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APPLIED SCIENCE DIVISION

**Separation of Low Molecular Weight Alcohols from
Dilute Aqueous Solutions by Reversible
Chemical Complexation**

D.R. Arenson* and C. J. King
*(Ph.D. Thesis)

April 1989

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SEPARATION OF LOW MOLECULAR WEIGHT ALCOHOLS FROM DILUTE AQUEOUS
SOLUTIONS BY REVERSIBLE CHEMICAL COMPLEXATION

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(*PhD Thesis)

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April 1989

SEPARATION OF LOW MOLECULAR WEIGHT ALCOHOLS FROM DILUTE
AQUEOUS SOLUTIONS BY REVERSIBLE CHEMICAL COMPLEXATION

Daniel Ray Arenson

ABSTRACT

The removal of alcohols from dilute solutions has traditionally been performed by distillation. Since this is an energy intensive process, a large amount of the total processing cost is due to the separation and purification of the alcohol. As an alternative to distillation, extraction is investigated from both a process and a chemistry point of view for several alcohols. The goals of the project were to find effective solvent systems for removal of alcohols and to investigate the interactions occurring in the organic phase during extraction.

Ethanol was examined both as a model compound and because of the interest in its production by fermentation. The four butanols were extracted in order to investigate the differences in extraction of the various isomers. Several propanols and propanediols were used also.

Phenols were found to provide much higher distribution ratios for extraction of ethanol than do other common solvents. Since most phenols are solids at room temperature, a mixed solvent system was employed. It was found that the type of diluent used could have a very large effect on the distribution ratio for the alcohol as well as on the water co-extraction and the solvent loss to the aqueous phase.

In extracting the butanol isomers it was found that the indicated activity coefficients in the organic phase were approximately the same when large concentrations of m-cresol were present. This indicates

that the majority of the difference in the distribution ratios of the isomers is due to the differences in solvation of butanol in the aqueous phase.

A mass-action-law model was used to obtain indicated stoichiometries for the complexes formed in the organic phase between the alcohol and m-cresol. Both multiple linear regression and curve-fitting methods were used to find the stoichiometries. The results seem to indicate the presence of a 1:1 alcohol:m-cresol complex with solvation modifications due to the changing concentrations of the components of the organic phase.

From the complex formation constants at different temperatures, the enthalpy of complex formation was calculated for the interaction between ethanol and m-cresol.

DEDICATION

To Shelley

for making it all worthwhile

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1. INTRODUCTION

1.1 Extraction

The need to remove and/or recover polar organics from relatively dilute aqueous solutions occurs in many industrial processes, as well as in the clean-up of plant effluent and waste streams. Alcohols and other chemicals bearing the aliphatic -OH group (e.g. diols) form an important class of substances often requiring separation from dilute aqueous solutions (Busche, 1983, 1985; Linko, 1985). Liquid-liquid extraction is a logical alternative in many of these situations (King, 1987). Increased use of fermentation to produce chemicals would lead to additional major recovery problems of this sort. An extraction process can remove and concentrate the solute if solvents of sufficient selectivity, capacity and regenerability can be found. This can avoid some of the high cost of energy-intensive processes, such as evaporation and distillation.

For the lower molecular weight alcohols, solvation and association effects are complex, and common solvents give relatively low equilibrium distribution coefficients (Kertes and King, 1987). Solvents that interact specifically, or preferentially, with the solute are likely to have higher distribution ratios, resulting in lower solvent flow rates, but the interaction must be readily reversible in order for the product to be recovered. Interactions with energies between 10 and 50 KJ/mol are generally strong enough to be specific, yet easily reversible (King, 1987). This fact provides incentive for identification of extractants giving stronger, yet still reversible, interactions with alcohol solutes.

The traditional method of production of alcohols from biomass consists of two steps, batch fermentation and subsequent separation and purification. The first step is a slow procedure. Ethanol fermentation is a typical example. The reaction vessel must first be cleaned and prepared before the sugar solution, supplemental nutrients and yeast inoculum are added. Initially the yeast is growing and the production of ethanol is slow. The production rate increases with the increasing numbers of yeast cells. After ~20 hours, the ethanol production rate reaches a maximum and begins decreasing as the yeast is being inhibited by the presence of the ethanol and/or lack of nutrients. The reaction tank is emptied and the broth is sent to the separation step, usually distillation (Maiorella et al., 1979).

In order to make the fermentation more efficient, a continuous feed of nutrient solution and maintenance of product and byproducts at levels below those that cause inhibition can be used to transform the batch process into a continuous fermentation/extraction process. Several alternative methods of achieving this more economical process are outlined by Maiorella et al. (1979) along with various methods of separating the products. Solvent extraction can be used to remove the product continuously by either contacting the solvent and the aqueous broth directly in the fermentation tank and recycling the regenerated solvent (combined) or by performing the extraction in a separate vessel and recycling both the depleted aqueous phase and the regenerated solvent (sequential).

One major problem with continuous extraction/fermentation systems is the potential toxicity of the solvent in the aqueous phase. This

problem can be approached in two different ways. The first is to use hardier strains of the organism, or to encapsulate the organism in a protective covering (Honda et al., 1986). The second is to reduce the amount of solvent dissolved in the aqueous phase. The idea is to reduce aqueous solubility of the solvent while retaining the properties which make it a useful extractant. Increased alkyl or aryl weighting is one approach, but this tends to reduce equilibrium distribution ratios. Alternatives are mounting the extractant functionality on a solid sorbent or imprisoning the solvent in a membrane. A low-solubility organic scavenger can also be used to remove residual dissolved solvent from the aqueous phase.

1.2 Ethanol

Ethanol has already seen much use as an alternative fuel, obtainable from renewable resources. Much attention has been given to technology for recovery of ethanol from aqueous solution, since costs for separation and purification tend to be large fractions of the total cost (Busche, 1983, 1985). A large number of solvents have been examined for recovery of ethanol by solvent extraction. Selected molar distribution ratios (D_{EtOH}) and selectivities with respect to water ($\alpha = D_{\text{EtOH}}/D_{\text{H}_2\text{O}}$) taken from the present work and several surveys are shown in Table 1.1. The ethanol concentrations are not shown because for moderate variations in alcohol concentration in dilute solutions there is little change in the distribution ratio (Arenson et al., 1986, 1988b; see also Figures 4.6 - 4.8). The underlying chemistry of the extraction has recently been reviewed (Kertes and

TABLE 1.1

4

Distribution Ratios, D_{EtOH} (concentration basis) and
Separation Factors, α , (selectivities) for
Extraction of Ethanol from Dilute Solution in Water
with Several Different Solvents

<u>Solvent</u>	D_{EtOH}	α	<u>Ref.</u>
m-cresol	2.17	13	present work; Arenson et al, 1988b
3,4-diethyl-pyridine	1.07	6	Murphy et al., 1984
2-ethyl hexanoic acid	0.52	44	Roddy, 1981
tributyl phosphate	0.54	8	Munson and King, 1984
2-ethyl hexanol	0.58	23	Munson and King, 1984
methyl i-butyl ketone	0.50	15	Roddy, 1981
n-butyl acetate	0.34	14	present work; Arenson et al, 1988b
chloroform	0.13	110	present work; Arenson et al, 1988b
toluene	0.08	120	present work; Arenson et al, 1988b

King, 1987), but understanding of it is still far from complete. Most solvents have low capacities, as reflected by distribution ratios less than unity. Oxygen-containing, polar extractants generally provide distribution ratios larger by up to two orders of magnitude than the hydrocarbons and halocarbons under comparable conditions (Kertes and King, 1987). These more polar compounds also co-extract large amounts of water and hence give lower selectivities. There is a roughly inverse relationship between the distribution ratio and the selectivity, as shown in Figure 1.1 (Roddy, 1981; Munson and King, 1984). A compromise between these two factors must be found to maximize the efficiency of the solvent. The solvent must also be thermally stable and interact rapidly with the solute. Low selectivity can be overcome to some extent by performing an extractive distillation of the extract in the presence of the solvent, thereby removing co-extracted water (Munson and King, 1984).

The review of the production of ethanol by fermentation by Maiorella et. al. (1979) discusses both the traditional distillation and the more recent alternative processes. The conventional atmospheric distillation process produces 96 wt% ethanol. Using an azeotropic distillation with benzene or other entrainers can increase this final product to 99.9 wt%, but the energy consumption is increased by ~40% for this extra step. Alternatives to these methods include vacuum distillation, extractive distillation, vapor phase water absorption, solvent extraction including use of supercritical CO₂, separation by selective membranes, and selective adsorption of water by zeolite molecular sieves or of ethanol by carbon. Each of

1.1 Separation factor versus distribution ratio for extraction of ethanol.

these methods has advantages and disadvantages depending on the feed composition, restrictions on the operating conditions and final product desired. The focus of this work, solvent extraction, possibly combined with a subsequent extractive distillation step, is probably most applicable for low concentration feeds when a high purity end product, greater than 95 wt%, is desired. If the problem of solvent toxicity is reduced to acceptable levels, extraction can also be useful in a continuous fermentation/purification process.

The utility of extraction for recovery of ethanol is held back by low solvent capacities and by the fact that the optimal ranges of feed and product composition for use of extraction are also the ranges where simple distillation is most efficient (King, 1988). However, studies of extraction of ethanol are also relevant to extraction of other alcohols, glycols and polyols. Also, identifying solvent systems giving higher equilibrium distribution ratios would make solvent extraction more competitive. Furthermore, continuous combined extraction/fermentation processes for ethanol with adequately immobilized extractants or rapid recycle through an external extraction/solvent removal loop could increase the efficiency of producing bulk chemicals and therefore be more competitive with distillation for recovery of ethanol.

As was noted by Munson and King (1984) and is shown in Figure 1.1, acidic solvents exhibit higher selectivities for ethanol for a given distribution ratio of ethanol. This occurs because ethanol is somewhat more basic than water in organic solutions (Chantooni and Kolthoff, 1978; Kamlet et al., 1983; Gutmann et al., 1982). Phenols

are somewhat more acidic and less basic than alcohols (Bellamy et al, 1966a). Hence, as shown in Figure 1.1 and Table 1.1, phenols in general, and m-cresol in particular, provide higher capacities for ethanol than do the higher alcohols, which are among the best of other solvents. This finding (Arenson et al, 1986, 1988a) is consistent with related results reported by others (Zudkevitch et al., 1984; Dadgar and Foutch, 1985; Cockrem et al, 1986; Honda et al., 1986).

Phenolic extractants for ethanol and butanols are the subject of the present research.

1.3 Butanol

Butanol has been produced by fermentation for many years. The best known process simultaneously produces acetone and ethanol using *Clostridium acetobutylicum*. However there are other strains that produce butanol with other combinations of co-products including isopropanol and acetic and butyric acids. Production of butanol by fermentation has been relatively inactive for many years, because there are economically more attractive catalytic processes using petroleum based feedstocks. However, the inevitable ultimate increase in cost of petroleum and increased efficiency of the fermentation have led to recent renewed interest in the fermentation process and methods to purify the products from it (Marlatt and Datta, 1986; Ennis et al., 1986).

Various types of distillation, including vapor recompression and multiple-effect distillation, are the traditional methods of recovery

(Ennis et al., 1986). However, there are a number of potentially more energy-efficient alternatives, which include membranes (reverse osmosis and pervaporation), adsorbents, liquid-liquid extraction (organic and two-phase aqueous) and chemical recovery (acetification etc.). In contrast to the recovery of ethanol, the distribution ratios of butanol into more common, cheaper solvents such as esters and ketones are high enough to make extraction economically competitive, if not actually cheaper than distillation processes. The need to discover a solvent with a much higher distribution ratio is not as pressing for the recovery of butanol as for recovery of ethanol, which gives distribution ratios nearly an order of magnitude lower (compare Tables 1.1 and 1.2). The capital cost of the equipment needed is substantial. The economics become dependent on the future outlook for the price of the products and cost of the raw materials (Marlatt and Datta, 1986).

An additional aspect of interest in the extraction of butanol is the opportunity to examine the relative distribution ratios of isomers. Information on isomeric differences can contribute substantially to an understanding of the underlying extraction chemistry. The four isomers of butanol afford an opportunity to investigate isomeric differences in the extraction of alcohols.

Although no explicit study appears to have been made of the structural isomer effect on extractability in general, several systematic observations have been reported. For the butanols under consideration the reported partition coefficients, as taken from a recent review (Kertes and King, 1987) and summarized in Table 1.2,

TABLE 1.2

10

Partition Coefficient* of Butanol Isomers
Between Water and Organic Liquids at 25°C

<u>Solvent</u>	<u>Isomer</u>			
	<u>n-</u>	<u>i-</u>	<u>s-</u>	<u>t-</u>
Benzene	0.66	0.69	0.54	0.24
Cyclohexane	0.13	0.14	0.11	0.07
Carbon Tetrachloride	0.51	0.39	0.29	0.14
Chloroform	2.8	2.2	2.0	1.0
Ether	7.8	6.9	4.5	2.4
n-Octanol	7.4	5.5	4.5	2.7
Oleyl Alcohol	3.2	2.9	2.0	1.2

* mol/L basis

show high extractability into alcohols and ether, but low extractability into hydrocarbons. The trend of decreasing extractability with increasing branching is evident: The highest distribution ratios are measured for the primary and the lowest for the tertiary isomer, differing by a factor of up to three.

Another goal of the present research was to examine and interpret isomeric differences in the extraction of butanols by a phenolic extractant (m-cresol).

1.4 Phenolic Extractants

1.4.1 Extraction and Solubility of Phenols

The strength of the phenol as an extractant correlates roughly with the solubility of the phenol in water and its partitioning into an organic solvent. Some background concerning the extraction and solution chemistry of phenols is therefore instructive.

Phenol and its derivatives are weak acids in aqueous solution, having pK_a values between 10 and 11. Because only undissociated phenols are soluble in common, inert organic solvents, the partitioning of phenols at infinite dilution is dependent on the pH of the aqueous solution, particularly in the pH range 8-12.5. For example, at 28°C m-cresol has a distribution ratio of 1.01 into cyclohexane at a pH of 6.7. However the distribution ratio decreases to 0.09 at a pH of 11.0 (Golumbic et al., 1949). For additional information on the effect of pH on the distribution ratio of phenols, see Greminger et al. (1982). The pK_a of a phenol derivative increases with addition of alkyl groups onto the phenol ring, which decreases

its acid strength (Golumbic et al, 1949); for example, pK_a values of m-cresol and 2,4-xylenol are 10.01 and 10.40, respectively, whereas that of phenol is 9.99 (Dean, 1985). The magnitude of this change is dependent on the position where the alkyl group is added, the effect being largest for an ortho group. At higher phenol concentrations, an increasingly lower fraction of the phenol is in the equilibrium aqueous phase due to formation of a larger amount of phenol dimer or higher oligamer, which favors solubility in the organic phase.

Inorganic salts and acids have a salting-out effect on the solubility of phenols in water, increasing the distribution ratio of the phenol into a solvent (Korenman and Makarova, 1974). The presence of alcohols in the aqueous phase will decrease the distribution ratio of phenols because of the increased solubility of the phenol in the alcohol-water mixture. This effect is most apparent at low pH because of the repressed ionization of the phenol (Golumbic et al., 1949).

Interactive solvents will also affect the partitioning of the phenols by forming 1:1 associations which in turn lead to increasing distribution ratios and low aqueous solubilities (Korenman, 1983). The solvent-solute interaction is energetically favored over the solute-solute interaction, although in the case of phenol and alcohol the difference is not large (Woolley and Rushforth, 1974; Korenman and Smirnov, 1980). In the case of a mixed solvent the stability of the complex is affected by the type of diluent used (see Table 1.3). The diluent does not actually participate in the complex formation but does affect the complexation by its ability to solvate the resultant adduct. The stability of the complex formed between the phenol and an

Table 1.3

Formation Constants of Cresol Complexes, K_{nm} , in Diluents of Differing Degrees of Interaction
(Korenman and Pavlovskaya, 1973)

$$K_{n,m} = \frac{[Cresol_n Extractant_m]}{[Cresol]^n [Extractant]^m}$$

<u>Extractant</u>	<u>Diluent</u>	<u>o-Cresol</u>	<u>m-Cresol</u>	<u>p-Cresol</u>
n-pentyl acetate (1:1 - n,m=1)	CCl ₄	46.8	85.0	
	benzene	19.1	26.3	24.0
	nitrobenzene		7.0	5.5
n-octanol (2:1 - n=2,m=1)	CCl ₄	34.0	79.4	52.5
	benzene	14.1	24.0	20.4
	CHCl ₃	7.4	16.6	16.6
	nitrobenzene	8.5	8.5	10.0

extractant is greater in an inert diluent than in diluents which have an affinity towards the phenol as can be seen in Table 1.3.

Association with other substances and the self-association of the phenols are both strongly affected by changes in temperature. Partition coefficients into inert solvents increase with increasing temperature, while the opposite occurs for reactive solvents (Eppel et al., 1980; Korenman et al., 1982). The enthalpy change of the partitioning process is made up of two terms, an endothermic enthalpy of dehydration of the phenol and an exothermic enthalpy of formation of the complex (Eppel et al., 1980). The overall enthalpy change is dependent on the value of the second term, since the first term is constant for any solvent. The more affinity a solvent has for interacting with phenol, the larger the exothermic enthalpy is. The term for the entropy change is smaller for reactive solvents due to the formation of strong complexes (Korenman et al., 1982).

The partitioning of the phenol is affected by its substituent groups. The effects fall into three categories -- type, quantity and position of the group or groups (Korenman, 1983). Hydrophilic groups such as hydroxy, amine, nitro, carbonyl and carboxyl increase the solubility of the phenol while alkyl and halogen groups decrease it. The larger the alkyl or halogen group, the larger the effect. Increasing the numbers of groups increases the overall effect. The isomeric effect is relatively minor compared to the first two effects, with the biggest difference being for substituents in the ortho- or 'sterically hindered position'. This effect tends to be larger for-- interactive solvents.

1.4.2 Phenols as Extractants

While phenols are very good extractants for alcohols, they have two drawbacks, significant aqueous solubility and potential toxicity to the organism. The aqueous solubility and the consequent toxicity may be diminished by alkyl weighting of the phenol ring and/or incorporation of phenol groups onto a solid sorbent or into membrane system. Other approaches are to use a low solubility organic scavenger for the phenol, to use a protective agent for the organism (Honda et al., 1986) or to use a membrane screen between the aqueous and organic phases (Maiorella et al., 1979). Alternatively, dissolved solvent may be recovered from the raffinate. Possible approaches for this purpose include atmospheric or vacuum steam stripping, extraction with a non-polar solvent, and adsorption (Senetar and King, 1987).

Toxic effects to humans must be considered for any process related to fermentation or water treatment.

1.5 Water Co-extraction

For most inorganic compounds or high value compounds, there is little economic incentive to be concerned about water that is co-extracted during the recovery process. The amount of water transferred to the organic phase is normally small for metals and inorganics, since the transfer of the solute is often by salt or complex formation, or via dipole-dipole solvation. In these cases, water does not seem to have a significant effect on the chemistry of the partition process (Marcus and Kertes, 1969), and the cost of an

extra dewatering step is low compared to the value of the product.

In the case of organic nonelectrolytes, the co-extraction of water is substantial, particularly if the solute is freely water miscible. In addition, for these lower-value solutes, the cost of the dewatering process step can be an appreciable fraction of the total recovery cost. All of the alcohols used in this work (C_2 - C_4) are quite soluble in aqueous solution, with those of lower molecular weight being miscible for any composition and temperature. The water solubilities of these compounds are strongly affected by temperature (Kertes and King, 1987).

Water can be co-extracted for two reasons -- its solubility in the organic solvent and/or its interaction with the solute or the complex in the organic phase (Roddy and Coleman, 1981). The interaction can be considered to be hydration of the alcohol/solvent complex or the complexing of the hydrated alcohol. There is some evidence for the formation of an alcohol monohydrate species in several solvents, particularly at low alcohol and water concentrations (Frank and Ives, 1966; Huyskens et al., 1980).

In addition to its effect upon process economics, water co-extraction can also have an important effect on the chemistry of the extraction process. Very little is known of the state of water in the organic phase. In the study of Huyskens et al. (1980) it was noted that, as more ethanol was extracted into different hydrocarbons, the amount of co-extracted water increased at a much greater, non-linear rate that was similar for all alcohols, assuming that the activity of water in the aqueous phase was the same. This was attributed to the

formation of hydrates of the alcohol in the organic phase. Roddy and Coleman (1981) also note an increase in water co-extraction despite the concurrent decrease in water activity in the aqueous phase. However, they show a linear dependence of co-extracted water on the amount of ethanol extracted. The reason for the increase in water co-extraction is formation of a monohydrate or simply higher solubility in a solvent containing larger amounts of ethanol.

The prevailing opinion is that water forms hydrogen-bond associations with the alcohol in the organic phase. Thus: "A priori, one could expect that the absorption of water would be influenced by the association of the alcohol in the organic phase." (Huyskens et al., 1980) These authors go on to state that no such effect was observed, and that the presence of water apparently does not effect the self-association of the alcohol. Rather water is incorporated in the alcohol chain such that the hydrated alcohol end behaves the same as the non-hydrated species in associating further. Thus the water molecule becomes part of the alcohol chain. They also conclude that the water, since it has two donor and acceptor sites, can interact with a second chain, through an alcohol or another water molecule, to create a larger branched chain. In contrast, Roux-Desgranges et al. (1986) indicate that the self-association of the alcohol causes large changes in the specific molar volume and heat capacity of water in the organic phase and is enhanced by the presence of water.

At lower concentrations in the organic phase, ethanol is more basic than water, and hence is more attracted to the acidic, hydrogen bonding extractants (Chantooni and Kolthoff, 1978; Kamlet et al.,

1983; Gutmann et al., 1982). The water molecule has four possible hydrogen-bonding sites, two acceptors and two donors. The basicity of the acceptor sites is improved by interactions at the donor sites (Huyskens et al., 1980). Therefore, when the concentration of alcohol has increased, the acceptor sites of the water molecules become more basic due to donor-site interactions and compete more for the acceptor site of the alcohol (Huyskens et al., 1980; Chantooni and Kolthoff, 1978). Simultaneously, water also becomes a better donor because of the interactions at the acceptor sites. Also, water seems to utilize its secondary sites to interact with other water molecules rather than with alcohols. This explanation accounts for the increase in the amount of water co-extracted per alcohol extracted to an organic solvent, with increasing alcohol concentration (Huyskens et al., 1980).

1.6 Alcohol Association

Hydrogen bonding between alcohols is still not particularly well understood. There is a definite lack of agreement with respect to the complexes formed in a simple solution of alcohol in an inert hydrocarbon. The suggested forms to be found in solution include the monomer, linear polymers or i-mers, cyclic polymers, cyclic dimer and a water-like structure (Van Ness et al., 1967). Several groups have proposed different models, such as 1-3, 1-4, 1-3-8, 1-2-3-..., and 1-2- ∞ , for the types of aggregates formed, based on several different techniques or combination of techniques (Bellamy and Pace, 1966a; Van Thiel et al., 1957; Fletcher and Heller, 1967; Tucker and Christian,

1977; Tucker and Becker 1973; Van Ness et al., 1967; Coggeshall and Saier, 1951; Murthy and Rao, 1968; Luck, 1967; Luck and Schrems, 1980; Frank and Ives, 1966; Singh and Rao, 1967). The major disagreements seem to be the existence or contribution of the dimer and the size and form of the polymer (i.e. cyclic, linear or a water-like structure). Depending on the spectroscopic method used, different values of the equilibrium constants for the different i-mers have been derived, although the values of the enthalpies of formation are of the same order of magnitude.

A significant amount of the investigative work is based on infrared spectra of the alcohol in an 'inert' solvent (see Figures 1.2 - 1.5). There is agreement that the 'monomer' peak is located at approximately $3600\text{--}3650\text{ cm}^{-1}$, although it is not agreed whether this peak is from only the true monomer or also contains a contribution from the free-proton end of the polymer. It is also agreed that there is a broad peak in the $3300\text{--}3450\text{ cm}^{-1}$ range, but not what size or range of sizes of the aggregate this represents. The small peak often visible near 3500 cm^{-1} has many explanations. It has been noted that the IR spectra can change considerably with composition (Van Ness et al., 1967) and temperature (Tucker and Becker, 1973). It has also been noted that there is a definite difference in the interaction from one solvent to another, even with solvents such as CCl_4 and benzene, which are usually thought to be inert (Van Ness et al., 1967; Spencer et al., 1985). There have been a few IR spectroscopic studies of alcohol-phenol hydrogen bonding (Fuchs and Rupprecht, 1983; Bellamy and Pace, 1966b).

Figure 1.2 Infrared absorption traces for n-butanol in octane. A, 0.037 mol/L; B, 0.059 mol/L; C, 0.086 mol/L; D, 0.118 mol/L. From Aveyard and Mitchell, 1969.

Figure 1.4 Near infrared spectra of ethanol in cyclohexane at various ethanol weight fractions; a, 0.001932; b, 0.003922; c, 0.005874; d, 0.010027. From Ibbitson and Moore, 1967.

Figure 1.3 Infrared survey spectra at 25°C; I, $n\text{-C}_{16}\text{D}_{34}$ vs. air; II, ~ 0.09 mol/L $t\text{-BuOH}$ in $n\text{-C}_{16}\text{D}_{34}$, solvent compensated. From Tucker and Becker, 1973.

Figure 1.5 Difference infrared absorption spectra for dry ethanol in n-undecane vs. dry n-undecane. From Roddy and Coleman, 1981.

Other types of investigations include calorimetry (Anderson et al., 1975; Spencer et al., 1985; Woolley et al., 1971), NMR (Dixon, 1970; Tucker and Becker, 1973; Fujiwara and Ikenoue, 1976; Saunders and Hyne, 1958; Griffiths and Socrates, 1966), Raman spectroscopy (Abramczyk et al., 1987), measurements of freezing point depression (Muhammed, 1975), dielectric polarization, dipole moment (Ibbitson and Moore, 1967) static dielectric permittivity (Kunst et al., 1976; Misra et al., 1985) and vapor pressure (Tucker and Becker, 1973; Tucker and Christian, 1977).

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2. EXPERIMENTAL

2.1 Goals

The purpose of this research project was to investigate the extraction of low molecular weight alcohols. The first part of the project was to find a suitable extractant. The qualities desired were: a large capacity for uptake of alcohol (high distribution ratio), preferential extraction of alcohol over water (adequate separation factor) and a small loss of solvent to the aqueous phase (low water solubility). The second aim of the project was to attempt to derive insight into the chemistry of the process of extraction by phenols, through applying an equilibrium, mass-action-law interaction model to the extraction data.

2.2 Materials

The materials used as solutes, diluents and extractants and listed in Table 2.1, were used as obtained. m-Cresol was also further purified by vacuum distillation to reduce impurities. There was no difference in the results obtained with the two grades of m-cresol. Also, no impurities were noticed during analysis of the phases by gas chromatography.

2.3 Distribution Ratios

Aqueous solutions of alcohol were prepared with concentrations between 0.1 and 1.0 mol/L. Likewise, 0.1 to 9.0 mol/L solutions of extractant in the various diluents were prepared. Five-mL aliquots of

the initial organic and aqueous phases (1:1 volume ratio) were placed in a 20 ml scintillation vial, which was capped, sealed with Parafilm and shaken vigorously in a constant temperature Labline Orbit Water Bath Shaker [Labline Instruments, Melrose Park, IL] for at least 24 hours. Experiments were carried out at 0, 25 and 50°C. The vial was centrifuged using an IEC-HN SII centrifuge [International Equipment Company, Needham Heights, MA] to ensure complete phase separation and was then replaced in a thermostatted bath for several hours. The organic phase was analyzed for alcohol content by means of a Varian Model 3700 gas chromatograph [Varian Corp., Palo Alto, CA] with a thermal conductivity detector. A Perkin-Elmer Model 3920 gas chromatograph [Perkin-Elmer Corp., Norwalk, CN] with a flame ionization detector was used to measure the alcohol and solvent contents of the aqueous phase. Two different 0.64 cm I.D. columns, 180 cm and 60 cm long, were used, each being packed with Poropak Q [Waters Associates, Milford, MA]. The oven temperature was initially 180°C, with temperature programming to 240°C in order to elute the extractant. Closure of the mass balance was within 10% and usually within 5%. The water content of the organic phase was analyzed with a Quintel MS-1 automatic Karl Fischer titrator [Quintel Corp., Tempe, AZ]. pH values of final aqueous solutions were well below pKa for m-cresol.

2.4 Vapor Headspace Analysis

— For the headspace-analysis studies, ~20 ml of an aqueous solution of n-butanol was placed in a 50-ml test tube capped with a teflon

stopper (resulting in a vapor space of ~28 ml). Sufficient m-cresol was added to saturate the aqueous phase and form a small amount of a second phase. The stopper had a small hole just large enough for a syringe needle. The test tube was shaken and placed in a water bath for a minimum of 48 hours. It was then centrifuged and put back in the water bath for at least another 24 hours. Again, all experiments were carried out at 25°C.

The gas phase from the vial was sampled by means of a water-jacketed syringe (Kieckbusch and King, 1979) to avoid effects due to condensation or adsorption on the walls of the syringe barrel. For the analysis of this gas sample, the Varian Model 3700 gas chromatograph with a flame-ionization detector was used. The aqueous phase was then analyzed, as described above for the extraction experiments. The gas phase was sampled first since sampling of the aqueous phase disturbed the vapor headspace.

Table 2.1
LIST OF CHEMICALS

alamine 336	Henkel	
1-butanol (n-BuOH)	Fischer Scientific	99%
2-butanol (s-BuOH)	Eastman Kodak	99%
n-butyl acetate	Matheson, Coleman and Bell	99%
4-t-butylcatechol	Aldrich	99%
chloroform	Matheson, Coleman and Bell	99%
4-chlorophenol	Aldrich	99%
2-cresol	Matheson, Coleman and Bell	97%
3-cresol	Matheson, Coleman and Bell	99%
4-cresol	Aldrich	99%
cumylphenol	Aldrich	99%
di-n-butyl ether	Morton Thiokol (Alfa)	99%
di-ethyl ether	Mallinckrodt	99%
di-2-ethyl hexyl phosphoric acid (D2EHPA)	Mobil	95%
1-dodecanol	Aldrich	98%
1-heptane	Baker	99%
4-n-hexyl resorcinol	Aldrich	99%
4-methyl-2-nitrophenol	Aldrich	99%
2-methyl-1-propanol (i-BuOH)	Mallinckrodt	99%
2-methyl-2-propanol (t-BuOH)	Mallinckrodt	99%
1-octane	Mallinckrodt	99%
1-octanol	Aldrich	99%
pentachlorophenol	Aldrich	99%
1,2-propanediol	BDH	95%
1,3-propanediol	Aldrich	98%
1-propanol (n-PrOH)	Baker	99%
2-propanol (i-PrOH)	Fischer Scientific	99%
toluene	Matheson, Coleman and Bell	99%
2,4,6-trichlorophenol	Aldrich	99%
1,3-xylene	Eastman Kodak	99%

Table 2.1 (continued)
LIST OF CHEMICALS

3,5-xyleneol	Aldrich	97%
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3. BUTANOLS

3.1 Distribution Ratios

The extraction of butanols was performed with low concentrations (≤ 1.0 mol/L) of both the butanol and m-cresol in order to examine the isomeric differences in the extraction of the four butanol isomers. n-Octane was used as an inert diluent which could be separated readily from the other constituents during analysis by gas chromatography. Since both butanol and m-cresol were kept at low concentrations, the densities of the aqueous and organic phases were different enough that there was no difficulty in achieving phase separation. The procedure used for these extractions was described in Chapter 2. The butanol isomers were extracted individually, rather than in mixtures. There was no apparent effect on the measured distribution ratios when the centrifugation step was omitted.

Figures 3.1 - 3.4 show the resultant distribution ratios (D), in mol/L concentration units, for each of the four butanol isomers at varying initial concentrations of aqueous butanol and m-cresol in n-octane. The distribution ratios are shown as functions of the initial butanol concentrations because the initial concentrations could be held constant. The full results, including final butanol concentrations, are tabulated in Appendix A. As can be seen from the graphs, there is little change in the distribution ratios with change in the initial aqueous butanol concentration, at least in the range investigated, 0.05 - 0.50 mol/L (0.4 - 3.7 wt%). A similar result was obtained for extraction of ethanol (Figures 4.6 - 4.8). The apparent

Figure 3.1 Distribution ratio for extraction of n-butanol versus m-cresol concentration, 25°C.

Figure 3.2 Distribution ratio for extraction of i-butanol versus m-cresol concentration, 25°C.

Figure 3.3 Distribution ratio for extraction of s-butanol versus m-cresol concentration, 25°C.

Figure 3.4 Distribution ratio for extraction of *t*-butanol versus *m*-cresol concentration, 25°C.

differences with respect to butanol concentration that do exist may be due to inaccuracy in measuring the butanol concentration, particularly in the organic phase. For concentrations of the organic phase alcohol less than 0.1 mol/L, the peak for butanol, obtained with the TCD detector, separated from water and solvent, was small enough and broad enough to be affected by the background noise from the gas chromatograph (up to ~10%) and by the criteria for determination of the peak beginning and end points supplied as input to the integrator (up to ~10%). The butanol concentration of the aqueous phase, measured by FID detector, can be measured with good precision at much lower concentrations. However, the broad peak which results from the separation of the alcohol from water and solvent still results in some imprecision (< 5%). In all cases the results are reproducible to within 10%, and the concentrations tabled in Appendix A are average values of at least two chromatographic measurements.

The lack of dependence of D upon the butanol concentration is an important factor because it facilitates the interpretation of the results. Also, the relationship between D and m-cresol concentration is essentially linear, with only a small value of D in the absence of m-cresol. This is taken to indicate that the interaction of butanol with m-cresol is the dominant factor in the extraction.

Figures 3.5 - 3.7 compare the equilibrium distribution ratios for the four butanol isomers at each of the three initial aqueous concentrations, for m-cresol concentrations in the solvent mixture ranging up to 1.0 mol/L. D decreases from normal to iso to secondary to tertiary butanol.

Figure 3.5 Distribution ratio for extraction of 0.1 mol/L initial aqueous concentrations of the butanol isomers versus m-cresol concentration, 25°C.

Figure 3.6 Distribution ratio for extraction of 0.3 mol/L initial aqueous concentrations of the butanol isomers versus m-cresol concentration, 25°C.

Figure 3.7 Distribution ratio for extraction of 0.5 mol/L initial aqueous concentrations of the butanol isomers versus m-cresol concentration, 25°C.

The limitations of the experimentally accessible distribution ratios should be recognized for an analysis of the differences in extractabilities of the isomers and formation constants of the adducts. As distinguished from thermodynamic partition coefficients (Kertes and King, 1987), distribution ratios are global quantities that include all aspects of the complex behavior of the alcohol solutes in both phases. Hydration via hydrogen bonding in water, self-association in non-polar solvents and adduct formation with *m*-cresol are all factors incorporated in the experimental distribution ratios.

3.2 Separation of Effects in the Two Phases

From the plots of the experimentally determined distribution ratios, it is apparent that there are significant differences among the isomers. For a better understanding of the causes for the isomer effect, it would be valuable to separate that effect into its aqueous and organic components. The activity coefficients of the butanol isomers, in both aqueous and organic phases, were used as measures of the differences among the isomers.

The activity coefficient is a global variable, like the distribution ratio, that can incorporate many different interactions and can be affected by the presence and concentrations of each of the other components in a phase. In order to make a significant comparison among the isomers, it is necessary that the effects of the other components be accounted for.

In the aqueous phase, the major component is water. Experimental

data can be found in the literature for the activity coefficients for each of the butanols in a binary aqueous solution. However, in the extraction, there is also a small amount of solvent in the aqueous phase at equilibrium (see Figure 3.8). It must be ascertained whether the presence of the solvent, especially m-cresol for which the aqueous solubility is much higher than that of n-octane (2.5 wt% versus 0.002 wt% -- Dean, 1985), affects the aqueous activity coefficient. If the aqueous m-cresol does not significantly affect the activity coefficient of butanol, then the binary aqueous butanol activity coefficient may be used to compare the isomers.

The organic activity coefficient of butanol can be found if the aqueous activity coefficient is known, since the activity of butanol in each phase must be the same at equilibrium and the equilibrium distribution ratio is the inverse ratio of activity coefficients. The indicated differences in the organic-phase activity coefficients among isomers can then be assessed and can be interpreted in terms of complexation strengths or other interactions.

3.3 m-Cresol Distribution Ratio

Though the room temperature solubility of m-cresol in water is substantial, its extractability from water into aliphatic hydrocarbons is still high (Korenman and Pereshein, 1970). Figure 3.8 shows equilibrium data measured in the present work for the distribution of m-cresol between octane and aqueous butanol solutions as a function of the initial m-cresol concentration in n-octane at 25°C.

Figure 3.9 shows the same data but plotted as the equilibrium

Figure 3.8 Equilibrium concentration of m-cresol in the aqueous phase versus initial organic concentration of m-cresol in n-octane during extraction of 0.3 mol/L initial aqueous concentrations of the butanol isomers, 25°C.

Figure 3.9 Equilibrium concentration of m-cresol in the aqueous phase versus that in the organic phase during extraction of 0.3 mol/L initial aqueous concentrations of the butanol isomers, 25°C.

concentration of m-cresol in the organic phase versus that in the aqueous phase. From this plot, the partition coefficient for m-cresol can be measured as the initial slope of the curve. The result is approximately equal to 1. The value is only an estimate since the concentrations used in these experiments were larger than those generally used to find partition coefficients. In addition, the presence of butanol in significant amounts precludes calculating a true partition coefficient of m-cresol between water and n-octane. Arro and Molder (1976) report that the partition coefficient of monomeric m-cresol between water and n-octane at 20°C is 0.44. The distribution of m-cresol is relatively unaffected by the particular butanol present in the aqueous phase at a 0.3 mol/L level.

These solubility data were also used as part of the mass-action law analysis interpretation of the partition process, described in Chapter 5.

3.4 Activity Coefficients

Differences in boiling point and vapor pressure indicate that the isomers of butanol differ with respect to self-association in the pure state (Mullens et al., 1971; Huyskens et al., 1980). This behavior persists when the isomers are dissolved in inert organic solvents such as benzene, cyclohexane or carbon tetrachloride (Mullens et al., 1971; Huyskens et al., 1980; Amidon et al., 1974). The tendency toward aggregation should decrease in the order of decreasing boiling point, normal to iso to secondary to tertiary. The difference in the degree of association is small, not exceeding 10%, and there is no evidence

that the energy of the bonds is any different among the isomer homoassociates (Kertes and King, 1987).

Dilute aqueous solutions of lower alcohols, including the butanols, exhibit significant deviations from ideal thermodynamic behavior (Kertes and King, 1987). The generally positive deviation from Raoult's law, and the extremes of the excess functions of mixing, are believed to be due to the effect of the nonelectrolyte solute on the complex network of hydrogen bonds in water (Butler et al., 1933; Butler et al., 1935; Naberuhkin and Rogov, 1971; Battino, 1971; Franks, 1968a, 1968b) even though the water-alcohol bonds are considered to be less stable than those in the water clusters.

Mole-fraction-based activity coefficients of butanol isomers in water at 25°C, as determined from vapor pressure measurements (Butler et al., 1933), were converted to the mole/L scale (Kertes et al., 1975) and are plotted in Figure 3.10 for the butanol concentration range of interest. The values agree well with data from other sources (Butler et al., 1935; Rytting et al., 1978; Randall and Weber, 1940; Pierotti et al., 1959). Activity coefficients, which disregard the exact solution model of the butanol solutes (Laiken and Nemethy, 1970), can be taken to relate to the fundamental tendency of the molecule to partition between the gas phase and water and reflect the intrinsic hydrophobic character of the isomers. In this specific case, hydrophobicity is primarily altered by the proton-donating and-accepting ability of the hydroxyl group. The isomer effect is substantial.

In order to assess the effect of m-cresol on the activity

Figure 3.10 Activity coefficients for the butanol isomers in water (literature) and in 1.0 mol/L initial concentration of *m*-cresol in *n*-octane (calculated) versus butanol concentration, 25°C.

coefficients of the butanols in water, the partial pressures of n-butanol over both pure water and m-cresol-saturated aqueous solutions were determined at various alcohol concentrations, as shown in Figure 3.11. The procedure for these experiments is described in Chapter 2. Although the experimental points in the figure show considerable scatter and are somewhat higher than those reported by Butler et al. (1933), both sets of points (with and without m-cresol present) are approximately the same. This indicates that, if there is an effect of the dissolved m-cresol on the aqueous activity coefficient of butanol, it must be small. We assume that a similar conclusion holds for other butanol isomers.

Figures 4.16 and 3.12 show the aqueous activity coefficients for ethanol and butanol respectively, plotted against the alcohol concentration. Literature values for the infinite dilution activity coefficient of ethanol are not in very good agreement. The values reported at 25°C range from 3.3 to 3.8 (see Figure 4.16). This may be explained by the data of Nord et al. (1984) which show a large increase in the aqueous activity coefficient with increasing alcohol concentration at very low concentrations. This may also explain the apparent deviation of the vapor pressures and activity coefficients in Figures 3.11 and 3.12 from the results of Butler et al. (1933).

Using the aqueous molar activity coefficients from Figure 3.10, the effective (Marcus and Kertes, 1969) molar activity coefficients of the isomers in the octane-cresol phase can be derived via the relationship

$$\gamma_a \cdot [B]_a = \gamma_o \cdot [B]_o \quad (3.1)$$

$$\gamma_o = \gamma_a / D \quad (3.2)$$

Figure 3.12 Aqueous activity coefficients of n-butanol versus the concentration of n-butanol, 25°C.

in which $[B]$ is the concentration of butanol, γ is the activity coefficient, D is the experimentally determined distribution ratio and subscripts a and o represent aqueous and organic phases, respectively. The pure solute was used as the standard state for the butanols. The calculated effective molar activity coefficients for the butanols in the organic phase at 1 mol/L (14.7 wt%) concentration of cresol, plotted at the bottom of Figure 3.10, show no substantial isomer effect.

Figure 3.13-3.15 shows the calculated organic-phase activity coefficients for constant initial aqueous concentrations (0.1, 0.3 and 0.5 mol/L) of each of the butanols during extraction with various initial concentrations of *m*-cresol. At very low *m*-cresol concentrations there is a substantial difference in the activity coefficients of the isomers. However as the concentration of the extractant increases, the difference decreases. The values of the calculated organic-phase activity coefficients for the extraction of butanol into *n*-octane (no *m*-cresol present), agree well with the activity coefficients measured from vapor pressures of solutions in cyclohexane for three of the butanol isomers (*n*-, *s*- and *t*-) by French (1983). The comparison is shown in Table 3.1 and in Figure 3.16. Similar results were obtained by Brown and Smith (1959) and Brown et al. (1969).

The absolute values of the activity coefficients in the two phases are not strictly comparable. Those for the aqueous phase are measured thermodynamic values, while those for the organic phase are apparent values calculated from equation 3.2 under the specific experimental

Figure 3.13 Equilibrium organic phase activity coefficients of butanols calculated for extraction of 0.1 mol/L initial aqueous butanol, versus m-cresol concentration in n-octane, 25°C.

Figure 3.14 Equilibrium organic phase activity coefficients of butanols calculated for extraction of 0.3 mol/L initial aqueous butanol, versus m-cresol concentration in n-octane, 25°C.

Figure 3.15 Equilibrium organic phase activity coefficients of butanols calculated for extraction of 0.5 mol/L initial aqueous butanol, versus m-cresol concentration in n-octane, 25°C.

Figure 3.16 Equilibrium organic phase activity coefficients of butanol calculated for extraction into n-octane versus organic phase butanol concentration, 25°C. Comparison with measured activity coefficients for butanols in cyclohexane (French, 1983).

TABLE 3.1

Infinite dilution aqueous
activity coefficients for butanol
(from Butler et al., 1935)

<u>Isomer</u>	<u>γ_{∞}</u>
n-	52.9
i-	43.2
s-	25.1
t-	11.8

conditions. It can nonetheless be concluded that the primary cause for the isomeric differences observed in the extractability of the different butanol isomers is the hydrophobic effect in the aqueous medium. Further interpretation of organic-phase interactions of the different butanol isomers is made in Chapter 5.

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4. ETHANOL

The extraction of ethanol was performed with both low and high concentrations of the extractant. For the extractions into dilute solutions of m-cresol, both the ethanol and m-cresol concentrations were less than 1.0 mol/L. These experiments were performed to investigate the chemistry of the interactions in the organic phase, as for the butanol work of Chapter 3. The more concentrated extractions were aimed at identifying an extractant with a high capacity for removal of the ethanol, in addition to discovering any differences in the extraction chemistry at higher concentrations. In these experiments, the initial ethanol concentration was between 0.86 and 1.0 mol/L (4-5 wt%), while the extractant composed from 0 to 100% of the solvent phase. The actual maximum concentration on a mol/L scale depended on the properties of the particular extractant. The procedure for these experiments was described in Chapter 2.

4.1 Phenolic Extractants

Figure 4.1 shows experimental distribution ratio data for 1 mol/L initial aqueous ethanol extracted into a few of the different phenolic extractants at varying concentrations of the extractant in the equilibrium organic phase. A complete tabulation of the results is included in Appendix B. For the relatively non-interacting diluents used, the dependence on the concentration of the phenolic extractant is nearly linear, and there is little difference in the capacities of the mono-hydroxybenzenes at similar molar concentrations despite the

Figure 4.1 Distribution ratio for 1.0 mol/L initial aqueous ethanol, extracted by various phenols in non-interactive diluents, versus initial extractant concentration, 25°C.

changing substituent groups. The exceptions to this are those phenols which have very strong intramolecular interactions between the hydroxy group and an active substituent. For the majority of phenols, these interactions are sterically hindered. However, in the case of the nitrophenols, the interaction of nitro and hydroxy groups is possible. Because of this interaction the available hydrogen bonding sites for ethanol become weaker and fewer in number. This leads to a markedly lower distribution ratio.

The diluents alone have very low capacities, which are negligible in relation to that of the extractant, even at relatively low extractant concentration. This suggests that the extraction of ethanol is due almost completely to hydrogen bonding between the hydroxy functionalities of ethanol and the phenol.

The di-hydroxybenzenes show a somewhat higher capacity for ethanol, but not twice as great as for the mono-hydroxybenzenes, as might be expected on the assumption that all the hydrogen-bonding sites are of equal strength and accessibility. However, the interaction of the first hydroxy group probably lessens the electron-withdrawing capability of the aromatic ring, making interactions with the second hydroxy group weaker. Similiar to the mono-hydroxybenzenes, the results are nearly the same for the different di-hydroxybenzenes at a given extractant concentration.

Chlorophenols can also lead to a slightly higher distribution ratio due to the large electron withdrawing capacity of the chloro- groups. However, the chloro- groups may also cause some steric hindrance when in the ortho postitions so that this rise in distribution ratio is

reduced, as in the case of 2,4,6-trichlorophenol.

4.2 Diluents

Most phenols are solids at room temperature and must be dissolved in a diluent in order to be used in the extraction. This means that, for extraction of ethanol from water at or near ambient temperature, most of the phenols can be used only at lower concentrations. The exceptions used here are m-cresol, 2,4-xyleneol and p-t-butyl catechol, which are liquids at or near room temperature. Additional functional groups tend to cause higher melting points and therefore lower solubilities, which limit the concentration of extractant attainable in the organic phase at a given temperature.

The choice of the diluent can be very important. The properties that are desirable in the diluent are: (1) The extractant is soluble in it over the entire range of conditions, (2) a high distribution ratio is maintained over the concentration range of interest, (3) the solubility of water in the diluent is low, (4) the solubility of the diluent in water is also low, (5) the diluent serves to lower the loss of the extractant to the aqueous phase and (6) the diluent has the correct physical and chemical properties for whatever regeneration method is to be used.

Figure 4.2 compares D values for solutions of m-cresol in chloroform, toluene and n-butyl acetate, for extraction of initially 1 mol/L aqueous ethanol. Chloroform, a Lewis acid, and n-butyl acetate, a Lewis base, show deviations from linear additivity of the

Figure 4.2 Distribution ratio for 1.0 mol/L initial aqueous ethanol, extracted by m-cresol in various diluents, versus initial extractant concentration, 25°C.

distribution ratios in the positive and negative directions, respectively. The negative effect of n-butyl acetate probably results from competitive interactions of the solute and the diluent with the acidic extractant. As is shown in Figure 4.3, n-butyl acetate as diluent serves to increase the distribution ratio for m-cresol (i.e., reduce the loss of m-cresol to the aqueous phase) over most of the range of compositions, in comparison to toluene as diluent, with the effect being particularly pronounced at low m-cresol concentrations. (The data reported in Figure 4.3 were measured in the presence of ethanol, during the extraction experiment with 1 mol/L initial aqueous ethanol.) Such behavior also corresponds to preferential interactions between the acidic cresol and the basic ester.

The acidic chloroform diluent serves to increase the distribution ratio for ethanol (Figure 4.2) and increases D for m-cresol over most of the concentration range (Figure 4.3). These results would correspond to preferential interactions between chloroform and an ethanol-cresol complex. Bellamy, et al (1966) have reported a tendency for hydrogen bonding of chloroform to either end of a linear oligomer complex formed between ethanol and phenol. The drop in distribution ratio for m-cresol at low concentrations of m-cresol in chloroform may result from positive deviations from ideality in binary mixtures of chloroform and m-cresol. In addition to increasing the distribution ratio for ethanol and m-cresol, the use of the chloroform as the diluent also raises the separation factor, α , as can be seen in Figure 4.4. The separation factor is defined as the distribution ratio of ethanol divided by the distribution ratio of water. The

Figure 4.3 Distribution ratio for m-cresol during extraction of 1.0 mol/L initial aqueous ethanol, versus initial extractant concentration in various diluents, 25°C.

Figure 4.4 Separation factor versus distribution ratio for extraction of 1.0 mol/L initial aqueous ethanol by m-cresol in toluene and chloroform, 25°C.

increase in the separation factor results mostly from the increase in the distribution ratio of ethanol, though the distribution ratio of water decreases slightly also.

Figure 4.5 shows the distribution ratio for ethanol, extracted by several different phenols using chloroform as the diluent, versus extractant concentration. A similar curvature is observed for each of these solvent systems as in the m-cresol/chloroform.

4.3 Dilute Solutions

Figures 4.6 - 4.11 show equilibrium distribution ratios, D , for extraction of ethanol from aqueous solutions of different initial molarities into solvents composed of relatively dilute m-cresol in both toluene and chloroform. Data were obtained at three temperatures -- 0° , 25° and 50°C . The results are also tabulated in Appendix B. As in Chapter 3 for butanol, there is very little effect of increasing ethanol concentration on the distribution ratio. However, this can be explained by the law of mass-action curve fitting model explored in Chapter 5. Figures 4.12 and 4.13 show the predictions of the model developed in Chapter 5 for ethanol extracted by m-cresol in toluene and chloroform for dilute solutions of both solute and extractant with varying initial concentrations of aqueous ethanol. As can be seen, the law of mass-action model predicts only a small deviation in the distribution ratio for an increase in the initial aqueous ethanol concentration. The magnitude of this increase is of the same order as the uncertainty of the experimental measurements.

Figure 4.5 Distribution ratio for extraction of 1.0 mol/L initial aqueous ethanol by various phenols in chloroform versus initial extractant concentration, 25°C.

Figure 4.6 Distribution ratio for extraction of 0.1, 0.3 and 0.5 mol/L initial aqueous ethanol by m-cresol in toluene versus extractant concentration, 0°C.

Figure 4.7 Distribution ratio for extraction of 0.1, 0.3 and 0.5 mol/L initial aqueous ethanol by m-cresol in toluene versus extractant concentration, 25°C.

Figure 4.8 Distribution ratio for extraction of 0.1, 0.3 and 0.5 mol/L initial aqueous ethanol by m-cresol in toluene versus extractant concentration, 50°C.

Figure 4.9 Distribution ratio for extraction of 0.1, 0.3 and 0.5 mol/L initial aqueous ethanol by m-cresol in chloroform versus extractant concentration, 0°C.

Figure 4.10 Distribution ratio for extraction of 0.1, 0.3 and 0.5 mol/L initial aqueous ethanol by m-cresol in chloroform versus extractant concentration, 25°C.

Figure 4.11 Distribution ratio for extraction of 0.1, 0.3 and 0.5 mol/L initial aqueous ethanol by m-cresol in chloroform versus extractant concentration, 50°C.

Figure 4.12 Predicted distribution ratio curves calculated from law of mass-action model at 0.1, 0.3, 0.5 and 1.0 mol/L initial aqueous ethanol extracted by m-cresol in toluene versus initial extractant concentration for $K_{12}=3.0$ L/mol, 25°C.

Figure 4.13 Predicted distribution ratio curves calculated from law of mass-action model for 0.1, 0.3, 0.5 and 1.0 mol/L initial aqueous ethanol extracted by m-cresol in chloroform versus initial extractant concentration, for $K_{12}=3.0 \text{ (L/mol)}^2$ and $K_{111}=0.1 \text{ (L/mol)}^2$, 25°C.

4.4 Temperature Effects

Figures 4.14 and 4.15 show the effect on the distribution ratio of increasing the temperature under which the extraction is preformed. As can be seen from each of the graphs, the temperature dependence of the distribution ratio over the temperature range from 0° to 50°C is relatively small. In the case of ethanol, the temperature range for operation at atmospheric pressure is restricted to 0°C (freezing point of water) to 78°C (boiling point of ethanol). Even if the boiling point of ethanol was not a restriction, the extraction would still be limited in temperature by the boiling point of water. The lack of large temperature dependence of the distribution ratio precludes the use of temperature-swing back extraction as a regeneration alternative. It still might be possible to use a solvent-swing regeneration with the extraction and regeneration steps at different temperatures to enhance the efficiency of the process. However, ethanol should in most cases be readily regenerable by distillation or stripping as opposed to back-extraction.

4.5 Activity Coefficient

The activity coefficient for dilute ethanol in water has been measured previously (see Figure 4.17). In the case of the infinite dilution activity coefficient, there are considerable differences in the results, which show a relatively wide range of values. The large concentration dependence for the lower concentration ranges, shown in Figure 4.16 and listed in Appendix B, is most likely the cause of the discrepancies in the reported values. Typically, the infinite

Figure 4.14 Distribution ratio for extraction of 1.0 mol/L initial aqueous ethanol by m-cresol in toluene versus initial extractant concentration at 0, 25 and 50 °C.

Figure 4.15 Distribution ratio for extraction of 1.0 mol/L initial aqueous ethanol by m-cresol in chloroform versus initial extractant concentration at 0, 25 and 50 °C.

Figure 4.16 Aqueous activity coefficient of ethanol versus the concentration of ethanol, 25°C.

dilution coefficient has been found by extrapolating the values of the activity coefficient. Because of the apparent increase in concentration dependence as the concentration decreases, the value at infinite dilution will be larger than predicted by the extrapolation. This effect may also be the cause for the difference in vapor pressures and activity coefficients for butanol at very low concentrations, shown in Figures 3.11 and 3.12. In addition the temperature dependence of the activity coefficient is significant. In order to calculate an organic activity coefficient for ethanol as was done in Chapter 3 for butanol, an aqueous activity coefficient must be assumed. The results of Nord et al. (1984) were used for the aqueous values. The resultant organic-phase activity coefficients, obtained from the measured distribution ratios and the aqueous activity coefficients, are similar to those for butanol and are shown in Figure 4.17.

4.6 Water Co-extraction

Since the goal of the extraction is to remove the ethanol from water, it would be interesting to see how the presence of water affects the extraction of ethanol, and how the presence of ethanol affects the extraction of water. Since it is not possible to remove the water from the extraction, the extraction experiment was performed in the absence of ethanol. The goal was to find out whether the distribution ratio of water is affected by the presence of ethanol. The experiment was performed as described in Chapter 2, but the initial aqueous phase was pure water. The results are shown in

Figure 4.17 Organic phase activity coefficient of ethanol calculated from equilibrium for extraction by m-cresol in toluene, versus the initial extractant concentration, 0, 25 and 50°C.

Figures 4.18 - 4.23. As can be seen, in each case, the amount of water extracted into the aqueous phase was the same regardless of whether ethanol was present or not. The conclusion is that the co-extraction of ethanol does not affect the extraction of water, which occurs independently. This agrees with the observation of Huyskens et al. (1980), that the alcohol hydrate interacts with other alcohols as if the water was not present.

Figure 4.18 Comparison of the distribution ratio of water extracted by m-cresol in toluene both with and without the presence of 1.0 mol/L initial aqueous ethanol, versus the initial extractant concentration, 0°C.

Figure 4.19 Comparison of the distribution ratio of water extracted by m-cresol in toluene both with and without the presence of 1.0 mol/L initial aqueous ethanol, versus the initial extractant concentration, 25°C.

Figure 4.20 Comparison of the distribution ratio of water extracted by m-cresol in toluene both with and without the presence of 1.0 mol/L initial aqueous ethanol, versus the initial extractant concentration, 50°C.

Figure 4.21 Comparison of the distribution ratio of water extracted by m-cresol in chloroform both with and without the presence of 1.0 mol/L initial aqueous ethanol, versus the initial extractant concentration, 0°C.

Figure 4.22 Comparison of the distribution ratio of water extracted by m-cresol in chloroform both with and without the presence of 1.0 mol/L initial aqueous ethanol, versus the initial extractant concentration, 25°C.

Figure 4.23 Comparison of the distribution ratio of water extracted by m-cresol in chloroform both with and without the presence of 1.0 mol/L initial aqueous ethanol, versus the initial extractant concentration, 50°C.

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5. MODELLING

In order to investigate the chemistry of the extraction more thoroughly, the results of the extractions were used to model the interactions occurring in the organic phase at equilibrium. The resulting stoichiometry and equilibrium formation constant of the complex might give some insight into ways to improve extraction conditions.

5.1 BUTANOL

It was seen in Chapter 3 that there appeared to be very little isomeric difference among the butanols in the organic phase, while the aqueous phase activity coefficients showed significant variation among the different isomers. In order to explore the organic phase characteristics further, the experimental data were assessed by means of a complexation model, with attention to the apparent relative stoichiometries and formation constants for the butanol/m-cresol complex.

For the complexation of n moles of butanol with m moles of m-cresol,

The complex formation constant is given by

$$K_{nm} = \frac{[B_n C_m]_o}{[B]_a^n [C]_o^m} \quad (5.2)$$

In order to obtain the concentration of the complex, it is assumed

that all of the butanol in the organic phase is part of the complex, except for the butanol that is solvated by the diluent. The concentration of butanol in the organic phase for extraction with n-octane is multiplied by the volume fraction of the organic phase that is n-octane. This is subtracted from the actual organic phase butanol concentration to get the modified butanol concentration for the organic phase.

$$[B]'_o = [B]_o - \theta [B]_{o,dil} \quad (5.3)$$

Since this modified concentration of organic butanol is assumed to be completely complexed, the concentration of the complex is given by

$$[B_n C_m]_o = \frac{1}{n} [B]'_o \quad (5.4)$$

Once the complex concentration is known, the concentration of m-cresol can be found by subtracting the amount of m-cresol that is complexed.

$$[C]_o = [C]_{o,T} - \frac{1}{m} [B_n C_m]_o \quad (5.5)$$

A simple linear regression can be performed assuming that the stoichiometry for either butanol (n) or m-cresol (m) is equal to unity. If n is assumed to be unity, Equation 5.6 is used. Alternatively, if m is assumed to be unity, then Equation 5.7 is used.

$$\text{Log} \frac{[B]'_o}{[B]_a} = m \text{Log} [C] + \text{Log} K_{1,m} \quad (5.6)$$

$$\text{Log} \frac{[B]'_o}{[C]_o} = n \text{Log} [B]_a + \text{Log} (n K_{n,1}) \quad (5.7)$$

The results of these two regressions are shown in Table 5.1, as well as in Figures 5.1 and 5.2. There appears to be a substantial amount of scatter in the data, but some of it is due to the process of taking the logarithms of small numbers, which tends to exaggerate the appearance of scatter. The regression by both methods indicates that the complex formed for each of the butanols is very nearly 1:1. Table 5.1 also reports results of a regression determining the values of the complex formation constant assuming a 1:1 complex.

A large aggregate complex with the same number of molecules of butanol and m-cresol might also give the same type of results. In addition, the calculation allows for only one type of complex to be formed, so the result is a weighted average over all the complexes formed, including the case where no complex is formed (unassociated organic phase butanol, solvated by m-cresol rather than diluent). Therefore, the stoichiometries that result from these calculations are average, relative values and without further information should not be taken as evidence for specific molecular interactions.

The apparent stoichiometries and complex formation constants can also be found by treating the experimental data by the multiple linear regression method. This method is described in detail for ethanol in section 5.2. The results of the calculation are also shown in Table 5.1. The stoichiometries and formation constants calculated by the different methods are all approximately the same. The result from the multiple regression discounts the possibility of large aggregates.

The major assumptions in these calculations are (1) that all the butanol in the organic phase, other than that solvated directly by the

Figure 5.1 Logarithm plot of the modified distribution ratio for butanol vs. the equilibrium m-cresol concentration in the organic phase, mol/L; 25°C. Test of Equation 5.4.

Figure 5.2 Logarithm plot of the modified butanol concentration in the organic phase, mol/L, divided by the equilibrium m-cresol concentration in the organic phase, mol/L, vs. the butanol concentration in the aqueous phase, mol/L; 25°C. Test of Equation 5.5.

Apparent Stoichiometry and Equilibrium Constant
for Extraction of Butanols with m-Cresol in
n-Octane, 25°C

	<u>n-butanol</u>	<u>i-butanol</u>	<u>s-butanol</u>	<u>t-butanol</u>
Assuming $n=1$:				
n	1.00	1.00	1.00	1.00
m	1.07±0.05	1.08±0.04	1.16±0.08	1.02±0.03
K_{rm}	3.31±0.75	2.82±0.44	2.12±0.79	1.39±0.22
Assuming $m=1$:				
n	1.06±0.07	0.95±0.05	0.86±0.11	0.95±0.04
m	1.00	1.00	1.00	1.00
K_{rm}	3.52±0.81	2.36±0.39	1.32±0.52	1.23±0.37
Assuming $n=m=1$:				
K_{11}	3.09	2.59	1.83	1.36
Multiple Regression:				
n	1.15±0.01	1.00±0.01	0.94±0.02	0.95±0.01
m	1.13±0.01	1.08±0.01	1.14±0.02	1.01±0.01
K_{rm}	4.37±0.08	2.83±0.04	1.94±0.07	1.32±0.02

diluent, is part of a butanol/m-cresol complex, (2) that there are not any other interactions involved, and (3) that the activity coefficients of each component and of the complex are constant over the range investigated, thereby allowing the use of concentrations rather than activities. Since such a large fraction of the butanol was in the organic phase and only dilute solutions of butanol and m-cresol were used, there would be very little m-cresol not in a complex and the activity coefficients should not vary very much. Therefore the formation of m-cresol dimers and higher oligamers was not considered important for the extraction of butanol. The interaction of n-octane was not considered important because of the small distribution ratio of the butanols into the pure diluent. Possible interactions with water were also considered to be insignificant due to the small amount of water co-extracted. For all but the highest concentrations of m-cresol, the extraction of water was too small to be measured precisely with the methods used for measuring the co-extracted water in the ethanol experiments, i.e., less than 0.1 mol/L. Coupled with the apparent 1:1 complex revealed through the linear regressions, the overall indication is that the butanol/m-cresol interaction is dominant in the organic phase, at least in the range of concentrations investigated.

The complex formation constants $K_{n,m}$ are heterogeneous because the aqueous phase concentration of butanol is included. In order to compare the formation constants of the different isomers with the effects of the partitioning between the aqueous and organic phases removed, the calculated values of the heterogeneous formation

constants were multiplied by the ratios of organic phase activity coefficients, without the extractant, to aqueous activity coefficients for each isomer (Butler et al., 1935; Rytting et al., 1978; see Table 5.2) to give a value of the homogeneous formation constant, K_{Hom} .

$$K_{Hom} = K_{Het} \frac{\gamma_o}{\gamma_a} \quad (5.8)$$

The results are listed in Table 5.2. With the effects of differences in solvation in the aqueous phase removed, there is very little difference in the values of the homogeneous formation constants of the different isomers of butanol. The strength of the hydrogen bonding interaction between butanol and m-cresol is therefore apparently essentially the same for all of the isomers. This corroborates the finding in Chapter 3 that the activity coefficients in the organic phase, in which the formation of the complex is dominant (m-cresol concentration greater than 0.3 mol/L initially), were approximately the same for the different isomers, while in the aqueous phase they were very different. The organic-phase activity coefficients reported in Table 5.2 are for solution in pure diluent (no m-cresol).

The dominant effect in the organic phase is the formation of the butanol/m-cresol complex, while the variation among the distribution ratios of the isomers is mostly due to the aqueous phase differences.

5.2 ETHANOL

The graphs of the distribution ratios for extraction of ethanol by m-cresol in toluene and in chloroform have significantly different

Infinite Dilution Activity Coefficients and Complex
Formation Constants for Butanol and m-Cresol in
n-Octane, 25°C

<u>Isomer</u>	K_{Het}	$\gamma_{\infty, a}$	$\gamma_{\infty, o}$	K_{Hom}
n-	3.09	52.9	33.4	1.95
i-	2.59	43.2	32.5	1.95
s-	1.83	25.1	27.9	2.03
t-	1.36	11.8	18.0	2.07

curvatures (see Figure 4.2). This difference was taken to indicate that the interactions in the two diluents are not the same. However, it was also noticed that the difference was most apparent for solvent mixtures containing about 50% extractant, so that it appears that it is the interaction of the diluent with the extractant or with the ethanol/cresol complex that causes the change in distribution ratios. Since one of the goals of the project was to investigate the chemistry involved in the extraction, it was desirable to understand why the two curves differ.

Determination of the stoichiometry of the complex or complexes formed between ethanol, m-cresol and the diluent, and of the complex formation constants, was pursued by two methods. The first involved assuming the stoichiometry and curve fitting the experimental data using the complex formation constants as independent parameters. The second method involved a regression of the experimental data to get the stoichiometries and complex formation constants.

For both methods, several other interactions had to be accounted for in addition to the formation of the ethanol/m-cresol complex. The other interactions that were considered to be of possible importance were water/m-cresol, water/diluent, diluent/ethanol, diluent/m-cresol, diluent/complex and m-cresol oligamerization. These interactions were considered for ethanol, but not for butanols, because the ethanol data extended to substantially higher concentrations of ethanol and m-cresol, some interactive diluents were used and co-extraction of water was much greater.

From Figures 1.1, 4.2 and 4.4 as well as Appendix B, the

distribution ratios and selectivities for toluene and chloroform can be compared. It can be seen that the two diluents do not interact with ethanol with equal strength. While the interactions of the diluents with ethanol are different, in comparison to the values for m-cresol, the differences between them are relatively insignificant. This leads to the conclusion that the interaction between the diluent and ethanol is relatively weak compared to that between m-cresol and ethanol. For this reason, other than for the solvation of ethanol into the diluent, the interaction between diluent and ethanol was not taken into account.

From Figure 4.3, at low concentrations of m-cresol, neither the chloroform nor the toluene has a large affinity for the m-cresol. This is demonstrated by the low distribution ratios for m-cresol, compared to the distribution ratios for n-butyl acetate which can hydrogen bond to the m-cresol. Thus the diluent/m-cresol interaction was considered to be small. As was demonstrated in Chapter 4, the presence of ethanol does not affect the extraction of water. The converse, the presence of water not affecting the extraction of ethanol, is also assumed to be true and the interaction of water and ethanol is not included in the calculations.

The diluent/complex and m-cresol oligamerization interactions were accounted for by inclusion of the 1:1:1 complex and by calculation of unassociated m-cresol, m-cresol dimer and trimer concentrations. Only dimer and trimer were used for the oligamerization of m-cresol. There is much disagreement about what types of aggregates are formed by phenols. Since the objective of incorporating the self-association of

m-cresol was to obtain an apparent concentration of unassociated m-cresol, one model system (1-2-3) was used with the experimentally determined formation constants measured in carbon tetrachloride, $K_{C2}=0.8$ L/mol and $K_{C3}=5.0$ L/mol (Wooley and Rushforth, 1974).

In order to incorporate the interaction of the active diluent, two complexes were used simultaneously, ethanol/m-cresol and ethanol/m-cresol/chloroform.

$$[E]_{o,T} = [EC] + [ECCl] \quad (5.9)$$

An apparent concentration of m-cresol was found by including the dimer and trimer in the ethanol equivalent to Equation 5.5.

$$[C]_{o,T} = [C]_o + 2[C_2]_o + 3[C_3]_o + [complex]_o \quad (5.10)$$

While the iterative procedures described below could all have been performed as a self-contained computer program, the iteration was done by hand. For the calculations with chloroform as the diluent, some of the iterative calculations showed instability and divergence. Due to the lack of precision in the data and the relatively low number of experimental points, alternate methods for carrying out the regression were not pursued.

5.2.1 Curve Fitting

Since the butanol data were fit well by use of a 1:1 complex, it was initially assumed that the ethanol data could also be fit using a 1:1 complex in the law of mass action model. However, in comparing the shape of the experimental distribution ratio data with the curve

generated by assuming that there is a 1:1 complex, it was noted that the extraction data with toluene as diluent did not resemble the 1:1 curve. Curves for several other complexes were generated and it was noted that the 1:2 curve resembled the toluene extraction data. It was also noted that the 1:1:1 complex did not model the chloroform extraction data particularly well by itself, but when it was combined with a 1:2 complex, the fit was much better. Some sample generated curves of distribution ratio versus m-cresol concentration for 1:1, 1:2, 1:3 ethanol/m-cresol, 1:1:1 and 1:1:2 ethanol/m-cresol/diluent complexes are shown in Figure 5.3.

The procedure used to generate the curves and determine the best fit for the complex formation constant is shown below.

From the curvatures of plots of the experimental data, it was determined that the dominant complex present was 1:2 ethanol/m-cresol for extraction of ethanol by m-cresol in toluene. For extraction of ethanol by m-cresol in chloroform, two complexes dominate, the 1:2 and the 1:1:1. The complexes assumed to be present are by no means the only ones allowed nor are they necessarily the actual complexes. However they fit the data reasonably well.

Both the 1:2 and the 1:1:1 complexes can also be thought of as solvated 1:1 complexes. The complex that is being formed must somehow be solvated by the solvent phase. The composition of the solvent changes as the initial concentration of m-cresol increases. The distribution ratio is then dependent on the solvent composition not only through formation of the 1:1 complex but also through changes in the ability of the non-complexed solvent to solvate the complex. Thus

Figure 5.3 Distribution ratios for extraction of ethanol vs. equilibrium total m-cresol concentration in the organic phase, mol/L, for different stoichiometries of the complex.

the solvation ability of the solvent must be taken into account. The additional m-cresol or chloroform would then modify the complex formation constant to account for the change in the solvation (i.e., the activity coefficient) of the complex in the mixed solvent as it changes from pure diluent to pure extractant. m-Cresol would solvate the complex better than does toluene, and chloroform would solvate the complex better than does m-cresol.

For extraction in the toluene diluent, the complexation between ethanol and m-cresol was fit to the 1:2 model

$$(E)_a + 2(C)_o \rightleftharpoons (EC_2)_o \quad (5.11)$$

with the equilibrium complex formation constant

$$K_{12} = \frac{[EC_2]_o}{[E]_a [C]_o^2} \quad (5.12)$$

The value for the complex formation constant was determined by minimizing the summation of the differences between the experimentally measured organic phase concentrations of m-cresol and the total m-cresol calculated from the following equation

$$[C]_{o,T} = [C]_o + 2[C_2]_o + 3[C_3]_o - 2[EC_2]_o \quad (5.13)$$

It is also assumed that all of the ethanol in the organic phase, less the ethanol that is solvated by the toluene, is complexed by the m-cresol.

$$[EC_2]_o = [E]'_{o,T} \quad (5.14)$$

$$[E]'_{o,T} = [E]_{o,T} - \theta \cdot [E]_{o,tol} \quad (5.15)$$

The unassociated m-cresol concentration was calculated from the aqueous ethanol concentration using Equation 5.12, rearranged to Equation 5.16, and assuming an initial value for K_{12} .

$$[C]_o^2 = \frac{[EC_2]_o}{K_{12}[E]_a} \quad (5.16)$$

The formation of dimers and trimers of m-cresol is described by the following equations

$$2(C)_o \rightleftharpoons (C_2) \quad (5.17)$$

$$3(C)_o \rightleftharpoons (C_3) \quad (5.18)$$

with formation constants

$$K_{c_2} = \frac{[C_2]_o}{[C]_o^2} \quad (5.19)$$

$$K_{c_3} = \frac{[C_3]_o}{[C]_o^3} \quad (5.20)$$

The total m-cresol concentration can be calculated from Equation 5.13. This is subtracted from the experimentally measured organic phase m-cresol concentration. The summation of the absolute values of the squares of the differences is the error.

$$Error = \sum \left| [C]_{o,T} - [C]_{o,Total} \right|^2 \quad (5.21)$$

The calculation is then repeated for new K_{12} , chosen manually, until a minimum in the error is located. The results are shown in Table 5.3.

Complex Formation Constants for Ethanol
and m-Cresol from Curve Fitting

Toluene Diluent

<u>Temperature (°C)</u>	<u>K₁₂</u>	<u>K₁₁₁</u>
Dilute:		
0	2.13	
25	2.77	
50	3.96	
Concentrated:		
0	2.71	
25	3.24	
50	4.15	

Chloroform Diluent

Dilute:		
0	2.13	0.039
25	2.77	0.036
50	3.96	0.129
Concentrated:		
0	2.71	0.048
25	3.24	0.120
50	4.15	0.121

'Dilute' refers to extractions in which the initial concentration of ethanol was 0.1, 0.3 or 0.5 mol/L and that of m-cresol was 1.0 mol/L or less.

'Concentrated' refers to extractions in which the initial concentration of ethanol was 1.0 mol/L and that of m-cresol was from 0 to 100% (9.56 mol/L).

In order to calculate predicted curves for distribution ratio versus m-cresol concentration, a series of organic phase ethanol concentrations was assumed. The aqueous phase ethanol concentration was calculated based on the ethanol mass balance.

$$[E]_T = [E]_{o,T} + [E]_a \quad (5.22)$$

The distribution ratio was calculated as

$$D = \frac{[E]_{o,T}}{[E]_a} \quad (5.23)$$

The organic phase unassociated m-cresol concentration was calculated from Equation 5.16. Using Equations 5.19 and 5.20, the dimer and trimer concentrations were then calculated. Equation 5.13 was used to get the total concentration of m-cresol in the organic phase. The predicted distribution ratio is plotted versus the total m-cresol concentration, and are compared to the experimental data in Figures 5.4 - 5.9. There is good agreement between the experimental points and the predicted curves.

In addition to the 1:2 complex, when chloroform was the diluent, a 1:1:1 complex was used to fit the data.

$$(E)_a + (C)_o + (Cl)_o \rightleftharpoons (ECCl)_o \quad (5.24)$$

with the equilibrium complex formation constant

$$K_{111} = \frac{[ECCl]_o}{[E]_a [C]_o [Cl]_o} \quad (5.25)$$

The same values for the 1,2 complexation constant as found for the toluene data were used for the chloroform case.

Figure 5.4 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in toluene, mol/L, 0°C. Dilute concentration range.

Figure 5.5 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in toluene, mol/L, 25°C. Dilute concentration range.

Figure 5.6 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in toluene, mol/L, 50°C. Dilute concentration range.

Figure 5.7 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in toluene, mol/L, 0°C. Concentrated solutions.

Figure 5.8 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in toluene, mol/L, 25°C. Concentrated solutions.

Figure 5.9 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in toluene, mol/L, 50°C. Concentrated solutions.

The procedure used was the same, but some of the equations were modified to account for the second complex. Equation 5.13 and 14 were replaced respectively by

$$[C]_{o,T} = [C]_o + 2[C_2]_o + 3[C_3]_o + [ECCl]_o + 2[EC_2]_o \quad (5.26)$$

$$[E]_{o,T} = [EC_2] + [ECCl] \quad (5.27)$$

The interaction with m-cresol and water was left out of Equation 5.26 because it is postulated that the water/m-cresol complex is able to interact with alcohols as if it were just m-cresol. Equations 5.16, 5.25, 5.26 and 5.27 were combined to get the concentration of unassociated m-cresol

$$[C]_o = \frac{-K_{111}[E]_o[Cl]_o + \sqrt{(K_{111}[E]_o[Cl]_o)^2 + 4K_{12}[E]_o[E]_{o,T}}}{2K_{12}[E]_o} \quad (5.28)$$

Since the concentration must be a positive quantity, only the positive root was used.

For the calculation of the predicted distribution ratio the procedure was also the same as for toluene diluent but with the modified equations. In addition the concentration of free chloroform was calculated by subtracting the amount of chloroform in the complex from the volume fraction of chloroform multiplied by the concentration of pure chloroform, less that in the 1:1:1 complex.

$$[Cl] = 12.33 \cdot 0 - [ECCl] \quad (5.29)$$

This leads to an iterative calculation since the concentration of chloroform was used to calculate the concentration of unassociated m-

cresol in Equation 5.29. However the calculation converged readily, in most cases, with realistic assumptions for the initial chloroform values.

The results of the curve fitting for chloroform diluent are given in Table 5.3. They also are plotted and compared to the experimental data in Figures 5.10 - 5.15. The agreement between the experimental data and the predicted curves is not quite as good as for the toluene case, but the model still predicts the experimental points fairly well. Only some of the points at the highest m-cresol concentrations are not predicted well. From Figure 5.3, the 1:1:2 complex is capable of rationalizing this curvature but, when it is included instead of the 1:1:1 complex, tends to cause the ideal curve to vary too much from the rest of the experimental points. Since it was desirable to avoid one more fittable parameter, the 1:1:1 complex was chosen.

5.2.2 Multiple Linear Regression

This method uses the same complexation equations as were used in section 5.2.1 (Equations 5.11, 5.12, 5.24 and 5.25) but calculates the stoichiometries of the complex or complexes formed as well as the value of each complex formation constant. The equivalent equations then become

$$n(E)_a + m(C)_o \rightleftharpoons (E_n C_m)_o \quad (5.30)$$

$$K_{nm} = \frac{[E_n C_m]_o}{[E]_a^n [C]_o^m} \quad (5.31) \quad --$$

$$n'(E)_a + m'(C)_o + p(Cl)_o \rightleftharpoons (E_{n'} C_{m'} Cl_p)_o \quad (5.32)$$

Figure 5.10 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in chloroform, mol/L, 0°C. Dilute concentration range.

Figure 5.11 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in chloroform, mol/L, 25°C. Dilute concentration range.

Figure 5.12 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in chloroform, mol/L, 50°C. Dilute concentration range.

Figure 5.13 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in chloroform, mol/L, 0°C. Concentrated solutions.

Figure 5.14 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in chloroform, mol/L, 25°C. Concentrated solutions.

Figure 5.15 Comparison of predicted and experimental ethanol distribution ratios versus equilibrium m-cresol concentration in chloroform, mol/L, 50°C. Concentrated solutions.

$$K_{n'm'p} = \frac{[E_n \cdot C_m \cdot Cl_p]_o}{[E]_o^n [C]_o^{m'} [Cl]_o^p} \quad (5.33)$$

As in the previous section, one complex is assumed to be present for the case of the toluene diluent and two for the chloroform diluent. However the stoichiometry is now allowed to vary for each of the complexes rather than being assumed.

All the apparent concentrations were first estimated assuming initial values for each of the stoichiometries and for the complex formation constant. Then the multiple linear regression was carried out for the logarithmic form of the concentration. The procedure was then repeated using the results of the previous regression in an iterative procedure until the results converged.

In the case of chloroform, the stoichiometric coefficients for the two complexes were each allowed to vary independently of the value for the other complex. This was done primarily because it was easier to calculate without the additional restraint of forcing the two complexes to have the same stoichiometries for ethanol and m-cresol. Also there is no reason, a priori, to assume the stoichiometries for ethanol and m-cresol should be the same in each of the complexes. In fact, with the changing composition of the solvent taken into account, there is reason to believe that the apparent stoichiometries should be different, at least in the case of m-cresol.

5.2.2.1 Unassociated m-Cresol Concentration

To calculate the concentration of unassociated m-cresol with toluene as the diluent, the following equations were used. The total

amount of m-cresol in the organic phase is shown in Equation 5.13. The equilibrium complex formation constants for the m-cresol dimer and trimer are shown in Equations 5.19 and 5.20. Combining these equations along with Equation 5.12 results in

$$[C]_{o,T} = [C]_o + 2K_{C_2}[C]_o^2 + 3K_{C_3}[C]_o^3 + mK_{nm}[E]_a^n[C]_o^m \quad (5.34)$$

Reorganizing the equation in terms of $[C]_o$

$$[C]_o^3 + \frac{2K_{C_2} + mK_{nm}[E]_a^n[C]_o^m}{3K_{C_3}}[C]_o^2 + \frac{1}{3K_{C_3}}[C]_o - \frac{[C]_{o,T}}{3K_{C_3}} = 0 \quad (5.35)$$

Equation 5.35 is a third-order polynomial in $[C]_o$. The method of solving it is outlined in Appendix C.

For the chloroform diluent, the $n':m':p$ complex is also present. However the procedure for the calculation of the unassociated m-cresol concentration is the same, except that Equations 5.13, 5.34 and 5.35 are replaced by the following

$$[C]_{o,T} = [C]_o + 2[C_2]_o + 3[C_3]_o + m[E_n C_m]_o + m'[E_{n'} C_{m'} Cl_p] \quad (5.36)$$

$$[C]_{o,T} = [C]_o + 2K_{C_2}[C]_o^2 + 3K_{C_3}[C]_o^3 + mK_{nm}[E]_a^n[C]_o^m + m'K_{n'm'p}[E]_a^{n'}[C]_o^{m'}[Cl]_o^p \quad (5.37)$$

$$[C]_o^3 + \frac{2K_{C_2} + mK_{nm}[E]_a^n[C]_o^m}{3K_{C_3}}[C]_o^2 + \frac{1 + m'K_{n'm'p}[E]_a^{n'}[C]_o^{m'}[Cl]_o^p}{3K_{C_3}}[C]_o - \frac{[C]_{o,T}}{3K_{C_3}} = 0 \quad (5.38)$$

Equation 5.38 is of the same type as Equation 5.35. The solution procedure was therefore similar and is shown in Appendix C.

5.2.2.2 Unassociated Ethanol Concentration

When the diluent was toluene, to calculate the concentration of complexed ethanol in the organic phase, the amount of ethanol in the organic phase solvated by the diluent was subtracted from the total concentration of ethanol in the organic phase, as was done in Equation 5.15. Under the assumption that all other ethanol is complexed, the concentration of the complex is then be given by Equation 5.14.

With the second complex present when chloroform is the diluent, Equation 5.15 is still used but Equation 5.14 is replaced by the following two equations, one for each complex, which multiply the total complexed ethanol in the organic phase by the fraction of the total ethanol present in each complex. The fraction of ethanol in each complex is calculated based on assumed stoichiometries and complex formation constants.

$$[E_n C_m] = \frac{1}{n} [E]_{o,T} \frac{K_{nm} [E]_a^n [C]_o^m}{[complex]_{o,T}} \quad (5.39)$$

$$[E_n \cdot C_m \cdot Cl_p] = \frac{1}{n} [E]_{o,T} \frac{K_{n \cdot m \cdot p} [E]_a^n [C]_o^m [Cl]_o^p}{[complex]_{o,T}} \quad (5.40)$$

$$[complex]_{o,T} = K_{nm} [E]_a^n [C]_o^m + K_{n \cdot m \cdot p} [E]_a^n [C]_o^m [Cl]_o^p$$

The logarithms of the concentrations of the two complexes are regressed separately along with the other necessary logarithmic concentrations to solve for new values of the stoichiometries and complex formation constants. Unlike in the curve-fitting analysis, the stoichiometries of ethanol and m-cresol are allowed to be different in the two complexes.

5.2.2.3 Simultaneous Linear Regression

The procedure used is the same for both toluene and chloroform diluents with the removal of the X_3 terms in the case of toluene.

For the chemical complexation reaction in Equation 5.24 with the equilibrium constant from Equation 5.25, the equilibrium mass-action law equation can be rewritten as

$$\log([complex]) = n' \log([E]_o) + m' \log([C]_o) + p \log([Cl]_o) + \log(n \cdot K_{n \cdot m \cdot p}) \quad (5.41)$$

There will be z equations of the type in Equation 5.41, one for each set of data points. The multiple linear regression method, detailed in Appendix C (Bevington, 1969), can be used to obtain the stoichiometries and complex formation constant.

The results of the multiple regressions for both diluents are shown in Table 5.4. For the toluene diluent, the indicated stoichiometries and complex formation constants are not particularly close to the assumed 1:2 ratio. Since this is an average value, it may reflect a combination of 1:1 and 1:2 complexes but there is no way to tell by the methods used here. There could be other complex ratios included also, or the effects could be ones of general solvation. Rather, most of the stoichiometries are about 1.5:1. The results for the chloroform diluent in dilute solution are also not very near the predicted values from the curve fitting. In addition, some of the dilute solution results show negative stoichiometries for chloroform. In dilute solutions, the variation in chloroform concentration is small, which can account for that problem. Part of the problem is

TABLE 5.4

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Stoichiometries and Complex Formation Constants
for Ethanol and m-Cresol
(concentrated and dilute as in Table 5.3)

Toluene Diluent

Dilute:	Temperature (°C)		
	0	25	50
n	1.06±0.06	1.08±0.04	0.96±0.06
m	1.52±0.06	1.54±0.05	1.46±0.08
K _{nm}	1.17±0.19	1.43±0.19	1.47±0.31
Concentrated:			
n	1.04±0.32	1.52±0.32	1.07±0.22
m	1.56±0.28	2.82±0.26	1.67±0.18
K _{nm}	4.02±0.35	6.60±0.48	6.13±0.31

Chloroform Diluent

Dilute:			
n	1.03±0.05	1.49±0.04	1.33±0.06
m	1.46±0.06	2.16±0.04	1.86±0.05
n'	0.47±0.38	1.48±0.04	1.32±0.05
m'	0.82±0.08	1.24±0.14	0.60±0.10
p	-0.35±0.72	2.48±1.76	-4.12±1.76
K _{nm}	2.02±0.26	8.35±0.31	3.95±0.54
K _{nmp}	0.20±0.05	0.01±0.01	0.02±0.01
Concentrated:			
n	1.05±0.27	1.46±0.04	0.62±0.07
m	0.77±0.06	1.75±0.16	1.64±0.04
n'	1.05±0.42	0.42±0.04	0.64±0.06
m'	0.75±0.22	0.68±0.08	0.62±0.11
p	1.01±0.03	1.03±0.02	1.01±0.02
K _{nm}	4.16±0.15	3.07±0.03	2.95±0.04
K _{nmp}	0.12±0.01	0.06±0.01	0.12±0.01

probably also due to the assumption that the m-cresol dimer and trimer formation constants are unchanged, not only in a more active diluent like chloroform, but also at different concentrations of m-cresol. This may also account for the variation in results for the concentrated solutions in toluene.

Another problem is that the solution is probably made up of other complexes and/or general solvation in addition to the two complexes assumed in these models. As was mentioned earlier, this type of model gives an average ratio for the complex. It does not identify a particular molecular species since there are at most two complexes allowed in the model. A larger number of complexes could be accounted for in principle. However, there is a limit to the usefulness of incorporating additional species in either of the modeling approaches since the experimental data are probably not plentiful or precise enough to warrant fitting parameters for more than the few complexes used here.

Despite the limitations of the regression model and the line fitting results, there is a strong indication for the formation of a complex with m-cresol in both a toluene and a chloroform diluent. The stoichiometry of the complex appears to be 1:1 from the butanol results as well as the results from the curve fitting section, with the change in solvent from pure diluent to pure extractant accounted for. However the results of the multiple regression do not correlate closely enough with the other results to substantiate the 1:1 complex.

5.2.3 Enthalpy of Complexation

From the complex formation constants the enthalpy of complexation can be calculated via the Gibbs-Helmholtz equation in the form

$$\frac{d(\ln K_{1,2})}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{\text{complex}}}{R} \quad (5.42)$$

In order to use this equation, the stoichiometries must be the same. For this reason, the complex formation constants resulting from the curve fitting were used instead of the results of the regression. The results are shown in Table 5.5 and Figure 5.16. These enthalpies include the enthalpy of phase change, since the complex formation constants are heterogeneous.

5.3 WATER

In chapter 4, it was shown that the presence of ethanol did not affect the extraction of water by m-cresol in either toluene or chloroform. It is assumed that the corollary is also true; that the presence of water in the organic phase does not affect the extraction of ethanol by m-cresol. However it would be interesting to compare the apparent stoichiometry and complex formation constant for ethanol and water extracted with m-cresol.

Using the experimental data obtained in the absence of ethanol, the apparent stoichiometry and formation constant for the water/m-cresol complex were found. Since it was found that an alcohol with a hydrogen bonded water attached to it still has the same strength of interaction with other alcohols (Huyskens et al., 1980), the

TABLE 5.5

Apparent Enthalpy of Complexation for Ethanol
and m-Cresol
(dilute and concentrated as in Table 5.3)

Diluent	$\Delta H_{\text{complex}}$ (Kcal/mole)	
	<u>1:2</u>	<u>1:1:1</u>
Toluene	dilute	2.2
	concentrated	1.5
Chloroform	dilute	2.2 4.0
	concentrated	1.5 3.3

Figure 5.16 Natural logarithm of the complex formation constant versus the inverse of the temperature for the 1:2 and 1:1:1 complex for both dilute and concentrated solutions. The slope is used to calculate the enthalpy of formation of the complex.

oligamerization of m-cresol needs to be taken into account. The complexation reaction is

with a complex formation constant

$$K_{rs} = \frac{[W_r C_s]_o}{[W]_a^r [C]_o^s} \quad (5.44)$$

The procedure used is a combination of that used for butanol and that used for ethanol. The concentration of water/m-cresol complex is found as in equations 5.3 and 5.4 with water in place of butanol. The unassociated m-cresol concentration is found as in section 5.2.1, with water replacing ethanol. The stoichiometry and formation constant are found as in equation 5.4 used with water replacing butanol. The only differences are that there is only one complex assumed even in chloroform diluent and, since the water/m-cresol complex can interact with another m-cresol as if the water was not present (Huyskens et al. 1980), the unassociated m-cresol concentration is actually the sum of the m-cresol monomer, dimer and trimer.

$$[C]_o' = [C]_o + [C_2]_o + [C_3]_o \quad (5.45)$$

The results are shown in Figures 5.17 - 5.28 and in Table 5.6. The results for the complexation of water and m-cresol in both the toluene and chloroform diluents do not differ greatly. This agrees with the plots of water distribution ratios shown in Figures 4.18 - 4.23, which are nearly the same for both diluents.

In comparing the results with those for complexation of ethanol

TABLE 5.6

Apparent Stoichiometry and Complex Formation Constants
for Water and m-Cresol
(dilute and concentrated as in Table 5.3)

Toluene Diluent

Dilute:

<u>Temperature (°C)</u>	<u>s</u>	<u>K_{1s} (x10⁴)</u>
0	1.57±0.14	1.21±0.32
25	1.53±0.05	2.39±0.33
50	1.56±0.08	4.18±0.89

Concentrated:

<u>Temperature (°C)</u>	<u>s</u>	<u>K_{1s} (x10²)</u>
0	2.30±0.06	3.92±0.36
25	2.03±0.17	5.87±0.74
50	2.10±0.06	7.42±0.76

Chloroform Diluent

Dilute:

<u>Temperature (°C)</u>	<u>s</u>	<u>K_{1s} (x10⁴)</u>
0	1.63±0.08	2.02±0.50
25	1.31±0.28	2.18±0.21
50	1.09±0.06	2.13±0.41

Concentrated:

<u>Temperature (°C)</u>	<u>s</u>	<u>K_{1s} (x10²)</u>
0	1.86±0.18	1.33±0.37
25	1.46±0.12	1.29±0.26
50	1.76±0.08	2.39±0.34

Figure 5.17 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for dilute solutions of m-cresol in toluene, mol/L; 0°C.

Figure 5.18 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for dilute solutions of m-cresol in toluene, mol/L; 25°C.

Figure 5.19 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for dilute solutions of m-cresol in toluene, mol/L; 50°C.

Figure 5.20 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for concentrated solutions of m-cresol in toluene, mol/L; 0°C.

Figure 5.21 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for concentrated solutions of m-cresol in toluene, mol/L; 25°C.

Figure 5.22 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for concentrated solutions of m-cresol in toluene, mol/L; 50°C.

Figure 5.23 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for dilute solutions of m-cresol in chloroform, mol/L; 0°C.

Figure 5.24 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for dilute solutions of m-cresol in chloroform, mol/L; 25°C.

Figure 5.25 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for dilute solutions of m-cresol in chloroform, mol/L; 50°C.

Figure 5.26 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for concentrated solutions of m-cresol in chloroform, mol/L; 0°C.

Figure 5.27 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for concentrated solutions of m-cresol in chloroform, mol/L; 25°C.

Figure 5.28 Logarithmic plot of the modified distribution ratio for water in the absence of alcohol vs. the equilibrium total concentration of m-cresol (monomer, dimer and trimer) for concentrated solutions of m-cresol in chloroform, mol/L; 50°C.

(Table 5.5), it can be seen that the stoichiometry for complexation of ethanol and water is approximately the same for complexing with m-cresol. The principal difference is in the complex formation constant, which is much larger for ethanol. The magnitude of the difference seems to depend on the concentration, although it is at least two orders of magnitude. The reason for the difference in the order of magnitude for the complex formation constant of water and m-cresol between the concentrated and dilute solutions of m-cresol is unclear. The difference between the complexation constants for water and ethanol with m-cresol demonstrates a high degree of preference for m-cresol to complex with ethanol instead of water. This selectivity is partially offset by the much greater driving force for complexation of water, due to its much higher concentration (two orders of magnitude). The offsetting effect due to the increase in driving force correlates with Figures 4.6 - 4.11 which show a small (<10%) predicted rise in the distribution ratio of ethanol as the initial aqueous concentration of ethanol increases from 0.1 mol/L to 1.0 mol/L.

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6. PROPANOLS AND PROPANEDIOLS

For extraction of ethanol and butanol, direct application of the results of this work to an industrial process is rather unlikely. In the case of ethanol, distribution ratios are not great enough for extraction to compete effectively with distillation over the range of compositions where extraction is most effective. Extraction is a more likely process for removal of butanols from water, but attractively large distribution ratios can be obtained using simpler and cheaper solvents. Therefore there may be little or no incentive to use more expensive extractants such as phenols. Two types of alcohols, for which extraction may be useful and for which phenols would be good candidates as extractants, are the propanols and diols.

6.1 Propanol

For removal of propanols from dilute aqueous solutions, extraction is a possible competitor to distillation. Distillation is more complicated than for ethanol because of mid-range azeotropes and the closeness of the boiling points of water and propanols, particularly n-propanol (n-propanol-97°C; i-propanol-82°C). In addition, distribution ratios obtained with the more common solvents are rather low, as shown in Table 6.1. Phenol extractants, as exemplified by m-cresol, can provide much larger capacities for removal of the propanol, as reflected in the distribution ratio. The values of the distribution ratios for ethanol, propanols and butanols in various solvents can be compared in Tables 1.1, 1.2 and 6.1.

Figure 6.1 shows the measured distribution ratios for n-propanol

Figure 6.1 Distribution ratios for 0.5 mol/L initial aqueous n-propanol and i-propanol extracted by m-cresol in toluene, versus initial extractant concentration, 25°C.

Table 6.1
Distribution Ratios for Extraction of Propanols
with Various Solvents, 25°C
(Kertes and King, 1987)

Solvent	<u>Distribution Ratio</u>	
	n-	i-
-----	----	----
cyclohexane	0.03	0.02
benzene	0.23	0.11
carbon tetrachloride	0.12	0.04
diethyl ether	0.40	0.64
n-octanol	1.80	1.10
m-cresol	16.61	9.00

and i-propanol, respectively, extracted by m-cresol in toluene. In a similar manner as for ethanol and butanol, the distribution ratio is approximately linear with respect to the concentration of the extractant. Figure 6.2 compares the distribution ratios for ethanol, propanols and butanols extracted by m-cresol. The relative extractabilities of the propanols are, as expected, intermediate between those of ethanol and the butanols, though there is some overlap, namely n-propanol and t-butanol.

The distribution ratios of the different alcohols at a given extractant concentration lie in approximately the same ratio as the activity coefficients. Table 6.2 lists infinite dilution activity coefficients for each of the alcohols along with their distribution ratios for extraction from 0.5 mol/L initial aqueous concentration by 1.0 mol/L initial m-cresol concentration. The ratio of the activity coefficient to distribution ratio is roughly the same for all the alcohols, though there is some deviation. This extends the finding in Chapter 3 for butanols that the interaction with m-cresol and subsequent solvation of the resultant complex is nearly the same for each of the alcohols and that the difference in distribution ratios is largely due to the aqueous phase activity.

Distribution ratios for propanol are high enough to consider extraction as a method of separation but low enough that complex solvent systems are probably needed to make the process economical.

6.2 Propanediols

Because the boiling points are so far removed from that of water

Figure 6.2 Comparison of distribution ratios for 0.5 mol/L initial aqueous ethanol, propanols and butanols extracted by m-cresol in a non-interactive diluent, versus extractant concentration, 25°C.

Table 6.2

Comparison of Infinite Dilution Activity Coefficients and Measured Distribution Ratios for 0.5 mol/L Initial Aqueous Alcohol Concentration Extracted by 1.0 mol/L Initial m-Cresol, 25°C (Activity Coefficients from Butler et al., 1935)

Alcohol	γ	D	γ/D
-----	----	----	----
ethanol	3.7	0.24	15.4
n-propanol	14.4	1.63	8.8
i-propanol	7.7	0.80	9.6
n-butanol	52.9	3.59	14.7
i-butanol	43.2	3.33	13.0
s-butanol	25.1	1.72	14.6
t-butanol	11.8	1.14	10.4

(1,2-propanediol: 189°C; 1,3-propanediol: 213°C), distillation of the diol/water mixture is relatively straightforward. However, because the diols generally appear in dilute aqueous solutions, distillation is an energy-intensive process since the majority of the solution is water being vaporized and removed in the distillate. The energy cost is roughly equivalent to simply boiling the water, although multi-effect evaporation is possible and part of the energy may be reusable in the form of steam heating.

Extraction offers a method of circumventing the need to remove most of the solution in the distillate stream, because only a fraction of the water is co-extracted. Assuming the distribution ratio is high enough (substantially greater than one), the resultant organic phase will be a more concentrated solution of the diol and therefore have less volume than the aqueous feed. However, what is needed, and is elusive, is a solvent or extractant providing such a high distribution ratio.

Figure 6.3 shows distribution ratios measured for both 1,2- and 1,3-propanediol at various initial concentrations of m-cresol in m-xylene. Both diols are extracted approximately the same amount at a given extractant concentration. 1,2-Propanediol was also extracted with chloroform as the diluent. The same roughly linear relationship for distribution ratio versus extractant concentration is observed for larger concentrations of m-cresol when toluene is the diluent, as was seen for extraction of ethanol. The deviation from linearity that leads to curvature at lower concentrations of the extractant for the case of toluene as diluent is more pronounced, possibly due to the

Figure 6.3 Distribution ratios for 1.0 mol/L 1,2-propanediol and 1,3-propanediol extracted by m-cresol in several diluents, versus extractant concentration, 25°C.

lesser degree of physical solvation of the uncomplexed diol in the diluent in comparison with ethanol.

The plot of the distribution ratio for chloroform as diluent also shows the same type of relationship as was found in the case of extraction of ethanol. Ethanol is found in low concentrations (~0.75 wt%) in chloroform as a stabilizer. Ordinarily, the ethanol was removed by contacting the chloroform with water prior to making up the initial organic phase. Since the distribution ratio for ethanol is so low for extraction from water into chloroform, the ethanol preferentially transferred to the water phase. When this ethanol stabilizer was not removed from the chloroform prior to use of the chloroform as diluent, the ethanol apparently inhibited the complexation between the diol and the m-cresol by competing with the diol to interact with the m-cresol. This is reflected in the lower distribution ratio when ethanol was present.

The distribution ratios for the propanediols extracted by m-cresol are all less than unity. Therefore the extraction does not give a concentrating effect. This increases costs for extracting the propanediols, but does not necessarily preclude use of extraction. Because of the additional $-\text{CH}_2-$, the butanediols should have higher distribution ratios.

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APPENDIX A

Experimental measurements for batch equilibrium extractions of butanols.

Table A.1
Experimental measurements for n-butanol

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
0.050	0.300	0.108	0.192	0.032	0.024	0.75	-----	-----	-----
0.050	0.500	0.138	0.362	0.022	0.034	1.54	-----	-----	-----
0.050	0.700	0.170	0.530	0.018	0.038	2.11	-----	-----	-----
0.100	0.000	0.000	0.000	0.086	0.013	0.16	0.000	0.000	0.00
0.100	0.100	0.055	0.045	0.082	0.020	0.24	0.007	0.035	0.08
0.100	0.200	0.093	0.107	0.068	0.032	0.35	0.017	0.073	0.25
0.100	0.300	0.0129	0.171	0.056	0.044	0.75	0.029	0.104	0.52
0.100	0.500	0.160	0.340	0.040	0.062	1.55	0.049	0.176	1.22
0.100	0.700	0.180	0.520	0.030	0.070	2.33	0.057	0.241	1.90
0.100	0.900	0.188	0.712	0.028	0.076	2.71	0.063	0.300	2.25
0.100	1.000	0.191	0.809	0.024	0.066	2.75	0.053	0.330	2.21
0.200	0.300	0.108	0.182	0.102	0.096	0.94	-----	-----	-----
0.200	0.500	0.116	0.384	0.066	0.110	1.67	-----	-----	-----
0.200	0.700	0.184	0.516	0.064	0.156	2.38	-----	-----	-----
0.300	0.000	0.000	0.000	0.264	0.043	0.17	0.000	0.000	0.00
0.300	0.100	0.044	0.056	0.234	0.080	0.34	0.037	0.025	0.16
0.300	0.200	0.071	0.129	0.202	0.108	0.53	0.065	0.062	0.32
0.300	0.300	0.095	0.205	0.162	0.138	0.85	0.095	0.094	0.57
0.300	0.500	0.130	0.370	0.132	0.176	1.33	0.133	0.160	1.01
0.300	0.700	0.153	0.547	0.100	0.210	2.10	0.167	0.219	1.67
0.300	0.900	0.166	0.734	0.084	0.216	2.57	0.173	0.280	2.06
0.300	1.000	0.160	0.840	0.076	0.232	3.05	0.189	0.307	2.49

Table A.1 (continued)

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
0.400	0.300	0.104	0.196	0.228	0.218	0.96	-----	-----	-----
0.400	0.500	0.120	0.390	0.162	0.250	1.54	-----	-----	-----
0.400	0.700	0.170	0.530	0.122	0.294	2.41	-----	-----	-----
0.500	0.000	0.000	0.000	0.387	0.088	0.25	0.000	0.000	0.00
0.500	0.100	0.041	0.059	0.314	0.151	0.57	0.061	0.010	0.19
0.500	0.200	0.067	0.133	0.268	0.224	0.84	0.136	0.021	0.51
0.500	0.300	0.094	0.206	0.220	0.260	1.18	0.172	0.054	0.78
0.500	0.500	0.134	0.366	0.170	0.320	1.88	0.232	0.119	1.36
0.500	0.700	0.162	0.538	0.138	0.364	2.64	0.276	0.181	2.00
0.500	0.900	0.182	0.718	0.118	0.392	3.32	0.304	0.239	2.57
0.500	1.000	0.185	0.815	0.108	0.388	3.59	0.300	0.272	2.78

Table A.2
Experimental measurements for i-butanol

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
0.050	0.300	0.128	0.172	0.042	0.024	0.55	-----	-----	-----
0.050	0.500	0.158	0.342	0.032	0.034	1.07	-----	-----	-----
0.050	0.700	0.174	0.526	0.024	0.042	1.75	-----	-----	-----
0.100	0.000	0.000	0.000	0.080	0.012	0.20	0.000	0.000	0.00
0.100	0.100	0.053	0.047	0.078	0.024	0.31	0.012	0.035	0.15
0.100	0.200	0.093	0.107	0.068	0.028	0.41	0.016	0.074	0.23
0.100	0.300	0.115	0.185	0.060	0.040	0.67	0.028	0.112	0.47
0.100	0.500	0.144	0.356	0.040	0.056	1.40	0.044	0.183	1.10
0.100	0.700	0.170	0.530	0.034	0.068	2.00	0.056	0.243	1.65
0.100	0.900	0.172	0.728	0.026	0.070	2.69	0.058	0.305	2.23
0.100	1.000	0.173	0.827	0.024	0.072	3.03	0.060	0.332	2.50
0.200	0.300	0.104	0.196	0.132	0.088	0.67	-----	-----	-----
0.200	0.500	0.134	0.366	0.098	0.136	1.39	-----	-----	-----
0.200	0.700	0.152	0.548	0.074	0.148	2.00	-----	-----	-----
0.300	0.000	0.000	0.000	0.240	0.047	0.19	0.000	0.000	0.00
0.300	0.100	0.047	0.053	0.212	0.082	0.39	0.035	0.017	0.16
0.300	0.200	0.080	0.120	0.180	0.104	0.60	0.061	0.051	0.34
0.300	0.300	0.110	0.190	0.160	0.136	0.85	0.089	0.079	0.56
0.300	0.500	0.143	0.357	0.122	0.166	1.36	0.119	0.151	0.98
0.300	0.700	0.165	0.535	0.098	0.196	2.00	0.149	0.212	1.52
0.300	0.900	0.180	0.720	0.084	0.212	2.52	0.165	0.270	1.96
0.300	1.000	0.181	0.819	0.078	0.218	2.79	0.171	0.298	2.19

Table A.2 (continued)

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
0.400	0.300	0.080	0.220	0.278	0.186	0.67	-----	-----	-----
0.400	0.500	0.102	0.398	0.212	0.260	1.23	-----	-----	-----
0.400	0.700	0.124	0.576	0.172	0.316	1.84	-----	-----	-----
0.500	0.000	0.000	0.000	0.384	0.114	0.29	0.000	0.000	0.00
0.500	0.100	0.040	0.060	0.346	0.156	0.45	0.042	0.017	0.12
0.500	0.200	0.067	0.133	0.296	0.188	0.64	0.074	0.050	0.25
0.500	0.300	0.083	0.217	0.254	0.232	0.91	0.118	0.078	0.46
0.500	0.500	0.129	0.371	0.194	0.300	1.55	0.186	0.127	0.96
0.500	0.700	0.149	0.551	0.152	0.338	2.22	0.224	0.190	1.47
0.500	0.900	0.165	0.735	0.134	0.358	2.67	0.244	0.250	1.82
0.500	1.000	0.171	0.829	0.122	0.406	3.33	0.292	0.266	2.39

Table A.3
Experimental measurements for s-butanol

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
0.050	0.300	0.128	0.172	0.038	0.020	0.53	-----	-----	-----
0.050	0.500	0.164	0.336	0.028	0.030	1.07	-----	-----	-----
0.050	0.700	0.182	0.518	0.024	0.032	1.33	-----	-----	-----
0.100	0.000	0.000	0.000	0.092	0.010	0.13	0.000	0.000	0.00
0.100	0.100	0.052	0.048	0.094	0.012	0.15	0.002	0.040	0.02
0.100	0.200	0.085	0.115	0.070	0.032	0.49	0.022	0.070	0.31
0.100	0.300	0.122	0.178	0.064	0.044	0.72	0.034	0.100	0.53
0.100	0.500	0.142	0.358	0.056	0.052	1.14	0.042	0.176	0.75
0.100	0.700	0.148	0.552	0.040	0.052	1.35	0.042	0.252	1.05
0.100	0.900	0.188	0.712	0.036	0.052	1.50	0.042	0.301	1.17
0.100	1.000	0.207	0.793	0.034	0.058	1.76	0.048	0.323	1.41
0.200	0.300	0.108	0.192	0.160	0.082	0.54	-----	-----	-----
0.200	0.500	0.138	0.362	0.128	0.136	0.90	-----	-----	-----
0.200	0.700	0.182	0.518	0.118	0.138	1.17	-----	-----	-----
0.300	0.000	0.000	0.000	0.262	0.033	0.15	0.000	0.000	0.00
0.300	0.100	0.051	0.049	0.250	0.052	0.24	0.019	0.024	0.08
0.300	0.200	0.085	0.115	0.218	0.078	0.39	0.045	0.052	0.21
0.300	0.300	0.118	0.182	0.188	0.102	0.59	0.069	0.079	0.37
0.300	0.500	0.149	0.351	0.148	0.146	1.04	0.113	0.142	0.76
0.300	0.700	0.168	0.532	0.126	0.172	1.43	0.139	0.206	1.10
0.300	0.900	0.181	0.719	0.112	0.194	1.80	0.161	0.262	1.44
0.300	1.000	0.187	0.813	0.104	0.196	1.96	0.163	0.291	1.57

Table A.3 (continued)

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
0.400	0.300	0.084	0.216	0.312	0.170	0.54	-----	-----	-----
0.400	0.500	0.114	0.386	0.262	0.220	0.85	-----	-----	-----
0.400	0.700	0.132	0.568	0.210	0.256	1.22	-----	-----	-----
0.500	0.000	0.000	0.000	0.450	0.072	0.12	0.000	0.000	0.00
0.500	0.100	0.042	0.058	0.440	0.090	0.20	0.018	0.019	0.04
0.500	0.200	0.070	0.130	0.372	0.116	0.31	0.044	0.052	0.12
0.500	0.300	0.091	0.209	0.340	0.146	0.43	0.074	0.082	0.22
0.500	0.500	0.118	0.382	0.260	0.230	0.88	0.158	0.125	0.61
0.500	0.700	0.143	0.557	0.228	0.262	1.15	0.190	0.187	0.83
0.500	0.900	0.156	0.744	0.194	0.306	1.62	0.244	0.235	1.26
0.500	1.000	0.167	0.833	0.184	0.316	1.72	0.244	0.264	1.33

Table A.4
Experimental measurements for t-butanol

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
0.050	0.300	0.124	0.176	0.040	0.016	0.40	-----	-----	-----
0.050	0.500	0.136	0.364	0.038	0.024	0.63	-----	-----	-----
0.050	0.700	0.144	0.556	0.030	0.024	0.80	-----	-----	-----
0.100	0.000	0.000	0.000	0.084	0.005	0.07	0.000	0.000	0.00
0.100	0.100	0.060	0.040	0.082	0.010	0.12	0.005	0.032	0.06
0.100	0.200	0.092	0.108	0.080	0.016	0.20	0.011	0.075	0.14
0.100	0.300	0.141	0.159	0.068	0.026	0.38	0.021	0.100	0.31
0.100	0.500	0.182	0.318	0.054	0.038	0.70	0.033	0.170	0.61
0.100	0.700	0.199	0.501	0.048	0.046	0.96	0.041	0.237	0.85
0.100	0.900	0.229	0.671	0.046	0.046	1.00	0.041	0.292	0.89
0.100	1.000	0.238	0.762	0.042	0.044	1.05	0.039	0.319	0.93
0.200	0.300	0.108	0.192	0.172	0.064	0.37	-----	-----	-----
0.200	0.500	0.118	0.382	0.152	0.082	0.54	-----	-----	-----
0.200	0.700	0.152	0.548	0.134	0.112	0.84	-----	-----	-----
0.300	0.000	0.000	0.000	0.292	0.019	0.08	0.000	0.000	0.00
0.300	0.100	0.053	0.047	0.276	0.036	0.13	0.017	0.030	0.06
0.300	0.200	0.081	0.119	0.254	0.056	0.22	0.037	0.067	0.14
0.300	0.300	0.109	0.191	0.224	0.078	0.35	0.059	0.098	0.26
0.300	0.500	0.142	0.358	0.186	0.114	0.61	0.095	0.162	0.51
0.300	0.700	0.153	0.547	0.164	0.138	0.84	0.119	0.227	0.72
0.300	0.900	0.166	0.734	0.142	0.158	1.11	0.139	0.282	0.98
0.300	1.000	0.164	0.836	0.130	0.164	1.26	0.145	0.310	1.11

Table A.4 (continued)

$[B]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[B]_a$ (mol/L)	$[B]_o$ (mol/L)	D	$[B]_o$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
0.400	0.300	0.096	0.204	0.296	0.100	0.34	-----	-----	-----
0.400	0.500	0.126	0.374	0.272	0.148	0.54	-----	-----	-----
0.400	0.700	0.134	0.572	0.198	0.188	0.95	-----	-----	-----
0.500	0.000	0.000	0.000	0.484	0.034	0.07	0.000	0.000	0.00
0.500	0.100	0.068	0.032	0.432	0.058	0.13	0.024	0.010	0.06
0.500	0.200	0.094	0.106	0.410	0.084	0.20	0.050	0.049	0.12
0.500	0.300	0.108	0.162	0.398	0.124	0.31	0.090	0.060	0.23
0.500	0.500	0.199	0.301	0.330	0.180	0.55	0.146	0.110	0.44
0.500	0.700	0.230	0.470	0.282	0.220	0.78	0.186	0.171	0.66
0.500	0.900	0.248	0.652	0.244	0.260	1.07	0.226	0.226	0.93
0.500	1.000	0.258	0.742	0.228	0.260	1.14	0.226	0.257	0.99

APPENDIX B

Experimental measurements for batch equilibrium extractions of ethanol.

Table B.1
Experimental measurements for ethanol extracted by
m-cresol in toluene, 0°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_{o,T}$ (mol/L)	$[E]_{o,T}$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	D	$[E]'_{o,T}$ (mol/L)	$[C]_o$ (mol/L)	D_{mod}
0.100	0.00	0.00	0.00	0.000	0.095	0.001	0.00	0.000	0.00	0.00
0.100	0.10	0.03	0.06	0.002	0.095	0.001	0.02	0.001	0.04	0.02
0.100	0.20	0.05	0.15	0.003	0.094	0.001	0.03	0.002	0.09	0.03
0.100	0.30	0.06	0.24	0.004	0.092	0.001	0.05	0.003	0.12	0.04
0.100	0.50	0.07	0.43	0.007	0.086	0.002	0.08	0.006	0.18	0.07
0.100	0.70	0.08	0.62	0.010	0.086	0.003	0.11	0.009	0.22	0.11
0.100	0.90	0.08	0.82	0.012	0.082	0.004	0.15	0.012	0.25	0.15
0.100	1.00	0.09	0.91	0.014	0.082	0.004	0.17	0.013	0.27	0.16
0.300	0.00	0.00	0.00	0.003	0.282	0.000	0.01	0.000	0.00	0.00
0.300	0.10	0.03	0.06	0.006	0.264	0.001	0.02	0.003	0.04	0.01
0.300	0.20	0.05	0.15	0.010	0.257	0.001	0.04	0.007	0.09	0.03
0.300	0.30	0.06	0.24	0.014	0.259	0.001	0.05	0.011	0.12	0.04
0.300	0.50	0.07	0.43	0.024	0.258	0.002	0.09	0.021	0.18	0.08
0.300	0.70	0.08	0.62	0.034	0.229	0.003	0.15	0.031	0.22	0.14
0.300	0.90	0.08	0.82	0.042	0.241	0.004	0.18	0.039	0.25	0.16
0.300	1.00	0.09	0.91	0.047	0.228	0.004	0.21	0.044	0.27	0.19
0.500	0.00	0.00	0.00	0.005	0.454	0.001	0.01	0.000	0.00	0.00
0.500	0.10	0.03	0.06	0.010	0.441	0.000	0.02	0.005	0.04	0.01
0.500	0.20	0.05	0.15	0.017	0.424	0.001	0.04	0.012	0.09	0.03
0.500	0.30	0.06	0.24	0.026	0.426	0.001	0.06	0.020	0.12	0.05
0.500	0.50	0.07	0.43	0.041	0.408	0.002	0.10	0.035	0.18	0.09
0.500	0.70	0.08	0.62	0.058	0.383	0.002	0.15	0.052	0.22	0.14
0.500	0.90	0.08	0.82	0.070	0.383	0.003	0.18	0.065	0.25	0.17
0.500	1.00	0.09	0.91	0.079	0.387	0.004	0.20	0.074	0.26	0.19

Table B.1 (continued)
Experimental measurements for ethanol extracted by
m-cresol in toluene, 0°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	D	$[E]_{o}$ (mol/L)	$[C]_{o,mod}$ (mol/L)	D_{mod}
1.000	0.00	0.00	0.00	0.020	0.960	0.043	0.02	0.000	0.00	0.00
1.000	1.00	0.08	0.92	0.090	0.920	0.189	0.10	0.070	0.21	0.08
1.000	2.00	0.11	1.89	0.210	0.770	0.487	0.27	0.190	0.32	0.25
1.000	3.00	0.15	2.85	0.330	0.630	1.108	0.52	0.310	0.39	0.49
1.000	4.00	0.16	3.84	0.410	0.540	1.720	0.76	0.390	0.44	0.72
1.000	5.00	0.17	4.83	0.440	0.510	2.304	0.86	0.420	0.49	0.82
1.000	6.00	0.18	5.82	0.510	0.470	2.828	1.09	0.490	0.53	1.04
1.000	7.00	0.20	6.80	0.520	0.450	3.947	1.16	0.500	0.57	1.11
1.000	8.00	0.22	7.78	0.550	0.420	3.713	1.31	0.530	0.60	1.26
1.000	9.00	0.12	8.88	0.570	0.350	5.611	1.63	0.550	0.63	1.57
1.000	9.56	0.22	9.34	0.580	0.320	6.747	1.81	0.560	0.65	1.75

Table B.2
Experimental measurements for ethanol extracted by
m-cresol in toluene, 25°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_a$ (mol/L)	$[E]_o$ (mol/L)	$[W]_o$ (mol/L)	D	$[E]'_o$ (mol/L)	$[C]_{o,mod}$ (mol/L)	D_{mod}
0.100	0.00	0.00	0.00	0.000	0.099	0.001	0.00	0.000	0.00	0.00
0.100	0.10	0.04	0.06	0.002	0.098	0.001	0.02	0.001	0.05	0.01
0.100	0.20	0.05	0.15	0.004	0.096	0.001	0.04	0.003	0.10	0.04
0.100	0.30	0.06	0.24	0.005	0.094	0.001	0.06	0.005	0.14	0.05
0.100	0.50	0.07	0.43	0.010	0.090	0.002	0.11	0.009	0.20	0.10
0.100	0.70	0.08	0.62	0.013	0.086	0.003	0.15	0.013	0.24	0.14
0.100	0.90	0.08	0.82	0.017	0.083	0.004	0.21	0.017	0.28	0.20
0.100	1.00	0.09	0.91	0.019	0.081	0.004	0.23	0.019	0.30	0.23
0.300	0.00	0.00	0.00	0.009	0.290	0.001	0.03	0.000	0.00	0.00
0.300	0.10	0.04	0.06	0.013	0.286	0.001	0.05	0.004	0.05	0.01
0.300	0.20	0.05	0.15	0.018	0.279	0.001	0.06	0.009	0.10	0.03
0.300	0.30	0.06	0.24	0.024	0.256	0.001	0.09	0.015	0.14	0.06
0.300	0.50	0.07	0.43	0.035	0.252	0.002	0.14	0.026	0.20	0.10
0.300	0.70	0.08	0.62	0.047	0.250	0.003	0.19	0.038	0.24	0.15
0.300	0.90	0.08	0.82	0.058	0.241	0.004	0.24	0.049	0.28	0.20
0.300	1.00	0.09	0.91	0.065	0.237	0.005	0.27	0.056	0.29	0.24
0.500	0.00	0.00	0.00	0.014	0.482	0.001	0.03	0.000	0.00	0.00
0.500	0.10	0.04	0.06	0.023	0.479	0.001	0.05	0.009	0.05	0.02
0.500	0.20	0.05	0.15	0.032	0.462	0.001	0.07	0.018	0.10	0.04
0.500	0.30	0.06	0.24	0.041	0.452	0.001	0.09	0.027	0.14	0.06
0.500	0.50	0.07	0.43	0.061	0.440	0.002	0.14	0.047	0.20	0.11
0.500	0.70	0.08	0.62	0.081	0.422	0.003	0.19	0.067	0.24	0.16
0.500	0.90	0.08	0.82	0.100	0.405	0.004	0.25	0.086	0.28	0.21
0.500	1.00	0.09	0.91	0.109	0.399	0.005	0.27	0.095	0.29	0.24

Table B.2 (continued)
Experimental measurements for ethanol extracted by
m-cresol in toluene, 25°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_a$ (mol/L)	$[E]_o$ (mol/L)	$[W]_o$ (mol/L)	D	$[E]'_o$ (mol/L)	$[C]_{o,mod}$ (mol/L)	D_{mod}
1.000	0.00	0.00	0.00	0.064	0.920	0.136	0.07	0.000	0.00	0.00
1.000	1.00	0.15	0.85	0.124	0.732	0.466	0.17	0.060	0.20	0.08
1.000	2.00	0.32	1.68	0.255	0.601	0.620	0.42	0.191	0.30	0.32
1.000	3.00	0.49	2.51	0.336	0.521	0.756	0.64	0.271	0.37	0.52
1.000	4.00	0.62	3.38	0.392	0.465	1.378	0.84	0.328	0.42	0.71
1.000	5.00	0.78	4.22	0.440	0.417	1.922	1.06	0.375	0.47	0.90
1.000	6.00	0.16	5.84	0.494	0.363	3.067	1.36	0.429	0.53	1.18
1.000	7.00	0.22	6.78	0.516	0.341	4.000	1.51	0.452	0.57	1.33
1.000	8.00	0.22	7.78	0.551	0.305	6.100	1.81	0.487	0.60	1.60
1.000	9.00	0.24	8.76	0.581	0.276	6.589	2.10	0.516	0.62	1.87
1.000	9.56	0.20	9.36	0.587	0.270	7.422	2.17	0.522	0.64	1.94

Table B.3
Experimental measurements for ethanol extracted by
m-cresol in toluene, 50°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	D	$[E]'_o$ (mol/L)	$[C]_{o,mod}$ (mol/L)	D_{mod}
0.100	0.00	0.00	0.00	0.005	0.078	0.001	0.06	0.000	0.00	0.00
0.100	0.10	0.04	0.06	0.007	0.078	0.001	0.08	0.002	0.05	0.03
0.100	0.20	0.05	0.15	0.009	0.079	0.002	0.11	0.004	0.10	0.06
0.100	0.30	0.06	0.24	0.009	0.069	0.002	0.13	0.004	0.14	0.06
0.100	0.50	0.07	0.43	0.014	0.070	0.003	0.20	0.010	0.20	0.14
0.100	0.70	0.08	0.62	0.018	0.070	0.004	0.26	0.014	0.24	0.20
0.100	0.90	0.08	0.82	0.021	0.056	0.005	0.37	0.016	0.28	0.29
0.100	1.00	0.09	0.91	0.022	0.053	0.005	0.42	0.018	0.30	0.34
0.300	0.00	0.00	0.00	0.017	0.248	0.001	0.07	0.000	0.00	0.00
0.300	0.10	0.04	0.06	0.024	0.237	0.001	0.10	0.007	0.05	0.03
0.300	0.20	0.05	0.15	0.029	0.231	0.001	0.12	0.012	0.10	0.05
0.300	0.30	0.06	0.24	0.036	0.222	0.002	0.16	0.019	0.14	0.09
0.300	0.50	0.07	0.43	0.047	0.194	0.003	0.24	0.031	0.20	0.16
0.300	0.70	0.08	0.62	0.060	0.205	0.004	0.29	0.043	0.24	0.21
0.300	0.90	0.08	0.82	0.068	0.182	0.005	0.38	0.052	0.28	0.28
0.300	1.00	0.09	0.91	0.081	0.182	0.005	0.45	0.065	0.29	0.36
0.500	0.00	0.00	0.00	0.026	0.389	0.001	0.07	0.000	0.00	0.00
0.500	0.10	0.04	0.06	0.034	0.404	0.001	0.09	0.009	0.05	0.02
0.500	0.20	0.05	0.15	0.040	0.404	0.001	0.10	0.014	0.10	0.04
0.500	0.30	0.06	0.24	0.055	0.377	0.002	0.15	0.029	0.14	0.08
0.500	0.50	0.07	0.43	0.074	0.375	0.002	0.20	0.048	0.20	0.13
0.500	0.70	0.08	0.62	0.101	0.361	0.003	0.28	0.075	0.24	0.21
0.500	0.90	0.08	0.82	0.117	0.338	0.004	0.35	0.091	0.27	0.27
0.500	1.00	0.09	0.91	0.128	0.335	0.005	0.38	0.102	0.29	0.31

Table B.3 (continued)
Experimental measurements for ethanol extracted by
m-cresol in toluene, 50°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	D	$[E]'_o$ (mol/L)	$[C]_{o,mod}$ (mol/L)	D_{mod}
1.000	0.00	0.00	0.00	0.040	0.920	0.204	0.04	0.000	0.00	0.00
1.000	1.00	0.07	0.93	0.250	0.600	0.418	0.42	0.210	0.18	0.35
1.000	2.00	0.12	1.88	0.410	0.530	0.982	0.77	0.370	0.27	0.70
1.000	3.00	0.16	2.84	0.500	0.470	2.415	1.06	0.460	0.34	0.98
1.000	4.00	0.18	3.82	0.520	0.420	3.440	1.24	0.480	0.40	1.14
1.000	5.00	0.20	4.80	0.560	0.360	3.529	1.56	0.520	0.45	1.44
1.000	6.00	0.20	5.80	0.570	0.340	4.904	1.68	0.530	0.50	1.56
1.000	7.00	0.22	6.78	0.580	0.310	5.639	1.87	0.540	0.54	1.74
1.000	8.00	0.24	7.76	0.610	0.280	6.724	2.18	0.570	0.57	2.04
1.000	9.00	0.25	8.75	0.620	0.260	7.778	2.38	0.580	0.60	2.23
1.000	9.56	0.26	9.30	0.620	0.250	8.505	2.48	0.580	0.62	2.32

Table B.4
Experimental measurements for ethanol extracted by
m-cresol in chloroform, 0°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	$[Cl]_{o,i}$ (mol/L)	D	$[E]_{,o}$ (mol/L)	$[C]'_o$ (mol/L)	$[Cl]_o$ (mol/L)
0.100	0.00	0.00	0.00	0.002	0.166	0.001	12.33	0.01	0.000	0.00	12.33
0.100	0.10	0.04	0.06	0.009	0.164	0.001	12.20	0.05	0.007	0.05	12.20
0.100	0.20	0.05	0.15	0.014	0.162	0.001	12.07	0.09	0.012	0.10	12.07
0.100	0.30	0.06	0.24	0.018	0.157	0.002	11.94	0.11	0.016	0.13	11.94
0.100	0.50	0.07	0.43	0.025	0.147	0.003	11.69	0.17	0.024	0.19	11.69
0.100	0.70	0.08	0.62	0.033	0.147	0.004	11.43	0.22	0.031	0.24	11.43
0.100	0.90	0.08	0.82	0.039	0.140	0.005	11.17	0.28	0.037	0.27	11.17
0.100	1.00	0.09	0.91	0.041	0.137	0.006	11.05	0.30	0.039	0.29	11.05
0.300	0.00	0.00	0.00	0.006	0.319	0.001	12.33	0.02	0.000	0.00	12.33
0.300	0.10	0.04	0.06	0.027	0.328	0.002	12.20	0.08	0.021	0.05	12.20
0.300	0.20	0.05	0.15	0.038	0.320	0.001	12.07	0.12	0.032	0.09	12.07
0.300	0.30	0.06	0.24	0.048	0.310	0.004	11.94	0.15	0.042	0.13	11.94
0.300	0.50	0.07	0.43	0.068	0.297	0.003	11.69	0.23	0.062	0.19	11.69
0.300	0.70	0.08	0.62	0.085	0.284	0.003	11.43	0.30	0.079	0.23	11.43
0.300	0.90	0.08	0.82	0.096	0.269	0.005	11.17	0.36	0.090	0.27	11.17
0.300	1.00	0.09	0.91	0.105	0.265	0.006	11.05	0.40	0.099	0.28	11.05
0.500	0.00	0.00	0.00	0.008	0.508	0.001	12.33	0.02	0.000	0.00	12.33
0.500	0.10	0.04	0.06	0.047	0.494	0.001	12.20	0.09	0.039	0.05	12.20
0.500	0.20	0.05	0.15	0.063	0.483	0.002	12.07	0.13	0.056	0.09	12.07
0.500	0.30	0.06	0.24	0.077	0.471	0.003	11.94	0.16	0.069	0.12	11.94
0.500	0.50	0.07	0.43	0.107	0.445	0.003	11.69	0.24	0.099	0.18	11.69
0.500	0.70	0.08	0.62	0.137	0.424	0.003	11.43	0.32	0.129	0.22	11.43
0.500	0.90	0.08	0.82	0.159	0.404	0.005	11.17	0.39	0.151	0.26	11.17
0.500	1.00	0.09	0.91	0.171	0.391	0.005	11.05	0.44	0.163	0.27	11.05

Table B.4 (continued)
Experimental measurements for ethanol extracted by
m-cresol in chloroform, 0°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	$[Cl]_{o,i}$ (mol/L)	D	$[E]_o$ (mol/L)	$[C]_o'$ (mol/L)	$[Cl]_o$ (mol/L)
1.000	0.00	0.00	0.00	0.030	1.280	0.081	12.33	0.02	0.000	0.00	12.33
1.000	1.00	0.06	0.94	0.350	1.000	0.392	11.05	0.35	0.320	0.11	10.78
1.000	2.00	0.09	1.91	0.440	0.670	0.817	9.74	0.66	0.410	0.23	9.49
1.000	3.00	0.08	2.92	0.560	0.600	0.994	8.46	0.93	0.530	0.31	8.20
1.000	4.00	0.12	3.88	0.630	0.550	1.783	7.18	1.15	0.600	0.37	6.94
1.000	5.00	0.14	4.86	0.630	0.480	2.006	5.89	1.31	0.600	0.43	5.71
1.000	6.00	0.18	5.82	0.630	0.440	2.972	4.59	1.43	0.600	0.48	4.44
1.000	7.00	0.20	6.80	0.620	0.400	3.922	3.30	1.55	0.590	0.53	3.20
1.000	8.00	0.22	7.78	0.620	0.380	4.833	2.02	1.63	0.590	0.57	1.96
1.000	9.00	0.24	8.76	0.620	0.370	5.883	0.72	1.68	0.590	0.60	0.69
1.000	9.56	0.34	9.22	0.620	0.360	6.472	0.00	1.72	0.590	0.62	0.00

Table B.5
Experimental measurements for ethanol extracted by
m-cresol in chloroform, 25°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	$[Cl]_{o,i}$ (mol/L)	D	$[E]_o$ (mol/L)	$[C]_o'$ (mol/L)	$[Cl]_o$ (mol/L)
0.100	0.00	0.00	0.00	0.014	0.125	0.002	12.33	0.11	0.000	0.00	12.33
0.100	0.10	0.04	0.06	0.017	0.139	0.003	12.20	0.13	0.003	0.05	12.20
0.100	0.20	0.05	0.15	0.020	0.131	0.004	12.07	0.15	0.006	0.09	12.07
0.100	0.30	0.06	0.24	0.026	0.132	0.002	11.94	0.20	0.012	0.13	11.94
0.100	0.50	0.07	0.43	0.031	0.117	0.003	11.69	0.27	0.017	0.19	11.68
0.100	0.70	0.08	0.62	0.040	0.122	0.005	11.43	0.33	0.026	0.24	11.42
0.100	0.90	0.08	0.82	0.046	0.117	0.006	11.17	0.39	0.032	0.27	11.16
0.100	1.00	0.09	0.91	0.051	0.118	0.007	11.05	0.43	0.037	0.29	11.04
0.300	0.00	0.00	0.00	0.037	0.298	0.001	12.33	0.13	0.000	0.00	12.33
0.300	0.10	0.04	0.06	0.045	0.288	0.002	12.20	0.16	0.007	0.04	12.20
0.300	0.20	0.05	0.15	0.055	0.282	0.002	12.07	0.20	0.018	0.09	12.06
0.300	0.30	0.06	0.24	0.066	0.236	0.003	11.94	0.28	0.029	0.13	11.93
0.300	0.50	0.07	0.43	0.083	0.236	0.004	11.69	0.35	0.046	0.18	11.67
0.300	0.70	0.08	0.62	0.100	0.235	0.005	11.43	0.43	0.063	0.23	11.40
0.300	0.90	0.08	0.82	0.109	0.232	0.007	11.17	0.47	0.071	0.26	11.14
0.300	1.00	0.09	0.91	0.122	0.225	0.007	11.05	0.54	0.085	0.28	11.02
0.500	0.00	0.00	0.00	0.052	0.395	0.002	12.33	0.13	0.000	0.00	12.33
0.500	0.10	0.04	0.06	0.066	0.388	0.003	12.20	0.17	0.014	0.04	12.19
0.500	0.20	0.05	0.15	0.084	0.432	0.002	12.07	0.20	0.032	0.08	12.05
0.500	0.30	0.06	0.24	0.102	0.406	0.003	11.94	0.25	0.049	0.12	11.92
0.500	0.50	0.07	0.43	0.137	0.379	0.004	11.69	0.36	0.084	0.17	11.65
0.500	0.70	0.08	0.62	0.157	0.360	0.005	11.43	0.44	0.105	0.22	11.39
0.500	0.90	0.08	0.82	0.191	0.347	0.006	11.17	0.55	0.139	0.25	11.12
0.500	1.00	0.09	0.91	0.205	0.306	0.007	11.05	0.67	0.153	0.27	11.00

Table B.5 (continued)
Experimental measurements for ethanol extracted by
m-cresol in chloroform, 25°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	$[Cl]_{o,i}$ (mol/L)	D	$[E]_o$ (mol/L)	$[C]'_o$ (mol/L)	$[Cl]_o$ (mol/L)
1.000	0.00	0.00	0.00	0.030	1.030	0.004	12.33	0.03	0.000	0.00	12.33
1.000	1.00	0.04	0.96	0.440	0.790	0.341	11.05	0.56	0.410	0.15	10.76
1.000	2.00	0.05	1.95	0.550	0.630	0.706	9.74	0.87	0.520	0.25	9.48
1.000	3.00	0.07	2.93	0.640	0.570	0.869	8.46	1.12	0.610	0.33	8.21
1.000	4.00	0.07	3.93	0.660	0.490	1.241	7.18	1.35	0.630	0.39	6.98
1.000	5.00	0.09	4.91	0.660	0.430	1.703	5.89	1.53	0.630	0.45	5.74
1.000	6.00	0.11	5.89	0.660	0.380	1.896	4.59	1.74	0.630	0.50	4.47
1.000	7.00	0.13	6.87	0.660	0.360	2.071	3.30	1.83	0.630	0.54	3.22
1.000	8.00	0.15	7.85	0.660	0.340	3.102	2.02	1.94	0.630	0.58	1.97
1.000	9.00	0.18	8.82	0.650	0.320	3.969	0.72	2.03	0.620	0.62	0.70
1.000	9.56	0.20	9.36	0.620	0.290	4.314	0.00	2.14	0.590	0.64	0.00

Table B.6
Experimental measurements for ethanol extracted by
m-cresol in chloroform, 50°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	$[Cl]_{o,i}$ (mol/L)	D	$[E]_{i,o}$ (mol/L)	$[C]'_o$ (mol/L)	$[Cl]_o$ (mol/L)
0.100	0.00	0.00	0.00	0.021	0.114	0.002	12.33	0.18	0.000	0.00	12.33
0.100	0.10	0.04	0.06	0.024	0.116	0.003	12.20	0.21	0.004	0.05	12.20
0.100	0.20	0.05	0.15	0.029	0.118	0.004	12.07	0.24	0.008	0.10	12.07
0.100	0.30	0.06	0.24	0.031	0.116	0.004	11.94	0.26	0.010	0.13	11.94
0.100	0.50	0.07	0.43	0.036	0.112	0.006	11.68	0.32	0.016	0.19	11.68
0.100	0.70	0.08	0.62	0.043	0.101	0.006	11.42	0.42	0.022	0.24	11.42
0.100	0.90	0.08	0.82	0.048	0.104	0.008	11.16	0.46	0.028	0.28	11.16
0.100	1.00	0.09	0.91	0.052	0.099	0.008	11.04	0.52	0.031	0.29	11.04
0.300	0.00	0.00	0.00	0.063	0.275	0.002	12.33	0.22	0.000	0.00	12.33
0.300	0.10	0.04	0.06	0.073	0.251	0.003	12.20	0.29	0.011	0.04	12.19
0.300	0.20	0.05	0.15	0.080	0.248	0.003	12.07	0.32	0.017	0.09	12.06
0.300	0.30	0.06	0.24	0.088	0.248	0.004	11.94	0.35	0.025	0.13	11.93
0.300	0.50	0.07	0.43	0.107	0.231	0.005	11.68	0.46	0.044	0.18	11.67
0.300	0.70	0.08	0.62	0.120	0.213	0.006	11.42	0.56	0.057	0.23	11.40
0.300	0.90	0.08	0.82	0.106	0.167	0.008	11.16	0.63	0.043	0.27	11.15
0.300	1.00	0.09	0.91	0.136	0.209	0.008	11.04	0.64	0.073	0.28	11.02
0.500	0.00	0.00	0.00	0.108	0.383	0.003	12.33	0.28	0.000	0.00	12.33
0.500	0.10	0.04	0.06	0.124	0.386	0.003	12.20	0.32	0.016	0.04	12.19
0.500	0.20	0.05	0.15	0.131	0.375	0.005	12.07	0.34	0.023	0.08	12.06
0.500	0.30	0.06	0.24	0.150	0.349	0.004	11.94	0.42	0.042	0.12	11.92
0.500	0.50	0.07	0.43	0.184	0.335	0.006	11.68	0.54	0.076	0.18	11.65
0.500	0.70	0.08	0.62	0.200	0.312	0.006	11.42	0.64	0.092	0.22	11.39
0.500	0.90	0.08	0.82	0.210	0.307	0.008	11.16	0.68	0.102	0.26	11.13
0.500	1.00	0.09	0.91	0.236	0.302	0.009	11.04	0.78	0.128	0.27	11.00

Table B.6 (continued)
Experimental measurements for ethanol extracted by
m-cresol in chloroform, 50°C

$[E]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	$[C]_a$ (mol/L)	$[C]_o$ (mol/L)	$[E]_o$ (mol/L)	$[E]_a$ (mol/L)	$[W]_o$ (mol/L)	$[Cl]_{o,i}$ (mol/L)	D	$[E]_{o,o}$ (mol/L)	$[C]_{o,o}$ (mol/L)	$[Cl]_o$ (mol/L)
1.000	0.00	0.00	0.00	0.060	0.900	0.264	12.33	0.07	0.000	0.00	12.33
1.000	1.00	0.12	0.88	0.390	0.590	0.731	11.05	0.66	0.330	0.16	10.76
1.000	2.00	0.14	1.86	0.540	0.490	1.372	9.74	1.10	0.480	0.27	9.42
1.000	3.00	0.17	2.83	0.600	0.430	2.028	8.46	1.40	0.540	0.34	8.16
1.000	4.00	0.20	3.80	0.630	0.390	2.617	7.18	1.62	0.570	0.41	6.92
1.000	5.00	0.24	4.76	0.620	0.330	3.539	5.89	1.88	0.560	0.46	5.69
1.000	6.00	0.25	5.75	0.630	0.310	5.033	4.59	2.03	0.570	0.51	4.42
1.000	7.00	0.24	6.76	0.630	0.280	5.572	3.30	2.25	0.570	0.55	3.18
1.000	8.00	0.21	7.79	0.630	0.260	6.867	2.02	2.42	0.570	0.60	1.95
1.000	9.00	0.22	8.78	0.610	0.250	8.178	0.72	2.44	0.550	0.63	0.69
1.000	9.56	0.24	9.32	0.590	0.240	9.489	0.00	2.46	0.530	0.65	0.00

Table B.7
Experimental distribution ratio measurements for ethanol
extracted by other solvents

Extractant	Diluent	T (°C)	V _O /V _A	[E] _{a,i} (mol/L)	[S] _{o,i} (mol/L)	[E] _a (mol/L)	[E] _o (mol/L)	D	[W] _o (mol/L)	[S] _o (mol/L)
alamine 336 w/HCl	heptane	25	1	1.00	0.50	0.82	0.17	0.21		
	n-octane	25	1	1.00	0.50	0.67	0.40	0.60		
	chloroform	25	1	1.00	0.50	0.86	0.22	0.26		
m-cresol	toluene	25	1	0.86	0.86	0.73	0.12	0.17		
	octanol	25	1	0.86	0.00	0.58	0.28	0.49		
			1	0.86	0.86	0.59	0.26	0.44		
			1	0.86	1.71	0.58	0.28	0.49		
			1	0.86	2.57	0.53	0.32	0.61		
			1	0.86	3.43	0.51	0.34	0.67		
			1	0.86	4.28	0.47	0.39	0.82		
			1	0.86	5.00	0.43	0.42	0.98		
			1	0.86	6.00	0.39	0.46	1.19		
			1	0.86	7.00	0.36	0.50	1.38		
			1	0.86	8.00	0.32	0.53	1.65		
			1	0.86	9.00	0.30	0.56	1.90		
	n-butyl acetate	25	1	0.86	0.00	0.70	0.14	0.21		0.00
			1	0.86	1.00	0.60	0.20	0.43		0.02
			1	0.86	2.00	0.57	0.27	0.50		0.04
			1	0.86	3.00	0.52	0.33	0.63		0.08
			1	0.86	4.00	0.50	0.38	0.71		0.11
			1	0.86	5.00	0.45	0.42	0.91		0.14
			1	0.86	6.00	0.42	0.44	1.05		0.18
			1	0.86	7.00	0.38	0.50	1.25		0.22

Table B.7 (continued)
Experimental distribution ratio measurements for ethanol
extracted by other solvents

Extractant	Diluent	T (°C)	V _o /V _a	[E] _{a,i} (mol/L)	[S] _{o,i} (mol/L)	[E] _a (mol/L)	[E] _o (mol/L)	D	[W] _o (mol/L)	[S] _o (mol/L)
m-cresol	n-butyl acetate	25	1	0.86	8.00	0.32	0.52	1.64		0.19
			1	0.86	9.00	0.30	0.56	1.86		0.21
o-cresol	toluene	25	1	0.86	0.86	0.71	0.16	0.22		
p-cresol	toluene	25	1	0.86	0.86	0.71	0.15	0.21		
			1	0.86	1.00	0.71	0.16	0.22		
			1	0.86	2.00	0.60	0.28	0.46		
			1	0.86	3.00	0.51	0.36	0.70		
			1	0.86	4.00	0.45	0.43	0.96		
			1	0.86	5.00	0.40	0.48	1.18		
	chloroform	25	1	1.07	1.00	0.65	0.36	0.55		
			1	1.05	2.00	0.50	0.49	0.99		
			1	1.02	3.00	0.42	0.57	1.33		
			1	1.00	4.00	0.37	0.61	1.66		
4-t-butyl catechol	toluene	25	1	0.86	1.00	0.68	0.24	0.35	0.051	
			1	0.86	2.00	0.52	0.38	0.73	0.142	
			1	0.86	2.50	0.47	0.43	0.91	0.237	
	chloroform	25	1	1.07	1.00	0.63	0.45	0.71	0.054	
			1	1.05	2.00	0.45	0.50	1.11	0.142	
			1	1.01	4.00	0.42	0.57	1.36		
		60	1	1.07	1.00	0.52	0.47	0.90		

Table B.7 (continued)
Experimental distribution ratio measurements for ethanol
extracted by other solvents

Extractant	Diluent	T (°C)	V _o /V _a	[E] _{a,i} (mol/L)	[S] _{o,i} (mol/L)	[E] _a (mol/L)	[E] _o (mol/L)	D	[W] _o (mol/L)	[S] _o (mol/L)
4-t-butyl catechol	toluene	60	1	1.05	2.00	0.40	0.48	1.20		
			1	1.01	4.00	0.33	0.56	1.70		
	di-n-butyl ether	25	1	1.00	0.00	0.98	0.05	0.05		
			1	1.00	1.00	0.88	0.16	0.18		
			1	1.00	2.00	0.78	0.30	0.38		
			1	1.00	4.00	0.58	0.48	0.83		
			1	1.00	6.48	0.43	0.61	1.42		
		60	1	1.00	0.00	0.87	0.09	0.10		
			1	1.00	1.00	0.73	0.23	0.32		
			1	1.00	2.00	0.68	0.36	0.53		
			1	1.00	4.00	0.51	0.60	1.18		
			1	1.00	6.48	0.34	0.70	2.06		
p-chlorophenol	toluene	25	1	1.00	1.00	0.71	0.27	0.39		
			1	1.00	2.00	0.55	0.43	0.78		
cumyl phenol	toluene	25	1	0.86	1.00	0.76	0.16	0.21	0.017	
			1	0.86	2.00	0.70	0.25	0.36	0.032	
	chloroform	25	1	1.07	1.00	0.69	0.36	0.49	0.036	
			1	1.05	2.00	0.55	0.44	0.80	0.064	
DEHPA (di-2-ethyl hexyl phosphoric acid)	i-octane	25	5	0.86	0.86	0.60	0.03	0.06		
			4	0.86	0.86	0.72	0.04	0.06		
			3	0.86	0.86	0.78	0.04	0.05		
			2	0.86	0.86	0.80	0.04	0.05		

Table B.7 (continued)
Experimental distribution ratio measurements for ethanol
extracted by other solvents

Extractant	Diluent	T (°C)	V _O /V _a	[E] _{a,i} (mol/L)	[S] _{o,i} (mol/L)	[E] _a (mol/L)	[E] _o (mol/L)	D	[W] _o (mol/L)	[S] _o (mol/L)
DEHPA	i-octane	25	1	0.86	0.86	0.82	0.05	0.06		
			1	0.17	0.86	0.16	0.01	0.07		
			1	0.86	3.02	0.70	0.19	0.29		
	chloroform	25	5	0.86	0.86	0.72	0.20	0.22		
			1	0.86	0.86	0.63	0.14	0.27		
	dodecanol	25	5	0.86	0.86	0.35	0.10	0.29		
1			0.86	0.86	0.69	0.17	0.25			
4-n-hexyl resorcinol	toluene	25	1	0.86	1.00	0.62	0.28	0.45	0.099	
			1	0.86	2.00	0.51	0.39	0.76	0.212	
	chloroform	25	1	1.07	1.00	0.61	0.51	0.84	0.102	
			1	1.05	2.00	0.49	0.55	1.12	0.255	
	toluene	25	1	1.00	1.00	0.94	0.04	0.04		
			1	1.00	2.00	0.90	0.05	0.06		
pentachloro- phenol	di-n-butyl ether	60	1	1.00	1.50	0.76	0.31	0.41		
2,4,6-tri- chlorophenol	toluene	25	1	1.00	1.00	0.82	0.10	0.12		
3,5-xylenol	m-xylene	25	1	0.86	0.43	0.78	0.08	0.10		
			1	0.86	0.86	0.74	0.11	0.15		

Table B.7 (continued)
Experimental distribution ratio measurements for ethanol
extracted by other solvents

Extractant	Diluent	T (°C)	V_o/V_a	$[E]_{a,i}$ (mol/L)	$[S]_{o,i}$ (mol/L)	$[E]_a$ (mol/L)	$[E]_o$ (mol/L)	D	$[W]_o$ (mol/L)	$[S]_o$ (mol/L)
3,5-xylenol	xylene	25	1	0.86	4.28	0.42	0.44	1.06		
		1	0.86	7.90	0.34	0.51	1.49			

Table B.8
Literature aqueous activity coefficient for ethanol, 25°C

Source	x (mol. fr.)	[E] _a (mol/L)	P (torr)	α
-----	-----	-----	-----	-----
Nord et al., 1984	0.0004	0.000024	23.86	3.52
	0.0008	0.000049	23.96	3.67
	0.0013	0.000073	24.05	3.60
	0.0035	0.000194	24.49	3.46
	0.0061	0.000337	25.01	3.41
	0.0083	0.000454	25.43	3.37
	0.0100	0.000543	25.76	3.37
	0.0131	0.000707	26.33	3.31
	0.0161	0.000863	26.89	3.28
	0.0212	0.001124	27.81	3.22
	0.0309	0.001605	29.49	3.13
	0.0412	0.002095	31.21	3.05
	0.0500	0.002498	32.64	3.00
	0.0603	0.002952	34.25	2.94
	0.0700	0.003362	35.70	2.88
	0.0803	0.003782	37.17	2.82
	0.0903	0.004174	38.52	2.76
	0.1001	0.004544	39.75	2.70
	0.1200	0.005256	41.93	2.56
	0.1406	0.005943	43.77	2.40
	0.1602	0.006553	45.19	2.26
	0.1806	0.007148	46.38	2.11
	0.2000	0.007678	47.32	1.99
	0.2200	0.008193	48.14	1.87
	0.2349	0.008557	48.67	1.79
Avila and Silva, 1970	0.1000	0.004540	39.10	2.93
Dobson, 1925	0.0523	0.002601	33.17	3.04

Table B.8 (continued)
Literature aqueous activity coefficient for ethanol, 25°C

Source	x (mol. fr.)	[E] _a (mol/L)	P (torr)	α
-----	-----	-----	-----	-----
Dobson, 1925	0.0916	0.004224	38.44	2.71
	0.1343	0.005738	43.42	2.47
	0.1670	0.006756	45.69	2.22
	0.2022	0.007737	47.21	1.96
Hall et al., 1979	0.0550	0.002721	33.33	2.94
	0.1246	0.005414	42.06	2.48
	0.2142	0.008047	47.98	1.91

Table B.9
Comparison of experimental distribution ratio measurements for water
extracted by m-cresol in toluene with and without ethanol present

T (°C)	[C] _{o,i} (mol/L)	<u>with ethanol present</u>		<u>without ethanol present</u>	
		[W] _o (mol/L)	D _w	[W] _o (mol/L)	D _w
0	0.00	0.000	0.00	0.000	0.00
	1.00	0.001	0.00	0.001	0.00
	2.00	0.002	0.01	0.003	0.01
	3.00	0.006	0.02	0.005	0.02
	4.00	0.009	0.03	0.009	0.03
	5.00	0.012	0.04	0.011	0.04
	6.00	0.014	0.05	0.017	0.06
	7.00	0.020	0.07	0.028	0.10
	8.00	0.019	0.07	0.027	0.10
	9.00	0.028	0.10	0.033	0.12
	9.56	0.034	0.12	0.038	0.14
25	0.00	0.000	0.00	0.000	0.00
	1.00	0.001	0.00	0.001	0.00
	2.00	0.003	0.01	0.003	0.01
	3.00	0.006	0.02	0.006	0.02
	4.00	0.010	0.03	0.010	0.04
	5.00	0.012	0.04	0.012	0.04
	6.00	0.015	0.05	0.018	0.06
	7.00	0.021	0.08	0.023	0.08
	8.00	0.028	0.10	0.028	0.10
	9.00	0.035	0.12	0.035	0.13
	9.56	0.038	0.14	0.039	0.14

Table B.9 (continued)
 Comparison of experimental distribution ratio measurements for water
 extracted by m-cresol in toluene with and without ethanol present

T (°C)	$[C]_{O,i}$ (mol/L)	<u>with ethanol present</u>		<u>without ethanol present</u>	
		$[W]_O$ (mol/L)	D_w	$[W]_O$ (mol/L)	D_w
50	0.00	0.001	0.00	0.000	0.00
	1.00	0.002	0.01	0.002	0.01
	2.00	0.005	0.02	0.004	0.01
	3.00	0.012	0.04	0.009	0.03
	4.00	0.017	0.06	0.016	0.06
	5.00	0.018	0.06	0.020	0.07
	6.00	0.025	0.09	0.023	0.08
	7.00	0.028	0.10	0.035	0.13
	8.00	0.034	0.12	0.031	0.11
	9.00	0.039	0.14	0.045	0.16
	9.56	0.043	0.15	0.045	0.16

Table B.10
Comparison of experimental distribution ratio measurements for water
extracted by m-cresol in chloroform with and without ethanol present

T (°C)	[C] _{o,i} (mol/L)	<u>with ethanol present</u>		<u>without ethanol present</u>	
		[W] _o (mol/L)	D _w	[W] _o (mol/L)	D _w
0	0.00	0.000	0.00	0.000	0.00
	1.00	0.002	0.01	0.002	0.01
	2.00	0.004	0.01	0.004	0.01
	3.00	0.005	0.02	0.006	0.02
	4.00	0.009	0.03	0.015	0.05
	5.00	0.010	0.04	0.013	0.05
	6.00	0.015	0.05	0.016	0.06
	7.00	0.020	0.07	0.020	0.07
	8.00	0.024	0.09	0.024	0.09
	9.00	0.029	0.11	0.036	0.13
	9.56	0.032	0.12	0.038	0.14
25	0.00	0.000	0.00	0.000	0.00
	1.00	0.002	0.01	0.003	0.01
	2.00	0.005	0.02	0.006	0.02
	3.00	0.006	0.02	0.008	0.03
	4.00	0.010	0.04	0.011	0.04
	5.00	0.013	0.05	0.015	0.06
	6.00	0.017	0.06	0.017	0.06
	7.00	0.022	0.08	0.019	0.07
	8.00	0.027	0.10	0.028	0.10
	9.00	0.038	0.14	0.036	0.13
	9.56	0.037	0.13	0.039	0.14

Table B.10 (continued)
Comparison of experimental distribution ratio measurements for water
extracted by m-cresol in chloroform with and without ethanol present

T (°C)	$[C]_{O,i}$ (mol/L)	<u>with ethanol present</u>		<u>without ethanol present</u>	
		$[W]_O$ (mol/L)	D_w	$[W]_O$ (mol/L)	D_w
50	0.00	0.001	0.00	0.001	0.00
	1.00	0.004	0.01	0.002	0.01
	2.00	0.007	0.02	0.006	0.02
	3.00	0.010	0.04	0.008	0.03
	4.00	0.013	0.05	0.019	0.07
	5.00	0.018	0.06	0.016	0.06
	6.00	0.025	0.09	0.021	0.08
	7.00	0.028	0.10	0.026	0.09
	8.00	0.034	0.12	0.032	0.12
	9.00	0.041	0.15	0.040	0.14
	9.56	0.047	0.17	0.045	0.16

APPENDIX C.

C.1 Solution to Third Order Polynomial (Beyer, 1984)

For the equation of the form

$$[C]_o^3 + \frac{2K_{c_2} + mK_{nm}[E]_o^n [C]_o^m}{3K_{c_3}} [C]_o^2 + \frac{1 + m'K_{n'm'p}[E]_o^n [C]_o^m [C]_o^p}{3K_{c_3}} [C]_o - \frac{[C]_{o,T}}{3K_{c_3}} = 0 \quad (C.1)$$

This equation can be solved for its only one real root by the following two sets of substitutions.

$$P = \frac{2K_{c_2} + mK_{nm}[E]_o^n [C]_o^m}{3K_{c_3}} \quad Q = \frac{1}{3K_{c_3}} \quad R = \frac{[C]_{o,T}}{3K_{c_3}} \quad (C.2)$$

which substituted into Equation C.1 becomes

$$[C]_o^3 + P[C]_o^2 + Q[C]_o + R = 0$$

$$y^3 + Py^2 + Qy + R = 0 \quad (C.3)$$

The second substitution is

$$x = y - \frac{P}{3} \quad (C.4)$$

Equation C.3 then becomes

$$x^3 + ax + b = 0 \quad (C.5)$$

The solution is of the form $x = A + B$ where

$$A = \sqrt[3]{-\frac{b}{2} + \left(\frac{b^2}{4} + \frac{a^3}{27}\right)^{\frac{1}{2}}} \quad B = -\sqrt[3]{+\frac{b}{2} + \left(\frac{b^2}{4} + \frac{a^3}{27}\right)^{\frac{1}{2}}} \quad (C.6)$$

for which

$$a = \frac{1}{3}(3Q - P^2) \quad b = \frac{1}{27}(2P^3 - 9PQ + 27R) \quad (C.7)$$

C.2 Multiple Linear Regression (Bevington, 1969)

For the equation in the form

$$Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 \quad (\text{C.8})$$

In fitting the experimental points to equation C.8, the resulting simultaneous equations, one for each of the z sets of data, may be combined to solve for a_0 .

$$\sum Y_i = a_0 Z + a_1 \sum X_1 + a_2 \sum X_2 + a_3 \sum X_3 \quad (\text{C.9})$$

$$\begin{aligned} a_0 &= \frac{1}{Z} [\sum Y_i - a_1 \sum X_1 - a_2 \sum X_2 - a_3 \sum X_3] \\ &= \bar{Y} - a_1 \bar{X}_1 - a_2 \bar{X}_2 - a_3 \bar{X}_3 \end{aligned} \quad (\text{C.10})$$

In order to solve for the remainder of the coefficients, minimize the sum of the square of the difference between each set of experimental values and the averages by setting the first derivative equal to 0:

$$\chi^2 = \frac{1}{\sigma^2} \sum \left[(Y_i - \bar{Y}) - a_1 (X_{i1} - \bar{X}_1) - a_2 (X_{i2} - \bar{X}_2) - a_3 (X_{i3} - \bar{X}_3) \right]^2 \quad (\text{C.11})$$

$$\sum (Y_i - \bar{Y}_i) (X_{ik} - \bar{X}_k) = \sum \left[a_j \sum (X_{ij} - \bar{X}_j) (X_{ik} - \bar{X}_k) \right] \quad (\text{C.12})$$

$$k, j = 1, 2$$

$$i = 1, Z$$

The linear correlation coefficients assuming that all the data points are given equal weighting, are

$$r_{fg} = \frac{s_{fg}^2}{s_{ff} s_{gg}} \quad f, g = X_1, X_2, X_3 \quad (\text{C.13})$$

$$s_{fg} = \frac{1}{N-1} \sum \left[\left(f - \bar{f} \right) \left(g - \bar{g} \right) \right] \quad (C.14)$$

Equation C.12 becomes z simultaneous equations of the form:

$$r_{iy} = \sum_{k=1}^z (b_k r_{ik}) \quad (C.15)$$

where the coefficients b_k are related to the coefficients a_k by

$$b_k = a_k \frac{s_{kk}}{s_{yy}} \quad (C.16)$$

in which the diagonal terms in the matrix r are unity: $r_{jj} = 1$.

The coefficients b_k can be determined by matrix inversion:

$$b_k = \sum (r_{iy} r_{jk}^{-1}) \quad (C.17)$$

where r_{jk}^{-1} is the jk th term of the inverse matrix of r .

By substitution into Equation C.16 the coefficients a_k can be determined:

$$a_k = \frac{s_{yy}}{s_{kk}} \sum (r_{iy} r_{jk}^{-1}) \quad (C.18)$$

To calculate the uncertainties of the constants, the following equations are used

$$\sigma_{a_i}^2 \cong \frac{1}{Z-1} \frac{s^2}{s_{ii}^2} r_{ii}^{-1} \quad (C.19)$$

where

$$s^2 = \frac{1}{Z-z-1} \sum \left[\left(Y_i - \bar{Y} \right) - \sum a_j \left(X_i - \bar{X}_j \right) \right]^2 \quad (C.20)$$

$$\sigma_{a_0}^2 = \frac{\frac{1}{Z} + \frac{1}{Z-1} \sum_{j=1}^z \sum_{k=1}^z \left(\bar{X}_j \bar{X}_k \frac{1}{s_{jj} s_{kk}} r_{jk}^{-1} \right)}{\frac{1}{Z} \sum \frac{1}{\sigma_i^2}} \quad (C.21)$$

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APPENDIX D

Experimental measurements for batch equilibrium extractions of propanols and propanediols.

Table D.1
Experimental measurements for n-propanol extracted by
m-cresol in toluene, 25°C

$[P]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	D
-----	-----	-----
0.500	0.10	0.30
0.500	0.50	0.84
0.500	1.00	1.63
0.500	2.00	3.14
0.500	4.00	5.47
0.500	8.00	13.18
0.500	9.56	16.61

Table D.2
Experimental measurements for i-propanol extracted by
m-cresol in toluene, 25°C

$[P]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	D
-----	-----	-----
0.500	0.10	0.03
0.500	0.20	0.05
0.500	0.50	0.20
0.500	1.00	0.80
0.500	2.00	1.54
0.500	4.00	4.63
0.500	8.00	7.61
0.500	9.56	9.00

Table D.3
Experimental measurements for 1,2-propanediol extracted by
m-cresol in 3,5-xylene, 25°C

$[P]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	D
-----	-----	-----
0.500	0.00	<0.01
0.500	1.00	<0.01
0.500	3.00	0.07
0.500	5.00	0.23
0.500	7.00	0.41
0.500	9.56	0.72

Table D.4
 Experimental measurements for 1,2-propanediol extracted by
 m-cresol in chloroform (without ethanol present), 25°C

$[P]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	D
0.500	0.00	<0.01
0.500	1.00	0.04
0.500	2.00	0.21
0.500	3.00	0.41
0.500	5.00	0.65
0.500	7.00	0.68
0.500	9.56	0.72

Table D.5
 Experimental measurements for 1,2-propanediol extracted by
 m-cresol in chloroform (with ethanol present), 25°C

$[P]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	D
-----	-----	-----
0.500	0.00	<0.01
0.500	1.00	0.04
0.500	2.00	0.14
0.500	3.00	0.24
0.500	5.00	0.37
0.500	7.00	0.57
0.500	9.56	0.72

Table D.6
Experimental measurements for 1,3-propanediol extracted by
m-cresol in 3,5-xylene, 25°C

$[P]_{a,i}$ (mol/L)	$[C]_{o,i}$ (mol/L)	D
-----	-----	-----
0.500	0.00	<0.01
0.500	1.00	<0.01
0.500	2.00	0.03
0.500	3.00	0.08
0.500	5.00	0.30
0.500	7.00	0.47
0.500	9.56	0.70

APPENDIX E

Nomenclature:

n, m	= stoichiometric constants for alcohol (ethanol, butanol) and m-cresol, respectively, in the n:m complex
$n', m', p,$	= stoichiometric constants for ethanol, m-cresol and chloroform, respectively, in the n:m:p complex
r, s	= stoichiometric constants for water and m-cresol, respectively, in the r:s complex
$[B]_a$	= concentration of butanol in the aqueous phase, mol/L
$[B]_{a,i}$	= initial concentration of butanol in the aqueous phase, mol/L
$[B]_o$	= concentration of butanol in the organic phase, mol/L
$[B]'_o$	= concentration of butanol in the organic phase, not solvated by the diluent, mol/L
$[B]_{o,dil}$	= concentration of butanol in the organic phase solvated by the diluent, mol/L
$[B_n C_m]_o$	= concentration of the butanol/m-cresol complex in the organic phase, mol/L
$[C]_a$	= concentration of m-cresol in the aqueous phase, mol/L
$[C]_{o,T}$	= total concentration of m-cresol in the organic phase, mol/L
$[C]_o$	= concentration of unassociated and uncomplexed m-cresol in the organic phase, mol/L
$[C]_{o,i}$	= initial concentration of unassociated and uncomplexed m-cresol in the organic phase, mol/L
$[C]'_o$	= total concentration of m-cresol monomer, dimer and trimer in the organic phase, mol/L
$[C_2]_o$	= concentration of m-cresol dimer in the organic phase, mol/L
$[C_3]_o$	= concentration of m-cresol trimer in the organic phase, mol/L
$[Cl]_o$	= concentration of chloroform in the organic phase, mol/L

Nomenclature (continued):

$[Cl]_{o,i}$	= initial concentration of chloroform in the organic phase, mol/L
D	= distribution ratio; organic phase concentration of solute divided by aqueous phase concentration of solute, mol/L
D_{mod}	= modified distribution ratio; organic phase concentration of solute not solvated by the diluent, divided by aqueous phase concentration of solute, mol/L
D_w	= distribution ratio of water; organic phase concentration of water divided by aqueous phase concentration of water, mol/L
$[E]_T$	= concentration of ethanol in the initial aqueous phase, mol/L
$[E]_a$	= concentration of ethanol in the aqueous phase, mol/L
$[E]_{a,i}$	= initial concentration of ethanol in the aqueous phase, mol/L
$[E]_{o,T}$	= total concentration of ethanol in the organic phase, mol/L
$[E]'_{o,T}$	= ethanol concentration in organic phase not solvated by diluent, mol/L
$[E]_{o,dil}$	= ethanol concentration in organic phase solvated by diluent, mol/L
$[E]_o$	= concentration of unassociated and uncomplexed ethanol in the organic phase, mol/L
$\frac{[E_n C_m]_o}{[EC_2]_o}$	= concentration of ethanol/m-cresol complex in the organic phase, mol/L
$\frac{[E_n C_m Cl_p]}{[ECCl]}$	= concentration of ethanol/m-cresol/chloroform complex in the organic phase, mol/L
K_{12} K_{rm}	= equilibrium formation constant of alcohol/m-cresol complex (ethanol, butanol)
K_{111} K_{rmp}	= equilibrium formation constant of ethanol/m-cresol/chloroform complex
K_{C2}	= equilibrium formation constant of m-cresol dimer
K_{C3}	= equilibrium formation constant of m-cresol trimer

Nomenclature (continued):

K_{rs}	= equilibrium formation constant of water/m-cresol complex
P	= total pressure, torr
$[S]_o$	= concentration of extractant in the organic phase, mol/L
$[S]_{o,i}$	= initial concentration of extractant in the organic phase, mol/L
T	= temperature of the extraction, °C
V_a	= volume of the initial aqueous phase, ml
V_o	= volume of the initial organic phase, ml
$[W]_a$	= concentration of water in the aqueous phase, mol/L
$[W]_o$	= concentration of water in the organic phase, mol/L
$[W_rC_s]_o$	= concentration of water/m-cresol complex in the organic phase, mol/L
x	= mole fraction of the solute, mol/mol
X_1	= log of concentration of unassociated ethanol in the aqueous phase $[E]_a$
X_2	= log of concentration of unassociated m-cresol in the organic phase $[C]_o$
X_3	= log of concentration of chloroform in the organic phase $[Cl]_o$
Y	= log of concentration of complex (~ concentration of ethanol) in the organic phase $[E_nC_mCl_p]_o$
$\bar{X}_i$	= average of X_i
$\bar{Y}$	= average of Y
z	= number of components
Z	= number of experimental points
α	= separation factor, distribution ratio of ethanol divided by the distribution ratio of water

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