Lawrence Berkeley National Laboratory
Recent Work

Title

Purification of Aqueous Cellulose Ethers. Extraction of Alkali Salts with Isopropanol and High-Pressure Carbon Dioxide

Permalink

https://escholarship.org/uc/item/79c011gb

Authors

Bartscherer, K.A.
Pablo, J.J. de
Bonnin, M.C.
et al.

Publication Date

1990-07-01

eScholarship.org Powered by the California Digital Library
University of California

LBL-29452
UC-401

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

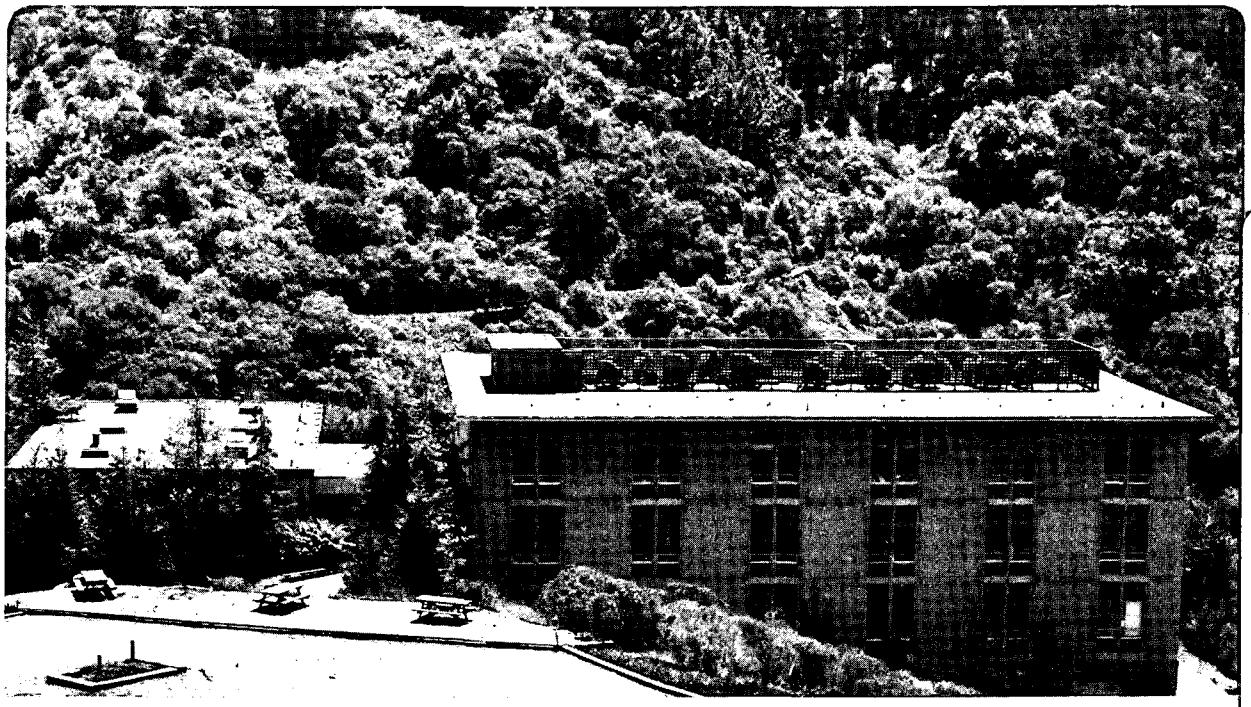
Purification of Aqueous Cellulose Ethers. Extraction of Alkali Salts with Isopropanol and High-Pressure Carbon Dioxide

K.A. Bartscherer, J.J. de Pablo,
M.C. Bonnin, and J.M. Prausnitz

July 1990

For Reference

Not to be taken from this room



LBL-29452
Copy 1
Bldg. 50 Library.

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-29452

Purification of Aqueous Cellulose Ethers. Extraction of Alkali Salts with Isopropanol and High-Pressure Carbon Dioxide

K.A. Bartscherer, J.J. de Pablo,
M.C. Bonnin, and J.M. Prausnitz
Department of Chemical Engineering
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Additional funding was provided by the Donors of the Petroleum Research Fund administered by the American Chemical Society.

Purification of Aqueous Cellulose Ethers. Extraction of Alkali Salts with Isopropanol and High-Pressure Carbon Dioxide

Kolja A. Bartscherer, Juan J. de Pablo, Marianne C. Bonnin

and John M. Prausnitz

Department of Chemical Engineering

and

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory

University of California, Berkeley, CA 94720

ABSTRACT

Manufacture of cellulose ethers usually involves high amounts of salt by-products. For application of the product, salt must be removed. In this work, we have studied the injection of high-pressure CO_2 into an aqueous polymer-salt solution; we find that upon addition of isopropanol in addition to CO_2, the solution separates into two phases. One phase is rich in polymer and water, and the other phase contains mostly isopropanol, water and CO_2. The salt distributes between the two phases, thereby offering interesting possibilities for development of a new purification process for water-soluble polymers. This work presents experimental phase-equilibrium data for hydroxyethyl cellulose and sodium carboxymethyl cellulose with sodium acetate and potassium sulfate, respectively, in the region 40°C and 30 to 80 bar. Based on these data, we suggest a process for the manufacture and purification of water-soluble cellulose ethers.

Introduction

Industrial production of certain cellulose derivatives yields a product that is soluble in water. The chemical steps leading to the desired product require strong alkali (sodium or potassium hydroxide) which must later be neutralized with acid (acetic, hydrochloric or sulfuric acid). The mixture containing the desired cellulose derivative, therefore, also contains salts. For application of the product, salt must be removed.

The experimental results presented in this work serve two purposes. First, they provide new data for the phase equilibria of a system containing five very different components: a water-soluble (cellulose derivative) polymer, an alkali salt, an organic co-solvent, water, and high-pressure CO_2. Second, they provide the basis for the development of a novel process for separating alkali salts from water-soluble polymers.

Two polymers were studied in this work. Both are water-soluble cellulose ethers which are derived from cellulose, a polymer consisting of linear chains of β-anhydroglucose rings. Figure 1 shows the structural unit of cellulose. $R_{cell}(OH)_3$ or simply $R_{cell}OH$ are convenient representations of the chemical structure of cellulose. Cellulose with substituents like CH_2COONa or CH_2CH_2OH for the hydrogen atom in one (or more) of the three hydroxyl groups of the β-anhydroglucose rings forms cellulose ethers, like sodium carboxymethylcellulose or hydroxyethylcellulose.

Sodium carboxymethylcellulose

Sodium carboxymethylcellulose, commonly called "CMC", is the most widely used water-soluble cellulose derivative. It has been commercially available in Germany since 1921 (1), and in the U.S. since 1946. In 1977, the total U.S. production of CMC exceeded 48,000 metric tons. CMC is used in detergents, textiles, pharmaceuticals, foods, paints and drilling muds.

Sodium carboxymethylcellulose is a polyelectrolyte prepared by the reaction of alkali cellulose with sodium chloroacetate. Alkali cellulose is prepared by soaking native cellulose in an aqueous solution of NaOH to break the cristallinity of cellulose, thereby facilitating chemical reactions. An excess of sodium hydroxide neutralizes the hydrogen chloride that is instantaneously formed, giving NaCl as byproduct:

$$R_{Cell}(OH)_3 + NaOH \rightleftarrows R_{cell}(OH)_3\ (NaOH) \qquad (1)$$

$$R_{Cell}(OH)_3\ (NaOH) + ClCH_2COONa \rightarrow R_{Cell}(OH)_2OCH_2COONa + NaCl + H_2O \qquad (2)$$

Another side reaction, the conversion of sodium chloroacetate to sodium glycolate, occurs simultaneously:

$$NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl \qquad (3)$$

An additional source of NaCl is provided by the subsequent neutralization of excess NaOH by an acid such as HCl. The properties of the final CMC product depend on the degree of substitution, defined as the average number of carboxymethyl groups per anhydroglucose unit in the cellulose, on the chain length or degree of polymerization, and on the uniformity of substitution as well as the purity. For some (but not all) applications, such as in detergents, CMC need not be purified. The crude material contains 30w% or more of by-product salts (mainly sodium chloride and sodium glycolate).

Hydroxyethylcellulose

Hydroxyethylcellulose (HEC) is a widely used nonionic water-soluble cellulose ether. It has applications similar to those of CMC but does not precipitate as easily as CMC in electrolyte solutions and dissolves better in water (2). It is prepared by the reaction of ethylene oxide with alkali cellulose:

$$R_{Cell}(OH)_3\ (NaOH) + n\ CH_2CH_2O \rightarrow R_{Cell}(OH)_2(OCH_2CH_2)_nOH + NaOH \qquad (4)$$

Ethylene and polyethylene glycol are by products of this reaction:

$$NaOH + n\ CH_2CH_2O \rightarrow HO(CH_2CH_2O)_nNa \quad (5)$$

$$HO(CH_2CH_2O)_nNa + H_2O \rightarrow HO(CH_2CH_2O)_nH + NaOH \quad (6)$$

In commercial processes for manufacture of HEC, another by-product, sodium acetate, results from the neutralization of excess sodium hydroxide (from alkali cellulose with acetic acid).

For food, pharmaceutical and other uses, it is necessary to purify cellulose ethers from their byproducts. CMC and HEC, which are soluble in both cold and hot water, are at present industrially purified by extraction with an aqueous-organic solvent mixture (3,4,5), such as aqueous acetone or aqueous ethanol. The purification process, including the recycling of water and solvents, contributes significantly to the total costs of these polymers (2).

The experimental data reported in this work were taken to provide a possible alternative purification process for water-soluble cellulose ethers. Phase equilibria were measured for polymer/salt/mixed-solvent systems. Although we kept a practical perspective for our experiments, sodium chloride could not be used in our equipment because chloride ions are highly corrosive. Further, our salt-concentration measurements by atomic absorption spectroscopy cannot distinguish between the sodium cations coming from the polyelectrolyte (CMC) and those coming from NaCl. Instead, in our CMC measurements we used potassium sulfate. For studies with HEC, phase equilibrium data were taken in the presence of sodium acetate.

In recent years, supercritical extraction processes have attracted much interest; several commercial extraction processes are already in operation (6). These offer different advantages, including environmental safety and energetic efficiency. In typical supercritical extraction (SCE) processes, a supercritical fluid (SCF) is used to dissolve a specific, non-

volatile component from a multicomponent mixture. In some cases, however, the SCF is a poor solvent for the component to be extracted. In such cases, the SCF cannot be used directly as a solvent but, as shown here, it can be used to induce phase separation, thereby enhancing the effectiveness of another, more suitable solvent. For the system of interest here, CO_2 does not dissolve the salt, but it enables the use of water/isopropanol mixtures to dissolve the salt selectively in a separate phase which does not dissolve the polymer.

Near the critical temperature of a hydrocarbon solvent, solutions of hydrocarbon polymers exhibit a lower critical solution temperature (LCST). Thirty years ago, Freeman and Rowlinson (7) observed, that upon heating, a homogeneous polymer solution may separate into two fluid phases. Such phase splitting could provide the basis for a separation process. Similarly, it has been known for many years that injection of a high-pressure gas into a binary liquid mixture can induce a phase separation, as shown, for example, by Kuk and Montagna (8) for the system isopropanol/water/CO_2. The supercritical gas reduces the LCST to lower temperatures, so that a phase split can be achieved at room temperature. At 40°C and 100 bar, water and isopropanol are completely miscible. However, upon injection of high-pressure CO_2 into an aqueous solution of isopropanol, the ternary system exhibits two liquid phases and one gas phase, at the same temperature and pressure.

More recently, McHugh and Guckes (9) reported phase separations in a two-solvent polymer solution. These authors found that addition of a supercritical fluid to a binary polymer solution can also reduce the lower critical solution temperature; the magnitude of the reduction depends on the molecular weight of the polymer and on its solubility in the SCF.

In our work, we induce liquid-liquid phase separations in aqueous polymer solutions by injection of high-pressure CO_2. The systems studied here contain sodium carboxymethylcellulose, potassium sulfate, isopropanol, water and CO_2, or hydroxyethylcellulose, sodium acetate, isopropanol, water and CO_2.

Our experiments indicate that, near 40°C and between 30 and 60 bar, there is a liquid-liquid-vapor region for these mixtures. Further, we have found that, while the

presence of polymer in these three-phase systems is restricted to the heavier, aqueous liquid phase, under certain circumstances the salt can distribute between the two coexisting liquid phases. This partitioning of the salt could provide the basis for a novel purification process for water-soluble cellulose ethers. It could also provide the basis for purification processes for water-soluble polymers in general (e.g. proteins or enzymes).

Equipment

Figure 2 shows a schematic diagram of the apparatus used for our experiments. The equilibrium cell is a high-pressure Jerguson Dual-Flat-Glass Cell (Model 17T32 with a cell volume of aproximately 150 cm^3). Figure 3 shows the construction of the cell. The cell consists of a one piece Hastelloy-C chamber, forged-steel covers and borosilicate-glass windows protected by mica shields; it has been tested for a maximum pressure of 200 bar at 40°C. The cell was placed in a constant-temperature oven from APPLIED TEST SYSTEMS equiped with an OMEGA-ENGINEERING heater-controller (The accuracy is about ± 0.1°C). Mixing was achieved through recirculation of upper and lower cell contents by two LDC-ANALYTICAL Simplex Minipumps.

Pressure was measured with a HEISE Optical Sensor Pressure Transducer (Model 623). It offers a calibration stability of 0.01% in the range from 1.0 to 2000 bar. The output of the transducer is indicated on the display of a digital voltmeter; calibration was carried out with a HEISE Bourdon Tube dial gage from 30 to 135 bar.

All valves used in the equipment were NUPRO "JB" Series needle valves for pressures to 200 bar and temperatures to 200°C. The connecting lines were made of high-pressure 316-stainless steel tubing with pressure ratings well above 200 bar.

Density Measurements

The densities of both liquid phases were measured continuously with two METTLER-PAAR Precision Density Meters, located in the recirculation circuits shown in Figure 2. Continuous density measurements provide a very sensitive method of monitoring the state of an experiment; little or no change of the density over a long period of time indicates that a state of equilibrium has been attained.

The measuring principle for the densimeter is based on the change in natural frequency of a hollow oscillator when filled with different fluids. A simple equation gives the relationship between the mass density of the sample ρ and the period of oscillation τ of the filled oscillator tube

$$\rho = A\ \tau^2 + B$$

where A and B are temperature-dependent apparatus constants, obtained by calibration with fluids of known density. We used pure CO_2, pure water and pure ethylene glycol to calibrate the densimeter. The accuracy of our density measurements was $\pm$ 0.0005 g/cm^3. This relatively low accuracy is due to our "homemade" temperature control which produces oscillations of ±0.1°C. However, this accuracy is sufficient for our purposes.

Concentration Measurements

To determine concentrations of the contents of the cell, discrete volumes of different phases were sampled by means of two VICI 6-port switching valves with zero dead volume, mounted in the recirculation lines shown in Figure 2. These two-position valves are made from Hastelloy-C and were tested for 200°C and 350 bar. The sample is pumped through a sampling loop of known volume; when equilibrium is attained, the volume of sample that is present in the loop at that moment is separated from the system which is now flowing through a shortcut in the valve. The sample can then be analysed separately. Figure 4 illustrates the operating principle of these valves.

A crucial point of our measurements is knowing the exact volumes of both sampling loops. These volumes are required to calculate concentrations inside the cell. The necessary volumetric calibration was achieved by sampling two different sodium-acetate-solutions of known concentration. The samples were rinsed out with a known amount of pure water, and their concentration was analysed by atomic absorption spectroscopy. From the concentration c_{sample}, the volume V_{sample} and the known concentration c_{loop}, the volume V_{loop} of each sampling loop was determined according to

$$V_{loop} = V_{sample} \frac{c_{sample}}{c_{loop}} \tag{7}$$

To minimize gravimetric and volumetric errors arising in the preparation of the samples, several calibration experiments were carried out; the resulting two values for each loop were averaged.

Sodium was detected at a wavelength of 589.0 nm, with a single-element hollow-cathode lamp.

Concentration of Carbon Dioxide

The concentration of CO_2 in the samples was determined by a volumetric method. The sampling lines were connected to a burette filled with CO_2-saturated water. The volume of CO_2 going out of solution after the valves were switched was monitored through the rising liquid level in the burette. Temperatures in the burette were measured with an accuracy of 0.1 K with an OMEGA ENGINEERING Digital Temperature Indicator and remote thermocouples; room pressure was measured with an accuracy of ± 0.01 bar with a precision mercury barometer. The amount of CO_2 in the sampling loop was then calculated using the ideal-gas law which is justified for CO_2 at room temperature and pressure.

$$c_{loop} = \frac{V_{CO_2}\, p_{room}\, M_{CO_2}}{T_{CO_2}\, R} \tag{8}$$

Figure 5 shows the equipment for our CO_2-measurements.

Concentration of Salt

Salt concentration was measured with a PERKIN-ELMER Atomic Absorption Spectrophotometer (model 2280). Since the detection range for this high-accuracy apparatus is very small, high dilution with a solvent is necessary to obtain reliable data. The detection of alkali metals requires special care; plastic bottles are used to prevent adsorption at glass walls and a different alkali salt is added to prevent ionisation effects. (Ionization interferences occur when the flame energy removes electrons from the atoms, forming ions. This reduces the number of atoms and thus the atomic absorption. Addition of an excess of an easily ionized element to the samples controls these effects.)

Concentrations of Alcohol and Polymer

The concentrations of 2-propanol and CMC or HEC in the samples were detected by High-Pressure Size-Exclusion Chromatography.

The column used was a BIORAD Bio-Gel SEC-30XL column(7.8 mm I.D.) packed with a hydrophilic-hydroxylated polyether material. These columns operate consistantly in the pH-range from 2 to 12 and are typically used for protein analysis. The hydrophilic packing with a pore size of 250 $\dot{A}$ and a particle size of 6μm separates molecular weights from about 10^2 to 10^6. To exclude effects from changes in room temperature, the column and the detector were thermostatised at 36±0.1°C.

A KNAUER Differential-Refractometer Type 198.00 was used as a detector. The integrator, a NELSON Analytical Chromatography 4100 system, was calibrated by injecting different solutions of selected components and by relating resulting peak areas (μV sec) to the known concentrations. Due to errors from sample injection, dilution and possible fluctuations in sample retention times, four measurements using the same sample solution have been averaged. Table 1 shows the results for the HPLC calibration.

The samples introduced in the HPLC contained up to 1.0 g/l of salt. Since the salts, K_2SO_4 in the CMC sample and CH_3COONa in the HEC sample unfortunatly had retention times close to that of the corresponding polymer, the peak areas of salt and polymer overlapped and could not be integrated separately. One way to solve this problem is to calibrate the HPLC for pure salt solutions and to substract the areas calculated from the salt concentrations measured by atomic absorption from the polymer areas resulting from the run of our samples. However, this method can be used only if a linear additive relation exists between polymer/salt concentrations and the resulting HPLC peak areas, i.e., if for all combinations of salt and polymer concentrations the resulting peak areas for the mixture are equal to the sum of the individual peak areas of the single components.

Our measurements indicate that additivity did not hold in our systems. For CMC, which is a charged polymer, configurational changes could be observed in the presence of potassium sulfate; with the ionic strength of the solution exceeding 0.5g/l CMC and 0.08g/l K_2SO_4, HPLC peak areas were not additive. This effect, a change in the configuration of a polymer upon addition of an ionic species in the solution is typical for polyelectrolytes. At infinite dilution, a single polymer molecule can be considered to be the microscopic analog of an osmotic cell. In the case of a polyelectrolyte, the osmotic cell would be of the size of the molecule, containing fixed (ionic substitutes in the chain) and mobile charges. As shown by Flory (10), the mobile counter-ions of the polyelectrolyte exert an osmotic pressure on the hypothetical membrane around the molecule, which may be very large. The polymer molecule should therefore expand enormously in solution if a substantial portion of its units are ionized. Addition of a salt to the solution tends to equalize the concentration of ions inside and outside the molecule, and thus to decrease the osmotic expansion force. The expansion of the molecule determines its size and shape, which are recognized by a size-exclusion column, giving different retention times and peak areas.

However, the different HPLC calibration measurements indicate a region of concentration of CMC and K_2SO_4, (concentration combinations below 0.08 g/l K_2SO_4 and 0.5 g/l

CMC) for which the peaks corresponding to individual components are additive. Figure 6 illustrates these results.

To determine the concentrations of CMC in our samples, sufficiently dilute solutions were run through the HPLC; the peak areas corresponding to the known concentrations of salt (measured by atomic absorption) were substracted to give the correct polymer peaks. For HEC, which is an uncharged polymer, no dilutions had to be made; according to our calibrations, the peak areas of HEC and sodium acetate were additive for all concentrations measured.

Experiments

Phase equilibria were measured for the two systems of the type POLYMER/SALT/WATER/2-PROPANOL/CO_2. The polymers studied in this work were hydroxyethylcellulose and sodium carboxymethylcellulose; the salts used for these studies were potassium sulfate and sodium acetate.

Materials

The CMC used was supplied by SIGMA, Chemical Company as product #C8758 Carboxymethylcellulose, sodium salt, low viscosity (2% aqueous solution at 25°C: 10-20 cps). It was washed with 10 times by weight of 80%vol absolute ethanol/water solution to remove salts. Further cleaning showed no significant change in salt content. Table 2 shows the sodium concentrations of differently intensive cleaned CMC samples; no change in salt content indicates that the amount of salt measured corresponds to the mobile sodium ions of the polymer.

The HEC was provided by UNION CARBIDE as Cellosize QP-09L with a degree of substitution of three and a molecular weight of about 70000. HEC was not purified prior to the experiments because commercially available HEC contains up to 30%w of sodium acetate; the polymer was used for our phase equilibrium measurements as supplied by UNION

CARBIDE and the content of sodium acetate was 4.8 %w.

Potassium sulfate was from J.T Baker Chemical Co. as 'Baker Analysed' reagant grade; the isopropyl alcohol was Certified A.C.S standard and the CO_2 came from a commercially available syphon-type bottle, filtered through a NUPRO 5 μm filterelement.

The water used for all the experiments was TYPE I reagent-grade water (equal to or exceeding standards established by ASTM, CAP and NCCLS), purified with a BARNSTEAD NANOPURE water purification system.

Operating Procedure

All experiments were carried out the same way to ensure reproducibility. Before each experiment, all lines of the equipment were rinsed with nanopure water for at least one, hour four times, at 40°C. No detergents were used. The cell and lines were rinsed with pure acetone for 15 minutes to wash out the remaining water and then emptied and dried under vacuum for one hour.

The polymer and (if added) the salt, were dissolved in the appropriate amount of water by stirring with a mechanical stirrer at low revolutions in a closed container for several hours. The stirring time depended on the concentration (viscosity) of the solution. After reaching a uniform solution, isopropanol was slowly added and carefully dissolved in the aqueous solution. Heavy stirring or shaking of this mixture before the alcohol dissolved inevitably led to undesired precipitation of solid polymer which stubbornly resisted redissolving. Since precipitation of small amounts of solid polymer was unavoidable, especially in the case of CMC, where the rate of alcohol to aqueous solution had to be very close to the precipitation point, the solution was filtered through a 0.1-mm wire gauze before each experiment.

A slight vacuum was then applied to the equipment and the mixture was sucked in through the bottom drain. This method offers the advantage of very short inlet tubing without plugging the CO_2-purge-lines at the top of the cell with the viscous initial mixture.

To determine volumetric contents of the equilibrium cell, its transparent glass walls were marked at intervals corresponding to 10 ml; the volumes of the recirculation lines were 10 ml for the lower cicuit and 2 ml for the upper circuit. These volumes were taken into account for feeding the initial solution because the construction of this cell required the upper phase to reach the suction inlet of the top circuit to sample that phase; the initial filling had to be at least up to this level as illustrated in Figure 3.1.

After activating the bottom recirculation pump and waiting for the fluid level to be constant (the lines are filled when the fluid drops out of the lower circuit outlet), the value for the density was measured by averaging the period of oscillation indicated by the density meter; this value had to be constant to ± 5 in the sixth digit of the display if the initial solution was homogeneous. Now the 6-port valve located in the lower phase circuit was switched and rinsed out with 200 ml of pure water; previous measurements with atomic absorption showed this amount to be sufficient to rinse out all loop contents. Sampling the initial cell composition before adding CO_2 and applying pressure in the same way as that used later for the equilibrium phases, guarantees that mass balances do not depend on the sampling loop calibration or preparing of the mixture.

The sampling valve was then switched back after drying the flushing lines under vacuum; pressure was then applied to the system through the CO_2-inlet line. To reach pressure rates above the bottle pressure (about 70 bar), the liquid CO_2 coming from the syphon at the bottom of the gas bottle was liquified at about 10°C before entering the pump (a LDC Analytical Simplex Minipump, identical to the metering pumps used to recirculate the cell contents). Since liquid CO_2 at 10 °C is almost incompressible, the desired pressure could be reached relatively fast by introducing compressed liquid CO_2 into the cell.

The inlet valve at the top was now closed and the system was allowed to equilibrate. Sine CO_2 dissolves gradually in the liquid solutions contained in the cell, to reach a desired equilibrium pressure CO_2 had to be added by trial and error. The equilibration time for a typical experiment ranged from 24 hours to several days. This time was required because of

the poor effectiveness of our mixing device (there are no mechanical stirrers inside the cell) and the high viscosity of the bottom phase which hinderes mass transfer.

Equilibrium was reached as indicated by stability of the density. The water inside the burettes and the connected reservoirs was then "bubbled" with gaseous CO_2 for 15 minutes to ensure saturation. The top sampling valve was switched and the CO_2 from the loop was slowly released into the flask by means of the upper flushing valve (see Figure 5). After determining the volume of CO_2 and the necessary temperature and pressure, the gas was released and the remaining parts of the sample were rinsed out with pure water to 200 ml. This procedure was repeated for the bottom sample. To make sure that the sampled phases were free of entrainment, the corresponding recirculation pumps were operated solely for at least three hours prior to each sampling.

The sampling of the bottom phase marked the end of an experiment. The pressure in the equipment was released slowly through the upper purge line and the cell was emptied via the bottom drain; while the apparatus was cleaned in various rinsing cycles, all three samples were analysed with the spectroscopic and chromatographic equipment described in the previous sections.

Measurement of CO_2 Solubility

Solubility of CO_2 in 10%w aqueous CMC solutions was measured at 40°C and pressures from 50 to 150 bar. Figure 8 shows these measurements compared to values from the literature for solubility of CO_2 in pure water.

No significant differences between the measured solubilities for CO_2 in the polymer solution and reported solubilities in pure water could be observed.

The system CMC-K_2SO_4-H_2O-C_3H_8O-CO_2

Equilibrium was measured for a variety of concentrations and pressures at a temperature of 40°C. In all experiments, the concentration of CMC in the aqueous salt solution was 10w% or 8w%. The concentration of salt(K_2SO_4) was 2.5w% throughout. This combination is equal to a salt content of the CMC of about 30w%, which is the amount of salt found in unpurified commercial CMC (2). We had to change the concentration of CMC from an initial 10w% in aqueous solution to 8w% because the viscosity of the bottom solution, especially in the presence of salt, caused mixing problems and extremely long equilibrium times (up to 3 days).

Special care was required to avoid precipitation inside the equipment to prevent blocking the lines. The recirculation lines outside the equilibrium chamber were made out of high-pressure tubing with very small inner diameters; solid particles in the mixture stopped the flow in the pumps and made mixing as well as sampling impossible. Entrainment of the heavy phase in the lighter phase blocked the circuit lines through precipitation of polymer induced by local concentration gradients. To prevent such precipitation, it was necessary to find the ratio of isopropanol to aqueous polymer-salt-solution where solid polymer precipitates out of solution; for all our experiments, the initial mixtures had to have alcohol/water ratios below this value. Table 3 shows the effect of isopropanol on the solubility of CMC in aqueous salt solution at room pressure and temperature.

The system HEC-CH_3COONa-water-2-propanol-CO_2

Experiments similar to those with CMC containing systems were carried out for HEC mixtures. Since HEC is a nonionic polymer, it tolerates higher concentrations of electrolytes than CMC. Also, the solubility of HEC in aqueous-organic solvents is higher. While the limit for addition of isopropanol to a 8w% aqueous solution of CMC without precipitation of the polymer is 25/50 volumetric ratio (see table 3), an aqueous HEC solution tolerates a volumetric ratio of 60/50. In addition, the viscosity of aqueous HEC samples is lower than

that of equal-concentration CMC solutions. These effects facilitate to a large extent the feasibility of our phase equilibrium measurements; problems with plugged recirculation pumps did not occur, and equilibrium periods were shorter.

Concentrations of HEC were 9.5w% and 8w% in aqueous solution throughout; this HEC already contained a part of sodium acetate of 4.8w% of polymer; salt concentrations were therefore about 0.46 to 0.38w% in aqueous solution.

Although mixing for our experiments with HEC systems was easier than that for CMC systems, entrainment of the heavy phase into the light phase was a serious problem. As could be observed from the change of the top phase from a milky state to a clear, transparent solution, top-phase sampling in HEC systems required at least 12 hours of recirculating the top phase through the bottom phase without recirculating the bottom phase. Three hours achieved the same result in CMC systems.

Results and Discussion

CMC-systems

Phase compositions were measured for sodium carboxymethylcellulose/potassium sulfate/water/iso-propanol/CO_2 systems in the LLV region at 40°C. This region was found by raising the pressure until the initial mixture separated in two liquid phases; Equilibrium phases were then sampled and analysed. The compositions of the feed mixture and of the resulting equilibrium phases are reported in Tables 4-6. Figure 9 also shows these results for experiments numbered 1 to 16.

In Tables 5-7, concentrations are given in g/l. This unit was chosen because initially, when this work was undertaken, only the density of the heavy bottom phase could be measured (12) water concentrations for the top phase could not be determined. For the last experiments, a second density-meter was available; the density of the top phase could then be measured to determine the concentration of water. For the concentration mesured, three

significant figures are reported.

Figure 9 shows phase compositions in bar graphs. This presentation facilitates the interpretation of our results.

Volumes of Equilibrium Phases

Depending on the initial alcohol concentration, for a given temperature, phase separation occurres at different pressures; in our experiments, the onset of this phase separation had to be determined visually. Therefore, the pressure where it occured could not be measured with high accuracy.. Another method to detect the onset of a phase separation of the initial mixture was to monitor the output of the density meter in the bottom recirculation circuit; equilibrium liquid-liquid phases had a density very different from that of the initial homogeneous mixture.

The volumes of the two liquid phases in equilibrium are highly dependent on the alcohol/water ratio in the feed mixture. For a feed volumetric ratio of 16/50, the volumes of the resulting top and bottom phases were 5 and 125 ml, respectively. For an initial composition of 20/50, the resulting phase volumes were 45 ml of top phase and 80 ml of bottom phase. As shown in experiments #14, #15 and #16, these volumes could change to 80 ml of top phase and 50 ml of bottom phase for a feed alcohol/water ratio of 25/50. The limiting volumetric ratio for the initial iso-propanol/aqueous-salt-polymer solution was 27/50 (see experiment #12, Table 3). For higher alcohol concentrations, solid polymer precipitates out of solution and it becomes impossible to sample the bottom phase.

Pressure does not have a significant effect on the volumes of the two phases in the LLV region. Although the top phase dissolves more CO_2 at elevated pressures, the dissolved CO_2 drives water back to the aqueous polymer-rich bottom phase, thereby resulting in almost constant phase volumes See experiments #9-11 which were actually one experiment that was sampled three times at different pressures.

From a physical-chemistry point of view, knowledge of the magnitude of phase volumes at equilibrium is of minor importance. From a chemical engineering point of view, however, these volumes are very important. Since the experiments reported here were carried out to find a novel purification process for water-soluble cellulose ethers, knowing the amounts of salt and polymer in both liquid phases is of great interest. To determine these amounts, we need information about the volumes of the equilibrium phases; for a constant concentration of salt and polymer we prefer a large top phase which removes large amounts of salt and small amounts of polymer.

Solubility of Carbon Dioxide

The solubility of CO_2 depends on the amount of isopropanol in solution as well as on the total pressure of the system; while the solubility of CO_2 in aqueous polymer does not change significantly with pressure, the solubility in isopropanol does.

Although overall pressures varied between 31 and 78 bar, the concentration of CO_2 in the aqueous polymer-rich bottom phase remained in the vicinity of 45 g/l. On the other hand, the solubility of CO_2 in the alcohol-rich top phase covered the range from 45 to 500 g/l. Figure 10 shows a plot of pressure versus CO_2-concentration in the alcohol-rich top phase for experiments #9-11 (Experiments #9-11 were samples of the same system at different pressures.)

Polymer and Salt Partitioning

Upon formation of the alcohol-CO_2-rich top phase, a change in the salt and polymer concentrations in the aqueous bottom phase takes place. Figure 11 gives the amounts of salt and polymer in the initial mixture as well as in the resulting two liquid phases.

Unfortunately, we were not able to keep the top phase free of entrainment in all our experiments; even if the reported polymer concentrations in the top phase are in some cases very low, it cannot be ruled out that these concentrations are partly or completely due to

bottom phase entrained into the top phase sample.

While CMC and potassium sulfate are both very soluble in water, their solubilities in isopropanol is low, even at elevated pressures. Only a sufficient amount of water dissolved in the alcohol-rich top phase allows the presence of CMC and potassium sulfate.

For some sets of conditions, no polymer and almost no salt were found in the top phase. This top phase usually had a relatively small volume, as shown in experiments #5 and #9-11. This small top phase contained large amounts of CO_2, thus reducing the solubility of water, and therefore also that of salt and polymer in this phase.

In cases where the top phase dissolved larger amounts of water, larger concentrations of salt were found in this phase (Experiments #1, #3, #4). For experiments #14 and #16, where the initial acohol/water ratio was optimized for the formation of a top phase containing a maximum of water, the distribution of potassium sulfate between top and bottom phase was much more significant than the distribution of CMC. Due to entrainment problems, however, quantitative statements have to be considered with caution. The results from measurements #14 and #16 indicate that, for the conditions reported, the lighter liquid phase dissolves about one third of the initial amount of water at 40 bar and 40°C; at most one tenth of the initial amount of CMC dissolves in the top phase.

These results show that the studied phase splitting phenomena can indeed be used to remove the by-product salts from an aqueous-organic CMC solution without significant loss of polymer.

HEC-systems

Phase equilibrium measurements similar to those for the CMC-systems were carried out for HEC-systems. Similar measurements for HEC-systems were conducted earlier by Krenzer et al.(12). Our measurements confirm that there is also a liquid-liquid-vapor region

for HEC mixtures, i.e. the initial HEC/sodium acetate/water/iso-propanol solution splits in two liquid phases upon addition of high-pressure CO_2. Table 7-9 give phase compositions for the experiments.

Volumes of equilibrium phases

The volumes and compositions of the forming two liquid phases were much less sensitive to the initial alcohol/water ratio for HEC systems than for the CMC-systems.

This effect was accompanied by higher alcohol solubilities in the aqueous polymer phase. However, the pressures necessary to induce a phase split were significantly higher for HEC than for CMC; while CMC experiment #15 exhibits a LLV region for 31 bar and 40°C, a pressure of at least 60 bar at 40°C was required to split an initial HEC mixture into two phases. This stronger effect on the lower critical solution temperature of the iso-propanol/water/CO_2-mixture by CMC is probably due to its ionic character, although it also depends on the degree of substitution of the polymer.

Pressure does not have a significant effect on the volumes of the two phases in the LLV region. Moreover, with increasing overall pressure of the system (exceeding the critical point of the mixture), the iso-propanol/water/CO_2 top phase disappears again and only two phases are left in the system: a fluid CO_2-rich phase and a liquid polymer-rich phase.

Partitioning of Salt and Polymer

The results for experiments #1 and #2 indicate that for HEC/sodium acetate the polymer distribution between top and bottom phase is equal to the distribution of CMC between the two phases; about $\frac{1}{10}$ of the initial amount of polymer dissolves in the top phase. As opposed to one third of the salt for CMC systems, however, one half of the overall amount of salt dissolves in the alcohol-rich top phase of the HEC system. This confirms the results of Krenzer et al. (12) who predicted a similar salt/polymer partitioning from mass balances

without measuring the top phase density.

The production of hydroxyethylcellulose is currently achieved in an isopropanol/water-mixture; by bringing the dilute product mixture in contact with high-pressure CO_2, half of the salt impurities could be removed in only one step.

Suggested Process

Figure 13 shows schematically the current process for manufacture of HEC. Alkali cellulose is prepared by soaking native cellulose in aqueous NaOH, thereby breaking its cristallinity, and filtering it to reduce water content. The reaction is typically conducted in an aqueous isopropanol-solution of near azeotropic composition. Ethylene oxide is added and the reaction is initiated by temperature (4-5 hours at 60°C (13) or 1-2 hours at 75°C (14)) or, in the case of continuous processes where the ethylene oxide is introduced as a liquid, by pressure (1 to 4 hours at 7 to 28 bar (15)). The educt alkali cellulose and the product hydroxyethyl cellulose, which are insoluble in this mixture, are kept as solids throughout the reaction. Excess sodium hydroxide is neutralized by acetic acid, and the slurry is purified by washing extensively with aqueous isopropanol. The solution is then centrifuged and the polymer is dried in a nitrogen atmosphere. The isopropanol has to be recovered by distillation.

Based on the results of our experiments, we suggest a different manufacturing and purification process for HEC. As before, the reaction is carried out under high pressure. However, in addition to ethylene oxide, carbon dioxide is used to induce a phase transition. The concentration of isopropanol is about 50vol%. HEC is soluble in the water-rich phase. In the neutralization step, the gas phase is recycled and the two liquid phases are flashed. The top-phase flash serves as an isopropanol recovery step. The bottom phase is freed from CO_2 and HEC is precipitated by addition of isopropanol. Filtration and drying with liquid CO_2 complete the process. Figure 14 shows a flowsheet of the suggested process.

The suggested process has several potential advantages over the current process. First, it is easier to process a liquid phase rather than a slurry. Second, reaction in two liquid phases might be more desirable than reaction in a solid phase, because it offers reaction uniformity and, for a similar degree of substitution, produces a more even distribution of subtituents on the cellulose chain than heterogeneous processes. The lower concentration of dissolved cellulose ethers in homogeneous processes makes them less economical than heterogeneous processes (2). In our case, however, the formation of two liquid phases and the fact that the polymer is restricted to only one of the phases make a homogeneous process an attractive alternative; at the end of the reaction, the heavier phase is sufficiently concentrated in polymer, while the lighter phase can be recycled. Thus, amounts of HEC equivalent to those of a heterogeneous process could be handled in a homogeneous process. To prove the superior quality of the HEC produced by the suggested process, kinetic and characterisation studies are now required.

Since the pressures required for the suggested process would not exceed 65 bar, such a process could be more energy-efficient, because no distillation steps for solvent recovery are necessary. With slight pressure reductions, most of the water condensates from the supercritical fluid mixture and the CO_2 can be recompressed and returned to the process.

It is worth while to point out that, for economic reasons, current processes for the recovery of ethanol and propanol from fermentation boths are shifting from distillation to supercritical fluid extraction (6). Finally, our preliminary results indicate that polymers of a higher purity could be obtained by recycling the flashed alcohol-rich top phase in the phase-separation/neutralization step several times before removing the (salt-free) polymer-rich bottom phase.

It is premature to claim that the suggested process is superior to the current processes. Clearly more information is required for a reliable economic analysis. Nevertheless, the results reported here suggest that there may be a significant economic advantage to development of a separation process using carbon dioxide as a phase splitter.

Conclusions

Measurements of phase equilibria for systems of polymer/salt/alcohol/water/carbon dioxide were carried out in the liquid-liquid-vapor region for several operating conditions. We found a partitioning of alkali salts between the two liquid phases that could be used as the basis for an industrial process to the water-soluble cellulose ethers studied in this work. Based on the results of our measurements, a new process for the manufacture and purification of hydroxyethylcellulose was suggested.

Because experimental studies of phase equilibria for viscous polymer systems are time-consuming, we were able to find only local optima for the partitioning of the salt with respect to the polymer. Only a small region of the phase diagram was explored; a model for correlating and predicting the thermodynamic behavior of these complex systems would be extremely useful. Such a model is now under development. The data measured in this work will provide model-parameters.

To the best of our knowledge, this is the first report of phase separation of CMC solutions in mixed aqueous-organic solvents upon contact with high-pressure CO_2. This effect, previously observed for HEC, is not restricted to water-soluble cellulose ethers. It also has promising applications for the purification of thermally sensitive polymers, such as proteins and enzymes.

Acknowledgments

The authors are grateful to Professor K.S.Pitzer for the loan of his densimeter, to P.Magin for assistance with chemical analysis and to M.Krenzer for construction of experimental apparatus in the early stage of this work. This research was supported by the Director, Office of Energy Resaerch, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract No.DE-AC03-76F00098.Additional funding was provided by the Donors of the Petroleum Research Fund administered by the American Chemical Society. For financial support, M.Bonnin is grateful to Rhone-

Poulenc-Corporation.

References

(1) Gerichtl. Offenbar. 322,586 (July 1, 1920), O.Leuchs (to Bayer A.G.)

(2) Kirk-Othmer. Encyclopedia of Chemical Technology, vol.3, p.226. J.Wiley & sons, (1979)

(3) U.S.Patent 2,572,039 (Oct. 23, 1951), E.D.Klug and H.G.Tennent (to Hercules Powder Co.)

(4) U.S.Patent 2,682,535 (June 29, 1954), A.E.Broderick (to Union Carbide)

(5) U.S.Patent 3,049,537 (Aug. 14, 1962), E.D.Klug and W.D.Robertson (to Hercules Powder Co.)

(6) Japan Alcohol Association, internal report 1988

(7) Freeman P.I., J.S.Rowlinson, Polymer, London 1(1960),20

(8) Kuk M.S., J.C.Montagna, Chemical Engineering at Supercritical Fluid Conditions, chapter 4. Editor M.E.Paulaitis et al.Ann Arbor Science, (1983)

(9) McHugh M.A., T.L.Guckes, Macromolecules 18(1985),674

(10) Flory P.J., "Principles of Polymer Chemistry", p. 629, Cornell University Press 1953

(11) Wiebe R., V.L.Gaddy, J. amer. chem. soc. 63(1941),475

(12) Krenzer M.E., J.J.de Pablo, and J.M.Prausnitz, LBL-report #28102, (1989)

(13) U.S.Patent 3,527,751 (Sep.8, 1970), J.E.Gill (to Imperial Chemical Industries, Ltd.)

(14) U.S.Patent 4,009,329 (Feb.22, 1977), W.C.Arney, C.A.Williams, and J.E.Glass, Jr. (to Union Carbide Corp.)

(15) U.S.Patent 4,015,067 (Mar.29, 1977), G.Y.T.Liu and C.P.Strange (to Dow Chemical Co.)

Component	Concentration	Area	Component	Concentration	Area
	[g/l]	[μV sec]		[g/l]	[μV sec]
CMC	0.5	704580	HEC	0.1	120630
	0.75	1045838		0.5	398918
	1.0	1370246		1.0	1349932
Potassium sulfate	0.08	77717	Sodium acetate	0.01	-
	0.15	123974		0.1	85836
				1.0	762416
CMC and Potassium sulfate	1.0/0.15	1179925	HEC and Sodium acetate	1.0/1.0	1739194
	1.0/0.08	942920		0.5/0.1	468006
	0.5/0.15	708620		0.1/1.0	752074
	0.5/0.08	769937	2-propanol	0.78	521726
	0.1/0.15	225853		1.56	874607
	0.1/0.08	168826		2.34	1502564

Table 1: Results for the HPLC calibration.

10 mg/l solution of	Absorption units
CMC crude	0.096
CMC 1*washed	0.088
CMC 2*washed	0.088
CMC 3*washed	0.087

Table 2: Effect of further washing on salt removal.

(atomic absorption studied at 589nm with a single-element hollow-cathode lamp)

Volumetric ratio of 2-propanol to an aqueous solution of 8w% CMC and 2.5w% K_2SO_4	Observed solution properties
1.0/5.0	Clear solution
2.0/5.0	Clear solution
2.5/5.0	Milky solution, no change
3.0/5.0	Milky solution, precipitate after 1 day
4.0/5.0	Precipitate phase forms immediately

Table 3: Solution properties of CMC in aqueous organic salt solution at 25°C, 1 bar.

Exp.	$i-C_3H_7OH/H_2O$	p	T	c_{CMC}	$c_{K_2SO_4}$	$c_{i-C_3H_7OH}$	c_{CO_2}	c_{H_2O}
#	[ml/ml]	[bar]	[°C]	[g/l]	[g/l]	[g/l]	[g/l]	[g/l]
1	22/50	1	40	-	-	-	-	-
2	22/50	1	40	-	-	-	-	-
3	20/50	1	40	107	20.1	223	-	-
4	18/50	1	40	104	19.4	201	-	663
5	18/50	1	40	44.0	18.9	201	-	717
6	18/50	1	40	65.8	22.7	213	-	684
7	16/50	1	40	-	-	-	-	-
8	20/50	1	40	73.9	16.3	209	-	681
9	17/50	1	40	70.3	3.73	163	-	756
10	17/50	1	40	70.3	3.73	163	-	756
11	17/50	1	40	70.3	3.73	163	-	756
12	27/50	1	40	56.7	14.9	239	-	651
13	28/50	1	40	43.4	0	221	-	696
14	25/50	1	40	34.4	14.1	138	-	780
15	26/50	1	40	36.5	12.0	250	-	670
16	25/50	1	40	30.3	12.7	211	-	712

Table 4: Composition of the initial mixture at pressure p and temperature T for CMC solutions.

Entry "-" indicates: NOT SAMPLED

Exp.	V_{phase}	p	T	c_{CMC}	$c_{K_2SO_4}$	$c_{i-C_3H_7OH}$	c_{CO_2}	c_{H_2O}
#	[ml]	[bar]	[°C]	[g/l]	[g/l]	[g/l]	[g/l]	[g/l]
1	60	72	40	137	23.5	164	46.4	651
2	90	68	40	117	24.7	167	44.3	677
3	80	63	40	200	22.5	122	46.5	630
4	90	49	40	105	17.2	227	42.3	616
5	120	78	40	39.3	16.9	189	52.1	700
6	120	69	40	57.3	21.8	177	49.2	814
7	125	79	40	74.1	16.7	158	50.9	708
8	80	54	40	104	20.9	169	44.7	672
9	125	44	40	80	18.6	126	40.2	753
10	115	48	40	81.4	20.0	101	40.2	780
11	110	62	40	80.0	20.0	90.0	39.5	797
12	-	48	40	-	-	-	-	-
13	130	66	40	39.7	0	208	64.3	660
14	55	53	40	67.3	21.3	99.9	41.0	784
15	65	32	40	55.3	16.4	173	28.3	728
16	50	38	40	77.1	21.3	181	29.9	700

Table 5: Composition of the heavier phase at pressure p and temperature T for CMC solutions. Entry "-" indicates: NOT SAMPLED

Exp.	V_{phase}	p	T	c_{CMC}	$c_{K_2SO_4}$	$c_{i-C_3H_7OH}$	c_{CO_2}	c_{H_2O}
#	[ml]	[bar]	[°C]	[g/l]	[g/l]	[g/l]	[g/l]	[g/l]
1	70	72	40	38.5	9.38	313	152	-
2	40	68	40	0	7.55	394	141	-
3	45	63	40	6.10	4.79	355	102	-
4	40	49	40	32.7	11.2	274	46.8	-
5	15	78	40	2.46	2.52	232	320	-
6	10	69	40	-	-	-	-	-
7	5	79	40	11.5	5.20	297	123	-
8	45	54	40	-	-	-	-	-
9	15	44	40	0	0.27	272	399	-
10	30	48	40	2.00	0.82	237	430	-
11	40	62	40	0	0.03	213	507	-
12	-	48	40	15.0	8.99	264	57.0	-
13	5	66	40	-	-	-	-	-
14	80	53	40	8.23	9.31	155	61.5	-
15	70	32	40	-	-	-	-	-
16	80	38	40	1.06	7.17	234	40.5	654

Table 6: Composition of the lighter top phase at pressure p and temperature T for CMC solutions. Entry "-" indicates: NOT SAMPLED

Exp.	$i-C_3H_7OH/H_2O$	p	T	c_{HEC}	c_{CH_3COONa}	$c_{i-C_3H_7OH}$	c_{CO_2}	c_{H_2O}
#	[ml/ml]	[bar]	[°C]	[g/l]	[g/l]	[g/l]	[g/l]	[g/l]
1	45/50	1	40	38.0	1.48	308	-	552
2	45/50	1	40	38.0	1.96	310	-	573

Table 7: Composition of the feed at pressure p and temperature T for HEC solutions.

Exp.	V_{phase}	p	T	c_{HEC}	c_{CH_3COONa}	$c_{i-C_3H_7OH}$	c_{CO_2}	c_{H_2O}
#	[ml]	[bar]	[°C]	[g/l]	[g/l]	[g/l]	[g/l]	[g/l]
1	60	62	40	66.3	2.57	258	73.0	560
2	50	66	40	71.8	2.22	236	73.8	583

Table 8: Composition of the heavier phase at pressure p and temperature T for HEC solutions.

Exp.	V_{phase}	p	T	c_{HEC}	c_{CH_3COONa}	$c_{i-C_3H_7OH}$	c_{CO_2}	c_{H_2O}
#	[ml]	[bar]	[°C]	[g/l]	[g/l]	[g/l]	[g/l]	[g/l]
1	80	62	40	6.72	1.27	311	96.5	-
2	90	66	40	4.84	1.42	324	103	480

Table 9: Composition of the lighter phase at pressure p and temperature T for HEC solutions.

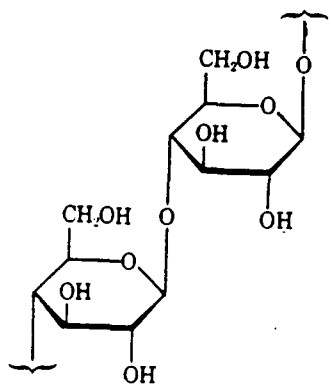


Figure 1: Structural units of cellulose (2 β-anhydroglucose rings).

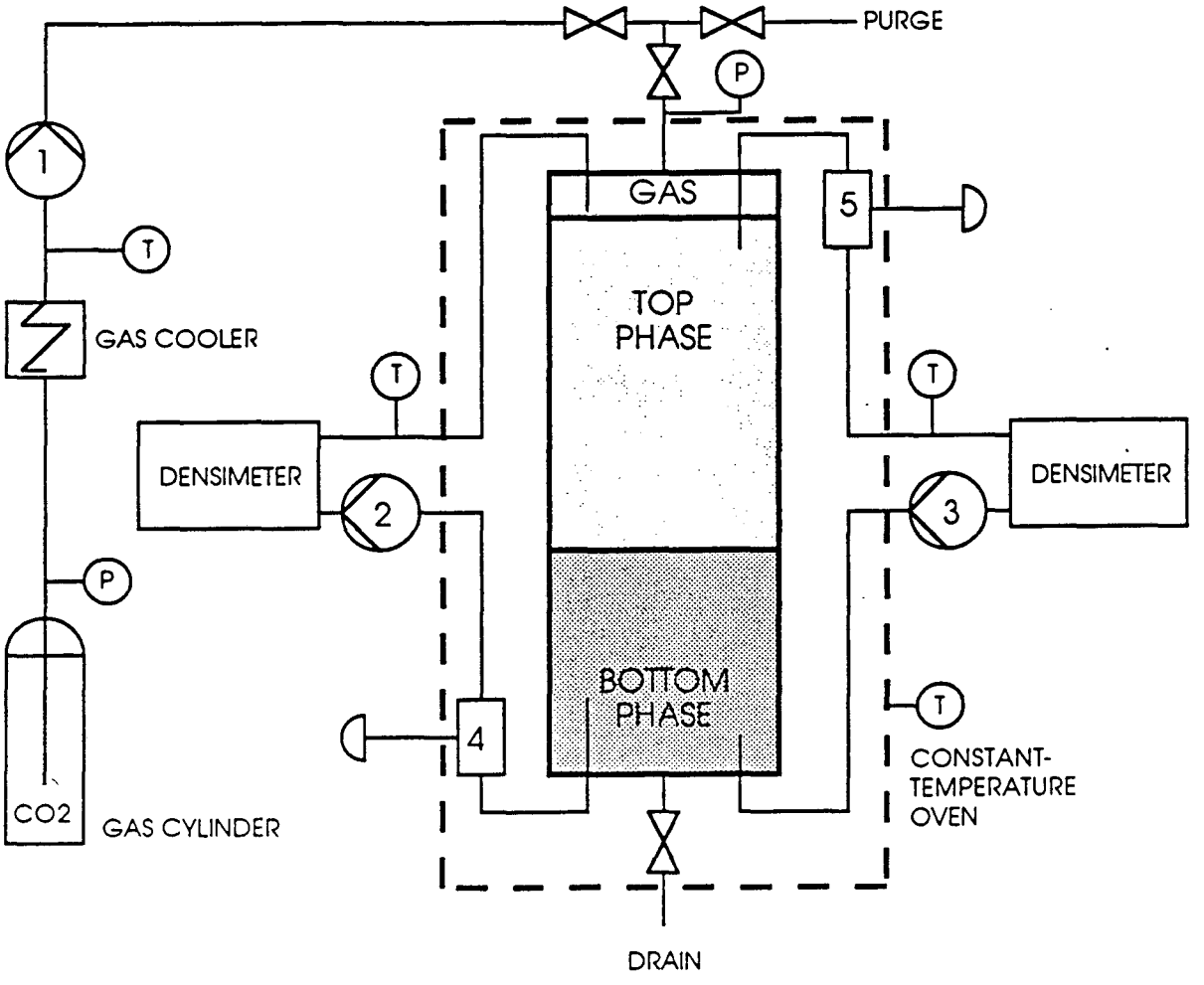


Figure 2: Phase-equilibrium apparatus.

(1) Liquid CO_2 feed pump. (2,3) Recirculation pumps. (4,5) 6-port sampling valves.

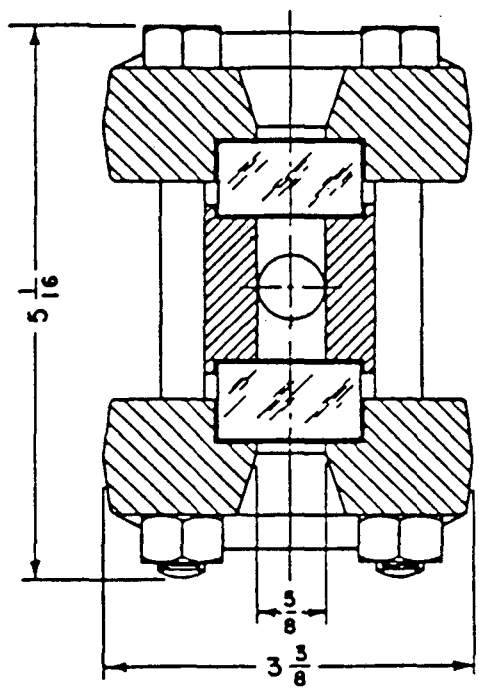


Figure 3: Equilibrium cell, cross-section.

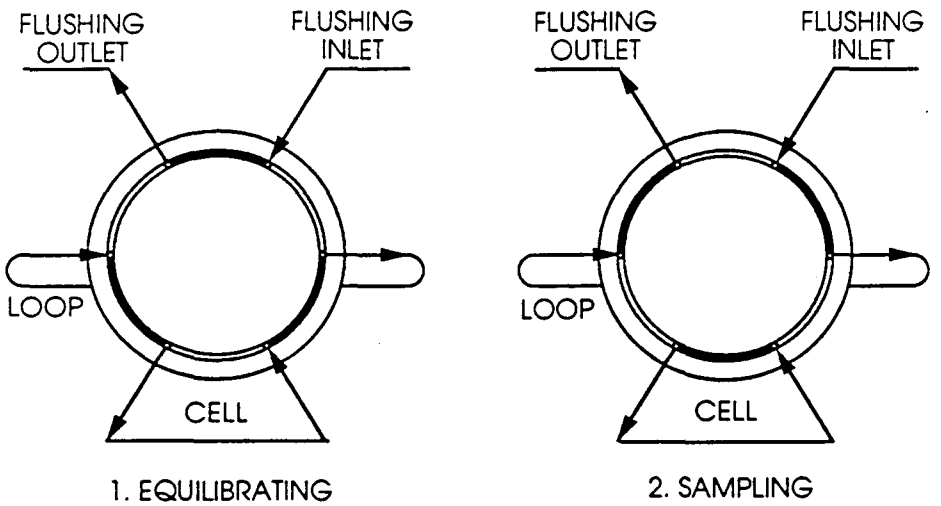


Figure 4: Operating principle of the sampling valves.

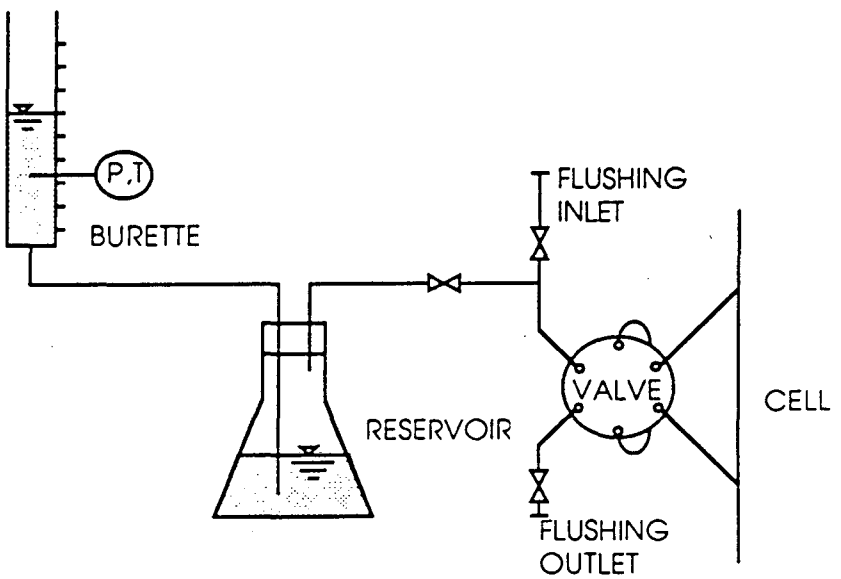


Figure 5: Equipment for CO_2 concentration measurements.

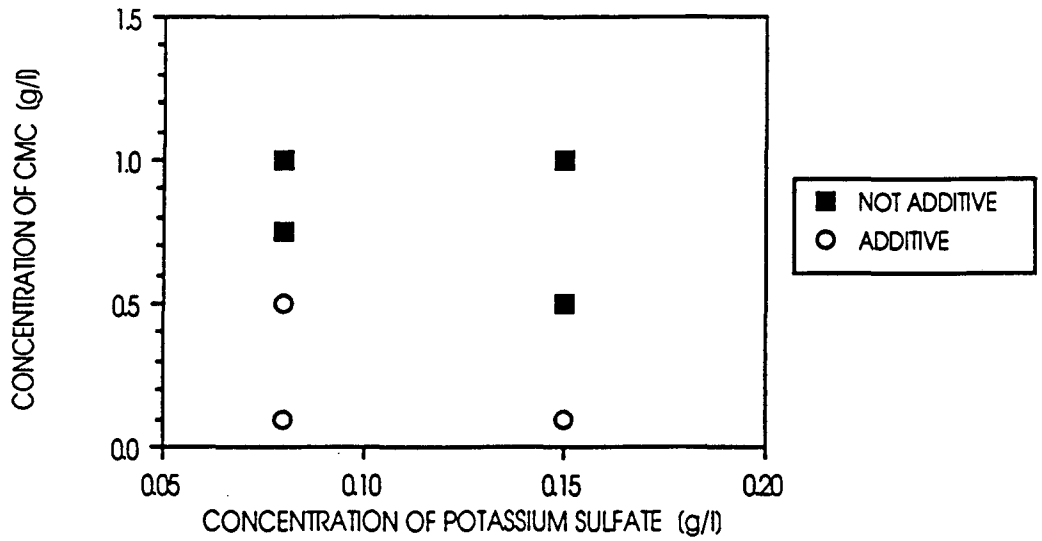


Figure 6: Additive and non-additive concentration combinations for CMC/salt.

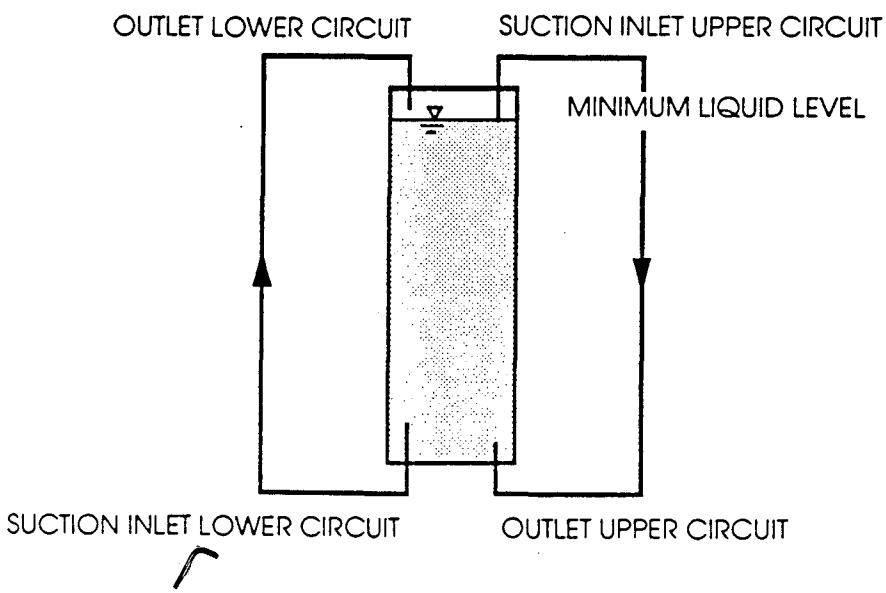


Figure 7: Required minimum liquid level in the cell for top-phase sampling.

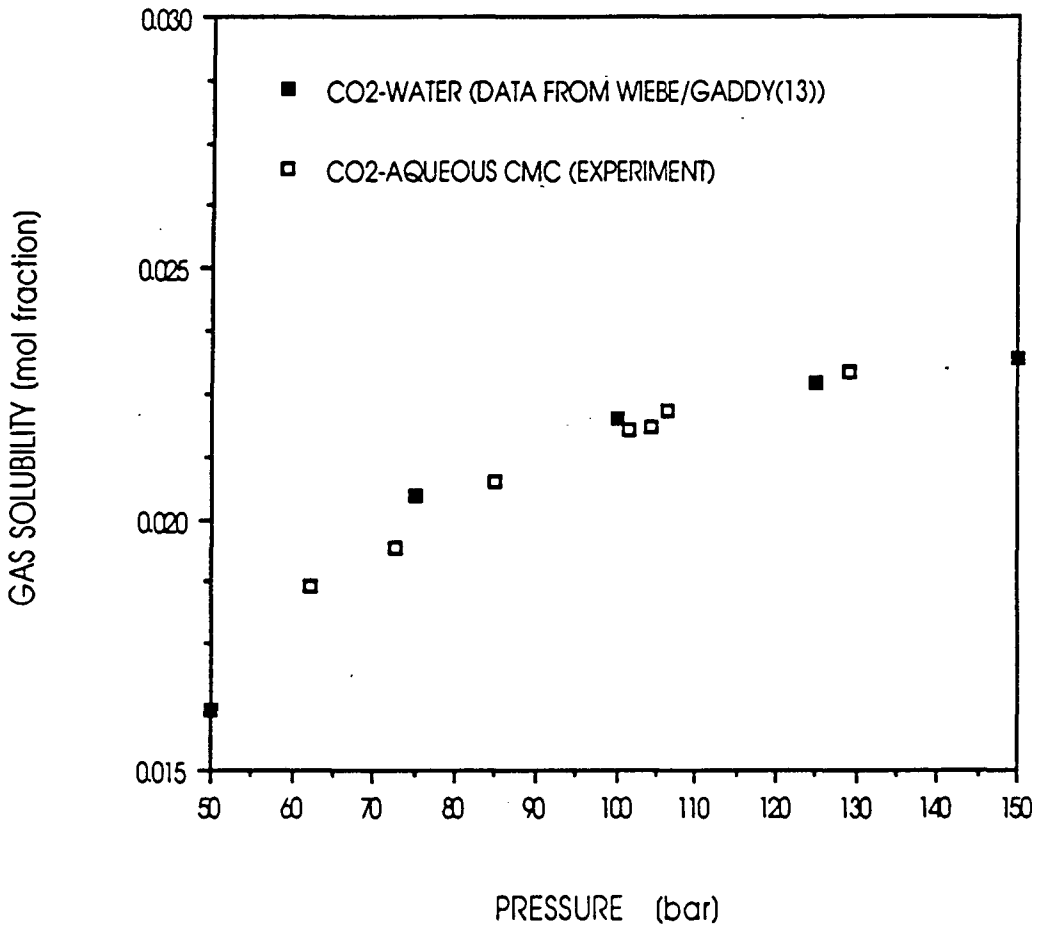


Figure 8: CO_2 solubilities in water and in aqueous polymer.

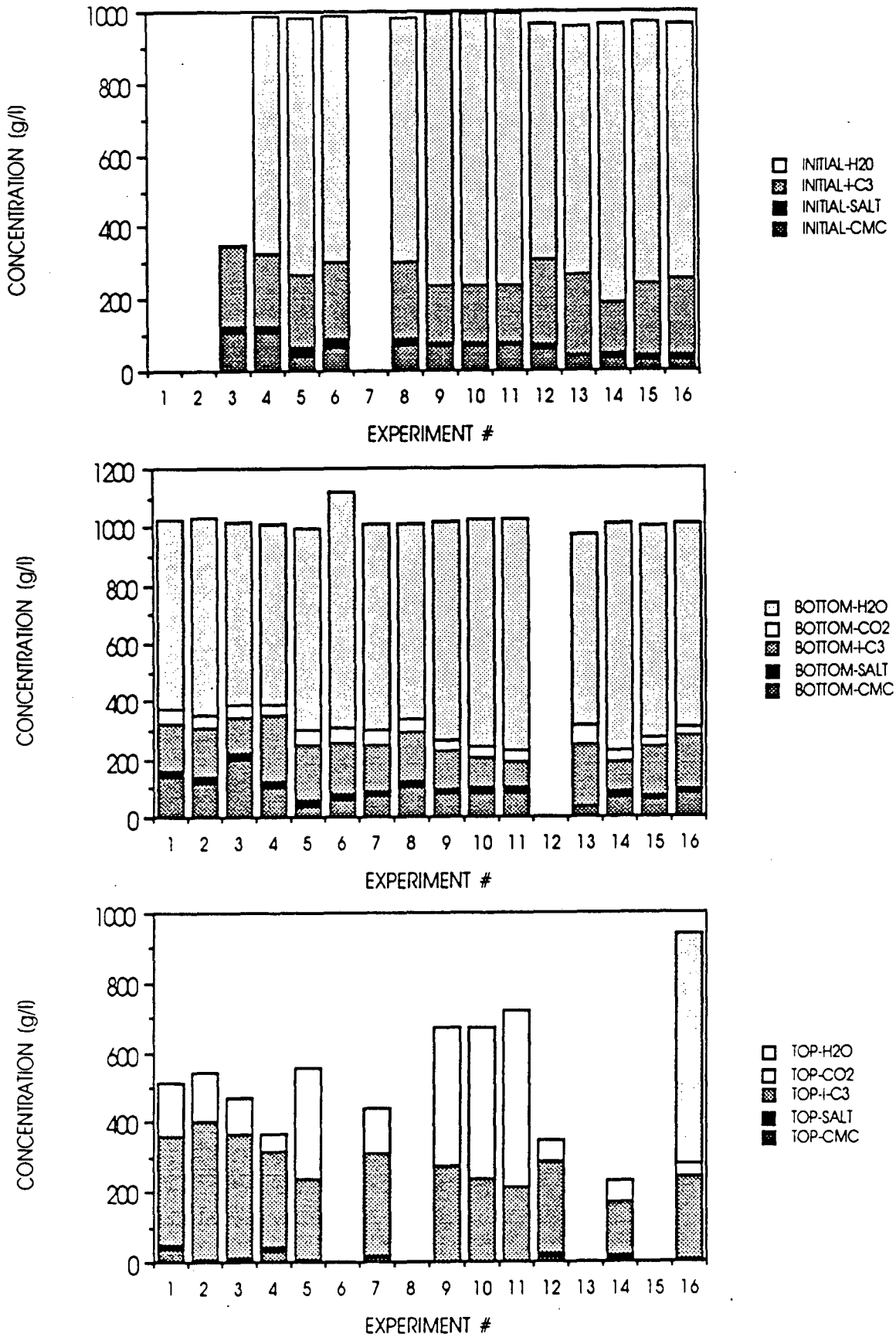


Figure 9: Initial-mixture and equilibrium phase compositions.

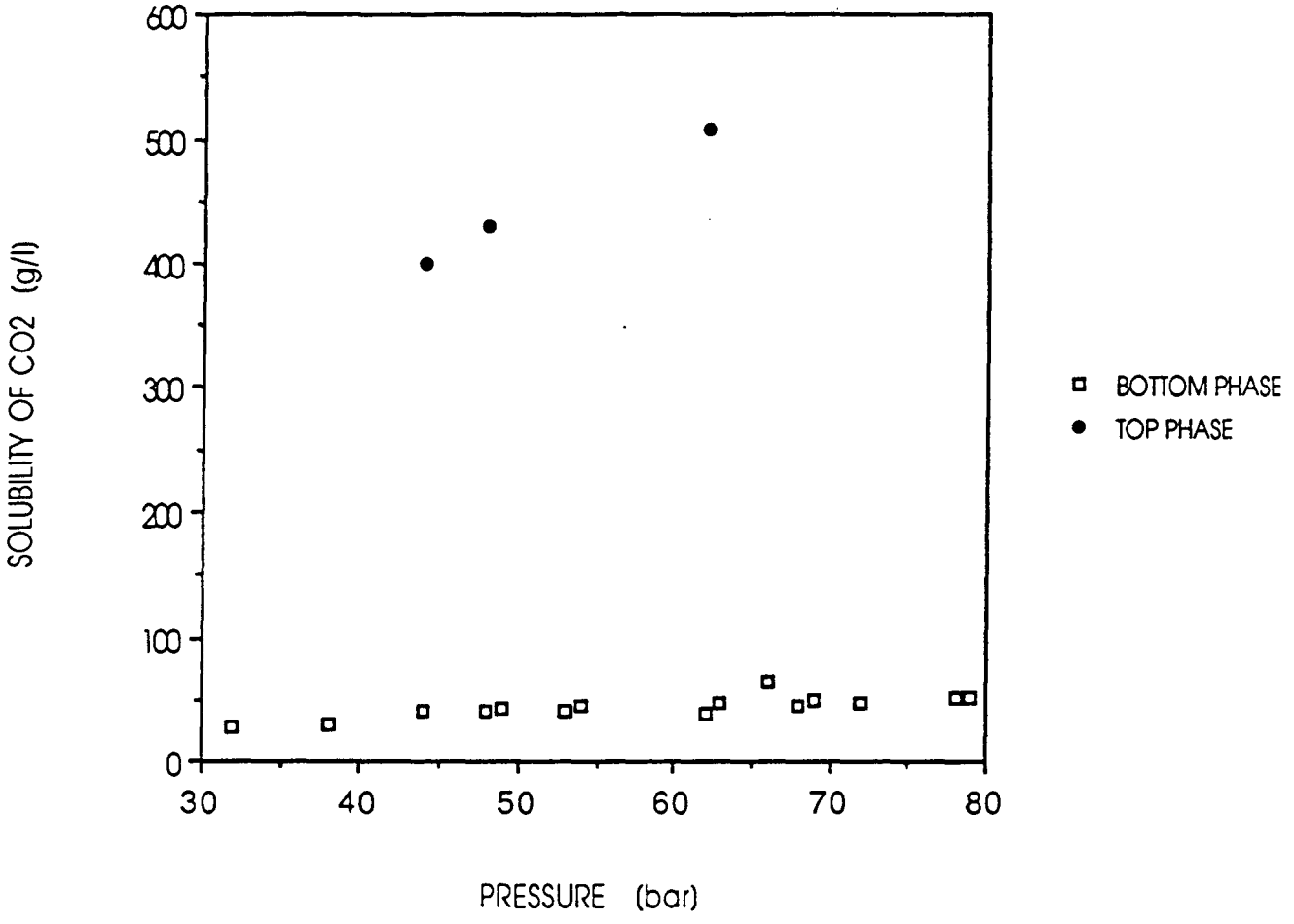


Figure 10: Change of solubility of CO_2 in the top phase with pressure.

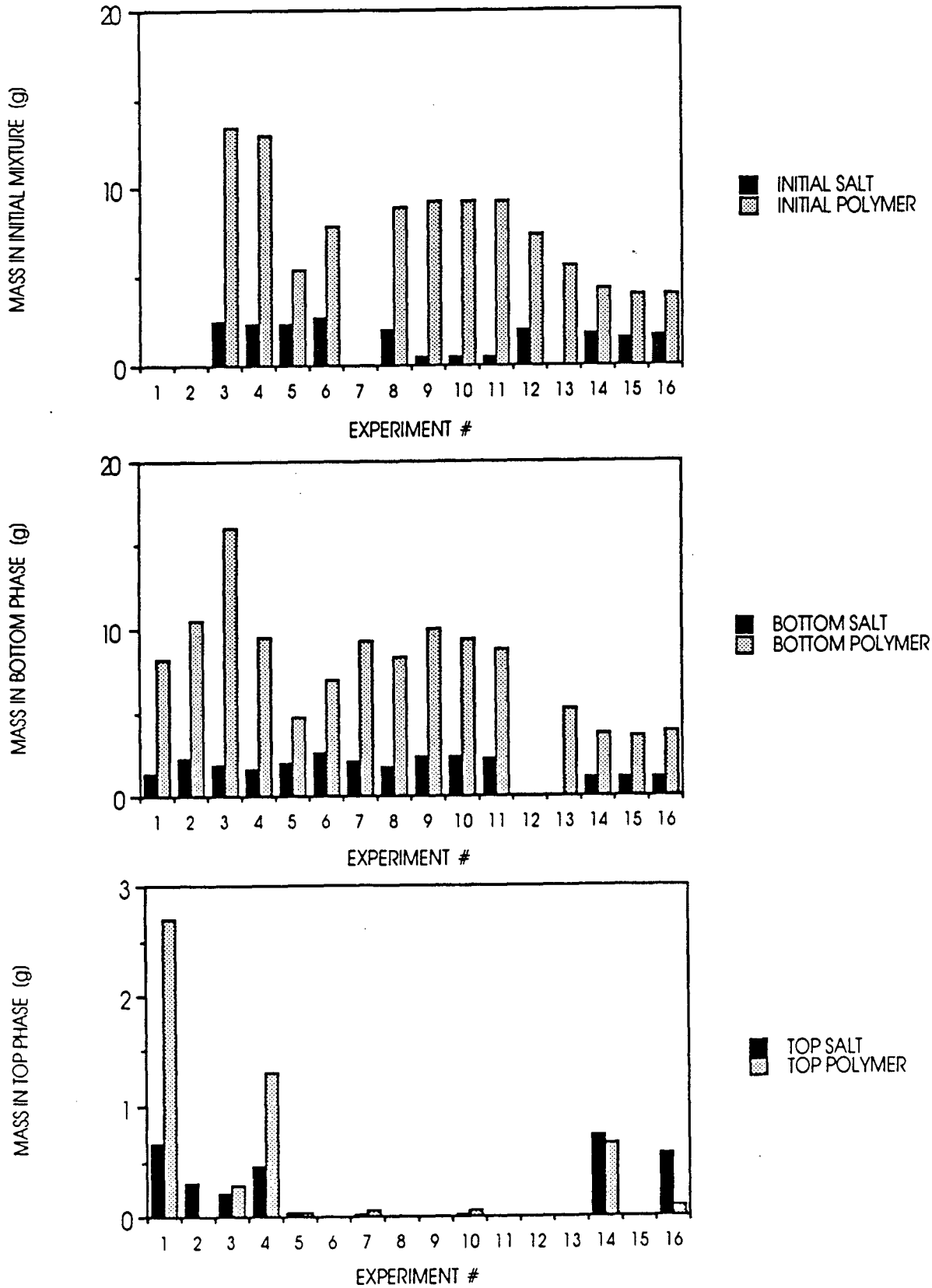


Figure 11: Distributions of CMC and K_2SO_4

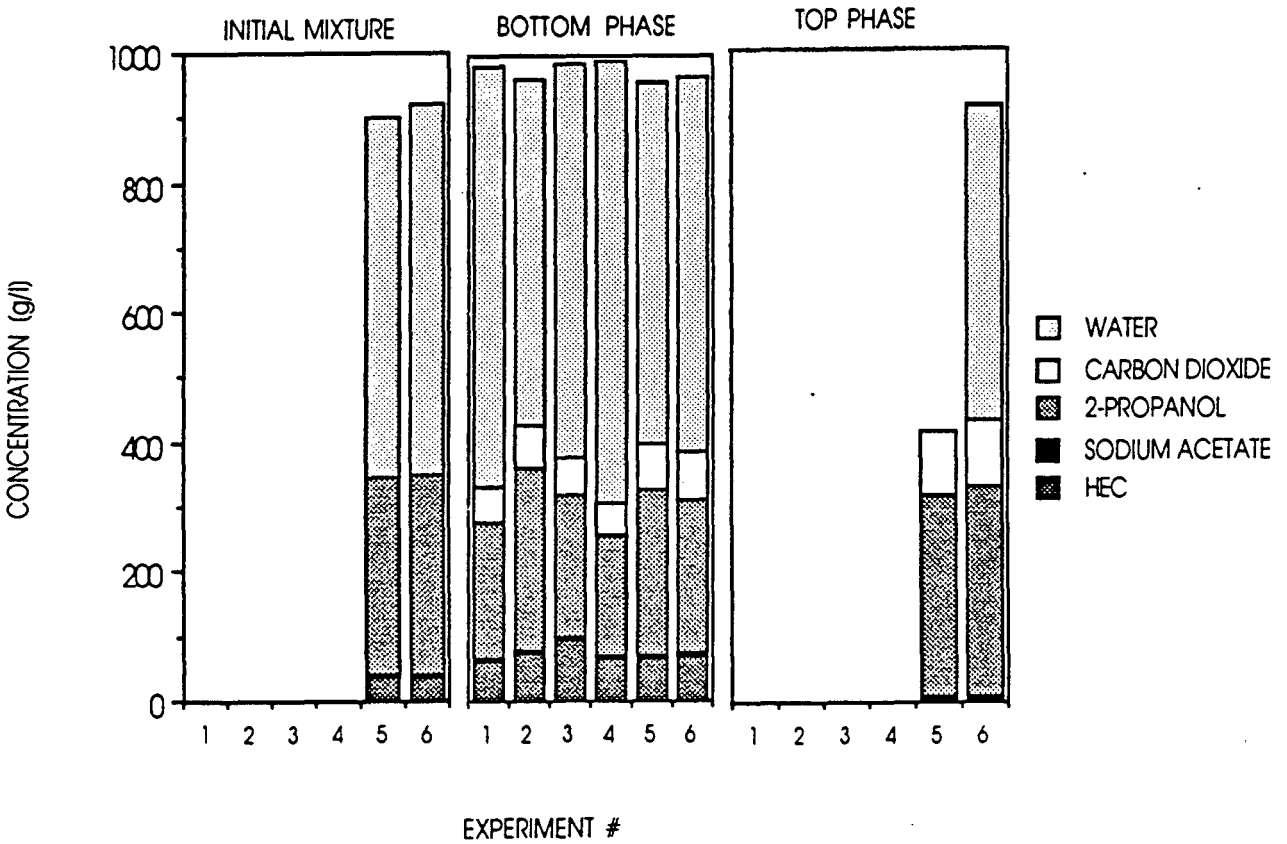


Figure 12: Initial mixture and equilibrium phase compositions for HEC solutions.

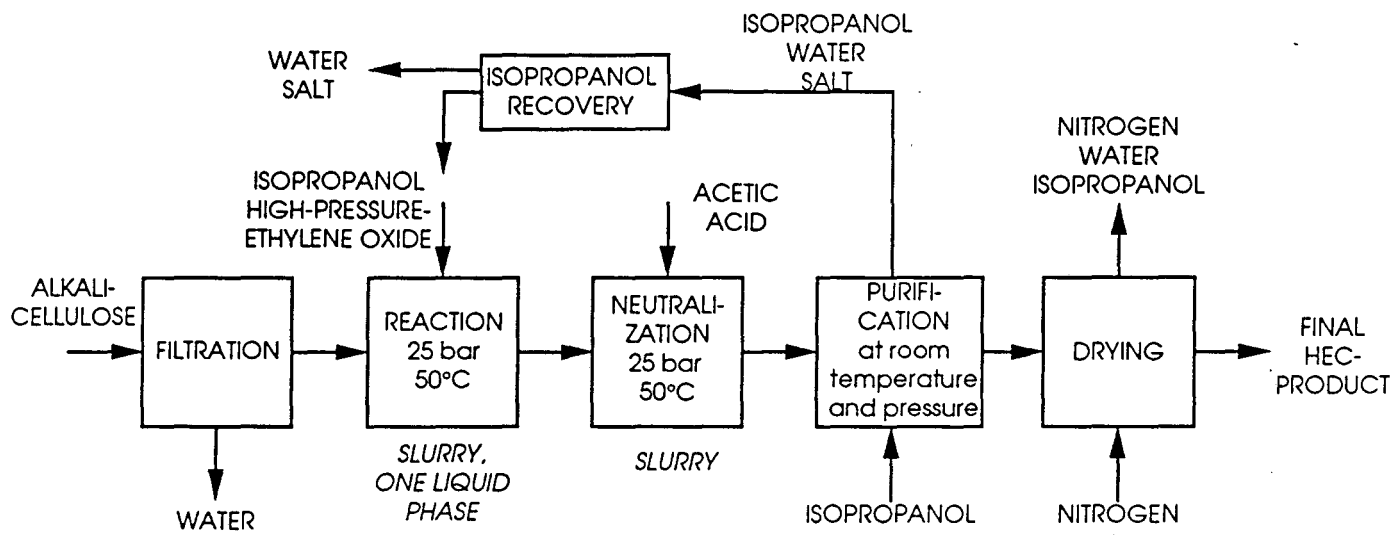


Figure 13: Current process for manufacture of HEC

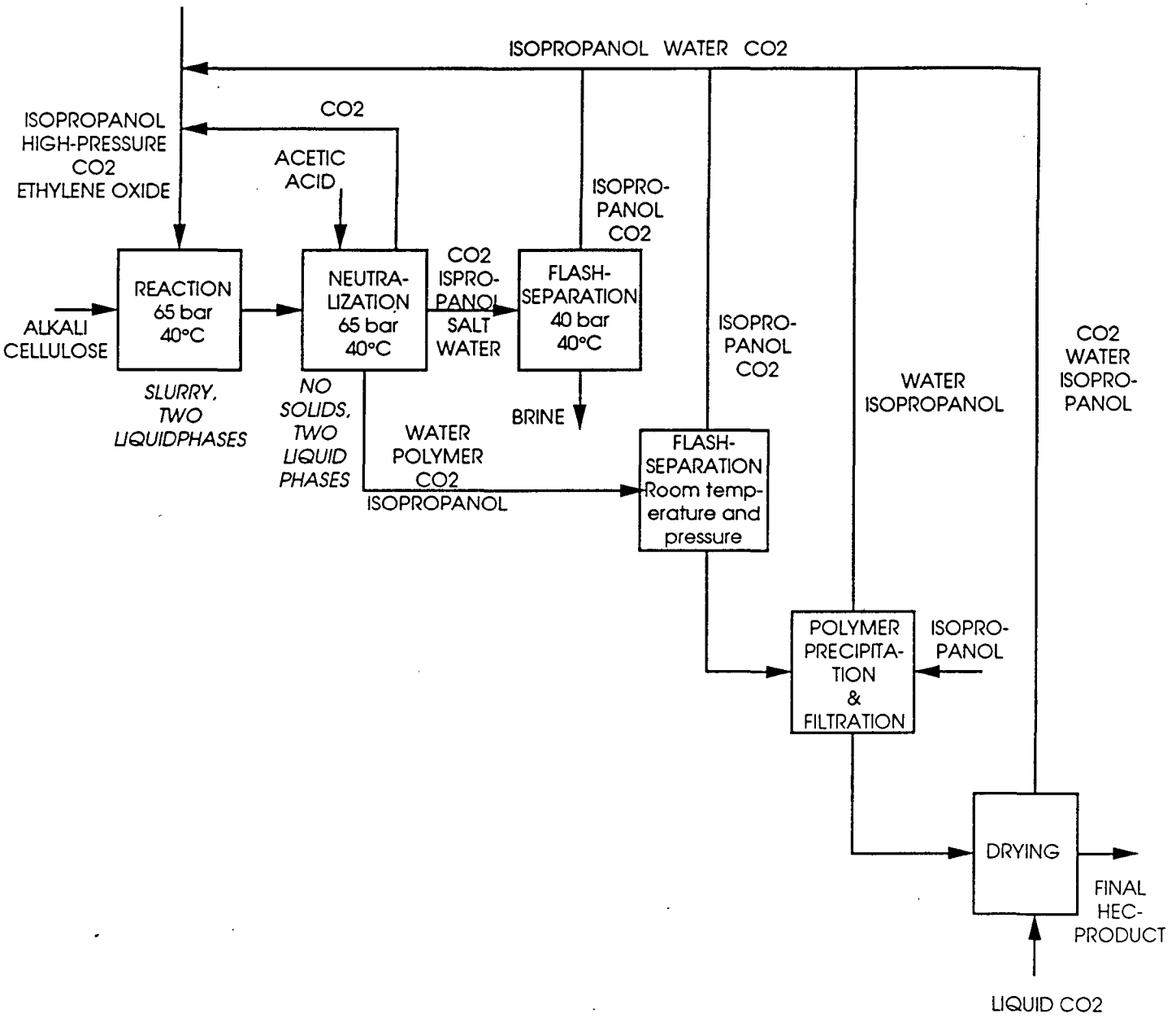


Figure 14: A possible process for manufacture of HEC.

Non optimized flowsheet based on limited experimental results.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720