Lawrence Berkeley National Laboratory

Title
THERMODYNAMICS OF LIQUID MIXTURES CONTAINING POLAR POLYMERS AND SOLVENTS

Permalink
https://escholarship.org/uc/item/5c39c6qs

Authors
Pfennig, A.F.
Prausnitz, J.M.

Publication Date
1984-12-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

To be submitted for publication

THERMODYNAMICS OF LIQUID MIXTURES CONTAINING
POLAR POLYMERS AND SOLVENTS

A.F. Pfennig and J.M. Prausnitz

December 1984

DISCLAIMER

THERMODYNAMICS OF LIQUID MIXTURES CONTAINING

POLAR POLYMERS AND SOLVENTS

A.F. Pfennig and J.M. Prausnitz

Molecular and Materials Research Division
Lawrence Berkeley Laboratory
and
Department of Chemical Engineering
University of California
Berkeley, CA 94720

ABSTRACT

The Helmholtz energy of mixing for a binary liquid mixture is given as a function of local composition as suggested by computer-simulation studies for mixtures with significant differences in intermolecular forces of the components. Particular attention is given to mixtures containing polar polymers in polar or nonpolar solvents. For a binary mixture, two parameters are required to represent solvent activity data for the entire range of concentration; these are the interchange energy ω_{12} and the contact-site parameter α_{12}.

The semi-theoretical expression presented here is used to reduce experimental results for solutions of polyglycols in benzene, dioxane, water, carbon tetrachloride, and chloroform.

The equations derived here are extended to multicomponent mixtures without further assumptions.

INTRODUCTION

Numerous attempts have been made to obtain expressions for the Helmholtz energy of a liquid mixture whose components mix in a nonrandom manner [11,13,4,34,2,20,25,26]. As discussed by Scott [29], for liquid mixtures at low pressures, the change of Helmholtz energy upon mixing at constant temperature and volume is essentially equal to the Gibbs energy of mixing at constant temperature and pressure.

A recent publication [16] discusses a semi-theoretical derivation of an expression based on the local-composition concept. For mixtures of small molecules, this concept is related to the quasi-chemical theory of mixtures; results reported in Ref. [16] agree well with computer simulations [22,23]. We here extend this derivation to liquid mixtures containing non-spherical molecules which differ appreciably in size and shape and which exhibit strong energetic interactions. We are particularly concerned with solutions of polar polymers in polar or nonpolar solvents.

Polymer molecules are generally viewed as flexible chains, consisting of equisized segments. Division into segments is usually performed in an arbitrary manner. The arbitrary segments are used to determine the number of external contact sites of a chain molecule, generally based on a lattice model of the liquid. It is then assumed that each segment has as many contact sites as a solvent molecule except that in each link between two segments two

contact sites take part. That model, however, cannot account correctly for differences in the molecular diameters of the segments that comprise the components. Therefore, inconsistencies may arise in the description of solutions containing polymer molecules with a large segment diameter and solvent molecules with a small molecular diameter, or vice versa. We avoid this inconsistency by choosing independently the hard-core volume and the surface area for the polymer and for the solvent, and by not making use of any lattice relation between them. This independent choice avoids subdivision of a polymer molecule into arbitrary segments.

THERMODYNAMIC FRAMEWORK

We consider a binary liquid mixture of components 1 and 2 at low pressure. The Helmholtz energy of mixing at constant temperature is given by the sum of three contributions:

$$\Delta A^M = \Delta A^M_{Comb} + \Delta A^M_{FV} + \Delta A^M_{EI} \ . \tag{1}$$

The first contribution follows from the entropy change of athermal mixing; the second, from the change of free volume experienced by each component upon mixing, and the third, from energetic interactions.

For polymer solutions, the first term in Eq.(1) is particularly important. The athermal combinatorial contribution accounts for the number of possible distinguishable arrangements of the molecules in the mixture:

$$\frac{\Delta A^M_{Comb}}{nRT} = \frac{1}{2} Q_M \ (\ \psi_1 \ln \psi_1 \ + \ \psi_2 \ln \psi_2 \ ) \ +$$

$$+ \ (\ 1 - \frac{1}{2} Q_M \ ) \ (\ \phi_1 \ln \phi_1 \ + \ \phi_2 \ln \phi_2 \ ) \ . \qquad (2)$$

Here n is the total number of moles, ϕ and ψ denote, respectively, hard-core-volume and contact-site fractions of the two components:

$$\phi_1 = \frac{x_1 v_1^*}{x_1 v_1^* + x_2 v_2^*} \qquad \text{and} \qquad \phi_2 = 1 - \phi_1 \ , \qquad (3)$$

$$\psi_1 = \frac{x_1 Q_1}{x_1 Q_1 + x_2 Q_2} \qquad \text{and} \qquad \psi_2 = 1 - \psi_1 \ , \qquad (4)$$

where x is the mole fraction:

$$x_1 = \frac{n_1}{n} \qquad \text{and} \qquad x_2 = 1 - x_1 \ , \qquad (5)$$

with

$$n = n_1 + n_2 \ . \qquad (6)$$

The hard-core volume is denoted by v^*. The number of contact sites per molecule, denoted by Q, is proportional to the external surface area of a molecule. For the mixture, we define

$$Q_M = x_1 Q_1 + x_2 Q_2 \ . \qquad (7)$$

Equation (2) is a modification of an expression proposed by Guggenheim [12].

The equation-of-state contribution is given by the Flory-Prigogine theory [10]:

$$\Delta A_{FV}^{M} = 3nRT \ [\ x_1 c_1 \ln(\ \tilde{v}_1^{1/3} - 1 \ ) + x_2 c_2 \ln(\ \tilde{v}_2^{1/3} - 1 \ ) -$$

$$- c_M \ln(\ \tilde{v}_M^{1/3} - 1 \ )] \ , \tag{8}[†]$$

where $3c$ is the number of external degrees of freedom per molecule, as introduced by Prigogine [28] and where $\tilde{v}_1$ and $\tilde{v}_2$ are the reduced volumes of the pure components:

$$\tilde{v}_1 = \frac{v_1}{v_1^*} \qquad \text{and} \qquad \tilde{v}_2 = \frac{v_2}{v_2^*} \ . \tag{9}$$

For the mixture, we assume that the volumes are additive. We set

$$\tilde{v}_M = \frac{x_1 v_1 + x_2 v_2}{x_1 v_1^* + x_2 v_2^*} \ , \tag{10}$$

$$c_M = x_1 c_1 + x_2 c_2 \ . \tag{11}$$

The contribution of attractive intermolecular forces to the Helmholtz energy of mixing is given by two parts:

$$\Delta A_{EI}^{M} = \Delta U^{M} - T\Delta S_{NR}^{M} \ . \tag{12}$$

Here subscript EI refers to energetic interactions and subscript NR to nonrandomness.

Assuming additivity of pair interactions, the change in internal energy upon mixing may be expressed by:

[†] If preferred, other equations of state suited for polymer solutions may be substituted; for example, the entropic contribution of the perturbed hard-chain equation [5] may be used.

$$\Delta U^M = \frac{1}{2} nQ_M [\; \psi_1^0 \epsilon_{11} + \psi_2^0 \epsilon_{22} -$$

$$- \psi_1 \psi_{11} \epsilon_{11} - \psi_1 \psi_{21} \epsilon_{21} - \psi_2 \psi_{12} \epsilon_{12} - \psi_2 \psi_{22} \epsilon_{22} \;].(13)$$

Superscript ^{0} refers to contact-site fraction ψ calculated with Q^0, the number of contact sites per molecule of the pure component. For any liquid i, we set $Q_i^0 = Q_i$. Local contact-site fraction ψ_{ji} denotes the fraction of contact sites of a central molecule i which are in contact with sites of species j. The interaction energy between molecules of species i and j per mole of contact sites is denoted by ϵ_{ij}.

The following constraints follow from site balances [9,21]:

$$\psi_1 \psi_{21} = \psi_2 \psi_{12} \quad , \tag{14}$$

$$\psi_{11} + \psi_{21} = \psi_{12} + \psi_{22} = 1 \quad . \tag{15}$$

The change from bulk composition to nonrandom local composition is accompanied by a change in entropy. Following earlier work [16], we assume that the entropy change per contact site is proportional to $\ln(\psi_j/\psi_{ji})$; we then obtain

$$\Delta S_{NR}^M = \frac{1}{2} nQ_M R [\; \psi_1(\; \psi_{11} \ln\frac{\psi_1}{\psi_{11}} + \psi_{21} \ln\frac{\psi_2}{\psi_{21}}) +$$

$$+ \psi_2(\; \psi_{12} \ln\frac{\psi_1}{\psi_{12}} + \psi_{22} \ln\frac{\psi_2}{\psi_{22}})] \quad . \tag{16}$$

The local contact-site fractions are determined such that they minimize the Helmholtz energy:

$$(\partial \Delta A^M / \partial \psi_{21})_{T,V,x} = 0 . \qquad (17)$$

Equations (14), (15) and (17) are then used to calculate the local compositions:

$$\psi_{21} = \frac{1 - \sqrt{1 - 4 \psi_1 \psi_2 \tau_{21}}}{2 \psi_1 \tau_{21}} \qquad (18a)$$

or

$$\psi_{21} = \psi_2 \lfloor \frac{2}{1 + \sqrt{1 - 4 \psi_1 \psi_2 \tau_{21}}} \rfloor . \qquad (18b)$$

Here

$$\tau_{21} = 1 - \exp(\tilde{\omega}_{12}) , \qquad (19)$$

with

$$\tilde{\omega}_{12} = \frac{\omega_{12}}{RT} \qquad (20)$$

and

$$\omega_{12} = (\varepsilon_{11} + \varepsilon_{22}) - 2\varepsilon_{21} . \qquad (21)^{\dagger}$$

The bracketed term in Eq.(18b) is a nonrandom factor [25], which corrects the bulk composition for nonrandomness. For a random mixture ($\tau_{21} = 0$), this factor is unity.

Equation (18b) can be simplified by expanding the square roots and neglecting higher-order terms in $\psi_1 \psi_2 \tau_{21}$:

$\dagger$ We here set $\varepsilon_{12} = \varepsilon_{21}$.

$$\psi_{21} = \psi_2 \left[\frac{1}{1 - \psi_1 \psi_2 \tau_{21} - \dots} \right] \quad . \tag{22}$$

Table I shows that Eq.(22) provides a good approximation for all reasonable values of $\tilde{\omega}_{12}$.

From Eqs.(1), (2), (8), (12), (13), (16), and (17), we find

$$\frac{\Delta A^M}{nRT} = \left(1 - \frac{1}{2} Q_M \right) \left(\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 \right) +$$

$$+ 3 \left[x_1 c_1 \ln \left(\tilde{v}_1^{1/3} - 1 \right) + x_2 c_2 \ln \left(\tilde{v}_2^{1/3} - 1 \right) - \right.$$

$$\left. - c_M \ln \left(\tilde{v}_M^{1/3} - 1 \right) \right] +$$

$$+ \frac{1}{2} Q_M \left(\psi_1 \ln \psi_{11} + \psi_2 \ln \psi_{22} \right) \quad . \tag{23}$$

For a random mixture ($\psi_{ji} = \psi_j$), the contribution due to energetic interactions is equivalent to that used in the Flory-Huggins [10] equation, where the hard-core-volume fractions are replaced by contact-site fractions.

In view of the three contributions to ΔA^M (Eq.(1)), the chemical potential of component 1 is

$$\Delta \mu_1 = \left(\partial \Delta A^M / \partial n_1 \right)_{T,V,n_2} = RT \ln a_1 =$$

$$= \Delta \mu_{1,Comb} + \Delta \mu_{1,FV} + \Delta \mu_{1,EI} \quad , \tag{24}$$

where a_1 is the activity of component 1. For the second part, arising from changes in free volume at low pressures, we use an approximation suggested by Oishi [24]:

$$\left(\frac{\Delta\mu_1}{RT}\right)_{FV} = 3c_1 \ln\left[\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_M^{1/3} - 1}\right] - c_1\frac{(\tilde{v}_1/\tilde{v}_M - 1)}{(1 - 1/\tilde{v}_1^{1/3})} \quad .(25)$$

The contribution due to energetic interactions is

$$\left(\frac{\Delta\mu_1}{RT}\right)_{EI} = \frac{1}{2}Q_1 \ln\frac{\psi_{11}}{\psi_1} \quad . \tag{26}$$

We assume that $v_i^{\ddagger}$, Q_i, c_i and ω_{12} are independent of composition. With the assumption that Q_i, ω_{12} and the equation-of-state contribution do not depend on temperature, we find, using the Gibbs-Helmholtz equation,

$$\Delta H^M \approx \Delta U^M = \frac{1}{2}nQ_M\psi_1\psi_{21}\omega_{12} \quad , \tag{27}$$

which is consistent with Eq.(13).

Multicomponent mixtures are discussed in the appendix.

EVALUATION OF PARAMETERS

To apply Equation (24) to real binary mixtures, we must estimate hard-core volumes $v_i^{\ddagger}$ for both components. To do so, we use the group-contribution method of Bondi [6], whose data agree well with the results of a similar compilation by Slonimskii et al. [31], which was especially developed for polymers.

Before using these molecular-volume data in the Flory-Prigogine equation, we normalize them. Comparison with compilations by Abe and Flory [1] and by Allen et al. [3] yields

- 9 -

$$v_i^* = 1.43 \ v_i^{Bondi} \qquad (28)^\dagger$$

at 20°C for substances in the v*-range from 30 to 200 cm^3/mole. Since the change of the hard-core volume with temperature is very small, as pointed out by Bondi [6], we assume v_i^* to be a constant for each substance in the temperature range of interest.

For typical small solvent molecules the number of external degrees of freedom is closely approximated by [24]

$$3c = 3.3 \ . \qquad (29)$$

For molecules whose V^{Bondi} exceeds 60 cm^3/mole, we find from data given by Abe and Flory [1] and by Allen et al. [3] the rough correlation

$$c = 0.5 + 0.01 \ V^{Bondi} \ , \qquad (30)$$

where V^{Bondi} is in cm^3/mole.

For v_1 and v_2, we use experimental densities or compilations reported by Brandrup and Immergut [8] or by van Krevelen [33].

For a binary mixture, we estimate the number of contact sites per molecule of species i by

$$Q_i = \alpha_{ij} \beta A_i^{Bondi} \ . \qquad (31)$$

Here A_i^{Bondi} is the surface area of a molecule of species i as reported by Bondi [6]. These surface areas are normalized through β to give the number of contact sites. Normalization

---

† The hard-core volumes v_i^* can also be obtained from UNIQUAC size parameters [27] upon multiplying the recommended UNIQUAC r-values by 21.70 cm^3/mole.

factor β accounts also for the reduction of the total surface area to that part which is effective for energetic interactions with other molecules. For polymers, the available surface area is less than the geometrical surface area because of folding back of the molecules. This effect increases with size and flexibility of the molecules. It is assumed to be independent of concentration.

For solutions of polymers in typical solvents, we use

$$\beta = 10^{-9} \text{ mole/cm}^2 \text{ for polymers and} \tag{32}$$

$$\beta = 1.4 \cdot 10^{-9} \text{ mole/cm}^2 \text{ for typical solvent molecules.} \tag{33}$$

For molecules of intermediate size, values between these limits should be chosen. These β-values yield a number of contact sites in the range 8 to 12 for most solvents (ranging in size from 1,4-dioxane to n-hexane) and a value of approximately 4 for water. Binary parameter α_{12} is of the order of unity and accounts for the decrease in the number of contact sites, which occurs when the molecules exhibit strong localized interactions (e.g. hydrogen bonding), where only a fraction of all possible contact sites is effective.

Binary parameters α_{12} and ω_{12} are adjusted to represent experimental activity data for various polymer-solvent pairs.

RESULTS AND DISCUSSION

Table II presents V^{Bondi} and A^{Bondi} used in this study. Table III and Figures 1 to 3 present results for binary mixtures.

Agreement with experimental data is very good; it is generally better than that obtained using the segment-interaction equation proposed by Heil [14], which is based on an expression for the local composition similar to that introduced by Wilson [34]. An advantage of our expression is that binary parameters α_{12} and ω_{12} account for different effects in the mixture (size and energy); therefore, they are not as strongly correlated as are the two adjustable energy parameters which are used in all equations of the Wilson form.

A theory for polar polymer solutions by Brandani [7] also uses local compositions; it contains two adjustable binary parameters which are strongly correlated. An expression by Heintz et al. [15] accounts for differences in molecular diameter of the components in the mixture, but does not introduce local compositions. Both of these earlier theories require volumetric (PvT) data for the pure components to obtain characteristic parameters. We do not require these here since we rely on the correlations of Bondi.

Figure 4 shows contributions to the Helmholtz energy of mixing as given in Eq.(1). In the highly nonideal system

poly(propylene oxide) - chloroform, hydrogen bonding occurs in the mixture but not in the pure components. In this system, the combinatorial contribution and that due to energetic interactions are of comparable magnitude. For the other systems studied here, the energetic part is of lower importance, and the equation-of-state contribution is always minor. Therefore, future efforts should be directed towards a better description of the Helmholtz energy of athermal mixing, i.e. towards better estimation of the size and shape parameters. It will be particularly desireable to replace Equations (32) and (33) for β by a continuous function of molecular size.

CONCLUSIONS

We have presented a semi-theoretical framework for representing thermodynamic properties of mixtures containing polar polymers and polar or nonpolar solvents. Pure-component parameters are evaluated from independent sources. With two adjustable binary parameters (interchange energy ω_{ij} and interaction-site parameter α_{ij}), very good agreement with experiment is obtained for five binary systems.

Possible improvement and extension should be directed towards better pure-component parameters, especially for medium-sized molecules which are not included in this study.

ACKNOWLEDGEMENTS

Appendix: MULTICOMPONENT MIXTURES

The framework outlined in this work can be extended to multicomponent systems without further assumptions. For a system containing k components, the contributions to Eq.(1) can be written as:

$$\frac{\Delta A_{Comb}^{M}}{nRT} = \frac{1}{2} Q_M \sum_{i=1}^{k} \psi_i \ln \psi_i - \left(\frac{1}{2} Q_M - 1 \right) \sum_{i=1}^{k} \phi_i \ln \phi_i \quad , \quad (A-1)$$

$$\Delta A_{FV}^{M} = 3nRT \left[\sum_{i=1}^{k} x_i c_i \ln(\tilde{v}_i^{1/3} - 1) - c_M \ln(\tilde{v}_M^{1/3} - 1) \right] \quad , (A-2)$$

$$\Delta U^{M} = \frac{1}{2} nQ_M \left[\sum_{i=1}^{k} \psi_i^0 \varepsilon_{ii} - \sum_{i=1}^{k} \sum_{j=1}^{k} \psi_i \psi_{ji} \varepsilon_{ji} \right] \quad , \quad (A-3)$$

$$\Delta S_{NR}^{M} = \frac{1}{2} nQ_M R \left[\sum_{i=1}^{k} \sum_{j=1}^{k} \psi_i \psi_{ji} \ln \frac{\psi_j}{\psi_{ji}} \right] \quad . \quad (A-4)$$

Where:

$$x_i = \frac{n_i}{n} \quad , \quad (A-5)$$

$$\phi_i = \frac{n_i v_i^{\ddagger}}{\sum_{j=1}^{k} n_j v_j^{\ddagger}} \quad , \quad (A-6)$$

$$\psi_i = \frac{n_i Q_i}{\sum_{j=1}^{k} n_j Q_j} \quad , \quad (A-7)$$

with

$$n = \sum_{i=1}^{k} n_i \quad . \quad (A-8)$$

For the mixture:

$$Q_M = \sum_{i=1}^{k} x_i Q_i \quad , \tag{A-9}$$

$$\tilde{v}_M = \frac{\sum_{i=1}^{k} x_i v_i}{\sum_{j=1}^{k} x_j v_j^*} \quad , \tag{A-10}$$

and:

$$c_M = \sum_{i=1}^{k} x_i c_i \quad . \tag{A-11}$$

The local contact-site fractions are again determined by minimizing the Helmholtz energy:

$$\left(\frac{\partial \Delta A^M}{\partial \psi_{ji}} \right)_{T,V,x_i,\psi_{lm}} = 0 \quad , \tag{A-12}$$

for all independent ψ_{ij} and for all ψ_{lm} independent of ψ_{ij}.

From Equation (A-12) we obtain $\frac{1}{2} k (k - 1)$ conditions of the form

$$\tilde{\omega}_{ij} = \ln \frac{\psi_{ii}\psi_{jj}}{\psi_{ij}\psi_{ji}} \quad , \tag{A-13}$$

where

$$\tilde{\omega}_{ij} = \frac{\omega_{ij}}{RT} \quad , \tag{A-14}$$

with

$$\omega_{ij} = (\varepsilon_{ii} + \varepsilon_{jj}) - 2\varepsilon_{ij} \quad . \tag{A-15}^{\dagger}$$

---

† We assume that $\varepsilon_{ij} = \varepsilon_{ji}$.

The generalizations of Eqs.(14) and (15) are

$$\psi_i \psi_{ji} = \psi_j \psi_{ij} \quad , \tag{A-16}$$

$$\sum_{j=1}^{k} \psi_{ji} = 1 \quad . \tag{A-17}$$

Equations (A-13), (A-16) and (A-17) must be solved simultaneously for all independent i-j pairs. A simple procedure for a ternary mixture has been devised by Panayiotou and Vera [25]. A simpler approximate procedure is to use Eq.(18) unaltered for all ψ_{ij}, substituting i and j for 1 and 2. Table IV shows that this procedure provides only a rough estimate for the local compositions, which influence ΔS_{NR}^{M} very strongly. These errors in entropy are partly compensated by opposite changes in the internal energy. The overall change in ΔA^{M} is minute.

Contributions to the chemical potential of component 1 due to free-volume changes and due to energetic interactions are analogous to those for binary mixtures, Eq.(25) and (26). The internal energy takes the form

$$\Delta H^{M} \approx \Delta U^{M} = \frac{1}{2} n Q_M \sum_{i=1}^{k} \sum_{j=1}^{i-1} \psi_j \psi_{ij} \omega_{ij} \quad . \tag{A-18}$$

To estimate the number of contact sites of species i, Q_i, in a multicomponent mixture, we propose the following interpolation method: Let Q_i^{ij} be the number of contact sites of a molecule i in the binary mixture of components i and j. We then define

$$Q_i = \sum_{j=1}^{k} x_i Q_i^{ij} \quad , \tag{A-19}$$

with

$$Q^{ii} = (1 - x_i)^{-1} \sum_{\substack{j=1 \\ j \neq i}}^{k} x_j Q_i^{ij} \quad , \tag{A-20}$$

which is the number of contact sites of molecule i averaged over all pair values, excluding i-i pairs. The number of contact sites of a molecule of species i depends on the binary partner. If that dependence is small, the concentration dependence of Q_1 may be neglected when calculating the chemical potential.

Table I

Local contact-site fractions calculated with Eq.(18) and with
the approximation, Eq.(22), for a binary mixture at $\psi_1 = \psi_2 = 0.5$,
for various values of $\tilde{\omega}_{12}$.

$\tilde{\omega}_{12}$	ψ_{21} Eq.(18)	ψ_{21} Eq.(22)	percent error[†]
- 0.30	0.53743	0.53464	7.45
- 0.20	0.52498	0.52373	4.98
- 0.10	0.51250	0.51219	2.50
0.10	0.48750	0.48719	2.50
0.20	0.47502	0.47378	4.98
0.30	0.46257	0.45979	7.44

[†] The error $\left| \dfrac{\psi_{21}^{Eq.(18)} - \psi_{21}^{Eq.(22)}}{\psi_{21}^{Eq.(18)} - \psi_2} \right|$ has its maximum value

at $\psi_1 = \psi_2 = 0.5$.

Table II

Pure-component parameters used in this study. For polymers,
parameters are given per repeating unit.

Fluid	Molecular Weight	V^{Bondi}	A^{Bondi}
	$\dfrac{g}{mole}$	$\dfrac{cm^3}{mole}$	$\dfrac{10^9 cm^2}{mole}$
water[†]	18.015	11.50	2.50
benzene	78.114	48.36	6.00
1,4-dioxane	84.075	46.62	5.90
chloroform	119.378	43.50	6.03
carbon tetrachloride	153.823	52.29	7.28
poly(ethylene oxide)	44.053	24.16	3.30
poly(propylene oxide)	58.080	34.38	4.64
poly(tetramethylene oxide)	72.107	44.62	6.00

[†] The geometric data for water are estimated using the inter-
atomic distances reported by Sutton [32].

Table III

Binary parameters

System	Polymer Molecular Weight	ref.	T	conc. range	No. of data points	ω_{12}	α_{12}	root mean square dev. of a_1 [†]
	g/mole		°C	wt. percent		J/mole		10^{-3}
poly(ethylene oxide) (2)								
- benzene (1)	4150	18	24.6	1-13	10	11.49	1.077	0.04
	4150	18	34.6	1-13	10	-9.93	1.084	0.13
- water (1)	4150	19	24.6	3-73	11	512.59	0.998	6.03
	4150	19	34.6	3-73	12	430.86	1.004	4.97
poly(tetramethylene oxide) (2)								
- 1,4-dioxane (1)	2000	30	30.0	5-95	13	100.83	0.994	7.04
	2000	30	40.0	5-95	13	56.79	0.983	4.93
poly(propylene oxide) (2)								
- carbon tetrachloride (1)	2050	17	5.53	10-98	12	-312.37	0.610	1.59
- chloroform (1)	2050	17	5.53	10-98	12	-1167.97	0.830	3.89

[†] The deviation is defined as $\sqrt{\left\{\frac{1}{N}\left[\sum_{i=1}^{N}(a_{calc.} - a_{exptl.})^2\right]\right\}}$, where N is the number of data points.

Table IV

Comparison of local compositions in a ternary system for $\psi_1 = \psi_2 = \psi_3 = 1/3$[†]. Eq.(A-13) denotes local contact-site fractions calculated by solving Eq.(A-13) simultaneously for all independent i-j pairs, Eq.(18) denotes those compositions which are calculated from Eq.(18) by substituting i and j for 1 and 2.

			ψ_{ij}	
i	j	$\tilde{\omega}_{ij}$	Eq.18	Eq.(A-13)
1	2	0.20	0.325	0.322
2	3	0.20	0.325	0.322
3	1	0.20	0.325	0.322
1	2	0.20	0.325	0.318
2	3	0.20	0.325	0.318
3	1	0.00	0.333	0.340
1	2	0.20	0.325	0.314
2	3	0.00	0.333	0.336
3	1	0.00	0.333	0.336
1	2	0.20	0.325	0.314
2	3	0.20	0.325	0.314
3	1	- 0.20	0.340	0.359
1	2	0.20	0.325	0.311
2	3	0.00	0.333	0.332
3	1	- 0.20	0.340	0.355
1	2	0.20	0.325	0.308
2	3	- 0.20	0.340	0.351
3	1	- 0.20	0.340	0.351

[†] The sum of relative errors has its maximum in an equimolar mixture.

Figure 1

Activity of water in poly(ethylene oxide) with a molecular weight of 4150 g/mole. Comparison with experimental data at 34.6°C.

Figure 2

Activity of carbon tetrachloride in poly(propylene oxide) with a molecular weight of 2050 g/mole. Comparison with experimental data at 5.53°C.
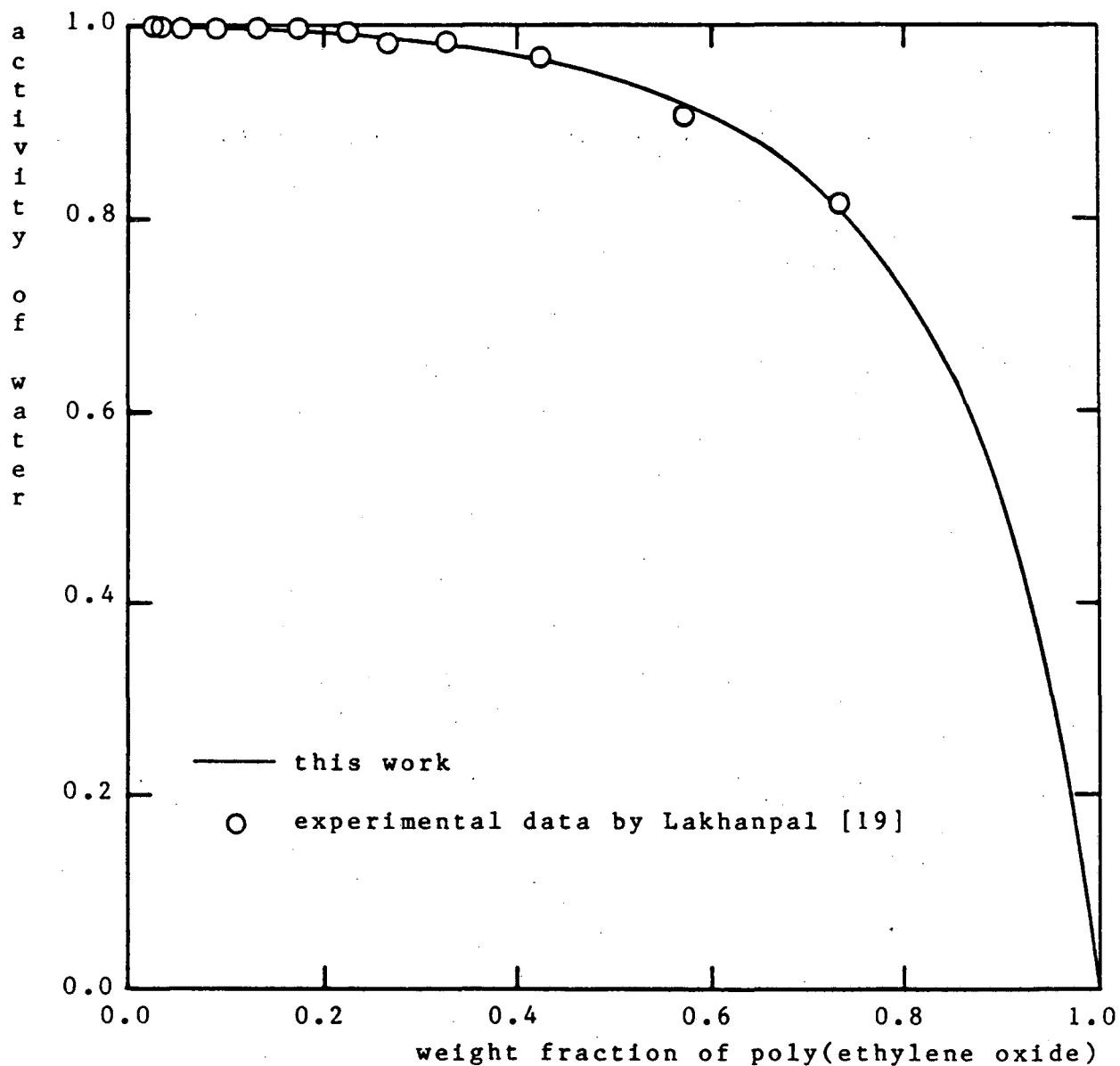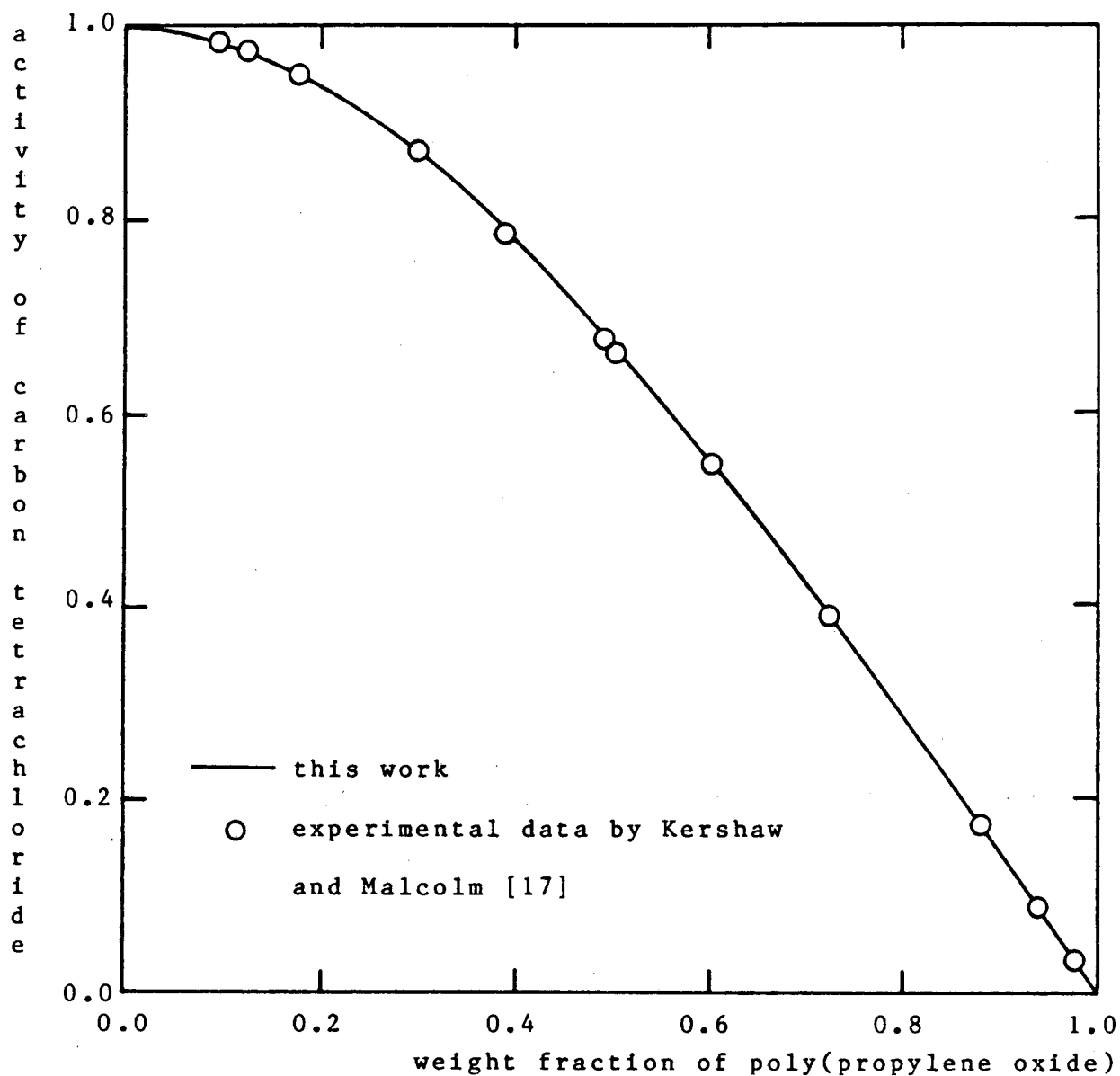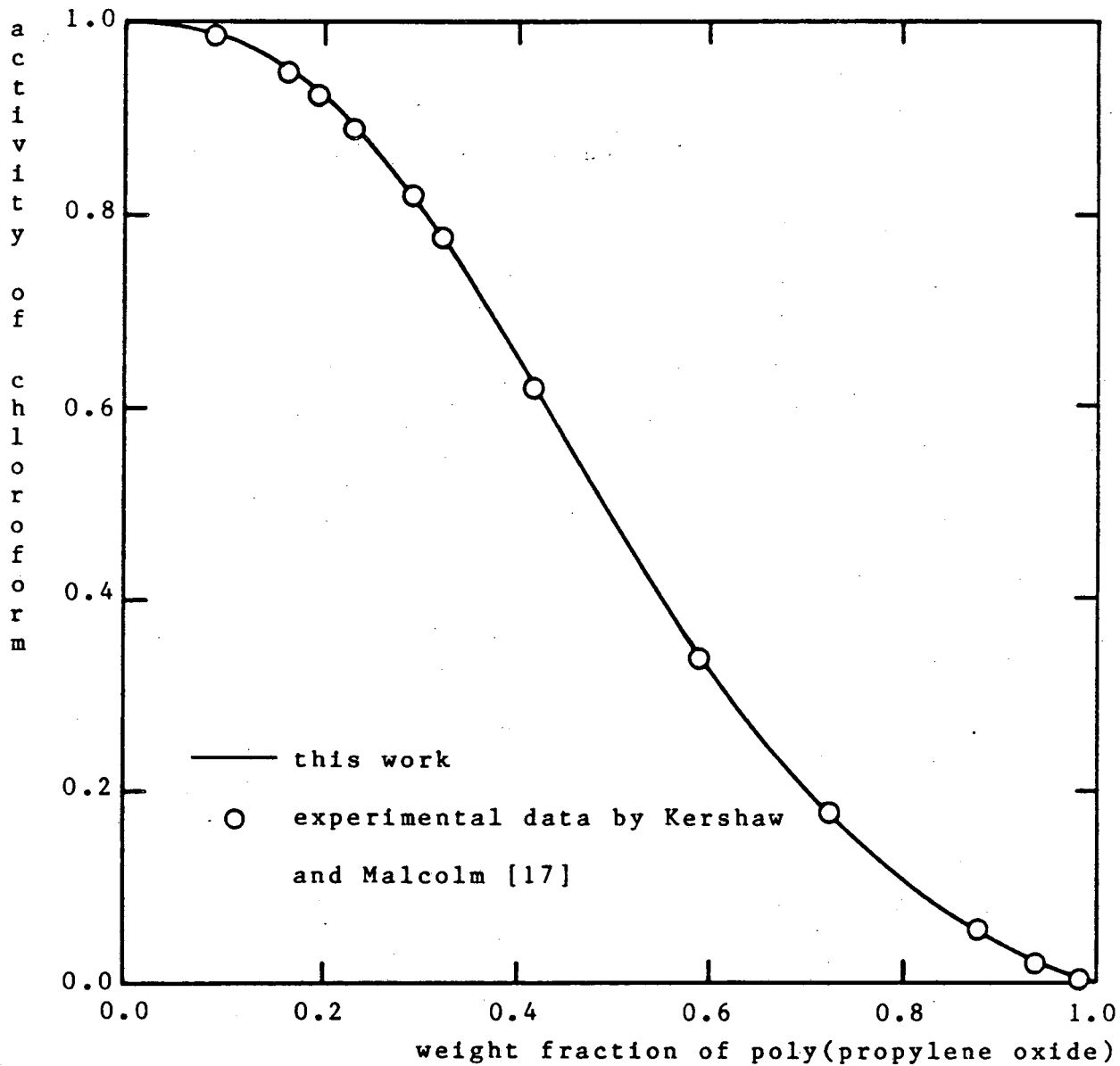
Figure 3

Activity of chloroform in poly(propylene oxide) with a molecular weight of 2050 g/mole. Comparison with experimental data at 5.53°C.
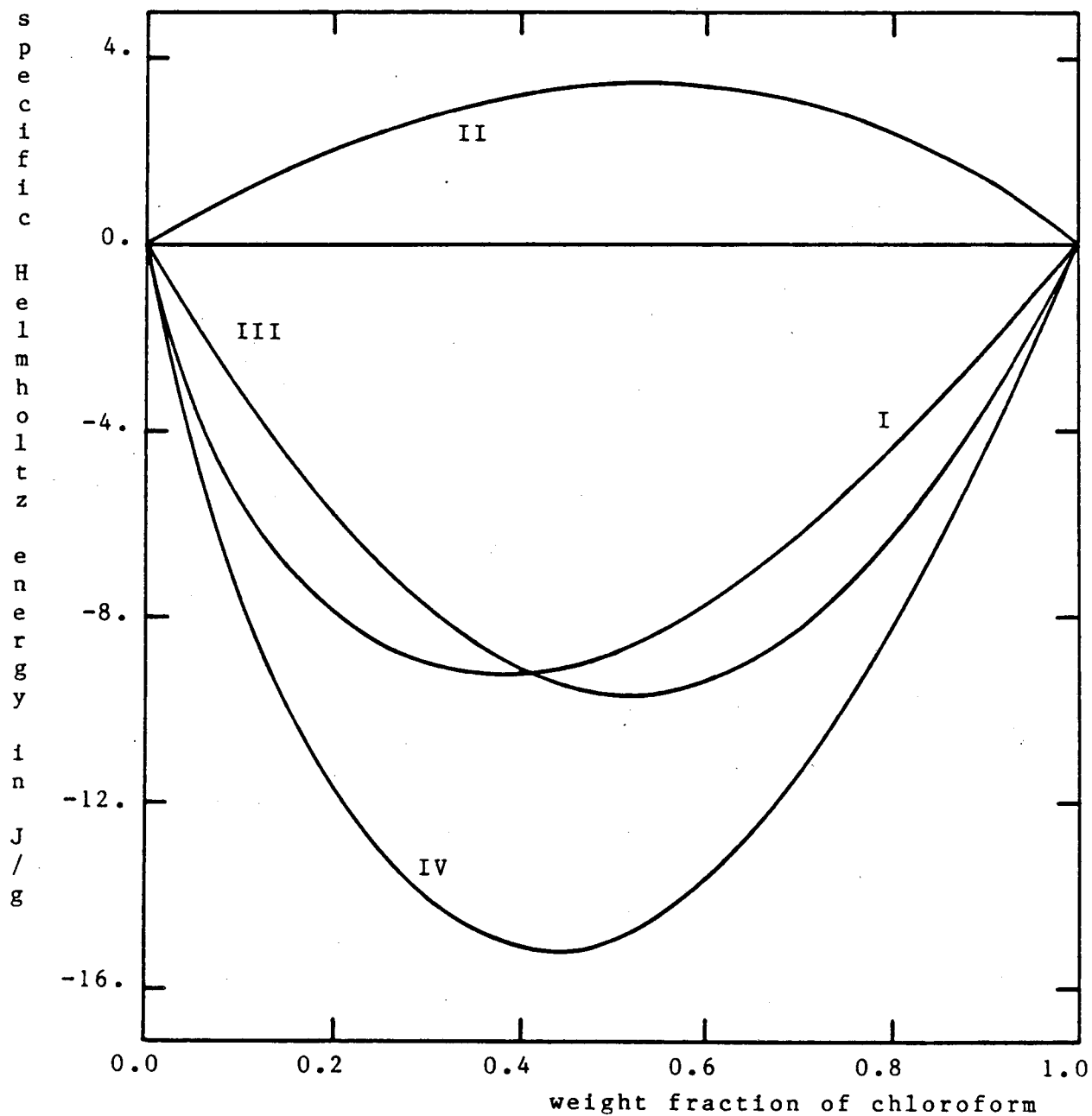
Figure 4

Relative magnitudes of contributions to the Helmholtz energy
for the system chloroform - poly(propylene oxide) with a
molecular weight of 2050 g/mole at 5.53°C.
Contributions: I - combinatorial, II - free volume,
III - energetic, IV - total.

NOMENCLATURE

A $\quad$ Helmholtz energy

A_i $\quad$ van-der-Waals surface area of a molecule

c $\quad$ external degrees of freedom per molecule

H $\quad$ enthalpy

Q $\quad$ number of contact sites per molecule

S $\quad$ entropy

T $\quad$ temperature

U $\quad$ internal energy

V_i $\quad$ van-der-Waals volume of a molecule

a $\quad$ activity

i, j $\quad$ summing indices

k $\quad$ number of components

n $\quad$ number of moles

v $\quad$ molar volume

x $\quad$ mole fraction

Greek letters

α $\quad$ binary surface parameter

β $\quad$ surface parameter

Δ $\quad$ change of property

ε $\quad$ interaction energy per mole contact sites

μ $\quad$ chemical potential

τ $\quad$ see Eq.(19)

ϕ $\quad$ hard-core-volume fraction

ψ $\quad$ contact-site fraction

ω $\quad$ interchange energy

superscripts

Bondi	from the compilations of Bondi [6]
Eq.(18)	calculated with Eq.(18)
Eq.(A-13)	calculated with Eq.(A-13)
ij	in a binary mixture of components i and j
M	upon mixing
0	of pure component
~	dimensionless quantity

subscripts

Comb	combinatorial
EI	arising from energetic interactions
FV	arising from free-volume effects
i, j	of component i or j
ij	binary parameter
ji	refers to local composition of j around a central molecule of type i
M	property of the mixture
NR	arising from nonrandomness
1, 2	of component 1 or 2

REFERENCES

[1]   Abe, A.   The Thermodynamic Properties of Small,
      Flory, P.J.   Nonpolar Molecules
                                J. Am. Chem. Soc. 87, 1838 (1965)

[2]   Abrams, D.S.   Statistical Thermodynamics of Liquid
      Prausnitz, J.M.   Mixtures: A New Expression for the
                                Excess Gibbs Energy of Partly or
                                Completely Miscible Systems
                                AIChE J. 21, 116 (1975)

[3]   Allen, G.   Intermolecular Forces and Chain
      Gee, G.   Flexibility in Polymers: I. Internal
      Wilson, G.J.   Pressures and Cohesive Energy
                                Densities of Simple Liquids
                                Polymer 1, 456 (1960)

[4]   Barker, J.A.   Cooperative Orientation Effects in
                                Solutions
                                J. Chem. Phys. 20, 1526 (1952)

[5]   Beret, S.   Perturbed Hard-Chain Theory: An
      Prausnitz, J.M.   Equation of State for Fluids Containing
                                Small or Large Molecules
                                AIChE J. 21, 1123 (1975)

[6]   Bondi, A.   Physical Properties of Molecular
                                Crystals, Liquids and Glasses
                                John Wiley and Sons, Inc., New York
                                1968

[7]   Brandani, V.   Effect of Nonrandomness in Polymer-
                                Solution Thermodynamics
                                Macromolecules 12, 883 (1979)

[8]   Brandrup, J.   Polymer Handbook
      Immergut, E.H.   John Wiley and Sons, Inc., New York
                                1966

[9]   Flemr, V.   A Note on Excess Gibbs Energy Equations
                                Based on Local Composition Concept
                                Coll. Czech. Chem. Commun. 41, 3347
                                (1976)

[10] Flory, P.J.   Thermodynamics of Polymer Solutions
                                Discuss. Farad. Soc. 49, 7 (1970)

[11] Guggenheim, E.A.   The Statistical Mechanics of Regular
                                Solutions
                                Proc. Roy. Soc. A148, 304 (1935)

[12]   Guggenheim, E.A.   Statistical Thermodynamics of Mixtures
                                 with Zero Energies of Mixing
                                 Proc. Roy. Soc. A183, 203 (1944)

[13]   Guggenheim, E.A.   Mixtures
                                 Oxford University Press, 1952

[14]   Heil, J.F.   Phase Equilibria in Polymer Solutions
       Prausnitz, J.M.   AIChE J. 12, 678 (1966)

[15]   Heintz, A.   Thermodynamics of Polydimethylsiloxane
       Neff, B.   Solutions. II. Applications of an
       Lichtenthaler, R.N.   Extended Flory-Theory.
                                 Ber. Bunsenges. Phys. Chem. 87, 1169
                                 (1983)

[16]   Hu, Y.   The Molecular Basis for Local
       Azevedo, E.G.   Compositions in Liquid Mixture Models
       Prausnitz, J.M.   Fluid Phase Equil. 13, 351 (1983)

[17]   Kershaw, R.W.   Thermodynamics of Solutions of
       Malcolm, G.N.   Polypropylene Oxide in Chloroform
                                 and in Carbon Tetrachloride
                                 Trans. Farad. Soc. 64, 323 (1968)

[18]   Lakhanpal, M.L.   Thermodynamic Properties of Solutions
       Singh, H.G.   of Polyoxyethyleneglycols in Benzene
       Sharma, S.C.   Indian J. Chem. 6, 436 (1968)

[19]   Lakhanpal, M.L.   Thermodynamic Properties of Aqueous
       Chhina, K.S.   Solutions of Polyoxyethyleneglycols
       Sharma, S.C.   Indian J. Chem. 6, 505 (1968)

[20]   Maurer, G.   On the Derivation and Extension of
       Prausnitz, J.M.   the UNIQUAC Equation
                                 Fluid Phase Equil. 2, 91 (1978)

[21]   McDermott, C.   Note on the Definition of Local
       Ashton, N.   Composition
                                 Fluid Phase Equil. 1, 33 (1977)

[22]   Nakanishi, K.   Free Energy of Mixing, Phase Stability,
       Okuzaki, S.   and Local Composition in Lennard-
       Ikari, K.   Jones Liquid Mixtures
       Higuchi, T.   J. Chem. Phys. 76, 629 (1982)
       Tanaka, H.

[23]   Nakanishi, K.   Molecular Dynamics Studies on the
       Tanaka, H.   Local Composition in Lennard-Jones
                                 Liquid Mixtures and Mixtures of
                                 Nonspherical molecules
                                 Fluid Phase Equil. 13, 371 (1983)

[24] Oishi, T.
     Prausnitz, J.M.
Estimation of Solvent Activities in Polymer Solutions Using a Group-Contribution Method
Ind. Eng. Chem. Process Des. Dev. $\underline{17}$, 333 (1978)

[25] Panayiotou, C.
     Vera, J.H.
The Quasi-Chemical Approach for Non-Randomness in Liquid Mixtures
Fluid Phase Equil. $\underline{5}$, 55 (1980)

[26] Panayiotou, C.G.
A Two-Fluid, Non-Random-Mixing Theory for Liquid Mixtures
Canad. J. Chem. Eng. $\underline{62}$, 578 (1984)

[27] Prausnitz, J.M.
     Anderson, T.F.
     Grens, E.A.
     Eckert, C.A.
     Hsieh, R.
     O'Connell, J.P.
Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria
Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1980

[28] Prigogine, I.
     Bellemans, A.
     Mathot, V.
The Molecular Theory of Solutions
North-Holland Publshing Co.
Amsterdam, 1957

[29] Scott, R.L.
Theoretical Models and Real Solutions
Disc. Farad. Soc. $\underline{15}$, 44 (1953)

[30] Sharma, S.C.
     Lakhanpal, M.L.
Thermodynamics of Mixtures of Poly(tetramethylene Oxide)s and 1,4-Dioxane
J. Polym. Sci.: Polym. Phys. $\underline{21}$, 353 (1983)

[31] Slonimskii, G.L.
     Askadskii, A.A.
     Kitaigorodskii, A.I.
About Packing of Macromolecules in Polymers
Visokomol. Soedin. $\underline{12}$, 494 (1970)

[32] Sutton, L.E.
Tables of Intermolecular Distances and Configuration in Molecules and Ions
Chem. Soc. London, Spec Publ. $\underline{11}$ (1958)
+ Supplement, ibid, $\underline{18}$ (1965)

[33] van Krevelen, D.W.
Properties of Polymers
Elsevier, Amsterdam 1976

[34] Wilson, G.M.
Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing
J. Am. Chem. Soc. $\underline{86}$, 127 (1964)