[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Phase Equilibria in Polymer–Solvent Systems. II. Thermodynamic Interaction Parameters from Critical Miscibility Data[1]

BY A. R. SHULTZ AND P. J. FLORY

RECEIVED APRIL 20, 1953

Studies of critical miscibility phenomena in polymer–solvent systems may be used to obtain reasonably trustworthy values of thermodynamic functions. The statistical thermodynamic theory of solutions has been applied to observed liquid–liquid phase separation data for fifteen solvent–polymer pairs. The solvent–polymer interaction parameters obtained by the theoretical analysis are entirely consistent with corresponding parameters for small molecule binary mixtures calculated from vapor pressure and calorimetric data. Deviations form normal entropies of mixing evaluated for polymer solutions by phase studies may be logically attributed to short range orientation effects superimposed upon the random mixing phenomenon treated by statistical theories. These deviations are comparable to those observed for small molecule mixtures and should not be considered peculiar to the chain structure of polymer molecules.

Introduction

In a recent paper[2] various aspects of experimentally observed liquid–liquid phase separation in binary polymer–solvent systems have been compared with theoretical predictions. The measured phase boundary curves exhibited qualitative agreement with theory although the two-phase regions were broader and the polymer fraction concentrations at the critical miscibility temperatures were greater than those predicted. The values of the polymer–solvent pair interaction parameters derived from the critical miscibility data were larger than those calculated from viscosity[3,4] and osmotic pressure[5] data. Because of these differences and the expected sensitivity of critical miscibility expressions to any slight error in the chemical potential formulation, the interaction parameters evaluated by the phase studies were viewed with considerable caution. However, the critical temperature was observed to depend on the polymer molecular weight precisely in the manner predicted by theory. This conformity encouraged further inspection of the thermodynamic parameters. Subsequent comparison with those for small molecule pairs, as calculated from the thermodynamic data of several investigators, has indicated that they are wholly reasonable and at least qualitatively in accord with expectation. It is the purpose of this paper to present the results of further polymer–solvent phase equilibria studies, and to examine in a systematic manner the nature of the thermodynamic interactions derived from critical miscibility measurements.

Theory

The chemical potential of component i in a binary mixture may be written quite generally as[6,7]

$$\mu_i - \mu_i^0 = RT\,[\ln(1 - v_j) + (1 - \mathrm{v}_i/\mathrm{v}_j)v_j + \chi_{ij}v_j^2] \quad (1)$$

where v_j is the volume fraction of component j, v_i and v_j are the molar volumes of the components, and χ_{ij} is a parameter characterizing first neighbor interactions. Thus, the quantity $RT\chi_{ij}v_j^2$ corresponds to the van Laar heat of mixing term. It is necessary, however, to interpret it more generally as the free energy resulting from local interactions between neighboring elements of the mixture.[8] χ_{ij} is considered to comprise both entropy and heat of dilution contributions from first neighbor interactions, which leads to the further specification that[2,8]

$$\chi_{ij} = (1/2 - \psi_{ii}) + \psi_{ij}\Theta_{ij}/T \quad (2)$$

where $R(\psi_{ij} - 1/2)v_j^2$ is the contribution to the entropy of dilution from these interactions, and $R\psi_{ij}\Theta_{ij}v_j^2$ represents the heat of dilution. According to the theory as developed for components differing in size, the entropy of dilution $\Delta\bar{S}_i$ for a binary mixture in which the local interactions make no contribution to the entropy is given by

$$\Delta\bar{S}_i^n = -R[\ln(1 - v_j) + (1 - \mathrm{v}_i/\mathrm{v}_j)v_j] \quad (3)$$

We shall refer to this as the "normal" entropy of dilution by analogy with the "ideal" entropy of dilution for a mixture of molecules of equal size ($\mathrm{v}_i = \mathrm{v}_j$); $\Delta\bar{S}_i$ will equal $\Delta\bar{S}_i^n$ if $\psi_{ij} = 1/2$. Improved agreement with experiment may be obtained, of course, through inclusion in equation (1) of terms in higher powers of the concentration v_j with arbitrary coefficients.[9]

It follows from equation (1) that the critical temperature T_c above which co-existence of two liquid phases in the binary system is impossible is given by[2,7]

$$1/T_c = (1/\Theta_{ij})[1 + (1/\psi_{ij})(1/x^{1/2} + 1/2x)] \quad (4)$$

where $x = \mathrm{v}_j/\mathrm{v}_i$, and the aforementioned resolution of the thermodynamic parameter χ_{ij} has been adopted. Thus, Θ_{ij} represents the critical miscibility temperature in the limit of infinite polymer molecular weight (*i.e.*, infinite x).

Determination of Polymer–Solvent Interaction Parameters from Liquid–Liquid Phase Equilibria.—The visual determination of phase separation temperatures in polymer solutions has been described previously.[2] Phase boundary curves thus determined for four polystyrene fractions mixed with cyclohexanol are shown in Fig. 1. The critical

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[1] A portion of this work was presented in partial fulfillment for the degree of Doctor of Philosophy at Cornell University. The research was in part carried out in connection with the Government Research Program on Synthetic Rubber under contract with the Synthetic Rubber Division, Reconstruction Finance Corporation.

[2] A. R. Shultz and P. J. Flory, THIS JOURNAL, **74**, 4760 (1952).

[3] T. G Fox and P. J. Flory, *ibid.*, **73**, 1909, 1915 (1951).

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[5] W. R. Krigbaum and P. J. Flory, *ibid.*, **75**, 1775 (1953).

[6] M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942); *J. Phys. Chem.*, **46**, 151 (1942).

[7] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

[8] P. J. Flory and W. R. Krigbaum, "Annual Reviews of Physical Chemistry," Vol. II, Annual Reviews, Inc., Stanford, California, 1951, p. 383 ff.

[9] H. Tompa, "Comptes Rendus de la deuxième Réunion Chimie Physique," Paris, 1952, p. 163.

precipitation temperatures T_c, *i.e.*, the maximal ordinates of the curves in Fig. 1 are plotted in Fig. 2 as $1/T_c$ against $1/x^{1/2} + 1/2x$. As has been found for a number of other systems,[2,10—12] the plot is accurately linear in agreement with theory as expressed by equation (4). The well-defined intercept and slope give Θ_{ij} = 358.9°K. and ψ_{ij} = 1.514 for this pair.

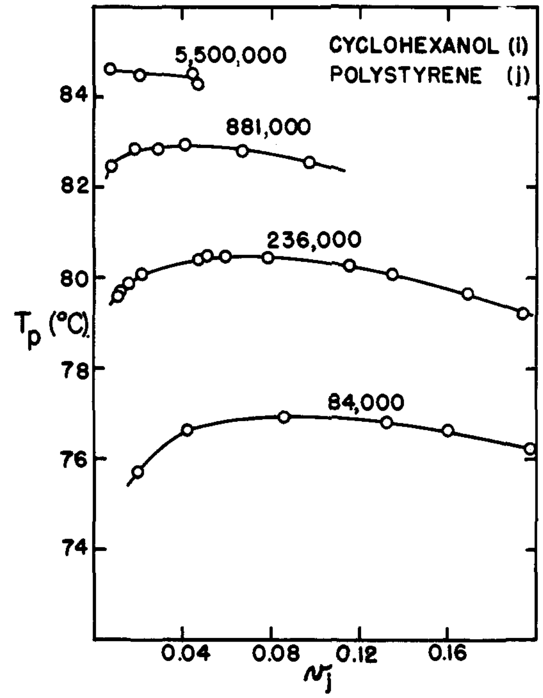

Fig. 1.—Precipitation temperatures, T_p, plotted against polymer volume fractions, v_j, for the system cyclohexanol (i)—polystyrene (j). Phase boundary curves are shown for four polystyrene fractions. The numbers adjacent to the curves are the molecular weights of the polymer fractions.

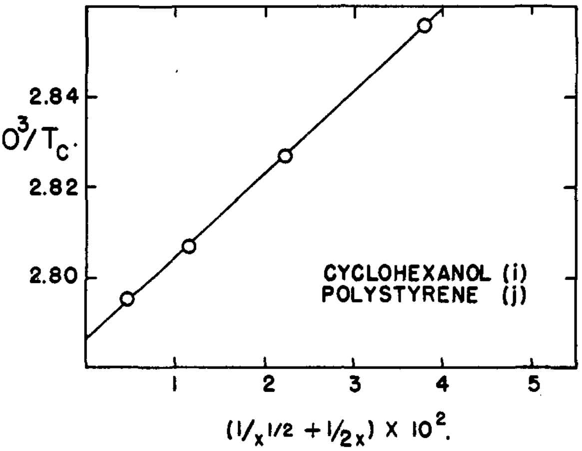

Fig. 2.—Reciprocal critical precipitation temperatures, $1/T_c$, against $(1/x^{1/2} + 1/2x)$ for the system cyclohexanol (i)-polystryrene (j). x is the polymer-to-solvent molar volume ratio.

With the aid of the values of the parameters Θ_{ij} and ψ_{ij} established in the above manner (see Table I), the observed precipitation temperatures T_p may be converted to values of χ_{ij} through the use of equation (4). Then the binary phase diagram, Fig. 1 for example, may be replotted with χ_{ij} as the ordinate. Precipitation results for cyclohexane-polystyrene (solid circles) and for cyclohexanol-polystyrene (open circles) are presented in this manner in Fig. 3. The broken lines are theoretical curves calculated according to equation (1) in the manner previously described[2,13] for polymer fractions having x = 10,950 (upper curve) and x = 768 (lower curve), respectively. Such a presentation of experimental results permits comparison of the cyclohexane-polystyrene and cyclohexanol-polystyrene phase equilibria data with theory and with each other.

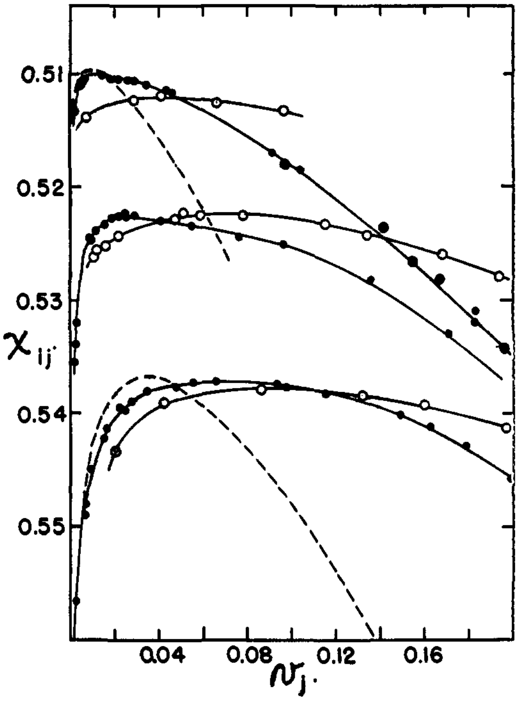

Fig. 3.—Phase boundary curves for cyclohexane (i)-polystyrene (j) (solid circles) and cyclohexanol (i)-polystyrene (j) (open circles) plotted as χ_{ij} against polymer volume fraction, v_j. The broken lines are theoretical curves corresponding to x = 10,950 (upper curve) and x = 768 (lower curve): ●, cyclohexane-polystyrene; ○, cyclohexanol-polystyrene; - - -, theoretical curves corresponding to upper and lower C_6H_{12}-PS data.

Critical miscibility temperatures, T_c, have been determined by several investigators for fractionated polymers in poor solvents. These measurements involved the observation of phase separation in solutions each of which possessed a polymer fraction concentration estimated to be the critical value, $(v_j)_c$. The broadness of the phase boundary curve peaks as illustrated in Fig. 1 revealed that precise estimation of the critical concentrations was not essential. Parameters derived from the above-mentioned studies are listed in Table I. Θ_{ij} and ψ_{ij} values were obtained from plots corresponding to Fig. 2. In every case the plots were satisfactorily linear in accordance with equation (4). The y-values listed

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TABLE I

THERMODYNAMIC PARAMETERS FROM PRECIPITATION DATA ON SOLVENT–POLYMER MIXTURES

Component i	Component j	Θ_{ij}(°K.)	ψ_{ij}	$R\psi_{ij}\Theta_{ij}$ (cal.)	y	Ref.
		Group 1				
Octadecanol-1	Polystyrene	474	1.30	1225	279	12, 2
Nitrobenzene	Polyethylene	503	1.09	1100	80	15
Cyclohexanol	Polystyrene	358.9	1.514	1080	115	14
		Group 2				
Cyclohexane	Polystyrene	307.2	1.056	645	116	2, 3b
Ethylcyclohexane	Polystyrene	343.2	0.875	598	154	3b
Phenetole	Polydimethylsiloxane	358	0.69	491	126	10
Pentanone-2	Natural rubber	287.5	0.80	458	97	11
Diisobutyl ketone	Polyisobutylene	331.1	0.65	428	162	2
n-Propyl acetate	Gutta percha	333	0.57	378	110	11
Heptanone-4	Poly-(methylmethacrylate)	305	0.61	370	166	16
		Group 3				
Dimethylformamide	Cellulose tricaprylate	413	0.39	320	76	11
Butanone	Polydimethylsiloxane	298.2	0.43	255	90	16
3-Phenylpropanol-1	Cellulose tricaprylate	323	0.21	135	149	11
		Group 4				
1,4-Dioxane	Poly-(acrylic acid)	302.2	−0.31	−187	95	16
Butanone	Poly-(methacrylonitrile)	279	−0.63	−350	99	16

TABLE II

THERMODYNAMIC PARAMETERS FOR SELECTED BINARY SMALL MOLECULE MIXTURES

i	j	χ_{ij}(30°C.)	ψ_{ij}	Θ_{ij}(°K.)	$\Delta H_i(v_j \to 1)$ cal./mole	Method	Ref.
C_6H_{12}	C_6H_6	0.557	1.194	317.6	755	a	17
					815	d	18
C_6H_{12}	$C_6H_5CH_3$	.51 ± 0.02	0.97 ± .02	306 ± 6		c	19
					610	d	18
C_6H_6	$C_6H_5CH_3$	.026 ± .009	0.593 ± .009	61 ± 1		b	20
		.030 ± .012	.589 ± .012	61 ± 1		b	21
					71	d	22
CCl_4	C_6H_{12}	.099	.594	98.3	116	a	23
CCl_4	C_6H_6	.127	.551	98.0	107	a	24
					120	d	22
CCl_4	$C_6H_5CH_3$	−0.14 ± 0.04	0.60 ± 0.04	−22 ± 3		b	25
					−26	d	22

refer to the calculation of x for the polymer–solvent pairs by the relation $x = M_j/y$ where M_j is the molecular weight of a polymer fraction. The solvent–polymer pairs are listed in order of decreasing $R\psi_{ij}\Theta_{ij}$.

Calculation of Small Molecule Interaction Parameters.—The interaction parameter χ_{ij} for a liquid pair may be evaluated from any valid measurement of the chemical potential for a binary solution. If the temperature coefficient of the chemical potential is known, the thermodynamic interaction is separable into its heat and entropy components. Accurate vapor pressure data are convenient sources from which liquid–liquid interactions may be calculated. Such calculations, leading to the parameters listed in Table II, have been carried out as follows.

a.—The most straightforward method of obtaining χ_{ij} is applicable when partial vapor pressures above liquid mixtures of known composition are available. To the approximation that the partial vapor pressure of a liquid in a binary mixture is equal to its fugacity, one obtains from equation (1)

$$(\mu_i - \mu_i^0)/RT = \ln (P_i/P_i^0) = \ln (1 - v_j) + [1 - (V_i/V_j)]v_j + \chi_{ij}v_j^2 \quad (5)$$

where P_i is the partial vapor pressure of component i above a solution of volume fraction composition v_j, and P_i^0 is the vapor pressure of pure i at the same temperature. According to equation (5) a plot of $\ln(P_i/P_i^0) - [\ln (1 - v_j) + (1 - V_i/V_j)v_j]$ against v_j^2 should yield a straight line passing through the origin and having a slope χ_{ij}. Dispersion forces predominate in the small molecule systems referred

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(24) G. Scatchard, S. E. Wood and J. M. Mochel, *ibid.*, **62**, 712 (1940).

(25) R. A. Lehfeldt, *Phil. Mag.* (London, Edinburgh and Dublin), [5] **46**, 42 (1898).

to in this paper, and the predicted linearity therefore obtains. When highly polar interactions and/or hydrogen bonding occur, equation (1) is not an adequate expression for the chemical potential.[25a]

b.—If the liquid–vapor equilibria of a binary system are described only in terms of the liquid mixture compositions and their total vapor pressures, it is necessary to adopt a different procedure for the calculation of χ_{ij}. From equation (5) and the corresponding expression for $(\mu_j - \mu_j^0)/RT$ one obtains

$$P_{\text{total}}^{\text{observed}} = v_i P_i^0 \exp\{[1 - (\mathrm{v}_i/\mathrm{v}_j)]v_j\} \exp\{\chi_{ij}v_j^2\} + v_j P_j^0 \exp\{[1 - (\mathrm{v}_j/\mathrm{v}_i)]v_i\} \exp\{(\mathrm{v}_j/\mathrm{v}_i)\chi_{ij}v_i^2\} \quad (6)$$

$$= P_i^{\text{n}} \exp\{\chi_{ij}v_j^2\} + P_j^{\text{n}} \exp\{(\mathrm{v}_j/\mathrm{v}_i)\chi_{ij}v_i^2\} \quad (6a)$$

where P_i^{n} and P_j^{n} are the "normal" partial pressures of components i and j which would be observed for a liquid mixture of the volume composition v_j if $\chi_{ij} = 0$. Expansion of the exponentials in equation (6a), subtraction of $P_{\text{total}}^{\text{n}} = P_i^{\text{n}} + P_j^{\text{n}}$ and rearrangement yields the approximate relation

$$\chi_{ij} \cong [P_{\text{total}}^{\text{observed}} - P_{\text{total}}^{\text{n}}]/[P_i^{\text{n}}v_j^2 + (\mathrm{v}_j/\mathrm{v}_i)P_j^{\text{n}}v_i^2] \quad (7)$$

For $\chi_{ij}^2 < 0.04$ this expression appears to be quite satisfactory.

c.—For systems in which χ_{ij}^2 is considerably greater than 0.04, equation (7) is not a good approximation. Terms which are quadratic and cubic in χ_{ij} in the exponential expansions of equation (6a) must then be retained for the evaluation of χ_{ij}.

d.—Calorimetric data are included in Table II for comparative and supplemental purposes. $\text{Lim}_{(v_j \to 1)}\Delta\bar{H}_i = R\psi_{ij}\Theta_{ij}$ is the amount of heat absorbed by a system when one mole of component i is dissolved in an infinite amount of component j. This partial molar heat of mixing at infinite dilution is obtained by plotting the heat absorbed, ΔH, when one mole of i is mixed with enough j to yield a concentration v_i against this concentration, v_i. Extrapolation to $v_i = 0$ gives the desired partial molar quantity as the intercept. The suggested plots proved to be approximately linear for the data treated in the compilation of Table II. For systems which conform to equation (1), calorimetric data furnish the means by which χ_{ij} may be separated into its component parts. Knowledge of χ_{ij} at a given temperature combined with the value of $\psi_{ij}\Theta_{ij}$ from $\Delta\bar{H}_i(v_j = 1)$ effects the resolution formulated in equation (2).

Table II has been compiled by application of the above-mentioned methods of analysis to selected data.

Discussion

The extent of agreement between predicted and observed phase boundary curves for the solvent—polymer systems cyclohexane–polystyrene and cyclohexanol–polystyrene is seen in Fig. 3. The distinguishing characteristics of the deviation of these and other systems from theory are the large two-phase regions observed and the correspondingly increased breadth of the phase boundary curves in the region of critical miscibility. Although this deviation from theory has not been explained, it is important to point out that it is not peculiar to polymer solutions. A discussion of the problem of critical phenomena in binary solutions by Hildebrand and Scott[26] contains references to several instances of similar behavior. Even binary mixtures conforming closely to the regular solution concept exhibit broadening of the coexistence curve in the region of critical miscibility.[27] The similarity of deviations from solubility theory of small molecule binary mixtures to those of polymer solutions encourages one to place equal confidence in thermodynamic parameters derived from critical miscibility data for polymer–solvent systems. Actually, determination of interaction parameters from phase equilibrium measurements has greater validity for polymer solutions than for small molecule solutions since less deviation from "normality" (*cf.* following paragraph) is required to produce phase separation in the former; thus, equation (1) should be a more accurate expression for the chemical potential of a polymer solution at critical miscibility.

Let us now examine the thermodynamic interactions between the polymer–solvent pairs listed in Table I. In the case of a solution exhibiting the "normal" entropy of dilution given by equation (3), $\psi_{ij} = 0.50$ as previously noted. The deviation from the normal entropy of dilution is therefore $R(\psi_{ij} - 0.5)v_j^2$, which may be considered to arise principally from a loss (or gain) in local order of the solution relative to that existent in the pure liquid components. The heat absorbed by the solution upon addition of one mole of component i to an infinite amount of solution of composition v_j is $R\psi_{ij}\Theta_{ij}v_j^2$, according to equations (1) and (2).

All of the data in Table I were obtained from precipitation measurements on polymers of comparatively high molecular weight, and this requires according to equation (4) that $\chi_{ij} \cong 0.50$ within the range of the observations for each of the systems studied. Hence, by equation (2), the entropy of dilution parameter is necessarily related to the heat of dilution parameter $\psi_{ij}\Theta_{ij}$ as follows

$$\psi_{ij} \cong \psi_{ij}\Theta_{ij}/T$$

under the conditions required to bring about precipitation. Since the temperature range over which the various measurements were made is limited (279 to 503°K.), variations in ψ_{ij} are correlated implicitly with those occurring in $R\psi_{ij}\Theta_{ij}$. This is a consequence of the experimental method adopted. With this restriction in mind, one may for convenience divide the solvent (i)–polymer (j) systems of Table I into four groups characterized as follows.

Group 1. A large positive heat of dilution and positive deviation from the normal entropy of dilution. ($R\psi_{ij}\Theta_{ij} > 700$; $\psi_{ij} > 1.10$)

Group 2. A moderate positive heat of dilution and a small positive deviation from the normal entropy of dilution. ($350 < R\psi_{ij}\Theta_{ij} < 700$; $0.50 < \psi_{ij} < 1.1$)

[25a] G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **68**, 1957, 1960 (1946).

[26] J. H. Hildebrand and R. L. Scott, "Annual Review of Physical Chemistry," Vol. I, p. 75 ff.; "The Solubility of Non-Electrolytes," Third edition, Reinhold Publ. Corp., New York, N. Y., p. 457 ff.

[27] B. H. Zimm, *J. Phys. Colloid Chem.*, **54**, 1306 (1950).

Group 3. A small positive heat of dilution and a small negative deviation from the normal entropy of dilution. ($0 < R\psi_{ij}\Theta_{ij} < 350$; $0 < \psi_{ij} < 0.50$)

Group 4. A small negative heat of dilution and a large negative deviation from the normal entropy of dilution. ($R\psi_{ij}\Theta_{ij} < 0$; $\psi_{ij} < 0$)

Group 1 includes polystyrene solutions in two considerably different aliphatic alcohols. The larger value of ψ_{ij} associated with cyclohexanol is in accord with the expected high degree of local order in the pure liquid of this compact, cyclic alcohol as compared to that of the long-chain octadecanol. The presence of hydroxyl groups, with consequent hydrogen-bridging, explains the absolute high degrees of local order present in the pure alcohols. Equation (1) is not a satisfactory expression for the chemical potential of an alcohol at low concentrations in a binary mixture with hydrocarbons.[16] However, at the high alcohol concentrations corresponding to the observed T_c for the above polymer–solvent systems equation (1) should offer a good approximation to the chemical potential, thus explaining the linearity of the plot in Fig. 2. The nitrobenzene–polyethylene system exhibits a large heat of dilution, which places it logically in group 1 despite the fact that its deviation from normal entropy of dilution is not as great as those of the alcohol–polystyrene pairs.

Group 2 contains the largest number of systems studied by phase equilibria measurements. It comprises mainly those components which are not highly oriented in their pure liquid states and which have little tendency toward mutual alignment or association upon mixing. The degree of orientation therefore changes little on mixing. The moderate endothermal heats of dilution are in accord with those of chemically analogous small molecule pairs. The last three pairs of group 2 and the first two pairs of group 3 are nearly normal solutions as defined above.

The liquid pairs of group 3, although yielding slightly endothermal mixtures, form solutions in which a greater degree of orientation occurs than in the pure liquid components. Since an appreciable degree of local order must exist in these pure liquid components, the mixtures must be rather highly ordered.

The two exothermal systems found in group 4 exhibit marked negative deviations from the normal entropy of dilution. Thus, as in group 3, the interaction of the solvent molecules with the polymer chain causes an increase in local order. In group 4 the loss of random character upon mixing is much greater and is accompanied by heat evolution.

The above observations indicate that the relative magnitudes and signs of the interaction parameter components as determined by liquid–liquid phase equilibria measurements are reasonable. In order to explore more quantitatively the correspondence between solvent–polymer and analogous binary small molecule pair interactions, the latter were analyzed as described above and the results were tabulated in Table II. Inspection of Tables I and II reveals that the values of ψ_{ij}, Θ_{ij} and $\Delta\bar{H}_i(v_j \rightarrow 1)$ for the cyclohexane–polystyrene pair lie in each case between the corresponding values for cyclohexane–toluene and cyclohexane–benzene. Furthermore, the cyclohexane–polystyrene and cyclohexane–toluene parameters are nearly identical. Upon the basis of this comparison a solubility parameter,[28] δ, of 8.9 is indicated for polystyrene in the region of 25°. Phase equilibria data[29] for the ternary system carbon tetrachloride (1)–cyclohexane (2)–polystyrene (3) at 15° yield $\chi_{13} = -0.12_5 \pm 0.05$. Within experimental error this is equal to the carbon tetrachloride–toluene $\chi_{ij} = -0.14 \pm 0.04$ at the same temperature. Again the choice of toluene as a thermodynamic interaction model for polystyrene is obvious.

The relationship between the interaction parameter components determined from phase studies and the corresponding quantities obtained from the temperature coefficient of intrinsic viscosities requires further investigation. Careful evaluation of previous[3] and more recent[15] viscosity data on the cyclohexane–polystyrene system reveals that the phase equilibria ψ_{ij} value is 7.7 times the viscosity ψ_{ij} for this pair. The Θ_{ij} values determined by either method are identical. Whether 7.7 is a general factor connecting the parameters (ψ_{ij} and, therefore, $\psi_{ij}\Theta_{ij}$) of viscosity measurements with those of critical miscibility must be determined by comparative studies on other systems. There are indications from the miscibility data[29] for carbon tetrachloride–cyclohexane–polystyrene that this factor is not satisfactory for the carbon tetrachloride–polystyrene pair.

ITHACA, N. Y.

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[28] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," Third edition, Reinhold Publ. Corp., New York, N. Y., Chapter VII.

[29] Data to be published.