Thermodynamic Interpretation of Solute–Polymer Interactions at Infinite Dilution

KHALID A. KARIM* and DAVID C. BONNER,*† *Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409*

Synopsis

Heats of solution at infinite dilution of solutes in poly(ethyl methacrylate) were estimated using gas–liquid chromatography over a temperature range of 417.74 K–427.55 K. The heat of solution is related to solute polarizability and dipole moment. Contributions of specific interactions such as hydrogen bonding and charge-transfer complexing to the enthalpy of solution were also determined.

Introduction

Gas–liquid chromatography (GLC) has proved to be an accurate technique for measuring thermodynamic properties of binary solutions, providing that the volatilities of the two components different considerably.[1-9] In recent years, various attempts have been made to develop a common approach for the determination of thermodynamic data for binary polymer solutions from GLC measurements.

Our objectives here is to identify the various types of intermolecular force interactions between polymer and solute in concentrated solution. This is done using a mathematical model of a type first described by Dwyer and Karim[10] for binary solutions of low molecular weight substances. The model of Dwyer and Karim[10] is

$$-\Delta H_s = a\alpha_1 + b\mu_1 + X \tag{1}$$

where α_1 is the solute polarizability; μ_1 is the solute dipole moment; X is the contribution of specific interactions such as hydrogen bonding, charge transfer, and the like; and a and b are empirically determined constants. The heat of solution of a solute in a solvent (a polymer in this case) at infinite dilution is represented by ΔH_s. (We have used the symbol ΔH_s with the same meaning as the symbol $\Delta \overline{H}_s$ of Dwyer and Karim.[10] We eliminate the superscript (−) to avoid confusion with partial molar quantities.) From gas–liquid chromatography (GLC), we determine ΔH_s using

$$\Delta H_s / RT^2 = d \ln V_g{}^0 / dT \tag{2}$$

As Dwyer and Karim[10] point out, eq. (2) only gives an approximate value of ΔH_s. However, due to uncertainties in the values of polarizability and dipole movement, further refinement of eq. (2) for use in conjunction with eq. (1) is unwarranted. The specific retention volume used here is defined by

$$V_g{}^0 = F(t_g - t_r)(273.15/T)(f_p/m_2) \tag{3}$$

* Present address: Chemical Engineering Department, Texas A & M University, College Station, Texas 77843.

† To whom correspondence should be addressed.

0021-8995/78/0022-1277$01.00

where F = carrier gas flow rate at column outlet, T = column temperature in K, t_g = retention time (to peak maximum) of solute, t_r = retention time (to peak maximum) of air, m_2 = mass of polymer coated on Fluoropak in the column f_p = gas compressibility correction = $\frac{3}{2}[(P_o)^2 - 1]/[(P_i/P_o)^3 - 1]$, P_i = column inlet pressure, and P_o = column outlet pressure.

In order to demonstrate the applicability of the technique embodied in eqs. (1) and (2) to polymer solutions, we use poly(ethyl methacrylate) as the stationary liquid phase (solvent) and a variety of monofunctional aliphatic and aromatic compounds as solutes.

Experimental

A Varian Aerograph Model 920 gas chromatograph containing thermal conductivity detectors was used in this study. Columns of stainless-steel tubes about 2 m long, with 2.2 mm I.D. and 0.47 mm wall thickness were packed with 3.30 g poly(ethyl methacrylate) supported on acid-washed, 80–100 mesh Fluoropak 80. The number-average molecular weight ($\overline{M}_n$) of the polymer determined by gel permeation chromatography is equal to 144,000. The polymer was carefully deposited on the solid support from solution in chloroform. The Fluoropak packing was coated with 1 g polymer per 10 g Fluoropak. Helium was used as the carrier gas and was dried by passage through a gas purifier containing silica gel and molecular sieves. The gas inlet pressure was measured by a Heise pressure gauge (0–100 psig, 0.1 div.). Flow rates in the range of 2–12 ml/min (S.T.P.) were used at room temperature and repeatedly checked during the experiment using a bubble flow meter. Injector and detector temperatures were kept 20°C higher than the boiling point of the highest-boiling solute. Our sampling technique was based on drawing a sample of a solute with a 1-μl Hamilton syringe and flushing out. Usually, traces of the sample are left in the syringe, and we will refer to these traces as "residual." Approximately 0.1 μl of the residual was injected into the chromatograph. By using such small samples, we found that there is no dependence of retention time on sample size over the range of sample sizes studied, i.e., 0.1–0.5 μl of the residual. Fluoropak 80 was used as solid support because of its low surface energy and resulting minimal adsorptive capacity.

A statistical treatment of errors involved in the determination of ΔH_s from retention data has been developed previously.[10] The same procedure for calculating error was adopted in this work. A maximum error of ±1% in reproducing $V_g{}^0$ values was observed, and the heat of solution was estimated on this basis to have an error of less than ±2%.

Results and Discussion

Specific retention volumes ($V_g{}^0$) of a variety of monofunctional organic solutes were determined. In order to obtain equilibrium retention volumes, it was necessary to extrapolate the values of $V_g{}^0$ to zero flow rate, as illustrated in Figure 1. Measurements of $V_g{}^0$ were performed at seven different flow rates, and over the range of 2–12 ml/min (S.T.P.) for all the solutes studied, the retention volumes were independent of the flow rate if the latter was less than 4 ml/min. Errors in $V_g{}^0$ values at flow rates of 2 ml/min become as large as 2%. Therefore,
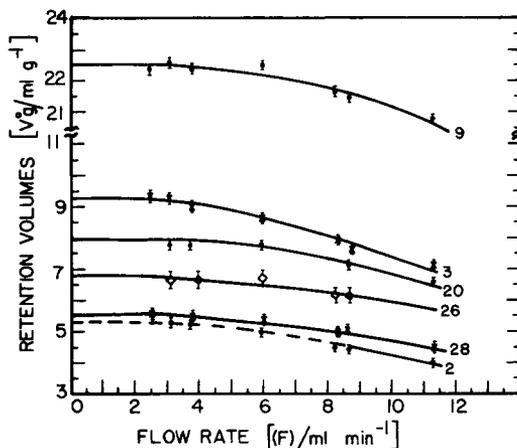
Fig. 1. Effect of flow rate on specific retention volume $V_g{}^0$ at 417.75 K.

we chose flow rates of approximately 4 ml/min in order to obtain equilibrium data with optimum reproducibility. A detailed discussion of the zero-flow rate extrapolation procedure was presented by Lichtenthaler et al.[11] The following empirical relation was suggested:

$$V_g{}^0 = c \exp{(-dF^2)} \tag{5}$$

where c and d are temperature-dependent constants and F is the flow rate in ml/min (S.T.P.).

Interactions between polar molecules are mainly due to (i) the permanent electrical forces (dipoles), (ii) quadrupoles and higher multipole moments, and (iii) hydrogen bonding together with charge-transfer and coordination forces. Interactions of type (iii) will be referred to in this work as "specific interactions."

For a nonpolar solute in solution with a polar polymer, interactions are mainly due to induced electric moments that arise from the short-lived perturbation of the electron positions during collision or near collision. Interactions due to dispersion forces are always present in any solute–solvent systems.

A similar procedure to that used by Dwyer and Karim[10] in determining the contribution of the above interaction parameters individually to the chromatographically measured heats of solution will be adopted in this work. Values of ΔH_s of the solutes in the polymer together with their molecular parameters are listed in Table I.

n-Alkanes were used to determine the reference curve when determining the dipolar and specific interaction contributions of the polar solutes to the heat of solution. A plot of the ΔH_S versus polarizability α of solutes is shown in Figure 2. The polarizabilities listed in Table I and used in Figure 2 are taken as the arithmetic average of the three principal components of polarizability, namely,

$$\alpha_i = \frac{\alpha_x + \alpha_y + \alpha_z}{3}$$

The curve for n-alkanes was found to be fit by the following polynomial:

$$-\Delta H_s = 1.3030\alpha_1 - 0.0086\alpha_1{}^2 + 0.0017\alpha_1{}^3 \tag{6}$$

TABLE I
Dipole Moments, Polarizability, and Heats of Solution of Solutes Poly(ethyl Methacrylate)

Solute	Code no.	Polarizability $\alpha \times 10^{24}/cm^3$	Dipole Moment $\mu \times 10^{30}/C\ m$	Heat of solution $-\Delta H_s$ (experimental), kJ/mole	ΔH_s calculated from eq. (11), kJ/mole	$X[\Delta H_s(\text{exp}) - \Delta H_s(\text{calc})]^a$
n-Heptane	1	13.71	0	20.22	20.63	0
n-Octane	2	15.54	0	24.82	24.55	0
n-Nonane	3	17.42	0	29.73	29.08	0
n-Decane	4	19.30	0	35.66	34.17	0
1-Octene	5	15.36	1.13	29.09	27.00	0
n-Butyl bromide	6	11.22	6.94	35.76	33.27	0
Nitromethane	7	4.95	11.91	36.71	36.20	0
Nitroethane	8	6.74	11.81	40.13	38.41	0
1-Nitropropane	9	8.48	12.01	43.69	41.34	0
Methyl cyanide	10	4.40	13.21	38.24	38.72	0
Ethyl Cyanide	11	6.26	13.51	39.12	41.82	0
Acrylonitrile	12	6.19	12.77	36.99	40.05	0
Di-n-propyl ether	13	12.57	3.43	25.50	29.23	0
n-Butylamine	14	9.72	3.33	30.37	21.75	8.62
Methyl ethyl ketone	15	8.24	9.24	33.68	34.19	0

Dimethyl ketone	16	6.43	9.60	34.35	32.48	0
Methylcyclohexane	17	12.90	0	15.60	15.48	0
Ethylcyclohexane	18	14.72	0	18.03	17.66	0
n-Butyl acetate	19	12.51	6.13	36.76	33.90	0
n-Propyl acetate	20	10.67	6.00	35.04	30.00	0
n-Butyraldehyde	21	8.17	6.00	33.93	33.67	0
Benzene	22	10.40	0	32.71	31.43	0
Toluene	23	12.34	1.23	37.38	37.38	0
Ethylbenzene	24	14.17	1.97	40.73	41.92	0
Chlorobenzene	25	12.32	5.70	45.45	48.53	0
Bromobenzene	26	13.49	5.67	45.75	50.19	0
n-Propyl alcohol	27	6.90	5.64	37.27	23.14	14.13
n-Butyl alcohol	28	8.76	5.57	38.03	25.81	12.22
n-Pentyl alcohol	29	10.64	5.54	38.70	28.77	9.93
Chloroform	30	8.32	3.40	34.29	13.32	20.97
Carbon tetrachloride	31	10.24	0	5.94	5.99	0
Propionic acid	32	6.90	5.83	32.91	23.72	9.19
Cyclohexane	33	10.71	0	12.23	12.85	0

a Small values of X are within experimental error and are set to zero.
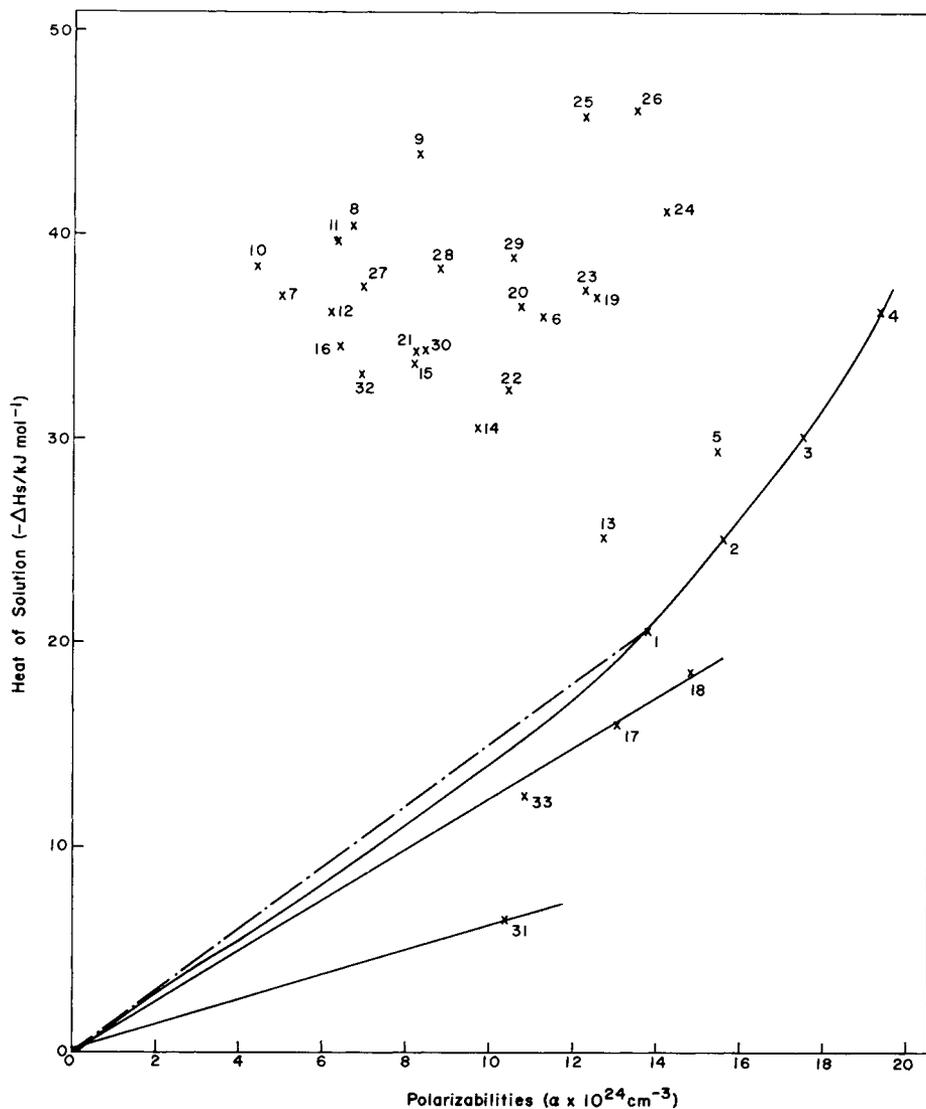
Fig. 2. Heat of solution as a function of polarizability for solutes in poly(ethyl methacrylate).

The solid curve through points 1, 2, 3, and 4 in Figure 2 is that determined using eq. (6).

The reference curve for chloroform was taken to be a line passing through the point of carbon tetrachloride and the origin (the solid line through point 31 in Fig. 2), while that for the aromatic compounds was initially taken to be a line having zero intercept and passing through the points of the cyclic alkanes (the solid line through points 33, 17, and 18 in Fig. 2).

The heats of solution of the polar compounds which are estimated from the vertical differences above the relevant reference curve will be referred to as ΔH_{ad}. These values are measures of the strength of the interaction due to the permanent electrical forces in the polar molecules and also due to specific interactions. Values below the relevant reference curve will be referred to as ΔH_n. It follows that ΔH_s is the sum of two contributions identified by the type of molecular interaction:

$$-\Delta H_s = \Delta H_{ad} + \Delta H_n. \tag{7}$$

For nonpolar solutes, eq. (7) will be reduced to the following form:

$$-\Delta H_s = \Delta H_n \tag{8}$$

The curve of the alkanes expression by eq. (6) can be approximated for simplicity by a straight line passing through the origin, introducing a maximum error of 4% in the values of ΔH_{ad}. Equation (6) will then be reduced to

$$-\Delta H_s = 1.47\alpha_1. \tag{9}$$

Equation (9) gives the dashed line in Figure 2.

A linear correlation was found to exist between ΔH_{ad} and the dipole moments of the solutes, as shown in Figure 3. A similar correlation also exists when ΔH_{ad} is estimated from the straight-line approximation represented by eq. (9), as shown in Figure 4. The slight scatter around the line is probably due to the exclusion of the contribution of the permanent quadrupoles and higher multipole moments and also the choice of the proper values of dipole moments. Vapor-state values for dipole moments were used whenever possible. The solid lines in Figures 3 and 4 are least-squares fits (forced through the origin) of data for compounds which, because of their chemical structures, should not have specific interactions with poly(ethyl methacrylate). Compounds not exhibiting specific interactions with the polymer are indicated by the symbol × in Figures 3 and 4.
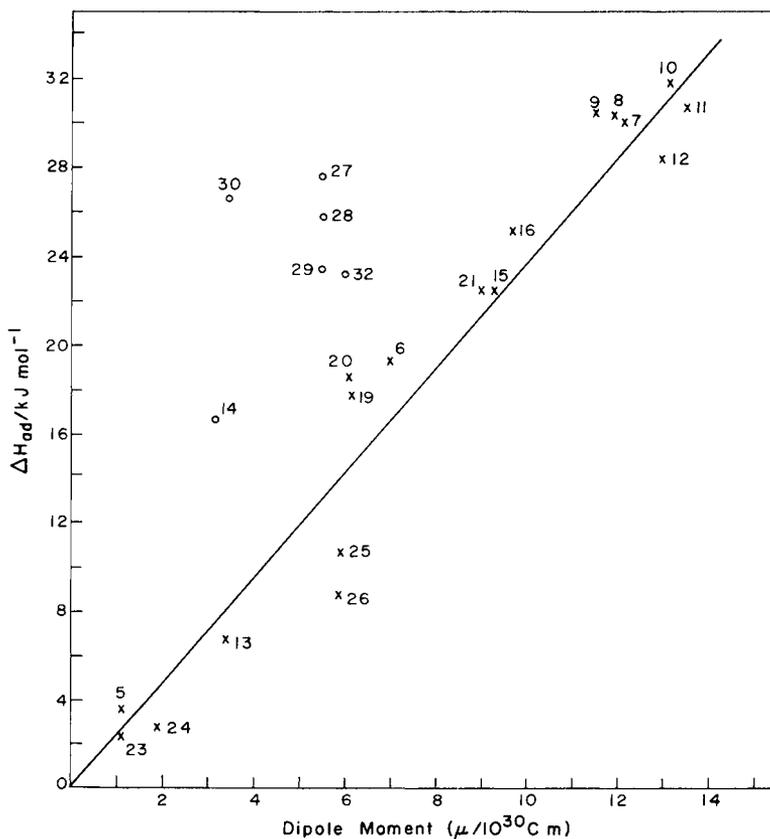
Fig. 3. Plot of ΔH_{ad} values for solutes in poly(ethyl methacrylate) vs their dipole moments.
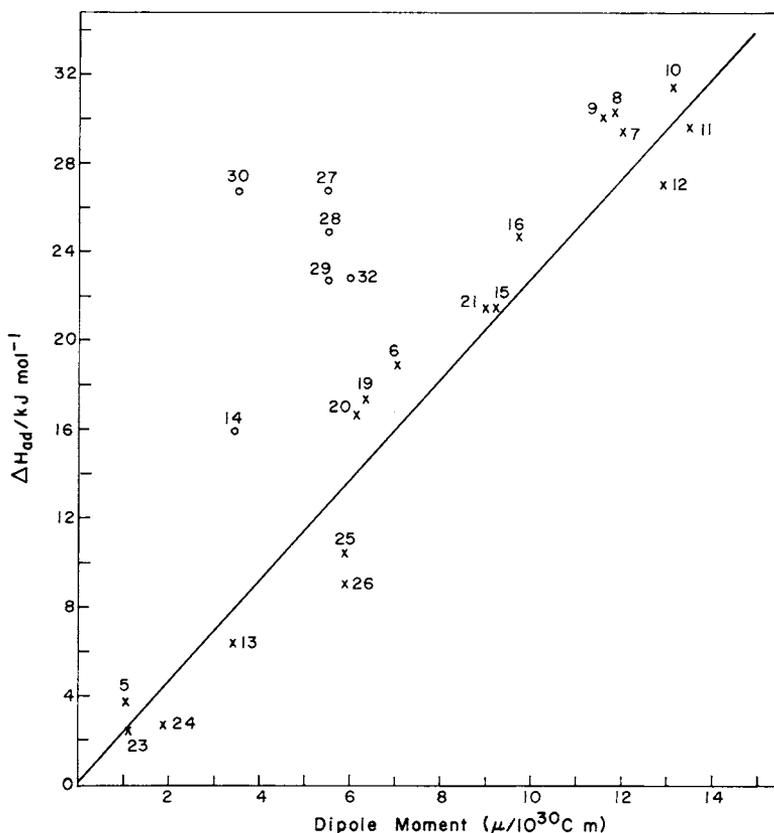
Fig. 4. Plot of ΔH_{ad} values (obtained from the straight-line approximation) for solutes in poly(ethyl methacrylate) vs their dipole moments.

Points which are well above the line belong to compounds exhibiting specific interactions. The vertical distances above the dipole–dipole line are measures of the magnitude of such interactions.

From Figures 2–4, we have determined a simple model which relates ΔH_s to the molecular properties of the solutes:

$$-\Delta H_s = 1.47\alpha_1 + 2.50\mu_1 + X \tag{10}$$

where the factors multiplying α_1 and μ_1 are empirical constants representing the slopes of plots of ΔH_s versus α and ΔH_{ad} versus μ, respectively.

According to eq. (6), a more accurate form of eq. (10) is

$$-\Delta h_s = 1.303\alpha_1 - 0.0086\alpha_1^2 + 0.0017\alpha_1^3 + 2.50\,\mu_1 + X. \tag{11}$$

Values of ΔH_s calculated from eq. (11) are listed in Table I.

Molecular Shape of Solutes

The shape of the nonpolar molecules forming the reference line was found to be an important criterion in justifying the above relationships. It was found by Dwyer and Karim[10] that branched polar compounds should have a reference curve composed of similarly branched alkanes. A method is developed here to account for such structural changes, and it is summarized by the following equation:

$$\frac{\Delta H_s(n\text{-alkane})}{\omega(n\text{-alkane})} = \frac{\Delta H_s(\text{branched alkane})}{\omega(\text{branched alkane})} \tag{12}$$

where ω is the acentric factor defined by Pitzer.[12,13] From the heat of solution of an n-alkane, it is possible to estimate with good accuracy the heat of solution of its isomers from eq. (12).

Taking the cyclic paraffins as a reference for the polar, aromatic compounds, the polar, aromatic solutes were found to have excessively large values of ΔH_{ad} when compared with the ΔH_{ad} that would be predicted by the solid line in Figure 3 for molecules having dipole moments equivalent to those of polar, aromatic compounds. Benzene, which is nonpolar, would have had a ΔH_{ad} corresponding to a dipole moment of approximately 7×10^{30} C m using cyclic paraffins as a reference. We conclude that the cyclic paraffins do not form a proper reference for the aromatics in the combined treatment of aliphatics and aromatics.

If benzene, toluene, and ethylbenzene were to be used as reference curve solutes for other polar aromatic compounds, the values of ΔH_{ad} for chlorobenzene and bromobenzene would be lower than the true values and would fall well below the lines of Figures 3 and 4. This is due to the additional heat of solution (ΔH_{ad}) that results from dipolar interaction of toluene and ethylbenzene with the polymer which is included in the values of ΔH_s for toluene and ethylbenzene. This value will then introduce an error in the measured ΔH_{ad} values for bromobenzene and chlorobenzene equivalent to about 1.5 kJ/mole. Knowing the dipole moments of toluene and ethylbenzene, this error was estimated from an extrapolation procedure in Figure 3. We may safely conclude that the reference curve for bromobenzene and chlorobenzene is a line passing through the point of benzene and below the points of toluene and ethylbenzene. Such a procedure is necessary in order to generalize the correlations developed here for combined study of aliphatic and aromatic compounds.

When considering aromatic systems only, it is possible to assume that the cyclic paraffins are reference solutes representing the reference curve. This assumption will not change the overall interaction selectivity scale, except for benzene.

From Figures 3 and 4, it appears that alcohols, amines, and chloroform exhibit significant specific interactions in the polymer solution. This behavior may be attributed to the formation of hydrogen bonds between these solutes and the polymer.

Specific Interactions

Acids, alcohols, amines, and chloroform had large values of ΔH_{ad} and X, indicating stronger interaction with the polymer than the rest of the solutes. Chloroform, which has the smallest dipole moment among the strongly interacting solutes, possess the highest value of X (Table I). The significance of this behavior will be explained later in terms of the hydrogen bond energy and other thermodynamic functions related to solubility. According to the molecular structure of the solutions and polymer studied, it is reasonable to propose that the type of interaction resulting in large values of ΔH_s and ΔH_{ad} is due to hydrogen bond formation or acid–base complexing rather than dipole–dipole or dispersion–force interactions.

The enthalpies of hydrogen bond formation (ΔH_f) determined by NMR and calorimetry between methyl acetate and each of two solutes, chloroform and

butanol (which are Lewis acids), are listed in Table II, together with the values of ΔH_{ad} of these Lewis acids obtained using poly(ethyl methacrylate) as a GLC stationary liquid phase. No values of enthalpy of hydrogen bonding between chloroform or butanol and poly(ethyl methacrylate) are available in the literature. Comparison of ΔH_{ad} values for several solutes in poly(ethyl methacrylate) and their ΔH_f values in methyl acetate (see Table II) indicates that ΔH_{ad} is of the same order of magnitude as ΔH_f. In making the comparison, note that only the interaction of the acetate group in the polymer and in methyl acetate is considered. No consideration is given to the number of alkyl groups attached to the acetate functional group in the two Lewis basis. These results suggest that values of ΔH_{ad} from GLC may be reasonable estimates of enthalpy of hydrogen bond formation. This hypothesis is currently under investigation in our laboratories using acid–base systems for which ΔH_f values have been reported.

Solubility Criteria

As indicated earlier, the nondispersion strength of interaction between solute and polymer is represented by the values of ΔH_{ad} and X. Chloroform gives the largest value of X of the solutes tested, indicating stronger interactions with the polymer than the rest of the solutes. This behavior, combined with similar solubility parameter values, may be considered a favorable solution criterion, and chloroform may be the best solvent tested for poly(ethyl methacrylate).

In order to prove this hypothesis, it was necessary to calculate other well-defined thermodynamic parameters, such as weight fraction activity coefficient (Ω_1^∞) and Flory-Huggins thermodynamic interaction parameter (χ) for solutes at infinite dilution in the polymer. Values of Ω_1^∞, χ, solubility parameters, vapor pressure and solute second virial coefficients are listed in Table III.

The weight fraction activity coefficient (Ω_1^∞) can be determined from the specific retention volume ($V_g{}^0$) of the solute at infinite dilution in the molten polymer by the following equation[16]:

$$\ln \Omega_1^\infty = \ln \left(\frac{a_1}{w_1} \right)^\infty = \ln \left(\frac{273.15R}{P_1{}^s V_g{}^0 M_1} \right) - \frac{P_1{}^s}{RT} (B_{11} - v_1) \qquad (13)$$

where a_1 and w_1 are the activity and the weight fraction of the solute, respectively; R is the gas constant, M_1 is the molecular weight of the solute; and $P_1{}^s$ is the solute saturation vapor pressure at the column temperature T. The terms B_{11} and v_1 are the second virial coefficient and molar volume of the pure solute at temperature T, respectively.

In order to estimate B_{11},[17-19] it was necessary to calculate vapor pressure of solutes at the column temperature,[20] critical volumes,[21] critical pressures,[21] and acentric factors.[12,13] The combined total error in estimating Ω_1^∞ did not exceed ±10% and for χ was less than ±5%.

The Flory-Huggins interaction parameter χ can also be calculated from values of $V_g{}^0$:

$$\chi = \ln \frac{273.15Rv_{2sp}}{V_g{}^0 M_1 P_1{}^s} - \left(1 - \frac{v_1}{\overline{M}_n v_{2sp}} \right) - \frac{P_1{}^s}{RT} (B_{11} - v_1) \qquad (14)$$

where v_{2sp} is the specific volume of the polymer and $\overline{M}_n$ is the number-average molecular weight of the polymer.

TABLE II

Enthalpies of Hydrogen Bond Formation (ΔH_f) and ΔH_{ad} for Some Acid–Base Systems

Acid	Base	Method	ΔH_f, kcal/mole	ΔH_{ad}, kcal/mole	Ref.
$CH_3COOC_2H_5$		NMR	2.5 ± 0.1		14
	poly(ethyl methacrylate)	GLC		2.38 ± 0.048	present work
n-C_4H_9OH	$CH_3COOC_2H_5$	calorimetry	2.43 ± 0.13		15
	poly(ethyl methacrylate)	GLC		2.70 ± 0.054	present work
n-C_3H_7OH	poly(ethyl methacrylate)	GLC		2.97 ± 0.059	present work
n-$C_5H_{11}OH$	poly(ethyl methacrylate)	GLC		2.45 ± 0.049	present work
n-C_3H_7COOH	poly(ethyl methacrylate)	GLC		2.47 ± 0.049	present work
n-$C_4H_9NH_2$	poly(ethyl methacrylate)	GLC		1.75 ± 0.035	present work

TABLE III
Physical Constants and Thermodynamic Parameters of Solutes in Poly(ethyl Methcrylate) at
417.74 K

Solute code no.	$P_1{}^s$, mm Hg	$-B_{11}$, cc/g-mole	$\Omega_1{}^\infty$	χ	δ at 25°C, (cal/cm³)^{1/2} [a]
1	2471	1104	19.226	1.232	7.4
2	1248	1506	18.571	1.263	7.6
3	641	2001	18.098	1.288	—
4	332	2606	17.759	1.310	6.6
5	1402	1412	14.232	1.015	—
6	2378	820	4.355	0.214	8.7
7	2597	1144	6.950	0.773	12.7
8	1793	1174	6.080	0.539	11.1
9	1133	1440	5.470	0.383	10.3
10	3939	1202	12.902	1.044	11.9
11	2659	1246	10.160	0.785	10.8
12	4571	985	8.543	0.605	10.5
13	3277	957	11.399	0.763	7.8
14	4547	430	10.44	0.641	9.1
15	4230	797	7.710	0.470	9.3
16	7607	593	9.037	0.620	9.9
17	2261	979	16.147	1.206	7.8
18	1076	1384	14.524	1.154	—
19	1273	1366	6.727	0.459	8.5
20	2412	1008	7.009	0.481	8.8
21	4784	773	7.575	0.376	9.0
22	3901	645	5.655	0.221	9.2
23	1820	955	5.878	0.298	8.9
24	946	1323	6.079	0.383	8.8
25[b]	1119	1173	3.916	0.142	9.5
26[b]	769	1278	2.815	0.008	10.5
27	3341	591	9.811	0.683	11.9
28	1782	764	8.339	0.528	11.4
29	969	965	7.400	0.422	10.9
30	6303	512	2.292	-0.220	9.3
31	4173	653	4.560	0.613	8.6
32	848	990	50.779	2.663	9.9
33	3688	741	16.142	1.189	8.2

[a] Solubility parameter of poly(ethyl methacrylate) at 25°C is 9.1 (cal/cm³)^{1/2}.
[b] Data calculated in 419.65 K.

In order to achieve good solubility, χ should be small or negative. For complete miscibility of polymer and solute, the largest permissible value for χ is 0.5.[17] Values of χ for halogenated polar aliphatic and aromatic compounds, C_4 and C_5 alcohols, aromatic hydrocarbons, butyraldehyde, methyl ethyl ketone, and propyl acetate were found to be less than 0.5. This indicates that these compounds are potential solvents for poly(ethyl methacrylate). Useful comparisons between the solubility parameter of the polymer at 25°C and those of the compounds listed in Table III can be made. (A more meaningful comparison between solvent and polymer solubility parameters could be made if the solubility parameters were available at 417.75 K, column temperature. However, due to lack of physical property data for the polymer, a reliable estimate of δ for the polymer at 417.75 K could not be made.)

The solubility parameters of compounds with $\chi < 0.5$ are of similar magnitude to that of the polymer. This is a favorable solubility criterion. Chloroform has

a negative χ value and a very small $\Omega_1{}^\infty$ value, suggesting that specific interaction is accompanying dissolution. This conclusion is supported by the large values of ΔH_{ad} and X of chloroform in poly(ethyl methacrylate). Other hydrogen-bonding compounds, such as propionic acid and propyl alcohol, also give large values of ΔH_{ad}, but according to their values of χ and δ, they are poor solvents. We, therefore, conclude that values of ΔH_{ad} or X alone are not sufficient to estimate solubility, but they are very useful in understanding molecular interactions or predicting a possible solvent.

Conclusions

The correlations between heats of solution at infinite dilution of binary systems and the molecular parameters of the two components developed by Dwyer and Karim[10] have been extended to describe interactions in polymer solutions. The correlations were found to apply to the polymer studied here. We have also extended the correlations of Dwyer and Karim[10] to allow for structural changes in the solute molecules by employing Pitzer's acentric factor.[12,13] In order to obtain true solution thermodynamic data, the study was conducted at temperatures greater than the melting range of the polymer. It was possible to isolate the contributions of solute polarizability, dipole moment, and other solute–polymer interactions contribution to the heat of solution. This approach can be used to help in predicting optimum solubility characteristics based on molecular parameters. By comparing values of ΔH_{ad}, χ, $\Delta_1{}^\infty$, and solubility parameters, one can obtain reliable predictions of solvents for polymers.

References

1. A. J. B. Cruickshank, W. B. Gainey, and C. L. Young, *Trans. Faraday Soc.*, **64**, 337 (1968).

2. A. J. B. Cruickshank M. L. Windsor, and C. L. Young, *Proc. R. Soc. Ser. A*, **295**, 259 (1966).

3. J. R. Conder, D. C. Locke, and J. H. Purnell, *J. Phys. Chem.*, **73**, 700 (1969).

4. D. F. Cadogan, J. R. Conder, D. C. Locke, and J. H. Purnell, *J. Phys. Chem.*, **73**, 708 (1969).

5. E. F. Meyer, *J. Chem. Educ.*, **50**, 191 (1973).

6. O. Smidsrød and J. E. Guillet, *Macromolecules*, **2**, 272 (1969).

7. W. R. Summers, Y. B. Tewari, and H. P. Schreiber, *Macromolecules*, **5**, 12 (1972).

8. R. D. Newman and J. M. Prausnitz, *A.I.Ch.E.J.*, **19**, 704 (1973).

9. Y. L. Cheng and D. C. Bonner, *Macromolecules*, **7**, 687 (19774.

10. J. Dwyer and K. A. Karim, *Ind. Eng. Chem., Fundam.*, **14**, 196 (1975).

11. R. N. Lichtenthaler, D. D. Liu, and J. M. Prausnitz, *Macromolecules*, **7**, 565 (1974).

12. K. S. Pitzer, *J. Am. Chem. Soc.*, **77**, 3427 (1955).

13. K. S. Pitzer, D. Z. Lippman, R. F. Curl, C. M. Huggins, and J. Petersen, *J. Am. Chem. Soc.*, **77**, 3433 (1955).

14. G. R. Wiley and S. I. Miller, *J. Am. Chem. Soc.*, **94**, 3287 (1972).

15. E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. Von R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2365 (1970).

16. D. D. Patterson, Y. B. Tewari, H. P. Shreiber, and J. E. Guillet, *Macromolecules*, **4**, 356 (1971).

17. J. M. Prausnitz, *Molecular Thermodynamics of Fluid-Phase Equilibrium*, Prentice-Hall, Englewood, New Jersey, 1969, p. 297.

18. C. Tsonopoulos, *A.I.Ch.E.J.*, **20**, 263 (1974).

19. C. Tsonopoulos, *A.I.Ch.E.J.,* **21,** 827 (1975).

20. R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids,* 2nd. ed., McGraw-Hill, New York, 1966, p. 125.

21. A. L. Lydersen, *Estimation of Critical Properties of Organic Compounds,* Coll. Eng. Univ. Wisconsin, Eng. Expt. Sta. Rept. 3, Madison, Wisconsin, April, 1955.