Estimation of thermodynamic parameters for poly(ethyl methacrylate)/isopropyl alcohol system from intrinsic viscosity measurements

Ayten Kuntman
Faculty of Electrical and Electronic Engineering, Technical University of Istanbul, Maslak, 80626, Istanbul, Turkey

and Bahattin M. Baysal*
Department of Chemical Engineering and Polymer Research Center, Bogazici University, Bebek, 80815, Istanbul, Turkey

(Received 23 July 1992; revised 26 January 1993)

Intrinsic viscosities of poly(ethyl methacrylate) (PEMA) solutions in isopropyl alcohol (IPA) above and below the theta (θ) temperature (36.9°C) have been measured by using a capillary viscometer. The equation-of-state exchange energy (X_{12}) and entropy (Q_{12}) parameters were estimated as 62.82 J cm^{-3} and 0.03 J cm^{-3} K^{-1}, respectively. The unperturbed dimension constant (K_θ) and characteristic ratio (C_∞) were determined as 5.91×10^{-4} dl mol$^{1/2}$ g$^{-3/2}$ and 9.3 using the intrinsic viscosity data obtained at the θ temperature for PEMA in IPA. The polymer–solvent interaction parameters (χ_1, χ_2) were calculated from equation-of-state theory as a function of temperature. The value of the ratio of contact sites (s_2/s_1) is found to be 0.73 for this PEMA–IPA pair.

(Keywords: thermodynamic parameters; intrinsic viscosity; poly(ethyl methacrylate); isopropyl alcohol)

INTRODUCTION

The equation-of-state exchange energy and entropy parameters which characterize a mixture have been determined for various polymer–solvent pairs in several works[1–9]. X_{12} and Q_{12} represent the exchange free energy and the entropy of interaction for formation of a contact between a solute segment and solvent molecule, respectively.

Recently, a simple procedure based on intrinsic viscosity measurements has been proposed to estimate these parameters for a polymer–solvent pair[9]. In this study X_{12} and Q_{12} parameters of poly(ethyl methacrylate) (PEMA)/isopropyl alcohol (IPA) system are evaluated from intrinsic viscosity measurements. In addition, polymer–solvent interaction parameters χ_1 and χ_2 were calculated by using equation-of-state theory as a function of temperature.

THEORETICAL BACKGROUND

Intrinsic viscosities of the solutions were determined by using the following equations:

$$\eta_{sp}/c=[\eta]+k_H[\eta]^2c \tag{1}$$

$$[\eta]=\lim_{c\to0}[\eta_{sp}/c] \tag{2}$$

where η_{sp} represents the specific viscosity, c is the polymer concentration (g dl^{-1}) and k_H is the Huggins constant.

The intrinsic viscosity may be expressed in the form[10]:

$$[\eta]_\theta=K_\theta M^{1/2} \tag{3}$$

$$K_\theta=\Phi_0(\langle r^2\rangle_0/M)^{3/2} \tag{4}$$

where M is the polymer molecular weight and Φ_0 is the Flory–Fox viscosity constant, which was taken as 2.5×10^{21} (if the intrinsic viscosity unit is dl g^{-1})[10]; $\langle r^2\rangle_0$ is the mean squared end-to-end distance of the unperturbed coil, $[\eta]_\theta$ is the intrinsic viscosity at the θ temperature; K_θ is the unperturbed dimension constant of the chain. The cubic expansion factor α_η^3 is defined[11–13] as:

$$\alpha_\eta^3=[\eta]/[\eta]_\theta \tag{5}$$

For flexible chains, α_η^3 is a function only of the excluded-volume parameter (Z):

$$\alpha_\eta^3=1+C_{1\eta}Z \tag{6}$$

where the coefficient $C_{1\eta}$ is a numerical constant. Its value is given[13] as $1.05<C_{1\eta}<1.55$. The above empirical relation is the best fit to the experimental data over the $0<\alpha_\eta^3<1.6$ range[13].

The excluded-volume parameter is related to the polymer–solvent interactions through the interaction density (B):

$$Z=(3/2\pi)^{3/2}(B\Phi_0/K_\theta)M^{1/2} \tag{7}$$

$$B=\bar{v}^2(1-2\chi_1)/V_1N_A \tag{8}$$

---

* To whom correspondence should be addressed

0032-3861/93/173723-04

where $\bar{v}$ is the specific volume of polymer, χ_1 is the polymer–solvent interaction parameter, V_1 is the molar volume of the solvent and N_A is the Avogadro number.

In general, χ depends on composition as well as temperature. It is appropriately expressed empirically by[2]:

$$\chi=\chi_1+\chi_2 v_2+\chi_3 v_2^2+\cdots \tag{9}$$

where χ_1 and χ_2 are functions of temperature and v_2 is the volume fraction of polymer segment.

On the other hand, according to the equation-of-state theory, χ_1 is given by the following equation[4,14]:

$$\lim_{v_2\to 0}\chi=\chi_1=(p_1^*V_1^*/\tilde{v}_1RT)(A^2\alpha_1T/2+Y_{12})-V_1^*Q_{12}(s_2/s_1)^2/R \tag{10}$$

where

$$A=(1-T_1^*/T_2^*)(p_2^*/p_1^*)-(s_2/s_1)^2X_{12}/p_1^* \tag{11}$$

$$Y_{12}=X_{12}(s_2/s_1)^2/p_1^* \tag{12}$$

Quantities appearing in these equations are defined as follows: R is the universal gas constant, α_1 is the thermal expansion coefficient of the solvent, V^*, p^* and T^* are the characteristic molar volume, pressure and temperature of solvent or polymer, the subscripts 1 and 2 refer to the value for pure solvent and solute, $\tilde{v}_1=(V_1/V_1^*)$ is the reduced volume, s_2/s_1 is the ratio of surface areas (or contact sites) for a polymer segment and solvent molecule, X_{12} and Q_{12} are the exchange energy and entropy parameters of interaction, respectively. The characteristic molar volumes and temperatures can be calculated by means of the following equations:

$$\tilde{v}^{1/3}=(V/V^*)^{1/3}=[\alpha T/3(1+\alpha T)]+1 \tag{13}$$

$$\tilde{T}=T/T^*=(\tilde{v}^{1/3}-1)/\tilde{v}^{4/3} \tag{14}$$

$$p^*=\gamma T\tilde{v}^2 \tag{15}$$

The thermal expansion coefficient, α, and the thermal pressure coefficient, γ, are defined as:

$$\alpha=V^{-1}(\partial V/\partial T)_p \tag{16}$$

$$\gamma=(\partial p/\partial T)_V \tag{17}$$

Equation (10) was rearranged and the following form was obtained:

$$\chi_1=p_1^*V_1^*\alpha_1A^2/2\tilde{v}_1R-(s_2/s_1)^2V_1^*Q_{12}/R+(s_2/s_1)^2V_1^*X_{12}/\tilde{v}_1RT \tag{18}$$

Assuming that all of the equation-of-state parameters are independent of temperature in the studied temperature range, equation (18) shows that the χ_1 *versus* $1/T$ plot must give a straight line. The slope and intercept of this line will give the following quantities:

$$\text{slope}\qquad (s_2/s_1)^2V_1^*X_{12}/\tilde{v}_1R \tag{19}$$

$$\text{intercept}\qquad p_1^*V_1^*\alpha_1A^2/2\tilde{v}_1R-Q_{12}(s_2/s_1)^2V_1^*/R \tag{20}$$

Accordingly, the χ_2 coefficient in the series expansion of χ as indicated in equation (9) is given as:

$$\begin{aligned}\chi_2=\{&2(1-s_2/s_1)(Y_{12}+Z_{12}T)\\&+[2Y_{12}+(1-p_2^*T_1^*/p_1^*T_2^*)A]A\alpha_1T\\&-(3+2\alpha_1T+2\alpha_1^2T^2)(2\alpha_1TA^3/9)\}(p_1^*V_1^*/\tilde{v}_1RT)\end{aligned} \tag{21}$$

where

$$Y_{12}=(s_2/s_1)^2(X_{12}/p_1^*) \tag{22}$$

$$Z_{12}=-Q_{12}(s_2/s_1)^2\tilde{v}_1/p_1^* \tag{23}$$

EVALUATION OF THE EQUATION-OF-STATE PARAMETERS

The thermal expansion coefficient (α_1) of isopropyl alcohol was calculated from equation (16).

The specific molar volume of IPA was determined using equation (24). The variation of the density of this solvent with temperature is given by the following equation[15]:

$$\rho_t=0.8014-0.809\times10^{-3}t-0.27\times10^{-6}t^2 \tag{24}$$

The thermal expansion coefficient of PEMA was assumed to be equal to that of PMMA and its value in the range 0–50°C has been reported as $7\times10^{-5}\,\mathrm{K}^{-1}$ in ref. 16.

The equation-of-state parameters $\tilde{v}$, V^* and T^* were calculated using equations (13) and (14).

The thermal pressure coefficients (γ) of the solvent and polymer were calculated by using the following equation and the argument given in refs. 5 and 6:

$$\gamma=\alpha/\beta \tag{25}$$

In equation (25) α and β represent thermal expansion (16) and pressure (17) coefficients, respectively. We used the following compressibility values of 2.45×10^{-4} (MPa^{-1}, 20°C) and 102 (Mbar, 18°C) for PMMA[17] and IPA[15], respectively. The characteristic pressure parameters p^* of the polymer and solvent were evaluated by using equation (15). The calculated values of the thermal expansion and pressure coefficients and equation-of-state parameters of the solvent and polymer are give in *Table 1*.

The ratio of surface areas (or contact sites) (s_2/s_1) for a polymer segment and solvent molecule was calculated by using equation (21). As is seen in equation (18), the equation-of-state contribution of χ_1 is insensitive to the ratio of s_2/s_1 (ref. 4), but χ_2 (equation (21)) is sensitive to this ratio. The s_2/s_1 value was calculated with

Table 1 The thermal expansion coefficients α, thermal pressure coefficients γ and equation-of-state parameters of isopropyl alcohol and poly(methyl methacrylate)

Substance	T (°C)	$\alpha\times10^{-3}$ (K^{-1})	γ ($\mathrm{J\,cm^{-3}\,K^{-1}}$)	$\tilde{v}$	V^* ($\mathrm{cm^3\,mol^{-1}}$)	$T^*\times10^{-3}$ (K)	p^* ($\mathrm{J\,cm^{-3}}$)
Isopropyl alcohol	35	1.159	1.136	1.283	60.23	4.92	579
	45	1.146	1.123	1.292	60.27	5.03	595
Poly(methyl methacrylate)	0–50	0.07					
	35	0.07	0.286	1.020	–	45.3	91.9
	45	0.07	0.286	1.021	–	45.5	95.0

optimization to the most suitable experimental values of χ_2. It is known from experimental and theoretical considerations that $\chi_2 \simeq 1/3$ near the theta point[14,18].

EXPERIMENTAL

Poly(ethyl methacrylate) (PEMA) was a product of Polysciences Inc., Warrington, PA. The sample was precipitated in a methanol/water mixture, filtered and dried in a vacuum oven for 48 h at 40°C. The intrinsic viscosity of this polymer was carried out in an Ubbelohde-type capillary viscometer. Intrinsic viscosity was converted to molecular weight by means of the following relation[19]:

$$[\eta]=3.46\times10^{-5}M_{\mathrm{v}}^{-0.81} \tag{26}$$

in methyl ethyl ketone at 30°C, and it was found to be 2.2×10^5. The intrinsic viscosities of PEMA solutions were measured in a constant-temperature bath controlled to ±0.002°C. Kinetic energy corrections were negligible.

In this study, the initial concentrations of PEMA solutions were smaller than 3×10^{-3} g ml^{-1}. In order to prevent coalescence the solutions were stored at 40°C in a constant-temperature bath prior to viscosity measurements. Experimental $[\eta]$ values have a precision of $\pm1\%$.

RESULTS AND DISCUSSION

The intrinsic viscosities of PEMA solutions in IPA around the θ temperature are tabulated in *Table 2*. The square values of expansion factor α^2 were calculated by using equation (5) and included in this table. For this purpose the intrinsic viscosity value of PEMA (0.295 dl g^{-1}) at 36.9°C (θ temperature) is used. The intrinsic viscosity values are plotted against temperature in *Figure 1*. The temperature coefficients of intrinsic viscosity $\partial\ln[\eta]/\partial T$ were found to be 0.122 and 9.36×10^{-3} dl g^{-1} K^{-1} below and above the θ temperature, respectively. α^2 values of expansion factor were plotted against T/θ in *Figure 2*.

Thermodynamic interaction parameters (χ_1) of poly(ethyl methacrylate) were obtained by using intrinsic viscosity data in isopropyl alcohol. Equations (3)–(8) represent the basic relations for this purpose. The calculated values of χ_1 were also included in *Table 2*. The variation of χ_1 with reciprocal values of absolute temperature is plotted in *Figure 3*.

The unperturbed dimension constant (K_θ) was evaluated as 5.91×10^{-4} dl mol$^{1/2}$ g$^{-3/2}$ from equations (3) and (4) using the intrinsic viscosity data at the θ temperature. The above value is comparable to the reported figure of 4.75×10^{-4} dl mol$^{1/2}$ g$^{-3/2}$ for this system[20]. The characteristic ratio (C_∞) for PEMA in IPA was obtained as 9.3 by the following relation:

$$C_\infty=\langle r^2\rangle_0/nl^2 \tag{27}$$

where n is the number of skeletal bonds and l is the length of one bond (1.54 Å).

The C_∞ value of this work for PEMA (9.3) can also be compared with literature results for unperturbed

Table 2 Intrinsic viscosities $[\eta]$, χ_1 parameters and expansion factors α^2 of poly(ethyl methacrylate) at various temperatures

T (°C)	$[\eta]$ (dl g^{-1})	χ_1	α_η^2
32	0.160	0.518	0.665
34	0.210	0.511	0.797
35	0.240	0.507	0.872
36	0.267	0.504	0.936
36.5	0.273	0.503	0.950
36.9	0.295	0.500	1.000
38	0.296	0.500	1.002
40	0.302	0.499	1.016
42	0.309	0.498	1.031

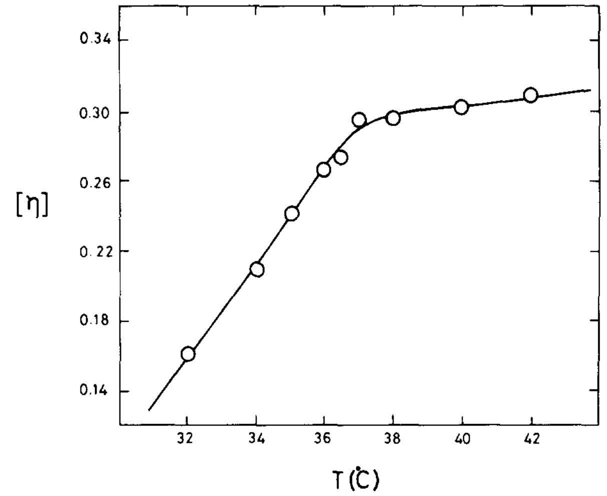

Figure 1 Dependence of intrinsic viscosities $[\eta]$ on temperature of PEMA in IPA solution

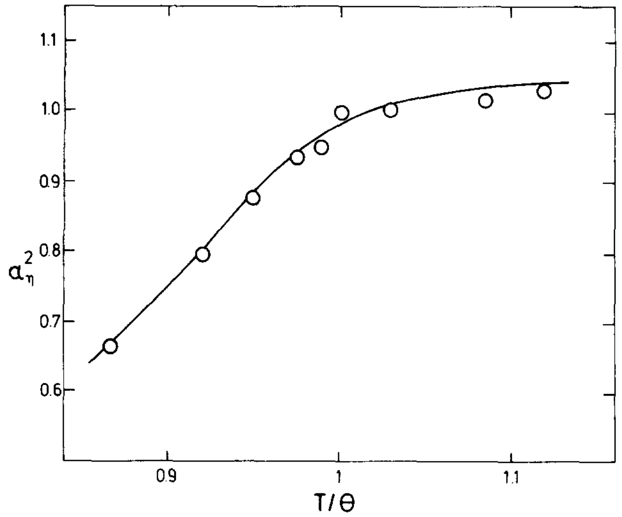

Figure 2 The variation of expansion factor α^2 with T/θ for PEMA–IPA solutions

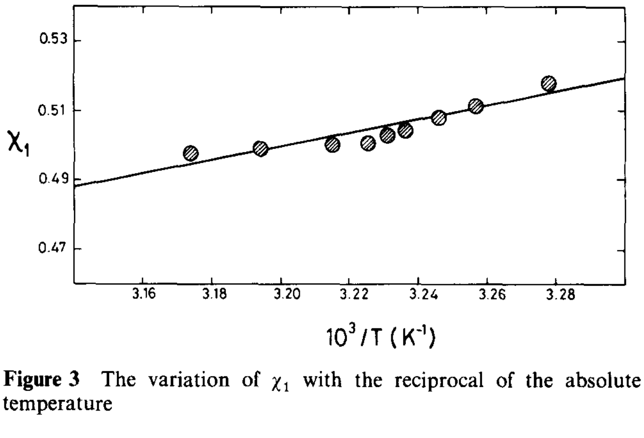

Figure 3 The variation of χ_1 with the reciprocal of the absolute temperature

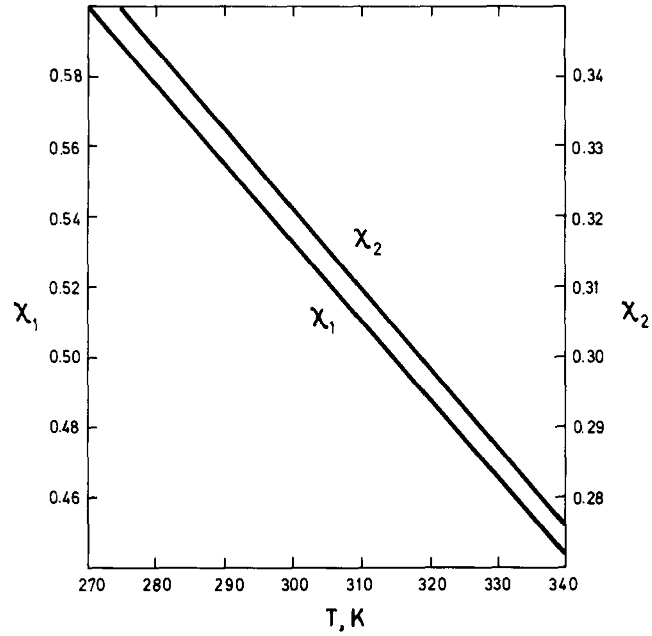

Figure 4 The values of χ_1 and χ_2 calculated according to the equation-of-state theory plotted as functions of temperature for the PEMA–IPA system

Table 3 Dependence of X_{12}, Q_{12} and χ_1 on the ratio s_2/s_1 at θ temperature (309.9 K) for PEMA–IPA system

s_2/s_1	X_{12} (J cm^{-3})	$Q_{12}\times 10^2$ (J cm^{-3})	χ_2
1.00	33.5	1.7	0.060
0.90	41.3	2.0	0.152
0.80	52.3	2.5	0.243
0.75	59.5	2.9	0.288
0.74	61.1	2.9	0.296
0.73	62.8	3.0	0.306
0.72	64.6	3.1	0.315
0.71	66.4	3.2	0.324
0.70	68.3	3.2	0.334
0.60	93.0	4.3	0.424
0.50	133.9	6.1	0.512

dimensions of polymers with related side groups. Poly(methyl methacrylate), poly(n-butyl methacrylate), poly(t-butyl methacrylate) and poly(2-ethylbutyl methacrylate) have C_∞ values, respectively, of 9 ± 0.5[20–22], 8.8[23], 10.2[24] and 9.8[25].

X_{12} and Q_{12} values were determined from the slope and intercept of the straight line that was plotted in *Figure 3* by using relations (19) and (20). The numerical values of X_{12} and Q_{12} are found to be 62.82 J cm^{-3} and 0.030 J cm^{-3} K^{-1}, respectively.

The polymer–solvent interaction parameters χ_1 and χ_2 were calculated from equation-of-state parameters for the PEMA–IPA pair using equations (18) and (21). The dependences of χ_1 and χ_2 on temperature are shown in *Figure 4*.

The variations of X_{12}, Q_{12} and χ_2 values with s_2/s_1 ratios are listed in *Table 3*. As a result of the proposed optimization it was shown that the ratio s_2/s_1 is 0.73 for PEMA–IPA system. This ratio has been reported as 0.476[4] and 0.833[26] for polystyrene in methyl ethyl ketone, and as 0.49[9] for poly(*p*-chlorostyrene) in n-propylbenzene and isopropylbenzene solvents.

REFERENCES

1 Abe, A. and Flory, P. J. *J. Am. Chem.* 1965, **87**, 1838
2 Flory, P. J. *Discuss. Faraday Soc.* 1970, 49
3 Höcker, H., Blacke, G. J. and Flory, P. J. *Trans. Faraday. Soc.* 1971, **67**, 2251
4 Flory, P. J. and Höcker, H. *Trans. Faraday Soc.* 1971, **67**, 2258
5 Höcker, H. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2270
6 Höcker, H., Shih, H. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2275
7 Orwoll, D. J. *Rubber Chem. Technol.* 1977, **50**, 3
8 Walsh, P. J. and Rostami, S. *Adv. Polym. Sci.* 1985, **70**, 119
9 Yilmaz, F. and Baysal, B. M. *Polym. Int.* 1993, **31**, 107
10 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953
11 Kurata, M. and Stockmayer, W. H. *Fortschr. Hochpolym. Forsch.* 1963, **3**, 196
12 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969
13 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
14 Erman, B. and Flory, P. J. *Macromolecules* 1986, **19**, 2342
15 National Research Council of the USA 'International Critical Tables of Numerical Data', Vol. 3, McGraw-Hill, New York, 1930
16 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', Wiley Interscience, New York, 1967, V-55
17 Hellwege, K. H., Knappe, W. and Lehmann, P. *Kolloid-Z.* 1962, **183**, 110
18 Uyanik, N. and Baysal, B. M. *Doğa-Tr. J. Chem.* 1988, **12**, 332
19 Khanna, S. N., Chatterfee, S. R., Handi, U. S. and Palit, S. R. *Trans. Faraday Soc.* 1962, **58**, 1827
20 Berry, G. C. and Yen, S. P. *Adv. Chem. Ser.* 1969, **91**, 734
21 Jenkins, R. and Porter, R. S. *Adv. Polym. Sci.* 1980, **36**, 1
22 Jenkins, R. and Porter, R. S. *Polymer* 1982, **23**, 105
23 Lath, D. and Bohdanecky, M. *J. Polym. Sci., Polym. Lett. Edn.* 1977, **15**, 555
24 Karandinos, A., Nan, S., Mays, J. W. and Hadjichristidis, N. *Macromolecules* 1990, **24**, 2007
25 Didot, F. E., Chinai, S. N. and Levi, D. W. *J. Polym. Sci.* 1960, **43**, 557
26 Bondi, A. *J. Phys. Chem.* 1964, **68**, 441