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Comparison of the intrinsic viscosity and inverse gas chromatography techniques in determination of the exchange enthalpy and entropy parameters

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The χ_1-interaction parameters of poly(dimethyl siloxane) with methyl ethyl ketone at very low polymer concentration were determined by means of intrinsic viscosity (IV) measurements at several temperatures. The χ_1^∞-total interaction parameters of the same system at infinitely high polymer concentration were also determined using inverse gas chromatography (i.g.c.) technique around the same temperature range. Then, exchange enthalpy, X_{12}, and entropy, Q_{12}, parameters in the Flory's equation of state theory were determined from the obtained interaction parameters. Both X_{12} and Q_{12} parameters obtained by IV are lower than those found by i.g.c.. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Recently, we suggested a new method to estimate average values of the exchange enthalpy, X_{12} and entropy, Q_{12} parameters of the equation of state theory in some polymer–solvent pairs by intrinsic viscosity (IV) measurements[1–4]. Later, we submitted two other manuscripts for determination of the X_{12} and Q_{12} parameters of poly(dimethyl siloxane) (PDMS) with some solvents by inverse gas chromatography (i.g.c.) technique[5,6]. The obtained values of the X_{12} and Q_{12} parameters were comparable with those determined earlier by other techniques at lower polymer concentration[7] although i.g.c. data are obtained at compositions where the polymer fraction approaches unity. This implies that X_{12} and Q_{12} parameters are independent of composition of the polymer–solvent system as it is assumed in the equation of state theory.

In the present study, we aimed to compare these two techniques for the PDMS-methyl ethyl ketone (MEK) system because this system is suitable to study with both techniques around room temperature.

In addition, since MEK is a theta solvent for PDMS at 20°C, it would be interesting to obtain the χ-interaction parameter of the system at theta point in order to predict the whole expansion of the empirical equation

$$\chi_t = \chi_1 + \chi_2\Phi_2 + \chi_3\Phi_2^2 + \dots \qquad (1)$$

where χ_1, χ_2, and χ_3 are coefficients that are constant for a given polymer–solvent pair and are a function of temperature. Φ_2 is segment fraction of the polymer, which will be defined in the next section. χ_1 and χ_2 are 1/2 and 1/3 at theta point, respectively[8], however, there is

no information about the magnitude of other coefficients in order, yet.

THEORETICAL BACKGROUND

The Flory formulation of the equation of state theory

In the theory, a pure liquid solvent or an amorphous polymer is described with a partition function[9–15]. By differentiation, it yields the equation of state for pure components and their mixtures, which can be expressed in a reduced form

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - (\tilde{v}\tilde{T})^{-1} \qquad (2)$$

The reduced volume, $\tilde{v}$, temperature, $\tilde{T}$ and pressure $\tilde{p}$ of a pure liquid or an amorphous polymer are defined as

$$\tilde{V} = V/V^* \qquad (3)$$

$$\tilde{T} = T/T^* \qquad (4)$$

$$\tilde{p} = p/p^* \qquad (5)$$

where V is actual molar volume of the liquid at actual T, temperature in K and p, pressure. Characteristic molar volume (or hard-core molar volume), V^*, characteristic temperature, T^* and characteristic pressure, p^* of the pure component can be calculated directly from experimental values of the molar volume, V, thermal expansion coefficient, α and the thermal pressure coefficient, γ of the pure component, by means of the equations

$$\tilde{v}^{1/3} = [(\alpha T/3)/(1 + \alpha T)] + 1 \qquad (6)$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (7)$$

$$\alpha = (1/V)(\partial V/\partial T)_{p=0} \qquad (8)$$

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$$p^* = \gamma T \tilde{v}^2 \tag{9}$$

$$\gamma = (\partial p/\partial T)_v \tag{10}$$

Generally, subscript 1 and subscript 2 are used for solvent and polymer, respectively. No subscript is used for their binary mixtures. Two different concentrations are defined in the theory. The segment fraction of the components are

$$\Phi_2 = m_2 v_2^* / (m_1 v_1^* + m_2 v_2^*); \qquad \Phi_1 = 1 - \Phi_2 \tag{11}$$

and the contact site fraction of the components are

$$\theta_2 = (s_2/s_1)\Phi_2 / [(s_2/s_1)\Phi_2 + \Phi_1]; \qquad \theta_1 = 1 - \theta_2 \tag{12}$$

where m is weight fraction and s_2/s_1 is the ratio of surface areas (or contact sites) for a polymer segment and solvent molecule.

Total interaction parameter, χ_t is defined in a whole concentration range in the theory as

$$RT\chi_t = p_1^* V_1^* / \Phi_2^2 \{ 3\tilde{T}_1 \, \mathrm{Ln}[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]$$
$$+ \tilde{v}_1^{-1} - \tilde{v}^{-1} \} + (X_{12} - T\tilde{v}Q_{12})V_1^* \theta_2^2 / \tilde{v}\Phi_2^2 \tag{13}$$

where R is universal gas constant. The exchange enthalpy, X_{12} and entropy, Q_{12} parameters in the parentheses in the last term of equation (13) are combined as an effective exchange energy parameter, $\bar{X}_{12}$

$$\bar{X}_{12} = X_{12} - T\tilde{v}Q_{12} \tag{14}$$

The total interaction parameter χ_t is the sum of enthalpy interaction parameter χ_h and entropy interaction parameter χ_s as

$$\chi_t = \chi_h + \chi_s \tag{15}$$

The enthalpy interaction parameter is defined in the theory in a whole concentration range as

$$\chi_h = (p_1^* V_1^* / RT\Phi_2^2)[(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + (\alpha T/\tilde{v})(\tilde{T}_1 - \tilde{T})/\tilde{T}]$$
$$+ V_1^*(1 + \alpha T)X_{12}\theta_2^2 / (\tilde{v}RT\Phi_2^2) \tag{16}$$

Intrinsic viscosity

IV, $[\eta]$ is related to the χ_1-interaction parameter by the following equation[16-20]

$$[\eta] = [\eta]_\theta + 1.05(3/2\pi)^{3/2}(\Phi_0/N_A)(M_2 v_2^2/V_1)(1 - 2\chi_1) \tag{17}$$

where $[\eta]_\theta$ is the intrinsic viscosity at the theta point, Φ_0 is universal viscosity constant being equal to 2.5×10^{-21} mol^{-1} if the unit of the IV is dl g^{-1}, M_2 and v_2 are molecular weight and partial specific volume of the polymer, respectively, V_1 is molar volume of the solvent and N_A is Avogadro's number.

Polymer concentration is considerably lower (10^{-4} g cm^{-3}) in an intrinsic viscosity measurement. Further, the ratios of specific viscosity, η_{sp} to the polymer concentration, c, are extrapolated to the zero polymer concentration to obtain the IV according to its definition, $[\eta] = \mathrm{Lim}_{c \to 0}(\eta_{sp}/c)$. Therefore, we may assume that the χ_1-interaction parameter in equation (17) is equal to the χ_1 interaction parameter at zero polymer concentration, i.e. $\Phi_2 \cong 0$, in equation (1).

On the other hand, from the series expansion of equation (13) in powers of Φ_2, the following equation is obtained for the infinitely dilute polymer

solutions[1-4,12]

$$\chi_1 = p_1^* V_1^* A^2 \alpha_1 / 2\tilde{v}_1 R - (s_2/s_1)^2 V_1^* Q_{12}/R$$
$$+ (s_2/s_1)^2 V_1^* X_{12}/\tilde{v}_1 RT \tag{18}$$

where

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

It is obvious that X_{12} and Q_{12} can be obtained from the slope and intercept of the linear straight line of the plot, χ_1 vs $1/T$ if we assume that all equation of state parameters are independent of temperature in the studied temperature range.

Inverse gas chromatography

The specific retention volume, V_g^0, is a quantity obtained from the i.g.c. technique and is the net volume of carrier gas required to move all solvent molecules through the column at $0°C$ and is related to the χ_{12}^∞-interaction parameter at infinitely high polymer concentration according to Flory–Huggins theory[21-24]

$$\chi_{12}^\infty = \mathrm{Ln}(273.2Rv_2/p_1^0 V_g^0 V_1) - (1 - V_1/M_2 v_2)$$
$$- p_1^0 (B_{11} - V_1)/RT \tag{19}$$

where p_1^0 and B_{11} are the saturated vapour pressure and second virial coefficient of the solvent, respectively. Solvent vapour pressures were computed from the well-known Antoine's equation and Antoin's constants have been obtained from the literature[25]. The densities of solvent and polymer were also obtained from the literature[12,15]. Second virial coefficients of MEK have been calculated from the expression given by Pitzer and Curl[26]. In order to obtain the χ_t^∞-interaction parameter in the equation of state theory, the corresponding ratio of molar hard-core volumes of the components are used instead of the ratio of their actual molar volumes as follows

$$\chi_t^\infty = \mathrm{Ln}(273.2Rv_2^*/p_1^0 V_g^0 V_1^*) - (1 - V_1^*/M_2 v_2^*)$$
$$- p_1^0 (B_{11} - V_1)/RT \tag{20}$$

Under the i.g.c. conditions, the segment and contact site fractions of polymer approaches to unity, i.e. $\Phi_2 \cong 1$, $\theta_2 \cong 1$. Therefore, it may be assumed that $v = v_2$, $T = T_2$, $\alpha = \alpha_2$. Consequently, for i.g.c. conditions, equations (13)–(16) can be rewritten, respectively, as follows:

$$RT\chi_t^\infty = p_1^* V_1^* \{3\tilde{T}_1 \mathrm{Ln}[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_2^{1/3} - 1)] + \tilde{v}_1^{-1} - \tilde{v}_2^{-1}\}$$
$$+ \bar{X}_{12} V_1^* \tilde{v}_2^{-1} \tag{21}$$

$$\bar{X}_{12} = X_{12} - T\tilde{v}_2 Q_{12} \tag{22}$$

$$\chi_t^\infty = \chi_h^\infty + \chi_s^\infty \tag{23}$$

$$\chi_h^\infty = (p_1^* V_1^*/RT)[(\tilde{v}_1^{-1} - \tilde{v}_2^{-1}) + (\alpha_2 T/\tilde{v}_2)(\tilde{T}_1 - \tilde{T}_2)/\tilde{T}_2]$$
$$+ V_1^*(1 + \alpha_2 T)X_{12}/(\tilde{v}_2 RT) \tag{24}$$

By means of i.g.c. measurements, χ_h^∞ is found from the slope of the linear straight line of the χ_t^∞ vs $1/T$ plot, according to its definition

$$\chi_h^\infty = [\partial(\chi_t^\infty)/\partial(1/T)]/T \tag{25}$$

EXPERIMENTAL

PDMS was a Petrarch Inc. (Bristol, USA) product with a number-average molecular weight of 2.8×10^4. MEK

was analytical reagent grade produced by Merck AG. Inc. (Darmstadt, Germany) and was used without further purification.

The IV was obtained using a home-made Ubbelohde type viscometer in a constant temperature bath controlled to $\pm 0.02°C$. The efflux time of 2 ml methyl ethyl ketone was 357.5 ± 0.1 s at 20°C. Five polymer concentrations were obtained in the viscometer by successive dilution of the initial PDMS solution. The concentrations of the solutions were kept below $10^{-4} g cm^{-3}$. The IV was found from the intercept of the linear regression of the experimental data.

Experimental details related to the i.g.c. technique were given in previous studies[5,6].

RESULTS AND DISCUSSION

In *Table 1*, we have reported IV data obtained in this study. Although we used equation (17) in calculation of χ_1 in our previous studies related to IV[1-4], we have applied a slight modification to equation (17) in this study. In a theta solvent favourable and unfavourable interactions compensate each other, so high volume change of mixing is not expected. According to experimental results[12-14,27-30], it was also found that the volume change of mixing is low in theta solvents, i.e. max. 0.3%, therefore it may be assumed that the volume change of mixing is negligible and the partial specific volume of polymer is approximately equal to its own specific volume in a theta solvent. On the other hand, Eichinger and Flory[27] have proposed a replacement of volume fractions with segment fractions and the ratio of molar volumes of polymer to that of solvent, V_2/V_1, with the ratio of molar hard core volume of polymer to that of solvent, V_2^*/V_1^*. Therefore, we have applied this proposal to equation (17), analogously to equations (19) and (20), and have rewritten equation (17) as

$$[\eta] = [\eta]_\theta + 1.05(3/2\pi)^{3/2}(\Phi_0/N_A)$$
$$\times (M_2 v_2^*/V_1^*)(1 - 2\chi_1)v_2 \qquad (26)$$

In *Figure 1*, we have plotted χ_1-interaction parameter by a linear regression as a function of the reciprocal of the absolute temperature using the above modified equation. From its slope and intercept, we have calculated X_{12} and Q_{12} parameters, respectively, which are presented in *Table 1*. In order to calculate X_{12}, and Q_{12}, the necessary reduced and characteristic parameters of the PDMS and MEK were taken from literature[12,15]. It should be noted that we have found higher values for X_{12} and Q_{12} if we used equation (17) instead of equation (26) in calculation of χ_1, for example 44.9 J cm^{-3} and -0.0596 J cm^{-3} K for the former and 40.6 J cm^{-3} and -0.0700 J cm^{-3} K for the latter, respectively, at 20°C.
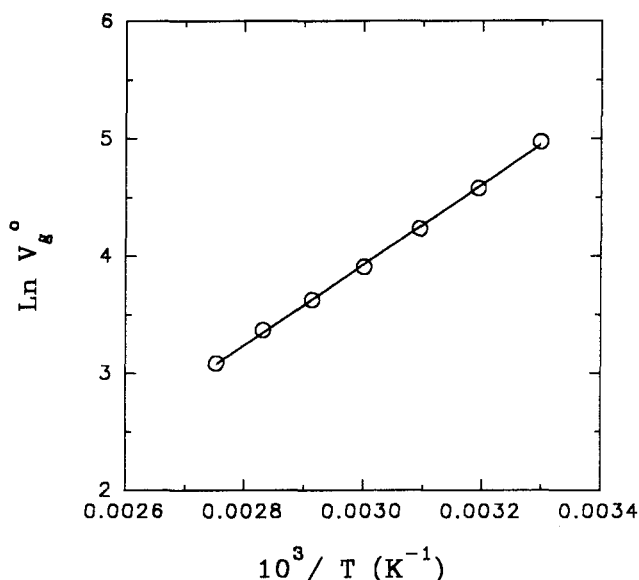

Figure 1 Variation of χ_1-interaction parameter obtained from IV measurements as a function of temperature
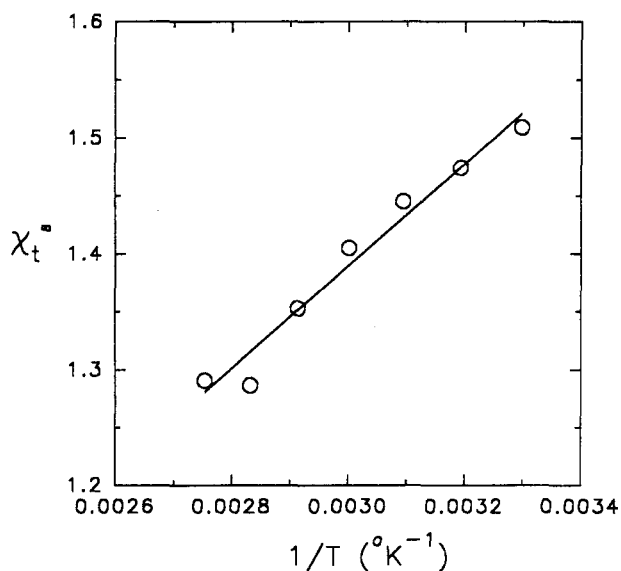

Figure 2 Variation of specific retention volume of MEK in PDMS in the i.g.c. measurements as a function of temperature

The specific retention volumes, V_g^o of the PDMS-MEK system were shown in *Figure 2* as a function of reciprocal of the absolute column temperature. The linear straight line shows that the equilibrium sorption is attained in the studied temperature range. The numerical data for V_g^o were given in *Table 2* together with other data obtained from i.g.c. measurements.

Figure 3 represents variation of the values of χ_t^∞ with temperature. We have assumed that they increased linearly with the reciprocal of the absolute temperature since variation of them with reciprocal of absolute temperature is a straight line according to our previous studies[5,6] and some studies in the literature[24,31]. Then, we have calculated χ_h^∞ values from its slope. We could not find any i.g.c. data related to χ_t^∞ and χ_h^∞ in literature to compare our data.

The X_{12} and Q_{12} parameters obtained from both techniques are shown in *Figure 4* where filled and hollow

Table 1 Intrinsic viscosities, $[\eta]$, χ_1-interaction parameters, exchange enthalpy, X_{12} and entropy, Q_{12} parameters of PDMS-MEK system at various temperatures

Temp. (°C)	$[\eta]$ (dl g^{-1})	χ_1	X_{12} (J cm^{-3})	$-Q_{12} \times 10^3$ (J cm^{-3} K^{-1})
20	0.1300	0.500	40.6	70.0
30	0.1390	0.491	41.0	69.9
40	0.1462	0.484	41.3	69.6
50	0.1591	0.472	41.6	69.3
60	0.1667	0.465	41.9	69.1

Table 2 The specific retention volumes, V_g^o, χ_t^∞-total interaction and χ_h^∞-enthalpic interaction parameters at infinitely high polymer concentration, and effective exchange energy $\bar{X}_{12}$, exchange enthalpy, X_{12} and exchange entropy Q_{12} parameters of PDMS-MEK system obtained from IGC measurements at various column temperatures

Column temp. (°C)	V_g^o (cm³ g pol⁻¹)	χ_t^∞	χ_h^∞	$\bar{X}_{12}$ (J cm⁻³)	X_{12} (J cm⁻³)	$-Q_{12} \times 10^3$ (J cm⁻³ K⁻¹)
30	144.5	1.51	1.45	64.7	52.8	32
40	97.3	1.47	1.40	65.3	49.9	40
50	69.0	1.44	1.36	64.2	54.6	24
60	49.8	1.40	1.32	64.0	53.8	24
70	37.6	1.35	1.28	62.4	54.7	18
80	29.1	1.29	1.24	60.5	53.7	16
90	21.9	1.29	1.21	60.9	55.5	16

symbols belong to IV and i.g.c. experiments, respectively. The X_{12} as well as Q_{12} parameters obtained from IV measurements have values lower than those obtained from i.g.c. measurements. This suggests that X_{12} and Q_{12}
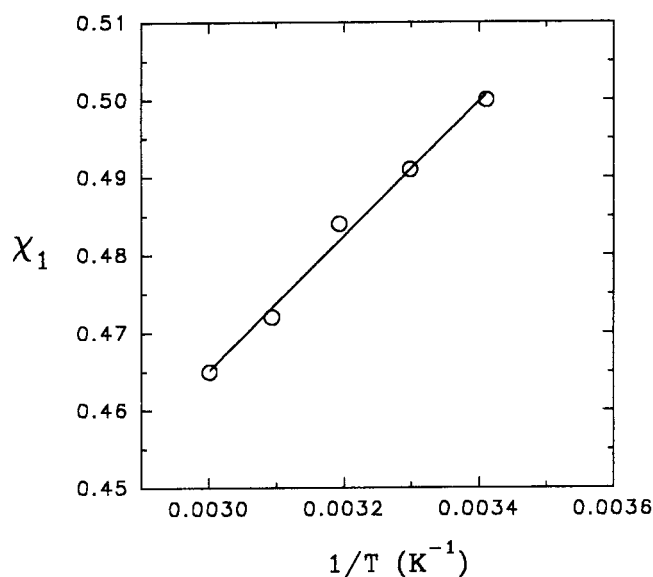
Figure 3 The χ_t^∞-total interaction parameters of PDMS-MEK system obtained from i.g.c. as a function of temperature

parameters are dependent on composition of the mixture at least for this polymer–solvent system. Both X_{12} and Q_{12} parameters slowly increase with temperature, so they may be independent of temperature.

In *Figure 5*, we have compared the total interaction parameter χ_t data obtained by osmotic pressure measurements in literature[32] with the expected values from the equation of state theory for the PDMS-MEK system at a whole composition range at 20°C. The solid line was theoretically produced by using the mean values of the X_{12} and Q_{12} parameters obtained from both techniques in equation (13). The ratio, s_2/s_1 was estimated as 0.58 by the approximation that the solvent may be represented by a sphere and the polymer by a cylinder. The experimental χ value is 0.50 at $\Phi_2 = 0$, that is obtained by IV at 20°C (θ-point) while the χ value is 1.58 at $\Phi_2 = 1$, that is obtained by extrapolation of the i.g.c. data at high temperatures to 20°C. The agreement between theory and experiments is satisfactory.

The dotted line in *Figure 5* was produced by assuming the empirical equation (1) as

$$\chi_t = 1/2 + (1/3)\Phi_2 + (1/4)\Phi_2^2 + (1/5)\Phi_2^3$$
$$+ (1/6)\Phi_2^4 + (1/7)\Phi_2^5 \qquad (27)$$

Therefore, at theta point at least for this polymer–solvent
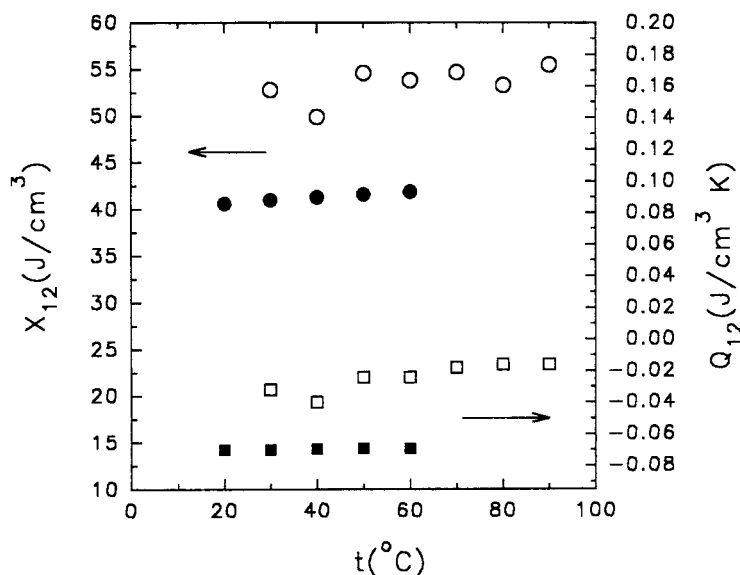
Figure 4 The exchange enthalpy, X_{12} and entropy, Q_{12} parameters of PDMS-MEK system as a function of temperature. The filled and hollow symbols were obtained from IV and i.g.c. measurements, respectively
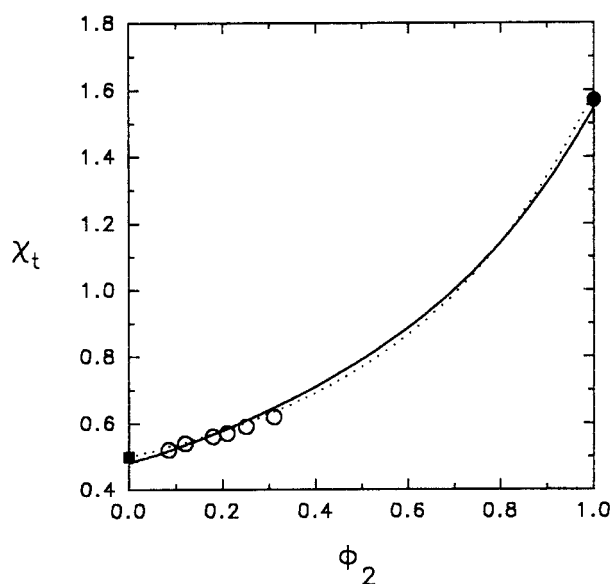
Figure 5 Comparison of the χ_t-total interaction parameter of the PDMS–MEK system at a whole concentration range at 20°C. The solid line was produced from the equation of state theory by using the mean values of the X_{12} and Q_{12} parameters obtained from both techniques in this study. The hollow symbols represent the data reported by Dolc *et al.*, obtained from the osmotic pressure measurements[25]. The filled square and the filled circle represent data obtained from IV and i.g.c. measurements, respectively, in this study. The dotted line was produced by using equation (27) in the text

system, we may write

$$\chi_t = \sum_{i=0}^{5} 1/(i+2)\Phi_2^i \tag{28}$$

It is concluded that the IV technique gives lower values for both X_{12} and Q_{12} parameters of the PDMS–MEK system. This suggests that the X_{12} and Q_{12} parameters depend on composition of this polymer–solvent pair. The increase of the X_{12} and Q_{12} parameters with temperature is almost negligible. The composition dependence of the X_{12} and Q_{12} parameters is in disagreement but negligible temperature dependence of them is in agreement with the assumptions of the equation of state theory of Flory.

ACKNOWLEDGEMENTS

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