Interaction parameters in ternary polystyrene solutions at high temperature

Abdel-Azim A. Abdel-Azim* and Malcolm B. Huglin
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK
(Received 6 June 1983)

A combination of dilute solution viscometry and Rayleigh light scattering has been used to evaluate experimentally the interaction parameters χ_{ij} in solutions comprising tetralin (1), polystyrene (2) and 3-methyl cyclohexanol (3). The measurements were carried out at 371.5 K, where binary solutions of the polymer in 3-methyl cyclohexanol are under θ-conditions and tetralin is a thermodynamically good solvent for polystyrene. For polymer–solvent interaction, values of $\chi_{12} = 0.40 \pm 0.01$ and $\chi_{23} = 0.50$ were obtained. The solvent–solvent interaction parameter χ_{13} was composition dependent, having limiting values of 0.52 and 0.73 at $X_1 = 0$ and $X_1 = 1$, respectively, where X_1 is the mol fraction of liquid 1 in binary mixtures of liquids (1) and (3).

INTRODUCTION

For a polymer (2) dissolved in a single solvent (1) the general thermodynamic behaviour and solubility in particular are governed by the magnitude of the Flory–Huggins interaction parameter χ_{12}. Thus, for a given temperature and molar mass (M) of polymer, the better the solvent the smaller is χ_{12}. There are several circumstances in which advantages may be gained by the inclusion of an additional solvent component (3). Substance 3 may be a low molecular weight liquid, a slat or even another polymer (see, e.g., refs. 1 and 2). Preliminary communications[3–5] have dealt with systems in which 1, 2 and 3 denote, respectively, 1,2,3,4-tetrahydronaphthalene (TET), polystyrene (PS) and 3-methyl cyclohexanol (MC). The findings indicated the necessity to invoke the relevant interaction parameters, which are not available in the literature.

Determination of the two polymer–solvent interaction parameters χ_{12} and χ_{23} as well as the solvent–solvent interaction parameter χ_{13} forms the basis for the present paper, which relates solely to 371.5 K. At this temperature MC is a θ-solvent for PS, whereas TET is a good solvent for the polymer. Moreover, as TET and MC are completely miscible, it is possible to examine polymer solutions and binary solvent mixtures encompassing the entire range of solvent composition, i.e. from $X_1 = 0$ to $X_1 = 1$, where X denotes mol fraction in the binary solvent mixture.

EXPERIMENTAL

Materials

MC and TET were purified as before[5]. For light-scattering calibration, AnalaR benzene was purified by passage through a region of aluminium oxide (mesh chromatogr.) above a lower layer of silica gel (60–120

mesh, chromatogr.). After subsequent standing over anhydrous $MgSO_4$ for 24 h, the benzene was filtered, dried with Na wire for 24 h and distilled at atmospheric pressure. For differential refractometry, a polydisperse PS sample of $M \approx 3 \times 10^5 \, \text{g mol}^{-1}$ was used (designation—PS3; courtesy of Mr L. J. Maisey, RAPRA, Shawbury, Shropshire, UK). Five monodisperse PS samples ($\bar{M}_w/\bar{M}_n \leqslant 1.09$), having molar masses of 1.06×10^5, 2.94×10^5, 4.20×10^5, 6.40×10^5 and $9.60 \times 10^5 \, \text{g mol}^{-1}$ were used for viscometry. These samples and their specifications were supplied by Polymer Laboratories Ltd., Church Stretton, Shropshire, UK. The sample of highest molar mass was used for light-scattering measurements.

Density, refractometry and viscometry

Eleven binary mixtures of MC/TET were made up gravimetrically. The densities of these and of the pure solvents were measured dilatometrically at several temperatures within the range 289–339 K. A similar temperature range was used for measuring the refractive indices with a Pulfrich refractometer at a wavelength in vacuo $\lambda_0 = 436 \, \text{nm}$. At the same wavelength the specific refractive index increment of sample PS3 in TET was measured at 371.5 K in a Brice–Phoenix differential refractometer fitted with an external recirculatory oil thermostat. The compartment of the stoppered cell was insulated by a winding of thick polyurethane foam. Calibration was effected at 298 K with aq. solutions of KCl of different concentrations C_s, where C_s is expressed in g salt/100 g of water. For several values of C_s the corresponding literature values of $\Delta \bar{n}$ are available[6], where $\Delta \bar{n}$ represents the difference in refractive index between solution and solvent. Rather than select one of the exact listed concentrations it proved more convenient to take a solution of any known C_s and calculate $\Delta \bar{n}$ from the following least squares form of literature data.

$$\Delta \bar{n} \times 10^6 = 1.862 + 1415.8 \, C_s - 17.699 \, C_s^2 + 0.428 \, C_s^3$$

Note that, although this expression yields a coefficient of

* Present address: Department of Chemistry, Military Technical College, Kobry El-Kobba, Cairo, Egypt

C_s^0 which is not the theoretical value of zero, this coefficient ($= 1.862 \times 10^{-6}$) is smaller than the lowest limit of detecting $\Delta \tilde{n}$ experimentally.

Intrinsic viscosities in TET and MC were measured as described previously[5].

Light scattering

A Sofica photometer (model 42000) was used with unpolarized incident light of $\lambda_0 = 436$ nm. Temperature constancy within $\pm 0.2°C$ was attained by means of the internal heater of the instrument. Solutions and solvents were clarified by passage through a porosity 4 sinter. Scattered light outputs, G, were registered on a digital voltmeter, the Cabannes depolarization factor being measured at an angle of 90° for liquid mixtures but not for polymer solutions. The absolute Rayleigh ratio for benzene at 90° was interpolated from its quoted dependence on temperature[7], yielding $R_{90} = 56.1 \times 10^{-4} \, m^{-1}$ at the working temperature.

A flint glass working standard is a convenient alternative to the use of benzene for calibration. The manufacturers quote a value for the ratio r [$= G(\text{glass})/G(\text{benzene})$], which eliminates the need to measure $G(\text{benzene})$, this latter quantity being replaced by the quotient of the measured reading $G(\text{glass})$ and r. By measuring directly the 90° scattering values of $G(\text{glass})$ and $G(\text{benzene})$ at seventeen temperatures over as wide a range as allowed by the f.p. and b.p. of benzene, it was established that the quoted value of r was applicable only to within approximately $\pm 5°C$ of ambient temperature. The observed decrease in r with temperature T was fitted to a polynomial from which the value of r appropriate to $T = 371.5$ K was obtained. This was used thereafter in conjunction with $G(\text{glass})$ for measurements on dilute solutions of PS in TET and on twenty-two different compositions of TET/MC mixtures .

RESULTS AND DISCUSSION

Physicochemical properties

The dependence of composition and temperature on the density ρ (kg dm^{-3}) of binary solvents is shown in a combined form in *Figure 1*. At a fixed temperature the variation of ρ with W_3 (where W_3 denotes weight fraction of MC) is quadratic, whereas at a fixed composition ρ varies rectilinearly with T. The dependence at 293.1 K and
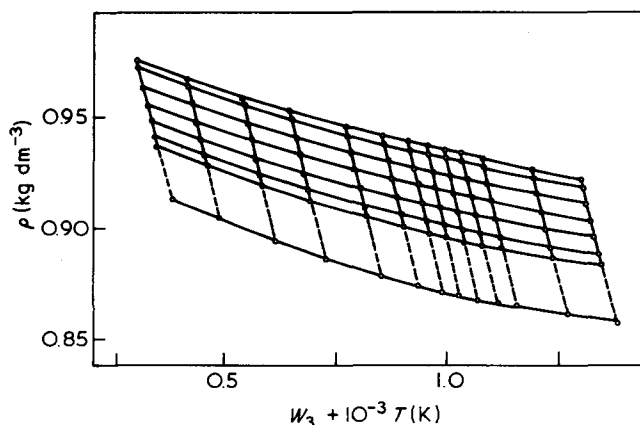

Figure 1 Variation of density of TQT/MC mixtures with temperature and composition. W_3 is the weight fraction of MC and broken lines indicate extrapolation to $T = 371.5$ K
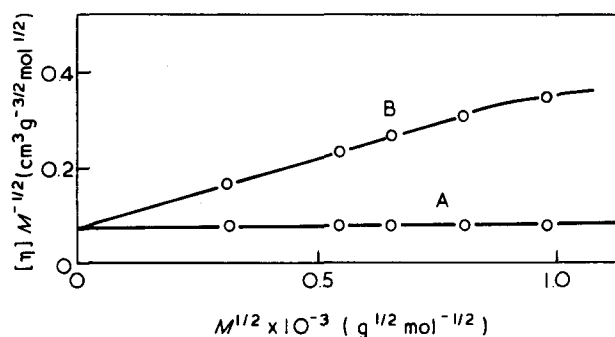

Figure 2 Stockmayer–Fixman plots for (A) PS in MC and (B), PS in TET

the extrapolated one at 371.5 K (used for subsequent calculations of concentration in viscometry) are:

293.1 K: $\rho = 0.9710 - 6.57 \times 10^{-2} \, W_3 + 1.23 \times 10^{-2} \, W_3^2$
371.5 K: $\rho = 0.9122 - 8.63 \times 10^{-2} \, W_3 + 3.02 \times 10^{-2} \, W_3^2$

A similar general form is applicable for the effect of composition and T on refractive index $\tilde{n}_0$. In terms of mol fraction, X, which is the compositional variable selected for light scattering from liquid mixtures, the extrapolated relation at 371.5 K is:

$$\tilde{n}_0 = 1.53494 - 8.64 \times 10^{-2} \, X_3 - 4.60 \times 10^{-3} \, X_3^2 \quad (1)$$

The specific refractive index increment $d\tilde{n}/dc_2$ for PS in TET was 0.0755 dm^3 kg^{-1}.

The parameter χ_{23}

The following results have been quoted previously[3-5] for the system PS/MC: (1) the θ-temperature is 371.5 K (via phase separation), (2) at this temperature the Mark–Houwink exponent is 0.50, the slope of the Stockmayer–Fixman plot[8] is zero and the second virial coefficient (via light scattering) is zero. These findings have been verified by repeating the relevant experiments with the present new set of monodisperse PS samples of different molar masses from those used previously. Only the present Stockmayer–Fixman plot is shown here (*Figure 2*). Under the θ-conditions prevailing, therefore, the polymer–solvent interaction parameter χ_{23} has a value of 0.50.

The parameter χ_{12}

For solutions of PS in TET the Mark–Houwink exponent was 0.82 and the slope (S) of the Stockmayer–Fixman plot (*Figure 2*) was $2.80 \times 10^{-4} \, m^3 \, kg^{-2}$ mol. The value of χ_{12} was calculated from S via:

$$S = 1.02 \, \Phi_0 \, \bar{v}_2^2 \, (0.50 - \chi_{12})/V_1 N_A \quad (2)$$

In equation (2), N_A is the Avogadro number, V_1 ($= 0.1449$ dm^3 mol^{-1}) is the molar volume of TET and $\bar{v}_2$ is the partial specific volume of PS in solution for which the literature value[9] of 0.9738 dm^3 kg^{-1} relating to amorphous PS was used. Hammel *et al.*[10] have confirmed that the interpolated value of $\bar{v}_2$ from data on liquid-like polymer is in good accord with the directly measured value. For the latter, $\bar{v}_2 = 0.9750$ dm^3 kg^{-1} for PS in *trans*-decalin at 371.5 K[11]. Moreover, Sutter and Burchard[12] have indicated that, at a given temperature, the nature of the solvent does not generally have a large effect on the partial specific volume. In fact, the use of 0.9650 dm^3 kg^{-1}

in place of the value of $0.9738\,dm^3\,kg^{-1}$ actually adopted here vor $\bar{v}_2$ changes the resultant value of χ_{12} by an insignificant amount of 0.002.

There is as yet no unanimity regarding the value of the Flory constant Φ_0 (see e.g. Yamakawa[13] and Bareiss[14]). Commonly adopted values of 2.87×10^{23} and $2.50 \times 10^{23}\,mol^{-1}$ yield from equation (2) $\chi_{12} = 0.41$ and 0.40, respectively. It is also possible to evaluate Φ_0 from the intrinsic viscosity $[\eta]$ of a polymer having known number-average values of molar mass M and mean square radius of gyration $\langle s^2 \rangle$:

$$[\eta] = \Phi_0 6^{3/2} \langle s^2 \rangle^{3/2} / M \qquad (3)$$

For the PS sample specified later, $[\eta] = 300\,dm^3\,kg^{-1}$ in TET, which yields from equation (3) $\Phi_0 = 2.71 \times 10^{23}\,mol^{-1}$. This value in conjunction with equation (2), gives $\chi_{12} = 0.41$.

Figure 3 illustrates the light-scattering results for the monodisperse sample of nominal $M = 9.60 \times 10^5$ g mol^{-1} in TET. The derived parameters are $\bar{M}_w = 9.81 \times 10^5\,g\,mol^{-1}$; $\langle s^2 \rangle_z^{\frac{1}{2}} = 43.3$ nm and second virial coefficient $A_2 = 3.16 \times 10^{-4}\,m^3\,kg^{-2}\,mol$. The first two quantities were utilized, as described, to calculate Φ_0 without conversion to the corresponding number-average values (in view of the very low degree of polydispersity). The close accord (to within 2%) between $\bar{M}_w$ and the specified value affords some justification for the procedures adopted in the Experimental section whereby (1) the factor r was not assumed to be constant, but was interpolated to the actual working temperature and (2) the absolute R_{90} of benzene was interpolated from its temperature dependence up to the working temperature, which is actually above the b.p. of benzene.

Next we consider alternative routes to the evaluation of χ_{12}. At a fixed temperature the Flory theory[15] affords:

$$\alpha^5 - \alpha^3 = 2C_m M^{\frac{1}{2}} (0.50 - \chi_{12}) \qquad (4)$$

there α is the chain expansion factor and C_m comprises *inter alia* $\bar{v}_2$, V_1, Φ_0 and K_θ (in the expression $[\eta] = K_0 M^{\frac{1}{2}} \alpha^3$). Use of the previously reported value[3] of K_θ gives $C_m = 0.0323\,mol^{\frac{1}{2}}\,g^{-\frac{1}{2}}$ and, hence, from equation (4), $\chi_{12} = 0.39$.

The second virial coefficient is given by equation (5):

$$\chi_{12} = 0.50 - A_2 (V_1/\bar{v}_2{}^2)/h(Z) \qquad (5)$$

Here $h(Z)$ is a function of the excluded volume parameter Z. Various expressions have been proposed for the function $h(Z)$ and $h(\bar{Z})$, where $\bar{Z} = Z/\alpha^3$. They are formulated in terms of either the viscometric expansion factor $(\alpha \equiv \alpha_\eta)$ or that based on the radius of gyration $(\alpha \equiv \alpha_s)$. From the intrinsic viscosities in TET and MC, $\alpha_\eta = 1.636$ and, via $\alpha_\eta^3 = \alpha_s^{2.43}$, the value of α_s is 1.837. The excluded volume functions collated by Yamakawa[16] as well as more recent ones of Tanaka[17,18] were evaluated. In each instance the result was combined with selected values of χ_{12} in equation (5) to ascertain which χ_{12} afforded agreement with the experimental A_2. In several instances fit was obtained for $\chi_{12} \approx 0.39$. However, the Casassa–Markowitz expression[19] for $h(Z)$, for example, led to an unrealistically low value of 0.18.

A related approach is embodied in the use of the penetration function:

$$\psi = A_2 M^2 / (4\pi^{3/2} N_A \langle s^2 \rangle^{3/2}) \qquad (6)$$

From the experimentally determined quantities in equation (6), $\psi = 0.279$. For each of several excluded volume theories the corresponding curve of ψ as a function of $\bar{Z}$ has been plotted by Yamakawa[16]. For certain of the theories the curves indicate that ψ cannot attain a value as high as 0.279. For the remainder, the value of $\bar{Z}$ read from the curve was inserted into the corresponding expression for $h(Z)$ and consistency examined by comparison with the $h(Z)$ known from the experimental expansion coefficient. The Flory–Krigbaum–Orofino function[20] modified by Stockmayer[21] afforded best consistency, yielding $\chi_{12} = 0.39$. In general, for theories capable of affording $\psi = 0.279$ the values of χ_{12} affording acceptable consistency were 0.39–0.41.

In a previous discussion[4] on the lattice co-ordination number PS in TET/MC mixtures, a value of $\chi_{12} = 0.41$ was used. In view of the overall sources of uncertainty associated with the present detailed findings, it appears more legitimate now to assign $\chi_{12} = 0.40 \pm 0.01$.

The parameter χ_{13}

Light scattering was used to obtain the concentration fluctuation Rayleigh ratio R_c in TET/MC over the whole range of composition. The directly measured total Rayleigh ratio R_t was converted to the isotropic Rayleigh ratio R_{iso} via the measured depolarization ratio σ_u of the horizontal to vertical components of the incident light

$$R_{iso} = R_t (6 - 7\sigma_u)/(6 + 6\sigma_u)$$

In a pure liquid or mixture the density fluctuation scattering R_d is given by equation (7) in which k_B, β and ε are, respectively, the Boltzmann constant, the coefficient of isothermal compressibility and the optical dielectric constant:

$$R_d = (\pi^2/2\lambda_0^4) k_B T \beta [\rho (\partial \varepsilon/\partial \rho)_T]^2 \qquad (7)$$

By invoking the Eykman expression[22] in conjunction with the equality $\varepsilon = \tilde{n}^2$, the factor $\rho(\partial \varepsilon/\partial \rho)_T$ in equation (7) may be written as:

$$\rho(\partial \varepsilon/\partial)_T = 2\tilde{n}(\tilde{n} + 0.4)(\tilde{n}^2 - 1)/(\tilde{n}^2 + 0.8\tilde{n} + 1)$$

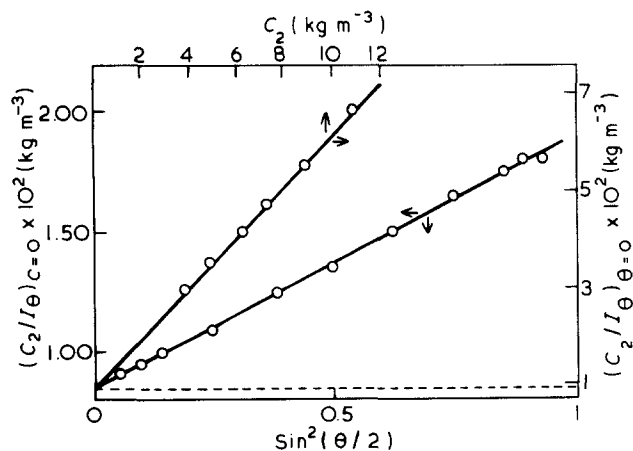For a pure liquid $R_d = R_{iso}$, thus allowing β to be

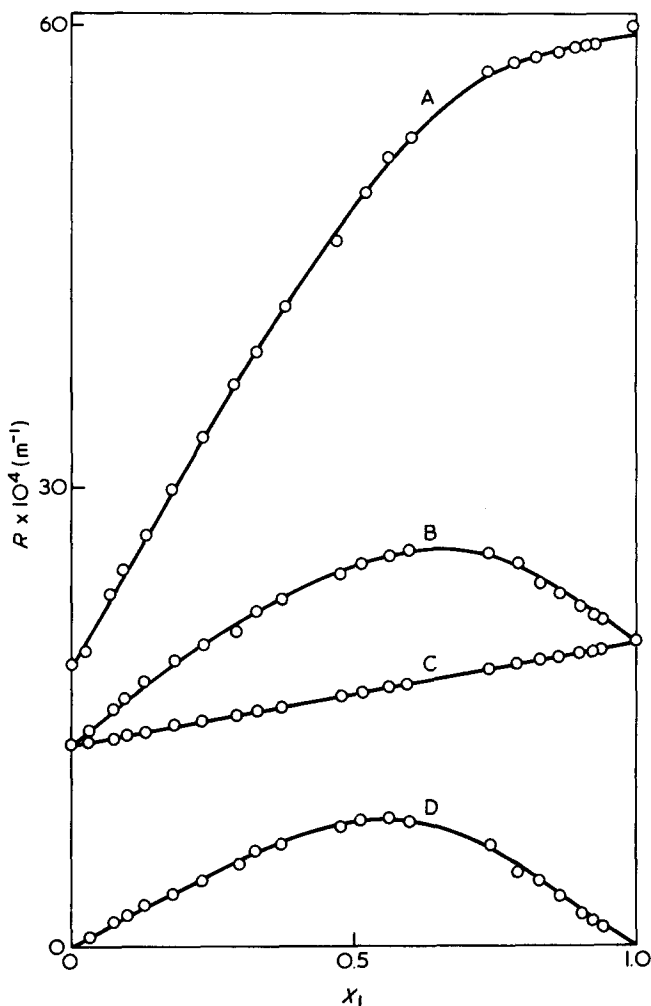Figure 3 Light-scattering plots for PS sample of highest molar mass in TET

Figure 4 Variation of the Rayleigh ratios A, R_t; B, R_{iso}; C, R_d; and D, R_c with mol fraction X_1 of TET in TET/MC mixtures
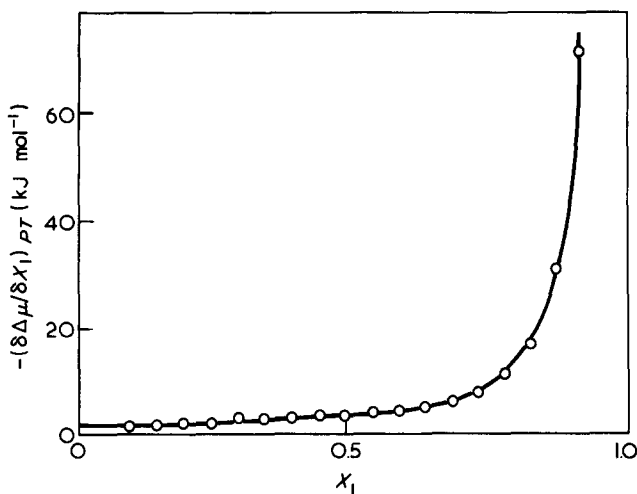

Figure 5 $\partial\Delta\mu_3/\partial X_1$ versus the mol fraction X_1 of TET in TET/MC mixtures

calculated as $\beta_1 = 10.27 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$ for pure TET and $\beta_3 = 9.27 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$ for pure MC. These values were used in a previously derived expression[23] to calculate the coefficient of isothermal compressibility β_{13} of a mixture of any known composition. The variations of R_t, R_{iso} and R_d with composition are shown in *Figure 4*. Also included in this Figure is the variation with X_1 of R_c, this

latter quantity being obtained by subtracting R_d from R_{iso}. At each composition the variation of chemical potential with composition[24,25] was calculated for TET via equation (8) and for MC via equation (9):

$$-(\partial\Delta\mu_1/\partial X_1)_{P,T} = (2\pi^2/\lambda_0^4)(k_B T V_{13} n_0^2)(\partial\tilde{n}_0/\partial X_3)^2 X_3/R_c \tag{8}$$

$$-(\partial\Delta\mu_3/\partial X_1)_{P,T} = (2\pi^2/\lambda_0^4)(k_B T V_{13}\tilde{n}_0^2)(\partial\tilde{n}_0/\partial X_1)^2 X_1/R_c \tag{9}$$

Here V_{13} is the molar volume of the mixture, which was obtained from the density; $\tilde{n}_0$ was obtained via equation (1), differentiation of which also yielded $\partial\tilde{n}_0/\partial X_3$. Note also that $(\partial\tilde{n}_0/\partial X_1) = -(\partial\tilde{n}_0/\partial X_3)$ as $(X_1 + X_3) = 1$. $\Delta\mu_1$ is (chemical potential of TET in the mixture)−(chemical potential of pure TET). A similar meaning in terms of MC is attached to $\Delta\mu_3$. The right-hand side of equation (8) was evaluated to give $(\partial\Delta\mu_1/\partial X_1)_{P,T}$ at each composition. Subsequent graphical integration gives $\Delta\mu_1$ at each of several selected compositions. The same procedure applies to the determination of values of $\Delta\mu_3$ via equation (9), the plot being shown in *Figure 5*. The variation of the resultant values of $\Delta\mu_1$ and $\Delta\mu_3$ with composition is illustrated in *Figure 6*. The free energies of mixing (ΔG_m), as well as their ideal (ΔG_{id}) and excess (ΔG_E) values were calculated from equations (10), (11) and (12), respectively:

$$\Delta G_m = X_1\Delta\mu_1 + X_3\Delta\mu_3 \tag{10}$$

$$\Delta G_{id} = RT(X_1\ln X_1 + X_3\ln X_3) \tag{11}$$

$$\Delta G_E = \Delta G_m - \Delta G_{id} \tag{12}$$

The variation of these quantities with X_1 over the whole composition range is shown in *Figure 7*. Finally, the interaction parameter χ_{13} was calculated from equation (13):

$$\chi_{13} = \Delta G_E/X_1 X_3 RT \tag{13}$$

As shown in *Figure 8*, χ_{13} undergoes only a small change in the interval $X_1 = 0$–0.25, but thereafter increases markedly with X_1. Least squares fitting of the data yields the polynomial:

$$\chi_{13} = 0.521 - 1.95 \times 10^{-2}\,X_1 + 0.339\,X_1^2 - 0.115\,X_1^3$$

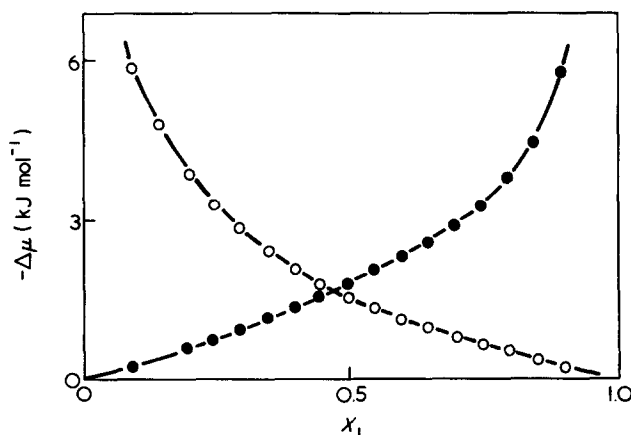Hence, over the whole range of composition χ_{13} varies

Figure 6 Chemical potentials of TET and MC as a function of mixed solvent composition. $\bigcirc$, $\Delta\mu_1$; $\bullet$, $\Delta\mu_3$
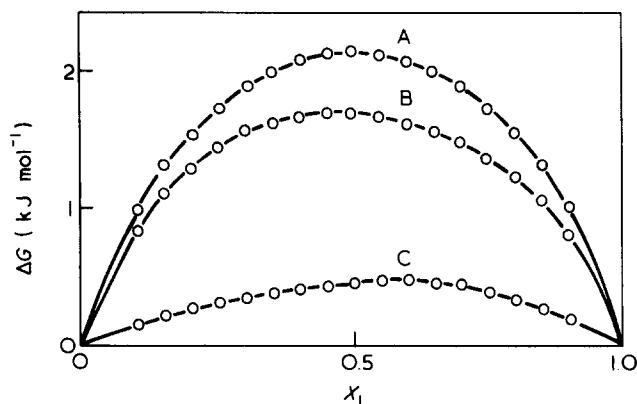
Figure 7 Free energies of mixing TET with MC as a function of composition. A, $-\Delta G_{id}$; B, $-\Delta G_m$; C, ΔG_E
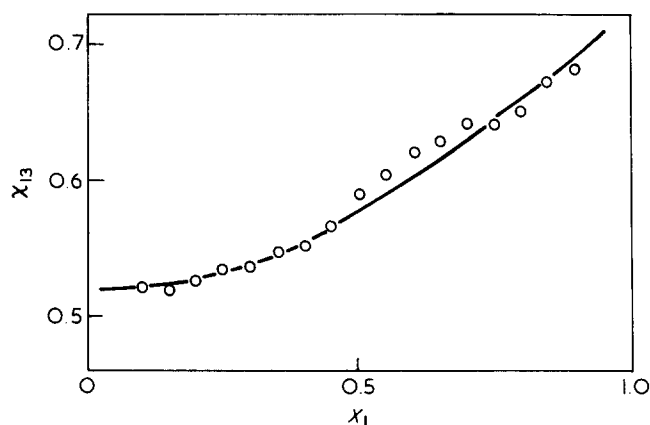

Figure 8 Dependence of the binary interaction parameter χ_{13} on mol fraction X_1 of TET in TET/MC mixtures at 371.5 K

between 0.521 and 0.725. No directly comparable published data are available. However, the overall trend is similar to that observed by Živný et al.[26] who used benzene and methanol in place of TET and MC, re-

spectively. Their values of χ_{13} displayed an appreciable increase with increasing content of benzene in the binary mixture.

REFERENCES

1 Kratochvíl, P. *J. Polym. Sci. C* 1975, **50**, 487
2 Huglin, M. B. *Topics in Current Chem.* 1978, **77**, 141
3 Abdel-Azim, A.-A. A. and Huglin, M. B. *Europ. Polym. J.* 1982, **18**, 735
4 Abdel-Azim, A.-A. A and Huglin, M. B. *Makromol. Chem. Rapid Commun.* 1982, **3**, 437
5 Abdel-Azim, A.-A. A. and Huglin, M. B. *Makromol. Chem. Rapid Commun.* 1981, **2**, 119
6 Huglin, M. B. in 'Light Scattering from Polymer Solutions (Ed. M. B. Huglin), Academic, London, 1972, Chap. 6
7 Scornaux, J. and Van Leemput, R. *Makromol. Chem.* 1976, **177**, 2721
8 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci. C* 1963, **1**, 137
9 Höcker, H., Blake, G. J. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2251
10 Hammel, G. L., Schulz, G. V. and Lechner, M. D. *Makromol. Chem.* 1981, **182**, 1835
11 Nyström, B. and Roots, J. *Polymer* 1977, **18**, 1289
12 Sutter, W. and Burchard, W. *Makromol. Chem.* 1978, **179**, 1961
13 Yamakawa, H. *J. Chem. Phys.* 1970, **53**, 436
14 Bareiss, R. E. *Makromol. Chem. Rapid Commun.* 1981, **2**, 523
15 Flory, P. J. 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, N.Y., 1953, Chap. 14
16 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, London, 1971
17 Tanaka, G. *Macromolecules* 1980, **13**, 1513
18 Tanaka, G. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 305
19 Casassa, E. F. and Markovitz, H. *J. Chem. Phys.* 1958, **29**, 493
20 Orofino, T. A. and Flory, P. J. *J. Chem. Phys.* 1957, **26**, 1067
21 Stockmayer, W. H. *Makromol. Chem.* 1960, **35**, 54
22 Eykman, J. F. *Rec. Trav. Chim.* 1895, **14**, 185
23 Huglin, M. B. and Sokro, M. B. *Polymer* 1980, **21**, 651
24 Fechner, B. M. and Strazielle, C. *Makromol. Chem.* 1972, **160**, 195
25 Scholte, Th. G. *Europ. Polym. J.* 1970, **6**, 1063
26 Živný, A., Pouchlý, J. and Šolc, K. *Coll. Czech. Chem. Commun.* 1967, **32**, 2753