Selective solvation of polystyrene in tetralin/cyclohexane mixtures

Abdel-Azim A. Abdel-Azim and Malcolm B. Huglin
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

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Refractive index increments and density increments have been measured at 307.6K for polystyrene in binary solvents of 1,2,3,4-tetrahydronaphthalene (tetralin, TET) and cyclohexane over the whole range of solvent composition. Comparison of these increments with the corresponding values obtained at dialysis equilibrium (i.e. at constant chemical potential of low molecular weight species) yielded the coefficients of selective adsorption (γ_1) of TET by the polymer. Positive values of γ_1 were exhibited at solvent compositions up to 78% (v/v) of the thermodynamically better solvent, TET. Theoretical curves of γ_1 vs. composition were calculated on the basis of, firstly, relevant interaction parameters and, secondly, interaction parameters in conjunction with solubility parameters. Both procedures afforded self-consistent results, which were, however, uniformly lower than the experimental values of γ_1.

Keywords Polystyrene; tetralin; cyclohexane; selective adsorption; interaction parameter; solubility parameter

INTRODUCTION

In a previous communication[1] we have discussed the lattice coordination number of polystyrene (PS; subscript 2) in binary solvents comprising 1,2,3,4-tetrahydronaphthalene (tetralin, TET; subscript 1) and cyclohexane (CH, subscript 3) at 307.6K, which is the θ temperature for PS in pure CH. The present report deals with different aspects of the same systems. Since TET is a thermodynamically good solvent for PS[2-4], it is possible to vary the solvent power of the medium by changing ϕ_1 (where ϕ denotes volume fraction) at constant temperature. One measure of such variations is the coefficient of selective adsorption of one of the two solvent constituents. The techniques that have been employed include sedimentation[5], adiabatic compressibility[6], viscometry[7,8], n.m.r.[8], gel permeation chromatography[9], light scattering[10-12], differential refractometry[11,13,14] and density increments[15-21]. The last two of these were employed in the present work. A temperature of 307.6K is implied throughout and, for refractometry, a wavelength *in vacuo* of 436 nm was used.

EXPERIMENTAL

Materials

The PS used was a sample designated as PS3 ($\bar{M}_w = 3.4 \times 10^5$ g mol^{-1}), which was prepared and provided by RAPRA, Shawbury, Shrewsbury, UK (courtesy Mr L. J. Maisey). TET and CH were dried over sodium wire and distilled twice at atmospheric pressure.

Refractometry

Using solvents made up accurately by weight, a calibration curve was constructed of refractive index ($\tilde{n}_0$) of solvent *versus* weight fraction of TET, Values of $\tilde{n}_0$ were measured with a Pulfrich refractometer fitted with an external circulatory thermostat. The solvents used subsequently for preparing polymer solutions were made up more conveniently by volume and the exact value of ϕ_1 for each was obtained from the measured value of $\tilde{n}_0$ in conjunction with the calibration curve and the densities of TET and CH.

Differential refractometry

With a Brice Phoenix differential refractometer the calibration constant correlating the observed image displacement Δd with the refractive index increment $\Delta\tilde{n}$ between solution and solvent was determined for aqueous solutions of KCl of known $\Delta\tilde{n}$[22]. A sealed cell with Teflon stoppers was used and the cell compartment, through which thermostating liquid was passed, was insulated with polyurethane foam. For a particular mixed solvent, values of $\Delta\tilde{n}$ were measured on PS solutions at five concentrations within the range 5–25 kg m^{-3}. After attainment of dialysis equilibrium, similar determinations were made on dialysed PS solutions using the dialysate in the solvent chamber of the cell.

Dialysis

Dialysis equilibrium between polymer solutions and the corresponding mixed solvent used to prepare them was achieved by means of the simple dialysis cells described previously[23]. The dialysis bags, made of regenerated cellulose (Visking tubing), were initially Soxhlet extracted with methanol for 5 h and then freed from methanol by successive washings with the mixed solvent. Prior to dialysis the bags were conditioned in the mixed solvent for 48 h at room temperature.

Density increment

Densities were measured with a Kratky digital densimeter Model DMA 02 (Anton Paar, Gratz, Austria) which was calibrated according to recommended pro-

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cedures[24]. The accuracy was verified by comparison of measured densities of CH and benzene with the literature values. Special care was taken to insulate and minimize the length of the rubber tubing connecting the external thermostat to the instrument. The measured quantities were the densities of (i) mixed solvents (ρ_0), (ii) polymer solutions (ρ), (iii) polymer solutions after dialysis (ρ') and (iv) the dialysates (ρ'_0).

RESULTS

Refractive index increments

From linear plots of $\partial\tilde{n}/\partial C_2$ *versus* C_2 (where C denotes concentration in mass of polymer per volume of solution), the specific refractive index increments at infinite dilution were obtained. These are denoted as $(\partial\tilde{n}/\partial C_2)_\phi$, indicating constancy in composition of the particular mixed solvent. The linear dependence of $(\partial\tilde{n}/\partial C_2)_\phi$ on solvent composition is shown in *Figure 1a*. The linearity is a consequence of the fact that, for these systems, the variation of $\tilde{n}_0$ with composition was found to be of the following linear form:

$$\tilde{n}_0 = 1.4276 + 0.1289\phi_1 \tag{1}$$

Hence the normal linear dependence[25] of $(\partial\tilde{n}/\partial C_2)_\phi$ on $\tilde{n}_0$ is equivalent here to a linear dependence also on ϕ_1. In *Figure 1a* the data for the present systems are seen to fit well with the line derived from data of Cowie and Bywater[10,12] on PS solutions in different solvents. For solutions at dialysis equilibrium the specific refractive index increments at infinite dilution were obtained similarly. These are denoted as $(\partial\tilde{n}/\partial C_2)_\mu$, indicating constancy of chemical potential (μ) of all diffusible low molecular weight species. *Figure 1b* shows that $(\partial\tilde{n}/\partial C_2)_\mu > (\partial\tilde{n}/\partial C_2)_\phi$, when $0.78 > \phi_1 > 0$.

It should be noted that, prior to determining $(\partial\tilde{n}/\partial C_2)_\mu$, it was necessary to establish the time for attainment of dialysis equilibrium. For this purpose one particular concentration ($C_2 \approx 20\,\mathrm{kg\,m^{-3}}$) was used and Δd was measured after intervals of time during the dialysis. Experiments were conducted with solvents of low ϕ_1 (*Figure 2a*) and high ϕ_1 (*Figure 2b*). Constant values of Δd were reached after 48 h and 72 h respectively, this difference probably being attributable to the higher viscosity of TET compared to that of CH. A dialysis time of 72 h was employed thereafter for all solvent compositions. The increase in Δd (and hence $\Delta\tilde{n}$) on approaching equilibrium (*Figure 2a*) indicates sorption of the liquid of higher refractive index (TET), whereas the opposite behaviour in *Figure 2b* indicates that the liquid of lower refractive index (CH) is adsorbed preferentially.

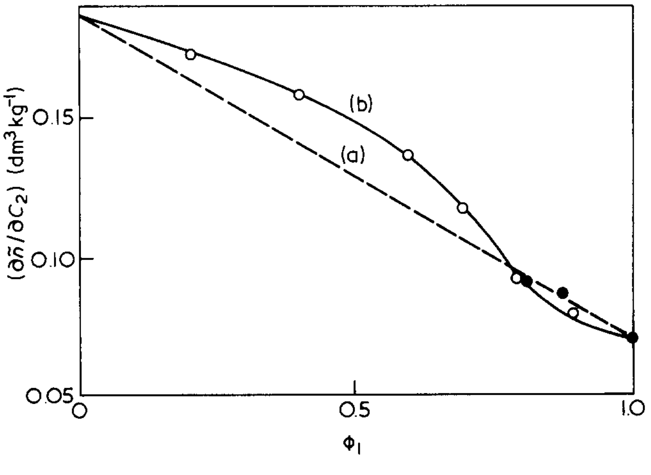

Figure 1 Specific refractive index increments for solutions of PS as a function of binary solvent composition (a) measured at constant composition and (b) measured at constant chemical potential. (Note that in (a) the broken line is the linear least-squares fit of several results of Cowie and Bywater[10,12] for PS in mixed solvents different from the present ones. These authors reported $(\partial\tilde{n}/\partial C_2)_\phi$ as a function of the refractive index ($\tilde{n}_0$) of the mixed solvent. These values of $\tilde{n}_0$ have been converted via equation (1) to the corresponding ϕ_1 of the present mixed solvents. Colinear data for the present system re shown as filled circles)

For each ϕ_1 the selective adsorption coefficient of TET (γ_1) was calculated from equation (2)[26] using $\partial\tilde{n}_0/\partial\phi_1 = 0.1289$ (see equation (1)):

$$\gamma_1 = \frac{(\partial\tilde{n}/\mathrm{d}C_2)_\mu - (\partial\tilde{n}/\mathrm{d}C_2)_\phi}{(\partial\tilde{n}_0/\partial\phi_1)} \tag{2}$$

The variation of γ_1 with ϕ_1 is illustrated in *Figure 3a*.

Density increments

Using the same range of polymer concentration C_2 as for differential refractometry, the density increments at

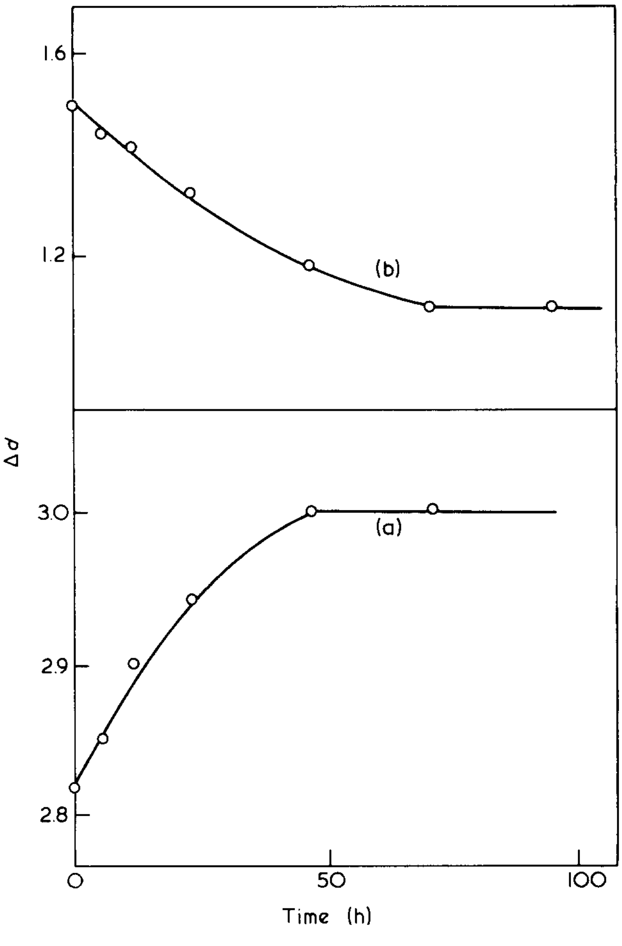

Figure 2 Approach to dialysis equilibrium for a PS solution in binary solvents having compositions (a) $\phi_1 = 0.10$ and (b) $\phi_1 = 0.90$ (the polymer concentration is ~20 kg m^{-3} in each case and Δd is the image displacement in the differential refractometer)

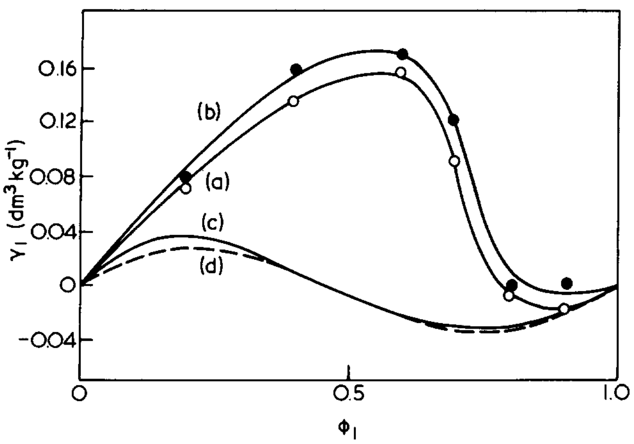

Figure 3 Coefficient of selective adsorption of TET to PS as a function of binary solvent composition. Coefficients determined (a) from refractive index increments, (b) from density increments, (c) by calculation via equation (5) using experimental values of χ_{13}, and (d) by calculation via equation (5) using calculated values of χ_{13}

constant solvent composition $(\partial \rho/\partial C_2)_\phi$ and at constant chemical potential of solvents $(\partial \rho'/\partial C_2)_\mu$ were obtained from linear plots of ρ *versus* C_2 and of ρ' *versus* C_2 respectively. In *Figure 4* it is seen that $(\partial \rho'/\partial C_2)_\mu > (\partial \rho/\partial C_2)_\phi$ when $0.78 > \phi_1 > 0$. Values of γ_1 were calculated from equation (3)[27] in which ρ_1 is the density of TET, $\bar{v}_3$ is the partial specific volume of CH in the TET/CH mixture and g_1/g_3 is the ratio of the weight of TET to that of CH in the binary solvent:

$$\gamma_1 = \left(\frac{g_1}{g_3}\right)\left(\frac{(\partial \rho/\partial C_2)_\phi - (\partial \rho'/\partial C_2)_\mu}{\rho_1(1-\bar{v}_3\rho_0)}\right) \qquad (3)$$

The variation of the resultant values of γ_1 with solvent composition is shown in *Figure 3b*.

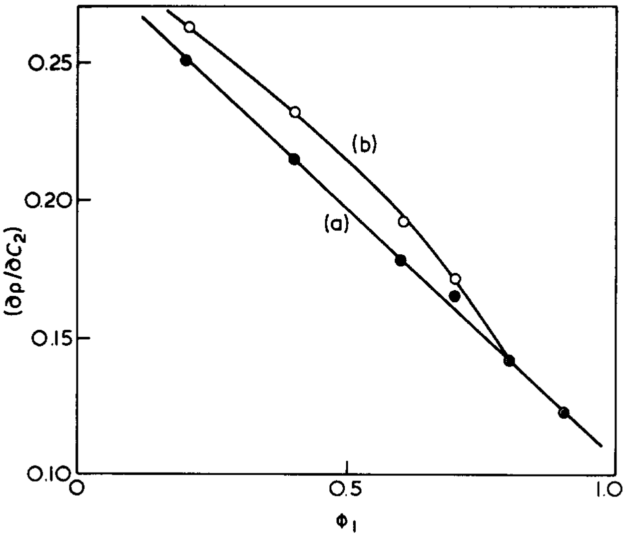

Figure 4 Density increments for solutions of PS as a function of binary solvent composition (a) measured at constant composition and (b) measured at constant chemical potential

Alternative forms of selective adsorption coefficient

The parameter γ_1 expresses selective adsorption on the basis of cubic decimetres of TET preferentially adsorbed per kilogram of polymer. In terms of selection adsorption of CH the corresponding coefficient is γ_3 where $\gamma_3 = -\gamma_1$. It is possible to convert these into coefficients expressing the weight of TET (or CH) selectively adsorbed per weight of polymer[15,28]. Perhaps more easily visualized is solvation on the basis of the number (n_1) of TET molecules adsorbed preferentially per monomer unit of the polymer chain, thus[14]:

$$n_1 = (M_0/\bar{V}_1)\gamma_1 \approx (M_0/V_1)\gamma_1 \qquad (4)$$

where M_0 is the molar mass of the monomer unit ($=104$ g mol^{-1}) and $\bar{V}_1$ and V_1 denote the partial molar volume and molar volume respectively of TET. For selective adsorption of CH the expression corresponding to equation (4) is:

$$n_3 \approx -(M_0/V_3)\gamma_1$$

The maximum extent of selective adsorption calculated via equation (4) was found to be $n_1 = 0.119$, which corresponds to 1 molecule of TET per 8.4 segments of PS. When the solvent medium is very rich in TET ($\phi_1 = 0.89$), there is selective desorption of TET, i.e. selective adsorption of CH corresponding to 1 molecule of CH per 66 segments of PS.

DISCUSSION

Theoretical formulations for γ_1 differ mainly in the number of parameters introduced. The expression of Read[29] includes both binary interaction parameters χ_{ij} and ternary parameters χ_{ijk}, the latter of which are absent in the simpler form given as[30]:

$$\gamma_1 = \frac{\bar{v}_2\phi_1\phi_3[V_r(\phi_3-\phi_1)\chi_{13} + \chi_{23} - V_r\chi_{12} + V_r - 1]}{\phi_1 + V_r\phi_3 - 2V_r\phi_1\phi_3\chi_{13}} \qquad (5)$$

In equation (5), $\bar{v}_2$ is the partial specific volume of PS in solution and V_r ($= V_3/V_1$) is the ratio of the molar volumes of CH and TET. For $\bar{v}_2$ we have used the literature value[31] of 0.9387 dm^3 kg^{-1} for amorphous PS. Since CH is a θ solvent, $\chi_{23} = 0.50$ and from viscometric studies[1] a value of $\chi_{12} = 0.416$ has been derived. With regard to the solvent–solvent interaction parameter χ_{13}, this is related to the excess free energy of mixing ΔG_E, as indicated in equation (6), where x denotes mole fraction:

$$\chi_{13} = \Delta G_E/(x_1/x_3RT) \qquad (6)$$

From values of ΔG_E measured by light scattering, χ_{13} was found[32] to vary as follows with composition:

$$\chi_{13} = 0.242 + 0.190x_3 + 0.0935x_3^2 \qquad (7)$$

The resultant values of γ_1 obtained from equation (5) are shown in *Figure 3c*.

Values of γ_1 have been obtained also by adopting an otherwise identical procedure except for the use of a calculated value for the TET/CH interaction parameter, χ_{13}^{calc}. This involves the use of a calculated value, ΔG_E^{calc}, for the excess free energy of mixing in equation (6). Prausnitz and Anderson[33] have proposed the following expression for non-polar liquids:

$$\Delta G_E^{calc} = (x_1V_1 + x_3V_3)\phi_1\phi_3(\delta_1 - \delta_3)^2 \qquad (8)$$

Using literature values[34] of 19.4 $(\mathrm{kJ\,dm^{-3}})^{1/2}$ and 16.8 $(\mathrm{kJ\,dm^{-3}})^{1/2}$ for the solubility parameters δ_1 and δ_3 respectively, the resultant values of $\chi_{13}^{\mathrm{calc}}$ were found to be:

$$\chi_{13}^{\mathrm{calc}} = 0.302 + 0.0768x_3 \qquad (9)$$

The values of γ_1 involving equation (5) and these values of $\chi_{13}^{\mathrm{calc}}$ are shown in *Figure 3d*. Good accord between the curves of *Figures 3c* and *3d* indicates that γ_1 is rather insensitive to the significant difference between χ_{13} (equation (7)) and its calculated value (equation (9)).

Good accord between the two different experimental techniques is demonstrated in *Figures 3a* and *3b*. The inversion point from selective adsorption to selective desorption of TET (at $\phi_1 \approx 0.78$) is however clearly evident only in *Figure 3a*. This inversion is considered to be a real effect, since the uncertainty of $\pm 0.0005\ \mathrm{dm^3\,kg^{-1}}$ in the specific refractive index increments has an exceedingly small effect on the resultant values of γ_1 calculated *via* equation (2). In contrast, it is a consequence of the form of equation (3) that the same estimated uncertainty in the density increments gives rise to a larger uncertainty of up to 3% in γ_1.

From a discussion by Cowie[35] on the discrepancy between experimental values of selective adsorption and theoretical ones calculated from equation (5), the importance of ternary parameters χ_{ijk} and χ_{ijj} is still not fully resolved. Read[29] has shown that only the χ_{ijk} term is significant and the inclusion of this parameter was necessary to obtain good accord with his experimental data for the system benzene(1)/PS(2)/CH(3). Strazielle and Benoit[30] have suggested that only the binary interaction parameters are required, and they found their experimental data to be in good agreement with the predicted behaviour of γ_1. They believe that the agreement obtained by Read is due to an overestimation of the refractive index increment used by him. One approach to estimating the χ_{ijk} term is *via* the method of Blanks and Prausnitz[36], which is based on solubility parameters. Cowie[35] has compared the results obtained by Yoshine and Tanzawa[37], Read[29] and Strazielle and Benoit[30] with the values calculated by means of the equations of Strazielle and Benoit[30] and Read[29]. In this comparison, values of χ_{ijk} were estimated *via* the method of Blanks and Prausnitz[36]. It was concluded that, although neither theoretical curve matched exactly, better agreement with experiment is obtained when using only χ_{ij}, thus suggesting that ternary interaction terms are unnecessary for this system. In the present system, the agreement between the theoretical and experimental values of γ_1 is worsened by invoking χ_{ijk} estimated by the same approach. Specifically, the calculated values of γ_1 were found thereby to decrease instead of undergoing the increase necessary for agreement with experiment.

In attempting to force better agreement between the present calculated and experimental values of γ_1, we have examined the values of χ_{ij} used in equation (5). By appropriate changes in χ_{12} and χ_{13} it was possible to obtain theoretical curves of γ_1 *versus* ϕ_1 which approached the experimental curves in the region $\phi_1 = 0$–0.6. However, at higher values of ϕ_1 the amended theoretical curve fell below the experimental one to an even greater extent than obtaining in *Figures 3c* and *3d*. Better agreement over the whole range of ϕ_1 is only obtainable by assigning $\chi_{23} = 0.65$, which is unrealistic in view of the fact that CH is a θ solvent.

The maximum value of γ_1 in the present study ($0.157\ \mathrm{dm^3\,kg^{-1}}$) is of a similar order to that found for solutions of PS in benzene/CH binary mixtures[29,30,37]. This agreement is probably attributable to the similar solvent power of TET and benzene for PS, as we have demonstrated by viscometric determinations[32]. However, Cowie and Bywater[10] have found a maximum value of $\gamma_1 = 0.236\ \mathrm{dm^3\,kg^{-1}}$ at $\phi_1 = 0.6$, for the system benzene(1)/PS(2)/heptane(3), which exceeds somewhat the present maximum γ_1. This can be readily explained on the basis of the higher χ_{13} $(=0.48)$[10] for benzene/heptane compared to $\chi_{13} = 0.33$ for TET/CH at the composition for maximum adsorption (the difference in χ_{13} values is also evident from the solubility parameters of the relevant solvents).

The observed inversion in selective adsorption has also been noted elsewhere for different ternary systems containing poly(methyl methacrylate)[7,9,38], nylon-6[14] and poly(4-tert-butylphenyl methacrylate)[39]. The inversion sorption detected here at high concentration of TET may lend further support to the 'cluster' model proposed by Suh and Liou[40], who postulated that the polymer molecule dissolved in a mixture of good solvent and bad solvent is surrounded mainly by molecules of the good solvent. The polymer–solvent cluster then behaves like the good solvent alone with respect to interactions with the bulk mixture. In other words, there exists an intermediate layer of excess good solvent between the polymer molecule and the bulk mixture, and this bulk mixture 'sees' the cluster as a compatible solute. One of the consequences proposed by these authors is as follows. When the molar volume of the bad solvent is less than that of the good one (i.e. the system under consideration here) and $\delta_1 < \delta_2$, then selective sorption of the small component 3 is important at low concentrations of this component in the binary phase, but decreases as the concentration of solvent 3 increases, rapidly giving way to adsorption of component 1. Suh and Liou[40] have stated that the cluster model need only be applied when $(\delta_3 - \delta_2) > 4.09\ (\mathrm{kJ\,dm^{-3}})^{1/2}$. However, in the present system $(\delta_3 - \delta_2) << 4.09\ (\mathrm{kJ\,dm^{-3}})^{1/2}$ and hence the cluster model need not be specially invoked to predict negative adsorption. This conclusion is consistent with that obtained by Cowie[35].

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