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Solvent/solvent/polymer ternary systems

1. Correlation between experimental data and theoretical predictions for acetonitrile/chlorobutane/poly(methyl methacrylate) system

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Dedicated to Prof. H.-J. Cantow on the occasion of his 70th anniversary

Summary

The paper investigates the agreement between experimental and theoretical data for the second virial coefficient A_2 and for the intrinsic viscosity $[\eta]$ for the acetonitrile/chlorobutane/poly(methyl methacrylate) ternary system.

Introduction

Solvent/solvent/polymer ternary systems exhibit many interesting properties. At infinite polymer dilution, the thermodynamic behaviour of such systems presents two main characteristics. First, one can note the appearance of the phenomenon of cosolvency, when the mixture of two nonsolvents for the given polymer acquires high solvent power, i.e., behaves as a good solvent for the given polymer. A second characteristic feature comes from the composition difference of the mixed solvent inside and outside the polymer domain.

The theoretical treatment of the excluded volume parameters and of the preferential adsorption coefficient λ_1 was performed through the thermodynamic theory - first by use of the Flory - Huggins (FH) model (1), as generalized by Pouchly et al. (FHP) (2), and later through the equation of state theory (Flory, Prigogine, Patterson formalism) (FPP) (3-5).

The present paper was aimed to investigate the agreement between experimental and theoretical data for the second virial coefficient A_2 and for the intrinsic viscosity $[\eta]$ for the acetonitrile (MeCN) ($\underline{1}$)/chlorobutane (ClBu) ($\underline{2}$)/poly(methyl methacrylate) (PMMA) ($\underline{3}$) ternary system, starting from different expressions for the preferential adsorption coefficient λ_1.

Theory

Preferential and total adsorption in different solvent/solvent/polymer systems was previously investigated (6) starting from various theoretical models. Generally, the mathematical expressions of the preferential adsorption coefficient, either starting from the Flory - Huggins model or from the equation of state theory (FPP model), differ only in the expression of the ternary interaction parameter χ_T (eq. /1/)

$$\chi_T = a_\chi\, g_{12}(u_1) \qquad /1/$$

a_χ being a constant independent of composition, and $g_{12}(u_1)$ the binary interaction function between the solvents. In different theories, a_χ appears as

$$a_\chi = (2g^\circ_{13}g^\circ_{23} - D)/[2(1 - D)] \qquad /2/$$

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or as

$$a_\chi = g^\circ_{13} g^\circ_{23}(1 - D'/2)/(1 - D') \qquad /3/$$

in the theory of Campos et al. (7,8) (FHP model), and as

$$a_\chi = (1/2)[1 - (\bar{V}_{12}/\bar{V}_3)^2(S^2 - S\alpha - \alpha')]g_{12}(u_1) \qquad /4/$$

in the FPP model, where u_i (i = 1, 2) is the volume fraction of the solvent mixture in the ternary phase, g°_{i3} is the interaction parameter between the two solvents in the ternary phase of the ternary solution or in the binary solution (between components i and 3) at infinite dilution of polymer,

$$D = g^\circ_{13}(dg_{23}/d\phi_3)_{\phi_3 \to 0} + g^\circ_{23}(dg_{13}/d\phi_3)_{\phi_3 \to 0} \qquad /5/$$

$$D' = D/2g^\circ_{13}g^\circ_{23} \qquad /6/$$

$$\bar{V}_i = V_i/V^*_i$$

$$S = S_i/S_{12}$$

$$\alpha = [(\partial \ln V_1)/(\partial \ln T)](p^*_3/p^*_1)(1 - T^*_1/T^*_3) \qquad /7/$$

$$\alpha' = (p^*_3/p^*_1)\alpha$$

where $g_{i3}(\phi_3)$ (i = 1, 2) is the interaction parameter between components i and 3 in the ternary phase of the ternary solution (between components i and 3), ϕ_i (i = 1, 2, 3) is the volume fraction of component i in the domain of the coil, V_i is the molar volume, p^*_i, V^*_i, T^*_i are reduced parameters for pressure, molar volume and temperature, respectively, and S_i is the molecular surface to volume ratio.

According to Pouchly et al. (9), the second virial coefficient A_2 can be defined by eq. /8/ and the intrinsic viscosity by eq. /9/:

$$A_2 = (\bar{v}^2_3/2V_1)[\phi_{10} + S\phi_{20} - 2\chi_{13}\phi_{10} - 2S\chi_{23}\phi_{20} + $$
$$+ 2(g_{12} - 2\chi_T)\phi_{10}\phi_{20}] \qquad /8/$$

$$\Delta[\eta]/M^{1/2} = \Delta K_\Theta + [2(0.51)\phi_0\bar{v}^2_3/N_0V_1](1 - 2a_\chi)^\infty M^{1/2}g_{12}\phi_{10}\phi_{20} \qquad /9/$$

Eq. /8/ can be also written as

$$\left\{[(2A_2V_1)/\bar{v}^2_3] - \phi_{10} - S\phi_{20} + 2\chi^{(M)}_{13}\phi_{10}\right\}/(2S\phi_{20}) =$$
$$= -\chi^{(M)}_{23} + (1 - 2a_\chi)^{(M)}(g_{12}\phi_{10}/S) \qquad /10/$$

where $\bar{v}_3$ is the partial specific volume of the polymer, V_1 is the molar volume of component 1, χ_{i3} is the interaction parameter between polymer and solvent i (i = 1, 2), M is the molecular weight, ϕ_0 is Flory's viscosity constant (equal to 2.5×10^{23} mol^{-1} for $[\eta]$ in $mlxg^{-1}$), N_0 is Avogadro's number, $\Delta K_\Theta = K^*_\Theta - K_\Theta$, K^*_Θ being the apparent unperturbed dimension of a macromolecular chain in a binary solvent mixture and K_Θ the real unperturbed dimension in a single theta solvent.

If the left hand side of eq. /10/ is denoted with Z, the correlation of Z with $g_{12}\phi_{10}/S$ should yield a linear dependence, as it has been veri-

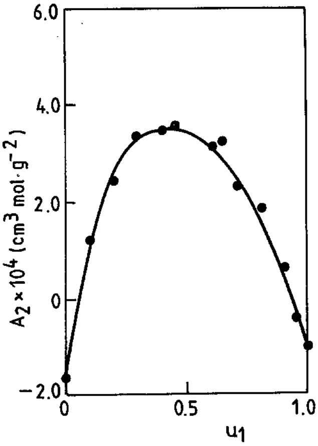

Fig. 1. Plot of the second virial coefficient A_2 vs. the volume fraction u_1 for the MeCN (1)/ClBu (2)/ /PMMA (3) ternary system. The data were taken from Ref. (10).

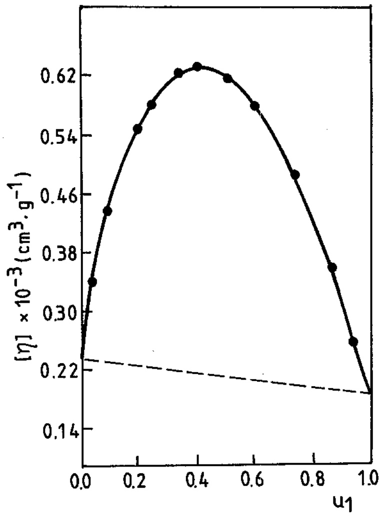

Fig. 2. Plot of the intrinsic viscosity [η] vs. the volume fraction u_1 for the MeCN (1)/ClBu (2)/ /PMMA (3) ternary system. The data were taken from Ref. (11).

fied in several ternary systems (9). At the same time, the proportionality represented in eq. /1/ is demonstrated.

Eq. /11/ allows the calculation of $\chi_{13}^{(M)}$:

$$A_{2,i3} = (\bar{v}_3^2/V_i)(\tfrac{1}{2} - \chi_{i3}) \qquad /11/$$

With the experimental values of $\chi_{23}^{(M)}$ and $(1 - 2a_\chi)^{(M)}$, one can calculate A_2 by use of eq. /8/ for every M.

In a true cosolvent system, where the single liquids are near theta conditions ($\chi_{i3}^{\infty} \simeq \chi_{i3}^{(M)}$, χ_{i3}^{∞} being the interaction parameter between polymer and solvent i at infinite dilution), the relation between ΔK_Θ and $\phi_{10}\phi_{20}g_{12}$ will remain unchanged.

Results and Discussion

The data of Campos et al. (7) were considered for the binary interaction function between solvents

$$g_{12}(\phi_{10}) = 2.679 - 11.183\phi_{10} + 45.401\phi_{10}^2 - 105.145\phi_{10}^3 + \\ + 134.168\phi_{10}^4 - 87.77\phi_{10}^5 + 23.009\phi_{10}^6 \qquad /12/$$

χ_{13}° was taken as 0.5 (MeCN being a theta solvent), and χ_{23}° as 0.52 (ClBu being a nonsolvent). By use of the relation of Nakata and Kaji (10) for $g_{i3}^{\circ} = (4/3)\,\chi_{i3}^{\circ}$, the values of $g_{13} = 0.67$ and $g_{23} = 0.69$ were found. The experimental data processed in this study were taken from Nakata and Kaji (10) for A_2 and from Prolongo et al. (11) for [η] (Figures 1 and 2).

The preferential adsorption coefficient λ_1 is plotted in Figure 3 as a function of solvent composition. A preferential adsorption of MeCN is observed over the composition range of MeCN 0 - 0.43, and then ClBu, i.e. the solvent less adequate from the thermodynamic point of view, is preferentially adsorbed. The phenomenon of inversion is associated with the values of g_{12} which are positive and high. Thus, inversion seems to be a common phenomenon for solvent/nonsolvent mixtures which persists even in mixtures of good solvents with marginal ones, or marginal (theta) solvents with nonsolvents.

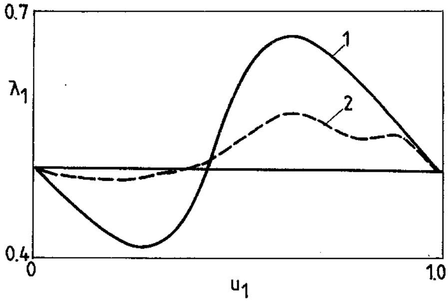

Fig. 3. Theoretical values of the preferential adsorption coefficient λ_1 as a function of the volume fraction u_1 in MeCN (1)/ClBu (2)/ /PMMA (3) ternary system.
1 - FH model; 2 - common curve obtained according to FHP and FPP models.

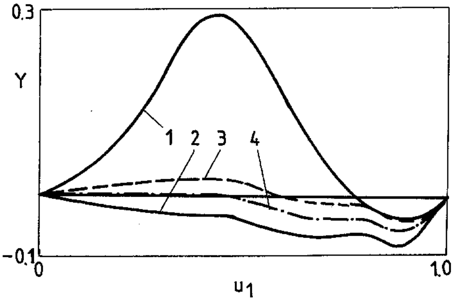

Fig. 4. Theoretical values of the total adsorption coefficient Y as a function of the volume fraction u_1 in MeCN (1)/ClBu (2)/PMMA (3) ternary system.
1 - FH model; 2 - FHP model, according to Ref. (7); 3 - FHP model, according to Ref. (8); 4 - FPP model.

The total adsorption coefficient Y is plotted in Figure 4 as a function of solvent composition. A detailed discussion on λ_1 and Y was previously published (6). An inversion of Y is observed for this ternary system.

Using eq. /9/ and the experimental data of Prolongo et al. (11) for $[\eta]$, the values of a_χ were calculated (Table 1) and then introduced in eq. /8/ to yield A_2 values. These values were plotted in Figure 5 as compared to those resulting from different theoretical models. The figure also presents the experimental values of A_2 reported by Nakata and Kaji (10).

Table 1. a_χ values obtained from different theories and from experimental data

	a_χ
FHP model, acc. to Ref. (7)	0.4509
FHP model, acc. to Ref. (8)	0.3504
FPP model	0.4887
from $A_2 = f(\chi_{i3}, \phi_{i0}, \chi_T)$, Ref. (10)	0.4460
from $[\eta] = f(\chi_{i3}, \phi_{i0}, \chi_T)$, Ref. (11)	0.4950

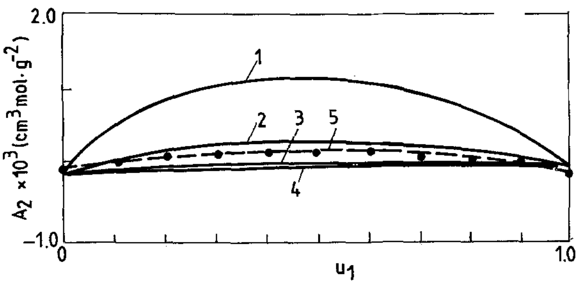

Fig. 5. Plots of the second virial coefficient A_2 vs. the volume fraction u_1 for the MeCN (1)/ ClBu (2)/PMMA (3) ternary system.
1 - FHP model, acc. to Ref. (7); 2 - FHP model, acc. to Ref. (8); 3 - FPP model; 4 - from exptl. values of [η]; 5 - exptl. values from Ref. (10).

For the present system, the experimental data for A_2 are much better predicted by the FPP model. This conclusion sustains our previous results describing ternary systems containing polystyrene (6). At the same time, A_2 values calculated from intrinsic viscosity data, according to eq. /9/, appear to be very close to those experimentally observed. As a practical consequence, one can analyse the behaviour of a given polymer in a binary solvent, when the individual interaction parameters are known, from viscometric data. Knowing the ternary interaction parameters, one can determine the preferential adsorption and hence, without experimental tests, some important solution properties. The disagreement between theory and experiment may be attributed to some specific interactions which are to be discussed in other studies.

References

1. Schultz A R, Flory P J (1955) J. Polym. Sci. 15:231
2. Pouchly J, Zivny A, Solc K (1968) J. Polym. Sci. Polym. Lett. Ed. 23:2451
3. Pouchly J, Patterson D (1973) Macromolecules 6:465
4. Horta A (1979) Macromolecules 12:785
5. Horta A (1985) Macromolecules 18:2498
6. Simionescu C I, Ioan S, Bercea M, Mitu N, Simionescu B C (1993) Eur. Polym. J. (in press)
7. Campos A, Gavara R, Tejero R, Gomez C, Celda B (1989) J. Polym. Sci. Part B: Polym. Phys. 27:1569
8. Campos A, Gavara R, Tejero R, Gomez C, Celda B (1989) J. Polym. Sci. Part B: Polym. Phys. 27:1599
9. Pouchly J, Zivny A (1983) Makromol. Chem. 184:2081
10. Nakata M, Kaji A (1988) Macromolecules 21:2514
11. Prolongo M G, Masegosa R M, Hernandez-Fuentes I (1981) Macromolecules 14:1526

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