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Registry No. (4-Aminobenzoic acid hydrazide)(terephthalic acid) (copolymer), 29258-54-6.

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Light-Scattering Study of Three-Component Systems. 3. Θ Point for Poly(methyl methacrylate) in the Binary Mixture 1-Chlorobutane + 2-Butanol

Mitsuo Nakata,* Yoshifumi Nakano, and Kohichiro Kawate

Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060, Japan. *Received July 20, 1987; Revised Manuscript Received March 1, 1988*

ABSTRACT: Light-scattering measurements have been made on the ternary system of poly(methyl methacrylate) (PMMA) in the isorefractive mixture 1-chlorobutane (BuCl) + 2-butanol (BuOH), which is a cosolvent for PMMA. For the sample with the molecular weight $M_w = 2.44 \times 10^6$ the mean-square radius of gyration $\langle s^2 \rangle$ and the second virial coefficient A_2 were determined at 40 °C as a function of the volume fraction u_2 of BuOH in the mixture. A_2 was zero near $u_2 = 0$ and 0.8 and showed a large maximum near $u_2 = 0.3$. The behavior of $\langle s^2 \rangle$ was analogous to that of A_2. For samples in the molecular weight range $M_w \times 10^{-4} = 3.66$–244 the second virial coefficient A_2 was determined at $u_2 = 0.800$ as a function of temperature. A_2 was found to vanish at 39.2 ± 0.5 °C irrespective of the molecular weight. The mean-square radius of gyration $\langle s^2 \rangle$ for $M_w = 2.44 \times 10^6$ determined at $u_2 = 0.800$ and at 39.2 °C agreed with the unperturbed one measured in the single solvent BuCl. The universal function Ψ for the excluded-volume effect obtained in the mixed solvent showed a similar behavior to those observed in single solvents.

Introduction

Ternary systems of polymer + mixed solvent exhibit many interesting features. The thermodynamic behavior of the ternary systems at infinite dilution of polymer has two characteristic features, for which the light-scattering measurement is a useful experimental means. One feature is a phenomenon of the cosolvency in which the mixture of two nonsolvents for a polymer acquires high solvent power for the polymer, comparable with that of a good solvent. Another characteristic feature of the system polymer + mixed solvent stems from the composition difference of the mixed solvent inside and outside the polymer domain. The preferential absorption was first investigated by Debye et al. to analyze the apparent molecular weight obtained by light-scattering measurements for systems polymer + solvent + precipitant.[1]

Strazielle and Benoit presented a light-scattering theory based on a molecular model and analyzed the data on the

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system polystyrene + benzene + cyclohexane.[2] The analysis suggested that benzene molecules are preferentially adsorbed along the polymer chain. For 10 mixed solvents Cowie determined the composition at which the second virial coefficient of polystyrene obtained by light-scattering measurements became zero at 35 °C.[3] The intrinsic viscosity and the root-mean-square radius of gyration of a polystyrene determined in the different Θ solvents varied with the solubility parameter but had little correlation with the observed preferential sorption coefficient. Dondos and Benoit[4] made viscosity measurements on polystyrenes with various molecular weights in the Θ solvents determined by Cowie. From the Stockmayer–Fixman plot they evaluated intramolecular interaction parameter, which was found to increase with increasing preferential sorption coefficient. For the Θ solvent dioxane + methanol both the intramolecular interaction parameter and the preferential sorption coefficient vanished, and the Θ solvent showed the same Θ condition as given by a single solvent. From the above facts Dondos concluded that the better solvent preferentially absorbed in the polymer domain brought about an expansion of polymer coil, because preferential adsorption along the polymer chain could cause the same effect on the intermolecular and intramolecular interactions. This interpretation appears to be inconsistent with those by Strazielle et al. and Cowie. On the other hand, Wunderlich has carried out light-scattering and viscosity measurements on poly(methyl methacrylate) in four mixed solvents.[5] The light-scattering measurements showed that the behavior of the mean-square radius of gyration was not affected by the mixed solvent. However, the hydrodynamic radius was found to depend on the enthalpy of mixing of the two solvent components. The contradictions in the above studies seem to be due to lack of experimental data. Cowie made the viscosity and light scattering measurements on a single sample of polystyrene. The experimental study by Dondos et al. lacks light-scattering measurements. The mixed solvent employed by Strazielle et al. is not a Θ solvent but rather a good one. Wunderlich did not observed the preferential sorption coefficient. In this situation of the experimental studies, it is difficult to draw definite conclusions on the behavior of polymer coil in mixed solvents.

In this paper we have made light-scattering measurements on the ternary system poly(methyl methacrylate) (PMMA) + 1-chlorobutane (BuCl) + 2-butanol (BuOH). The mixture BuCl + BuOH has been known to be a cosolvent for PMMA from cloud-point measurements.[6] Furthermore, since the refractive index difference between BuCl and BuOH is very small,[7] the light-scattering measurements on the system allowed us to perform a reliable determination of the mean-square radius of gyration. The Θ condition, at which the second virial coefficient vanishes, was explored with samples of different molecular weight and the mean-square radius of gyration was determined at that point. Thermodynamic analyses of the cosolvent phenomenon of the present system will be given in a subsequent paper.[8]

Experimental Section

Materials. PMMA was prepared by bulk polymerization of freshly distilled methyl methacrylate with 2,2-azobis(isobutyronitrile) (AIBN) as initiator at 50 °C. To prepare low molecular weight PMMA, n-butyl mercaptan was added as a chain-transfer agent. By changing the amount of the initiator and the chain-transfer agent we obtained four original polymers, which were fractionated by the fractional solution technique, i.e., the extraction method, and each middle fraction was used for the present study. The samples with molecular weight $M_w = 2.44 \times 10^6$ (MA-F9) and $M_w = 7.6 \times 10^5$ (M7-F4) are the same ones as those used in a previous study.[9] The samples with $M_w = 2.64 \times 10^5$ (M10-F9) and $M_w = 3.66 \times 10^4$ (M9-F6) were extracted from the original polymers, which were prepared with AIBN of 0.200% weight fraction and n-butyl mercaptan of 0.070% volume fraction and with AIBN of 0.200% and n-butyl mercaptan of 1.00%, respectively. The molecular weight distribution of the samples MA-F9 and M10-F9 was estimated from gel permeation chromatograms to be $M_w/M_N = 1.20$ and 1.11, respectively. BuOH was dried over anhydrous potassium carbonate and distilled before use. BuCl was purified as described in a previous paper.

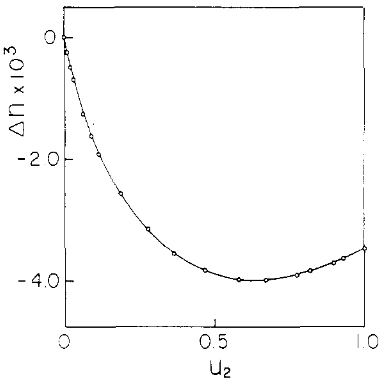

Figure 1. Refractive index difference Δn ($=n - n_1$) between the mixture 1-chlorobutane (1) + 2-butanol (2) and 1-chlorobutane at 40 °C as a function of the volume fraction u_2.

Refractive Index Increment and Light-Scattering Measurements. A differential refractometer of the Brice type was operated at 435.8 nm of a mercury arc and at 40 °C in accordance with the light scattering measurements. The instrument was calibrated for aqueous solutions of sodium chloride, for which refractometric data has been reported.[10] Refractive index increments $(\partial n/\partial c_3)_{u_2}$ cm^3 g^{-1} were measured for the sample M7-F4 at various compositions of the mixture BuCl (1) + BuOH (2), where c_3 and u_2 are the polymer concentration and the volume fraction of BuOH in the mixture, respectively.

Light-scattering measurements were made with a Shimadzu light-scattering photometer as in the previous study.[9] For the sample MA-F9 the second virial coefficient A_2 and the mean-square radius of gyration $\langle s^2 \rangle$ were determined at various compositions of the mixture BuCl + BuOH at 40 °C. At the volume fraction $u_2 = 0.800$, the second virial coefficient was measured for the samples MA-F9, M10-F9, and M9-F6 with varying temperature. The temperature coefficient of the refractive index increment at $u_2 = 0.800$ was taken as 4×10^{-4} cm^3 g^{-1} K^{-1}, because a constant molecular weight independent of temperature was obtained for the value. To determine A_2, measurements were carried out at five polymer concentrations in the range $c_3 < 1.5 \times 10^{-3}$ g cm^{-3} for the sample MA-F9 and in a higher concentration range for the lower molecular weight samples.

Experimental Results

The components of the present ternary system were assigned as BuCl (1), BuOH (2), and PMMA (3). The experimental data were represented by using the two compositions, that is, the polymer concentration c_3 (g cm^{-3}) and the volume fraction u_2 of BuOH in the binary mixture BuCl + BuOH. In Figure 1 the refractive index n of the mixture BuCl + BuOH at 40 °C[7] is given by plotting the refractive index difference $\Delta n = n - n_1$ from that of BuCl against the volume fraction u_2. Δn decreases rapidly near $u_2 = 0$ with increasing u_2 and has a shallow minimum near $u_2 = 0.65$. The refractive index difference between BuCl and BuOH is 3.41×10^{-3}, and the maximum slope is evaluated as $(\partial n/\partial u_2)_0 = -0.025$ at $u_2 = 0$. Figure 2 shows the refractive index increment $(\partial n/\partial c_3)_{u_2}$ at 40 °C as a function of u_2. Data in the range $u_2 > 0.8$ could not be obtained because of precipitation of PMMA.

From Figures 1 and 2 the value of $(\partial n/\partial u_2)_0/(\partial n/\partial c_3)_{u_2}$ is found to be very small compared with those for usual ternary systems of polymer + mixed solvent. Near $u_2 =$

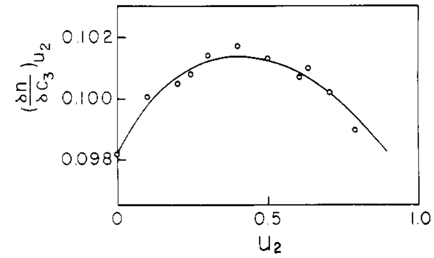

Figure 2. Refractive index increment $(\partial n/\partial c_3)_{u_2}$ (cm^3/g) for PMMA in the mixed solvent 1-chlorobutane (1) + 2-butanol (2) at 40 °C as a function of the volume fraction u_2.

Table I
Light-Scattering Data of Poly(methyl methacrylate) in the Binary Mixture 1-Chlorobutane + 2-Butanol at 40 °C

u_2	$10^{-6}M_w$	10^5A_2, cm^3 mol g^{-2}	$10^{11}\langle s^2\rangle$, cm^2	$10^5A_2{}^0$,[a] cm^3 mol g^{-2}
0	2.44	0	1.61	0
0.0120	2.69	3.4	2.21	5.6
0.0331	2.46	5.6	2.66	10.8
0.0628	2.48	8.3	2.97	20.1
0.1056	2.50	10.8	3.43	27.8
0.2001	2.47	12.3	3.47	37.5
0.2786	2.43	12.8	3.68	36.1
0.3947	2.44	12.5	3.52	37.8
0.4868	2.43	11.5	3.51	30.8
0.5881	2.40	9.7	3.19	25.0
0.7038	2.51	5.8	2.73	11.1
0.7991	2.53	0.5	1.67	6.0

[a] Calculated from the data of A_2 and $\langle s^2\rangle$ by using eq 9.

0.65 the value vanishes. Therefore, the light-scattering data of the present system could be analyzed as in the case of the binary system of polymer + single solvent. Considering the higher order contributions in the light-scattering equation,[11] we assumed the relation

$$(Kc_3/R_\theta)^{1/2} = M_3^{-1/2} + A_2(u_2)M_3^{1/2}c_3 + (8\pi^2n^2/3\lambda^2)\langle s^2(u_2)\rangle M_3^{-1/2}\sin^2(\theta/2) \quad (1)$$

with $K = (2\pi^2n^2/N_A\lambda^4)(\partial n/\partial c_3)_{u_2}{}^2$, where R_θ is the excess scattering from polymer molecules, M_3 is the molecular weight of the polymer, N_A is Avogadro's number, and λ is the wavelength in a vacuum. $A_2(u_2)$ and $\langle s^2(u_2)\rangle$ are the second virial coefficient and the mean-square radius of gyration at the volume fraction u_2, respectively. The plots of $(Kc_3/R_\theta)^{1/2}$ against c_3 and $\sin^2(\theta/2)$ were represented by a straight line. The slope of the $(Kc_3/R_\theta)^{1/2}$ versus $\sin^2(\theta/2)$ plot at each concentration was extrapolated to zero concentration to determine the mean-square radius of gyration $\langle s^2(u_2)\rangle$. The second virial coefficient $A_2(u_2)$ was determined by extrapolating the slope of the $(Kc_3/R_\theta)^{1/2}$ versus c_3 plot to zero angle. Table I shows the values of M_3, A_2, and $\langle s^2\rangle$ obtained for the sample MA-F9 at each volume fraction u_2. As expected from the very small value of $(\partial n/\partial u_2)_0/(\partial n/\partial c_3)_{u_2}$ the obtained molecular weights seem to be constant near the value $M_3 = 2.44 \times 10^6$ observed in the single solvent BuCl. An exceptionally high value is obtained at $u_2 = 0.012$. Since the magnitude of $(\partial n/\partial u_2)_0/(\partial n/\partial c_3)_{u_2}$ at $u_2 = 0.012$ is still small, -0.22, the high value of $M_3 = 2.69 \times 10^6$ could not be attributed to an effect of the preferential sorption. The high value at small u_2 was also observed in the previous study.[9] In Figure 3, the observed values of A_2 are plotted against u_2. The behavior of the data points is described by the solid curve, which appears to intersect the line of $A_2 = 0$ at $u_2 = 0$ and near 0.80. In Figure 4, the expansion factor $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_0$ is plotted against u_2, where $\langle s^2\rangle_0 = 1.58 \times 10^{-11}$ cm^2 is employed for the unperturbed mean-square radius of gyration. In accordance with the behavior of A_2 in Figure 3, α^2 increases rapidly with u_2 near $u_2 = 0$ and has a maximum near $u_2 = 0.3$. As in the case of binary systems of polymer + single solvent, α^2 tends to be unity near $u_2 = 0.80$ where the second virial coefficient A_2 vanishes.

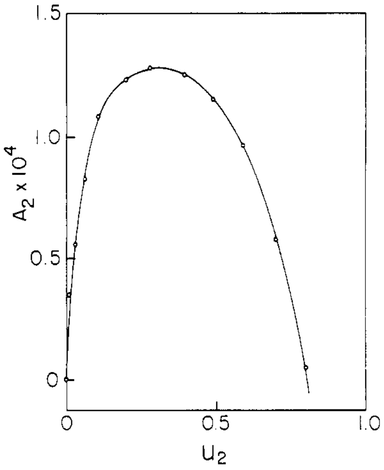

Figure 3. Plot of the second virial coefficient A_2 ((cm^3 mol)/g^2) versus the volume fraction u_2 for PMMA in the mixed solvent 1-chlorobutane (1) + 2-butanol (2) at 40 °C.

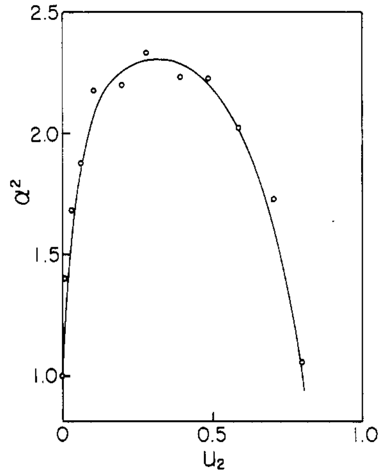

Figure 4. Plot of the square of the expansion factor α versus the volume fraction u_2 for PMMA in the mixed solvent 1-chlorobutane (1) + 2-butanol (2) at 40 °C.

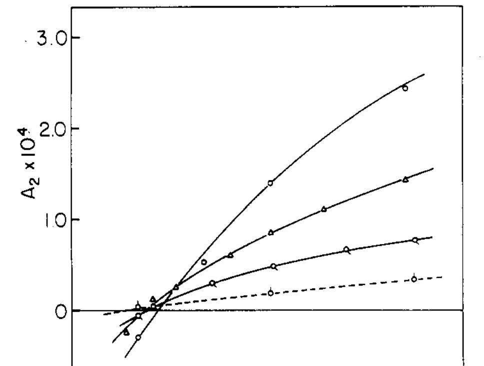

Figure 5. Second virial coefficient A_2 ((cm^3 mol)/g^2) versus the temperature t (°C) for PMMA in the mixed solvent 1-chlorobutane (1) + 2-butanol (2) at the volume fraction $u_2 = 0.800$. The data are obtained for three different molecular weights: $M_w = 3.66 \times 10^4$ (○), 2.64×10^5 (△), and 2.44×10^6 (ǫ). The points (ȯ) described by the broken line are the data for $M_w = 2.44 \times 10^6$ in the single solvent 1-chlorobutane.

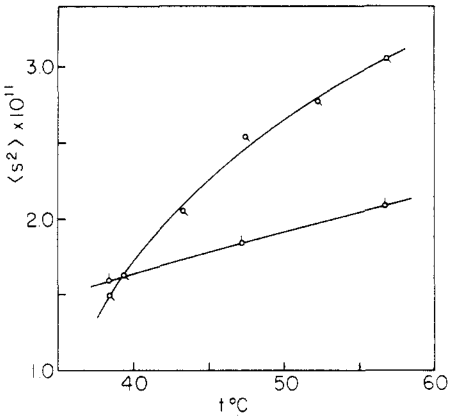

Figure 6. Mean-square radius of gyration $\langle s^2 \rangle$ versus temperature t (°C) for PMMA of M_w = 2.44 × 10^6 in the single solvent 1-chlorobutane (⦶) and in the mixed solvent 1-chlorobutane (1) + 2-butanol (2) at u_2 = 0.800 (⦸).

In Figure 5, the second virial coefficient A_2 observed for the samples MA-F9, M10-F9, and M9-F6 in the mixed solvent at u_2 = 0.800 is represented as a function of temperature. The solid curves for $M_3 \times 10^{-6}$ = 0.264 (M10-F9) and 2.44 (MA-F9) intersect the line of A_2 = 0 at 38.9 °C and the curve for $M_3 \times 10^{-4}$ = 3.66 (M9-F6) at 39.7 °C. This difference of the temperatures could not be taken seriously because of the scattering of the data points and a possible end effect in the low molecular weight sample. In this experimental situation the temperature at which A_2 vanishes is considered to be independent of the molecular weight and can be determined as 39.2 ± 0.5 °C. In Figure 5 the broken line for the open circles with a vertical bar describes the behavior of A_2 for the sample MA-F9 in the single solvent BuCl. On account of the small temperature dependence of A_2, a slight uncertainty in A_2 results in a large error in the estimate of the Θ temperature. A reasonable Θ temperature will be 38.0 ± 2.0 °C.

In Figure 6 the mean-square radius of gyration $\langle s^2 \rangle$ observed for the sample MA-F9 is plotted against temperature, where the open circles with an oblique bar are the data in the mixture BuCl + BuOH at u_2 = 0.800 and the open circles with a vertical bar are the data in the single solvent BuCl. At each temperature at which A_2 vanishes in Figure 5, the mean-square radius of gyration is estimated as $\langle s^2 \rangle_0 = 1.58 \times 10^{-11}$ cm^2 in BuCl and $\langle s^2 \rangle = 1.59 \times 10^{-11}$ cm^2 in the mixture BuCl + BuOH. The value of $\langle s^2 \rangle$ in the mixed solvent agrees well with the unperturbed value in BuCl. Thus, the mixture BuCl + BuOH was found to yield a Θ condition for PMMA at 39.2 °C and u_2 = 0.800 in view of the value of the unperturbed dimension and the molecular weight independence of the Θ temperature. Wunderlich also found Θ conditions for PMMA in other mixed solvents from the same viewpoint.[5] To compare the present value of $\langle s^2 \rangle_0$ with literature ones, we have corrected the observed ratio $\langle s^2 \rangle_0 / M_w = 6.5 \times 10^{-18}$ cm^2 for molecular weight polydispersity by multiplying the factor $(1 + U)/(1 + 2U)$ to it.[12] From the definition $U = M_w/M_N - 1$ we have the corrected ratio $(\langle s^2 \rangle_0 / M_w)_{\mathrm{corr}} = 5.6 \times 10^{-18}$ cm^2. This value should be compared with those determined for atactic PMMA samples, because the unperturbed radius of gyration of PMMA has been known to depend on its stereoregularity.[13] Wunderlich obtained the value $(\langle s^2 \rangle_0 / M_w)_{\mathrm{corr}} = 5.2 \times 10^{-18}$ cm^2 in BuCl after the correction for molecular weight polydispersity.[5] For fractionated samples, Schulz et al. have determined the ratio as 4.8×10^{-18} cm^2 in BuCl.[14] The present value is comparable with that by Wunderlich, but considerably higher than the value by Schultz et al. We have tried a viscosity measurement on the sample MA-F9 in BuCl at 38 °C. With a Ubbelohde type viscometer the intrinsic viscosity $[\eta]_\theta$ was determined to be 0.760 dL g^{-1} and after a 2% correction for polydispersity the value of K $(=[\eta]_\theta / M^{1/2})$ was obtained as 4.97×10^{-4} dL g^{-1}. Then, the Flory viscosity constant Φ $\{=K_\theta/(6\langle s^2 \rangle_0/M)^{3/2}\}$[15] was estimated as 2.6×10^{21}. The present value $K_\theta = 4.97 \times 10^{-4}$ dL g^{-1} is in agreement with those obtained by Wunderlich[5] and Fox,[16] and the value of $\Phi = 2.6 \times 10^{21}$ is compared with those determined for polymers of narrow molecular weight distribution.[17] The lower value of $\langle s^2 \rangle_0 / M = 4.8 \times 10^{-18}$ cm^2 by Schulz et al. appears to be attributed to a small difference in the overall tacticity of the samples.[18]

Comparison with Two-Parameter Theory and Discussion

The ternary system BuCl + BuOH + PMMA has been known to be a cosolvent system. Figures 3 and 4 demonstrate this property. The behavior of A_2 can be ascribed to both the cosolvent and excluded-volume effects. Quantitative analyses of A_2 can be made by examining the two effects separately. According to the two-parameter theory of dilute polymer solutions,[19,20] the second virial coefficient A_2 can be written in the form

$$A_2 = A_2^0 h(z/\alpha^3) \tag{2}$$

$$A_2^0 = N_A r^2 \beta / (2M^2) \tag{3}$$

where β is the binary cluster integral, r is the number of segments in a chain, and z is the excluded-volume parameter defined by

$$z = (4\pi^{3/2} N_A)^{-1} A_2^0 M^2 / \langle s^2 \rangle_0^{3/2} \tag{4}$$

The function $h(z/\alpha^3)$ in eq 2 represents the excluded-volume effect and A_2^0 is a measure of the polymer-solvent interaction inherent to systems. The excluded-volume effect is estimated from experimental data with the universal function Ψ defined by

$$\Psi = (4\pi^{3/2} N_A)^{-1} A_2 M^2 / \langle s^2 \rangle^{3/2} \tag{5}$$

The relation between the function $h(z/\alpha^3)$ and Ψ is obvious from the analogous expressions of eq 4 and 5. The two-parameter theory has been elaborated for systems of polymer + single solvent. It is interesting to use the two-parameter theory for the comparative study of the solutions in a single solvent and in a mixed solvent to reveal a characteristic feature due to the mixed solvent. In Figure 7 Ψ is plotted against α^2. The open circles were calculated from the data in Table I. The open circles with the vertical and oblique bars correspond to the data for the samplle MA-F9 in the single solvent BuCl and in the mixed solvent BuCl + BuOH at u_2 = 0.800, respectively. The filled circles were taken from the previous study on the sample MA-F9 in the mixture 1-chlorobutane + 2-methoxyethanol (MOEt).[9] The curves a, b, c, and d are described, respectively, by the modified Flory–Krigbaum–Orofino theory (FKO.m),[21,22] the Kurata–Yamakawa theory (KY),[19,20,23] the Stockmayer equation (S),[24] and the Casassa–Markovitz theory (CM)[25] in the same manner as in the previous paper. The data for the mixtures BuCl + BuOH and BuCl + MOEt show a similar behavior. BuOH is a nonsolvent for PMMA, while MOEt is a moderate solvent. This difference in solvent power is not reflected in the plot of Ψ versus α^2. As a whole the experimental points are fairly well described by the curve b or c, which is just the case for data observed in single solvents.[11,26–28] The cosolvency of the mixture BuCl + BuOH does not appear to bring about a different behavior from that in

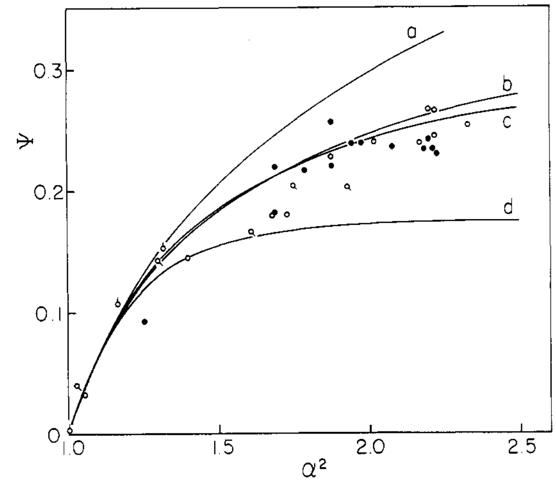

Figure 7. Plot of the universal function Ψ against the square of the expansion factor α for PMMA with $M_w = 2.44 \times 10^6$. Points ○ and ● were obtained in the mixed solvents 1-chlorobutane + 2-butanol and 1-chlorobutane + 2-methoxyethanol at 40 °C, respectively. Points ⚬ and ⚬ were obtained in the mixed solvent 1-chlorobutane (1) + 2-butanol (2) at $u_2 = 0.800$ and in the single solvent 1-chlorobutane with varying temperature, respectively. The solid curves a, b, c, and d represent the modifed Flory–Krigbaum–Orofino theory, the Kurata–Yamakawa theory, the Stockmayer equation, and the Cassassa–Markovitz theory, respectively.

single solvents in the excluded-volume effect.

According to the interpretation of the viscosity and preferential sorption data made by Dondos et al.,[4] the agreement of the mean-square radius of gyration observed in the mixed solvent at $u_2 = 0.800$ with the unperturbed one indicates that the preferential sorption vanishes or is very small in the mixed solvent at $u_2 = 0.800$. The thermodynamic analysis for the present system given in the subsequent paper also shows very small preferential sorption in a whole range of composition.[8] Therefore, the open circles showing a lower value in Figure 7 could be ascribed to an experimental uncertainty rather than the effect of the preferential sorption.

Since the excluded-volume behavior in the mixed solvent is not different from that in single solvents, we tried to evaluate the parameter $A_2{}^0$ in eq 3 by using the theories for $h(z/\alpha^3)$. The argument z/α^3 in eq 2 can be written as

$$z/\alpha^3 = (1/5.73)GA_2{}^0 \qquad (6)$$

where G is the experimentally determinable quantity defined by

$$G = 5.73\Psi/A_2 \qquad (7)$$

By substituting eq 6 into eq 2 combined with the theoretical equation for $h(z/\alpha^3)$ and solving for $A_2{}^0$ we obtained[9]

$$A_2{}^0 = [\exp(GA_2) - 1]/G \qquad \text{(FKO.m)} \qquad (8)$$

$$A_2{}^0 = [(1 - 0.319GA_2)^{-2.135} - 1](0.681G) \qquad \text{(KY)} \qquad (9)$$

$$A_2{}^0 = -(1/G)\ln(1 - GA_2) \qquad \text{(CM)} \qquad (10)$$

$$A_2{}^0 = A_2/(1 - GA_2/2) \qquad \text{(S)} \qquad (11)$$

Equations 8–11 were obtained for the modified Flory–Krigbaum–Orofino theory,[21,22] the Kurata–Yamakawa theory,[19,20,23] Casassa–Makovitz theory,[25] and the semi-empirical equation of Stockmayer,[24] respectively. In Figure 8 the calculated values of $A_2{}^0$ are plotted against u_2. The open circles were calculated with eq 9 and the solid curve b describes their behavior. The broken curves a and c illustrate the calculations due to eq 8 and 11, respectively.

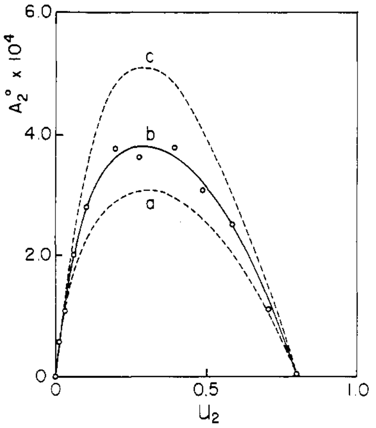

Figure 8. Plot of $A_2{}^0$ defined by eq 2 against the volume fraction u_2 for PMMA in the mixed solvent 1-chlorobutane (1) + 2-butanol (2). Open circles described by the solid curve b were calculated from experimental data with eq 9. The broken curves a and c are due to eq 8 and 11, respectively.

Equation 10 is not pertinent, for the value of GA_2 exceeds unity except for the small values of A_2. The calculated value of $A_2{}^0$ depends considerably on the choice of the theoretical equation for $h(z/\alpha^3)$, though the characteristic behavior of $A_2{}^0$ as a function u_2 is essentially same for eq 8, 9, and 11. The values of $A_2{}^0$ due to the Kurata–Yamakawa theory are given in the last column in Table I and will be used for a thermodynamic analysis in the subsequent paper, because this theory has been found to explain experimental data in single solvents reasonably. The value of $A_2{}^0$ depends strongly on the composition of the mixture BuCl + BuOH. The maximum value of $A_2{}^0$ near $u_2 = 0.3$ is comparable with those in good solvents, showing a typical cosolvent phenomenon. This observation is compatible with the cloud-point measurements made by Wolf and Blaum.[6]

Registry No. PMMA, 9011-14-7; BuCl, 109-69-3; BuOH, 78-92-2.

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Light-Scattering Study of Three-Component Systems. 4. Thermodynamic Properties of Poly(methyl methacrylate) in 1-Chlorobutane + 2-Butanol and 1-Chlorobutane + Acetonitrile

Mitsuo Nakata* and Atsushi Kaji

Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

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ABSTRACT: The second virial coefficient and the preferential sorption coefficient of the two ternary systems poly(methyl methacrylate) (PMMA) + 2-butanol (BuOH) + 1-chlorobutane (BuCl) and PMMA + acetonitrile (AcN) + BuCl were analyzed on the basis of the generalized Flory–Huggins equation. For the solvent mixtures the interaction function g_{12} was determined by boiling point measurements and the heats of mixing were roughly determined. An entropy contribution to the excess free energy was found to be very large in the mixture BuOH + BuCl, while it was small in AcN + BuCl. The ternary functions $g_T{}^0$ and $(\partial g_T/\partial \phi_3)^0$ were determined in different ways for the two ternary systems. As conjectured by Figueruelo et al., the ratio $g_T{}^0/\{g_{12} + (\partial g_T/\partial \phi_3)^0\}$ was nearly constant with the average values 0.43 for PMMA + BuOH + BuCl and 0.44 for PMMA + AcN + BuCl. This correlation between the ternary functions and the function g_{12} indicates that the specific thermodynamic properties of the solvent mixtures are reflected on the behavior of the ternary systems only through the function g_{12}.

Introduction

For systems of polymer + mixed solvent, cosolvency is a marked phenomenon, in which the binary mixture composed of poor solvents and/or nonsolvents for a polymer shows an enhanced solvent power as strong as a good solvent for the polymer. The cosolvent effect has been found for polymers in various mixed solvents and became recognized as a widespread phenomenon.[1-6] Furthermore, the inversion phenomena of the preferential sorption coefficient have been observed for many ternary systems.[6-10] This behavior seemed to be incompatible with the conventional notion that polymer molecules should tend to attract the better solvent preferentially in mixed solvent. Based on the thermodynamic analysis of three-component systems, it has been revealed that the properties of the ternary system polymer + mixed solvent are not deduced from those of the binary systems composed of each component.[7,11,12] To explain the observed behavior of the second virial coefficient A_2 and the preferential sorption coefficient λ, there has been introduced in the generalized Flory–Huggins equation the ternary function g_T, which represents the specific properties acquired by the ternary systems. Hence, a quantitative analysis of the experimental data of the ternary systems means to estimate the ternary function g_T. The function g_T can be evaluated directly only when a set of the data for A_2, λ, and the interaction parameters g_{ij} is known from experiments. *For the mixed solvent, the interaction parameter* g_{12} should be known as a function of the composition. However, it is not easy to obtain the complete set of the data. For nonsolvents, which are used in experiments of cosolvent phenomenon, the interaction parameters g_{i3} between polymer and solvent cannot be determined by usual experiments. Moreover, the second virial coefficient is not directly connected with the parameter g_{i3} but with the parameter χ_{i3}. Data of excess free energy for solvent mixtures is sparse in literature and a large difficulty occurs in evaluating the function g_{12}. Light scattering measurements for ternary systems cannot yield reliable data of A_2 and λ, when the refractive indices of the components are close to each other. Despite these difficulties it has been suggested that the solvent power of mixed solvents correlates chiefly to the excess free energy of the solvent mixture.[3,13] Recently, some attempts have been made to find a relation between the ternary function g_T and the binary interaction function g_{12} of the mixed solvent.[14-17] However, the relation could not be revealed, unless the function g_T is examined for a wide variety of ternary systems.

In this paper we have analyzed the light-scattering data for poly(methyl methacrylate) (PMMA) + 2-butanol (BuOH) + 1-chlorobutane (BuCl) obtained in the preceding study[18] and PMMA + acetonitrile (AcN) + BuCl by Horta et al.[4] Boiling point measurements were performed to obtain the excess free energy for the solvent mixtures and a rough determination was tried for the heats of mixing. The entropy contribution to the excess free energy was found to be very large for the mixture BuCl + BuOH and small for BuCl + AcN. It is interesting to know how these different properties of the mixed solvents are reflected to the behavior of present ternary systems.

Experimental Section

Boiling Point Measurements. The boiling temperature was determined at the constant pressures 120 ± 0.5 and 200 ± 0.5 mmHg for the mixture BuCl + BuOH and at 200 ± 0.5 mmHg for the mixture BuCl + AcN. The apparatus and method for the measurements were virtually the same as in a previous study.[19] The mixture boiling at the constant pressure in a vessel was cooled down slowly, observing small bubbles from the bottom. We tried to observe the lower limit of the temperature at which the bubbles ceased. For the pure liquids the lower limit temperature was higher by about 0.6 °C than the temperature in the vapor phase, which agreed with literature values at the pressure. Therefore, we used as a boiling temperature the lower limit temperature decreased by 0.5 °C for the mixtures BuCl + BuOH and BuCl + AcN. We tried our boiling point measurement for the mixture methanol + benzene at the pressure 148 ± 0.5 mmHg to compare the measured values of the excess free energy with literature ones. For this system the measured lower limit temperature was cor-

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