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Light-Scattering Study of Three-Component Systems. 5. Poly(methyl methacrylate) in the Nearly Ideal Mixture 1-Chlorobutane + Isoamyl Acetate

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ABSTRACT: Light-scattering measurements have been made on the ternary system of poly(methyl methacrylate) (PMMA) in the mixed solvent 1-chlorobutane (BuCl) + isoamyl acetate (IAA) for the two fractionated samples of the weight-average molecular weight $M_w = 1.95 \times 10^6$ and 9.8×10^4. BuCl and IAA have θ-temperatures for PMMA near 40.0 and 58.0 °C, respectively. The binary mixture BuCl + IAA was found to be a nearly ideal solution by vapor pressure measurements and to be an isorefractive mixture by refractive index experiments. The mean-square radius of gyration, $\langle s^2 \rangle$, was determined in the mixed solvent at the condition of vanishing second virial coefficient, A_2. The values of $\langle s^2 \rangle$ at $A_2 = 0$ agreed with the unperturbed value obtained at the θ-temperature in the single solvent BuCl. A_2 and $\langle s^2 \rangle$ measured at 50.0 °C decreased almost linearly with increasing volume fraction of IAA in the mixed solvent. The analysis of the observed behavior of A_2 by the generalized Flory–Huggins theory yielded the relation $g_T = 0.48 g_{12}$, where g_{12} and g_T are the binary interaction function for the mixed solvent and the ternary function for the ternary system. The relation was consistent with those obtained for cosolvent systems.

Introduction

The thermodynamic behavior of dilute polymer solutions in mixed solvent is described in terms of the preferential sorption coefficient λ, the second virial coefficient A_2, and the polymer dimension, i.e., the mean-square radius of gyration $\langle s^2 \rangle$ or the intrinsic viscosity $[\eta]$. The preferential sorption coefficient represents the composition difference of the mixed solvent between inside and outside the polymer domain. The second virial coefficient and the polymer dimension reflect the solvent power of mixed solvents.

A mixed solvent exhibits a different solvent power from the average solvent power of the two-component solvents. The increment of $[\eta]$ in mixed solvents was suggested to be correlated to the excess free energy G^E of the mixtures, though the values of $[\eta]$ estimated roughly with G^E were by a factor of 10 or more larger than observed ones.[1-3] The solvent power gained by mixed solvents has been argued also from the viewpoint of the molecular structure and the specific interaction in the mixture in addition to the effect of G^E.[4-10] The polymer dimension, A_2, and λ can be related to G^E by the Flory–Huggins theory.[11-14] This thermodynamic relation showed that a ternary function should be introduced in the Flory–Huggins theory to represent the properties acquired by the ternary system polymer + mixed solvent. The ternary function g_T was found to have a strong correlation with the interaction function g_{12} of mixed solvent.[15-22] According to the above analysis based on the Flory–Huggins theory, cosolvency[4-10,23,24] is not a peculiar phenomenon but is expected to occur in mixed solvents with a large value of g_{12} or G^E. By assuming g_T to be proportional to g_{12}, Pouchlý and Živný analyzed data of λ obtained for 19 ternary systems with large g_{12} values except for one.[15] The proportionality constant was positive and smaller than unity for most systems. Figueruelo et al.[17] deduced a relation between g_{12} and g_T from data of λ for some ternary systems with large g_{12} values. So far reliable experimental studies are very sparse for ternary systems with small or negative value of g_{12}. To reveal the characteristics of g_T, the relation between g_T and g_{12} should be investigated for various ternary systems with different values of g_{12}.

The preferential sorption may bring about different excluded volume effects for the polymer dimension and the second virial coefficient. This means that the polymer behavior in a mixed solvent may deviate from that predicted by the two-parameter theory.[25] Dondos and Benoit[26] determined intrinsic viscosities by varying the molecular weights for a few polymers in mixed solvents at the θ temperature corresponding to $A_2 = 0$.[27] The observed exponents in the Mark–Houwink–Sakurada viscosity law were larger than 0.5, and the slopes of the Stockmayer–Fixman plot[28] were positive for $\lambda > 0$. To examine the θ condition in mixed solvents, it is necessary to determine A_2 and $\langle s^2 \rangle$ by light-scattering measurements.

In this study, we have employed the system poly(methyl methacrylate (PMMA) + 1-chlorobutane (BuCl) + isoamyl acetate (IAA). The binary mixture BuCl + IAA was expected to be a nearly ideal mixture from viscosity[8] and cloud-point[29] measurements on PMMA in BuCl + amyl acetate. The solvents BuCl and IAA have θ temperatures near 40 °C[24,30] and 57 °C,[31] respectively. Moreover, since the mixed solvent BuCl + IAA is an isorefractive mixture, the light-scattering measurement can be made on the ternary system as in the case of the binary solution of polymer in a single solvent. We have carried out vapor-pressure measurements on the mixture BuCl + IAA and light-scattering measurements on the ternary system to clarify the relations between A_2 and g_{12} and A_2 and $\langle s^2 \rangle$.

Experimental Section

A. Materials. PMMA was prepared by bulk polymerization of freshly distilled methyl methacrylate with 2,2-azobis(isobutyronitrile) (AIBN) as initiator at 50 °C. Original polymers were fractionated by the fractional solution technique, i.e., the extraction method in the mixture toluene + methanol or benzene + methanol. The samples with weight-average molecular weights

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$M_w = 1.95 \times 10^6$ (MA-F8) and $M_w = 2.37 \times 10^5$ (M10-F8) belong to the same fraction series as MA-F9 and M10-F9 used in a previous study, respectively.[24,30] The sample with $M_w = 9.8 \times 10^4$ (M16-F9) is the ninth fraction in 13 fractions extracted from the original polymer which was prepared with AIBN of 0.200 wt % and *n*-butyl mercaptan of 0.30 vol %. The molecular weight distribution of the samples MA-F8 and M16-F9 was estimated by gel permeation chromatograms to be $M_w/M_n = 1.17$ and 1.19, respectively. The molecular weight distribution of the sample M10-F8 could be compared with that of M10-F9, which has $M_w/M_n = 1.11$.

Reagent-grade IAA was washed with saturated sodium hydrogen carbonate and sodium chloride solutions. It was dried with anhydrous magnesium sulfate for a couple of days and fractionally distilled in a 180-cm column packed with Raschig rings. BuCl was purified as described in a previous paper.[30]

B. Vapor-Pressure Measurements. The vapor-pressure apparatus was made of a 100-mL flask equipped with a Teflon valve and a mercury manometer of a Pyrex glass tubing of 8-mm inside diameter and 35-cm height.[32] A sample liquid of 30 mL and of known composition was transferred to the vapor-pressure apparatus by injector and was degassed by repeated operations of freezing, pumping, and melting. The bubble formation was not observed on melting in the first freeze-and-thaw operation, and the manometer showed null pressure on the subsequent freezing. This was the case for the pure solvents BuCl and IAA and the mixtures. In the present vapor-pressure measurements we repeated the freeze-and-thaw operation three times for degassing. We did not try a gas-release method for degassing,[32] because BuCl was much more volatile than IAA, and the gas-release procedure was considered to cause composition variation.

The vapor-pressure apparatus was immersed in a water bath, the temperature of which was controlled to within ±0.01 K. The sample liquid was continuously stirred by a magnetic stirrer for a rapid attainment of equilibrium state. The meniscus height in the mercury manometer was measured with a cathetometer to 0.1 mm.

C. Refractive Index Variation and Light-Scattering Measurements. In the light-scattering study on polymer(3) in the mixture solvent(1) + solvent(2) it is necessary to determined the derivatives $(\partial n/\partial c_3)_{u_2}$ and $(\partial n/\partial u_2)_{c_3=0}$ of the refractive index n of the system, where c_3 is the mass concentration of polymer(3) and u_2 is the volume fraction of the solvent(2) in the solvent mixture. The refractive index measurement was made at 435.8 nm of a mercury arc with a differential refractometer of the Brice type which was calibrated for aqueous solution of sodium chloride with relevant refractometric data.[33] The increment $(\partial n/\partial c_3)_{u_2}$ cm^3/g was measured for the sample M10-F8 at various values of the volume fraction u_2. Since the refractive index of BuCl is very close to that of IAA, we could determine the refractive index difference between the mixture BuCl + IAA and pure BuCl by the differential refractometer.

Light-scattering measurements were carried out with unpolarized incident light at 435.8 nm. The photometer was calibrated with benzene, taking its Rayleigh ratio as 46.5×10^{-6} cm^{-1}.[34] For optical clarification each solution was filtered through Sartorius membrane filter (SM 116) of 0.45-μm pore size into a solution cell of 19-mm i.d. and again filtered into the same cell. The solution cell was immersed in a cylindrical cell filled with the solvent and set in the photometer. Scattered intensities were measured at interval of 15° in the angular range from 30° to 150°. The measurements were made on the PMMA samples M16-F9 and MA-F8 at four or five concentrations in the ranges $c_3 < 2.0 \times 10^{-2}$ and $c_3 < 1.5 \times 10^{-3}$ g/mL, respectively.

Data Analyses and Results

In Figure 1 the total vapor pressures P (kPa) of the mixture BuCl(1) + IAA(2) measured at 40, 45, and 50 °C are given as a function of the mole fraction x_2 of IAA. The open circles represent experimental points. The vapor pressures of the pure BuCl and IAA determined at 40 °C were 0.65 and 0.23 kPa higher than literature values, respectively.[35,36] These slightly high values of P seemed to be caused by a trace of impurity gases, and the total vapor pressures obtained for the mixture also would be affected by the impurity gases. In Figure 1 the straight lines are given by connecting the points for the pure BuCl and IAA. The points for the mixture deviate downward from the straight lines.

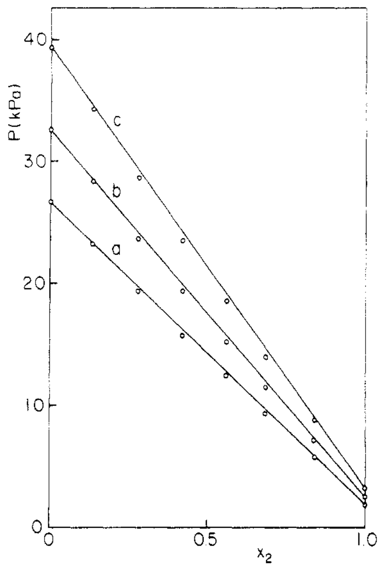

Figure 1. Plots of total vapor pressure P (kPa) against mole fraction x_2 for the mixture 1-chlorobutane(1) + isoamyl acetate(2) at the three temperatures 40.0 °C (a), 45.0 °C (b), and 50.0 °C (c). The open circles are the experimental data. The straight lines connect the two data points at the pure liquids.

The total vapor pressure P of binary mixtures is related to the chemical potential $\Delta\mu_i$ of mixing for component i by[37]

$$P = P_1 \exp(\Delta\mu_1/RT + D_1) + P_2 \exp(\Delta\mu_2/RT + D_2) \quad (1)$$

where P_i is the vapor pressure of component i, RT has the usual meaning, and D_i represents the correction given by

$$D_i = (V_i - B_{ii})(P - P_i)/RT \quad (2)$$

Here, V_i is the molar volume of component i and B_{ii} is the second virial coefficient of component i. In eq 2, the term due to the cross second virial coefficient B_{ij} is neglected because of its small contribution. The second virial coefficient B_{ii} was calculated using Berthelot's equation from the values of the critical temperature and pressure.[38]

The excess free energy G^E can be related to the chemical potential $\Delta\mu_i$ through the Gibbs free energy ΔG of mixing expressed with the mole fraction as

$$\Delta G/(N_1 + N_2) = RT(x_1 \ln x_1 + x_2 \ln x_2) + G^E(T,x_2) \quad (3)$$

where x_i and N_i are the mole fraction and number of moles of component i, respectively. Since, as shown in Figure 1, the deviation from Raoult's law is very small, we assumed a simple x_2 dependence of G^E given by

$$G^E = RTx_1x_2(a + bx_2) \quad (4)$$

where a and b depend only on temperature. The coefficients a and b were determined at each temperature by using Barker's method, i.e., a successive approximation with a least-squares method for total vapor pressure analysis.[39] The analysis yielded the values $a = -0.106$, $b = 0.120$ at 40 °C, $a = -0.109$, $b = 0.124$ at 45 °C, and $a = -0.100$, $b = 0.107$ at 50 °C. The obtained values of a and b do not seem to depend on temperature when experi-

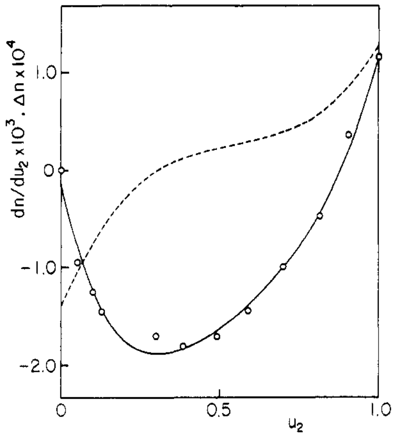

Figure 2. Refractive index behavior as a function of the volume fraction u_2 for the mixture 1-chlorobutane(1) + isoamyl acetate(2) at 50.0 °C. The solid curve with the experimental points ○ represent the refractive index difference Δn ($=n - n_1$) between the mixture and the pure 1-chlorobutane. The broken line is for the derivative dn/du_2.

Table 1. Refractive Index Increments for Poly(methyl methacrylate)(3) in the Mixed Solvent 1-Chlorobutane(1) + Isoamyl Acetate(2) Measured at 50.0 °C and at Some Other Temperatures

temp, °C	u_2	$(\partial n/\partial c_3)_{u_2}$, cm³/g
50.0	0	0.1017
	0.1956	0.1015
	0.3928	0.1010
	0.5977	0.1010
	0.7987	0.1003
	1	0.0996
40.0	0	0.0982
	1	0.0970
68.0	1	0.1051

mental errors are taken into consideration. Thus, we employ the average values $a = -0.105$ and $b = 0.117$ independent of temperature for subsequent analyses. The total vapor pressures calculated with these values of a and b agreed with the observed ones within an error of ±0.13 kPa or ±1.2%. Effects caused by impurity gases appear to be canceled out in the above analysis by using the observed vapor pressures for BuCl and IAA.

By a least-squares method, the difference Δn ($=n - n_1$) between the refractive index n of the mixture BuCl + IAA and the one n_1 of BuCl at 50 °C was fitted to the fourth-degree polynomial as

$$\Delta n \times 10^4 = -0.16 - 14.06u_2 + 38.74u_2^2 - 42.59u_2^3 + 19.28u_2^4 \quad (5)$$

Figure 2 shows the plots of Δn and the derivative dn/du_2 versus u_2. The open circles represent the experimental points of Δn, and the solind line is described by eq 5. The broken curve shows the derivative dn/du_2 due to eq 5.

The refractive index increments $(\partial n/\partial c_3)_{u_2}$ measured at 50 °C are given in Table 1. The values of $(\partial n/\partial c_3)_{u_2}$ in BuCl and IAA measured at some other temperatures are also given. Figure 3 shows the plot of $(\partial n/\partial c_3)_{u_2}$ versus u_2 at 50 °C.

For the ternary system solvent(1) + solvent(2) + polymer(3), a practical equation for the analysis of excess light-scattering data can be written as[25,40]

$$(Kc_3/R_\theta)^{1/2} = M_3^{-1/2} + A_2(u_2)M_3^{1/2}c_3 + {}^1/_6\langle s^2(u_2)\rangle M_3^{-1/2}q^2 \quad (6)$$

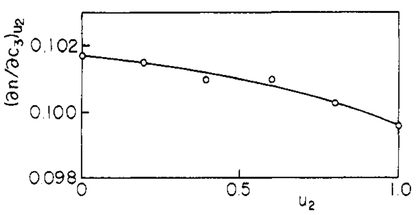

Figure 3. Plot of refractive index increment $(\partial n/\partial c_3)_{u_2}$ (cm³/g) against the volume fraction u_2 for PMMA(3) in the mixed solvent 1-chlorobutane(1) + isoamyl acetate(2) at 50.0 °C. The open circles are the experimental point.

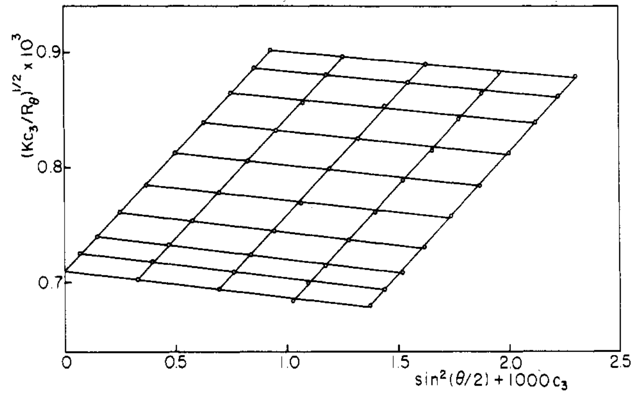

Figure 4. Zimm plot of the light-scattering data for PMMA-(sample MA-F8)(3) in the mixed solvent 1-chlorobutane(1) + isoamyl acetate(2) at 50.0 °C. The data were obtained at the volume fraction $u_2 = 0.6498$ of isoamyl acetate in the solvent.

with

$$K = (2\pi^2n^2/N_A\Lambda^4)(\partial n/\partial c_3)_{\mu_2}^{\ 2} \quad (7)$$

$$q = (4\pi n/\Lambda)\sin(\theta/2) \quad (8)$$

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 of incident light in a vacuum. $(\partial n/\partial c_3)_{\mu_2}$ in eq 7 is the refractive index increment at a constant chemical potential μ_2 and can be rewritten with the preferential sorption coefficient $\lambda(u_2)$ as[13]

$$(\partial n/\partial c_3)_{\mu_2} = (\partial n/\partial c_3)_{u_2} - \lambda(u_2)(\partial n/\partial u_2)_{c_3=0} = 0 \quad (9)$$

where λ (>0) means an excess of solvent(1) in the polymer domain.

For mixed solvents with relatively small $(\partial n/\partial u_2)_{c_3=0}$, the polymer dimension $\langle s^2(u_2)\rangle$ can be evaluated from scattering data with eq 6.[25] In the present ternary system the second term of the right-hand side of eq 9 can be neglected, because the magnitude of λ is usually smaller than unity and $(\partial n/\partial c_3)_{u_2}$ is much larger than $(\partial n/\partial u_2)_{c_3=0}$ as shown in Figures 2 and 3. Thus, by putting $(\partial n/\partial c_3)_{\mu_2} = (\partial n/\partial c_3)_{u_2}$, we can analyze the present data as in the case of the binary system of polymer + single solvent. In Figure 4, light-scatering data for the sample MA-F8 at $u_2 = 0.6498$ and at 50 °C are given by the Zimm plot, from which M_3, $A_2(u_2)$, and $\langle s^2(u_2)\rangle$ can be evaluated in a usual manner. In Table 2 the obtained values of M_3, A_2, and $\langle s^2\rangle$ are listed. As expected from the very small value of $(\partial n/\partial u_2)_{c_3=0}$, the values of M_3 determined in the mixed solvent agree with those determined in the pure solvents. For the molecular weight of the samples MA-F8 and M16-F9, we took the average values $M_3 \times 10^{-5} = 19.5$ and 0.98, respectively. In Figures 5 and 6 A_2 and $\langle s^2\rangle$ are plotted against u_2, respectively. The data points ○ and △ are for samples MA-F8 and M16-F9, respectively. For the sample M16-F9, A_2 was determined in pure IAA by varying

Table 2. Light-Scattering Data of Poly(methyl methacrylate) in the Mixed Solvent 1-Chlorobutane + Isoamyl Acetate at 50.0 °C

sample	u_2	$10^{-5}M_3$	$10^5 A_2$, cm^3 mol g^{-2}	$10^{11}\langle s^2\rangle$, cm^2
MA-F8	0	19.6	1.9	1.44
	0.1811	19.8	1.0	1.27
	0.2578	19.7	0.4	1.27
	0.5080	19.0	−0.9	1.11
	0.6498	19.8	−1.6	1.07
	0.7622	19.5	−1.9	0.99
	1	19.2	−2.3	0.99
	0[a]	19.6	0	1.19
	0.1811[b]	19.4	0	1.21
M16-F9	0	0.98	2.1	
	0.0523	0.98	1.7	
	0.2074	0.98	0.7	
	0.4033	0.97	0	
	0.5912	1.00	−0.6	
	0.7958	0.98	−1.2	
	1	0.97	−1.9	

[a] Measured at 40.0 °C. [b] Measured at 45.0 °C.

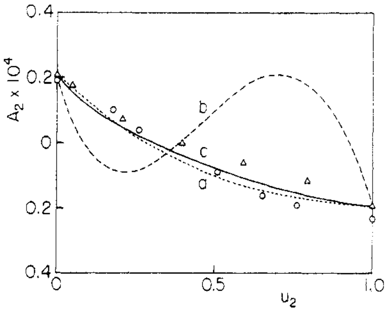

Figure 5. Plots of the second virial coefficient A_2 (cm^3 mol g^{-2}) against the volume fraction u_2 for PMMA in the mixed solvent 1-chlorobutane(1) + isoamyl acetate(2) at 50.0 °C. The points ○ and △ represent the experimental data for the samples MA-F8 and M16-F9, respectively. The dotted curve a was calculated with $g_{12} = g_T = 0$. Calculations with g_{12} given by eq 12 yield the broken curve b and the solid curve c for $g_T = 0$ and $g_T = 0.48g_{12}$, respectively.

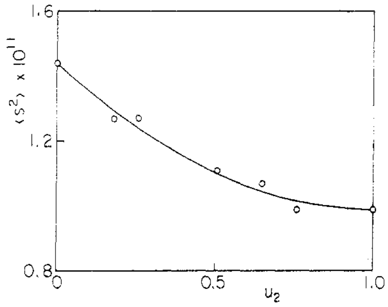

Figure 6. Plot of the mean-square radius of gyration $\langle s^2\rangle$ (cm^2) against the volume fraction u_2 for PMMA(sample MA-F8) in the mixed solvent 1-chlorobutane(1) + isoamyl acetate(2) at 50.0 °C. The open circles represent the experimental data.

temperature as $A_2 \times 10^5 = -4.6$ (40.0 °C), −3.5 (44.6), −1.9 (50.0), −0.7 (55.0), 1.4 (64.9), and 2.3 (70.0).

θ Condition and Unperturbed Dimension. The θ temperature of PMMA in pure BuCl has been found near 40 °C.[24,41] In Table 2 a vanishing second virial coefficient is observed at 40.0 °C in BuCl. The value of $\langle s^2\rangle_0 = 1.19 \times 10^{-11}$ cm^2 at the temperature can be taken as an unperturbed one. The vanishing second virial coefficient is also obtained at 45.0 °C in the mixture at $u_2 = 0.1811$, where $\langle s^2\rangle$ gives 1.21×10^{-11} cm^2. In Figure 5 the second virial coefficient becomes zero near $u_2 = 0.35$, where $\langle s^2\rangle$ is estimated as 1.18×10^{-11} cm^2 in Figure 6. The latter two values of $\langle s^2\rangle$ in the mixed solvent agree with the unperturbed one in BuCl. This behavior of A_2 and $\langle s^2\rangle$ in the mixed solvent indicates an occurrence of the usual θ condition.

The unperturbed dimension obtained at 40.0 °C in BuCl gives the ratio $\langle s^2\rangle_z/M_w = 6.1 \times 10^{-18}$ cm^2 which can be corrected for the molecular weight distribution $M_w/M_n = 1.17$ as $(\langle s^2\rangle/M)_{corr} = 5.3 \times 10^{-18}$. Within experimental errors this value agrees with the one 5.6×10^{-18} in a previous study[24] and 5.2×10^{-18} obtained by Wunderlich.[42] Fujii et al.[41] determined the θ temperature of PMMA in BuCl as 40.8 °C and obtained unperturbed ratios close to $\langle s^2\rangle_z/M_w = 6.5 \times 10^{-18}$, which gives corrected ratios very near $(\langle s^2\rangle/M)_{corr} = 6.1 \times 10^{-18}$. This value is considerably higher than the present one. However, we are not certain whether this difference is caused by experimental errors or polymerization conditions of PMMA. The present PMMA samples were polymerized at 50 °C, while the samples used by Fujii et al. were at 60 °C.

In IAA the temperature dependence of A_2 obtained for the sample M16-F9 yields a θ condition at 58.0 °C, which agrees with the observation by Kirste et al.[31]

Analysis by Generalized Flory–Huggins Theory. For the ternary system solvent(1) + solvent(2) + polymer(3), the generalized Flory–Huggins equation for the Gibbs free energy of mixing ΔG_{mix} can be written as[11-13]

$$\Delta G_{mix}/RT = N_1 \ln \phi_1 + N_2 \ln \phi_2 + N_3 \ln \phi_3 + g_{12}(u_2)N_1\phi_2 + g_{13}(\phi_3)N_1\phi_3 + g_{23}(\phi_3)N_2\phi_3 + g_T(u_2,\phi_3)N_1\phi_2\phi_3 \quad (10)$$

where ϕ_i is the volume fraction of component i and u_i $[=\phi_i/(\phi_1+\phi_2)](i = 1,2)$ is the volume fraction of component i in the mixed solvent, g_{ij} is the binary interaction function for components i and j, and $g_T(u_2,\phi_3)$ is the ternary function characteristic to the ternary system. On the basis of thermodynamic relations for the three-component systems, equations for A_2 and λ can be derived from eq 10 as a function of u_2. The present experimental data of A_2 were compared with the second virial coefficient A_2^L due to eq 10, which is given explicitly in a previous study.[21] The data of A_2 were not corrected for the excluded volume effect because of the small values of A_2.[24,30]

Assuming the relation $g_{i3}^0 = 4/3\chi_{i3}^0$, values of g_{i3}^0 and χ_{i3}^0 were calculated from the values of A_2 observed for the sample M16-F9 in the pure solvents, where the superscript 0 refers to the limit of zero polymer concentration. Thus, we obtained $\chi_{13}^0 = 0.4968$ and $g_{13}^0 = 0.6624$ for BuCl(1), and $\chi_{23}^0 = 0.5041$ and $g_{23}^0 = 0.6721$ for IAA(2). The function $g_{12}(u_2)$ can be related with the excess free energy $G^E(x_2)$ by

$$g_{12}(u_2) = [G^E/RT + x_1 \ln(x_1/u_1) + x_2 \ln(x_2/u_2)]/(x_1u_2) \quad (11)$$

The g_{12} function calculated with the values of $a = -0.105$ and $b = 0.117$ was slightly curved when plotted against u_2 but approximated by

$$g_{12} = -0.03 + 0.08u_2 \quad (12)$$

For the specific volume v_3 of PMMA at 50.0 °C, we used the value 0.8415 cm^3/g estimated from the density data above the glass transition temperature.[43] The molar volume ratio r_2 of IAA to BuCl was obtained as 1.423 from the density data 0.8526 g/cm^3 for BuCl and 0.8427 g/cm^3 for IAA at 50.0 °C.

First we made a calculation of A_2^L, assuming $g_{12}(u_2) = 0$ and $g_T(u_2,\phi_3) = 0$, because the magnitude of $g_{12}(u_2)$ for the present system is smaller than the magnitude for ordinary binary systems by a factor of 0.1 or less. In Figure 5 the calculation gives the dotted line a, which describes the behavior of the experimental points. On the other hand, the calculation of A_2^L with $g_{12}(u_2)$ given by eq 12 and $g_T(u_2,\phi_3) = 0$ gives the broken line b. The behavior of the line b is very different from that of the dotted line a. Although the present determination of g_{12} is not so accurate, it indicates that the ternary function $g_T(u_2,\phi_3)$ should not be neglected even in ternary systems with small g_{12}.

We tried to evaluate the ternary function $g_T(u_2,\phi_3)$ which brings about an agreement between the second virial coefficients observed and calculated with A_2^L. At the limit of zero polymer concentration, the function g_T can be expressed as

$$g_T = \alpha(u_2) + \beta(u_2)\phi_3 \qquad (13)$$

with $\alpha(u_2) = g_T^0$ and $\beta(u_2) = (\partial g_T/\partial \phi_3)^0$. It is difficult to determine the functional forms of $\alpha(u_2)$ and $\beta(u_2)$ from the data of A_2. Thus, we assumed the proportionality relations

$$\alpha(u_2) = Ag_{12}(u_2) \qquad (14)$$

$$\beta(u_2) = Bg_{12}(u_2) \qquad (15)$$

where A and B are a constant.[15-18] By repeating calculations of A_2^L for various values of A and B, we determined the constants as $A = 0.48$ and $B = 0$, which yield the solid curve c in Figure 5.

Discussion

We tried to evaluate the preferential sorption coefficient λ for the three cases: $g_{12} = g_T = 0$, g_{12} by eq 12 and $g_T = 0$, and g_{12} by eq 12 and $g_T = 0.48g_{12}$. In all the cases λ was positive and smaller than 0.024 in the whole range of u_2. The calculated value of λ is as small as about one-tenth of those measured for usual ternary systems. This small λ is consistent with the θ state found at $u_2 = 0.1811$ and $u_2 = 0.35$, where the unperturbed dimension $\langle s_2\rangle_0$ was obtained for vanishing A_2.

In Figures 5 and 6 the experimental points may be represented roughly by a straight line connecting the two points for pure solvents: The solvent power of the mixed solvent is given approximately by the average solvent power of the pure solvents. This is just what we have expected from the ideal behavior $g_{12} \simeq 0$ of the mixed solvent. In the present analysis the ternary function g_T was very small in magnitude but could not be neglected. Figueruelo et al. proposed an empirical relation among $g_{12}(u_2)$, $\alpha(u_2)$, and $\beta(u_2)$ as[17,18]

$$\alpha(u_2) = K[g_{12}(u_2) + \beta(u_2)] \qquad (16)$$

where K is a constant and conjectured to have the value of $g_{13}^0g_{23}^0$. For the present system the value of K is equal to $A = 0.48$, which is close to the value of $g_{13}^0g_{23}^0 = 0.45$. In a previous study[21] we have analyzed experimental data of A_2 for PMMA in the two cosolvents BuCl + 2-butanol and BuCl + acetonitrile and obtained nearly constant values of K comparable with $g_{13}^0g_{23}^0$. The above behavior of K indicates a simple relation between the functions g_{12} and g_T for various ternary systems with different values of g_{12}.

A few measurements for A_2 and $[\eta]$ have been carried out for ternary systems of mixed solvent with $g_{12} < 0$.[1,44,45] The solvent power of these mixed solvents was lower than the average solvent power of the pure solvents but has not been analyzed quantitatively by the thermodynamic equations.

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