(24) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.
(25) Casassa, E. F.; Markovitz, H. *J. Chem. Phys.* **1958**, *29*, 493.
(26) Takashima, K.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 245.
(27) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 799.
(28) Norisuye, T.; Kawahara, K.; Teramoto, A.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4330.

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. *Received July 20, 1987; Revised Manuscript Received March 1, 1988*

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-

0024-9297/88/2221-2514$01.50/0

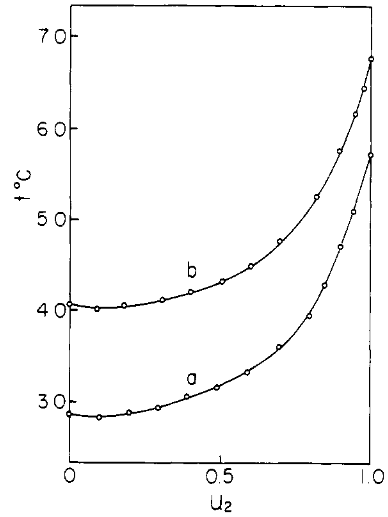

Figure 1. Plots of boiling temperatures observed at 120 (a) and 200 mmHg (b) against the volume fraction u_2 for the binary mixture 1-chlorobutane (1) + 2-butanol (2).

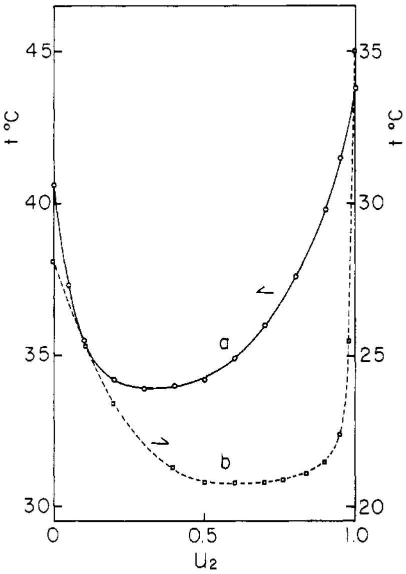

Figure 2. Boiling temperature as a function of the volume fraction u_2. Curve a was measured at 200 mmHg for the mixture 1-chlorobutane (1) + acetonitrile (2) and curve b at 148 mmHg for methanol (1) + benzene (2).

rected by −0.7 °C to obtain the boiling temperature. In Figure 1 the observed boiling temperatures for the system BuCl (1) + BuOH (2) are plotted against the volume fraction u_2 of BuOH. Figure 2 shows the boiling temperatures for the systems BuCl (1) + AcN (2) and methanol (1) + benzene (2) as a function of the volume fraction u_2 of component 2.

Heats of Mixing of the Solvent Mixtures. A rough determination of the heats of mixing was made by measuring the temperature change on mixing. Two liquids separated by thin Teflon sheet and at thermal equilibrium were mixed in a Dewar vessel and the temperature change was measured by a Beckmann thermometer. The effect of heat flow through the Dewar vessel was corrected by measurements on mixtures of known heats of mixing as described in a previous paper.[19] The heats of mixing were calculated from the temperature change by using the molar heat capacity of the mixture estimated with the assumption of additivity of the values of each component. The molar heat capacities of each component were evaluated according to the group-contribution method of Missenard.[20] The main error in the heats of mixing thus determined comes from the molar heat capacities estimated with the assumption of the additivity rule. Observed excess heat capacities range from a few percent for usual mixtures to several percent as a high value.[21] Considering other sources of error, the uncertainty in the observed heats of mixing was inferred to be less than 10%.

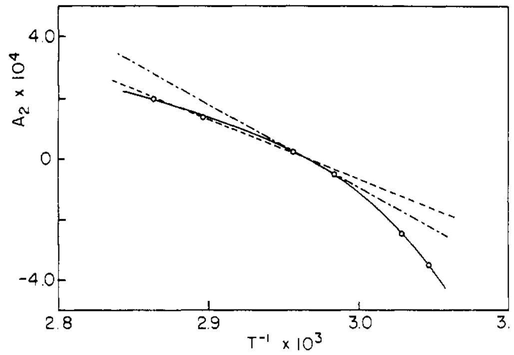

Figure 3. Plot of the second virial coefficient A_2 ((cm^3 mol)/g^2)) versus the reciprocal of absolute temperature for PMMA in 2-butanol with $M_w = 3.66 \times 10^4$. Extrapolation to 40 °C is made with the data above the Θ temperature (- - -) and with the tangent at the Θ temperature (– – –).

Light-Scattering Measurements. By light-scattering measurements the second virial coefficient for the system PMMA + BuOH was determined for the sample (M9-F6)[18] of molecular weight $M_w = 3.66 \times 10^4$ in the temperature range from 55 to 76 °C. For optical clarification, solutions flame-sealed in the light-scattering cells were left undisturbed at a temperature above the cloud point for a few days, rendering dust sedimentation, which could eliminate large forward scattering due to dust particles. The light-scattering data were analyzed so as to give the correct molecular weight, which was obtained by using the refractive index increment (cm^3 g^{-1}), depending on the temperature t (°C) as $dn/dc = 0.0802 + 0.0004t$. In Figure 3 the observed values of A_2 are plotted against the reciprocal of the absolute temperature T. The value of A_2 at 40 °C was determined as $A_2 = -4.6 \times 10^{-4}$ cm^3 mol g^{-2} by extrapolating the data above the Θ temperature with the broken line to $T^{-1} \times 10^3 = 3.19$.

Phenomenological Equation of Three-Component Systems

The preferential sorption coefficient λ and the second virial coefficient A_2 for the system polymer + mixed solvent can be related to the free energy of mixing ΔG_{mix}. For the ternary system solvent (1) + solvent (2) + polymer (3) the Flory–Huggins equation could be generalized as[7,12]

$$\Delta G_{\text{mix}}/RT = N_1 \ln \phi_1 + N_2 \ln \phi_2 + N_3 \ln \phi_3 + g_{12}(u_2)N_1\phi_2 + g_{13}(\phi_3)N_1\phi_3 + g_{23}(\phi_3)N_2\phi_3 + G_T \quad (1)$$

where N_i and ϕ_i are the number of moles and the volume fraction of component i, respectively, u_2 is the volume fraction of component 2 in the mixed solvent ($u_2 = \phi_2/(\phi_1 + \phi_2)$), and RT has its usual meaning. The binary interaction function g_{ij} in eq 1 covers all the thermodynamic properties of the binary system of components i and j. The function G_T depicts all deviations of the real ternary systems from the idealized system represented by the binary interaction function g_{ij} alone. Pouchlý et al.[12] and Chu et al.[7] assumed the functional form of G_T written as

$$G_T = g_T(u_2,\phi_3)N_1\phi_2\phi_3 \quad (2)$$

We refer to the function g_T in the above equation as a ternary function because of the product of three compositions multiplied to it. We use eq 1 as a phenomenological equation in the sense that the ternary function g_T is defined by eq 1 and 2 and should be evaluated with the binary interaction functions determined by experiments on the binary mixtures. On the basis of the thermodynamic equations of three component systems, Chu and Munk[7] derived the explicit equations for A_2 and λ from eq 1 and 2 in the form

$$A_2^0 = [\bar{v}_3^2/(2\bar{V}_1)][(b_{22}b_{33} - b_{23}^2u_1u_2)/b_{22}] \quad (3)$$

$$\lambda^0 = \bar{v}_3(b_{23}/b_{22})u_1u_2 \quad (4)$$

where $\bar{V}_1$ is the partial molar volume of component 1, $\bar{v}_3$ is the partial specific volume of component 3, and the superscript zero on A_2 and λ refers to the lattice theory as a base of eq 1. b_{ij}s in eq 3 and 4 are given by

$$b_{22} = (1/r_2)u_1 + u_2 - u_1u_2[2g_{12} - 2(u_1 - u_2)(\partial g_{12}/\partial u_2) - u_1u_2(\partial^2 g_{12}/\partial u_2{}^2)] \quad (5)$$

$$b_{23} = 1 - (1/r_2) + (1/r_2)g_{23}{}^0 - g_{13}{}^0 - (u_1 - u_2)(g_{12} - g_T{}^0) + u_1u_2[(\partial g_T/\partial u_2)^0 - (\partial g_{12}/\partial u_2)] \quad (6)$$

$$b_{33} = u_1 + (1/r_2)u_2 + 2u_1u_2[(g_{12} - g_T{}^0) - \chi_T{}^0] - 2[(1/r_2)\chi_{23}{}^0u_2 + \chi_{13}{}^0u_1] \quad (7)$$

with

$$\chi_{i3}{}^0 = g_{i3}{}^0 - (\partial g_{i3}/\partial \phi_3)^0 \quad (8)$$

$$\chi_T{}^0 = g_T{}^0 - (\partial g_T/\partial \phi_3)^0 \quad (9)$$

Here, the superscript zero on the right-hand side of eq 6–9 refers to the limit of zero polymer concentration and r_2 is the ratio of partial molar volume of solvent 2 to that of solvent 1.[19] For the binary system polymer + single solvent i, eq 3 with eq 5–9 reduces to

$$A_{2,i}{}^0 = (\bar{v}_3{}^2/\bar{V}_i)(1/2 - \chi_{i3}{}^0) \quad (10)$$

Within the scope of the lattice theory, the function g_{i3} depends on ϕ_3 as

$$g_{i3} = g_{i3}{}^0/[1 - (2/z)\phi_3] \quad (11)$$

where z is the coordination number of the lattice. Equations 8 and 11 yield the relation

$$\chi_{i3}{}^0 = (1 - 2/z)g_{i3}{}^0 \quad (12)$$

We have estimated $g_{i3}{}^0$ from the observed values of $A_{2,i}$ for $z = 8$, i.e., with the relation $g_{i3}{}^0 = (4/3)\chi_{i3}{}^0$.

Comparison of Phenomenological Equations and Experimental Data

The present experimental data was compared with the phenomenological equations by assigning the components as BuCl (1) + BuOH (2) + PMMA (3) and BuCl (1) + AcN (2) + PMMA (3). For the system BuCl + BuOH + PMMA the second virial coefficient $A_2{}^0$ corrected for the excluded-volume effect by the Kurata–Yamakawa theory was employed for the comparison.[18] The second virial coefficients of the systems BuCl + AcN + PMMA by Horta et al.[4] and BuOH + PMMA obtained in this study were used without the correction, because the measurements have been made for low molecular weight samples and the mean-square radius of gyration has not been measured. Since eq 6–9 are taken at the limit of zero polymer concentration, the ternary function g_T can be written as

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

where $\alpha(u_2)$ and $\beta(u_2)$ are a function of the volume fraction u_2 alone. The purpose of this section is to determine the function $\alpha(u_2) = g_T{}^0$, and $\beta(u_2) = (\partial g_T/\partial \phi_3)^0$ for PMMA in the two mixed solvents which are different in thermodynamic properties.

Evaluation of the Binary Interaction Functions. For the binary systems PMMA + solvent the interaction function g_{i3} was determined with eq 10 and 12. The observed values of $A_2 = 0$ in BuCl and $A_2 = -4.6 \times 10^{-4}$ in BuOH at 40 °C give $g_{13}{}^0 = 0.667$ and $g_{23}{}^0 = 0.749$, respectively. Horta's data of $A_2 = -1.56 \times 10^{-4}$ in BuCl and $A_2 = -1.0 \times 10^{-4}$ in AcN at 25 °C give $g_{13}{}^0 = 0.698$ and $g_{23}{}^0 = 0.68$, respectively.

For the partial specific volume of PMMA we used $\bar{v}_3 = 0.833$ at 25 °C and 0.838 at 40 °C, which were obtained by extrapolating the specific volume in the pure state from above the glass temperature.[22] The molar volume ratios were calculated as $r_2 = 0.876$ for BuCl (1) + BuOH (2) and $r_2 = 0.503$ for BuCl (1) + AcN (2) from the molar volumes for pure substance.

The binary interaction function g_{12} for the solvent mixtures was calculated from the boiling point data. The total vapor pressure p of binary mixtures is given by the equation

$$p = p_1 \exp(\Delta\mu_1/RT) + p_2 \exp(\Delta\mu_2/RT) \quad (14)$$

where p_1 and p_2 are the vapor pressure for pure components. The excess chemical potentials $\Delta\mu_1$ and $\Delta\mu_2$ in eq 14 are derived from the free energy of mixing

$$\Delta G/RT = N_1 \ln (1 - u_2) + N_2 \ln u_2 + g_{12}(T,u_2)N_1u_2 \quad (15)$$

which can be obtained from eq 1 by putting $N_3 = 0$. Since excess free energy measured on binary mixtures usually varies slightly with temperature,[23] we assumed that the function g_{12} depends on temperature as

$$g_{12}(T,u_2) = f(u_2)/T \quad (16)$$

where $f(u_2)$ is a function of the volume fraction alone. The functional form of $f(u_2)$ was assumed to be written as

$$f(u_2) = a + bu_2 + cu_2{}^2 \quad (17)$$

for the systems BuCl (1) + BuOH (2) and BuCl (1) + AcN (2). For the system methanol (1) + benzene (2) we have expressed the free energy of mixing with the mole fraction x_2 to obtained the molar excess free energy G^e given by

$$G^e = f_{12}'(T,x_2)x_2(1 - x_2) \quad (18)$$

The function $f_{12}'(T,x_2)$ was assumed to be independent of T and to be written as

$$f_{12}'(T,x_2) = a' + b'/(c' + x_2) \quad (19)$$

The total vapor pressure p can be calculated from the observed boiling point data with eq 14–17 or eq 14, 18, and 19. The parameters a, b, and c in eq 17 and a' b' and c' in eq 19 were determined by trial and error so as to give the constant pressures at which the boiling temperatures were measured. This analysis yielded a constant pressures within an error of ±3 mmHg for the system BuCl + BuOH, ±1 mmHg for BuCl + AcN, and ±2 mmHg for methanol + benzene. The errors seemed to be attributed to the experimental uncertainties rather than the above method for determining the function g_{12}. For the system methanol + benzene the correction of −0.7 °C for the measured lower limit temperature increased the molar excess free energy by 4–8%. The results of the data analyses of the boiling point are summarized as

$$g_{12} = 1.95 - 1.37u_2 + 0.57u_2{}^2 \quad (20)$$

for the system BuCl (1) + BuOH (2) at 40 °C,

$$g_{12} = 2.92 - 1.54u_2 + 0.54u_2{}^2 \quad (21)$$

for BuCl (1) + AcN (2) at 25 °C, and

$$G^e = x_2(1 - x_2)[860 + 310/(1.41 - x_2)] \quad (22)$$

for methanol (1) + benzene (2) at 25 °C. The above excess free energy for methanol + benzene was found to agree with literature values within the error of a few percent except at $x_2 = 0.1$ and 0.9, where the present values are lower by 7 and 6% than literature data, respectively.[23] The uncertainties in g_{12} for the systems BuCl + BuOH and BuCl + AcN could be comparable with those for methanol + benzene.

Horta et al. measured the molar excess free energy of the system BuCl + AcN at 25 °C by a light-scattering method.[25] The relation between the function g_{12} and the molar excess free energy G^e is written as

$$G^e = RT[g_{12}x_1u_2 - x_1 \ln (x_1/u_1) - x_2 \ln (x_2/u_2)] \qquad (23)$$

which allows us to compare the present results with Horta's data. The molar excess free energy calculated from eq 21 was found to be smaller than that found by Horta et al. Their values are about 17% larger than the present ones in the range $x_2 > 0.5$, and the difference becomes more than 30% in the range $x_2 < 0.2$. The light-scattering technique does not appear to be a pertinent method for the system BuCl + AcN, because the light-scattering intensity due to concentration fluctuation would be relatively low on account of the small refractive index difference between BuCl and AcN. Therefore, we will use the interaction function g_{12} given by eq 21 for the analyses of the second virial coefficient and the sorption coefficient.

Heats of mixing for solvent mixtures can be expressed as

$$\Delta H = Rh_{12}N_1u_2 \qquad (24)$$

corresponding to eq 15, and the Gibbs–Helmholtz equation gives

$$h_{12} = -T^2(\partial g_{12}/\partial T)_{p,u_2} \qquad (25)$$

The observed heats of mixing were represented by

$$h_{12} = 441 + 187/(0.127 + u_2) \qquad (26)$$

for the system BuCl (1) + BuOH (2) at 40 °C and

$$h_{12} = 391 + 139/(0.249 + u_2) \qquad (27)$$

for BuCl (1) + AcN (2) at 25 °C. According to eq 16 we obtain $h_{12} = f(u_2)$. However, this is not the case for the present systems. For the system BuCl + AcN the ratio $f(u_2)/h_{12}$ varies between 1.0 and 1.2, depending on the composition, while for the system BuCl + BuOH the ratio is small and varies from 0.3 to 0.6 with increasing u_2. For the system methanol + benzene the ratio of the molar excess free energy to the heats of mixing changes from 1.0 to 3.0 with decreasing x_2 at 25 °C.[23,24] The assumed temperature dependence of the interaction function given by eq 16 and 19 is not compatible with the observed heats of mixing especially for the systems BuCl + BuOH and methanol + benzene. However, the fairly good agreement of the present values of G^e with literature ones for the system methanol + benzene indicates the temperature dependence of eq 16 and 19 is a relevant approximation to estimate the excess free energy at a constant temperature from boiling point data in a restricted temperature range.

Since the binary interaction function g_{ij} was estimated, the second virial coefficient can be calculated by eq 3 assuming $g_T = 0$. The calculated maximum values of A_2^0 were 10 and 6 times larger than the observed ones for the systems PMMA + BuCl + AcN and PMMA + BuCl + BuOH, respectively. This large discrepancy between calculation and observation also has been shown in other systems[6,7] and therefore, the ternary function $g_T(u_2,\phi_3)$ should be introduced in eq 1 for the system polymer + mixed solvent.

Generalized Flory–Huggins Equation for the System BuCl (1) + BuOH (2) + PMMA (3). For this system an assumption was made for the sorption coefficient λ for lack of the experimental data. For many cosolvent systems, the inversion in λ has been observed at the composition where the second virial coefficient has its maximum value.[10] Therefore, we assumed $\lambda = 0$ at $u_2 = 0.3$ (see Figure 4). On account of this limited information on the sorption coefficient, we have analyzed the functions $\alpha(u_2)$ and $\beta(u_2)$ with a minimum number of parameters, that is

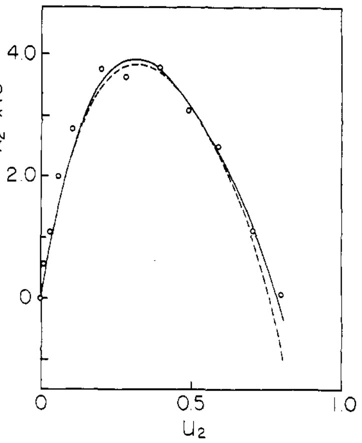

Figure 4. Plot of the second virial coefficient A_2^0 ((cm^3 mol)/g^2) versus the volume fraction u_2 for the system 1-chlorobutane (1) + 2-butanol (2) + PMMA (3). A_2^0 is corrected for the excluded-volume effect. Solid curve and broken curve were calculated by using eq 28 and 29 with the optimal parameters for the two values of $A_2(u_2{=}1) = -4.6 \times 10^{-4}$ and -6.3×10^{-4}, respectively.

$$\alpha(u_2) = A + Bu_2 \qquad (28)$$

$$\beta(u_2) = C + Du_2 \qquad (29)$$

where A, B, C, and D are constants. Since as shown by eq 4–6 the sorption coefficient includes only the function $\alpha(u_2)$ and its derivative, we determined the parameters A and B so as to yield $\lambda^0 = 0$ at $u_2 = 0.3$. For the values of A and B thus determined, we sought the values of the parameters C and D which brought about an agreement between the calculated and the observed second virial coefficient. The above analysis was repeated for the various values of the parameters A, B, C, and D, until an agreement in the second virial coefficient was attained in the whole range of $0 \leq u_2 \leq 0.8$. The behavior of the observed values of A_2^0 was found to be well represented by eq 3 combined with the parameters $A = 1.72$, $B = -0.95$, $C = 2.04$, and $D = -1.25$. In Figure 4, A_2^0 is plotted against u_2, where the solid curve is calculated with the above values of the parameter and the open circles are the experimental data. The calculated values of λ^0 changed from negative to positive at $u_2 = 0.3$ with increasing u_2 and their magnitude was very small as $|\lambda^0| < 0.024$, which would be about one-tenth of usual experimental values for cosolvent systems. In the preceding paper the mixture BuCl (1) + BuOH (2) at $u_2 = 0.80$ was found to give a Θ condition at 39.0 °C in light of $A_2 = 0$ and the mean-square radius of gyration equal to the unperturbed one.[18] The very small value of $\lambda^0 = 0.02$ at $u_2 = 0.80$ seems to legitimate this Θ condition. In Figure 5 the functions $g_{12}(u_2)$,$\alpha(u_2)$ and $\beta(u_2)$ are plotted against u_2. All the functions are of the same magnitude and decrease monotonously with increasing u_2.

The value of A_2 at 40 °C in pure BuOH determined by extrapolation is not so convincing because of the rapid decrease of A_2 with decreasing temperature as shown in Figure 3. As another estimate of A_2 at $u_2 = 1$, the extrapolation to 40 °C was made with a straight line tangent at $A_2 = 0$ to the smooth curve for the data points. The tangent described by the chain line in Figure 3 gives $A_2 = -6.3 \times 10^{-4}$ at 40 °C. This value of A_2 yields $g_{23} = 0.779$, for which we repeated the same analysis to determine the parameters A, B, C, and D in eq 28 and 29. The result of the analysis was represented by $A = 1.84$, $B = -1.20$, $C =$

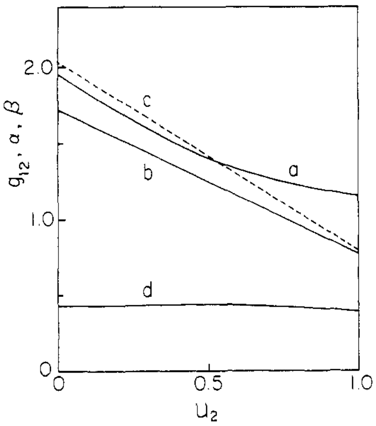

Figure 5. Plots of the binary interaction functin $g_{12}(u_2)$ (curve a), the ternary functions $\alpha(u_2)$ (curve b), and $\beta(u_2)$ (curve c) versus the volume fraction u_2 for the system 1-chlorobutane (1) + 2-butanol (2) + PMMA (3). Curve d represents the ratio $\alpha(u_2)/[g_{12}(u_2) + \beta(u_2)]$.

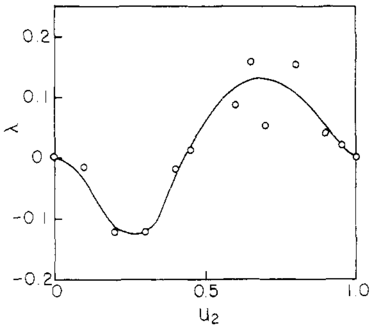

Figure 6. Plot of the sorption coefficient λ versus the volume fraction u_2 for the system 1-chlorobutane (1) + acetonitrile (2) + PMMA (3). The data were taken from ref 4. The solid curve was used for the estimation of the function $\alpha(u_2)$.

2.28, and $D = -1.65$. The second virial coefficient A_2^0 calculated with these values is described by the broken curve in Figure 4. The smaller value near $u_2 = 0.8$ shown by the broken curve is likely from an underestimate of $A_2 = -6.3 \times 10^{-4}$. The sorption coefficient λ^0 calculated with $g_{23} = 0.779$ again gave low values ranging from -0.01 to 0.032. The functions $\alpha(u_2)$ and $\beta(u_2)$ obtained for $g_{23} = 0.779$, which could be overestimated, are not largely different from those obtained for $g_{23} = 0.749$. Therefore, the uncertainties in g_{23} have a minor effect in determining the functions. Thus, the characteristic behavior of the function $\alpha(u_2)$ and $\beta(u_2)$ could be well represented by the parameters A, B, C, and D obtained for $A_2 = -4.6 \times 10^{-4}$.

Generalized Flory–Huggins Equation for the System BuCl (1) + AcN (2) + PMMA (3). For this system we first tried the same analysis as for the system BuCl + BuOH + PMMA with eq 28 and 29. However, the behavior of the observed second virial coefficient as a function of u_2 could not be represented by the four parameters in eq 28 and 29. This implied that the functional form of $\alpha(u_2)$ and $\beta(u_2)$ for this system is different from that for the system BuCl + BuOH + PMMA. Hence, we followed the analysis due to Chu and Munk to determine the functions $\alpha(u_2)$ and $\beta(u_2)$.[7] They defined a new function $L(u_2)$ by

$$L(u_2) = \lambda/(u_1 u_2 \bar{v}_3) \qquad (30)$$

Combining eq 30 with eq 4 and then substituting it into eq 3 we get

$$b_{23} = L(u_2) b_{22} \qquad (31)$$

$$b_{33} = (2\bar{V}_1/\bar{v}_3^2)A_2^0 + L^2(u_2) b_{22} u_1 u_2 \qquad (32)$$

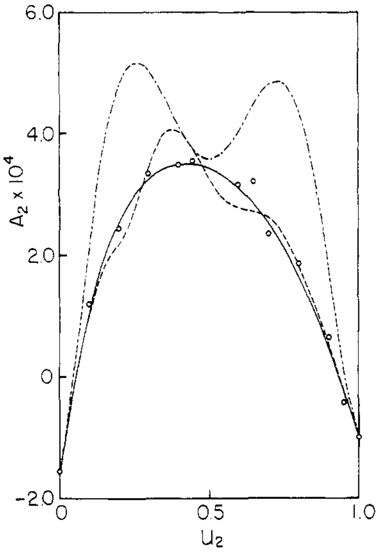

Figure 7. Plot of the second virial coefficient A_2 ((cm^3 mol)/g^2) versus the volume fraction u_2 for the system 1-chlorobutane (1) + acetonitrile (2) + PMMA (3). Experimental data were taken from ref 4. Solid curve was used for the estimation of the function $\beta(u_2)$. The broken curve and the chain curve were calculated with and without the term due to b_{23} (eq 6), respectively.

Thus, b_{23} and b_{33} can be determined as a function of u_2, because $L(u_2)$, A_2^0, and b_{22} are obtained by experiment. By using eq 31 the integration of eq 6 with respect to u_2 gives

$$(1 - u_2)u_2(g_T^0 - g_{12}) = [-1 + g_{13} + (1 - g_{23})/r_2]u_2 + \int_0^{u_2} L(u_2) b_{22}\, du_2 \qquad (33)$$

Considering the boundary value at $u_2 = 1$, the function $\alpha(u_2)$ [$=g_T^0$] can be expressed as

$$\alpha(u_2) = g_{12} - [1/(1 - u_2)]\int_0^1 L(u_2) b_{22}\, du_2 + [1/(u_1 u_2)]\int_0^{u_2} L(u_2) b_{22}\, du_2 \qquad (34)$$

with

$$g_{13} - g_{23}/r_2 = 1 - (1/r_2) - \int_0^1 L(u_2) b_{22}\, du_2 \qquad (35)$$

Then, from eq 7 $\beta(u_2)$ [$=(\partial g_T/\partial \phi_3)^0$] is obtained as

$$\beta(u_2) = \{b_{33}/2 - (u_2/r_2)[(1/2) - \chi_{23}] - (1 - u_2)[(1/2) - \chi_{13}] - (1 - u_2)u_2(g_{12} - 2g_T^0)\}/[(1 - u_2)u_2] \qquad (36)$$

Thus, we can calculate the functions $\alpha(u_2)$ and $\beta(u_2)$ from the experimental data of λ and A_2.

Figure 6 shows the relation of λ versus u_2 for the system BuCl (1) + AcN (2) + PMMA (3) obtained by Horta et al.[4] Since we consistently use the volume fraction u_2 of AcN as a variable, λ in Figure 6 has an opposite sign to that by Horta et al. and corresponds to the excess number of BuCl molecules in a polymer domain. The solid curve in Figure 6 depicts the behavior of the experimental data points. In Figure 7 A_2 is plotted against u_2. The solid curve illustrates the experimental data of the open circles. The estimation of the function $\alpha(u_2)$ and $\beta(u_2)$ was carried out as follows. The values of λ and A_2 were read from the solid lines in Figures 6 and 7 at intervals of $u_2 = 0.05$. $L(u_2)b_{22}$ calculated from the values of λ and g_{12} was fitted by a fifth-degree polynomial of u_2 with a least-squares method. Then, $\alpha(u_2)$ was obtained by a straightforward integration of eq 34. b_{33} was calculated from λ and A_2 according to eq 32. The obtained expression for $\alpha(u_2)$ and the values of b_{33} were substituted into eq 36 to calculated

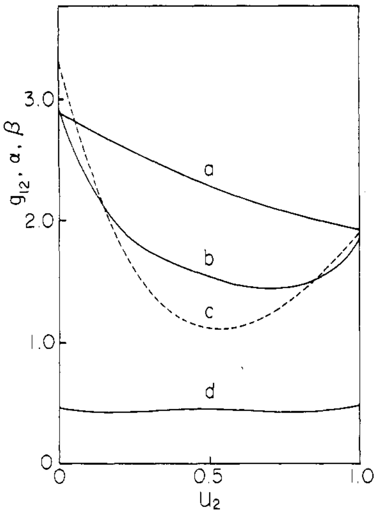

Figure 8. Plots of the binary interaction function $g_{12}(u_2)$ (a), the ternary functions $\alpha(u_2)$ (b), and $\beta(u_2)$ (c) versus the volume fraction u_2 for the system 1-chlorobutane (1) + acetonitrile (2) + PMMA (3). Curve d describes the ratio $\alpha(u_2)/[g_{12}(u_2) + \beta(u_2)]$.

$\beta(u_2)$. The somewhat lengthy expression for $\alpha(u_2)$ and the values of $\beta(u_2)$ thus obtained were fitted by a fourth-degree polynomial of u_2 as

$$\alpha(u_2) = 2.94 - 7.89u_2 + 18.61u_2^2 - 21.85u_2^3 + 10.03u_2^4 \tag{37}$$

$$\beta(u_2) = 3.33 - 9.90u_2 + 13.76u_2^2 - 6.27u_2^3 + 0.97u_2^4 \tag{38}$$

In Figure 8 $\alpha(u_2)$ and $\beta(u_2)$ are plotted against u_2 according to eq 37 and 38, respectively. The function $g_{12}(u_2)$ is also given in this Figure.

In Figure 7 the behavior of A_2 reproduced with eq 37 and 38 is shown by the broken curve, which has shoulders near $u_2 = 0.2$ and 0.65. Equation 37 could represent the calculated values of $\alpha(u_2)$ within an error of 0.1%, while eq 38 could approximate the calculated values of $\beta(u_2)$ within an error of 3.0%. The comparison of the solid curve and the broken curve in Figure 7 indicates that the calculation of A_2 is very sensitive to the value of $\beta(u_2)$, because the different shapes of the solid and broken curves are mainly due to the approximate expression of eq 38. Horta et al. calculated A_2 assuming $b_{23} = 0$, that is, with the single-liquid approximation.[26] In the present case the estimation of A_2 with $b_{23} = 0$ gives the chain curve with two peaks in Figure 7. The term due to b_{23} is not negligibly small. Except for the range $u_2 = 0.25$–0.75 the term $b_{23}^2u_1u_2$ amounts to more than a half of the term $b_{22}b_{33}$ in eq 3. The competition of the two terms makes the behavior of the calculated A_2 sensitive to the value of $\beta(u_2)$.

Comments and Conclusions

For the system BuCl + BuOH + PMMA the behaviors of $g_{12}(u_2)$, $\alpha(u_2)$, and $\beta(u_2)$ are parallel to each other both in magnitude and u_2 dependence as shown in Figure 5. For the system BuCl + AcN + PMMA the u_2 dependences of $g_{12}(u_2)$ and $\beta(u_2)$ are considerably different and the values of $g_{12}(u_2)$, $\alpha(u_2)$, and $\beta(u_2)$ are comparable only near $u_2 = 0$ and 1.

Figueruelo et al. proposed an empirical relation among $g_{12}(u_2)$, $\alpha(u_2)$, and $\beta(u_2)$, which is written as

$$\alpha(u_2) = K[g_{12}(u_2) + \beta(u_2)] \tag{39}$$

with K being a constant.[16,17] They conjectured that K is expressed by the binary interaction parameters as $K = g_{13}{}^0g_{23}{}^0$. In Figures 5 and 8 the ratio $\alpha(u_2)/[g_{12}(u_2) + \beta(u_2)]$ is depicted by the solid curve d. For the system BuCl + BuOH + PMMA the ratio varies between 0.442 and 0.425 in the range $0 \leq u_2 \leq 0.8$ and decreases from 0.425 to 0.397 in $0.8 \leq u_2 \leq 1$. The average value of the ratio could be 0.43. For the system BuCl + AcN + PMMA the ratio lies between 0.456 and 0.425 in the range $0.05 \leq u_2 \leq 0.95$ and shows the somewhat high values of 0.470 at $u_2 = 0$ and 0.483 at $u_2 = 1$. The average value could be 0.44. The constancy of the ratios for the two systems is remarkable when compared with the large u_2 dependences of $g_{12}(u_2)$, $\alpha(u_2)$, and $\beta(u_2)$. The average values 0.43 for BuCl + BuOH + PMMA and 0.44 for BuCl + AcN + PMMA are considerably lower than the respective values 0.50 and 0.48 estimated by $K = g_{13}{}^0g_{23}{}^0$ and eq 12. Figueruelo et al.[16] demonstrated the validity of eq 39 for six ternary systems, though their methods for estimating the functions $\alpha(u_2)$ and $\beta(u_2)$ are not clear. In the present studies the functions $\alpha(u_2)$ and $\beta(u_2)$ were evaluated in different ways for the two systems. For the system BuCl + AcN + PMMA Figueruelo et al. obtained $K = 0.455$ with values of g_{12} considerably different from ours. Thus, the constant values of K obtained with the different methods support an intimate correlation between the functions $g_T(u_2,\phi_3)$ and $g_{12}(u_2)$, though the each function of $\alpha(u_2)$ and $\beta(u_2)$ is not related to $g_{12}(u_2)$ explicitly.

The solvent mixtures BuCl + BuOH and BuCl + AcN are different in the thermodynamic properties. For the system BuCl + BuOH the excess free energy is about a half of the heats of mixing, while for the system BuCl + AcN an entropy term has a small contribution in the excess free energy. However, the strong correlation between $g_{12}(u_2)$ and $g_T(u_2,\phi_3)$ shown by eq 39 indicates that the behavior of the present ternary systems is governed only by the function $g_{12}(u_2)$. The specific properties of the solvent mixtures due to the entropy contribution in the excess free energy affect the behavior of the function $g_T(u_2,\phi_3)$ only through the function $g_{12}(u_2)$.

Horta[27,28] has applied the equation-of-state theory[29] to the ternary system polymer + mixed solvent and showed that the ternary function can be represented by the molecular parameters of the pure components and the interaction function g_{12}. In the final expressions for eq 6 and 7 by Horta's theory, the ternary functions are unnecessary but the interaction function g_{12} is multiplied by constant factors. Equation 5 for b_{22} remains in the same form in Horta's theory. Therefore, the comparison of the present phenomenological equations with Horta's leads to the relations

$$g_{12} - g_T{}^0 = fg_{12} \tag{40}$$

$$g_{12} - g_T{}^0 - \chi_T{}^0 = f'g_{12} \tag{41}$$

where the constants f and f' are given by

$$f = \tilde{V}_1/\tilde{V}_3(s - \alpha) \tag{42}$$

$$f' = (\tilde{V}_1/\tilde{V}_3)^2(s^2 - \alpha' - s\alpha) \tag{43}$$

Here, $\tilde{V}_i$ is the reduced molar volume of component i, s is the ratio of contact sites per segment of polymer to solvent, α is proportional to the difference in characteristic temperature between polymer and solvent, and α' is the product of α and the ratio of characteristic pressure of polymer to solvent. According to eq 40 and 41, $g_T{}^0$ and $(\partial g_T/\partial\phi_3)^0$ are proportional to the function g_{12} and K in eq 39 is given by

$$K = (1 - f)/(2 - 2f + f') \tag{44}$$

For the system BuCl + AcN + PMMA Horta estimated the constants f and f' as $f = 0.41$ and $f' = 0.03$, which give

$K = 0.49$. This value is close to the observed value, 0.44, and agrees with the value due to the relation $K = g_{13}{}^0 g_{23}{}^0$ and eq 12. Since the average values of the characteristic quantities for the two solvent components are used to estimate the values of f and f', the value of $K = 0.49$ could be also compared with the value for the system BuCl + BuOH + PMMA. In view of the parallel behavior of $g_{12}(u_2)$, $\alpha(u_2)$, and $\beta(u_2)$ shown in Figure 5 the system BuCl + BuOH + PMMA appears to be better explained by Horta's theory. Thus, according to Horta's theoretical calculation the observed ternary function g_T could not be attributed to the specific properties of the solvent mixture but was due to the equation-of-state effect.

Registry No. PMMA, 9011-14-7; BuOH, 78-92-2; BuCl, 109-69-3; AcN, 75-05-8.

References and Notes

(1) Deb, P. C.; Palit, S. R. *Macromol. Chem.* **1973**, *166*, 277.
(2) Wolf, B. A.; Blaum, G. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1115.
(3) Cowie, J. M. G.; McCrindle, J. T. *Eur. Polym. J.* **1972**, *8*, 1185.
(4) Horta, A.; Fernandez-Pierola, I. *Macromolecules* **1981**, *14*, 1519.
(5) Prolongo, M. G.; Masegosa, R. M.; Hernandez-Fuentes, I.; Horta, A. *Macromolecules* **1981**, *14*, 1526.
(6) Masegosa, P. M.; Prolongo, M. G.; Hernandez-Fuentes, I.; Horta, A. *Macromolecules* **1984**, *17*, 1181.
(7) Chu, S. G.; Munk, P. *Macromolecules* **1978**, *11*, 879.
(8) Aminabhavi, T. M.; Munk, P. *Macromolecules* **1979**, *12*, 607.
(9) Katime, I.; Strazielle, C. *Makromol. Chem.* **1977**, *178*, 2295.
(10) Gavara, R.; Celda, B.; Campos, A. *Eur. Polym. J.* **1986**, *22*, 373.
(11) Read, B. E. *Trans. Faraday Soc.* **1960**, *56*, 382.
(12) Pouchlý, J.; Ziviny, A.; Šolc, K. *J. Polym. Sci., Part C* **1968**, *23*, 245.
(13) Dondos, A.; Patterson, D. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 209.
(14) Pouchlý, J.; Zivny, A. *Makromol. Chem.* **1982**, *183*, 3019.
(15) Pouchlý, J.; Zivny, A. *Makromol. Chem.* **1983**, *184*, 2081.
(16) Figueruelo, J. E.; Celda, B.; Campos, A. *Macromolecules* **1985**, *18*, 2504.
(17) Figueruelo, J. E.; Campos, A.; Celda, B. *Macromolecules* **1985**, *18*, 2511.
(18) Nakata, M.; Nakano, H.; Kawate, K. *Macromolecules*, preceding paper in this issue.
(19) Nakata, M.; Numasawa, N. *Macromolecules* **1985**, *18*, 1741.
(20) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; 3rd ed.; McGraw-Hill: New York, 1977.
(21) Fortier, J.-L.; Benson, G. C. *J. Chem. Thermodyn.* **1976**, *8*, 411.
(22) Olabisi, O.; Shimha, R. *Macromolecules* **1975**, *8*, 206.
(23) Scatchard, G.; Ticknor, L. B. *J. Am. Chem. Soc.* **1952**, *74*, 3724.
(24) Goates, J. R.; Snow, R. L.; James, M. R. *J. Phys. Chem.* **1961**, *65*, 335.
(25) Fernândez-Piĕrola, I.; Horta, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77*, 271.
(26) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 268.
(27) Horta, A. *Macromolecules* **1979**, *12*, 785.
(28) Horta, A. *Macromolecules* **1985**, *18*, 2498.
(29) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.

Statistical Theory of Rayleigh Scattering of Light in Deformed and Swollen Heterogeneous Amorphous Polymer Networks

S. A. Patlazhan

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, Moscow Region, 142432 USSR.

Received April 13, 1987; Revised Manuscript Received September 4, 1987

ABSTRACT: A statistical theory of Rayleigh scattering of light in heterogeneous Gaussian amorphous polymer networks, subjected to deformation or swelling, is developed. The scattered intensity is shown to depend on the mean square of fluctuations of the shear modulus and increases in a nonlinear way with the degree of network elongation or swelling. Results of the calculation agree with experimental data on the angle distribution of scattered intensity on the screen.

1. Introduction

Knowledge of light-scattering characteristics in a condensed medium provides one of the main sources of information about the structure of the medium.[1–3] Such a method of diagnosis is being widely used in scientific research and applications. At the same time there is an imperative of further development of theoretical concepts of the light scattering. A problem of this kind arises, in particular, when analyzing optical properties of deformed polymers. This is caused by several factors. One of them is that polymer materials are characterized by complex inhomogeneities of various types.[4] For example, in amorphous networks there are random spatial fluctuations of the cross-link concentration which produce regions with different elastic properties (namely, different values of the elastic modulus). Such inhomogeneities do not have abrupt borders. Their spatial distribution reflects conditions of network formation. Experiments show that deformation or swelling of such systems results in qualitative changes in the light-scattering pattern. Therefore the main objective of theory in reconstruction of basic structural characteristics of inhomogeneous networks based upon the light-scattering data.

Two main approaches have been developed for studying properties of heterogeneous materials, namely, the "regular" approach and the statistical approach.[2] The former treats inhomogeneity regions as inclusions having specific geometric form (sphere, rod, disk). The resultant scattering intensity is thus determined by a sum of contributions of different inclusions to the scattering. This approach was successfully applied to describe the small-angle light scattering from spherulites[2–5] and from assemblies of oriented rods and plates.[6–9] The regular approach made it possible to interpret observable patterns of polarized light scattering in swelled and deformed polymer films filled with solid spheres.[10–12] It was shown, in particular, that an additional scattering in deformed media is caused by a nonuniform distribution of dielectric permeability, induced by elastic stress fields in the vicinity of inclusions.

It should be noted that within the framework of the regular approach one has to invoke data on the structure