Note on Polymer-mixed Solvents System. III. Selective Adsorption

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A recent paper by Ewart, Roe, Debye, and McCartney (E. R. D. M.)$^{(1)}$ on the light scattering of polymer dissolved in binary mixtures suggests that this method should yield interesting information regarding the interaction of polymer not only with good solvents but with non-solvents. As was shown by the authors mentioned above, the addition of a third component to a polymer-solvent mixture should cause a change in light scattering due to preferential adsorption of one or other of the solvent components by the polymer. Result obtained by them may be written

$$\lim_{c\to 0}(\tau/c)=M\times(32\pi^3n^2/3\lambda^4N_0)(\partial n/\partial c+\alpha\,\partial n/\partial\varphi)^2, \qquad (1)$$

where τ = turbidity, c = concentration of polymer, M = molecular weight of polymer, n = refractive index, λ = wave-length of exciting radiation, N_0 = Avogadro's number, φ = volume fraction of solvent in a solvent-diluent mixture exclusive of the volume occupied by the polymer, and $\alpha=-\partial\varphi/\partial c$.

The significance of this factor α can bn understood as a measure of the change ie composition of the solvent-diluent mixture (surrounding the polymer) due to selective adsorption. Thus, if the solvent component adsorbed has a higher refractive index than the diluent ($\partial n/\partial\varphi>0$), the ratio of polymer concentration to turbidity in the limit of zero concentration, $(c/\tau)_0$, should decrease. The contrary would be true if the refractive indices were in the reverse order.

On the other hand, a comprehensive theory of composition fluctuations in multi-component systems has been developed independently by Kirkwood and Goldberg,$^{(2)}$ and Stockmayer.$^{(3)}$ In their discussions, the deviation

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(1) R. H. Ewart, C. P. Roe, P. Debye and J. R. McCartney, *J. Chem. Phys.*, **14**, 687 (1946).

(2) J. G. Kirkwood and E. J. Goldberg, *J. Chem. Phys.*, **18**, 54 (1950).

(3) W. H. Stockmayer, *J. Chem. Phys.*, **18**, 58 (1950).

of the value of M calculated from the limiting value, $(\tau/c)_0$, from the true molecular weight was interpreted as showing that the thermodynamic interaction between a polymer and a diluent may cause the former to induce composition fluctuations with respect to the latter of the same order of magnitude as composition fluctuations with respect to the polymer species itself. Therefore, the approximate treatment of E. R. D. M., in which such deviation was discussed under the consideration of selective adsorption of one of the solvent components by polymer, should be regarded as a supplementing one on some molecular assumption rather than the basis for an exact analysis of turbidity data. However, such an approximate treatment may give some interesting information concerning selective adsorption in the actual polymer-mixed solvents systems. It will be shown in the present paper that the magnitude of selective adsorption can be well interpreted quantitatively by the interaction parameters characterizing the polymer-mixed solvents system, which were introduced in the free energy expression presented in the previous paper.⁽⁴⁾ This will enable us to estimate the magnitude of selective adsorption in any system if the values of the interaction parameter are known. (The various methods by which the interaction parameters can be calculated were already presented in the previous paper.⁽⁵⁾) Here it is also shown that these parameters can be computed from turbidity data by considering the dependence on polymer concentration.

The Significance of the Factor α

The theoretical treatments of light scattering in multi-component systems permit us to express the results of light scattering measurements in the language of thermodynamics. According to Stockmayer,⁽³⁾ turbidity τ is adequately represented by an equation of the form

$$\tau = HV\sum_i\sum_j\psi_i\psi_jA_{ij}/\mid a_{ij}\mid \qquad (2)$$

where $H=32\pi^3n^2kT/3\lambda^4$, $\psi_i=(\partial n/\partial m_i)_{T,P,m}$ (n is the refractive index, and the quantities m_i of the component i in volume V may be measured by any desired units, the definitions of their chemical potentials μ_i varying accordingly), $a_{ij}=(\partial\mu_i/\partial m_j)_{T,P,m}$, $\mid a_{ij}\mid$ represents the determinant of all the a_{ij}, and A_{ij} is the co-factor. From Eq. (2) the difference $\Delta\tau$, between the turbidity of the polymer 3-solvents 1 and 2 system⁽⁶⁾ and that of the solvents mixed in the same proportion in the absence of polymer, may be written

$$\Delta\tau/HV=\frac{\psi_3{}^2a_{22}-2\psi_2\psi_3a_{23}+\psi_2{}^2a_{33}}{a_{33}a_{22}-a_{23}{}^2}-\frac{\psi_2{}^2}{a_{22}{}^0}$$
$$=\frac{[\psi_3-(a_{23}/a_{22})\psi_2]^2}{a_{33}-a_{23}{}^2/a_{22}}+\psi_2{}^2\left(\frac{1}{a_{22}}-\frac{1}{a_{22}{}^0}\right), \qquad (3)$$

where the superscript zero denotes a solution containing no polymer. Obviously from the discussion in the last section on the dependency of the a's on polymer concentration, $(\Delta\tau/HC)_0$ at infinite dilution, may be given by

$$(\Delta\tau/HC)_0=M[\psi_3-(a_{23}/a_{22})\psi_2]^2. \qquad (4)$$

Eq. (4) agrees with the result of E. R. D. M (Eq. (1)). The correspondence is better seen when the equality

$$a_{23}/a_{22}=\frac{(\partial\mu_2/\partial m_3)_{T,P,m_3}}{(\partial\mu_2/\partial m_2)_{T,P,m_2}}$$
$$=-(\partial m_2/\partial m_3)_{T,P,\mu_2} \qquad (5)$$

is examined. It is clear that the ratio a_{23}/a_{22} is the analogue of the factor α. Thus, we can assume the factor α as a measure of the magnitude of selective adsorption, because the significance of the factor can be interpreted through the thermodynamic description of light scattering in the multi-component system.

Theoretical Treatment of Selective Adsorption

In the previous paper⁽⁴⁾ a general free energy expression covering much of the experimental data has been derived for the polymer-mixed solvents system, removing the Scott's assumptions,⁽⁷⁾ which are not always applicable to the actual cases. The partial molal free energy of components may be written⁽⁸⁾

$$\Delta\bar{F}_1=RT[(V_1/V_3)\{\ln v_1+(1-1/x)v_3+\mu_sv_3{}^2\}$$
$$+(V_1/RT)\{A_{12}v_2{}^2+A_{13}v_3{}^2$$
$$+(A_{12}+A_{13}-A_{23})v_2v_3\}] \qquad (6a)$$
$$\Delta\bar{F}_2=RT[(V_2/V_3)\{\ln v_2+(1-1/x)v_3+\mu_sv_3{}^2\}$$
$$+(V_2/RT)\{A_{12}v_1{}^2+A_{23}v_3{}^2$$
$$+(A_{12}+A_{23}-A_{13})v_1v_3\}]. \qquad (6b)$$

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(4) T. Kawai, This Bulletin, **25**, 336 (1952).

(5) T. Kawai, This Bulletin, **25**, 341 (1952).

(6) Here we adopt the same notation of components 1, 2, 3 as employed in the previous papers (reference 4 and 5) instead of that of Stockmayer.

(7) R. L. Scott, *J. Chem. Phys.*, **17**, 268 (1949).

(8) See Eq. (19a, b) in reference 4. As discussed there, the volume of polymer submolecule is larger than molecular volumes of both solvent and diluent in the actual systems.

The notation of these equations is similar to that was employed in the previous paper.⁽⁴⁾

Generally, when two phases co-exist in equilibrium,

$$\Delta\bar{F}_1' = \Delta\bar{F}_1'' \tag{7a}$$

$$\Delta\bar{F}_2' = \Delta\bar{F}_2'' \tag{7b}$$

$$\Delta\bar{F}_3' = \Delta\bar{F}_3'' \tag{7c}$$

must be fulfilled in a three component system. (Here we distinguish the two phases by primes and double primes.) Combining Eqs. (7a) and (7b)⁽⁹⁾ through respective substitution from Eqs. (6a) and (6b), there is obtained

$$\begin{aligned}\ln(v_1'/v_2') - \ln(v_1''/v_2'') = (V_3/RT)[\{A_{12}v_2''^2 \\ - A_{13}v_1''^2 + (A_{13} - A_{23})v_3''^2 + (A_{12} + A_{13} \\ - A_{23})v_2''v_3'' - (A_{12} + A_{23} - A_{13})v_1''v_3''\} \\ - \{A_{12}v_2'^2 - A_{13}v_1'^2 + (A_{13} - A_{23})v_3'^2 + (A_{12} \\ + A_{13} - A_{23})v_2'v_3' - (A_{12} + A_{23} - A_{13})v_1'v_3'\}].\end{aligned} \tag{8}$$

If we write $v_2'/v_1' = \theta'$, $v_2''/v_1'' = \theta''$, $v_1 = v_0/(1+\theta)$, and $v_2 = \theta v_0/(1+\theta)$, Eq. (8) may be converted to the form

$$\begin{aligned}\ln(\theta''/\theta') = (V_3/RT)\Big[(v_0'' - v_0')\Big\{-\Big(\frac{1-\theta'}{1+\theta'}\Big)A_{12} \\ - A_{13} + A_{23}\Big\} - v_0''\Big\{\Big(\frac{1-\theta''}{1+\theta''}\Big) - \Big(\frac{1-\theta'}{1+\theta'}\Big)\Big\}A_{12}\Big].\end{aligned} \tag{9}$$

Here we rewrite $\theta' = \theta$, and $\theta'' = \theta + \Delta\theta$. Then, expanding the terms $\ln(\theta''/\theta')$ and $\Big\{\Big(\frac{1-\theta''}{1+\theta''}\Big) - \Big(\frac{1-\theta'}{1+\theta'}\Big)\Big\}$ in series of $\Delta\theta/\theta$, and neglecting terms after the first two, it follows that

$$\begin{aligned}\Delta\theta/\theta \doteqdot (V_3/RT)\Big[-\Delta v_3\Big\{-\Big(\frac{1-\theta}{1+\theta}\Big)A_{12} - A_{13} \\ + A_{23}\Big\} + \{2(1 - v_3'')\Delta\theta/(1+\theta)^2\} \times A_{12}\Big]\end{aligned} \tag{10}$$

$$\begin{aligned}\{1/\theta - [2(1 - v_3'')/(1+\theta)^2] \times A_{12}V_3/RT\}\Delta\theta \\ \doteqdot -(V_3/RT)\Delta v_3\Big\{-\Big(\frac{1-\theta}{1+\theta}\Big)A_{12} - A_{13} + A_{23}\Big\}\end{aligned} \tag{11}$$

where $\Delta v_3 = v_3'' - v_3' = v_0' - v_0''$.

Now, let us turn our attention to a polymer molecule in the solvent and consider the influence of its environments on it. It may be assumed that each molecule is distributed within an effective volume such as is often considered in the treatments of high polymer solutions especially for coiled molecules.⁽¹⁰⁾ The relations concerning the partition of the two solvents inside and outside of this effective volume pervaded by a polymer molecule will be obtained from the condition of the equilibrium between the above region and its environments. Approximately Eq. (10) may be applicable to this equilibrium, although, strictly speaking, the partial molal entropy in the region assumed could not be expressed by the entropy terms in Eqs. (6a, b).

Since the values of $A_{12}V_3/RT$ are supposed to be comparatively small in usual cases,⁽¹¹⁾ the term $\{2(1-v_3'')/(1+\theta)^2\} \times A_{12}V_3/RT$ in Eq. (11) can be neglected as compared with $1/\theta$, if θ were sufficiently small. (We assumed here liquid 1 is a principal solvent, and liquid 2 a diluent.) Thus, Eq. (11) becomes

$$\begin{aligned}-\Delta\theta/\theta \\ \doteqdot (V_3/RT)\Delta v_3\Big\{-\Big(\frac{1-\theta}{1+\theta}\Big)A_{12} - A_{13} + A_{23}\Big\}.\end{aligned} \tag{12}$$

Since $\Delta\theta/\theta$ is assumed to be a measure of the magnitude of selective adsorption and the A's are the interaction parameters characterizing the polymer-mixed solvents system, Eq. (12) enables us to estimate roughly the magnitude of selective adsorption in any system.

It was shown in the previous paper⁽⁵⁾ that the medium containing non-solvent to some extent sometimes behaves as a better solvent than the pure solvent itself, and that the solvent power of the mixture shows a maximum at the solvent-precipitant composition which fulfils the condition;

$$(V_0/RT)\Big\{-\Big(\frac{1-\theta}{1+\theta}\Big)A_{12} + A_{23} - A_{13}\Big\} = 0. \qquad (13)^{(12)}$$

Thus, we can draw an interesting conclusion from Eqs. (12) and (13) as follows. Namely, when the solvent has a strong solvent power and the diluent has a strong precipitating power, a polymer molecule exhibits a conspicuous preference for the solvent molecules in its statistical environment. In this case, of course, the solvent ability of the mixture decreases uniformly with increasing θ as was

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(9) Eq. (7 a) × V_3/V_1 − Eq. (7 b) × V_3/V_2

(10) For example, see T. Kawai, This Bulletin, **24**, 70 (1951).

(11) Although the exact values of V_3 cannot be deduced, the A_{12} values calculated from vapor pressure data in various two liquids systems show that the values of $A_{12}V_3/RT$ are anticipated in the range from 0.5 to 2.0.

(12) See Eq. (7) in reference (5). V_0 is a mean value of the volumes of the solvent and the diluent.

discussed in the previous paper(5)(when$A_{23}-A_{13}>A_{12}$, the solutions of Eq. (13) cannot afford any physical meaning). When the solvent abilities of the two liquids do not differ very much from each other, selective adsorption is not notable. However, the contribution of the parameter A_{12} must be considered. When the $(A_{23}-A_{13})$ value becomes comparable to the A_{12} value, the magnitude of selective adsorption depends considerably on the solvent-diluent composition as seen in Eq. (12). Actually, this can be true only when the $(A_{23}-A_{13})$ values are tolerably small since the values of A_{12} are comparatively small. If $A_{23}-A_{13}<A_{12}$, an inversion in the sign of $\Delta\theta/\theta$ in Eq. (12) occurs with increasing θ, i. e., the diluent is rather preferentially adsorbed by the polymer until $\theta=\theta_c$, at which Eq. (13) is satisfied, and hereafter the solvent is adsorbed much more than the diluent as in usual cases. This corresponds to the fact that the solvent ability of the medium is improved in the first stage of addition of the diluent, and, after a certain solvent-diluent composition is reached, it decreases as the content of the diluent increases. As was discussed in the previous paper,(5) it appears also from experiments that this phenomenon occurs sometimes in polymer-mixed solvents systems. The turbidity data presented by Blaker and Badger(13) for nitrocellulose-two liquids systems can well be interpreted from the above reasoning. Quantitative discussion is impossible because the above treatment can not be applied to non-flexible chains such as nitrocellulose. However, considering that the energy term in the free energy expression gives predominant contribution to the result obtained in the above approximate treatment, it may be clear that we can roughly estimate the magnitude of selective adsorption even in such a case. The experiments of Blaker and Badger can be understood from the above procedure as follows; the diluent is positively adsorbed by the polymer in the solvent-diluent composition range used $(\theta<\theta_c)$. As Blaker and Badger pointed out, rather strong interaction between nitrocellulose and non-solvents is not surprising from many experimental facts.(13)

Comparison with Experimental Data

The factor α is not a characteristic constant of any one system, because it does not appear to behave in the same way for different systems. The value of α varies with the volume occupied by the polymer in the solvent (accordingly with molecular weight and concentration of the polymer etc.) and solvent-diluent composition. If we adopt the assumption of E. R. D. M. concerning the physical size of the effectively pervaded volume of a polymer molecule in the solvent, the factor α may be written as

$$\alpha=-\frac{\partial\varphi}{\partial c}=\left(\frac{v}{m}-\bar{v}\right)(\varphi_1''-\varphi_1') \qquad (14)$$

where v is the volume effectively occupied by a polymer molecule, m its mass, $\bar{v}$ the partial specific volume of the polymer and $(\varphi_1''-\varphi_1')$ is the difference in the volume fractions of solvent between in the effectively pervaded volume and in its environment.(14) The value of v/m can be calculated from the intrinsic viscosity of the solution by employing the relation $[\eta]=2.5\,v/m$ (with concentration measured in grams per cc.). Since $\Delta\theta/\theta$ in Eq. (12) can easily be computed from the $(\varphi_1''-\varphi_1')$ value thus obtained, we can examine the validity of Eq. (12) comparing with turbidity data. (Since $\Delta v_3 \doteqdot v_3''$ in the present situation, Δv_3 can be estimated from the relation $[\mu]=2.5/v_3''\rho$, where ρ is the density of the polymer.) For this purpose the light scattering data of E. R. D. M. on solution of polystyrene in benzene-methanol mixture is cited. As will be discussed in the next section, the interaction parameters μ_{13}, μ_{23}, and μ_{12} have been employed instead of A_{13}, A_{23}, and A_{12} respectively ($\mu_{13}=(V_0/RT)A_{13}$, $\mu_{23}=(V_0/RT)A_{23}$, $\mu_{12}=(V_0/RT)A_{12}$)(15), and these parameters have been calculated from the dependency of turbidity on polymer concentration. Thus Eq. (12) may be rewritten as

$$-\Delta\theta/\theta$$

$$\doteqdot(V_3/V_0)\left\{-\left(\frac{1-\theta}{1+\theta}\right)\mu_{12}+\mu_{23}-\mu_{13}\right\}\Delta v_3. \qquad (15)$$

In Table 1 the numerical calculation of Eq. (15) for this system is illustrated. The V_3/V_0 values calculated by Eq. (15) show a satisfactory constancy for different compositions of the solvent-diluent mixtures as was shown in the last column in Table 1. In spite of the approximation supposed here, the result is rather surprising.

Owing to the scantiness of available data, we cannot show that the theory presented here gives a satisfactory explanation of the

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(13) R. H. Blaker and R. H. Badger, *J. Am. Chem. Soc.*, **72**, 3129 (1950).

(14) Considering that the $(\varphi_1''-\varphi_1')$ values depend on the solvent-diluent composition, we assume $\Delta\theta/\theta$ as a measure characteristic to the system with regard to the magnitude of selective adsorption.

(15) V_0 is a certain mean value of the molal volumes of solvent and diluent as employed in reference (4).

Table 1

Numerical Calculation of Eq. (15) for Polystyrene-benzene-methanol System

$\mu_{13}=0.45,\ \mu_{23}=3.20,\ \mu_{12}=2.67$

φ_1'	$\varphi_1''-\varphi_1'$	$-\Delta\theta/\theta$	$-\left(\frac{1-\theta}{1+\theta}\right)\mu_{12}+\mu_{23}-\mu_{13}$	$[\mu]$	Δv_3	V_3/V_0
1	0	0	0.45	131.5	0	
0.925	0.25	0.0359	0.48	122.0	0.0224	3.96
0.90	0.51	0.0563	0.61	118.7	0.0208	4.75
0.875	0.79	0.0679	0.75	110.6	0.0194	4.53
0.85	1.00	0.0775	0.88	102.6	0.0189	3.93

experiments in many other systems. The interaction parameters for polystyrene-butanone-isopropanol system are calculated as $\mu_{12}=0.168$, $\mu_{13}=0.487$, and $\mu_{23}=0.711$ from the turbidity data in the same paper. ($\mu_{13}=0.471$ from the osmotic pressure data of Doty, Brownstein and Schlener(16)) In this system $\alpha\,\partial n/\partial\varphi$ is negligible compared with $\partial n/\partial c$, and the limiting value of τ/HC at infinite dilution gives polymeric molecular weights in agreement with those found in pure solvents. Since this condition is fulfilled if either α or $\partial n/\partial c$ is sufficiently small and $\partial n/\partial c$ is extremely small in this case ($\partial n/\partial c=0.0004$), the value of α cannot be deduced from the turbidity data. It is supposed, however, from the μ's that α is probably very small in this system. Since the interaction parameters can be estimated from various other measurements of the colligative properties of polymer solutions as discussed in the previous paper, we can anticipate the magnitude of selective adsorption in any system.

Calculation of the Interaction Parameters

The theories of light scattering in multicomponent systems presented by the above mentioned authors provide a complete description of turbidity in the language of thermodynamics, although the significance of the interaction parameters employed individually by them is a little different in each case. If the relations between the parameters employed in our treatment and those of the others are given, we can compute the parameters in Eq. (15) from turbidity data.

The statistical treatment of general multicomponent systems by McMillan and Mayer(17) permits us to express the activity coefficient γ_s of component as

$$\ln\gamma_s=-\frac{1}{c_s}\sum_{\nu n}n_s B^*_{\nu n}\left(\frac{\Delta\alpha}{\gamma}\right)^{\nu}\pi(c_r)^{n_r} \tag{16}$$

from Eq. (82b) in their paper (the notation is entirely the same with what employed by them), which may be written for the present system(18)

$$\ln\gamma_1=2B^*_{20}C_1+B^*_{11}C_2+B^*_{12}C_2^2+2B^*_{21}C_1C_2+\cdots \tag{17a}$$

$$\ln\gamma_2=2B^*_{02}C_2+B^*_{11}C_1+B^*_{21}C_2^2+2B^*_{12}C_1C_2+\cdots, \tag{17b}$$

where the irreducible integral, B^*_{ij}, shows that the integral for i molecules of component 1 (diluent) and j molecules of component 2 (polymer).(18) Now, according to the notation employed by Kirkwood and Goldberg, the activity coefficient either of the solvent additive 1 or of the polymer 2 is represented by the form

$$\ln\gamma_i=\sum_{k=1}^{2}A_{ik}C_k+\sum_{j,k=1}^{2}B_{ijk}C_jC_k. \tag{18}$$

Comparing Eq. (18) with Eqs. (17a, b), it is clear that the interaction parameters of Kirkwood and Goldberg correspond to the above irreducible integral B^*_{ij}.

On the other hand, the parameter β of Stockmayer may be written from Eq. (18)

$$\beta_{12}=d\ln\gamma_1/dm_2=A_{12}M_2+2B_{122}M_2^2m_2+2B_{112}M_1M_2m_1+\cdots \tag{19a}$$

$$\beta_{21}=d\ln\gamma_2/dm_1=A_{21}M_1+2B_{211}M_1^2m_1+2B_{212}M_1M_2m_2+\cdots, \tag{19b}$$

where M_i is molecular weight of component i. (the quantities m_i have been expressed in molalities.)

Obviously from the definition of β,

$$\beta_{12}=\beta_{21}. \tag{20}$$

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(16) P. Doty, M. Brownstein and W. Schlener, *J. Phys. Chem.*, **53**, 213 (1949).

(17) W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

(18) For convenience, the notation of components 1, and 2 employed by Kirkwood and Goldberg was used throughout in this section.

So, the following relations exist between the parameters of Kirkwood and Goldgerg;

$$A_{12}/A_{21}=B_{112}/B_{211}=B_{122}/B_{212}=M_1/M_2. \qquad (21)$$

And

$$\beta_{11}=A_{11}M_1+2B_{112}M_1M_2m_2+\cdots\cdot \qquad (22a)$$

$$\beta_{22}=A_{22}M_2+2B_{212}M_1M_2m_1+\cdots\cdot \qquad (22b)$$

Similarly, the expressions for the α's in Eqs. (2)∼(5) are easily obtained, but are not presented here.

Although the interaction parameters μ_{12}, μ_{13}, and μ_{23} in Eq. (15), which have been used throughout in our preceding papers, can strictly be related to those of the above mentioned authors, the following approximate method offers a convenient means for calculation of the parameters μ_{12}, μ_{13}, and μ_{23}. To indicate clearly the dependency of turbidity on polymer concentration, Eq. (3) may be rewritten (from Eq. (3, 5) in reference 3)

$$HVm_2/\Delta\tau RT=\{1/[\psi_2-(m_1\beta_{12}\psi_1)/(1+\beta_{11}m_1)]^2\}\{1+[\beta_{22}-(m_1\beta_{12}^2)/(1+\beta_{11}m_1)]m_2+\cdots\cdot\}. \qquad (23)^{(18)}$$

On the other hand, Scatchard⁽¹⁹⁾ showed that the osmotic pressure P in two diffusible components-one non-diffusible solute systems may be expressed by the equation

$$P=AM_2(m_2+BM_2m_2^2+\cdots\cdot) \qquad (24)$$

where $2BM_2=\beta_{22}-(m_1\beta_{12}^2)/(1+\beta_{11}m_1)$. (See Eq. (35) in reference 19) It is easily seen from Eq. (23) and (24) that we can calculate the second virial coefficient in the osmotic pressure expression by power series expansion in polymer concentrations from the light scattering data in polymer-mixed solvent systems. The method of estimating the parameters μ_{12}, μ_{13} and μ_{23} from the second virial coefficient in the osmotic pressure expression for various solvent-diluent compositions, is already represented in the previous paper.⁽⁵⁾

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(19) G. Scatchard, *J. Am. Chem. Soc.*, **68**, 2315 (1946).