Note on the Polymer-Mixed Solvent System. IV. Deviation from the Single Liquid Approximation in Osmotic, Viscometric and Swelling Measurements

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Introduction

In discussing the problems encountered in the treatment of the interaction of a polymer with a mixed solvent, the single liquid approximation is often used, assuming that the mixture of the two liquids behaves as a homogeneous liquid to the polymer. For the sake of its simplicity, the experimental results of osmotic pressure, viscosity, swelling ratio and other measurements for mixed solvents have been interpreted with considerable confidence by the terms usually employed in the binary system of a polymer and a liquid. In some polymer-mixed solvent systems, however, the deviation from the single liquid approximation cannot be ignored, due to selective adsorption. In the preceding paper[1], the relation between the liquid compositions in the two phases has been derived for the equilibrium between a mixed solvent and an isolated polymer molecule in solution. In this paper we shall apply this treatment to the equilibrium between a mixed solvent and a cross-linked polymer, or between a polymer-mixed solvent solution and a mixed solvent through a semi-permeable membrane, and shall investgate how the influence of the selective adsorption must be considered in osmotic, viscometric, and swelling measurements.

Theoretical

In the two-phase systems, the thermodynamical condition for equilibrium requires that the partial molar free energy of each component (liquid 1 or liquid 2) be the same in both phases:

$$\varDelta\bar{F}_1=\varDelta\bar{F}_1' \tag{1a}$$

$$\varDelta\bar{F}_2=\varDelta\bar{F}_2' \tag{1b}$$

The partial molar free energies of the components in the binary phase of the two liquids may be written as[2]

$$\varDelta\bar{F}_1=\ln\theta_1+\theta_2\{1-(V_1/V_2)\}+(V_1/RT)A_{12}\varphi_2^2 \tag{2a}$$

$$\varDelta\bar{F}_2=\ln\theta_2+\theta_1\{1-(V_2/V_1)\}+(V_2/RT)A_{12}\theta_1^2 \tag{2b}$$

where θ_1 and θ_2 are compositions (volume fractions), V_1 and V_2 molar volumes of the two liquids, and A_{12} is a constant related to the heat interaction between the liquids 1 and 2.

For the ternary phase which consists of a cross-liked gel and the two liquids, Flory's expression for entropy change in swelling of a cross-linked gel in a single liquid may be applied to the present system in somewhat modified form. We may represent the entropy change associated with the swelling of a network of functionality f formed from ν chains in a single liquid as the sum of two terms, the osmotic and elastic contributions, and according to Flory[3], may write,

$$\varDelta S_{sw}=\varDelta S_{osm}+\varDelta S_{el} \tag{3a}$$

$$\varDelta S_{osm}=-R\{n\ln(1-v_3)\} \tag{3b}$$

$$\varDelta S_{el}=-R\{(3/2)\nu(v_3^{-2/3}-1)+(\nu/2)\ln v_3\} \tag{3c}$$

where n is the number of solvent molecules and v_3, volume fraction of the polymer in the gel phase.

Since the effect of the segment size must be considered for the calculation of the entropy of dilution as in our previous treatments[1],[4],[5], Eq. (3b) should be rewritten as

$$S_{osm}=-R[\{(n_1V_1+n_2V_2)/V_3\}\{\ln(1-v_3)+\mu_s'v_3\}] \tag{3b'}$$

for the present three component system, where n_1 and n_2 are the numbers of molecules of liquid 1 and liquid 2 respectively, V_3, molar volume of a polymer segment and μ_s' may be assumed to involve all the complicated factors except the effect of the segment size in the calculation of the entropy of dilution[5],[6]. Replacing v_3 in Eqs. (3b') and (3c)

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[1] T. Kawai, This Bulletin, 26, 6 (1953).

[2] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes", 3rd Ed. Reinfold Publishing Corp., New York (1950).

[3] P. J. Flory, *J. Chem. Phys.*, 18, 108 (1950).

[4] T. Kawai, This Bulletin, 25, 336 (1952); 25, 342 (1952).

[5] T. Kawai, This Bulletin, 26, 409 (1953).

[6] The parameter μ_s' differs from the entropy contribution μ_s in the customarily used parameter μ, since the effect of segment size is not considered in the usual treatment of polymer solutions (μ_s' is the same with f in reference 5).

by $Z\nu V_3/(n_1V_1+n_2V_2+Z\nu V_3)$ (Z is the number of segments between the cross links) and differentiating the resultant expressions of Eqs. (3b′) and (3c) with respect to n_1 and n_2, the following equations are obtained,

$$\Delta\bar{S}_1=-R(V_1/V_3)[\ln(1-v_3)+\{1-(2/Zf)\}v_3+\mu_s'v_3^2+(1/Z)v_3^{1/3}] \quad (4a)$$

$$\Delta\bar{S}_2=-R(V_2/V_3)[\ln(1-v_3)+\{1-(2/Zf)\}v_3+\mu_s'v_3^2+(1/Z)v_3^{1/3}] \quad (4b)$$

Adding the terms for the mixing of the two liquids⁴⁾, and employing the expressions already given in the preceding paper [Eqs. (2a) and (2b) in the reference (4)] for the partial molar heat of mixing, the right hand sides of Eq. (1a) and (1b) are obtained, and then, combining them with Eqs. (2a) and (2b), Eqs. (1a) and (1b) may be written as follows,

$$\begin{aligned}&\ln\theta_1+\{1-(V_1/V_2)\}\theta_2+(V_1/RT)A_{12}\theta_2^2\\&=(V_1/V_3)[\ln(1-v_3')+\{1-(2/Zf)\}v_3'\\&+\mu_s'v_3'^2+(1/Z)v_3'^{1/3}]+\ln\theta_1'\\&+\{1-(V_1/V_2)\}\theta_2'+(V_1/RT)\{A_{12}v_2'^2\\&+A_{13}v_3'^2+(A_{12}+A_{13}-A_{23})v_2'v_3'\}\end{aligned} \quad (5a)$$

$$\begin{aligned}&\ln\theta_2+\{1-(V_2/V_1)\}\theta_1+(V_2/RT)A_{12}\theta_1^2\\&=(V_2/V_3)[\ln(1-v_3')+\{1-(2/Zf)\}v_3'\\&+\mu_s'v_3'^2+(1/Z)v_3'^{1/3}]+\ln\theta_2'\\&+\{1-(V_2/V_1)\}\theta_1'+(V_2RT)\{A_{12}v_1'^2\\&+A_{23}v_3'^2+(A_{12}+A_{23}-A_{13})v_1'v_3'\}\end{aligned} \quad (5b)$$

where the A's are the constants characteristic to each pair of the components (the gel phase being designated by a prime).

From Eqs. (5a) and (5b), there is easily obtained,

$$\begin{aligned}&\ln(\theta_1/\theta_1')-(V_1/V_2)\ln(\theta_2/\theta_2')\\&=(V_1/RT)[\{A_{13}-A_{23}-A_{12}(\theta_2'-\theta_1')\}v_3'\\&+A_{12}\{(\theta_2'-\theta_1')-(\theta_2-\theta_1)\}]\end{aligned} \quad (6)$$

If we write $\theta_1=\theta$, $\theta_1'=\theta+\Delta\theta$, $\theta_2=(1-\theta)$, and $\theta_2'=(1-\theta)-\Delta\theta$⁷⁾, Eq. (6) may be converted to the form,

$$\begin{aligned}&(V_1/V_2)\ln\{1-(\Delta\theta)/(1-\theta)\}-\ln\{1+(\Delta\theta/\theta)\}\\&=-(V_1/V_2)\{\Delta\theta/(1-\theta)\}-(\Delta\theta/\theta)\\&-(1/2)(V_1/V_2)\{\Delta\theta/(1-\theta)\}^2\\&+(1/2)(\Delta\theta/\theta)^2-\cdots\fallingdotseq(V_1/RT)[\{A_{13}\\&-A_{23}-A_{12}(1-2\theta-\Delta\theta)\}v_3'-2A_{12}(\Delta\theta)]\end{aligned} \quad (7)$$

Hence, to a satisfactory approximation⁸⁾,

$$\begin{aligned}\Delta\theta\fallingdotseq&-(1/RT)\{A_{13}-A_{23}-A_{12}(1-2\theta)\}v_3'/\\&\{[(1/V_1\theta)+\{1/V_2(1-\theta)\}]\\&-(A_{12}/RT)(2-v_3')\}\end{aligned} \quad (8a)$$

And when

$$(1/V_1\theta)+\{1/V_2(1-\theta)\}\gg(A_{12}/RT)(2-v_3'),$$

$$\begin{aligned}\Delta\theta\fallingdotseq&\{-\theta(1-\theta)/[(\theta/V_2)+\{(1-\theta)/V_1\}]\}\\&(1/RT)\{A_{13}-A_{23}-A_{12}(1-2\theta)\}v_3'\end{aligned} \quad (8b)$$

Since $\Delta\theta/\theta$ is assumed to be a measure of the magnitude of selective adsorption, Eq. (8) shows the relation between its magnitude and the compositions, molar volumes of the two liquids or the interaction parameters. The magnitude of the selective adsorption for various types of the polymer-mixed solvent systems was discussed in details in the preceding paper¹⁾. It must be noted, however, that the effect of molar volumes of the two liquids should be considered also. The smaller the values of both V_1 and V_2, the smaller the magnitude of the selective adsorption. As seen from Eq. (8), however, the smaller V_2 values of nonsolvents would be effective in solvent-rich compositions to make the above magnitude smaller, and vice versa.

Now, the μ^* values, which are customarily used to express the polymer-solvent interaction, are often calculated from the experiments of swelling of cross-linked polymers, even in mixed solvents, by the equation,

$$-\mu^*v_3'^2=\ln v_0'+v_3'+(V_0/ZV_3)\,v_3'^{1/3} \quad (9)$$

which Flory presented for the cross-linked polymer-single liquid (designated by 0) system⁹⁾. (For mixed solvents, the "single liquid approximation", assuming that the mixture of the two solvents behaves as a homogeneous liquid, is widely used. Then, $v_o=v_1+v_2$, and $V_0=x_1V_1+x_2V_2$, where the x's are mole fractions of the two liquids). Let us consider how the calculation of the μ^* values from this equation must be corrected for the cross-linked polymer-mixed solvent system, owing to the effect of the selective adsorption.

Since the terms involving the θ's in Eqs. (5a) and (5b) can be expressed as $(\Delta\theta/\theta)-1/2(\Delta\theta/\theta)^2+\cdots$ and $-(\Delta\theta/1-\theta)-1/2(\Delta\theta/1-\theta)^2\cdots$ respectively, multiplying Eq. (5a) by $\theta V_0/V_1$ and Eq. (5b) by $(1-\theta)V_0/V_2$, and adding the resultant two equations, there is obtained,

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7) It must be noted that the ratio of volume fractions of the two liquids was expressed by θ in reference 1.

8) Since $\Delta\theta$ is supposed to be far smaller than θ or $(1-\theta)$ in usual cases, and the second terms in the expanded equations of the logarithmic terms in Eq. (7) are inclined to be canceled with each other, Eq. (8a) may afford a satisfactory approximation, unless θ or $(1-\theta)$ is extremely small. Further more, the last terms $(A_{12}/RT)(2-v_3')$ in Eq. (8a) can be ignored so long as $\{(V_1/V_2)\theta_1+\theta_2\}/\theta_1\theta_2>2A_{12}V_1/RT$. (this condition is usually satisfied except in the systems having extremely large values of A_{12}) as mentioned also in reference 1.

9) P. J. Flory, J. Rehner, Jr., *J. Chem. Phys.*, **11**, 512 (1943).

$$\begin{aligned}
&(V_0/V_3)[\ln(1-v_3')+\{1-(2/Zf)\}v_3'+\mu_s'v_3'^2\\
&+(1/Z)v_3'^{1/3}]=-(V_0/V_1)\theta\ln\{1+(\varDelta\theta/\theta)\}\\
&-(V_0/V_2)(1-\theta)\ln\{1-(\varDelta\theta/1-\theta)\}\\
&+\{(V_0/V_1)-(V_0/V_2)\}\varDelta\theta\\
&-(A_{12}V_0/RT)(\varDelta\theta)^2-(V_0/RT)\{A_{13}(\theta+\varDelta\theta)\\
&+A_{23}(1-\theta-\varDelta\theta)\\
&-A_{12}(\theta+\varDelta\theta)(1-\theta-\varDelta\theta)\}v_3'^2\\
&-(V_0/RT)\{\theta(1-\theta-\varDelta\theta)\\
&-(1-\theta)(\theta+\varDelta\theta)\}[A_{13}-A_{23}\\
&-A_{12}\{1-2(\theta+\varDelta\theta)\}]v_3'\\
&\fallingdotseq(V_0/2)[(1/V_1\theta)+\{1/V_2(1-\theta)\}](\varDelta\theta)^2\\
&-(A_{12}V_0/RT)(1-2v_3'+v_3'^2)(\varDelta\theta)^2\\
&-(V_0/RT)\{A_{13}\theta+A_{23}(1-\theta)\\
&-A_{12}\theta(1-\theta)\}v_3'^2\\
&+(V_0/RT)\{A_{13}-A_{23}\\
&-A_{12}(1-2\theta)\}v_3'(1-v_3')\varDelta\theta \qquad (10)^{10)}
\end{aligned}$$

Substituting the expression of Eq. (8a) for $\varDelta\theta$ in Eq. (10), and combining Eq. (9) with (10),

$$\begin{aligned}
&\mu^*v_3'^2\fallingdotseq[1/2-(V_0/V_3)(1/2-\mu'_s)\\
&+(V_0/RT)\{A_{13}\theta+A_{23}(1-\theta)\\
&-A_{12}\theta(1-\theta)\}]v_3'^2\\
&+[\{1-(V_0/V_3)\}\{(1/3)v_3'^3\\
&+(1/4)v_3'^4+\cdots\}-(2V_0/V_3Zf)v_3']\\
&+[\{1/(RT)^2\}\{A_{13}-A_{23}\\
&-A_{12}(1-2\theta\}^2\theta(1-\theta)/\{(\theta/V_2)\\
&+(1-\theta)/V_1\}\{(\theta/V_1)+(1-\theta)/V_2\}]\\
&\times[1/2-v_3'+B\{1-4v_3'+(5/4)v_3'^2+\cdots\}\\
&+B^2\{2-12v_3'+(17/2v_3'^2)+\cdots\}+\cdots]\,v_3'^2 \qquad (11)^{10)}
\end{aligned}$$

where, $B=(A_{12}/RT)/[(1/V_1\theta)+\{1/V_2(1-\theta)\}]$ (B is very small in usual cases[8]). The last bracketed terms are due to the selective adsorption, and the first and second bracketed terms correspond to the expresion for a single liquid, which usually may be written,

$$\mu=\mu_s+(V_0RT)A_{30} \qquad (12)$$

where μ_s is a correction factor, mentioned in reference (6). It is easily seen from Eq. (11) that Eq. (12) must be replaced by

$$\begin{aligned}
&\mu=1/2-(V_0/V_3)(1/2-\mu_s')+(V_0/RT)A_{30}\\
&-(2V_0/V_3Zf)v_3'^{-1}+\{1-(V_0/V_3)\}\\
&\{(1/3)v_3'+(1/4)v_3'^2+\cdots\}. \qquad (13)
\end{aligned}$$

On this point, strictly speaking, lies an important source of inaccuracy in the customary calculation of the μ values from swelling measurements, which will be discussed in detail elsewhere (In extremely poor solvents, the dependency of μ upon v_3' can not be ignored).

Actually, even for single liquids, the μ values determined from swelling measurements are often larger than those obtained from osmotic pressure measurements[11],[12], and the influence of the molar volume of the solvent must be considered when the solvent power of the solvent is estimated from the μ value thus obtained[5].

For the present three-component system, however, we shall confine ourselves to the investigation of the effect of the selective adsorption, and assuming that all the complicated factors, such as those seen from Eq. (13), are involved in the term μ_s in Eq. (12), may write for the "single liquid approximation"[4],[13],

$$\mu^{**}=\mu_{13}\theta+\mu_{23}(1-\theta)-\mu_{12}\theta(1-\theta) \qquad (14)$$

where $\mu_{13}=\mu_s+(V_0/RT)A_{13}$, $\mu_{23}=\mu_s+(V_0/RT)A_{23}$, and $\mu_{12}=(V_0/RT)A_{12}$[14] (Eq. (14) corresponds to the expression in Part II[4], which is a somewhat improved form of Scott's[13]). Thus, Eq. (11) reduces to

$$\begin{aligned}
&\mu^*=\mu^{**}+[\{(1/RT)^2\}\{A_{13}-A_{23}\\
&-A_{12}(1-2\theta)\}^2\theta(1-\theta)/\{(\theta/V_2)\\
&+(1-\theta)/V_1\}\{(\theta/V_1)+(1-\theta)/V_2\}]\\
&\times[1/2-v_3'+B\{1-4v_3'+(5/4)v_3'^2+\cdots\}\\
&+B^2\{2-12v_3'+(17/2)v_3'^2+\cdots\}+\cdots] \qquad (15).
\end{aligned}$$

It may be notable that, as seen in Eq. (15), μ^* always gives a larger value than that expected for its original meaning due to the selective adsorption ($1/2>v_3'$, except in the case of swelling in an extremely poor solvent i.e. in the nonsolvent-rich region). Moreover, its deviation increases, of course, with the magnitude of the selective adsorption (accordingly, with the content of the nonsolvent), but, decreases rapidly in the neighbourhood of pure nonsolvent.

Several attempts[15],[16] have been made to correlate intrinsic viscosities with the thermodynamic properties of the solution. The writer[4] has developed the procedure of Flory[15], who treated the interaction of an isolated polymer molecule with solvent as a

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[10] For the same reason as mentioned in reference (8), Eqs. (10) and (11) would give a satisfactory approximation.

[11] T. Kawai, This Bulletin, 24, 69 (1951).

[12] P. Doty, M. Brownstein, W. Schlener, *J. Phys. Colloid Chem.*, 53, 213 (1949).

[13] R.S. Scott, *J. Chem. Phys.*, 17, 268 (1949).

[14] Eq. (14) is merely a convenient representation of μ^{**} by employing μ_s. And, strictly speaking, the parameter μ_{13}, or μ_{23} employed here differs from that calculated from experiments in the polymer 3–single liquid 1 (or 2) system, also because V_0 is a function of θ (cf. Eqs. (16) and (17)).

[15] P.J. Flory, *J. Chem. Phys.*, 17, 303 (1949).

[16] T.G. Fox, Jr., P.J. Flory, *J. Am. Chem. Soc.*, 73, 1904; 1909; 1915 (1951)

swelling phenomenon, to the polymer-mixed solvent system, and formulated the relation between intrinsic viscosity and the parameter μ for the single liquid approximation. Now, we can apply the treatment developed in the preceding pages for the swelling of a cross-linked polymer in a mixed solvent to discuss the effect of the selective adsorption on intrinsic viscosities. In another treatment[5], which is developed in consideration of the effect of segment size, the writer pointed out a more satisfactory correspondence of the volume swelling ratio of polymer gels, or intrinsic viscosities of polymer solutions with the values of $(1/2-\mu)/V_0$ rather than with the μ values themselves. There[5], the parameter μ which has been usually interpreted in terms of Flory-Rehner's theory, was expresed by

$$\mu=1/2-(V_0/V_3)(1/2-\mu_s')+(V_0/RT)A_{30} \tag{16}$$

instead of Eq. (13)[17]. The last bracketed terms in the right hand side of Eq. (13) were ignored in Eq. (16), since this can afford a satisfactory approximation when the values of v_3' is sufficiently small[18]. The similar approximation may be applied to the present problem on intrinsic viscosity, and we may write for the single liquid approximation,

$$\begin{aligned}\mu^{**}=&1/2-(V_0/V_3)(1/2-\mu_s')\\&+(V_0/RT)\{A_{13}\theta+A_{23}(1-\theta)\\&-A_{12}\theta(1-\theta)\}\end{aligned} \tag{17}$$

Considering the effect of the selective adsorption, the values of intrinsic viscosity in mixed solvents are expected to vary with

$$\begin{aligned}(1/2-\mu^*)/V_0=&(1/V_3)(1/2-\mu_s')\\&-(1/RT)\{A_{13}\theta+A_{23}(1-\theta)-A_{12}\theta(1-\theta)\}\\&-\{1/(RT)^2\}[\{A_{13}-A_{23}\\&-A_{12}(1-2\theta)\}^2\theta(1-\theta)/\{(\theta/V_2)\\&+(1-\theta)/V_1\}]\times[1/2-v_3'\\&+B\{1-4v_3'+(5/4)v_3'^2+\cdots\}\\&+B^2\{2-12v_3'+(17/2)v_3'^2+\cdots\}+\cdots]\end{aligned} \tag{18}$$

Finally, the treatment developed above will be applied to the interpretation of osmotic pressure in mixed solvents. The expressions for osmotic pressure π in the present system were already derived by Gee[19], Scott[13] and Scatchard[20]. Here, the errors introduced by employing the "single liquid approximation" in the customary calculations of the μ values will be discussed. The condition for equilibrium between both sides of the membrane in an osmometer may be expressed thus:

$$\begin{aligned}\ln\theta_1&+\{1-(V_1/V_2)\}\theta_2+(V_1/RT)A_{12}\theta_2^2\\&=(V_1/V_3)[\ln(1-v_3')+\{1-(1/x)\}v_3'\\&+\mu_s'v_3'^2]+\ln\theta_1'+\{1-(V_1/V_2)\}\theta_2'\\&+(V_1/RT)\{A_{12}v_2'^2+A_{13}v_3'^2\\&+(A_{12}+A_{13}-A_{23})v_2'v_3'\}+(\pi V_1/RT),\end{aligned} \tag{19a}$$

$$\begin{aligned}\ln\theta_2&+\{1-(V_2/V_1)\}\theta_1+(V_2/RT)A_{12}\theta_1^2\\&=(V_2/V_3)[\ln(1-v_3')+\{1-(1/x)\}v_3'\\&+\mu_s'v_3'^2]+\ln\theta_2'+\{1-(V_2/V_1)\}\theta_1'\\&+(V_2/RT)\{A_{12}v_1'^2+A_{23}v_3'^2\\&+(A_{12}+A_{23}-A_{13})v_1'v_3'\}+(\pi V_2/RT),\end{aligned} \tag{19b}$$

where x is the number of segments (number average) in a polymer molecule. Meanwhile, the μ values for mixed solvents have been usually calculated by

$$\begin{aligned}-\pi V_0=&RT[\ln(1-v_3')+\{1-(V_0/xV_3)\}v_3'\\&+\mu^*v_3'^2]\end{aligned} \tag{20}$$

Combining Eqs. (19a, b) and (20), an entirely analogous evaluation to the derivation of Eq. (11) leads to

$$\begin{aligned}\mu^*=&1/2-(V_0/V_3)(1/2-\mu_s')\\&+(V_0/RT)\{A_{13}\theta+A_{23}(1-\theta)-A_{12}\theta(1-\theta)\}\\&+[\{1/(RT)^2\}\{A_{13}-A_{23}\\&-A_{12}(1-2\theta)\}^2\theta(1-\theta)/\{(\theta/V_2)\\&+(1-\theta)/V_1\}\{(\theta/V_1)+(1-\theta)/V_2\}]\\&\times[1/2-v_3'+B\{1-4v_3'+(5/4)\,v_3'^2+\cdots\}\\&+B^2\{2-12v_3'+(17/2)v_3'^2+\cdots\}+\cdots]\end{aligned} \tag{21}$$

The last bracketed terms in Eq. (21) give the contribution of the selective adsorption and the other terms are equivalent to those obtained for the binary system of a polymer and a solvent in consideration of the effect of the segment size.

Applications of the above treatment will be given in the next paper to the osmotic, viscometric, and swelling data in a few polymer-mixed solvent systems.

After this paper had been read at the Special Meeting on High polymers, held by the Chemical Society of Japan, and the Society of High Polymer, Japan, at Tokyo University, on 31st Oct., 1953, Dr. Krigbaum sent me a copy of the manuscript of his paper, which was due to appear on J. Polymer Sci., He dealt with the composition

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[17] The complications, which arise from the last bracketed terms in Eq. (13) and from Flory's modification of his own original equation (cf. Eqs. (3c) and (9)), are avoided in Eq. (16), and this approximation is equivalent to assuming an equal μ value for both osmotic and swelling measurements.

[18] When the v_3' values are considerably large (i.e. $v_3'>0.1$), it may be suitable to express μ by Eq. (13) instead of Eq. (16). Actually, the validity of the approximate treatment (Eq. (16)) in reference 5 fails when it is applied to the swelling in extremely poor solvents.

[19] G. Gee, *Trans. Faraday Soc.*, 40, 463 (1944).

[20] G. Scatchard, *J. Am. Chem. Soc.*, 68, 2315 (1946).

relationship of the two phases in equilibrium between a polymer and a mixed solvent, and drew the conclusion similar to that of my preceding paper[1), except for the effect of the difference in molar volumes of the two liquids. Also this effect of molar volumes of the liquids had been involved in this treatment, although somewhat different results had been obtained because the effect of the segment size was considered in this treatment. A few points of difference between my treatment and Krigbaum's will be explained elsewhere, after an exchange of views with him.

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