Note on Polymer-Mixed Solvent System. V. Certain Consequences of the Previous Treatment

By Tōru KAWAI

(Received February, 1, 1955)

Introduction

In polymer-mixed solvent systems, thermodynamic properties of the ternary mixtures such as osmotic pressure and swelling, are usually explained by employing the approximation that the mixture of the two liquids can be treated as a hypothetical single liquid having intermediate properties. Sometimes, this single liquid approximation produces a considerable error in osmotic measurements due to non-uniform composition of a mixed solvent in both sides of a semi-permeable membrane. Similarly, swelling of a crosslinked gel or viscosity (especially intrinsic viscosity) of a polymer solution in a mixed solvent may have, more or less, the influence of this selective adsorption. The deviation of these properties from those for the single liquid approximation, have been formulated in Part IV. With the aid of the expressions of these deviations, several experimental results on osmotic, vicometric, and swelling measurements in polymer-mixed solvent systems will be investigated in this paper.

The Magnitude of the Deviation from the Single Liquid Approximation

As mentioned in Part II(1) and Part III(2) there exist two types of interaction between polymers and mixed solvents. When a nonsolvent is added to a polymer solution, the solvent ability of the medium usually decreases uuiformly with its addition (in this case, $A_{23}-A_{13}>A_{12}$(1)). In some cases, however, the first portion of the addition of the nonsolvent improves the solvent ability of the medium, and the solvent power shows a maximum value at a certain composition, $\theta_c(=(1/2)+(A_{23}-A_{13})/A_{12})$,(1,2,3) and then, decreases (in this case, $A_{23}-A_{13}<A_{12}$(1)). Such behaviors are attributable to the repulsive force acting between solvent and nonsolvent molecules (which is expressed by the parameter A_{12}). The solvent ability of mixed solvent is improved by the strong repulsive force between the solvent and nonsolvent molecules in the latter case (hereafter, designated by Case II), whereas a stronger precipitating power of a nonsolvent overcomes the effect of the above repulsive force in the former case (designated by Case I).

If the phenomenon of the selective adsorption may be explained by the assumption that a polymer molecule exhibits a preferential adsorption to the solvent molecules in its statistical environments, the magnitude of the selective adsorption may be usually larger with the larger difference of the solvent powers of the two liquids. The repulsive force between the two liquids, however, act so as to drive the solvent molecules into the polymer-rich phase, and this tendency may be promoted as the content of the nonsolvent increases. For instance, Schulz and Jirgens-

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1) T. Kawai, This Bulletin, 25, 341 (1952).

2) T. Kawai, This Bulletin, 26, 6 (1953).

3) As mentioned in Part IV, θ represents the composition of the solvent and not of the nonsolvent.

one[4] found that at 70% (by volume) of methanol the methanol-benzene ratio was 0.131 in a polystyrene gel phase and 3.00 in the solvent phase. In Case II, the magnitude of the selective adsorption depends considerably on the composition. In the composition range, $\theta > \theta_c$, the nonsolvent molecules are rather preferentially adsorbed by the polymer molecules owing to the fact that a majority of the solvent molecules drive the nonsolvent molecules into the environments of the polymer molecules through the strong repulsive force between the solvent and nonsolvent molecules. The magnitude of this "inverse" solective adsorption[5] decreases as the content of the nonsolvent increases until $1-\theta=1-\theta_c$, at which the solvent ability of the mixed solvent has a maximum value and at which the "inverse" selective adsorption vanishes. When the content of the nonsolvent becomes larger than $1-\theta_c$, many more solvent molecules are absorbed by the polymer molecules than the nonsolvent, and the magunitude of the solective adsorption increases with the increasing content of the nonsolvent as in usual cases.

Of course, the larger the manitude of the selective adsorption, the larger the deviation from the single liquid approximation. The deviation of the μ value is, however, to become smaller with increasing polymer concentration in the polymer-rich phase, whereas the magnitude of the selective adsorption must be larger with the polymer concentration (see Eqs. (8_a), (8_b) and (15) in Part IV). While, this deviation would increase with the addition of the nonsolvent until a certain nonsolvent-rich composition is reached, and then rapidly decrease to zero, although the effect of molar volumes of the two liquids is considerably comlicated. Therefore, the contribution of the selective adsorption to the μ value may be most remarkable when the solvent abilities of the two liquids differ very much from each other, and especially in a certain nonsolvent-rich composition. As will be shown later, this deviation sometimes amounts to 12% of the μ values observed in swelling measurements of a cross-linked gel in such a mixed solvent. In osmotic and viscometric measurements, however, this deviation exists generally in the range, 0~5% of the μ values, because the selective adsorption is not so remarkable at the compositions usually used in these measurements as in the swelling measurements. Intrinsic viscosity enables us, however, to detect the effect of the selective adsorption owing to its sensitivity to the solvent power.

Osmotic Pressure

According to the treatment developed in Part IV, the second virial coefficient in osmotic pressure expression, a_2, may be expressed, to a satisfactory approximation, by

$$\begin{aligned} a_2 &= (RT/\rho^2 V_0)(1/2-\mu^*) \\ &= (RT/\rho^2)[(1/V_3)(1/2-\mu'_s) \\ &\quad -(1/RT)\{A_{13}\theta+A_{23}(1-\theta)-A_{12}\theta(1-\theta)\}] \\ &\quad -\{1/(RT)\rho^2\}[\{A_{13}-A_{23} \\ &\quad -A_{12}(1-2\theta)\}^2\theta(1-\theta)/\{(\theta/V_2) \\ &\quad +(1-\theta)/V_1\}]\times[1/2-v_3'+B\{1-4v_3' \\ &\quad +(5/4)v_3'^2+\cdots\cdots\}+B^2\{2-12v_3' \\ &\quad +(17/2)v_3'^2+\cdots\cdots\}+\cdots\cdots] \end{aligned} \tag{1a}$$

(The notation is exactly the same as that employed in Part IV, and ρ is the density of the polymer), which may be converted to the form,

$$\begin{aligned} a_2 &= \{A^*_{13}\theta+A^*_{23}(1-\theta)+A^*_{12}\theta(1-\theta)\} \\ &\quad -(\rho^2/RT)\{A^*_{13}-A^*_{23}+A^*_{12}(1-2\theta)\}^2 \\ &\quad \times[\theta(1-\theta)/\{(\theta/V_2)+(1-\theta)/V_1\}][1/2-v_3' \\ &\quad +B\{1-4v_3'+(5/4)v_3'^2+\cdots\cdots\} \\ &\quad +B^2\{2-12v_3'+(17/2)v_3'^2+\cdots\cdots\}+\cdots\cdots] \end{aligned} \tag{1b}$$

where

$$A^*_{13}=(RT/\rho^2 V_3)(1/2-\mu_s')-A_{13}/\rho^2,$$
$$A^*_{23}=(RT/\rho^2 V_3)(1/2-\mu_s')-A_{23}/\rho^2,$$
and $A_{12}^*=A_{12}/\rho^2$.

On the other hand, the expression for the single liquid approximation,

$$a_2=A^*_{13}\theta+A^*_{23}(1-\theta)+A^*_{12}\theta(1-\theta) \tag{2}$$

has been usually applied to the experimental data for its simplicity.

As was discussed in the preceding section, the contribution of the selective adsorption to the μ value is comparatively small (0~5%) in usual osmotic measurements. Considerable errors of the a_2 values, however, may often be introduced by employing the single liquid approximation. A few examples will be presented, in which this deviation may be supposed to be remarkable, considering such factors having effects upon it as discussed in the preceding section. Kawai and Furukawa[6] measured the osmotic pressure of cellulose acetate solution in acetone-alkyl phthalates mixtures at 20°C. In Table I, the a_2 values are given for a few different com-

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[4] G. V. Schulz and B. Jirgensone, *Z. physik. Chem.*, B46, 131 (1940).

[5] Experimentally, Endo proved this phenomenon for polyvinyl acetate-acetone-water system. (Private communication from Mr. K. Endo, the Chemical Laboratory of Tokyo University).

[6] T. Kawai and T. Furukawa, *J. Chem. Soc. Japan, Ind. Chem. Section*, 57, 436 (1954).

TABLE I

THE EFFECTS OF THE SELECTIVE ADSORPTION UPON THE a_2 VALUE AND THE INTERACTION PARAMETERS (CELLULOSE ACETATE-ACETONE-ALKYL PHTHALATES SYSTEMS)

at 20°C, $V_1=73.3$ cc $\rho=1.30$ g/cc a_2, A^*(atm.(cc./g.)^2)

Nonsolvents	Dimethyl phthalate ($V_2=166.4$)	Diethyl phathalate ($V_2=197.9$)	Dibuthyl phthalate ($V_2=264.9$)
Interaction parameters from Eq. (2)	$A_{13}^*=1.43\times10$ $A_{23}^*=0.08_8\times10$ $A_{12}^*=1.48\times10$	$A_{13}^*=1.43\times10$ $A_{23}^*=-0.99\times10$ $A_{12}^*=2.64\times10$	$A_{13}^*=1.43\times10$ $A_{23}^*=-2.43\times10$ $A_{12}^*=0.26\times10$
Interaction parameters from Eq. (Ib)		$A_{13}^*=1.43\times10$ $A_{23}^*=-0.73_5\times10$ $A_{12}^*=2.32\times10$	$A_{13}^*=1.43\times10$ $A_{23}^*=-2.60\times10$ $A_{12}^*=1.16\times10$

Content of solvent by volume fraction	$a_2\times10$ (exp.)	$a_2\times10$ (calc.)	The contribution of selective adsorption $\times10$	$a_2\times10$ (exp.)	$a_2\times10$ (calc.)	The contribution of selective adsorption $\times10$	$a_2\times10$ (exp.)	$a_2\times10$ (calc.)	The contribution of selective adsorption $\times10$
0.856	1.42	1.42	0.0013	1.40	1.40	0.0019	0.91	0.91	0.085
0.750	1.35	1.36	0.0074	1.30	1.31	0.0092	0.51	0.51_5	0.125
0.667							0.20	0.19_4	0.150
0.500	1.10	1.09	0.0206	0.88	0.88	0.046			

The terms $[1/2-v_3'+B\{1-4v_3'+(5/4)v_3'^2+\cdots\cdots\}+B^2\{2-12v_3'+(17/2)v_3'^2+\cdots\cdots\}]$ in Eq. (Ib) are approximated by 1/2 in the above calculations. ($v_3'=0.005\sim0.02$)

positions. Since the contribution of the selective adsorption is supposed to be considerable when diethyl and dibutyl phthalates are used as the nonsolvent, the interaction parameters, A^*_{13}, A^*_{23}, and A^*_{12}, are calculated by employing Eq. (Ib) from the a_2 values for these two nonsolvent in Table I and are compared with those obtained by applying Eq. (2) in the same table. Merely for dimethyl phthalate, the interaction parameters are calculated only by Eq. (2), because this calculation does not seem to introduce any serious error. In order to estimate the contribution of the selective adsorption to the a_2 values, the last bracketed terms in Eq. (Ib) are evaluated for each composition of the three solvent-nonsolvent pairs also in Table I. Reasonable values of the parameters have been obtained by employing Eq. (Ib), whereas the A^*_{12} value calculated by Eq. (2) is unacceptably small especially for acetone-dibutyl phthalate in consideration of the strong repulsive force between the two liquids. Furthermore, an extremely good agreement has been obtained between the experimental and calculated a_2 values in all the composition range investigated.

Intrinsic Viscosity

As discussed in Part IV, intrinsic viscosities of a polymer in various liquids including mixed solvents might be correlated with the $(1/2-\mu)/V_0$ values. It is confirmed in Part IV and in another paper[7] that an entirely similar relationship may be expected between swelling ratio of a polymer gel in various liquids and the values of $(1/2-\mu)/V_0$[8]. Thus, a good correspondence is to be expected also between $[\eta]$ values and the equilibrium swelling ratio in a series of solvents or for various compositions of a mixed solvent. Actually, Staudinger and Heuer[9] found that the liquid which shows the greatest value of specific viscosity in the solvents for polystyrene, is the best swelling agent for polystyrene-divinyl benzene gels. Frith[10] also mentioned that $[\eta]$ values for a series of neoprence solutions in benzene-various esters mixtures are linearly related to the swelling of a vulcanized Neoprene in the corresponding esters[11]. Furthermore, the relationship between the equilibrium swelling ratio and the cohesive energy densities of the swelling agents, which was established by Gee[12] and has been widely used, can be well interpreted from the above procedure[7,13]. Also the a_2

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

[8] Strictly speaking, the μ values for the swelling of a cross-linked polymer are somewhat different from those used in the discussion of intrinsic viscosity, as mentioned in Part IV.

[9] H. Staudinger and W. Heuer, *Z. physik. Chem.*, **A171**, 129 (1934).

[10] E.M. Frith and F.R. Tuckett, "Linear Polymers", p. 231 (1950).

[11] Although the swelling agents are not the same as the liquids employed in the viscometric measurements, but are pure esters, it is not impossible to assume that this example may be interpreted by our procedure, as is seen from Eqs. (16) and (17) in Part IV.

[12] G. Gee, "Advances in Colloid Science", Vol. II, Interscience Publishers, Inc., New York (1946), p. 179.

[13] In the usual explanations for this relationship, the effect of segment size (see reference 7)) is not considered.

values would keep pace with the $[\eta]$ values in a series of solvents, as will be shown in the coming pages.

Now, the effect of the selective adsorption could be assumed to appear through the $(1/2-\mu^*)/V_0$ values upon intrinsic viscosities in mixed solvents. In case I, mentioned in the preceding section, $[\eta]$ value decreases with the addition of the nonsolvent, and its value may be somewhat smaller for each composition than that expected from the $(1/2-\mu^{**})/V_0$ values for the single liquid approximation. Although the magnitude of the selective adsorption may be notable in this case, its contribution to the $[\eta]$ value cannot be detected from the above procedure since only the $(1/2-\mu^*)/V_0$ value has been correlated with the selective adsorption, and $[\eta]$ itself has not yet been formulated in an analytical form in consideration of the above contribution.

In case II, however, this treatment leads to an interesting bit of information on the effect of the selective adsorption. It is evident Eqs. (17) and (18) in Part IV, that the $[\eta]$ values at the two compositions equally apart from the content of the solvent θ_c at which the solvent power of the mixed solvent shows a maximum, should be exactly equal to each other[14], if the single liquid approximation were valid. Namely, the $[\eta]\sim$composition curve is symmetrical with respect to the line $\theta=\theta_c$, as is shown by the dotted curve in Fig. 1. In actual system, the curve might deviate from this symmetrical one as is given by the rigid curve in the same figure. It is easily seen from Eq. (18) in Part IV, that $[\eta]$ values may be somewhat smaller than those expected from the single liquid approximation, either when $\theta<\theta_c$ or $\theta>\theta_c$. However, these deviations are likely to be larger when $\theta<\theta_c$ than when $\theta>\theta_c$ as will be discussed later. Thus, the $[\eta]\sim\theta$ curve becomes an asymmetric one, the degree of which depends upon the magnitude of the selective adsorption. At the two compositions equally apart by δ from θ_c, the contribution of the selective adsorption to the $(1/2-\mu^*)/V_0$ value may be written,

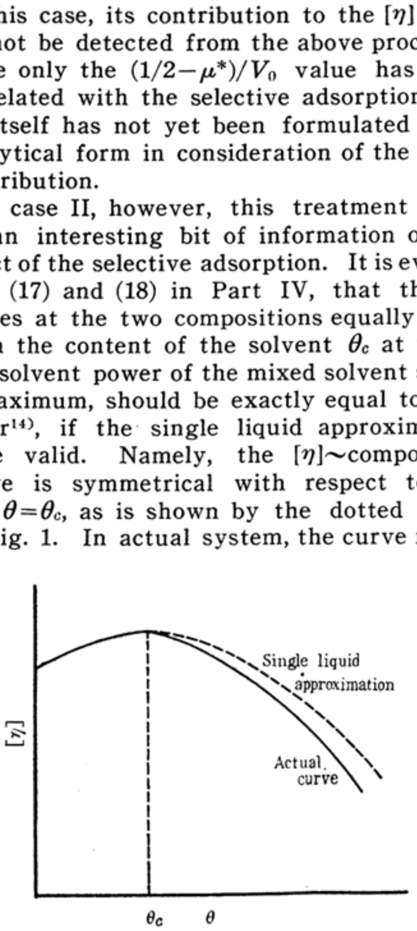

Fig. 1. Illustration of the effect of selective adsorption on the $[\eta]\sim\theta$ curve.

$$\Delta_1=\{1/(RT)^2\}(A_{12}\delta)^2(\theta_c+\delta)(1-\theta_c-\delta)\\(1/2-v_3'+C)/\{(\theta_c+\delta)/V_2+(1-\theta_c-\delta)/V_1\} \tag{3a}$$

at the composition, $\theta_1(=\theta_c+\delta)$, and

$$\Delta_2=\{1/(RT)^2\}(A_{12}\delta)^2(\theta_c-\delta)(1-\theta_c+\delta)\\(1/2-v_3'+C)/\{(\theta_c-\delta)/V_2+(1-\theta_c+\delta)/V_1\} \tag{3b}$$

at the composition, $\theta_2(=\theta_c-\delta)$, where the terms, $B\{1-4v_3'+(5/4)v_3'^2+\cdots\cdots\}+\cdots\cdots$ in Eqs. (1a) and (1b) are replaced by C $(1-\theta_c>\delta>0)$.

As easily seen from Eqs. (3a) and (3b), the above asymmetry of the $[\eta]\sim\theta$ curve arises mainly from the fact that the values of the term $\theta(1-\theta)$ in Eq. (18) in Part IV, are greater in the composition, $\theta_2(=\theta_c-\delta)$ than in the composition, $\theta_1(=\theta_c+\delta)$, although the effect of molar volumes of the two liquids has to be taken into account. The smaller the θ_c values, the less the difference of the $\theta(1-\theta)$ values between the above two compositions for a constant value of δ, and vice versa $(\theta_c\geqq1/2)$. For instance, Palit, Colombo and Mark[15] obtained the $[\eta]\sim\theta$ relation, giving an almost symmetrical curve with respect to the line $\theta=\theta_c=0.56$ for polystyrene-methylcyclohexane-acetone system. In this system, the effect of the selective adsorption can be ignored due to the extremely small difference between the $\theta_1(1-\theta_1)$ and $\theta_2(1-\theta_2)$ values. In many cases the selective adsorption seems, however, to give a considerable deviation from the "ideal" symmetry of the $[\eta]\sim\theta$ curve, owing to the sensitive variation of the $[\eta]$ value to the solvent power. In Part II[1], the $[\eta]$ value was correlated with the value of μ for the single liquid approximation and was discussed from a few experimental data in mixed solvents. More precise knowledge on the $[\eta]\sim\theta$ relation will be obtained with the aid of the treatment developed here.

It is evident from Eqs. (3a) and (3b) that the A_{12} value might also play an important role in the factors governing the asymmetry of the $[\eta]\sim\theta$ curve, when the degrees of the asymmetry are compared for various sys-

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[14] It is assumed, of course, that $[\eta]$ gives an equal value for the liquids having an equal value of $(^1/_2-\mu^*)V_0$ for a polymer.

[15] S.R. Palit, G. Colombo and H. Mark, *J. Polym. Sci.*, 6. 295 (1951).

tems[16]. In Fig. 2~5[17,18,19] the $[\eta]\sim\theta$ curves are given for several polymer-mixed solvent systems, which were cited also in Part II[1]. The θ_c and μ_{12} values are written for each system in the same figures, showing that the degree of the asymmetry of the curves is greater for the greater value of μ_{12} and for the smaller value of θ_c. Strictly speaking, the A_{12} values should be givin in these figures instead of μ_{12}, as understood from the above treatment. For the present purpose, however the μ_{12} values[1] may be sufficient to represent the relative magnitude of the parameter A_{12}. In Fig. 2 and Fig. 3,

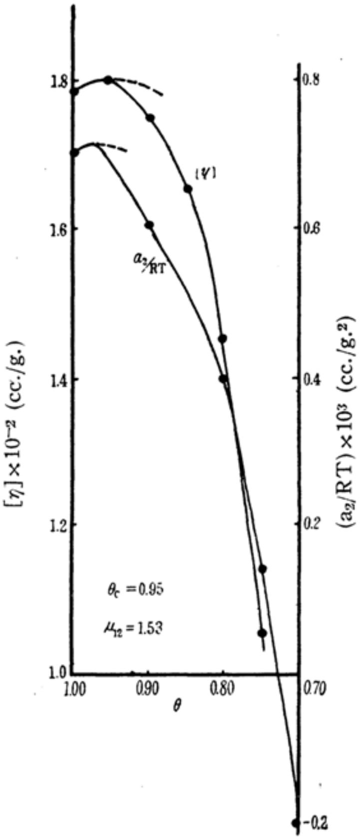

Fig. 2. $[\eta]\sim\theta$, and $a_2\sim\theta$ relationships for polyvinyl acetate-acetone-water system at 20°C.

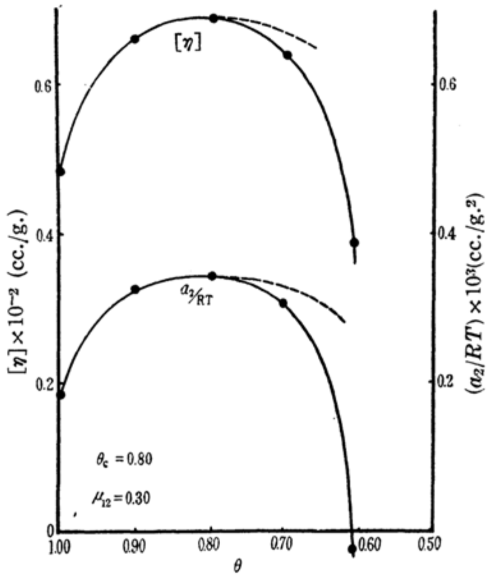

Fig. 3. $[\eta]\sim\theta$ and $a_2\sim\theta$ relationships for Polyvinyl acetate-methanol-watersystem at 20°C.

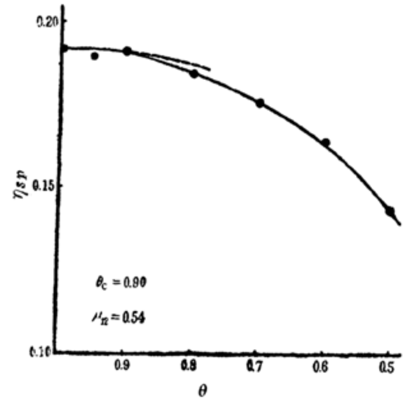

Fig. 4. The $\eta_{sp}\sim\theta$ relationship of 0.001 g./cc. polyvinyl acetate in acetone-ether mixture.

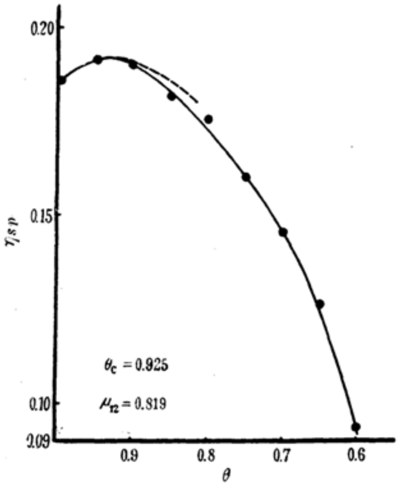

Fig. 5. The $\eta_{sp}\sim\theta$ relationship of 0.001 g./cc. polyvinyl acetate in acetone-petroleum benzin mixture.

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[16] Of cource, the deviation from the asymmetry of the $[\eta]\sim\theta$ curve increases with δ. These discussions are those for a constant value of δ.

[17] K. Yoshioka, *J. Chem. Soc. Japan*, **72**, 767 (1951).

[18] K. Endo, *J. Chem. Soc. Japan*, **72**, 885 (1951).

[19] K. Yoshioka, *J. Chem. Soc. Japan*, **72**, 664 (1951).

also the $a_2 \sim \theta$ curves are given from Endo's osmotic data[18,20], showing a satisfactorily good correspondence between the $[\eta]$ and a_2 values in all the composition ranges rather than between the $[\eta]$ and μ values[1], as is expected from the above treatment.

In order to investigate quantitatively the factors which have effects on the degree of the asymmetry in the $[\eta] \sim \theta$ curves, we have calculated numerically the right hand sides of Eqs. (3a) and (3b) in Table II,, having compared the polyvinyl acetate-acetone-water system (Fig. 2) with the polyvinyl acetate-methanol-water system (Fig. 3). The difference of the $(\Delta_2 - \Delta_1)$ values is remarkable between these two systems, mainly due to the superposed effects of the θ_c and A_{12} values.

TABLE II

ILLUSTRATION OF THE FACTORS RULING THE DEGREE OF THE ASYMMETRY IN THE $[\eta] \sim \theta$ CURVE (EXAMINATION OF EQS. (3a) AND (3b) FOR P.V.AC.-ACETONE-WATER[20] AND P.V.AC.-METHANOL-WATER SYSTEMS[18])

	P.V.Ac.-acetone-water system $\mu_{12}=1.53$[1], $\theta_c=0.95$[1]					P.V.Ac.-methanol-water system $\mu_{12}=0.30$[1], $\theta_c=0.80$[1]				
δ	$(\mu_{12}\delta)^2 \times 10^4$	$\theta(1-\theta) \times 10^2$	$\dfrac{\left\{\left(\frac{\theta}{V_1}\right)+\frac{(1-\theta)}{V_2}\right\}^2}{\left(\frac{\theta}{V_1}\right)+\frac{(1-\theta)}{V_2}} \times 10^3$	$\Delta^* \times 10^8$	$(\Delta_2-\Delta_1)^* \times 10^8$	$(\mu_{12}\delta)^2 \times 10^4$	$\theta(1-\theta) \times 10^2$	$\dfrac{\left\{\left(\frac{\theta}{V_1}\right)+\frac{(1-\theta)}{V^2}\right\}^2}{\left(\frac{\theta}{V_2}\right)+\frac{(1-\theta)}{V_1}} \times 10^3$	$\Delta^* \times 10^8$	$(\Delta_2-\Delta_1)^* \times 10^8$
0.01	2.34	3.84	4.35	1.95	1.30	0.09	15.39	19.85	1.38	0.09
−0.01		5.64	4.96	3.25			16.59	19.64	1.47	
0.02	9.36	2.91	4.08	5.57	10.33	0.36	14.76	18.11	4.80	1.42
−0.02		6.51	5.22	15.90			17.16	20.15	6.22	
0.03	21.06	1.96	3.84	7.91	34.96	0.81	14.11	17.63	10.08	4.76
−0.03		7.36	5.54	42.87			17.71	20.69	14.84	
0.04	31.44	0.99	3.64	6.74	82.67	1.44	13.44	17.18	16.61	11.27
−0.04		8.19	5.85	89.41			18.24	21.22	27.88	
0.10						9.00	9.00	14.81	60.04	173.64
−0.10							21.00	25.40	233.68	

* These Δ values are an approximate values, which were calculated by the relation, $\Delta=(1/2)(\mu_{12}\delta)^2\theta(1-\theta)\{(\theta/V_1)+(1-\theta)/V_2\}^2/\{(\theta/V_2)+(1-\theta)/V_1\}$.

Now, the effect of the molar volumes of the two liquids should be considered. When the molar volume of the solvent is larger than that of the nonsolvent $(V_1 > V_2)$, the asymmetry of the $[\eta] \sim \theta$ curve is increasingly promoted by this effect, since the terms represented by $1/\{(\theta/V_2)+(1-\theta)/V_1\}$, are greater in Eq. (3b) (at θ_2) than in Eq. (3a) (at θ_1). When $V_2 > V_1$, this effect of the molar volumes behaves as if it makes the degree of the asymmetry to be rather decreased. It is possible, however, to prove from Eqs. (3a) and (3b) that the deviation Δ_2 at the composition θ_2 is always greater than the deviation Δ_1 at θ_1 even when $V_2 > V_1$, owing to the predominant influence of the $\theta(1-\theta)$ values. When the degree of the asymmetry is compared for different systems, moreover, the magnitude of the terms, $1/\{(\theta/V_2)+(1-\theta)/V_1\}$ must be considered for the different systems. Therefore, it is no wonder that the degree of the asymmetry is sometime greater in the latter case $(V_2 > V_1)$ than in the former case $(V_1 > V_2)$ even if the comparison were made between the systems having equal θ_c and A_{12} values. Naito[21] pointed out that the $[\eta] \sim \theta$ curves show a remarkable asymmetry in the ternary systems, which involve acetone, *n*-propyl alcohol, and dioxane as the nonsolvents in polyvinyl alcohol-water solutions. These systems belong to the case, $V_2 > V_1$, although the effects of the θ_c and A_{12} values may predominate over the degree of the asymmetry.

Equilibrium Swelling

Boyer and Spencer[22] measured equilibrium swelling of polysyrene-divinyl benzene gels in solvent-nonsolvent mixtures. Fig. 6 is a semilogarithmic plot of μ, calculated by the Flory-Rehner equation (Eq. (9) in Part *IV*), against the composition of the solvent from their data for toluene-propanol mixture, which according to them, consists of three straight line portions, the first break occuring at $\mu \doteqdot 0.5$, the second at $\mu \doteqdot 1.0$. In the author's opinion, however, the $\mu \sim \theta$ relatino

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[20] K. Endo, *J. Chem. Soc. Japan*, 71, 232 (1950).

[21] R. Naito and T. Kominami, *Chem. of High Polymer, Japan*, II, 444 (1954).

[22] R.F. Boyer and R.S. Spencer, *J. Polymer Sci.*, 3, 97 (1948).

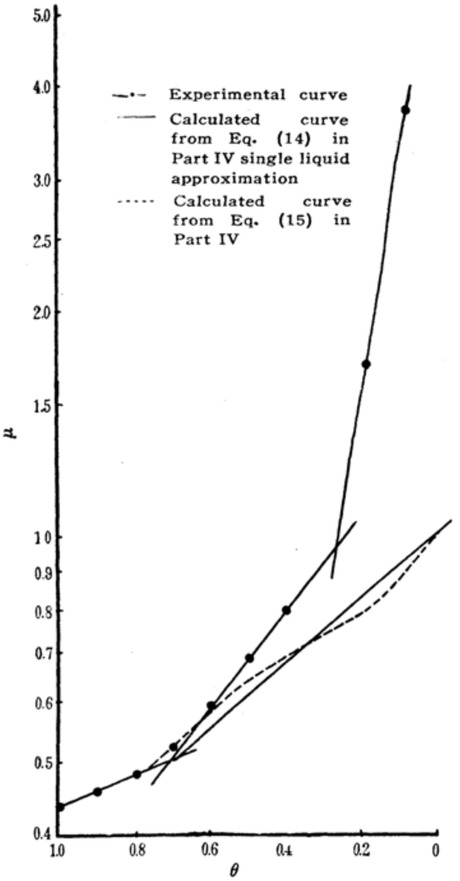

Fig. 6. Comparison of the theoretical $\mu\sim\theta$ curve considering the effect of selective adsorption with the experimental curve (Polystyrene-divinyl benzene gel-toluene-*n*-propanol).

should be represented by a smooth curve instead of the three straight lines. Although we can easily show that one of the origins of the break at $\mu=0.5$ resides in the choice of a semilogarithmic type of plot[23], the $\mu\sim\theta$ "curve" for this system clearly goes upward considerably in the neighbourhood of $\mu=0.5$ and also of $\mu=1.0$. These phenomena may imply the breakdown of the μ concept for poor solvents, as was pointed out by Boyer and Spencer[22]. This failure of the μ concept may be due to some complicated factors including those discussed in their paper[22], and may be due in part to the approximation of Eq. (12) applied instead of Eq. (13) in Part IV. For the present purpose, however, we shall confine ourselves to a discussion of the effect of the selective adsorption on the μ values. Also in order to make the other factors clear, it may not be meaningless, because this effect is supposed to be an important one of the above factors.

It is possible to calculate the contribution of the selective adsorption to the μ value from the equations derived in Part IV. Employing Eq. (14) in Part IV for the single liquid approximation[24], the interaction para-

TABLE III

THE CONTRIBUTION OF THE SELECTIVE ADSORPTION EFFECT TO THE μ VALUE OBTAINED FROM EQUILIBRIUM SWELLING OF POLYSTYRENE-DIVINYL BENZENE GELS (0.0462% D.V.B.) IN TOLUENE-N-PROPANOL MIXTURES AT 23°C.

$V_1=107,\ V_2=75.1,\ \mu_{13}=0.434,\ \mu_{23}=1.02,\ \mu_{12}=0.451$

θ	v_3'	μ (experimental)	μ (calculated for the single liquid approximation)	Contribution of selective adsorption*
1.0	0.0596	0.434	0.434	0
0.9	0.0650	0.452	0.452	0.0022
0.8	0.0780	0.479	0.479	0.0079
0.7	0.1225	0.523	0.505	0.0155
0.6	0.2362	0.592	0.562	0.0259
0.5	0.3880	0.688	0.614	0.0247
0.4	0.5195	0.800	0.677	0.0150
0.3	0.6256	0.925	0.750	(−0.0011)
0.2	0.8941	1.72	0.831	(−0.0458)
0.1	0.9906	3.80	0.921	(−0.0480)
0	0.9973	4.84	1.02	0

The contribution of the selective adsorption to the μ value has been calculated by $\{\mu_{23}-\mu_{13}+\mu_{12}(1-2\theta)\}^2[\theta(1-\theta)\{(\theta/V_1)+(1-\theta)/V_2\}/\{(\theta/V_2)+(1-\theta)/V_1\}]\times[1/2-v_3'+\mu_{12}\theta(1-\theta)\{1-4v_3'+(5/4)v_3'^2\}+\{\mu_{12}\theta(1-\theta)\}^2\{2-12v_3'+(17/2)v_3'^2\}]$ instead of Eq. (15) in Part IV, which may give a satisfactory approximation.

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[23] It is derived from the condition, $\frac{d^2(\ln\mu)}{d\theta^2}=0$, that the point of inflexion of the $\ln\mu\sim\theta$ curve occurs at $\mu=0,5$, so long as the single liquid approximation and the relation, $(\mu_{12})^{1/2}=(\mu_{23})^{1/2}-(\mu_{13})^{1/2}$, which corresponds to Scott's approximation [*J. Chem. Phys.*, **17**, 268 (1949)], hold their validity (cf. Eq. (14) in Part IV).

[24] In these calculations of the interaction parameters, it is assumed that $\mu_{13}={}^1/_2-(V_1/V_3)({}^1/_2-\mu_s')+(V_1/RT)A_{13}$ and $\mu_{23}={}^1/_2-(V_2/V_3)({}^1/_2-\mu_s')+(V_2/RT)A_{23}$, where the last terms should be written $(V_0/RT)A_{13}$ and $(V_0/RT)A_{23}$ respectively, but these expressions may be permitted as approximate ones (cf. Eq. (14) in Part IV).

meters are evaluated from the μ values for 0, 10, and 20 percent propanol, since the errors due to the selective adsorption and other factors are supposed to be very slight in such solvent-rich compositions ($\mu_{12}=0.434$, $\mu_{23}=1.02$, and $\mu_{12}=0.451$[24]). The statement of Boyer and Spencer that this toluene-propanol mixture does not show a maximum swelling at any composition, is well explained from these values of the interaction parameters (i.e. this ternary system belongs to Case I mentioned in the preceding section), whereas it is unacceptable from Gee's treatment[25] as they pointed out[22].

Employing these values of the interaction parameters, the contribution of the selective adsorption to the μ value has been estimated from Eq. (15) in Part IV, and is given in Table III, being compared with the μ values calculated for the single liquid approximation, and with those from the experiments. These are also shown in Fig. 6. Until a certain composition is reached, the contribution of the selective adsorption increases with the addition of the nonsolvent, and amounts to a considerable percentage of the total μ value as was discussed in Part IV. It is interesting to note that this contribution begins to decrease from this composition, owing both to the increase of v_3' and to the decrease of θ in Eq. (15) in Part IV, and finally, gives a negative value in the composition range above 80% propanol (the condition, $1/2-v_3'+B\{1-4v_3'+(5/4)v_3'^2+\cdots\cdots\}+B^2\{2-12v_3'+(17/2)v_3'^2+\cdots\cdots\}+\cdots\cdots>0$ cannot be satisfied for the extremely great content of the nonsolvent. Thus, the dependency of the above contribution upon v'_3 and B_1 may appear in various complicated ways such as are represented by Eq. (15) in Part IV, whereas it can be ignored approximately in the treatments of osmotic pressure and intrinsic viscosity.

The writer wishes to thank Prof. H. Maeda, and Assist. Prof. K. Makishima for constant encouragement and many helpful suggestions.

Laboratory of Textile Chemistry,
Tokyo Institute of Technology
Tokyo

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[25] G. Gee, *Trans. Faraday Soc.*, **40**, 468 (1944).