Notes on The Polymer-Mixed Solvents System. I The refinement of the free energy expression

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(Received January 18, 1952)

Introduction

While the thermodynamic systems involved in the problems of fractionation of high polymer are essentially multicomponent ones, they are normally simplified or approximated by assuming that the mixture of two solvents behaves as a homogeneous liquid with resspect to the polymer.(1)(2) Although this single liquid approximation is useful in obtaining semi-quantitative information concerning the polymer-mixed solvents interaction, it requires that the proportions of the two liquids are the same in both phases or in both sides of the membrane. Employing the single liquid approximation and some other approximation methods, Scott(3) has considered the problems of phase equilibria in a ternary system of polymer and two liquids. The free energy expression in his treatment contains, however, two serious assumptions which are not always applicable to the practical cases. Namely,

(a) the interaction energy between unlike pairs of molecules of the constituents is the geometric mean of those between respective like pairs (the Scatchard's approximation).(4)

From this assumption Scott derived the heat of mixing in the ternary system by employing two constants A_{13}, A_{23} characteristic of the corresponding binary systems, polymer-liquid 1 and polymer-liquid 2.

(b) the unit submolecule of the polymer and the molecules of the two solvents are all the same in shape and size.

Concerning the above two assumptions, the free energy expression will be refined and the single liquid approximation will be discussed in the present paper.

The Heat of Mixing of the System

Scatchard(4) has shown that if we make an assumption entirely equivalent to a binary components system we obtain for the heat of mixing in the ternary system

$$\Delta H^{M}{}_{123}=V_m(A_{12}v_1v_2+A_{13}v_1v_3+A_{23}v_2v_3),$$
$$V_m=x_1V_1+x_2V_2+x_3V_3, \qquad (1)$$

where the A's are the constants characteristic to each pair of the components, the v's volume fractions, the x's mole fractions and the V's molal volumes of the constituents. Differentiation leads to the partial molal heat of mixing,

$$\Delta\bar{H}_1=V_1[A_{12}v_2^2+A_{13}v_3^2+(A_{12}+A_{13}-A_{23})v_2v_3] \qquad (2a)$$
$$\Delta\bar{H}_2=V_2[A_{12}v_1^2+A_{23}v_3^2+(A_{12}+A_{23}-A_{13})v_1v_3] \qquad (2b)$$
$$\Delta\bar{H}_3=V_3[A_{13}v_1^2+A_{23}v_2^2+(A_{13}+A_{23}-A_{12})v_1v_2]. \qquad (2c)$$

Without the assumption (a) previously noted, we can derive the partial molal heat of mixing $\Delta\bar{H}_0$, corresponding to the single liquid approximation, directly from Eq. (1) as follows; when the ratio of compositions of solvents 1 and 2 is constant,

$$\theta N_1V_1=N_2V_2,\ N_1V_1+N_2V_2=(1+\theta)N_1V_1=N_0V_0,$$
$$N_0=N_1+N_2,\quad V_0=(1+\theta)V_1/(1+\theta V_1/V_2),$$

and then, Eq. (1) becomes

$$\begin{aligned}\Delta H^{M}{}_{123}&=A_{12}\{N_0V_0/(1+\theta)\}\\&\times\{N_0V_0\theta/(1+\theta)\}/(N_0V_0+N_3V_3)\\&+A_{13}\{N_0V_0/(1+\theta)\}\times N_3V_3/(N_0V_0+N_3V_3)\\&+A_{23}\{N_0V_0\theta/(1+\theta)\}\times N_3V_3/(N_0V_0+N_3V_3). \qquad (3)\end{aligned}$$

Differentiating with respect to N_0,

$$\begin{aligned}\Delta\bar{H}_0&=V_0\{[\theta/(1+\theta)^2]A_{12}(1-v_3^2)+[1/(1+\theta)]A_{13}v_3^2\\&+[\theta/(1+\theta)]A_{23}v_3^2\}=V_0\{-[\theta(1+\theta)^2]A_{12}\\&+[1/(1+\theta)]A_{13}+[\theta/(1+\theta)]A_{23}\}v_3^2\\&+[\theta/(1+\theta)^2]V_0A_{12}, \qquad (4)\end{aligned}$$

where the term $[\theta/(1+\theta)^2]V_0A_{12}$ vanishes when the mixture of solvents 1 and 2 are assumed to be a homogeneous liquid. Hence,

$$\begin{aligned}\Delta\bar{H}_0=V_0A_{30}v_3^2,\quad A_{30}&=-[\theta/(1+\theta)^2]A_{12}\\&+[1/(1+\theta)]A_{13}+[\theta/(1+\theta)]A_{23}. \qquad (5)^{(5)}\end{aligned}$$

The Entropy of Mixing of the System

The familiar expression of Huggins(6) and Flory(7) for the entropy of high polymer solutions may be written (binary system)

$$\begin{aligned}\Delta S=R\ln W=-R\{&N_1\ln[N_1/(N_1+xN_3)]\\&+N_3\ln[xN_3/(N_1+xN_3)]+u_s[N_1xN_3/(N_1+xN_3)]\}. \qquad (6)\end{aligned}$$

(The notation of this equation is similar to what is usually employed.)

Here we adopt an approximate method introducing the effect of volume difference between the polymer submolecule and the solvent molecule. At first, we consider a binary system of polymer 3 and liquid 1, where the molal volume V_1 of the solvent differs from the equivalent quantity V_3 of the polymer submolecule. In hypothetical lattice sites the operation of packing the solvent molecules which are equal in size and shape to the submolecule in the remaining sites is exactly equivalent to that of setting the polymer molecules in the sites without considering the existence of the solvent molecules. (This situation leads to Eq. (6)) When $V_1>V_3$, however, the configurations of polymer molecules are constrained by larger solvent molecules. The total number of

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(1) R. S. Scott, *J. Chem. Phys.*, **13**, 178 (1945).

(2) G. Gee, *Trans. Faraday Soc.*, **40**, 468 (1944).

(3) R. S. Scott, *J. Chem. Phys.*, **17**, 268 (1949).

(4) G. Scatchard, *J. Am. Chem. Soc.*, **56**, 995 (1934); *Trans. Faraday Soc.*, **33**, 160 (1937).

(5) Applying the "geometric mean rule" to Eq. (5), we can easily derive Scott's result $\mu_{30}=[(A\phi_1-B\phi_2)/(\phi_1+\phi_2)]^2$ in reference 3.

(6) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *Ann. N. Y. Acad. Sci.*, **43**, I (1942).

(7) P. J. Flory, *J. Chem. Phys.*, **9**, 666 (1941); Ibid., **13**, 453 (1945).

different configurations in this case W'', will be obtained from W', when N_1V_1/V_3 is substituted for N_1 in the above expression of W (Eq. 6), multiplying by a factor due to the fact that V_1/V_3 sites must be in one group. Thus,

$$W''=W'\times W_1\Big/\binom{N_1V_1/V_3+xN_3}{N_1V_1/V_3}, \qquad (7)$$

where W_1 is the number of different ways in which N_1 molecules each occupying V_1/V_3 sites can be packed in $(N_1V_1/V_3)+xN_3$ sites without overlapping. Ōsawa(8) calculated W_1 for certain cases, but we may replace $R\ln W_1$ with the usual expression of the entropy of mixing, $-R[N_1\ln v_1+N_2\ln v_2]$. Thus,

$$\begin{aligned}\varDelta S''=\varDelta S'-R\{&N_1\ln[N_1V_1/(N_1V_1+xN_3V_3)]\\ &+xN_3\ln[xN_3V_3/(N_1V_1+xN_3V_3)]\}\\ +R\{&(N_1V_1/V_3)\ln[N_1V_1/(N_1V_1+xN_3V_3)]\\ &+xN_3\ln[xN_3V_3/(N_1V_1+xN_3V_3)]\} \qquad (8)\end{aligned}$$

where $\varDelta S'=R\ln W'$.
And

$$\begin{aligned}\varDelta\bar{S}_1''=&-R[(V_1/V_3)\{\ln v_1+(1-1/x)v_3+\mu_s v_3^2\}\\ &+\{1-(V_1/V_3)\}(\ln v_1+v_3)]\\ &=R[(V_1/V_3x)v_3+(1/2-\mu_s V_1/V_3)v_3^2+\cdots]. \qquad (9)\end{aligned}$$

When $V_3>V_1$, simply,(9)

$$\varDelta S''=\varDelta S' \qquad (10)$$

$$\begin{aligned}\varDelta\bar{S}_1''=(V_1/V_3)\varDelta\bar{S}_1'=&-(RV_1/V_3)[\ln v_1+(1-1/x)v_3\\ &+\mu_s v_3^2]=R(V_1/V_3)[v_3/x+(1/2-\mu_s)v_3^2+\cdots]. \qquad (11)\end{aligned}$$

This result agrees with the Flory's formula.(10)

The first bracketed terms in Eq. (8), which correspond to W_1, are considered to be the entropy change in the case when isolated xN_3 molecules were mixed with other N_1 molecules different in size. The second bracketed terms, of course, correspond to $\binom{N_1V_1/V_3+xN_3}{NV_1/V_3}$. Thus it is easily seen that the first bracketed terms may be replaced with the usual expression of the entropy of mixing in a three components system $-R[N_1\ln v_1+N_2\ln v_2+N_3\ln v_3]$, when we deal with polymer-mixed solvents system. Therefore, when $(1+\theta)V_1/(1+\theta V_1/V_2)>V_3$,

$$\begin{aligned}\varDelta S''=\varDelta S'_{30}-R\{&N_1\ln[N_1V_1/(N_1V_1+N_2V_2+xN_3V_3)]\\ &+N_2\ln[N_2V_2/(N_1V_1+N_2V_2+xN_3V_3)]\\ &+xN_3\ln[xN_3V_3/(N_1V_1+N_2V_2+xN_3V_3)]\}\\ +R\{&[(N_1V_1+N_2V_2)/V_3]\ln[(N_1V_1\\ &+N_2V_2)/(N_1V_1+N_2V_2+xN_3V_3)]\\ &+xN_3\ln[xN_3V_3/(N_1V_1+N_2V_2+xN_3V_3)]\} \qquad (12)\end{aligned}$$

where $\varDelta S'_{30}$ corresponds to $\varDelta S'$ in Eq. (8).(11)
Hence,

$$\begin{aligned}\varDelta\bar{S}_1''=-R\{&\ln v_1+(1-V_1/V_2)v_2+(1-V_1/V_3)v_3\\ &+(V_1/V_3)[(1-1/x)v_3+\mu_s v_3^2]\} \qquad (13a)\end{aligned}$$

$$\begin{aligned}\varDelta\bar{S}_2''=-R\{&\ln v_2+(1-V_2/V_1)v_1+(1-V_2/V_3)v_3\\ &+(V_2/V_3)[(1-1/x)v_3+\mu_s v_3^2]\} \qquad (13b)\end{aligned}$$

When, $(1+\theta)V_1/(1+\theta V_1/V_2)<V_3$,

$$\begin{aligned}\varDelta S''=\varDelta S'_{30}-R[&N_1\ln\{N_1V_1/(N_1V_1+N_2V_2)\}\\ &+N_2\ln\{N_2V_2/(N_1V_1+N_2V_2)\}]. \qquad (14)^{(11)}\end{aligned}$$

Hence,

$$\varDelta\bar{S}_1''=-(RV_1/V_3)[\ln v_1+(1-1/x)v_3+\mu_s v_3^2] \qquad (15a)$$

$$\varDelta\bar{S}_2''=-(RV_2/V_3)[\ln v_2+(1-1/x)v_3+\mu_s v_3^2]. \qquad (15b)$$

Now we can write for the single liquid approximation that

$$\begin{aligned}\varDelta S'''=\varDelta S''+R\{&N_1\ln[N_1V_1/(N_1V_1+N_2V_2)]\\ &+N_2\ln[N_2V_2/(N_1V_1+N_2V_2)]\},^{(11)}\end{aligned}$$

$$N_1=N_0V_0/(1+\theta)V_1,\ N_2=\theta N_0V_0/(1+\theta)V_2,$$

and then, expressing Eqs. (12) and (14) with N_0, N_3, differentiation leads to $\varDelta\bar{S}_0'''$; When $V_0>V_3$,

$$\begin{aligned}\varDelta\bar{S}_0'''=-R\{&(V_0/V_3)[\ln v_0+(1-1/2)v_3+\mu_s v_3^2]\\ &+(1-V_0/V_3)(\ln v_0+v_3)\}=R[V_0/V_3x)\times v_3\\ &+(1/2-\mu_s V_0/V_3)v_3^2+\cdots\cdots]. \qquad (16)\end{aligned}$$

When $V_0<V_3$,

$$\begin{aligned}\varDelta\bar{S}_0'''=&-(RV_0/V_3)[\ln v_0+(1-1/x)v_3+\mu_s v_3^2]\\ &=(RV_0/V_3)[v_3/x+(1/2-\mu_s)v_3^2+\cdots\cdots]. \qquad (17)\end{aligned}$$

The Partial Molal Free Energy

Combining the equations of the previous sections for the partial molal entropy and heat of mixing, there is obtained for the partial molal free energy.

When $V_1(1+\theta)/(1+\theta V_1/V_2)>V_3$,(12)

$$\begin{aligned}\varDelta\bar{F}_1=RT\{&\ln v_1+(1-V_1/V_2)v_2+(1-V_1/V_3)v_3\\ &+(1-1/x)v_3+\mu_s v_3^2+(V_1/RT)[A_{12}v_2^2+A_{13}v_3^2\\ &+(A_{12}+A_{13}-A_{23})v_2v_3]\} \qquad (18a)\end{aligned}$$

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(8) F. Osawa, *Busseiron Kenkyu*, **12**, 27 (1948); ibid., **14**, 40 (1949).

(9) Employing Osawa's approximation, the writer estimated the effect of size and shape of solvents on $\varDelta\bar{S}_1$ for the solution of rodlike molecules ($V_3>V_1$), and the result is included in Eq. (II) as a special case. This Bulletin, **24**, 264 (1951).

(10) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(11) The bracketed terms in Eq. (14) arise from the fact that the term $\varDelta S'_{30}$ means the entropy change of mixing polymer molecules with the hypothetical homogeneous liquid assumed in the single liquid approximation. Thus these terms vanish for the single liquid approximation. This is also true for Eq. (12). It is easily seen that Eq. (12) and (14) can be also derived considering two processes, namely, mixing of liquid 1 and 2, and that of polymer 3 and this "new liquid".

(12) These conditions result from our approximate treatment of the entropy term as discussed in the previous section.

$$\Delta\bar{F}_2 = RT\{\ln v_2 + (1 - V_2/V_1)v_1 + (1 - V_2/V_3)v_3 + (1 - 1/x)v_3 + \mu_s v_3^2 + (V_2/RT)[A_{13}v_1^2 + A_{23}v_3^2 + (A_{12} + A_{23} - A_{13})v_1 v_3]\}. \tag{18b}$$

When $V_1(1+\theta)/(1+\theta V_1/V_2) < V_3$,(12)

$$\Delta\bar{F}_1 = RT\{(V_1/V_3)[\ln v_1 + (1 - 1/x)v_3 + \mu_s v_3^2] + (V_1/RT)[A_{12}v_2^2 + A_{13}v_3^2 + (A_{12} + A_{13} - A_{23})v_2 v_3]\} \tag{19a}$$

$$\Delta\bar{F}_2 = RT\{(V_2/V_3)[\ln v_2 + (1 - 1/x)v_3 + \mu_s v_3^2] + (V_2/RT)[A_{13}v_1^2 + A_{23}v_3^2 + (A_{12} + A_{23} - A_{13})v_1 v_3]\} \tag{19b}$$

For the single liquid approximation,

when $V_0 > V_3$,

$$-\Delta\bar{F}_0 = RT(V_0/V_3 x)v_3 + (1/2 - \mu_s V_0/V_3 - V_0 A_{30}/RT)v_3^2 + \cdots\cdots] \tag{20}$$

when $V_0 < V_3$,

$$-\Delta\bar{F}_0 = RT\{(V_0/V_3)[v_3/x + (1/2 - \mu_s - V_3 A_{30}/RT)v_3^2 + \cdots\cdots]\}. \tag{21}$$

Using the above Eqs. (18a, b) and (19a, b), we can compute the equilibrium phase diagrams for this ternary system by the usual conditions;

$$\Delta\bar{F}_1' = \Delta\bar{F}_1'', \ \Delta\bar{F}_2' = \Delta\bar{F}_2'', \ \Delta\bar{F}_3' = \Delta\bar{F}_3''. \tag{22}$$

(The expression for $\Delta\bar{F}_3$ is easily derived from the heat and entropy expressions which have been obtained previously.)

Now, if we consider the entropy term only, we obtain from Eqs. (15a, b) and (22)

$$(V_1/V_3)[\ln v_1' + (1 - 1/x)v_3' + \mu_s v_3'^2] = (V_1/V_3)[\ln v_1'' + (1 - 1/x)v_3'' + \mu_s v_3''^2] \tag{23a}$$

$$(V_2/V_3)[\ln v_2' + (1 - 1/x)v_3' + \mu_s v_3'^2] = (V_2/V_3)[\ln v_2'' + (1 - 1/x)v_3'' + \mu_s v_3''^2]. \tag{23b}$$

Hence,

$$\ln(v_1'/v_2') = \ln(v_1''/v_2'') \quad \text{or} \quad \theta' = \theta''. \tag{24}$$

Thus, the single liquid approximation is satisfied only when $\Delta\bar{H}_1 = 0$, and the invalidity of the single liquid approximation in the usual cases is due to the heat term only.(13) As immediately seen from Eqs. (13a, b), this is not true for the case when $V_3 < V_0$. In most of the actual cases, however, V_3 is anticipated to be larger than V_0 from the data of the molecular construction of polymer molecules, although the exact values of V_3 cannot be deduced.(14) From this point of view the problems of the selective adsorption will be discussed in future.

A Special Treatment of Associated Liquids

It is interesting to assume polymer-two liquids systems in which one or two of the liquids are associated liquids as an extreme case when $V_0 > V_3$. In this case, the deviation from the single liquid approximation may be attributable to the entropy term as well as to the heat term. Tobolsky and Bratz,(15) and Flory(16) have treated solutions of associated liquids with high polymer equations. The situation becomes more complicated in our case, but it does not seem to be inadequate to assume that the associated liquid consists of an equiliblium mixture of polymer molecules of various sizes, in order to estimate roughly the above volume effect.

To avoid complications we assume now that the submolecule of polymer and the "submolecule" of associated liquid and the molecule of non-asociated liquid have all the same volume. This assumption may be sufficient to obtain a rough picture of the volume effect on the entropy of mixing in polymer-two liquids systems in which one or two components are associated liquid. First of all, let us consider the binary system polymer 3-associated liquid 1.

(A) Polymer 3-associated liquid 1 system.—We can assume this system as a special case where the size and shape of solvent differ extremely from that of polymer submolecule. Thus, employing Eq. (7), the entropy of mixing in this system may be written,

$$\begin{aligned}\Delta S'' &= \Delta S'_{30} + \Delta S_{10} - \Delta S^0_{31} = -R[yN_1\ln\{yN_1/(yN_1 + xN_3)\} + N_3\ln\{xN_3/(yN_1 + xN_3)\}] \\ &\quad - R[N_1\ln\{yN_1/(yN_1 + xN_3)\} + xN_3\ln\{xN_3/(yN_1 + xN_3)\}] + R[yN_1\ln\{yN_1/(yN_1 + xN_3)\} \\ &\quad + xN_3\ln\{xN_3/(yN_1 + xN_3)\}] \\ &= -R[N_1\ln\{xN_3/(yN_1 + xN_3)\} + N_3\ln\{yN_1/(yN_1 + xN_3)\}]\end{aligned} \tag{25}$$

where $\Delta S'_{30} = R\ln W'$ = the entropy of mixing N_3 polymer molecules with randomly distributed yN_1 separate submolecules of liquid 1, $\Delta S_{10} = R\ln W_1$ = the entropy of mixing N_1 molecules of associated liquid with xN_3 separate submolecules of polymer 3, and ΔS^0_{31} (which corresponds to $\binom{yN_1 + xN_3}{yN_1}$ = the entropy of mixing both sorts of the submolecules at random. (the number average degree of "polymerization" of associated liquid $1 = y$).

The terms containing μ_s in the entropy expression vanishes in this case as can be easily understood from Huggins' theory(17) from which

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(13) This is also true for Scott's result of Eqs. (9abc) in reference 3.

(14) One submolecule is supposed to be several times larger than the monomeric unit of the polymer, although the molal volume of the solvent could be a little larger than the equivalent quantity of the monomeric unit of the polymer.

(15) A. V. Tobolsky, P. J. Bratz, *J. Chem. Phys.*, **13**, 379 (1945).

(16) P. J. Flory, *J. Chem. Phys.*, **14**, 49 (1945).

(17) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942)

the terms were derived.

Differentiating Eq. (25) with respect to N_1,

$$\Delta\bar{S}_1'' = -R[\ln v_1 + (1-y/x)v_3]\,. \tag{26}$$

This result corresponds to Scott's for the polymer-polymer system⁽¹⁵⁾ (Eq. (1a) in reference 18). Here we attempt to apply a somewhat paradoxical situation to the present problem. Namely, it may be permissible to assume that the associated liquid in both sides of the membrane were diffusible as separate submolecules, although it behaves thermodynamically as if it were a mixture of macromolecules in both sides. Thus, differentiating Eq. (25) with respect to yN_1 (not N_1), we can obtain an "effective" partial molal entropy of mixing,

$$\begin{aligned}\Delta\bar{S}_1'' &= -R[(1/y)\ln v_1 + (1/y-1/x)v_3]\\ &= R[v_3/x + v_3^2/2y + \cdots\cdots]\end{aligned} \tag{27}$$

Since the y values are supposed to be considerably large in the polymer-polymer system, two polymers would be often incompatible if there were any positive heat of mixing.⁽¹⁹⁾ Considering that such incompatibility does not appear in the actual polymer-associated liquid systems, the average degree of "polymerization" is supposed to be not so large as that of the actual polymer.

Therefore, it may be rather suitable to assume y as a measure of the effect of "association" of solvent on the partial molal entropy of mixing.

(B) Polymer 3-liquid 1-associated liquid 2.—In this case, we can assume two processes separately, namely, the mixing of polymer 3 and associated liquid 2, ΔS_{23} (which has been given by Eq. (25)), and the dilution of this "mixture" by liquid 1, $\Delta S_{\widehat{23}1}$. Then,

$$\begin{aligned}\Delta S'' = \Delta S_{23} + \Delta S_{\widehat{23}1} &= -R\{N_2\ln[yN_2/(yN_2+xN_3)]\\ &\quad + N_3\ln[xN_3/(yN_2+xN_3)]\}\\ &\quad - R\{N_1\ln[N_1/(N_1+yN_2+xN_3)]\\ &\quad + (N_2+N_3)\ln[(xN_3+yN_2)/(N_1+yN_2+xN_3)]\\ &\quad + \mu_s^{\widehat{23}1}\times N_1(xN_3+yN_2)/(N_1+yN_2+xN_3)\}.\end{aligned} \tag{28}$$ ⁽²⁰⁾

Differentiation leads to

$$\begin{aligned}\Delta\bar{S}_1'' &= -R[\ln v_1 + (1-1/y)v_2\\ &\quad + (1-1/x)v_3 + \mu_s^{\widehat{23}1}(v_2+v_3)^2]\end{aligned} \tag{29a}$$

$$\Delta\bar{S}_2'' = -R[\ln v_2 + (1-y)v_1 + (1-y/x)v_3 + y\mu_s^{\widehat{23}1}v_1^2] \tag{29b}$$

$$\Delta\bar{S}_3'' = -R[\ln v_3 + (1-x)v_1 + (1-x/y)v_2 + x\mu_s^{\widehat{23}1}v_1^2]. \tag{29c}$$

When $\mu_s^{12} = \mu_s^{13} = \mu_s^{\widehat{23}1}$, these results coincide with the result of Scott' (Eqs. (5a, b, c) in reference 18).

If the single liquid approximation may be applicable, assuming $\theta N_1 = yN_2$, $N_0 = (1+\theta)N_1$, and

$$\begin{aligned}\Delta S''' = \Delta S'' &+ R\{N_1\ln[N_1/(N_1+yN_2)]\\ &+ N_2\ln[yN_2/(N_1+yN_2)] + \mu_s^{12}\\ &\times N_1 yN_2/(N_1+yN_2)\}\,,\end{aligned} \tag{30}$$ ⁽¹¹⁾

$$\begin{aligned}\Delta\bar{S}_0''' &= -R\{[1/(1+\theta)+\theta/(1+\theta)y]\ln v_0 + [1/(1+\theta)\\ &\quad - 1/x + \theta/(1+\theta)y]v_3 + \mu_s^{\widehat{23}1}[\theta/(1+\theta)]^2 v_3^2\}\\ &= R[v_3/x + \{(1/2)[1/(1+\theta)+\theta/(1+\theta)y]\\ &\quad - \mu_s^{\widehat{23}1}[\theta/(1+\theta)]^2\}v_3^2 + \cdots\cdots\ ]\,.\end{aligned} \tag{31}$$

Combining Eq. (31) with Eq. (5),

$$\begin{aligned}-\Delta\bar{F}_0 &= RT[v_3/x + \{(1/2)[1/(1+\theta)+\theta/(1+\theta)y]\\ &\quad - \mu_s^{\widehat{23}1}[\theta/(1+\theta)]^2 - (\bar{V}_0/RT)[-\theta/(1+\theta)^2\times A_{12}\\ &\quad + 1/(1+\theta)\times A_{23} + \theta/(1+\theta)\times A_{13}]\}v_3^2 + \cdots].\end{aligned} \tag{32}$$

This result shows that the entropy term contributes in some way to the solubility and the phase separation in the system and that whether associated liquid 2 is solvent or non-solvent makes a considerable difference in the above contribution. Namely, the mixed solvents show poorer solvent power than that supposed from the true energetical solvent power, and this is more notable when the associated liquid is solvent than when it is non-solvent.

(C) Polymer 3-associated liquids 1 and 2 system.—The above procedure by which we derived Eq. (28) can be applied to introduce the entropy of mixing in polymer 3- associated liquids 1 and 2 system. Hence,

$$\begin{aligned}\Delta S'' = \Delta S_{31} + \Delta S_{\widehat{31}2} &= -R\{N_1\ln[xN_3/(yN_1+xN_3)]\\ &\quad + N_3\ln[yN_1/(yN_1+xN_3)]\} - R\{N_2\ln[zN_2/(yN_1\\ &\quad + zN_2+xN_3)] + (N_1+N_3)\ln[(yN_1+xN_3)/(yN_1\\ &\quad + zN_2+xN_3)]\} = -R\{N_1\ln[yN_1/(yN_1+zN_2\\ &\quad + xN_3)] + N_2\ln[zN_2/(yN_1+zN_2+xN_3)]\\ &\quad + N_3\ln[xN_3/(yN_1+zN_2+xN_3)]\}\,,\end{aligned} \tag{33}$$

where ΔS_{31} = the entropy of mixing polymer 3 with associated liquid 1, (see Eq. (25)) and $\Delta S_{\widehat{31}2}$ = that of mixing this mixture with associated liquid 2. (The average degree of "polymerization" of associated liquid $2 = z$.) Hence,

$$\Delta\bar{S}_1'' = -R(\ln v_1 + v_2 + v_3 - yv_2/z - yv_3/x) \tag{34a}$$

$$\Delta\bar{S}_2'' = -R(\ln v_2 + v_3 + v_1 - zv_3/x - zv_1/y) \tag{34b}$$

$$\Delta\bar{S}_3'' = -R(\ln v_3 + v_1 + v_2 - xv_1/y - xv_2/z) \tag{34c}$$

For the single liquid approximation,

$$\theta yN_1 = zN_2, \quad N_0 = yN_1 + zN_2 = (1+\theta)yN_1\,,$$

$$\begin{aligned}\Delta S''' = \Delta S'' &+ R\{N_1\ln[yN_1/(yN_1+zN_2)]\\ &+ N_2\ln[zN_2/(yN_1+zN_2)]\},\end{aligned} \tag{35}$$ ⁽¹¹⁾

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(18) R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).

(19) For two polymers, the critical value of μ ($\Delta\bar{H}_1 = RTy\mu v_3^2$) is several orders of magnitude smaller than that for two normal liquids ($\mu = 2$) or for a polymer-solvent system ($\mu = 1/2$) see Eq. (2) in reference 18).

(20) This expression of $\Delta S_{\widehat{23}1}$ is a rough approximation obtained by assuming hypothetically that the mixture of polymer 3 and associated liquid 2 is a homogeneous polymer.

and then,

$$\Delta\bar{S}_0''' = R\{v_3/x + (1/2)[1/(1+\theta)y + \theta/(1+\theta)z]v_3^2 + \cdots\cdots\cdots\} . \qquad (36)$$

Actually, the problem of "association" is far more complicated than appears above. Thus the present treatment includes many questions to be discussed. First, somewhat questionable situation in separate evaluation of the entropy and energy term may not be permissible especially in the systems in which one or two components are associated liquids. Next, we must distinguish between hydrogen bonded liquids and those associated simply because of the dipole moment of the molecules, and between, a three dimentional "polymer" network such as water which is able to form tetrahedral bonds per molecule and the linear "polymer" such as alcohols in which molecules with capacity for only two bonds per molecule are combined with each other. In short, the essential feature of the potentials between like and unlike pairs must be clearer. It is the purpose of this chapter, however, to indicate the possible applicability of the above procedure for rough estimation of the entropy in these systems.

Summary

The free energy expression derived by Scott for the polymer-mixed solvents system are refined and amplified, removing the assumptions which are not always applicable to the actual cases, although it was introduced by him for the sake of simplicity.

Owing to scantiness of the available data and to difficulties of exact calculation, the phase diagrams of the system using the results obtained are not given here. Determination of plait points and the problems in the osmotic pressure measurement in mixed solvents will be discussed elsewhere. Here, we confined ourselves to formulate the free energy expression for various systems also involving the systems in which one or two of the constituents are associated liquids as a special case where the assumption (b) is far from true. Application of the result obtained to some problems in viscosity, osmotic pressure, and swelling phenomena will be presented in the following articles.

This paper was presented at the Annual Meeting of the Tokyo Institute of Technology, where the treatment of associated liquids was discussed with particular reference to the applicability of the above methods to the thermodynamic problems of association.

In the writer's opinion, the generality of the thermodynamic function derived here in the application to equilibria involving transformation between various "polymeric" species of the associated liquid may be accessible when the volume effect of the associated liquid on the entropy term in these systems must be encountered. Obviously the Flory-Tobolsky-Bratz treatment is applicable only to the linear "polymer" such as alcohol, and we may go too far to say that our treatment is also applicable to the three dimentional "polymer". Our treatment is supposed, however, to be not far from true even in such a case, since the entropy of mixing in the above systems containing associated liquids as one or two components was formulated on the assumption that the submolecules of the "polymer" are distributed at random. i. e., this corresponds to the Bragg-Williams approximation.

The author expresses his appreciation to Professor A. Harajima and S. Ichimura for their kind reading and some suggestions, and to the director, K. Makishima, for his encouragement and support to this work.

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