A Remark on Solvent Power of Various Solvents for High Polymers

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The process of the interaction of long chain molecules with low molecular weight solvent molecules, which includes solubility, swelling, and plasticization, is of great importance both to research and to industry. The definition of solvent power still lacks precision; namely, the term of "good" or "bad" solvent has been employed vaguely in the discussions of viscosity, osmotic pressure, swelling, and other measurements.

The empirical parameter μ, which was introduced by Huggins1) in his statistical treatment of high polymer solutions is well used as a measure of thermodynamic interaction between polymer and solvents. Although this parameter μ can be considered as a measure of solvent power, it cannot always explain the experimental results of viscosity, osmotic pressure, and swelling measurements. Indeed, systematic study, choosing various liquids for one polymer substance, reveals that the second virial coefficient in osmotic pressure expression represented by power series expansion in polymer concentrations, intrinsic viscosity and swelling ratio do not always show a good correspondence to the μ values. In this paper we shall analyse the meaning of μ in a more improved and empirically satisfying approximation, considering principally the volume effect of the solvent, and shall examine some experimental results in the light of this procedure.

Analysis of Parameter μ

From the well-known Flory-Huggins' theory of high polymer solutions the partial molal free energy of solvent is expressed by

$$\Delta\overline{F}_1 = RT\{\ln(1-v_2)+(1-1/x)v_2+\mu v_2^2\} \quad (1)$$

where v_2 is volume fraction of polymer, and x the volume ratio of polymer molecule to solvent molecule (number average). With the use of Eq. (1) justified to a large measure by experiment, a more careful consideration of the parameter μ is desirable. In the initial statistical treatment of Huggins,1) μ consisted of a term $1/z'$, introduced from the calculation of the entropy of mixing (z': effective co-ordination number in hypothetical lattice sites1)), to which was added a contribution from the heat of mixing. As mentioned in the later sections, the necessity of choosing unreasonably low values of z (co-ordination number) to fit the data has lead to abandonment of this original interpretation, but the separation of μ into entropy and heat terms is of quite general validity, and we may write2)

$$\mu = \mu_S + \mu_H \quad (2)$$

Let us first consider μ_S for athermal solutions. In Table 1 the expressions of μ_S are summarized, being calculated from the results of the statistical evaluation of the entropy of dilution by several authors1)3)4)5).

Table 1

Theoretical Expression of μ_s by Several Authors

Authors	$\Delta\overline{S}_1$	μ_s	
Flory3)	$-R[\ln(1-v_2)+v_2]$	0	
Huggins1)	$-R[\ln(1-v_2)-(1-1/x)(Z'/2)\ln\{1-)2v_2/Z')\}]$	$(1-1/x)/Z'$	
Miller4)	$-R[\ln(1-v_2)-(Z/2)\ln\{1-(2/Z)v_2(1-1/x)\}]$	$(1-1/x)^2/Z$	
Guggenheim5)	$-R[\ln(1-v_2)-(Zq_1/2)\ln\{1-(2/Zq_2)(x_2-x_1)v_2/x_2)\}]$ $(q=\{x(Z-2)+2\}/Z)$	$(1-1/x)^2/Z$	$(x_2 \gg x_1)$

Except Flory's original formulation3), the theoretical expressions of μ_S are nearly equal to $1/z$. Experimentally μ_S falls between 0.3 and 0.5, far too high to be explained as merely $1/z$. This discrepancy is well interpreted in the following sections by consider-

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

2) Within the accuracy of experiments μ is nearly independent on polymer concentration for many systems, but the μ_s or μ_H is not constant except in very dilute range. Therefore, our discussion is limited to that of high dilution.

3) P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941).

4) A. R. Miller, *Proc. Camb. Phil. Soc.*, **35**, 109 (1942); ibid., **39**, 54, 131 (1943).

5) E. A. Guggenheim, *Proc. Roy. Soc.*, A**183**, 203 (1944).

ing chiefly the effect of segment size.

In the case when the heat of dilution is not zero, we must consider the problem of the preferential ordering induced in the solution by difference in the interaction energy. However, it was shown by Orr[6] and Guggenheim[7] that this effect does not introduce a serious error for high polymer solutions, and therefore, we shall neglect this effect for the time being. Thus we must consider the nature of μ_S and μ_H separately, in considerable detail, examining error due to over-simplified approximations or inadequate assumptions in the existing theories, which are not always applicable to the actual systems.

The Effect of Segment Size

In the majority of the existing theories of high polymer solutions, it has been assumed that the unit segment of polymer chain and solvent molecule are the same in shape and size. It requires that a section of the polymer chain which occupies a volume equal to that of one solvent molecule is also not very different in shape from the solvent molecule, and that it is equally free to occupy any one of $(z-1)$ cells in purely stereometric mean without considering the flexibility of the polymer chain. Considering the effect of flexibility of the chain also in addition to the above hindrance, perhaps steric in nature, Flory[8] modified his initial formulation of the entropy of dilution. If the solvent molecule is very small, or if there are limitations on the tortuosity which the chain may comfortably assume, then the size of the section of the chain which is free to orient itself at random, irrespective of the orientation of the preceding sections, may be equivalent to the volume occupied by several solvent molecules. Thus, he constructs a new lattice in which one cell will accomodate either β solvent molecules or one segment of the polymer chain, and obtains the same results as that of the writer[9] when the volume of "segment" is larger than that of solvent molecule as mentioned later. In the earlier papers[9][10], the writer calculated this effect of size and shape of solvent molecule and polymer "segment", and the result obtained may be written (Eqs. (9) and (11) in reference 9),

when $V_1 > V_2$,

$$\Delta\bar{S}_1 = -R\{(V_1/V_2[\ln v_1+(1+1/x)v_2+\mu_S v_2^2]+ [1-(V_1/V_2)](\ln v_1+v_2)\} = R[(V_1/V_2x)v_2+(1/2-\mu_S V_1/V_2) v_2^2+\cdots\cdots] \tag{3}$$

when $V_1 < V_2$,

$$\begin{aligned}\Delta\bar{S}_1 &= -(RV_1/V_2)[\ln v_1+(1-1/x)v_2+\mu_S v_2^2]\\ &= R(V_i/V_2)[v_2/x+(1/2-\mu_S)v_2^2+\cdots],\end{aligned} \tag{4}$$

where V_1 and V_2 are molal volumes of solvent molecule and polymer "segment" respectively. Here, we assume the "segment" as a unit submolecule which must be determined by steric factor only[11], and is characteristic to the polymer chain without regard to the types of the solvent, whereas Flory[8] assumed it as a section of the polymer chain which occupies a volume equal to the solvent molecule. Considering that the above approximation of Flory may not be allowed when the section of the polymer chain extremely differs in shape from the solvent molecule the validity of the usual expression of the entropy of mixing, $\Delta S = -R[N_1\ln v_1+N_2\ln v_2]$, fails when the section of polymer chain and the solvent molecule are extremely different in shape from each other even if the molal volumes are the same (See Eq. (8) in reference (9).) It is therefore evident that our assumption on the "segment" is more reasonable than that of Flory. Furthermore, it may be proper that this effect of segment size is separated from the effect of flexibility of the chain as in our treatment. Thus, we can improve the degreeof approximation because the term $(1-2\mu_S)$ may be considered as a probability factor modifying the purely random probability of finding adjacent polymer segments, whereas the Flory's modification was applied to his first approximation treatment[3] of high polymer solutions, which is an obvious oversimplification, as Flory himself recognized. It must be noted here that all the factors except the effect of the "segment" size are involved in μ_S in our treatment, because this treatment is proved to be very useful although it must be regarded as semi-empirical, and the theoretical limitations for further analysis of μ_S are increasingly apparent. In these factors, however, the effect of flexibility of the polymer chain is supposed to play the most important role, and hereafter, we are to employ f instead of μ_S which

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[6] W. J. C. Orr, *Trans. Faraday Soc.*, **11**, 320 (1944).

[7] E. A. Guggenheim, *Proc. Roy. Soc.*. A**183**, 213 (1944).

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

[9] T. Kawai, This Bulletin, **25**, 336 (1952).

[10] T. Kawai, This Bulletin, **24**, 269 (1951).

[11] The types of the hypothetical lattice sites are determined by the stereometric relation between the solvent and the polymer (the shape and size of the solvent molecule and the polymer "segment"). However, the "segment" should be determined uniquely by the stereometric factors of the polymer molecule itself.

was usually employed and which involved the effect of segment size. This parameter f corresponds to the μ_S value theoretically estimated when the polymer segment and the solvent molecule are the same in shape and size (its value is nearly equal to $1/z$)[12], and depends upon properties (mainly flexibility) of the polymer chain alone. Thus, Eqs. (3) and (4) may be rewritten when $V_2<V_1$,

$$\varDelta\breve{S}_1=R[(V_1/V_2x)v_2+\{1/2-(f\,V_1/V_2)\}v_2^2+\cdots\cdots] \qquad (5)$$

when $V_2<V_1$,

$$\varDelta\breve{S}_1=R\,[(V_1/V_2)\{v_2/x+(1/2-f)v_2^2+\cdots\cdots\}] \qquad (6)$$

Application of The Above Treatment to The Osmotic, Viscosimetric and Swelling Measurements

We are going to examine the effect of segment size mentioned above on the results of the measurements of osmotic pressure, viscosity, and swelling ratio. Combining the expression of the partial heat of dilution of the solvent,

$$\varDelta\breve{H}_1=KV_1v_2^2 \qquad (7)^{13)}$$

with Eqs. (5) and (6), the usually employed μ may be expressed by

$$\mu=fV_1/V_2+KV_1/RT, \qquad (8)$$

when, $V_2<V_1$ and

$$\mu=1/2-(V_1/V_2)(1/2-f)+KV_1/RT, \quad (9)$$

when $V_2>V_1$.

Osmotic Pressure: The second virial coefficient, A_2, in osmotic pressure expression represented by power series expansion in polymer concentrations, may be given as follows;

when $V_2<V_1$,

$$\begin{aligned}A_2&=(RT/\rho^2V_1)(1/2-\mu)\\&=(RT/\rho^2\{1/2V_2-f/V_4+K/RT\} \quad (10)\end{aligned}$$

when $V_2>V_1$,

$$A_2=(RT/\rho^2\{1/2-f)/V_2+K/RT\} \quad (10)$$

(ρ is density of the polymer). Therefore, the order of magnitude of the A_2, values (accordingly the slope of the line drawn through points of π/C plotted against C) obtained in a series of measurements with a polymer substance and different solvents, may not always agree with that of the $(1/2-\mu)$ values. One of such examples was reported in an earlier paper.[14]

Viscosity: The intrinsic viscosity of dilute solutions of a given high polymer varies with the nature of the solvent. For flexible linear polymers, this variation of intrinsic viscosity may, according to Flory[15], be treated as a swelling phenomenon, and be interpreted in terms of the interaction between solute and solvent molecules, although only the long range interferences between segments belonging to remotely connected portions of the chain were considered in his treatment. In an earlier paper[16] the writer formulated exactly the relation between intrinsic viscosity and the thermodynamic parameter μ. This formulation was exactly equivalent to that for swelling phenomenon. Thus, we shall confine ourselves to show that the above treatment, in which the effect of "segment" size has been considered, can be applied to the formula of swelling equilibrium.[17]

Swelling:—According to Flory-Rehner,[18] when solvent in gel is in equilibrium with excess solvent, the condition attained is that the partial molal free energy of the solvent in the gel equals zero;

$$\begin{aligned}\varDelta\breve{F}_{1g}&=\varDelta\breve{F}_{1m}+\varDelta\breve{F}_{1el}\\&=RT\,\{\ln(1-v_{2g})+v_{2g}+\mu_g v_{2g}^2\}\\&\quad+RT(\rho V_1/M_c)v_{2g}^{1/3}=0 \qquad (12)\end{aligned}$$

, where $\varDelta F_{1m}$ is the osmotic and $\varDelta F_{1el}$ the elastic contribution to the partial molal free energy. The notation of this equation is similar to what is usually employed.

Here, applying the above effect of "segment" size to Eq. (12), there is obtained

$$\begin{aligned}&\ln(1-v_{2g})+v_{2g}+f\,(V_1/V_2)v_{2g}^2\\&\quad+(KV_1/RT)v_{2g}^2+AV_1v_{2g}^{1/2}=0 \qquad (13)\end{aligned}$$

when $V_2<V_1$, and

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[12] B. H. Zimm, *Am. Chem. Soc.*, Meeting Sept. 1947.

[13] For application to the case in which strong mutual energy exists between unlike pairs, the constant K is employed here in a rather empirical meaning, instead of the form

$$\varDelta\breve{H}_1=V_1[(\varDelta E_1/V_1)^{1/2}-(\varDelta E_2/V_2)^{1/2}]^2$$

($\varDelta E_i/V_i$: cohesive energy density).

[14] K. Ishikawa and T. Kawai, *J. Chem. Soc. Japan* (Ind. Chem. Section), **55**, 73 (1952).

[15] P. J. Flory, *J. Chem. Phys.*, **17**, 103 (1949).

[16] T. Kawai, This Bulletin, **25**, 341 (1952).

[17] Yamaguchi deduced analogous results concerning the relation between intrinsic viscosity and the nature of solvents from an entirely different procedure (B. Yamaguchi and T. Ōki. Paper read at the rheological meeting held by the Chemical society, the High Polymer Society, and the Physical society, on 4th, Dec. 1952, in Tokyo.)

[18] P. J. Flory and J. Rehner Jr., *J. Chem. Phys.*, **11**, 512 (1943).

$$(V_1/V_2)\,[\ln(1-v_{2g})+v_{2g}+fv_{2g}{}^2]+(KV_1/kT)v_{2g}{}^2+AV_1v_{2g}{}^{1/3}=0 \quad (14)^{19)}$$

, when $V_2>V_1$.

Hence,

$$\mu_g=(V_1/V_2)f+KV_1/RT$$

, when $V_2<V_1$, and (15)

$$\mu_g={}^1/_2-(V_1/V_2)({}^1/_2-f)+KV_1/RT$$

, when $V_2>V_1$. (16)

Therefore, when $V_2>V_1$, volume swelling ratio $(={}^1/v_{2g})$ is a function of $({}^1/_2-\mu_g)/V_1$, and is independent upon V_1. When $V_2<V_1$, volume swelling ratio may be determined in somewhat different manner from the case when $V_2>V_1$. These problems will be discussed in the next section in more detail, being compared with experimental results.

Comparison with Experimental Results

Eqs. (13) and (14) will be tested from the measurement of the swelling of Boyer and Spencer[20] on styrene-divinylbenzene gels, which is one of the systematic studies in a large number of liquids differing widely in chemical type and in solvent power for a gel sample. In Table 2, one of their experimental results is analysed, attempting to show the better correspondence of the observed volume swelling ratio ${}^1/v_{2g}$ with $({}^1/_2-\mu_g)/V_1$ calculated from the above procedure, rather than with the parameter μ_g which have been usually interpreted in terms of the Flory-Rehner theory.

Table 2

Swelling of 0.0333% Divinyl Benzene Gels in Various Solvents at 23°C.

Solvents	Volume Swolling Ratic	μ_g	$(1/2-\mu_g)/V_1$ $\times 10^4$	$(1/2-\mu_g+\Delta\mu)$ $/V_1\times 10_4$	V_1
Phenyl Cyclohexane	18.57	0.417	4.85	6.02(14)	171
sym-Tetrachloroethane	23.92	0.417	7.83	9.72 (1)	106
Styrene	21.96	0.424	6.61	8.35 (5)	115
Phenyl Acetylene	22.43	0.426	6.73	8.54 (4)	110
o-Xylene	20.98	0.427	6.03	7.69 (7)	121
m-Xylene	20.02	0.433	5.45	7.07 (9)	123
p-Xylene	19.63	0.436	5.18	6.80(11)	124
Toluene	20.72	0.440	5.63	7.51 (8)	107
Trichloroethylene	21.84	0.444	6.23	8.45 (6)	89.9
Thiophene	22.99	0.450	6.31	8.83 (2)	79.3
cis-Dichloroethylene	22.49	0.453	6.19	8.82 (3)	75.9
Cyclohexanone	19.08	0.453	4.53	6.45(13)	104
Tetrahydrofuran	21.0	0.455	2.18	3.00	217
Dimethylfuran	18.00	0.458	2.87	5.71(16)	104
sym-Triethylbenzene	13.72	0.458	2.27	3.35(18)	103
Perchlorethylene	18.31	0.459	3.99	5.93(15)	120.9
Pyridine	19.82	0.464	4.46	6.94(10)	80.7
Ethylidene Chloride	18.41	0.469	0.83	1.37	372
trans-Dichloro-1-nitroethane	19.24	0.469	3.70	6.08(12)	83.8
Nitrobenzene	15.72	0.475	2.44	4.39(17)	103
Aniline	11.99	0.503	−0.33	1.86(19)	91.4
Diethyl Carbonate	10.79	0.503	−0.25	1.40(20)	122
Ethyl Chloroacetate	10.29	0.510	−0.94	0.94(22)	106
γ-Valerolactone	10.96	0.510	−1.10	1.10(21)	91.0
Propylene Oxide	12.7	0.590	−14.4	−1.01	69.4
Ethyl Laurate	65.3	0.570	−2.63	−11.5	266

The order of magnitude of the volume swelling ratios for the liquids given in Table 2 does not always correspond to that of the μ_g valves[21]. On the other hand, the order of their magnitude shows a better correspondence with that of the $({}^1/_2-\mu_g)/V_1$ values. (The larger the $({}^1/_2-\mu_g)/V_1$ values, the greater

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[19] Speculation of the "network" theory of Flory-Rehner leads to the conclusion that ΔF_{1el}, the elastic contribution to the partial molal free energy, should be expressed by the form $AV_1v_{2g}{}^{1/3}$, where A is a constant characteristic to the network structure, rather than by the form $(\rho V_1/M_c)v_{2g}{}^{1/3}$, which involves M_c explicitly.

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

[21] In many cases, the molal volumes of solvents do not differ very much from each other, and in such cases, the order of magnitude of the volume swelling ratios agrees with that of the μ_g values.

the solvent power, whereas the smaller the μ_g, the greater the solvent power.)

However, the regularity of this correspondence fails for a few liquids which are given under the line of ethylchloroacetate in Table 2. These discrepancies are completely removed by applying the following correction. In an earlier paper[22] it was pointed out that the values of μ_g calculated from swelling measurements are usually larger than those of μ obtained by osmotic measurements, and that, generally, the magnitude of these discrepancies is about 0.02[22] (which was determined approximately from many experimental results). These corrected values, $(^1/_2-\mu_g+\Delta\mu)/V_1$, are given in the fourth column in Table 2, where the number in the parentheses shows the order of magnitude of these values. A satisfactory correspondence is obtained between the volume swelling ratio and these values, whereas such a complete correspondence fails for the μ_g values. Now, there are three exceptional cases of tetrahydrofran, ethyl laurate and ethyliden chloride, in which the V_1 values are much larger than in the other cases. This exception may be well interpreted by Eq. (15), although the solvent power of these three liquids cannot be compared with that of the other liquids due to the uncertainty of the V_2 value[23].

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[22] T. Kawai, This Bulletin, **24**, 691 (1951). Probably, these discrepancies are due to over-simplification in the network theory of Flory (See P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).

[23] In the writer's opinion, the V_2 values should be determined through systematic study of experimental results, employing Eqs. (15) and (16). In this experiment of Boyer and Spencer, available data is too scanty to discuss quantitatively the case of $V_2>V_1$. From Table 2, the value of V_2 of this polymer is supposed to be about 100. It must be noted, however, that Eq. (16) may hold approximately even in the range $V_1>V_2$ so long as the difference between V_1 and V_2 is not considerably large, because the μ value should, according to Eqs. (15) and (16), decrease as V_1 increases ($V_1<V_2$), and become equal to that calculated from Eq. (1) when $V_1=V_2$, and then increases ($V_1>V_2$).