Statistical Thermodynamics of Solution of Rigid Rod-like Molecules

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(Received June 13, 1951)

Introduction

Recent theories of polymer solutions may be classified into two types, namely, the one based on the lattice model which was developed by Flory,(1) Huggins,(2) and others, and the other represented by Zimm's treatment(3) formally equivalent to that of imperfect gas theory. These two, however, include many questions to be discussed. The former involves a somewhat paradoxical situation in the separate evaluation of the entropy and energy terms in the partial molal free energy expression, although the success of the semi-empirical free energy expression justifies considerable confidence being placed in its application to thermodynamic properties of polymer solutions. Namely the statistical configurations of polymer molecules in solution must be influenced by the energetical interaction between polymer and solvent, and the heat of dilution must be determined by these configurations. The latter is more reasonable on this point, but often its calculation is not so easy as applicable to the practical cases. Furthermore, polymer-solvent interaction is not taken up explicitly, although the "average force potential" between segments involves it implicitly.

Now in the case of rigid large molecules circumstances are extremely simplified because the cofigurations are not affected by the energetical interaction. Thus the separate evaluation of the energy and entropy terms will be possible in this case. From this point of view, the above two methods were discussed in the present paper in relation to the most simple model for rigid rod-like molecules.

Discussion of Zimm's Result

In spite of its great simplicity, the theory of solution of rigid rod-like molecules has not been presented except by Zimm, who obtained the following result(3)

$$A_2 = \pi N_0 d l^2 / 4M^2, \qquad (1)$$

where A_2(4) is the second coefficient in the

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(1) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **9**, 660 (1941).

(2) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *J. Phys. Chem.*, **46**, 151 (1942).

(3) B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

(4) The A_2 values characterize the most important deviation from Raoult's law.

equation expressing osmotic pressure as power series in concentration analogous to the virial expression for gases, N_0 Avogadro's number, d the diameter, l the length, and M the molecular weight of the rod-like molecules. Employing the relationship $\pi d^2 l/4 = M/N_0\rho$, Eq. (1) reduces to

$$A_2 = 1/\rho^2(\pi/4)d^3N_0, \qquad (2)$$

where ρ is density of the solute. This result shows that Eq. (1) is not adequate in distinguishing th enature of actual polymer-solvent systems, since A_2 is a function of only ρ and d, and these values will not differ so much for various cellulose derivatives which are supposed to be rod-like molecules.(5)

In recent theories osmotic pressure expression involves one or two parameters which were introduced through some approximate treatments. These parameters are insufficient to account for experimental data or are not of theoretical significance (for example, the well used μ is merely an empirical one characterizing a given system). Actually, the partial molal free energy of dilution is a function of size and shape of solvent and solute molecules (spacial factors) and energetical interaction between solvent and solute. But even if the above factors were introduced in the osmotic pressure expression through amplification and refinement of the existing theory, we cannot compare them with osmotic data without estimating some of these factors in some other way. It may be said, however, that the approximate treatments in current theories must be improved by knowledge of the actual polymer. Now it must be noted that Zimm's treatment (the "rigid body approximation" for large molecules) is obviously an approximation applicable only to the case of long rigid rod-like molecules suspended in an effectively continuous and structureless solvent. Thus the effect of the above spacial factors on the entropy term must be investigated theoretically as well as experimentally. For this purpose, we adopted a lattice model consistent with the information obtained from the molecular constructions of solute and solvent.

Eq. (2) may be written

$$A_2 = \{V_1/(\pi/4)d^3N_0\}/V_1\rho^2$$
$$= \frac{1}{2}\{(V_1/N_0)/(\pi/8)d^3\}/V_1\rho^2 \qquad (3)$$

where V_1 is molal volume of solvent. Thus Zimm's result coincides with Flory's(1), based on lattice model as seen in his first paper on polymer solutions, when the volume of the segment equals $(\pi/8)d^3$. It is interesting that this volume equals that of the submolecule assumed in the following section.

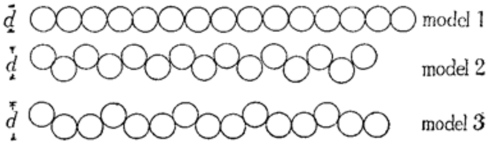

Fig. 1.—Hypothetical model of long rigid rod-like molecules.

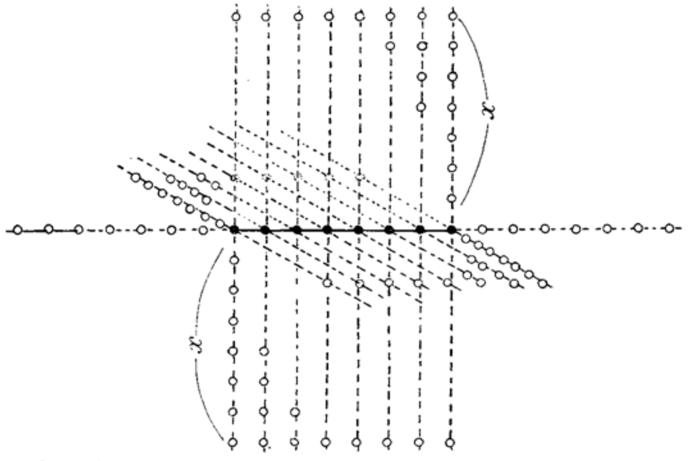

Fig. 2.—Illustration of the region $v\cdot$ (cubiclattice) : •–•–•–• indicates the first molecule A_1.

New Treatment of Solution of Rigid Rod-like Molecules

Let us consider a hypothetical model of the

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(5) It is supposed from the information on viscosity and light scattering etc., that the molecules of cellulose derivatives are not entirely rigid rods, but are somewhat flexible especially when they are long. Our procedure may also be applicable to such cases if the effect of energetical interaction on configurations of polymer molecules can be neglected, since it involves little bending of successive submolecules (See Fig. 1).

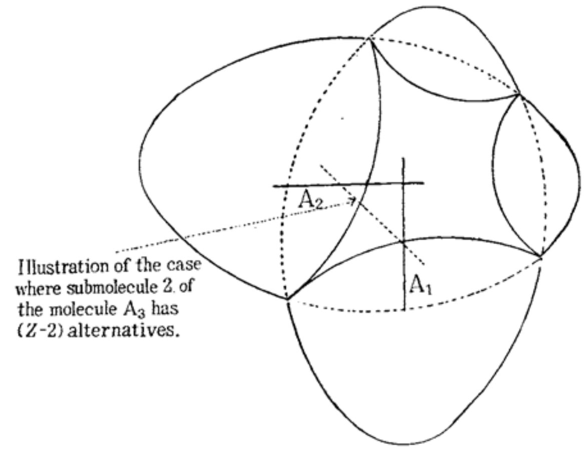

Fig. 3.—Illustration of the rigion v'.

rod-like molecules consisting of x spherical submolecules as illustrated in Fig. 1. For model 1 the volume of the submolecule is $\pi(d/2)^3$ and agrees with that mentioned above. The following procedure may be allowed for models 2, 3, etc.,(5) although somewhat different values must be adopted for the volume of the submolecule.(5) Now we assume N_0 lattice sites throughout the solution and make the above submolecule correspond to one lattice site. The type of lattice must be determined by the relative position of the submolecules in solution (accordingly by coordination number z). The solute molecules are first added one at a time, then the solvent molecules, counting the number of different ways setting each molecule in the lattice sites one after another in order to obtain the total number of configurations.

Submolecule 1 of molecule A_1 (the first solute molecule) can be placed in any of N_0 sites. Submolecule 2 of this molecule has a number of alternatives, z, equal to the coordination number. The position of the molecule A_1 is fixed when that of its first two submolecules is, because the successive submolecules must be connected linearly.(5) Thus the number of the configuration for the molecule A_1 is zN_0. Next, the second molecule A_2 is added. Here we consider linearly connected x sites starting from each submolecule of the first molecule for all coordinations in the circumference of the molecule, as illustrated in Fig. 2. The total number of these sites is given by(6)

$$v=(z-2)(x-1)x+3x-2\doteqdot(z-2)x^2-(z-5)x. \quad (4)$$

When submolecule 1 of the molecule A_2 is added in these sites, the number of configurations for the molecule A_2 is $v(z-1)$.(7) When it is added in other (N_0-v) sites, the number of configurations is $(N_0-v)z$.

Similarly for the third molecule A_3, we may write $(N_0-v')z+(v'-2x)(z-1)^*$ when the molecule A_2 was added in the above v sites, and $(N_0-2v)z+2(v-x)(z-1)$ when it was added in other (N_0-v) sites. Here the meaning of v' may be seen from Fig. 3, and $(z-1)^*$ is not strictly equal to $(z-1)$, although the difference between them is negligibly small.(8)

Proceeding in this manner to the N-th solute molecule, making the product of corresponding factors, and summing up all of them, a great number of terms are obtained. When concentration of solute is very small, these terms can be arranged as follows, assuming that the terms containing more than two of $(v-x)$ or $(v'-2x)$ etc. may be neglected, and that $v'\doteqdot 2v$(9):

$$\begin{aligned}&N_0(N_0-v)(N_0-2v)\cdots\{N_0-(N-1)v\}z^N\\&\quad+[N_0(N_0-v)\cdots\{N_0(N-2)v\}(N-1)(v-x)\\&\quad+N_0(N_0-v)\cdots(N-2)(v-x)\{N_0-(N-1)v\}\\&\quad+N_0(v-x)(N_0-2v)\cdots\\&\qquad\qquad\{N_0-(N-1)v\}]z^{N-1}(z-1)\\&\quad=z^N\{N_0(N_0-v)\cdots[N_0-(N-1)v]\}\times\\&\qquad[1+(v-x)/(N_0-v)\times(z-1)/z+\cdots\\&\quad(N-1)(v-x)/[N_0-(N-1)v]\times(z-1)/z] \quad (5)\end{aligned}$$

Thus the total number of configurations for N solute molecules is given by(10)

$$\begin{aligned}W=&z^N/2^N N!\times\{N_0(N_0-v)\cdots[N_0-(N-1)v]\}\\&\times\{1+(v-x)/(N_0-v)\times(z-1)/z+\cdots\end{aligned}$$

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(6) The v values given by Eq. (4) are a little larger than what we need, owing to overlapping of some of the v sites in a certain type of lattice, but are approximately available to such cases. One of the most simple cases where Eq. (4) holds strictly (cubic lattice) is illustrated in Fig. 2.

(7) The second molecule overlaps with the first in any one of x linearly connected sites starting from submolecule 1 of the second molecule A_2 for one coordination of it.

(8) When one of certain sites on the plane containing the previously added two molecules with in the range v' is occupied by submolecule 1 of the molecule A_3, the number of alternatives of its second submolecule is Z-2, but the number of these sites are very small in this range (see Fig. 3).

(9) Obvioluy from Fig. 3, this approximation is unsatisfactory, but the calculation is tedious and it is almost hopeless to thihk of getting results without employing it.

(10) This procedure is formally equivalent to Ichimura's on dilute solutions of coiled polymer (*J. Phys. Soc. Japan*, **3**, 308 (1948)).

$$\times(N-1)(v-x)/[N_0-(N-1)v]\times(z-1)/z\} \qquad (6)^{(11)}$$

$$\doteqdot z^N/2^N N!\times(N_0/v)!/(N_0/v-N)!\times\{1+(z-1)/z\times N^2/2N_0\times(v-x-2vxN/3N_0)\}, \qquad (6')$$

where the value 2 is the symmetrical number. Here N_0 is replaced by its equivalent $n+xN$ and n is regarded as the number of solvent molecules when each of them equals the submolecule in size and shape. After addition of all the solute molecules, the remaining sites are filled with the solvent molecules. This introduces no increase in the number of distinguishable configurations. Introducing the relationship $\varDelta S/R=\ln W$ and replacing factorial terms with Stirling's approximation, the entropy of the system is obtained. Then, deriving the entropy of mixing by the usual manner and differentiating it with respect to n, the partial molal entropy becomes

$$\begin{aligned}\varDelta\bar{S}_1&=R\{1/v\times\ln[1-vN/(n+xN)]\\&\quad-(z-1)/2z\times(v-x)[N/(n+xN)]^2\\&\quad+vx(z-1)/6z\times[N/(n+xN]^3+\cdots\cdot\}\\&=R\{v_2{}^2/x+[v/2x^2-(z-1)/2z\\&\quad\times(v-x)/x^2]v_2{}^2+\cdots\cdot\},\end{aligned} \qquad (7)$$

where $v_2=xN/(n+xN)=$ volume fraction of solute.

In our case, formulation of the energy term is simplified because we can evaluate it apart from the configurations of the system. Thus the heat of mixing may be written(12)

$$\varDelta H=K(z-2)xN(1-v_2), \qquad (8)$$

where $K=\varepsilon_{12}-(\varepsilon_{11}+\varepsilon_{22})/2.$

Or $\varDelta\vec{H}_1=K(z-2)v_2{}^2=\alpha v_2{}^2 \qquad (9)$

(these notations are similar to those employed usually).

Combining Eq. (9) with Eq. (7), there is obtained for partial molal free energy

$$\varDelta\bar{F}_1=\varDelta\bar{H}_1-T\varDelta\bar{S}_1=-RT\{v_2/x+[v/2x^2-(z-1)/2z\times(v-x)/x^2-\alpha/RT]v_2{}^2\}. \qquad (10)$$

Hence, according to the definition of A_2,

$$\begin{aligned}A_2&=1/V_1\rho^2\times\{v/zx^2+(1-1/z)/x-\alpha/RT\}\\&=1/V_1\rho^2\times\{(z-2)/2z+(z-3-2/z)/2x\\&\quad-\alpha/RT\}\doteqdot 1/V_1\rho^2(1/2-1/z-\alpha/RT).\end{aligned} \qquad (11)^{(13)}$$

This result coincides with that of Huggins, who derived it on solution of coiled molecules. However, it is possible to point out that the coordination number, z, holds its original significance explicitly in our case, since such approximation averaging the "distribution density" as used by Huggins is not adopted here.

Next, we adopted an approximate method introduing the effect of size and shape of solvent on the viewpoint that Flory's modification(1) for the entropy expression owing to the volume ratio β of segment for solvent may be unsatisfactory and that the spacial factors should be considered in more detail. When the above submolecule is a times larger than the solvent molecule, we assume conventionally a lattice sites in each submolecule, taking the coordination number, z', determined by the spacial factors of the solvent.

As mentioned above, the operation of packing the solvent molecules which equal in size and shape the submolecule in the remaining sites is exactly equivalent to that of setting solute molecules in the sites without considering the existence of solvent molecules. Therefore, the total number of different configurations W'' in this case will be obtained from W', which is substituted by aN_0 for N_0, an for n, and axN for xN, in the above expression for W, multiplying by a factor due to the fact that a solvent molecules must be in a group in the new lattice sites. Hence

$$W''=W'W_1\Big/\binom{aN_0}{an}, \qquad (12)$$

where W_1 is the number of different ways in which n molecules, each occupying a sites, can be packed in aN_0 sites without overlapping. Affording a good approximation for small and spherical molecules, W_1 was evaluated by Ōsawa as follows(14):

$$W_1=\left\{\binom{N_0}{n}z'^N\right\}^a\Big/\binom{z'N_0}{n}^{a-1} \qquad (13)$$

Entropy of this system is obtained in the

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(11) The terms in the latter bracket in Eq. (6) are arranged as seen here, employing the relations: $(N-1)(v-x)/[N_0-(N-1)v]\doteqdot(N-1)\times v/N_0-(N-1)\times n/N_0\times[1+(N-1)v/N_0]$, $(v/N_0\ll1,\ n/N_0\ll1)$; $1+2+\cdots\cdots+(N-1)=N(N-1)/2$; $1^2+2^2+3^3+\cdots\cdots+N^2=N(N+1)\times(2N+1)/6$.

(12) This result is the same as that for coiled molecules, since the number of polymer-solvent pairs are expressed as seen here in all cases.

(13) Perhaps employing another procedure, Zimm obtained a similar result (J. H. Hildebrand and R. L. Scott "The Solubility of Non-electrolytes," Reinfold Publishing Corp., New York, 1950.

(14) F. Osawa, *Busseiron Kenkyu*, **8**, 10 (1947).

same manner as mentioned previously. Differentiating the entropy of mixing with respect to *an*, there is obtained for the partial molal entropy:

$$\varDelta\overline{S}_1{}'' = \varDelta\overline{S}_1 + R\{(a-1)/a \times \ln(1-v_2) + (z'-1)\ln(1+v_2/(z'-1))\} \quad (14)$$

$$= R\{v_2/x + [1/2 - 1/z - (a-1)/2a + (a-1)/a(z'-1)]v_2^2 + \cdots\}. \quad (14')$$

Hence,

$$A_2 = 1/V_1\rho^2 \times [1/2a - 1/z + (a-1)/a(z'-1) - \alpha/RT]. \quad (15)$$

This procedure may detect the effect of size and shape of solvent on the entropy term approximately, although strictly speaking it can be reasonable only when the types of the above two lattices are one and same ($z=z'$). When $z=z'$, $z \gg 1$, Eq. (15) reduces to

$$A_2 \simeq 1/V_1\rho^2 \times (1/2a - 1/az - \alpha/RT). \quad (16)$$

Eq. (16) corresponds to Flory's modification for Eq. (11). The values of entropy terms in Eq. (15) and (16) are estimated for cellulose derivatives-various solvents systems, assuming $z=z'=12$(closely compacted) and that the volume of the submolecule$=\pi d^3/8 \doteqdot 1000$ Å.^{3}($d \doteqdot 7$Å.)$^{(15)}$. These values are shown in Table 1, being compared with the values of $1/2a$. Obviously from our assumption, this procedure is concerned only with dilute solutions. At high concentrations, Flory's result$^{(1)}$ $\varDelta\overline{S}_1 = v_2/x + 1/2a \times v_2^2 + \cdots$ in his early papers may be also applicable to our case. As is shown in the preceding section, Zimm's result corresponds to Flory's approximation, if we assume the "segment" as mentioned above. In the commonly used range of concentrations, the true value of A_2 is supposed to be a little greater than that calculated by Eq. (15) owing to the terms neglected in Eq. (5).

Table 1

Estimation of Values of the Entropy Term for Various Solvents

Solvent	a	$1/2a-1/az$	$1/2a-1/z+(a-1)/a(z'-1)$	$1/2a$
Acetone	8.22	0.050	0.058	0.061
Methyl acetate	7.59	0.055	0.062	0.066
Ethyl acetate	6.17	0.068	0.074	0.081
Butyl acetate	4.63	0.091	0.096	0.108
Cyclo-hexanone	5.76	0.072	0.079	0.087
Dioxan	7.07	0.059	0.066	0.071
Chloroform	7.51	0.056	0.063	0.067

Now the well-used parameter μ is usually expressed by the form $\beta + \alpha/RT$. Regarding the correlation of the value of β with molecular details of polymer solutions, Zimm$^{(16)}$ has shown that β would have a value of 0.49 for long rigid rods. When the effect of the size of the solvent is not considered, the value 0.49 for β corresponds to $z \doteqdot 2.0$, showing that the relation $\beta = 1/z$ is not available to practical cases. On the other hand, our procedure anticipates values of β in the range 0.40∼0.44, depending principally on the values of a. The exact values to be assigned to a, however, cannot be deduced theoretically because of the difficulty of bridging the gap between the actual polymer in solution on one hand and the idealized model composed of submolecules arranged in the hypothetical lattice on the other. Namely, the difficulty in our estimation of the entropy terms lies in the estimation of the size of the above submolecule. It is supposed, however, that the values of β estimated here may be rather appropriate from Zimm's evaluation in Hildebrand's book quoted in the footnote (13), although we cannot know his procedure in detail.

Many osmotic data for samples selected systematically and the facts from other physicochemical measurements will enable us to estimate the entropy and energy terms respectively. As is shown in Table 1, the contribution of the entropy of dilution to A_2 will not differ so much for the systems of cellulose derivatives and various solvents, and especially if more data were available to the systems, in a series of solvents for a given polymer, we could estimate

Table 2

Comparison with Experiments

System	Temp., °C.	$A_2V_1\rho^2$ entropy	A_2entropy $\times 10^4$(calc.)	$A_2 \times 10^4$ (exper.)
Nitrocellulose in acetone	20	0.054	4.13	10.89
	40			10.23
Nitrocellulose in methyl acetate	20	0.062	3.35	11.97
	40			11.17
Nitrocellulose in ethyl acetate	20	0.074	3.23	11.68
	40			10.07
Nitrocellulose in butyl acetate	20	0.096	3.15	7.85
	40			7.32

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(15) From our knowledge of viscosity, and light scattering etc. d is supposed to be in the range of 8∼15Å.

(16) B. H. Zimm, Am. Chem. Soc. Meeting, Sept. 1947. (P. Doty, M. Brownstein and W. Schlener, *J. Phys. Coll. Chem.*, **53**, 213 (1949)).

the energy term and solvent power from them. In Table 2, the A_2 values calculated from our experiment(17) on nitrocellulose (N content 10.5 %) are compared with those evaluated above.(18) Table 2 shows that acetone, methyl acetate, and ethyl acetate are alike better solvents than butyl acetate.

Summary

(1) A new thermodynamic relationship applicable to dilute solution of rigid rod-like molecules was derived, employing a lattice model.

(2) Small deviation from Zimm's result for rigid rod was discussed here, considering the effect of size and shape of solvent and solute.

(3) Although quantitative discussion is impossible because of the difficulty of the estimation of the size of the submolecule, it may be said that the contribution of entropy of dilution to A_2 (the second virial coefficient in osmotic pressure expression as power series in concentration) will be less for rigid rod-like molecules than for coiled molecules, and furthermore, the difference between such systems as cellulose derivatives in a series of solvents will be very small.

The author wishes to thank his director K. Makishima for constant encouragement and many helpful suggestions. This report was presented at the Fourth Meeting of the Chem. Soc. Japan, at Tokyo University, April, 1951.

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(17) K. Ishikawa and T. Kawai, paper read at the Fourth Meeting of Chem. Soc. Japan, April, 1951.

(18) The usual relations, $\Delta\bar{S}_1=(V_1\pi-V_1'\pi')/(T-T')$ and $\Delta\bar{H}_1=(V_1\pi/T-V_1'\pi'/T')/(1/T-1/T')$, often give the values of $\Delta\bar{S}_1$ and $\Delta\bar{H}_1$ with error as great as 100—200%.