The Effect of the Segment Size upon Thermodynamic Properties of Polymer Solutions

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Introduction

The statistical mechanical theories of polymer solutions currently in use do not entirely conform with observed thermodynamic data. Recently it has become apparent from the extensive measurements on the polymer-solvent systems, that the entropy of dilution differs widely for a given polymer in different solvents, and that, moreover, these entropy values are many times lower than can be accounted for by current theories[1,2].

The crucial point in all these theories lies in the expression for the second virial coefficient A_2. Various theories based on the idealized lattice model are essentially equivalent[3], and may be written uniquely as

$$A_2=(1/V_1\rho^2)\left\{\frac{1}{2}-\left(\frac{1}{Z}\right)\left(1-\frac{1}{m}\right)\right\} \tag{1}$$

where V_1 is the molar volume of the solvent, ρ, density of the polymer, Z, the coordination number of the lattice sites, and m, the number of submolecules in a polymer molecule. (Hereafter we shall designate the degree of the approximation in these theories as the first order approximation.) A number of osmotic measurements, however, give evidence that the observed values of A_2, in general, are much less than is predicted by Eq. (1).

Various attempts have been made to eliminate this lack of conformity; however, none of them seems to have successfully removed it. Accounting for the influence of a bending back of the polymer chain on to itself (long-range interference), Flory and Krigbaum[4] derived an expression for the second virial coefficient. When the polymer is homogeneous, their expression may be written

$$A_2=(1/V_1\rho^2)(\varphi_1-\kappa_1)F(\mathcal{X}) \tag{2}$$

$$\mathcal{X}=2(\alpha^2-1) \tag{3}$$

where φ_1 and κ_1 are the entropy and energy parameters respectively. The function $F(\mathcal{X})$ is a definite integral the evaluation of which is discussed in reference (4). The quantity α is a factor by which the spatial distribution of segments is expanded due to the long-range interference. Thus, the effect of the long-range interference (designated, for convenience, as the "long-range excluded volume effect") upon A_2 appears only through the function $F(\mathcal{X})$. Actually, Eq. (2), in combinaton with Eq. (3), well interprets the dependency of the molecular weight of the polymer on A_2, which has been borne out by experiments. As an example, the A_2 values were cited in Table I from the osmotic data of Bawn et al. for various molecular weights of polystyrene in toluene[5]. The values of $F(\mathcal{X})$ are calculated for the corresponding molecular weights, employing the α values evaluated from the data of intrinsic viscosities[2,6]. The ratio $A_2/F(\mathcal{X})$ may be regarded as constant in a wide range of molecular weights (M).

TABLE I

EXAMINATION OF THE DEPENDENCY OF A^2 UPON MOLECULAR WEIGHTS (M: NUMBER AVERAGE MOLECULAR WEIGHT) BY THE THEORY OF FLORY ET AL. (POLYSTYRENE-TOLUENE)

At 25°C

$M\times10^{-4}$	$A_2\times10^4$ g^{-2} cc	α	$F(\chi)$	$A_2/F(\chi)$
158	2.89	1.52	0.82	3.52
87	3.01	1.44	0.87	3.46
32	3.28	1.32	0.89_5	3.66
28.8	3.09	1.31	0.90	3.43
24.8	3.32	1.30	0.90_5	3.67
16.2	3.36	1.25	0.91_5	3.67
9.4	3.89	1.21	0.93_5	4.16

However, the question how the abnormally low values of $(\varphi_1-\kappa_1)$ should be explained remains unsolved; since the value of $F(\mathcal{X})$ is seldom far from unity (the α values are smaller than 2 apparently including all practical cases for any polymer-solvent pair so far investigated), the "long-range excluded

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[1] M. J. Schick, P. Doty and B. H. Zimm, *J. Am. Chem. Soc.*, **72**, 530 (1950).

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

[3] T. Kawai, This Bulletin, **26**, 409 (1953); **25**, 336 (1952).

[4] P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

[5] C. E. H. Bawn and M. A. Wajid, *J. Polymer Sci.*, **12**, 109 (1954).

[6] P. J. Flory and T. G. Fox, Jr., *J. Am. Chem. Soc.*, **73**, 1904 (1951).

volume effect" cannot eliminate the above lack of conformity between theory and experiment. Moreover, the definition of the parameters φ_1 and κ_1 still lacks precision; a more careful analysis of the meaning of these parameters is desirable.

At first, we must consider the problem of the preferential ordering induced in the solution by difference in the interaction energies, when the heat of dilution is not zero. However, it was shown that Eq. (I) did not conform with observed thermodynamic data for several systems which can be regarded as more or less athermal[7].

Another possible reason for this nonconformity may exist in neglecting the excluded volume effect in a short range scale, which will be discussed in the next section together with the segment size effect; the excluded volume for a segment in a polymer chain (not for a polymer molecule as the whole) would have to be taken into account, beside the effect in a long-range scale mentioned above.

It may be remarked here that existing theories of polymer solutions fail to take into account the specific geometrical character of the solvent in relation to the polymer segment. Considering the widely different entropies of dilution exhibited by different solutions of the same polymer at the same concentration, it is obvious that this is a serious deficiency which must be made up. In order to establish a unique explanation of these thermodynamic data in terms of molecular concept, an attempt will be made in this paper by proceeding with the idea of the segment size effect, which was already discussed briefly in the previous paper[3].

Athermal Solutions

Most of the existing theories involve an over-simplified assumption which usually has escaped notice; it was assumed that the solvent molecule and segment are the same in size and shape. Some investigators arrived within crude approximations, at the conclusion that the choice of any length of the submolecule along the polymer chain as a segment has no appreciable effect on the resultant formula for the entropy of dilution[8,9]. However, no one has taken into account the dependence of the entropy of dilution and of other related quantities on the relative dimensions of the solvent molecules and the solute molecule cross sections. As was shown in the treatment of rod-like molecules[10], this might play an important role on the explanation of unreasonably low values of φ_1. Zimm[11] also has shown an analogous effect for athermal solutions of various infinite chains in an artificial cubic lattice.

Here, the modification of the entropy expression by Flory[12], who first introduced the effect of the segment size, may be recalled, although his definition of the segment was somewhat ambiguous. In our treatment the segment in a thermodynamical sense will be redefined as a purely stereometric one in character. The essential feature of it is that it has to satisfy the condition that it is isotropic and spherical. The effect of anisotropy in the force fields around the segment can be ignored in athermal solutions; however, the geometrical anisotropy, i. e. its shape factor, must be taken into account. If the segment is assumed as a section of the polymer chain which occupies a volume equal to that of the solvent molecule, the resultant expression of the entropy must fail its validity, since it is quite different from the solvent molecule in shape when the dimensions of the polymer cross sections differ extremely from those of the solvent molecule. Therefore, we must construct a more realistic model with regard to the molecular constructions of the solvent and solute. The restriction of the lattice model, which arise from its artificiality, may possibly be removed by choosing a suitable size and shape of the segment as well as by introducing the coordination number characterizing the type of the lattice.

Let us consider four cases; (a) both the polymer and solvent are "aliphatic" (The term "aliphatic" used here means, for convenience, the "effectively" small dimensions of the solvent molecule and the polymer molecule cross sections. The solutions of the polymer consisting of a linear sequence of carbon atoms without any bulky side chains or branches in the open chain solvents belong to this case.) (b) the polymer consists of a sequence of rings[13] (the polymers in

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[7] H. Stuart, "Das Makromolekül in Lösungen", Berlin (1953).

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

[9] B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

[10] Exactly the same expression was derived for the solutions of large rigid rod-like molecules as Eq. (1). Even for these solutions, where both the excluded volume effect and ordering effect mentioned above need not be considered, Eq. (1) does not coincide with the formula obtained by methods using molecular distribution function, without considering the segment size effect (This Bulletin, **24**, 269 (1951)).

[11] B. H. Zimm, ref. (20), p. 364.

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

[13] These rings may be contained not only in the main chain but in the side chains; the bulky nature of the effective cross sections of such polymer chain is speculated here.

this class are designated by " aromatic polymer "), and the solvent is " aliphatic ". (c) the polymer is " aliphatic ", and the solvent is " aromatic " (of course, all rigid cyclic compounds such as cyclohexane or dioxane are also involved). (d) both the polymer and solvent are " aromatic ". These are hypothetically illustrated in Fig. 1.

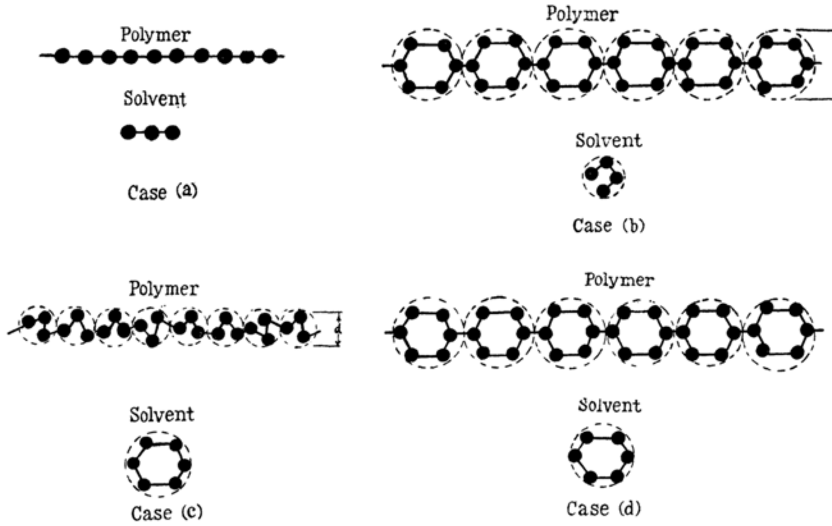

Fig. 1. Hypothetical models of polymer and solvent molecules.

For the case (a) Guggenheim obtained, within a crude approximation, an expression of entropy of dilution, which does not much differ from the results (for instance, Eq. (1)) deduced from the usual assumption that the solvent molecule and segment are the same in size and shape[14]. Here, considering the effect of the flexibility of the polymer chain[15,16], it would be preferable to write

$$A_2=(1/V_1\rho^2)\varphi_1^*. \qquad (4)$$

The parameter φ_1^* is characteristic to the polymer chain, irrespective of the solvent, and the effect of flexibility of the chain, if it gives rise to some alteration in the expression of A_2, may be involved into this parameter[15,16].

For the case (b) the author derived[3]

$$A_2=(1/V_1\rho^2)\,(V_1/V_2)\varphi_1^* \qquad (5)$$

which is formally analogous to the Flory's formula in reference (12). In our derivation of Eq. (5), however, the segment was assumed to be a sphere of radius $d/2$ (d is the diameter of the cross section of the polymer chain), the " molar " volume of which is V_2. Thus, the segment is defined by the steric factor only, and is characteristic of the polymer without regard to the type of the solvent.

To the case (c) our equation derived previously[3] is also applicable;

$$A_2=(1/V_1\rho^2)\{1/2-(V_1/V_2)(1/2-\varphi_1^*)\}. \qquad (6)$$

In arriving at this equation, the probability that V_1/V_2 sites must be in one group was calculated to an approximation which corresponds to that employed usually for the mixing of substances of low molecular weight[3], leading to the expression of the entropy of mixing;

$$\Delta S=-R[N_1\ln v_1+N_2\ln v_2]$$

(the N's are the numbers of the molecules and the v's, the volume fractions of the two components).

To the case (d) Eqs. (5) and (6) may be applicable again, according to the respective cases when $V_1>V_2$ and when $V_1<V_2$.

The above simplified models would not be able to provide the comprehensive picture of actual polymer solutions. It seems difficult, however, to take into account the molecular structure of the two components in more detail, because of the complicated character including the effect of the side chains, the non-uniformity of the cross sections along the polymer chain, and the spatial factors of the solvent molecule (our treatment of copolymer solutions may be suggestive in this point[17]).

Therefore, it seems to be rather preferable

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[14] E. A. Guggenheim, " Mixture ", Oxford Univ. Press, London (1952), p. 197.

[15] M. Kurata, M. Tamura and T. Watari, *J. Chem. Phys.*, 23, 991 (1955).

[16] M.L. Huggins, *J. Polymer Sci.*, 16, 209 (1955).

[17] T. Kawai, Meeting of Soc. of High Polymer, Japan, 11th Dec., 1954.

to introduce effective volumes of the solvent molecule and segment, V_1^* and V_2^*, involving all the complicated factors mentioned above, instead of V_1 and V_2, and use Eq. (5) when $V_1^*<V_2^*$ and Eq. (6) when $V_1^*>V_2^*$.

Furthermore, as was pointed out by Rushbrook et al.[18], even small molecules such as trimer or tetramer (in their terms) provide some difference in the entropy of mixing between rigid and flexible chains. This difference may be considered to arise from such effect of the excluded volume in a short-range scale as was mentioned previously. Zimm[9] showed an analogous effect on polymer solutions in somewhat different way; in his expression of A_2, the higher segment interaction integrals cannot be ignored in some cases. These integrals describe the effect of the interaction of the neighbouring segments on the probability of a meeting between a segment of one polymer molecule and that of the other molecule at a particular place. Thus, this effect depends on the local structure of the chain molecule and is more or less appreciable, except in the case where the segments are many times longer than their width (such long segments may be inadequate from our viewpoint in this treatment).

Here, the effect of the higher segment interaction, in Zimm's term, upon A_2 has been separated into two factors; the segment size effect (represented by V_1^*/V_2^*) and the effect of the chain flexibility (expressed by the parameter φ_1^*). The flexibility parameter φ_1^*, in other words, represents the just mentioned excluded volume effect in a short-range scale, and, if necessary, the expression of Kurata et al.[15] for A_2 may be utilized:

$$\varphi_1^*=1/3-(1/24)\{6\gamma+(1-\gamma)^2\} \qquad (7)$$

where γ is a parameter adjustable between zero and one, which increases with increasing flexibility of the polymer chain and reaches unity when polymer chains coil up tightly.

Taking account of the "long-range excluded volume effect", the final formulas may be written:

when $V_1^*<V_2^*$

$$A_2=(1/V_1\rho^2)(V_1^*/V_2^*)\varphi_1^*F(\chi) \qquad (8)$$

when $V_1>{}^*V_2^*$

$$A_2=(1/V_1\rho^2)\{1/2-(V_1^*/V_2^*)(1/2-\varphi_1^*)\}F(\chi). \qquad (9)$$

Since the segment in this treatment is characteristic of the polymer chain regardless of the solvent, Eqs. (8) and (9) would be very useful especially when we inquire into the effect of the solvent type on the thermodynamic properties of polymer solutions[3]. However, unless the spatial character of the solvent molecule (including the average configurations of its flexible carbon chains) may be represented by the "effective sphere" of volume V_1^*, the validity of this treatment fails[19]. The theoretical limitations for further analysis of this spatial factor would be apparent.

Solutions not Athermal

In this section, we shall consider the segments and solvent molecules of different sizes, each being approximated by an effective sphere in shape as was considered in the previous section, and we shall discuss the case when mixing of them is not athermal. Let us assume Z_{11} unit sites around the solvent molecule, and similarly Z_{22} unit sites around the segment; i.e., Z_{11} or Z_{22} corresponds to the surface area of each molecule and approximately, to its volume (in the latter case, this procedure is analogous to the usual treatment employing the cohesive energy density[20]). In their pure state, both the solvent molecule and segment may be assumed to have Z nearest neighbor contacts, and then, each one contact occupies Z_{11}/Z and Z_{22}/Z unit sites, respectively (Z is determined by the steric character of the segment and solvent molecule. When both

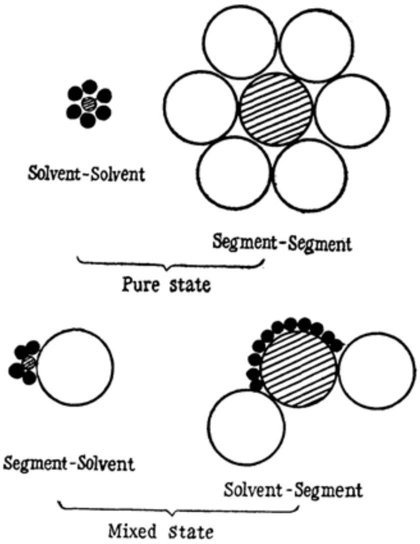

Fig. 2. Illustration of kinds of contacts.

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[18] G.S. Rushbrook, H.I. Scoins and A.J. Wakefield, *Trans. Faraday Soc., Discussion*, 15, 57 (1953).

[19] The value of V_1^* is to be determined by the spatial character of the solvent. When the solvent molecule consists of a long flexible carbon chain, "the flexibility entropy" of the solvent molecule contributes to the partial molal entropy of the solvent (see reference (16)).

[20] J.H. Hildebrand and R.L. Scott, "The Solubility of Nonelectrolyes", 3rd edition, Reinhold Publ. Co., New York (1950).

are effectively spherical, we can assume $Z=12$ for the closely compacted state).

When the two kinds of elements are mixed, we can suppose that, of the $Z_{11}n_1/2$ sites around the solvent molecule, X'_{12} sites come from the segments (n_1: the total number of the solvent molecules), and that, similarly, of the $Z_{22}n_2/2$ sites around the segment, X'_{12} sites come from the solvent molecules (n_2: the total number of the segments). (see Fig. 2).

One solvent molecule occupies Z_{11}/Z unit sites both around the solvent molecule and segment, and, similarly, one segment occupies Z_{22}/Z unit sites. Therefore the number of each contact in the mixture may be written as follows:

kinds of contacts	number of contacts expressed by that of the unit sites	actual number of contacts
solvent-solvent	$\frac{Z_{11}n_1}{2}-X'_{12}$	$X_{11}=a\left(\frac{Z_{11}n_1}{2}-X'_{12}\right)$
solvent-segment	X'_{12}	aX'_{12}
segment-solvent	X'_{12}	bX'_{12}
segment-segment	$\frac{Z_{22}n_2}{2}-X'_{12}$	$X_{22}=b\left(\frac{Z_{22}n_2}{2}-X'_{12}\right)$

$$(a=Z/Z_{11}, \qquad b=Z/Z_{22}).$$

Here, we have distinguished between the solvent-segment contacts (solvent molecules around a segment) and the segment-solvent contacts (segments around a solvent molecule).

Introducing the combinatory method developed by Guggenheim[14], the above assumptions lead to

$$g=g^*\times\frac{X_{11}^*!\,(aX_{12}'^*)!\,(bX_{12}'^*)!\,X_{22}^*!}{X_{11}!\,(aX'_{12})!\,(bX'_{12})!\,X_{22}!} \tag{10}$$

where g^* is the number of configurations for the athermal mixing of the two kinds of the elements, which was discussed in the previous section, and g, that for specified n_1, n_2 and X'_{12} (the asterisk means the athermal mixing).

For a given value of X'_{12} the configurational energy is given by

$$E_c=X_{11}w_{11}+X_{22}w_{22}+(a+b)X'_{12}w_{12} \tag{11}$$

where the w's denote the energies of the respective contacts. Consequently the configurational partition function Ω may be written

$$\Omega=\sum_{X'_{12}}g(n_1, n_2, X'_{12})\exp\{E_c(n_1, n_2, X'_{12})\}. \tag{12}$$

By replacing the sum of g on all X'_{12} values by its maximum term,

$$\Omega=g(n_1, n_2, X'_{12})\exp\{X_{11}w_{11}+X_{22}w_{22}+(a+b)X'_{12}w_{12}\}. \tag{13}$$

Now, X'_{12} should have the value determined by

$$\partial\ln\Omega/\partial X'_{12}=0.$$

From this condition the following relationship is obtained;

$$(u-y)^a(v-y)^b=Ay^{(a+b)} \tag{14}$$

where $A=e^{W/kT}$,

with $W=(a+b)w_{12}-aw_{11}-bw_{22}$.

In arriving at Eq. (14) we have introduced such abbreviations as Guggenheim[14] did:

$$u=\frac{Z_{11}n_1}{Z_{11}n_1+Z_{22}n_2}, \qquad v=\frac{Z_{22}n_2}{Z_{11}n_1+Z_{22}n_2}$$

$$y=\frac{X'_{12}}{Z_{11}n_1+Z_{22}n_2}. \tag{15}$$

Similarly, since $X_{12}'^*$ denotes the values of X'_{12} which maximizes the expression, $X_{11}!\,(aX'_{12})!\,(bX'_{12})!\,X_{22}!$, there is obtained

$$(u-y^*)^a(v-y^*)^b=y^{*(a+b)}\left(y^*=\frac{X_{12}'^*}{Z_{11}n_1+Z_{22}n_2}\right). \tag{16}$$

Eqs. (14) and (16) cannot be solved straightforwardly; however, writing $y=y^*+\Delta y$, we can evaluate y in spite of the crude approximation involved in its calculation[21]. The resultant equation is given by

$$y\doteqdot Kuv+(1-A^{1/b})(v-Kuv). \tag{17}$$[21]

We thus obtain the energy of mixing ΔE:

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[21] Expanding Eq. (14) into the binomial series with respect to Δy, we may write

$$A^{\frac{1}{b}}\left\{y^{*\frac{a+b}{b}}(u-y^*)^{-\frac{a}{b}}+\left[\left(\frac{a+b}{b}\right)y^{*\left(\frac{a+b}{b}\right)-1}\right.\right.$$
$$\left.\left.\times(u-y^*)^{-\frac{a}{b}}-\left(\frac{a}{b}\right)y^{*\frac{a+b}{b}}(u-y^*)^{-\left(\frac{a+b}{b}\right)}\right]\Delta y+\cdots\right\}$$
$$=v-y^*-\Delta y.$$

Since we can neglect safely the coefficient of Δy in the left hand side of this equation in comparison to that in the right (i.e. $(-1)\times\Delta y$) when $y^*<v\ll 1$ (for dilute solutions), except the case when $a\ll b$, the relation, $y=y^*+(1-A^{1/b})(v-y^*)$ is obtained to a satisfactory approximation provided that $\Delta y<y^*$. Next, Eq. (16) can be solved approximately as follows: when $a=b$, $y^*=uv$, and at infinite dilution, $y^*=uv$ when $a\gg b$ aud $y^*=uv/2$ when $a\ll b$. So long as the extremely dilute region (say, 0-2% polymer) is concerned, it is possible to show that y^* may be written approximately as Kuv, where K is about unity when $a>b$ and decreases with the decreasing values of a/b when $a<b$.

$$\Delta E=(Z_{11}n_1+Z_{22}n_2)Wy=(Z_{11}n_1+Z_{22}n_2)W\{Kuv+(1-A^{1/b})(v-Kuv)\}. \tag{18}$$

From this we may obtain the Helmholtz free energy of mixing, ΔF, by integration, assuming W independent of temperature T;

$$-\frac{\Delta F}{T}=\int\frac{\Delta E}{T^2}\mathrm{d}T+C. \tag{19}$$

The temperature independent term C is of course the athermal entropy of mixing (ΔS^*). The integration yields ΔF, and the partial molal quantities may be written as follows;

$$\Delta\bar{F}_1=\Delta\bar{S}_1{}^*+KZ_{11}W[1+(1/2)\{W/(bkT)\}+(1/6)\{W/(bkT)\}^2+\cdots\cdots]v^2+\cdots\cdots \tag{20}$$

$$\Delta\bar{E}_1=KZ_{11}W[1+W/(bkT)+(1/2)\{W/(bkT)\}^2+\cdots\cdots]v^2+\cdots\cdots \tag{21}$$

$$\Delta\bar{S}_1=\Delta\bar{S}_1{}^*+KZ_{11}W[(1/2)\{W/(bkT)\}+(1/3)\{W/(bkT)\}^2+\cdots\cdots]v^2+\cdots\cdots. \tag{22}$$

In the above treatment the connection between the segments in the chain molecule is not essentially taken into account. So far as the second virial coefficient is concerned, however, it was shown[4,9] that the neglect of it does not bring out any serious difference in the resultant formula. Evidently from the theory of Flory and Krigbaum[4], only interaction between pairs of the segments belonging to two different polymer molecules was considered in the introduction of the parameters φ_1 and κ_1. Therefore, the treatment in this section may be available to discuss the parameters φ_1 and κ_1, and the second virial coefficient may be written

$$A_2=(1/V_1\rho^2)(\varphi_1-\kappa_1)F(\mathcal{X}),$$

with

$$\varphi_1=\varphi_1{}^{**}+KZ_{11}(V_1Z_{22}/V_2Z_{11})^2W[(1/2)\times\{W/(bkT)\}+(1/3)\{W/(bkT)\}^2+\cdots\cdots] \tag{23}$$

where $\varphi_1{}^{**}=(V_1{}^*/V_2{}^*)\varphi_1{}^*$ when $V_1{}^*<V_2{}^*$,
and $\varphi_1{}^{**}=1/2-(V_1{}^*/V_2{}^*)(1/2-\varphi_1{}^*)$
when $V_1{}^*>V_2{}^*$.

And

$$\kappa_1=KZ_{11}(V_1Z_{22}/V_2Z_{11})^2W[1+W/(bkT)+(1/2)\{W/(bkT)\}^2+\cdots\cdots] \tag{24}$$

Comparison with Experiment

Unfortunately, there are very few polymer-solvent systems which have been investigated accurately enough either with respect to the temperature dependency of osmotic pressure or to (the direct measurements of) the heat of dilution to permit anything but a rough estimate of the adequacy of the treatment developed here for calculating $\Delta\bar{S}_1$ (or φ_1) and $\Delta\bar{E}_1$ (or κ_1). The treatment of intrinsic viscosities presented by Flory and Fox[6] affords very good agreement with the experiment as was pointed out elsewhere[22], and fortunately, the ($\varphi_1-\kappa_1$) values deduced from intrinsic viscosity measurements[2] well coincide with those from osmotic data[1,5,23], at least for the polymer solutions investigated here. This is illustrated in Table II (for polyisobutyrene solutions) and in Table III (for polystyrene solutions). These values of φ_1 and κ_1 may be available for the present purpose.

TABLE II

COMPARISON BETWEEN THEORY AND EXPERIMENT FOR POLYISOBUTYRENE SOLUTIONS

At 25°C

Solvent	($\varphi_1-\kappa_1$) from [η][2]	($\varphi_1-\kappa_1$) from osmotic data	$(\varphi_1)_{\text{exp.}}$	κ_1	$\varphi_1{}^{**}$	V_1 cc.
Benzene	0	0[23]	0.15	0.15	0.21^8	89.4_7
Cyclohexane	0.081	0.074_2[23]	0.14	0.059	0.15_7	108.7
Toluene	0.02		0.14	0.12	0.16_3	106.8
Ethylbenzene	0.023		0.14	0.117	0.11_4	122.4
75:25 E.B.:P.E.	0		0.17	0.17	(0.10_1)	126.3
50:50 E.B.:P.E.	−0.03		0.21	0.24	(0.07_7)	133.9_5
Diisobutyrene	0.040		0.056	0.016	0.04_7	156.9
n-Hexadecane	0.039		0.094	0.055	(−0.42)	291.9_2
n-Heptane	0.035		0.035	0	0.03_5	147.3_2
Triptane	0.047		0.047	0	—	—

TABLE III

COMPARISON BETWEEN THEORY AND EXPERIMENT FOR POLYSTYRENE SOLUTIONS

At 25°C

Solvent	($\varphi_1-\kappa_1$) From [η][2]	($\varphi_1-\kappa_1$) From osmotic data	$(\varphi_1)_{\text{exp.}}$	κ_1	V_1 cc
Cyclohexane	0	0.003_7[1]	0.13	0.13	108.7
Toluene	0.05	0.050_2[1]	0.11	0.06	106.8
Benzene	0.06	—	0.09	0.03	89.4_7
Dichloro-ethane	0.022	—	0.06	0.038	84.3
Methyl ethyl ketone	0.006	0.005_8[5]	0.006	0	90.1_2

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[22] T. Kawai and R. Kashiwagi, Annual Meeting of Chem. Soc. Japan, April 1955.

[23] P. J. Flory, *J. Am. Chem. Soc.*, 65, 372 (1943).

All these φ_1 values are much smaller than those predicted from Eq. (1). Furthermore, it has become apparent that the entropy of dilution differs widely for a given polymer in different solvents. For athermal mixing, the φ_1 values are predicted from Eqs. (8) and (9) to decrease with the increasing V_1^* values when $V_1^*>V_2^*$ and with the decreasing V_1^* when $V_1^*<V_2^*$.

To polyisobutyrene solutions Eq. (9) may be applicable, since it seems reasonable to choose the isobutene unit as the segment, which is considered to be smaller than the solvents used. Assuming $\varphi_1^*=0.2$[24], for convenience, the ratio V_1^*/V_2^* has been calculated from the $(\varphi_1)_{\text{exp.}}$ value (experimental values of φ_1) for heptane solution, which can be regarded as athermal. This ratio is 1.55 for heptane and then, assuming $V_1^*=V_1$, $V_2^*=95$ cc. This value of the segment volume V_2^* corresponds approximately to the isobutene unit. Regardless of these values of V_2^* and φ_1^*, we can evaluate the φ_1^{**} values for the solvents used from Eq. (9), regarding the heptane solution as a standard. Also these values are given in Table II (by employing the approximation, $V_1^*=V_1$ again), together with the molar volumes of the solvents. Except the two mixed solvents (ethylbenzene (E. B.)-phenyl ether (P. E.)) and n-hexadecane, the agreement between the $(\varphi_1)_{\text{exp.}}$ and φ_1^{**} values is rather satisfactory, considering the crudity of the assumptions on the one hand and the uncertainty of absolute magnitude of $(\varphi_1)_{\text{exp.}}$ on the other[25]. There appears to be no correlation between $(\varphi)_{\text{exp.}}$ and κ_1. In the systems having great κ_1 values such as the two mixed solvent solutions, however, there might be some contribution of the heat of mixing to φ_1. For n-hexadecane, the long asymmetrical solvent capable of assuming a number of different configurations, the assumption $V_1^*=V_1$ could no longer hold its validity[19].

The situation is entirely different for polystyrene solutions. For methyl ethyl ketone, in which $\kappa_1=0$, the $(\varphi_1)_{\text{exp.}}$ value is unexpectedly small. Considering the bulky nature of the aromatic side chain of polysyrene, we are inclined to apply Eq. (8) to these solutions. However, Eq. (8) leads us to an unreasonably large value of V_2^*; from this φ_1^{**} value we obtain $V_1^*/V_2^*=0.02$ and $V_2^*=7370$ cc. (assuming $\varphi_1^*=0.3$ and $V_1^*=V_1$)[26]. The reason for this is not known, and probably, this might be partly due to the same reason as was mentioned in reference (25). Nevertheless, it may be easily supposed from the chemical structure of the polystyrene chain that the value of V_2^* is fairly great, and the values of φ_1^{**} would not exceed, at the greatest, 0.1 for all the solvents cited in Table III (see the V_1 values given in the same table)[27]. The apparent discrepancy between thus estimated value of φ_1^{**} and the $(\varphi_1)_{\text{exp.}}$ values cannot be interpreted until Eq. (23) is introduced for the expression of φ_1. We can find semiqantitatively good correspondence between $(\varphi)_{\text{exp.}}$ and κ_1 values in Table III. This, of course, may be expected from Eqs. (23) and (24).

It must be emphasized that the preferential ordering induced by the difference in the interaction energies gives rise to a notable contribution to φ_1 for polystyrene solutions, whereas it does not appear to bring out so much influence for polyisobutyrene solutions. This result is in good agreement with Eq. (23), since the value of $(1/b)$ may be supposed to be much larger for polystyrene than for polyisobutyrene. It is an important conclusion in our theory that the above ordering effect is governed to a large extent by the size of the segment (strictly speaking, by its surface area, and approximately by V_2^*) as well as by the value of κ_1. At this point it is of interest to note that in an osmotic investigation of dilute polyvinylchloride solutions the highest entropy values were obtained in the solvents capable of the least specific interaction with the polymer[28].

In view of the simplicity of the concepts involved and of the paucity of available data, the good agreement between our theory and the experiments such as mentioned above may be to some extent fortuitous, and further improvement of the present theory and more extensive measurements would be necessary to establish the unique explanation of experimental data in terms of more detailed molecular concept. It may be said, however,

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[24] According to Eq. (7) the value of φ_1^* decreases from 0.292 to 0.083 with increasing flexibility (γ) of the chain. Here, for convenience, we adopt $\varphi_1^*=0.2$, obtained with $\gamma=0.5$ for polyisobutyrene.

[25] The free energy is fairly insensitive to the errors introduced in any over-simplified treatment, but the entropy and heat are not. Therefore, even if the $(\varphi_1-\kappa_1)$ values coincide with those obtained from osmotic data, we cannot conclude that the precise values of φ_1 and κ_1 have been obtained. Especially in the case of the good solvent, estimated uncertainties in φ_1 and κ_1 amount to 20-30%, whereas they are very little (0-5%) for the bad solvent.

[26] We have assumed $\varphi_1^*=0.3$, with $\gamma=0$ for polystyrene (see Eq. (7)).

[27] It may be remarked that the $(\varphi_1)_{\text{exp.}}$ value is larger for the polyisobutyrene-n-heptane system (a fairly flexible chain) than for the polystyrene-methyl ethyl ketone (a less flexible chain). This is approved by our treatment, but is in contradiction with the theories in which only the flexibility of the chain was taken into account.

[28] P. Doty and E. Mishuck, *J. Am. Chem. Soc.*, **69**, 1631 (1947).

that the widely different entropies of dilution exhibited by different solutions of the same polymer and abnormally low values of them have been semiquantitatively interpreted by the above treatment.

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