A Note on the Schulz's Osmotic Pressure Equation

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Introduction

It is well known that there exist two types of osmotic pressure expressions, one presented by Wo. Ostwald:

$$\pi/c = RT/M + Bc^{n-1} \qquad (1)$$

and the other presented by Schulz:

$$\pi/c = RT/M(1-cs). \qquad (2)$$

The notation of these equations is similar to what is usually employed. Recently, many theoretical treatments for high polymer solutions have been accomplished by Flory,(1),(2) Huggins(3),(4) and others, and osmotic pressure was represented by power series expansion in concentrations in all their reports as follows :

$$\pi/c = RT/M + A_2c + A_3c^2 + \cdots. \qquad (3)$$

These are regarded as an interpretation of Ostwald type. Concerning the Schulz's equation (SE), however, there has not been any theoretical explanation in spite of its empirical use.

This paper presents an explanation of the SE, which may offer some empirical knowledge for the following points.

(1) For the purpose of computing molecular weight of polymer more accurately, it is necessary to obtain the precise form of the π/c *vs.* c curve. Although recent theories demand upward curve, straight lines were obtained from many experimental data, showing that the accuracy of osmotic measurements cannot predict the higher terms in Eq. (3) at low concentrations. On the other hand, the SE leads to opposite curvature at very low concentrations. Thus it is required to examine the degree of approximation of the SE and to obtain the condition for its application.

(2) In order to investigate the state of polymer molecules in solution, it may be useful to inquire the source of parameters in osmotic pressure equations. The parameters in the equations derived by Flory, Huggins, and others have no clear physical meaning. Although s in the SE is also merely a simple parameter, he gave a physical meaning on it, that is, the "specific

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

(2) P. J. Flory, *Ibid.*, **13**, 453 (1945).

(3) M. L. Huggins, *Ibid.*, **9**, 440 (1941).

(4) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942).

covolume" of solute. It is necessary to examine whether s calculated by Eq. (2) represents the true value for the above physical meaning.

Formal Transformation of the Schulz's Equation

First of all, on the view-point discussed above, we try to equate the right-hand side of the SE with that of the Huggins, which is expressed as

$$\pi/c = RT/M + RT\left(\frac{1}{2}-\mu\right)c/V_1\rho_2^2, \quad (4)$$

where V_1 is the molal volume of solvent, ρ_2, the density of polymer, and μ a constant for any given system.

Obeying the Flory's expression $c = \rho_2 v_2$ (v_2 is the volume fraction of polymer), and $M/V_1\rho_2 = x$, Eq. (4) is reduced to

$$A = 1+x\left(\frac{1}{2}-\mu\right)v_2, \quad (5)$$

where A is the so-called "osmotic pressure coefficient" ($A = \pi/RTc/M$). Substituting $cs = s'v_2$, the SE is reduced to

$$A = 1/(1-s'v_2). \quad (6)$$

From Eqs. (5) and (6)

$$1/s' = 1/x(\frac{1}{2}-\mu) + v_2 \quad (7)$$

is obtained. It must be noted that s' corresponds to the Flory's "swelling factor," which is defined as the ratio of the volume effectively occupied by a polymer molecule in solvent to that in its unswollen state.⁽²⁾ While the SE was presented as an approximation, Eq. (5) was derived theoretically, showing that x and μ are predominant factors for osmotic pressure. So if Eq. (7) is derived in any other way, it may be said that the SE is interpreted theoretically, s in the SE being provided with a certain physical meaning.

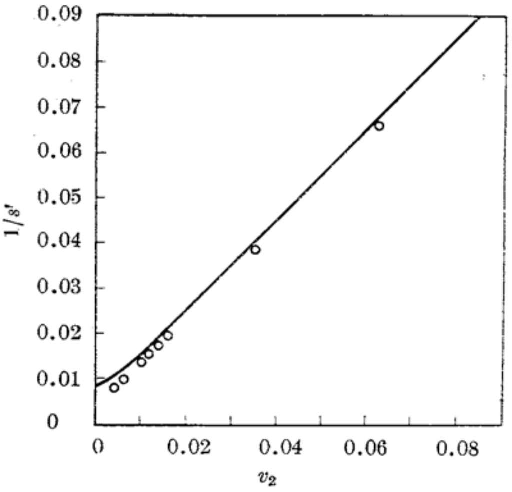

Fig. 1.—Comparison between the theoretical $1/s'$ *vs.* v_2 curve and the experimental plots (PVAc—methyl-ethyl ketone at 25°C.)

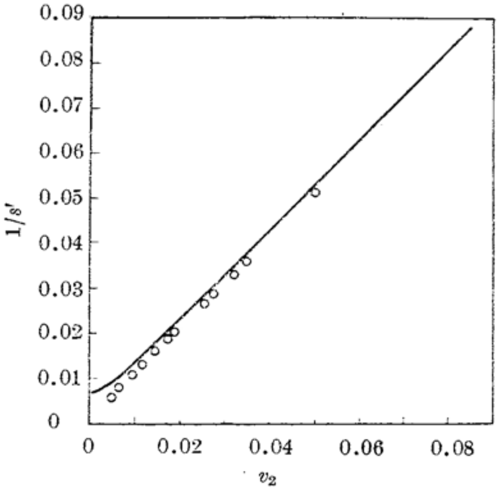

Fig. 2.—Comparison between the theoretical $1/s'$ *vs.* v_2 curve and the experimental plots (PVAc—1, 2, 3—trichloropropane at 15°C.)

Before discussing this subject, it is necessary to confirm the agreement of Eq. (7) with experimental results. We quote the Brown and Ferry's data,⁽⁵⁾ one of the most reliable results. And $1/s'$ values are plotted against v_2 in Figs. 1 and 2. These plots are on a line with gradient 1/1 within probable experimental error, satisfying Eq. (7). This fact is merely a reiteration of the previously noted agreement of Eqs. (2) and (4) with experimental results, but we can confirm that Eq. (7) is to be allowed in this case.

Theoretical Treatment

As discussed above, since Eq. (7) has been introduced by combining the SE with the theoretical Eq. (4), the independent derivation of Eq. (7) will bring in the theoretical basis of the SE and the condition under which its approximation may be permitted.

It seems an appropriate assumption that very dilute solution consists of two regions, one completely unoccupied by solute, and the other possessing an average "concentration"

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(5) G. Bown and J. D. Ferry, *J. Chem. Phys.*, **17**, 1107 (1949).

of solute determined by the statistical configurations of the polymer chain. It must be noted, however, that the state of affairs in the commonly used "dilute solution" differs from that in very dilute solution. In the former case, the intermolecular interaction cannot be neglected but in the latter case it may be neglected. Here, we are concerned with the former case.

We are going to turn our attention to one polymer molecule and consider the influence of its environment on it. The actual domain pervaded by a polymer chain cannot be defined sharply. It may be assumed that each molecule is distributed within an effective volume of sphere of radius R_e. Thus the swelling factor s' employed previously is considered to be the value for this effective volume. The s' *vs.* v_2 relation will be introduced from the condition of the equilibrium between inside and outside of this sphere.

The Flory's treatment⁽⁶⁾ of configurations of polymer chain may be acceptable by some modification for the region occupied by a polymer molecule, although his intramolecular statistic treatment as a swelling phenomenon does not indicate the total interferences within the random coiled molecule as the result of neglecting "short range interference." The free energy in the region occupied by a polymer molecule is given by

$$\varDelta F/kT = n \ln v_1 + \mu x v_1 + 3(\alpha^2-1)/2 - 3 \ln \alpha \tag{8}$$

(from Eq. (22) in the Flory's report⁽⁶⁾), where n is the number of solvent molecules, v_1, the volume fraction of solvent in this region, x, the number of the "lattice segments," that is, the ratio of the volume of a polymer molecule to the volume of the assumed cell, α, the factor by which linear dimension of the distribution of segments becomes larger than that of the "random flight" configurations owing to long range interference, and μ is a parameter introduced from the van Laar's expression; $\varDelta H/kT = \mu x v_1$. This definition of μ is related to μ_1 employed usually in the thermodynamic treatment of polymer solutions as $\mu = \mu_1/x_s$ (where x_s is the number of the lattice cells in a solvent molecule).

Adopting the above equivalent sphere of radius R_e,

$$n = (4\pi R_e^3/3 - xV)/x_s V, \tag{9}$$

where V is the volume of the lattice cell, and R_e is calculated from Eq. (13) in the Flory's report⁽⁶⁾ ($R_e = 0.52\,\alpha l z^{1/2}$, where l is the length of each segment for the "equivalent chain" and z is the number of the segments in a molecule.)

Applying the relations $lz = l'x$, $l' = V^{1/3}$, and $c = l/l'$, to the above expression for R_e, Eq. (9) gives

$$\alpha = \{2c^{3/2} x_s (n + x/x_s)/x^{3/2}\}^{1/3}. \tag{10}$$

Substituting this expression for α and $nx_s/(nx_s + x)$ for v_1 in Eq. (8) and differentiating with respect to n, there is obtained for the partial molal free energy

$$\ln a_s = \varDelta \overline{F}_{1s}/kT = \ln(1-v_{2s}) + v_{2s} + \mu_s v_{2s} + A v_{2s}^{1/3} - B v_{2s},^{(7)} \tag{11}$$

where a_s is the activity of solvent, and v_{2s} the volume fraction of polymer, subscript s showing the equivalent sphere ($A = 2^{2/3} c x_s / x^{4/3}$, and $B = x_s/x$).

Next, the activity of solvent in the environment region must be investigated. For the range of 0.01 to 0.10 volume fraction, we assume that the Huggins' expression for the activity of solvent in high polymer solutions is applicable to that in the environment region.⁽⁸⁾ Therefore,

$$\ln a_e = \varDelta \overline{F}_{1e}/kT = \ln(1-v_{2e}) + (1-1/x) v_{2e} + \mu_e v_{2e}^2, \tag{12}$$

where subscript e illustrates the environment region.

Thus the activity of solvent in the environment region is replaced to the mean value in the whole region of the system. This approximation may be permitted as far as we deal with the equilibrium between one solute molecule and its environment in the vast region involving other polymer molecules. Namely, the activity of solvent in the environment can be put approximately equal to that in the whole region on a statistic average, considering the intermolecular interaction.

For the condition of the equilibrium between the above two regions, $\ln a_s = \ln a_e$ is obtained. Hence from Eqs. (11) and (12),

$$\ln(1-v_{2s}) + v_{2s} + \mu_s v_{2s}^2 + A v_{2s}^{1/3} - B v_{2s} = \ln(1-v_{2e}) + (1-1/x) v_{2e} + \mu_e v_{2e}^2. \tag{13}$$

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(6) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

(7) This formula is analogous to the Flory's (Eq. (7) in *J. Chem. Phys.*, **18**, 108 (1950)) obtained for the swelling of network structure, except the coefficient B is two times larger than that of the Flory's.

(8) In very dilute solution ($s'v_2 \ll 1$), the activity of the region completely unoccupied by solute can be calculated and the result is $\ln a_e = \ln(1-8s'v_2)/8s'x$.

Since v_{2s} obviously equals to $1/s'$, the $1/s'$ *vs.* v_2 relationship has been derived here ($v_{2e} \doteqdot v_2$). Because Eq. (13) cannot be solved readily, numerical values of both sides of it are calculated by substituting suitable values for v_{2s} and v_{2e} respectively. Then equating the numerical values of these two sides, $1/s'$ *vs.* v_2 relation is obtained numerically.

In the above calculation constants A, B, μ_s and μ_e, must be estimated:

(1) A. The exact values of c cannot be deduced from theory, but are anticipated in the range from 0.1 to 1.0. We can select the proper dimension of the lattice cell freely and assume that $x_s = 1$, and $x = M/\rho_2 V_1$. Thus A is calculated for the proper values of c such as to illustrate the case that might arise in practice. ($A = 2^{2/3}\, c x_s / x^{4/3}$)

(2) B is calculated readily. ($B = x_s/x$)

(3) μ_e is obtained by usual manner from the osmotic data.

(4) μ_s may not equal numerically to μ_1 in the Flory's report. While μ_1 is applied to the interaction of an individual polymer molecule with its immediate environments, μ_s is indicative of the total polymer-solvent interaction within the region occupied by a polymer molecule. In order to eliminate the deviation of the Flory's treatment from the true thermodynamical value, it may be appropriate that the Huggins' expression for the partial molal free energy of dilution(9) ($\bar{F}_{1\,\mathrm{dil}} = kT[\ln(1-v_2) + (1-1/x)v_2 + \mu v_2^2]$) should be applicable to this spherical region, instead of that attained from the Flory's procedure ($\Delta\bar{F}_{1\,\mathrm{dil}} = kT[\ln(1-v_2) + v_2 + \mu_1 v_2^2]$), resulting that $\mu_1 = \alpha/RT$ is transffered to $\mu = 1/\beta + \alpha/RT$ without any alteration of the expression of the activity of solvent. This procedure is not yet satisfactory because circumstances in the above spherical region differ from those in polymer solutions. μ_s is supposed to be a little larger than the Huggins' μ, owing to the restriction(10) imposed on the possible number of configurations in the above spherical region.

Flory and co-workers used the μ-value determined on a polymer solution for the μ-value of the gel swollen in the same liquid in the treatments(11),(12) of the swelling of gels. In this point, as pointed out by Doty and co-workers,(13) lies an important source of inaccuracy in the Flory's procedure. The difference between μ-values determined by swelling and osmotic pressure is calculated by Doty and co-workers to be about 0.06 unit for a cross-linked polymer (polystylene) in various solvents. Although we can assume the above spherical region as if it were an extremely loose gel, the distinction between the spherical region and its environment is obscure. The difference between μ_s and μ_e, is supposed to be very small in our case. Thus we estimate this difference to be approximately 0.01 unit. Further quantitative discussion may be difficult owing to the complication of the above restriction to configurations and the weakness of the theoretical basis of μ itself.

Now employing these values of A, B, μ_e and μ_s, examples of the numerical calculation and the graphical method for the purpose of solving Eq. (13) are shown in Table 1 and Fig. 3 respectively, and the theoretical curve thus obtained is illustrated in Figs. 1 and 2, compared with the previously inserted experimental plots. A good coincidence between the theoretical curve and the experimental plots is observed.

Table 1

An Example of the Numerical Calculation of Eq. (13)
(methylethyl ketone solution of P. V. Ac.(5))
($M = 300,000$).

(Right-hand side) $x = 2800$, $c = 1$, $A = 4.0 \times 10^{-5}$, $B = 3.57 \times 10^{-4}$, $\mu_s = 0.44$

v_{2s}	$\ln(1-v_{2s}) - v_{2s} \times 10^4$	$A v_{2s}^{1/3} \times 10^4$	$-B v_{2s} \times 10^4$	$\mu_s v_{2s}^2 \times 10^4$	$\ln a_s \times 10^4$
0.01	− 0.5039	0.0862	−0.0357	0.44	−0.0134
0.03	− 4.5948	0.1243	−0.1072	3.96	−0.6183
0.05	−12.9364	0.1474	−0.1786	11.00	−1.9676
0.07	−25.7127	0.1648	−0.2500	21.56	−4.2379
0.09	−43.1127	0.1792	−0.3214	28.16	−7.6149

(left-hand side) $\mu_e = 0.43$, $x = 2800$

v_{2e}	$\ln(1-v_{2e}) \times 10^4$	$(1-1/x)v_{2e} \times 10^4$	$\mu_e v_{2e}^2 \times 10^4$	$\ln a_e \times 10^4$
0.01	−100.5039	99.9643	0.43	−0.1096
0.03	−304.5948	299.8929	3.87	−0.8367
0.05	−512.9364	499.8214	10.75	−2.3676
0.07	−725.7127	699.7500	21.07	−4.8927
0.09	−943.1127	899.6781	34.83	−8.6042

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(9) In our case, v_2/x term in the Huggins' expression vanishes when the entropy of dilution is combined with the entropy of elastic deformation of the molecule.

(10) This restriction is caused by the fact that the spherical region consists of a sequence of segments. Namely in this region the number of configurations is constrained owing to the expectancy for the occurrence of a segment in a cell immediately adjacent to a cell known to be occupied, while in the treatments of polymer solutions the effect of this expectancy is averaged as a whole in some manners considering the discontinuous nature of the solutions.

(11) P. J. Flory and J. J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).

(12) H. F. Boyer, *J. Chem. Phys.*, **13**, 363 (1945).

(13) P. Doty, M. Brownstein and W. Schlener, *J. Phys. Coll. Chem.*, **53**, 213 (1949).

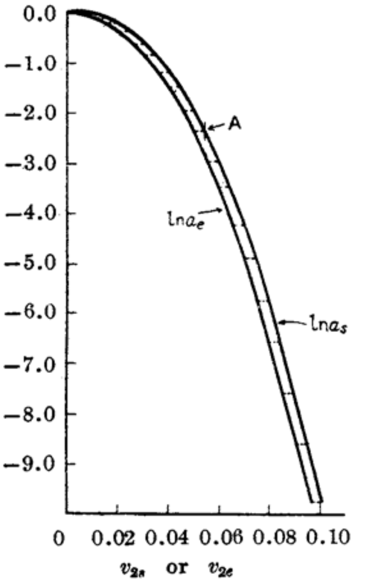

Fig. 3.—An example of the graphical method of Eq. (13). A: Volume fraction of polymer in the spherical region which is in equilibrium with a 0.05 by volume solution of polymer.

Now, expanding the logarithmic terms in Eq. (13) in series and neglecting terms beyond the first two,

$$-(1/2-\mu_s)v_{2s}^2+v_{2s}/x+Av_{2s}^{1/3} \\ =-(1/2-\mu_e)v_{2e}^2-v_{2e}/x \qquad (14)$$

is obtained. If the relation

$$Av_{2s}^{1/3}+\Delta\mu v_{2s}^2=2v_{2s}/x, \qquad (15)$$

where $\Delta\mu=\mu_s-\mu_e$, is satisfied, then follows

$$v_{2s}=v_{2e}+1/x(1/2-\mu_e). \qquad (16)$$

Eq. (16) coincides entirely with Eq. (7). Therefore, Eq. (15) is the necessary condition to satisfy Eq. (7) and for the SE to afford a theoretical basis.

The trial substitution of the above numerical values for A, x, $\Delta\mu$ and v_{2s} in Eq. (15) shows that Eq. (15) affords a legitimate approximation as illustrated in Table 2. In spite of the considerable large deviation from Eq. (15) in the range of moderately concentrated solutions, *i.e.*, over 0.07 volume fraction, a good agreement with experimental results is obtained as illustrated in Figs. 1 and 2, probably owing to the fact that the higher terms neglected in the derivation of Eq. (14) is more effective to cover the above deviation as concentration increases. In the above calculation we assume that $c=1$, from the viewpoint that each segment for the "equivalent chain" is supposed to correspond to one monomer unit of polyvinyl acetate, whose volume roughly equals to the molecular volume of the solvents. However, it must be noted that the deviation from Eq. (15) due to the c-values is rather small as illustrated in Table 2.

Table 2

The Test of the Validity of Eq. (15) for Various Values of c
(Methylethyl ketone and 1,2,3-trichloropropane solutions of P. V. Ac.)(5)

x	v_{2s}	$\Delta\mu v_{2s}^2+Av_{2s}^{1/3}\times10^4$			$2v_{2s}/x$ $\times10^4$
		$c=0.25$	$c=0.5$	$c=1.0$	
2,800	0.01	0.033	0.056	0.096	0.071
	0.03	0.121	0.152	0.214	0.213
	0.05	0.286	0.322	0.397	0.355
	0.07	0.532	0.573	0.655	0.497
	0.09	0.855	0.900	0.989	0.639
2,400	0.01	0.030	0.051	0.091	0.083
	0.03	0.119	0.149	0.207	0.250
	0.05	0.285	0.319	0.388	0.417
	0.07	0.529	0.568	0.645	0.583
	0.09	0.852	0.894	0.978	0.750

Meanwhile, Schulz found the following relation form experiments

$$\pi=ks^{-\nu}, \qquad (17)$$

where k and ν are constants characteristic to the polymer-solvent system. The theoretical basis of Eq. (17) may be interpreted as follows: it is obvious from the above assumption that the activity of solvent in the whole region may be approximated to that within the spherical region. Thus it results that the activity of solvent in polymer solutions is the function of $v_{2s}\,(=1/s\rho_2)$ only (see Eq. (11)). Hence

$$\pi=-\Delta\overline{F}_1/V_1=-RT\ln a_s/V_1 \\ =-RT\{\ln(1-v_{2s})+v_{2s}+\mu_s v_{2s}^2 \\ +Av_{2s}^{1/3}-Bv_{2s}\}/V_1. \qquad (18)$$

Substituting the numerical values calculated from the Staudinger's experimental data(14) on polyvinyl acetate-acetone system for A, B and μ_s in Eq. (18), the numerical calculation is carried out. The $\log\pi$ *vs.* $\log s$ relations thus obtained are illustrated in Fig. 4, compared with the experimental plots. The calculated

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(14) H. Staudinger and H. Warth, *J. prak. Chem.*, **155**, 261 (1940).

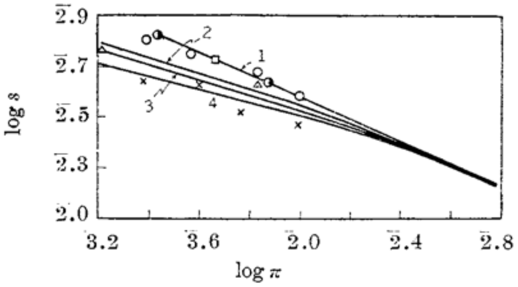

Fig. 4.—Comparison between the theoretical $\log \pi$ vs. $\log s$ curves and the experimental plots. Curve 1, Pro. No. 2 ($x=3350$); curve 2, Pro. No. 3R ($x=2250$); curve 3, Pro. No. 4R ($x=1600$); curve 4, Pro. No. 3 ($x=1870$); □, Pro. No. 2; ○, Pro. No. 3; ◑, Pro. No. 3R; △, Pro. No. 4R; ×, Pro. No. 5.

plots are approximately on straight lines and the experimental plots are also not so far from them.[15] Thus it is proved not only that Eq. (18) can be approximated to Eq. (17), but also that the theoretical values of k and ν agree with those values determined by the experiments. Because swelling pressure is assumed to be an expression of the activity of solvent within the spherical region, it is appropriate that k and ν are applicable to the swelling pressure of the same system.

Conditions for the Establishment of the Schulz's Equation

As discussed above, the influence of both c and $\varDelta\mu$ on Eq. (15) are not predominant enough to the considered significant. Now the test of the validity of Eq. (15) for various values of x and v_{2s} is illustrated in Table 3. Eq. (15) holds its validity over the considerable wide range of x. However, it must be noted that Eq. (15) affords a satisfactory approximation only in a limited range of concentration corresponding to x. Considering the influence of the higher terms neglected in Eq. (14) and the uncertainty of $\varDelta\mu$ on Eq. (15), we roughly estimate the range of concentration, to which the SE might be applicable, as follows; $v_2=0.04\sim0.08$ for $x=100$, $v_2=0.01\sim0.07$ for $x=1{,}000$ and $v_2=0.01\sim0.05$ for $x=10{,}000$.

Table 3

The Test of the Validity of Eq. (15) for Various Value of x and v_{2s} ($c=1$, $\varDelta\mu=0.01$)

v_{2s}	$x=100$ ($A=3.42\times10^{-3}$)		$x=1000$ ($A=1.59\times10^{-4}$)		$x=10000$ ($A=1.34\times10^{-7}$)	
	$\varDelta\mu {v_{2s}}^2 + A{v_{2s}}^{1/3} \times 10^4$	$2v_{2s}/x \times 10^4$	$\varDelta\mu {v_{2s}}^2 + A{v_{2s}}^{1/3} \times 10^4$	$2v_{2s}/x \times 10^4$	$\varDelta\mu {v_{2s}}^2 + A{v_{2s}}^{1/3} \times 10^4$	$2v_{2s}/x \times 10^4$
0.01	7.38	2.0	0.352	0.2	0.012	0.02
0.03	10.72	6.0	0.583	0.6	0.092	0.06
0.05	12.85	10.0	0.835	1.0	0.253	0.10
0.07	14.58	14.0	1.144	1.4	0.493	0.14
0.09	16.14	18.0	1.521	1.8	0.813	0.18

Conclusion

(1) We have given a theoretical basis to s in the Schulz's equation (2).

(2) Since the deficiency of this approximate treatment lies in the uncertainty of $\varDelta\mu$, a comprehensive investigation including both the experimental and theoretical study of the above "restriction imposed on possible configurations" is necessary for the refinement of our theory.

(3) The above treatment does not concern with extremely dilute solution ($sv_2 \ll 1$).

I should like to express my appreciation to the diretcor K. Makishima for his encouragement and support to this work.

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(15) When x is extremely small, Eq. (17) fails its validity.