

The Apparent Specific Volume of Polymers in Solution

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The physical meaning of the apparent specific volume v_2^* of macromolecules in solution is discussed on the basis of the statistical thermodynamical theory. It is pointed out that the v_2^* -value for macromolecules provides a measure for the interaction between segment and solvent molecules and is rather insensitive to changes in the molecular weight. Thus is emphasized here an important relation between the v_2^* -value and the chemical structure of solute. Some examples of application of this theory are described in connection with the chemical structure of certain polymers such as in copolymers of different monomers, in isomeric copolymers and in biological polymers.

1. INTRODUCTION

For sometime past there have been considerable numbers of studies made on the apparent specific or molal volume of various substances as calculated from the density of solutions. In particular for amino acids and proteins fairly systematic investigations have been carried out. It was found out that there was an additivity rule for volumes; that is, the apparent specific (or molal) volume is approximately an additive function of the volumes of the constituent atoms or atomic groups. In this paper the author presents a historical survey of this problem, a summary of recent experimental studies on linear macromolecules and also a brief discussion of the problem from the standpoint of the statistical thermodynamical theory developed by Kobatake and Inagaki. The last section of the paper discusses the application of this theory to the relation between the apparent specific volume of polymers and their chemical structure and about the significance of this quantity as one of physical characteristics of macromolecules.

2. THE DEFINITION OF THE APPARENT SPECIFIC VOLUME

When the composition and density, d , of a two component system are known, the specific volume, v_{12} , of the system is given as

$$1/d = v_{12} = g_1 v_1 + g_2 v_2, \quad (1)$$

where v_1 , v_2 and g_1 , g_2 are partial specific volume and weight fraction of the solvent (subscript 1) and the solute (subscript 2) respectively, in the solution. If one introduces the specific volume of the pure solvent, $v_1^0 = 1/d_0$, where d_0 is the density of the solvent alone, into Eq. (1) and attributes the difference between v_1 and v_1^0 to the contribution of the solute, then an apparent specific volume of the solute, v_2^* , can be defined as follows:

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$$v_{12} = g_1 v_1^0 + g_2 v_2^* \quad (2)$$

Generally v_2^* can be related to v_2 as

$$v_2 = v_2^* + g_2 \frac{\partial v_2^*}{\partial g_2} \quad (3)$$

In an aqueous solution with concentration of about 1%, one may say that v_2^* is substantially equal to v_2 since $v_2 \approx 1$, $g_2 \approx 0.01$ and $\partial v_2^* / \partial g_2 \approx 10^{-2}$ and therefore $v_2 - v_2^*$ is of the order of 10^{-4} . For substances of known molecular weight one often uses a partial molal volume, V_2 , and an apparent molal volume, V_2^* which are obtained by multiplying the corresponding specific volumes by the molecular weight, M .

3. HISTORICAL SURVEY

The study of the apparent molal volume has yielded many interesting results, especially in the study of the molecular structure of amino acids and proteins. The fundamentals for the study were brought together in a paper by Traube published as early as 1899. He discovered the additivity rule, that is, the apparent molal volume of a molecule is given by the sum of the volumes of the constituent atoms and arrived at the following atomic volumes¹⁾:

	C	H	N	O*)			S
				C-O-H	C=O	-OH	-SH
atomic volume (cc)	9.9	3.1	1.5	0.4	5.5	2.3	15.5

From these values the volume (in cc) of the following groups are, therefore, given as: $-\text{NH}_2 = 7.7$, $-\text{CH}_2 = 16.1$, $-\text{COOH} = 18.9$ and $-\text{CONH}- = 20.0$; and further, for example, the volume of glycine, $\text{NH}_2\text{CH}_2\text{COOH}$, one of the simplest α -amino acids is evaluated as 42.7 (cc/mole), which turned out to be in good agreement with the observed value of 43.5.

In 1930's E. J. Cohn *et al*²⁾, carried out a further investigation of the Traube rule for homologous series of aliphatic amino acids, amines and amides. By subtracting 16.3 (cc/mole) for each methylene group from the total volume they obtained the residual volume of a pair of end groups such as H and COOH, H and NH_2 and H and H. This residual volume is a constant characteristic of each pair of end groups. Direct evidence for the authenticity of this value for the volume of a methylene group was obtained from X-ray diffraction analysis and the study of surface films²⁾.

It turned out to be rather fortuitous that a good correspondence did exist between calculated and experimental volumes of certain compounds such as glycine and other amino acids. Now it is known that at least two correction factors should be considered. By comparing experimentally determined values of V_2^* for various neutral compounds with the sum of the atomic volumes, Traube found that the latter was almost always greater than the former by a nearly constant factor of the order of 13 (cc/g) called by Traube the *covolume*. These facts were already recognized as early as the 1880-90's by Ostwald³⁾ and also by Drude and Nernst⁴⁾, and was discussed from a quantitative point of view by Weber⁵⁾ and by

* For oxygen, different values were given depending on a position appearing in a group.

Cohn and associates⁶⁹. For example, the experimentally determined value of V_2^* for glycine, which exists in aqueous solution as a dipolar ion (Zwitterion, $^+\text{H}_3\text{NCH}_2\text{COO}^-$), is 43.5cc; while V_2^* of glycol amide $\text{CH}_2\text{OHCONH}_2$, which is a structural isomer of glycine and is present in the solution as an uncharged molecule, is 56.2cc. The difference of 12.7cc between the volumes of glycine and glycol amide is characteristic of α -amino acids and their uncharged isomers. This difference increases with increase in the number of methylene groups between the NH_3^+ and COO^- groups in such a way that it is about 15cc for β -amino acids and 18–20cc for those with two groups separated by a larger distance. The differences between the V_2^* of lactamide ($V_2^*=74\text{cc}$) and that of α -alanine ($V_2^*=61\text{cc}$) or that of β -alanine ($V_2^*=59$) also follow the general tendency stated above. For compounds with two dipoles such as ϵ , ϵ' -diamino di (α -thio-*n*-caproic acid), lysylglutamic acid and peptides of cystine, the observed values of V_2^* are always smaller than the calculated values by amounts of 12–22cc. In sum, for a large number of compounds in aqueous solutions the following relations apparently hold:

$$\begin{aligned} V_2^*(\text{expt}) &= V_2^*(\text{calc}) + (11 \sim 20)\text{cc} && \text{(for neutral compounds),} \\ V_2^*(\text{expt}) &= V_2^*(\text{calc}) && \text{(for dipolar ions)} \end{aligned}$$

and

$$V_2^*(\text{expt}) = V_2^*(\text{calc}) - (12 \sim 22)\text{cc} \quad \text{(for tetra polar ions),}$$

where $V_2^*(\text{calc})$ means the sum of the constituent atomic volumes neglecting a covolume correction. These facts are explained on the basis of a so-called electrostriction of the solvent. The orientation and close packing of water molecules around the charged groups result in an apparent reduction of the volumes of the solutes⁷⁰.

4. THE APPARENT SPECIFIC VOLUME OF PROTEINS

For proteins considered as condensation polymers of amino acids, it seems reasonable to assume that the apparent specific volume v_2^* might be calculated by an equation

$$v_2^* = \sum_i f_i (v_2^*)_i, \quad (4)$$

where $(v_2^*)_i$ and f_i denote the apparent specific volume and the weight fraction of the i -th constituent amino acid residue, respectively, and the summation extends over all different types of residues of the protein. According to Charlwood's careful measurements of various protein solutions⁸¹, observed values at the isoelectric point were always slightly higher than those calculated by Eq. (4), even though the reduction of the volume due to the electrostriction were neglected. If one considers a volume reduction due to electrostriction by a factor of 18cc per charge pair accessible to titration, this difference between observed and calculated values becomes even greater and reaches an amount of about the order of 3–4% of the observed value⁸¹. It was also found in proteins, especially in serum albumins, that the difference diminished with the change of molecular conformation from a folded compact form near the isoelectric point to an expanded or unfolded form at low pH⁹¹. This fact could presumably be attributed

to the pronounced molecular expansion which would facilitate penetration by solvent molecules. In other words, the expansion of polymer coils results in bringing solvent molecules into closer contact with solute molecules. This correction factor was termed the "excluded volume", Δ^{ex} , and was defined as follows:

$$\Delta^{ex} = [v_2^*]^{obs} - \{[v_2^*]^{calc} - \Delta^{el}\}, \quad (5)$$

in which Δ^{el} is the electrostrictive factor.

5. THE APPARENT SPECIFIC VOLUME OF LINEAR CHAIN POLYMERS

The study of the apparent specific volume, v_2^* , of linear chain polymers has been made mainly for the purpose of determining the Archimedes factor which is fundamental in the evaluation of molecular weights by ultracentrifugation methods. Detailed studies were carried out by Rosen¹⁰⁾ for polystyrene solutions and by Schulz and associates¹¹⁾ for polymethacrylate ester solutions. In particular Schulz and Hoffmann¹²⁾ deduced the following conclusions from the results of extensive measurements on these systems:

i) The apparent specific volume, v_2^* , for linear chain polymers is dependent on molecular weight, M_z , in such a way that

$$v_2^* = v_2^*_{(M_z \rightarrow \infty)} + K/M_z \quad (6)$$

where K is a constant factor (see Table 1).

ii) v_2^* is rather insensitive to the type of solvent (see Table 2).

iii) The difference and the ratio of the v_2^* 's of polystyrene and polymethyl methacrylate measured in a common solvent are almost always constant irrespective of the type of solvents (see Table 2).

Among these results it is particularly interesting that the parameter K in Eq. (6) takes either a positive or negative value, as is seen in Table 1, depending on the condition of the polymerization and especially on the type of initiator. The theoretical explanation of this result will be given in the next section. The results (ii) and (iii) are presumably accounted for by the concept of the additivity of the volumes due to Cohn *et al.*

Inagaki and Teramoto¹³⁾ carried out an accurate measurement of v_2^* for two types of cellulose derivatives and examined the applicability of the additivity

Table 1. k -values in Eq. (6) (according to Schulz and Hoffmann¹²⁾)

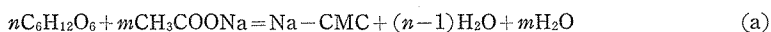
Polymer	Initiator	Solvent used in polymerization	k
polymethyl methacrylate	Bz ₂ O ₂	benzene	+39.4
	Bz ₂ O ₂	ethyl acetate	+39.3
	Bz ₂ O ₂	dioxane	+39.5
	AIBN	benzene	+50
polystyrene	Bz ₂ O ₂	benzene	-23
	Bz ₂ O ₂	ethyl acetate	-23
	AIBN	ethyl acetate	-10
	H ₂ SO ₄ /CCl ₄	ethyl acetate	+10

Bz₂O₂: benzoyl peroxide; AIBN: azobisisobutyronitrile.

Table 2. Changes of v_2^* for polymethyl methacrylate (PMM) and polystyrene (PST) in various solvents (Schulz and Hoffman)

Solvent	$v_2^*(M_2 \rightarrow \infty) = -(\mathfrak{B}_{11}^0/m_2)$		Difference	Ratio
	PMM	PST		
<i>o</i> -dichlorobenzene	0.8187	0.9289	0.1102	1.135
dioxane	0.8181	0.9270	0.1089	1.133
chlorobenzene	0.8118	0.9207	0.1089	1.134
<i>m</i> -xylene	0.8101	0.9260	0.1159	1.143
tetrahydrofuran	0.8085	0.9260	0.1017	1.145
butyl acetate	0.8080	0.9162	0.1082	1.134
toluene	0.8070	0.9169	0.1099	1.136
benzene	0.8069	0.9175	0.1106	1.137
carbon tetrachloride	0.8039	0.9087	0.1048	1.130
dimethyl ethyl ketone	0.8015	0.9106	0.1091	1.136
methyl ethyl ketone	0.7993	0.9078	0.1085	1.136
ethyl acetate	0.7963	0.9132	0.1169	1.147
acetone	0.7947	0.8990	0.1043	1.131
chloroform	0.7942	0.9110	0.1168	1.147

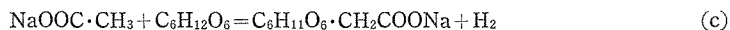
rule to these polymers. For sodium carboxymethyl cellulose (hereafter referred to as Na-CMC) with degree of substitution 0.51 the measurements were made in pure aqueous solution and in NaCl-solution with concentration range up to 0.1%, and for methyl cellulose (hereafter referred to as MC) with degree of substitution 1.26 in aqueous solution. The observed values are compared with calculated values which are obtained by applying the additivity rule. The calculation is made by first assuming a chemical process for the formation of the polymer and then deducing the volume change due to this process from the v_2^* values of low molecular weight compounds. Taking Na-CMC as an example, we assume the following process:



where m/n gives the degree of etherification α . For the formation of the glycosidic linkage between *d*-glucoses and ether linkage between *d*-glucose and sodium acetate we assume:



and



Now we define the volume changes associated with the processes (a), (b) and (c) as Δ , Δ_1 and Δ_2 , respectively, and further assume that the volume change due to the condensation of one *d*-glucose molecule to a cellulose chain end is also given by Δ_1 . Then finally we reach the following equation:

$$\Delta = (n-1)\Delta_1 + m\Delta_2 \quad (d)$$

The volume changes Δ_1 and Δ_2 may be deduced from the volume change due to processes (b) and (c)¹³⁾. Then by using the Δ -value from Eq. (d) we can calculate the apparent specific volume, v_2^* , for Na-CMC. Table 3 shows both measured

and calculated values of v_2^* of Na-CMC and MC and also of polyvinyl alcohol (hereafter referred to as PVA) measured by Nakanishi and Kurata¹⁴). In these results it is noticeable that:

i) v_2^* of Na-CMC increases with the increases in extraneous salt concentration; ii) the observed values of Na-CMC are much lower than the calculated value; and iii) the agreement between observed and calculated values is fairly good in neutral, non-electrolytic polymers such as MC and PVA. The theoretical discussion of these results will also be given in the following section.

Table 3. Apparent specific volume of cellulose derivatives and polyvinyl alcohol

Polymer	Solvent	v_2^*	
		observed	calculated
CMC	Pure Water	0.506 ₄	
	0.0050% NaCl	0.505 ₆	0.545
	0.0583% NaCl	0.510 ₆	
	0.1005% NaCl	0.512 ₅	
Methylcellulose	Pure Water	0.735 ₆	0.70-0.75 ^{*)}
PVA ^{**)}	Pure Water	0.755	0.743

^{*)} The value depends on the way of estimation of Δ_2 but the difference between upper and lower limits is only 0.05cc/g, and an intermediate value between 0.73 and 0.74 will be most reasonable.

^{**)} According to Nakanishi and Kurata.¹⁴⁾

6. THE STATISTICAL THERMODYNAMICAL THEORY

A thermodynamical study of the density of solutions was made first by Tamman¹⁵⁾ and subsequently by Hildebrand¹⁶⁾ and Scatchard¹⁷⁾. Kobatake and Inagaki have also applied the general theory of McMillan and Mayer¹⁸⁾ for multicomponent systems to this problem¹⁹⁾. Let us consider a two component solution under a constant pressure. Since the difference of vapor pressure between the pure solvent and the solution is negligible, the activity coefficient Y_0 of the solvent in the solution should differ from that of the pure solvent by an amount corresponding to the change of the activity of the solute. Such a change in activity results in a change of the density of the solution. Therefore the problem is to find out the change of activity of the solvent. This can be derived from the general equation of McMillan and Mayer for the pressure $P(z^0+y)$ of the solution relative to the pressure $P(z^0)$ of a standard state defined by the fugacity z^0 (see Eq. (83) in the original text)¹⁸⁾:

$$P(z^0+y) - P(z^0) = kT \left[c + Y_0 - \sum_{n,\nu} (n+\nu-1) B_{\nu n}^0 Y_0^\nu c^n \right] \quad (7)$$

The condition of a constant pressure, under which the density measurements are usually performed, gives the relation:

$$P(z^0+y) = P(z^0) \quad (8)$$

That is, the right hand side of Eq. (7) is identically equal to zero. Thus the change of the activity coefficient of the solvent is given as a function of concen-

tration c and virial coefficients, $B_{\nu n}^0$, which are derived from the molecular distribution function at the standard state (always assigned by the superscript 0). The final results for the density of the solution is given as:

$$d = d^0 \left\{ 1 + \frac{1}{\rho_1^0} \left[\frac{M_2}{M_1} - \rho_1^0 B_{11}^0 - 2\rho_1^0 B_{20}^0 - 1 \right] c + O(c^2) \right\}, \quad (9)$$

in which ρ_1^0 is the density of the pure solvent in number of molecules per ml, M_1 and M_2 are the molecular weight of the solute and solvent, respectively, B_{11} and B_{20} are the second virial coefficients (or the cluster integrals) between the *solute* and *solvent* molecules and between solvent molecules, respectively, in the McMillan Mayer expressions¹⁸⁾.

The reciprocal of Eq. (9) gives the expression of v_{12} in the form of a series expansion with respect to c . After substituting weight fractions g_1 and g_2 for the concentration c we obtain the expression for the apparent specific volume:

$$v_2^* = \frac{M_1}{M_2 d^0} - (2\rho_1^0 B_{20}^0 + 1 - \rho_1^0 B_{11}^0), \quad (10)$$

in which B_{20}^0 is related to the isothermal compressibility, κ_1^0 , of the solvent by the relation²⁰⁾:

$$\kappa_1^0 kT = (2\rho_1^0 B_{20}^0 + 1) / \rho_1^0 \quad (11)$$

From Eqs. (10) and (11) we get

$$v_2^* = \frac{1}{M_2} (\kappa_1^0 kT - B_{11}^0) \quad (12)$$

Here we introduce the Zimm approximation²¹⁾ for B_{11}^0 , that is, we assume N identical segmets in a polymer chain and assume that

$$B_{11}^0 = N \mathfrak{B}_{11}^0 \quad (13)$$

where $\mathfrak{B}_{11}^0$ is the second virial coefficient between each segment and the solvent. From Eqs. (12) and (13) we finally obtain

$$v_2^* = - \frac{\mathfrak{B}_{11}^0}{m_2} + \frac{\kappa_1^0 kT}{M_2} \quad (14)$$

where $m_2 = M_2/N$ is the weight of one segment. The equation (14) shows an apparent resemblance to the empirical equation of Schulz and Hoffman, Eq. (6). As was shown in Table 1, however, the empirical coefficient K , which is defined as $\kappa_1^0 kT$ in the theory, takes either positive or negative value depending on the type of the initiator used for polymerization and apparently does not satisfy the physical meaning of the theoretical coefficient, which should always be positive. And also the magnitude of the theoretical value is far too small to explain the experimental results.

To avoid these difficulties we have adopted a different second virial coefficient, $\mathfrak{B}_E^0$, for segments at the chain ends and write B_{11}^0 as

$$B_{11}^0 = 2\mathfrak{B}_E^0 + (N-2)\mathfrak{B}_{11}^0 \quad (15)$$

This assumption seems to be quite reasonable judging from the kinetics of radical polymerization. By using Eq. (14), K , in Eq. (12) is now written as:

$$K = \kappa_1^0 kT - 2(\mathfrak{B}_E^0 - \mathfrak{B}_{11}^0) \quad (16)$$

Taking into account the behavior of initiator fragments in polymerization reactions, we can explain at least qualitatively the variation of K -values for different series of polymers with different initiator fragments at the ends and also get satisfactory results about the order magnitude of K . By comparing Eqs. (6) and (14), it is readily seen that the first term of the right hand side of eq. (14), $-(\mathfrak{B}_{11}^0/m_2)$, corresponds to $v_2^*_{(M_2 \rightarrow \infty)}$. From its definition $\mathfrak{B}_{11}^0$ is always negative and therefore the first term is always positive. Also by considering the meaning of the Zimm model it can be said that this term gives the free volume possessed by one segment in the solvent. The fact that v_2^* for neutral (non-electrolytic) polymers is almost always independent of the type of solvent suggests that $\mathfrak{B}_{11}^0$ can be given at least as a first order approximation by a rigid sphere model for the segments. On the other hand if the potential of average force between the solute and solvent molecules has a long range nature, these assumption ceases to be valid and accordingly the additivity rule of Eq. (4) is no longer applicable. This effect was considered as the electrostriction effect. The large discrepancy between calculated and observed values of v_2^* for Na-CMC, as was shown in Table 3, is presumably attributed to this effect. Also the dependence of v_2^* upon extraneous salt concentration is explained as a balance between the electrostriction effect and the excluded volume effect defined by Eq. (5).

As mentioned above, we can cite the following three effects to explain why the v_2^* of polymer molecules does not satisfy the simple additivity rule, Eq. (4): i) the effect of end groups in polymer chains, ii) the nature of the potential of average force between polymer segment and solvent and iii) the excluded volume effect.

Traube had earlier introduced the concept of the covolume for the effect of end groups on v_2^* (or V_2^*) of low molecular weight compounds. From the Eqs. (12) and (14), however, all of the above three effects can be interpreted from the physical meaning of the interaction parameter, B_{11} , between solute and solvent molecules, thus we have introduced the concept of the "total covolume" including all of these three effects.

7. THE SIGNIFICANCE OF THE SPECIFIC VOLUME IN THE STUDY OF PHYSICAL PROPERTIES OF POLYMER SOLUTIONS

In conclusion we discuss the significance of the specific volume and also the kind of information which might conceivably be obtained from its measurement. The apparent specific volume v_2^* of a polymer is uniquely related to its chemical structure and is rather insensitive to changes of the molecular weight as long as the molecule is sufficiently large. Therefore if there are differences in the chemical structure of certain polymers such as in copolymers of different monomers, in isomeric copolymers (heterotactic polymers) and in branched polymers, the differences in the v_2^* s might become appreciable. It should be noted that if it were possible, a measurement by the specific volume method of the extent of the heterotacticity of polymer chains would give a heterotacticity measure in which solute molecules are separated from each others and are free from inter-molecular interaction. This is in contrast to previous methods mainly based on

the colligative properties in a solid state. In fact Buchdahl and associates found that isotactic polystyrene has a higher partial specific volume than atactic polystyrene²²⁾ by using density gradient sedimentation²³⁾. This method also was adopted to detect the structural change of deoxyribonucleic acids²⁴⁾ and a similar principle was applied to the fractionation of polymers with respect to the degree of branching²⁵⁾. Furthermore, the excluded volume effect in the sense of Charlwood⁸⁾ is presumably observed in helix-coil transitions of biological polymers and synthetic polypeptides. The measurement of v_2^* could be an important method in the study of helix-coil transitions, supplementing the measurements of optical properties.

The above mentioned theory also suggests that we could obtain from the measurements of v_2^* the modes of monomer sequence in copolymers. This study is now in progress in our laboratory. In copolymers with sufficiently high molecular weight the dependence of v_2^* on monomer composition might be mainly due to the mode of monomer sequence; in other words, in a copolymer such as



the contribution of AB and BA pairs to v_2^* might differ from that of pairs such as AA or BB.

If the interaction between monomers and solvent is of a short range nature, the $\mathcal{B}_{0,1}$ of a monomer (A or B) in a long sequence of the same monomer might be equal to that in the corresponding homopolymer. Therefore a deviation of v_2^* from simple sum of volumes with respect to the monomer composition might reflect the mode of the appearance of AB and BA pairs. Since the distribution of AB and BA sequence has already been predicted by the kinetic theory of copolymerization²⁶⁾, experimental results of the relation of v_2^* and monomer composition would provide a useful criterion on this theory of kinetics. In connection with the study of v_2^* in copolymers it was found that the v_2^* -value was widely changed with the monomer composition in a given solvent, and this observation was explained by the change of molecular extension of a chain in the solvent²⁷⁾. This seems to be implausible, however, since the change of v_2^* due to chain conformation, which is mainly described by the excluded volume effect in the sense of Charlwood, is at most a few per cent even in cases of such drastic conformation change as the unfolding of protein helices⁹⁾ and as the electrostatic expansion-contraction of polyelectrolytes¹³⁾. Furthermore we already know that the v_2^* of neutral polymers is almost independent of types of solvents (see Table 2).

As previously mentioned, measurement of the v_2^* of polymers, in spite of its usefulness, has not yet received the attention it deserves. A potential advantage to the study of specific volumes is that we can obtain solution density data with very high accuracy. For example, it is not at all formidable by using a float method under optimum conditions to get a value accurate to as many as six decimal places¹³⁾. Also by using the density gradient sedimentation method²³⁾ we can get a value with very high relative accuracy, and can hence detect a very small difference of densities of polymers. It does not seem to be too much to say that the further study of specific volume would provide much interesting information and suggest new problems.

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