The Relation between the Second Virial Coefficient of Osmotic Pressure and the Molar Volume of Solute (Abstract)⁽¹⁾

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Equation for the Osmotic Pressure in Dilute Ideal Solution

The osmotic pressure P, of a solution is thermodynamically related to the vapour-

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pressure of pure solvent p_1°, and that of solution p_1 according to the equation

$$P=-\frac{RT}{\bar{v}_1}\ln\frac{p_1}{p_1^\circ} \tag{1}$$

where $\bar{v}_1$ represents the partial molar volume of solvent in solution, R the gas constant and T absolute temperature. As a special case, when the solution is ideal, the partial molar volume of the solvent $\bar{v}_1$ can be put down as equal to the molar volume of pure solvent v_1°, and p_1/p_1° to the mole fraction of the solvent in the solution N_1, according to the Raoult's law, so that eq. (1) becomes

$$P=-\frac{RT}{v_1^\circ}\ln N_1\,. \tag{2}$$

And if the solution is composed from n_1 moles of solvent and n_2 moles of solute, the mole fraction of solvent N_1 is clearly

$$N_1=\frac{n_1}{n_1+n_2} \tag{3}$$

and the total volume of the solution V can be expressed as

$$V=n_1v_1^\circ+n_2v_2^\circ \tag{4}$$

where v_1° and v_2° are the molar volumes of the solvent and the solute in pure state respectively.

Putting eqs. (3) and (4) in eq. (2), we obtain

$$P=\frac{n_1RT}{V-n_2v_2^\circ}\ln\left(1+\frac{n_2}{n_1}\right). \tag{5}$$

This eq. (5) can, however, be further simplified to the eq. (6) for which is shown below for a sufficiently dilute solution by expanding the logarithmic factor in the right hand side and neglecting higher terms than the second

$$P=\frac{n_2RT}{V-n_2v_2^\circ}\,. \tag{6}$$

Dilute Solutions of Low Molecular Weight Substances

In real solutions solute molecules are generally solvated, that is, a number of solvent molecules are loosely attached to a solute molecule. But it may be a plausible assumption that the degree of solvation, i. e. the number of solvent molecules attached to a solute molecule increases with increasing dilution; finally a saturated state is reached and thereafter the degree of solvation does not increase with further increase of dilution. Accordingly in this state of saturation the solution may be treated as a sort of ideal solution, when we regard the solvated solute molecule as a whole as a molecule of the solute. Then, by expressing the maximum degree of solvation in this saturated state by $N_{\max}$, we can put the number of free solvent molecules in the solution at a sufficiently large dilution

$$n_1'=n_1-N_{\max}\,n_2 \tag{7}$$

the mole fraction of the free solvent

$$N_1'=\frac{n_1'}{n_1'+n_2}=\frac{n_1-N_{\max}\,n_2}{n_1-N_{\max}n_2+n_2} \tag{8}$$

and the total volume of the solution

$$V=n_1'v_1^\circ+n_2(v_2^\circ+v_1'N_{\max}) \tag{9}$$

where v_1' represents the molar volume of the solvent in the solvated state. Hence if we put eqs. (8) and (9) in eq. (2) we obtain for a sufficiently dilute solution

$$P=\frac{n_1'RT}{V-n_2(v_2^\circ+v_1'N_{\max})}\ln\left(1+\frac{n_2}{n_1'}\right) \tag{10}$$

or

$$P(V-n_2b_{\max})=n_2RT \tag{11}$$

where

$$b_{\max}=v_2^\circ+N_{\max}\,v_1'\,. \tag{12}$$

The $b_{\max}$ represents the maximum molar volume of the solvated solute, that is, the molar volume of the solvated solute in the state of saturated solvation.

Dilute Solutions of Chain Polymers

As is well known, the abnormal character of the solution of high polymers especially that of chain polymers is generally attributed to the random motion of the sections of the chain molecules in soln. But if we assume the extension of a chain molecule due to its random motion having a saturated or maximum value in sufficient dilution, such a solution can be treated in exactly the same way as the solution of low molecular weight substances in its saturated state of solvation. We obtain exactly the same form of the equation as (11) for the relation between the osmotic pressure, the volume of the solution and the temperature for a sufficiently dilute solution of high polymer, if we assume $b_{\max}$ representing the maximum molar volume of the solute, that is, the volume occupied by the solute molecule at its highest degree of expansion.

The Second Virial Coefficient and the Molar Volume of the Solute

The relation between the osmotic pressure P and the concentration c expressed in gram per liter of a solution is expressed by a well known equation

$$P=RT\left(\frac{c}{M}+A_2c^2+A_3c^3+\cdots\right) \qquad (13)$$

where M represents the molecular weight of the solute and A_2 and A_3 are the so-called the second and the third virial coefficient respectively. Hence, it may be of interest to compare eq. (11) obtained above with this eq. (13). For this purpose eq. (11) is deformed into the form

$$P=\frac{n_2RT}{V-n_2b_{\max}}=\frac{RT}{\frac{M}{c}-b_{\max}}$$

$$=RT\frac{c}{M}\left(1-\frac{c}{M}b_{\max}\right)^{-1},$$

and by expanding the right hand side of this equation and neglecting higher terms, we obtain

$$P=RT\left(\frac{c}{M}+\frac{b_{\max}}{M^2}c^2\right). \qquad (14)$$

By comparing the second terms in the right hand sides of eqs. (13) and (14) we see that the second virial coefficient A_2 is related to the maximum molar volume $b_{\max}$ and the molecular weight M of the solute according to the equation:

$$A_2=b_{\max}/M^2. \qquad (15)$$

As a verification of this eq. (15) we have compared the value of $b_{\max}$ of polystyrene in toluen solution calculated by this equation using the data obtained from the osmotic pressure measurement with that computed from the light scattering measurement. We have obtained namely from the data of osmotic pressure measurement made by Mark and others$^{(2)}$ at 25°C. for the toluene solution of polystyrene having a mean molecular weight of 1,580,000 as a value of $b_{\max}$ 3.74×10^5 liter/mole according to eq. (15). This value agrees, however, sufficiently well with the value of $b_{\max}=3.68\times10^5$ liter/mole obtained from the light scattering measurement made by Zimm and others$^{(3)}$ at 22°C. for the toluene solution of polystyrene having a mean molecular weight of 1,610,000.

Degree of Hydration of Sucrose and Glucose

When we calculate $b_{\max}$ for sucrose in aqueous solution by eq. (15) using the data of osmotic pressure measurement made by Morse$^{(4)}$ at 20°C., we obtain 0.382 liter/mole. But $b_{\max}$ is related with the molar volume of pure solute v_2^0 and the molar volume of the hydrated water v_1' according to eq. (12). Hence, if we assume v_2^0 being equal to the molar volume of pure solid sucrose (0.216 liter/mole) and v_1' being equal to the molar volume of pure water (0.018 liter/mole), we obtain as a maximum degree of hydration $N_{\max}$ of sucrose a value of about 9 accoring to eq. (12). In the same way we obtain as $N_{\max}$ for glucose at 10°C. a value of about 3.5 from the osmotic pressure measurement made by the same author.

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