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EFFECT OF THE SOLUTE AND SOLVENT MOLECULAR VOLUMES ON THE OSMOTIC PRESSURE

M. Podolak

*Institute of Physics, Opole University
Oleska 48, 45-052 Opole, Poland
podolak@uni.opole.pl*

In the present paper, the formula for osmotic pressure is derived on the grounds of the kinetic-molecular theory. The considerations which lead to obtaining the formula stem from reference to a system containing two solutions of differing solute concentrations, separated from each other with a semi-permeable membrane. As it follows from van't Hoff equation, which is well-known in the literature of the subject, osmotic pressure is a function of the difference in the concentrations of solutions and temperature. The formula obtained in this work, apart from the mentioned factors, contains a molar volumes ratio (or proper volumes of molecules) of the solute and the solvent. It follows from the formula, among others, that in the case of equal molar volumes of the solution components, the osmotic pressure is equal to zero. However, if the solute molar volume is twice bigger than that of the solvent, then the formula obtained in the paper acquires the form of van't Hoff one.

Key words: osmotic pressure, van't Hoff formula, molecular volumes.

If two chambers containing solutions of different solute concentrations are separated from each other with a porous membrane of differing permeability for the solute and the solvent, then in such a system there will occur, the phenomenon of osmosis. The term “osmosis” derives from the Greek language and means “pushing”. The phenomenon itself is induced by the difference in the volume streams of the solvent and the solute flowing through the membrane. The stream of the solvent is, generally, of higher value, and due to this, in the system, there follows a net flow through the membrane of this component. The flow can be stopped by influence relatively high external pressure on the solution of the higher solute concentration. In the case of a semi-permeable membrane, which allows passing of the solvent only, the pressure is equal to osmotic pressure (π). For dilute solutions the osmotic pressure is described by means of van't Hoff formula, widely-known in the literature of the subject [1], [2], [3], in the following form $\pi = RT\Delta c$, where R means gas constant, T – temperature in Kelvin degrees, Δc – the difference in solute concentrations. The formula was introduced into the literature by van't Hoff in 1885 [3]. It is a result of application of the ideal gas equation to describe dilute solutions with the assumption that there exists an analogy between gas closed in a vessel and a solute in a solvent.

Van't Hoff proved that there exist a close dependence between the osmotic pressure and saturated vapour pressure of the solvent over the surface of the solution [3]. In turn, vapour pressure, similarly as the osmotic pressure, depends on the concentration of the

solution [1], [3]. Thanks to this dependence, quantitatively described by Raoult's law, it is possible to derive van't Hoff formula from this law as well.

It follows from van't Hoff formula that the $\pi/\Delta c$ ratio should be independent from the concentration. This conclusion is not generally true with reference to real solutions [1], [2]. In consequence, in order to describe the osmotic pressure in such solutions, the virial equation in the form of $\pi = RTx(I+Bx+Cx^2+\dots)$ is applied, in which x denotes concentration of the solution, and $B, C \dots$ are virial coefficients. The values of these coefficients depend on temperature, and they determine intra-molecular interactions of double molecules (B) and triple ones (C). Van't Hoff formula constitutes the first term of the sum in this equation.

The aim of this work was to provide an analysis of the phenomenon of osmosis and derivation of a formula for osmotic pressure on the grounds of the kinetic-molecular theory, neglecting intra-molecular interactions and the contraction phenomenon.

Let us consider a two-chambers system (Fig. 1) containing water (w), as the solvent, and two water solute solution (s) of c_{s1} (chamber 1) and c_{s2} (chamber 2) concentrations. The chambers are separated with the membrane (M).

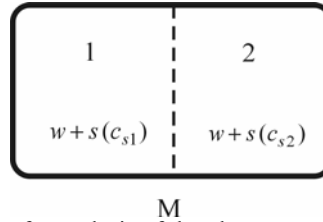


Fig. 1. Two-chambers system for analysis of the phenomenon of osmosis: w – water, s – solute, M – membrane

It follows from the kinetic-molecular theory concerning ideal gas that the pressure of gas exerted on the walls of a vessel is a linear function of the kinetic energy of gas molecules, which is described with the following equation:

$$p = \frac{2}{3} \frac{E_k}{V}, \quad (1)$$

in which E_k denotes the sum of the kinetic energies of all gas molecules in the vessel, and V – volume of the vessel [4], [5], [6]. The kinetic energy of molecules E_k can be written in the following form:

$$E_k = N\bar{e}_k, \quad (2)$$

where N denotes the number of molecules in the vessel and \bar{e}_k – mean kinetic energy of one molecule. The mean kinetic energy of a molecule is a function of temperature, which is described with one of the most fundamental equations of the kinetic-molecular theory and has the following form:

$$\bar{e}_k = \frac{3}{2} kT, \quad (3)$$

where k denotes Boltzmann constant.

On including equations (3 and 2) into equation (1) we will obtain:

$$p = \frac{N}{V} kT \quad \text{or} \quad p = \frac{N}{N_a V} RT, \quad (4)$$

where N_a denotes Avogadro's number.

Assuming that equation (4) can be applied to describe the pressure exerted by of water and solute molecules on the membrane (M) (Fig. 1), we can write a formula to determine the pressure of water and solute in chamber (1) and in chamber (2) in the form as follows:

$$p_1 = \frac{N_{w1}}{N_a V} RT + \frac{N_{s1}}{N_a V} RT = \frac{RT}{N_a V} (N_{w1} + N_{s1}), \quad (5)$$

and

$$p_2 = \frac{N_{w2}}{N_a V} RT + \frac{N_{s2}}{N_a V} RT = \frac{RT}{N_a V} (N_{w2} + N_{s2}), \quad (6)$$

where p_1 and p_2 denotes the pressure of water and solute in the chamber 1 and 2 respectively; N_{w1} and N_{w2} – the number of water molecules in this chambers; N_{s1} and N_{s2} – the number of solute molecules; V – the solution volumes ($V=V_1=V_2$).

Taking into account the proportions: $\frac{N_{w1}}{V_{w1}} = \frac{N_a}{\bar{V}_w}$, $\frac{N_{s1}}{V_{s1}} = \frac{N_a}{\bar{V}_s}$ as well as,

$\frac{N_{w2}}{V_{w2}} = \frac{N_a}{\bar{V}_w}$, $\frac{N_{s2}}{V_{s2}} = \frac{N_a}{\bar{V}_s}$ in which \bar{V}_w and \bar{V}_s denotes the water and solute molar volumes, V_{w1}, V_{w2} and V_{s1}, V_{s2} – volumes occupied by water and solute in chambers, equations (5) and (6) can be written in the following form:

$$p_1 = \frac{RT}{V} \left(\frac{V_{w1}}{\bar{V}_w} + \frac{V_{s1}}{\bar{V}_s} \right) \quad (7)$$

and

$$p_2 = \frac{RT}{V} \left(\frac{V_{w2}}{\bar{V}_w} + \frac{V_{s2}}{\bar{V}_s} \right). \quad (8)$$

Assuming that the phenomenon of contraction does not occur in the solution, we can write that $V_{w1} + V_{s1} = V$ as well as $V_{w2} + V_{s2} = V$, and then:

$$p_1 = \frac{RT}{V} \left(\frac{V}{\bar{V}_w} - \frac{V_{s1}}{\bar{V}_w} + \frac{V_{s1}}{\bar{V}_s} \right), \text{ or } p_1 = \frac{RT}{\bar{V}_w} \left(1 - \frac{V_{s1}}{V} + \frac{V_{s1} \bar{V}_w}{V \bar{V}_s} \right), \quad (9)$$

and

$$p_2 = \frac{RT}{\bar{V}_w} \left(1 - \frac{V_{s2}}{V} + \frac{V_{s2} \bar{V}_w}{V \bar{V}_s} \right). \quad (10)$$

Taking into account the dependences, $V_{s1} = n_{s1} \bar{V}_s$ and $V_{s2} = n_{s2} \bar{V}_s$, in which n_{s1}, n_{s2} denotes the number of moles of the solute in chambers, the expression determining the pressure in this chambers can be written in the following form:

$$p_1 = \frac{RT}{\bar{V}_w} \left(1 - \frac{n_{s1}}{V} \bar{V}_s + \frac{n_{s1}}{V} \bar{V}_w \right), \quad (11)$$

and

$$p_2 = \frac{RT}{\bar{V}_w} \left(1 - \frac{n_{s2}}{V} \bar{V}_s + \frac{n_{s2}}{V} \bar{V}_w \right). \quad (12)$$

On introducing, into equations (11) and (12), the molar concentrations of the solute (c_{s1}, c_{s2}) expressed with the dependences: $c_{s1} = \frac{n_{s1}}{V}$ and $c_{s2} = \frac{n_{s2}}{V}$, we obtain:

$$p_1 = \frac{RT}{\bar{V}_w} (1 - c_{s1} \bar{V}_s + c_{s1} \bar{V}_w), \quad (13)$$

and
$$p_2 = \frac{RT}{\bar{V}_w} (1 - c_{s2}\bar{V}_s + c_{s2}\bar{V}_w). \quad (14)$$

The difference in the pressures ($p_1 - p_2$) is equal to osmotic pressure (π) and amounts to:

$$\pi = p_1 - p_2 = \left(\frac{\bar{V}_s}{\bar{V}_w} - 1 \right) RT\Delta c, \quad (15)$$

where $\Delta c = c_{s2} - c_{s1}$.

It follows from equation (15) (in contrast to van't Hoff formula) that osmotic pressure depends not only on the solute concentration and temperature, but also on the ratio of the molar volumes of the solution components (thus on the ratio of proper volumes of their molecules). If the molar volumes of the solvent and the solute are equal, then the osmotic pressure equals zero. If the molar volumes of the solute are smaller as that of the solvent than the osmotic pressure change its direction. Equation (15), take on the form of van't Hoff formula, when the proper volume of a solute molecule is twice as big as that of the solvent.

For multi-atomic molecules, which consist of two, three or a greater number of atoms, equation (3) should be written in the following form:

$$\bar{e}_k = \frac{i}{2} kT = \frac{i}{2} \frac{R}{N_a} T \quad (16)$$

in which i denotes the number of degrees of freedom of the molecule. This number equals 3 for one-atomic molecules, and for others it can assume values such as 5 (two-atomic molecules), or 6 for greater. Substituting equation (16) in (2) and (1) we will obtain the following:

$$p = \frac{i}{3} \frac{N}{VN_a} RT. \quad (17)$$

If the number of freedom degrees of the solvent molecules (i) differs from that of the solute (for example j) then, in accordance with equation (17), each of the components of the solution will exert different pressure on the membrane.

Let us assume that in chamber 1 of the system represented in fig. 1, there are a solvent (*e.g.* water – w) and solute – (s) of a concentration of c_{s1} , and in chamber 2 there are a solvent and the same solute of a concentration of $c_{s2} > c_{s1}$. The pressures in chambers, analogous to equations (13) and (14), can be written as follows:

$$p_1 = \frac{1}{3} \frac{RT}{\bar{V}_w} (i - ic_{s1}\bar{V}_s + jc_{s1}\bar{V}_w) \quad (18)$$

and
$$p_2 = \frac{1}{3} \frac{RT}{\bar{V}_w} (i - ic_{s2}\bar{V}_s + jc_{s2}\bar{V}_w). \quad (19)$$

From equations (18) and (19) there follows a formula for osmotic pressure, which includes the number of degrees of freedom of the solvent molecules (i), as well as those of the solute (j), which has the following form:

$$\pi = p_1 - p_2 = \frac{1}{3} \left(i \frac{\bar{V}_s}{\bar{V}_w} - j \right) RT\Delta c, \quad (20)$$

where $\Delta c = c_{s2} - c_{s1}$.

Equation (20) acquires the form of equation (15) assuming that both the solvent and the solute consist of one-atomic molecules for which $i=j=3$.

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ЕФЕКТ РОЗЧИНУ ТА РОЗЧИННИКА МОЛЕКУЛЯРНОГО ОБ'ЄМУ ПІД ДІЄЮ ОСМОТИЧНОГО ТИСКУ

М. Подоляк

*Інститут фізики, Університет Ополье
ул. Олеска 48, 45-052 Ополье, Республіка Польща*

У статті виведено формулу для осмотичного тиску з молекулярно-кінетичної теорії. Як видно з відомого у науці рівняння Вант Гоффа, осмотичний тиск залежить від різниці в концентрації розчинів і температури. Одержана в дослідженні формула містить молярне співвідношення об'ємів у розчині і розчиннику. Показано, що в разі рівності молярних об'ємів компонент розчину – осмотичний тиск дорівнює нулю. Однак, якщо молярний об'єм розчину удвічі більший від об'єму розчинника, то отримана формула перетворюється у формулу Вант Гоффа.

Ключові слова: осмотичний тиск, формула Вант Гоффа, молярний об'єм.

ЭФФЕКТ РАСТВОРА И РАСТВОРИТЕЛЯ МОЛЕКУЛЯРНОГО ОБЪЕМА ПОД ДЕЙСТВИЕМ ОСМОТИЧЕСКОГО ДАВЛЕНИЯ

М. Подоляк

*Інститут фізики, Університет Ополье
ул. Олеска 48, 45-052 Ополье, Республіка Польща*

В статье выведена формула для осмотического давления из молекулярно кинетической теории. Как видно из известного в науке уравнения Вант Гоффа, осмотическое давление зависит от разницы в концентрации растворов и температуры. Полученная формула содержит молярное соотношение объемов в растворе и растворителе. Показано, что в случае равенства молярных объемов компонент раствора осмотическое давление равно нулю. Однако, если молярный

объём раствора вдвое больше от объёма растворителя, то полученная формула превращается в формулу Вант Гоффа.

Ключевые слова: осмотическое давление, формула Вант Гоффа, молярный объём.

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