

CALCULATION OF OSMOTIC PRESSURE USING A CLOSED SYSTEM MODEL

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Abstract

In this work we have used a closed system model to derive an analytical equation for the osmotic pressure of two component electrolyte and non-electrolyte solutions. In order to do so, we have used an equation of state, known as the dense system equation of state (DSEOS), for the model system. Based on the model, a new definition is given for the osmotic pressure of a closed system. Good agreement between the calculated and experimental osmotic pressure is obtained. Using the results obtained for the osmotic pressure along with some exact thermodynamic arguments, we have calculated the solvent activity for some electrolyte and non-electrolyte solutions. The calculated activities are found to be in good agreement with the experiment, in such a way that for the NaCl solutions the deviations for the calculated activities are less than 0.02% for solutions up to six molal.

1. Introduction

Osmotic pressure, which is one of the colligative properties, plays a key role in biological and industrial phenomena. In plants, osmosis is attributed to the transfer of water and mineral salts from the soil to the different parts of the plant via roots. In living creatures, osmotic pressure is the determining factor in the phase equilibria between different fluids in the body. The equilibrium between the transfer of blood particles and intercellular space is controlled by the hydrostatic pressure of the heart and the osmotic pressure of the blood proteins. Kidney operation in the body is another example of osmosis. The

main function of the kidney is to remove the wasted metabolic materials and impurities from the blood flow which is done by osmotic phenomena. Reverse osmosis is widely used in the desalinating of water. Here, osmotic pressure is discussed from two different points of view, namely in an open system and in a closed system. The latter is originally introduced in this work.

2. Osmotic Pressure in an Open System

Consider a system divided into two parts by a rigid, thermally conducting, semipermeable membrane. In the left part we put pure solvent A, and in the right a solution of B in A. Let us assume that the membrane allows solvent A to pass through it but does not allow the passage of solute B. Suppose that we have initially a system which is at the thermal and mechanical equilibrium ($T = T_r = T_L$, $P_0 = P_R = P_L$) but at non-material equilibrium [1] ($\mu_{A,R} \neq \mu_{A,L}^*$) at which $h_r = h_l$; where T , P , and h are temperature,

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pressure and height of fluid in both sides of the system and subscripts stand for right and left; and that $\mu_{A,L}^*(T, P_0)$ is the chemical potential of A on the left and $\mu_{A,R}^*(T, P_0, x_A)$ is for the right side (x_A is the mole fraction of A in solution). Considering the fundamental equation $\mu_A = \mu_A^* + RT \ln a_A$ (a_A is the activity of A in solution), the presence of solute B in solution causes that $\mu_{A,L}^* > \mu_{A,R}^*$ (the entropy increment is the main factor for this thermodynamic stability). Owing to the fact that the chemical potentials of A are different in each side of the membrane, substance A will flow through the membrane from left to right and as a result the height and pressure of the right part will increase. Partial molar volume of solvent (\bar{V}_A) is generally positive in dilute solution, the increase in pressure causes that $\mu_{A,R}$ increases because $\bar{V}_A = (\partial\mu/\partial P)_T$. The increase of $\mu_{A,R}$ will be continued until the equilibrium is eventually reached, at which $\mu_{A,L}^* = \mu_{A,R}$ (Figure 1a). The osmotic pressure (π) is defined at such an equilibrium state and is equal to $\pi = P_R - P_L$. For simplicity, we define $P_R \equiv P$ and $P_L \equiv P_0$ and (P_0 is atmospheric pressure and is considered to be equal to one atmosphere in our calculation). Therefore:

$$\pi = P - P_0 \quad (1)$$

Alternatively the osmotic pressure can be viewed as an extra mechanical pressure that must be applied on the solution in such a way that there will be no volume change in either sides, i.e. such a pressure prevents any net molecular migration through the membrane, and it will also increase the solvent chemical potential, to cancel out

exactly its reduction by the presence of solute in solution [Figure (1.b)]. Such a definition for osmotic pressure is appropriate for an open system, because of the fact that solvent molecules can pass through the membrane.

3. Osmotic Pressure in a Closed System Model

As we noted before, it is possible to prevent the decrease of the chemical potential of a solvent in an open system by applying an external pressure π on the solution [Figure (1)].

Consider a closed system at a constant temperature and pressure which is formed from 1 kg of solvent A (The moles of A are $n = 1\text{kg}/M_A$, where M_A is the molecular weight of solvent) and m mole of solute B (m is the solute molality). Let us suppose that the volume of the solution V [figure (2.b)] is larger than that of the pure solvent A (V_A^*) [figure (2a)]. The osmotic pressure may be defined so that it satisfies two constraints:

(i) The osmotic pressure equals that pressure which equalizes the chemical potential of solvent (μ_A) in a solution with that of pure solvent (μ_A^*) at the same temperature:

$$\mu_A(T, P_0 + \pi, x_A) = \mu_A^*(T, P_0) \quad (2)$$

(ii) Due to the fact that the increasing of pressure causes the reduction of volume, we define the osmotic pressure such that it will equalize the volume of the solution (V) at the temperature T and pressure $\pi + P_0$ with the volume of 1 kg of the pure solvent (V_A^*) at P_0 and T . Since we are interested in aqueous solutions in which the water mole fraction is more than 0.9, it is possible to assume that the

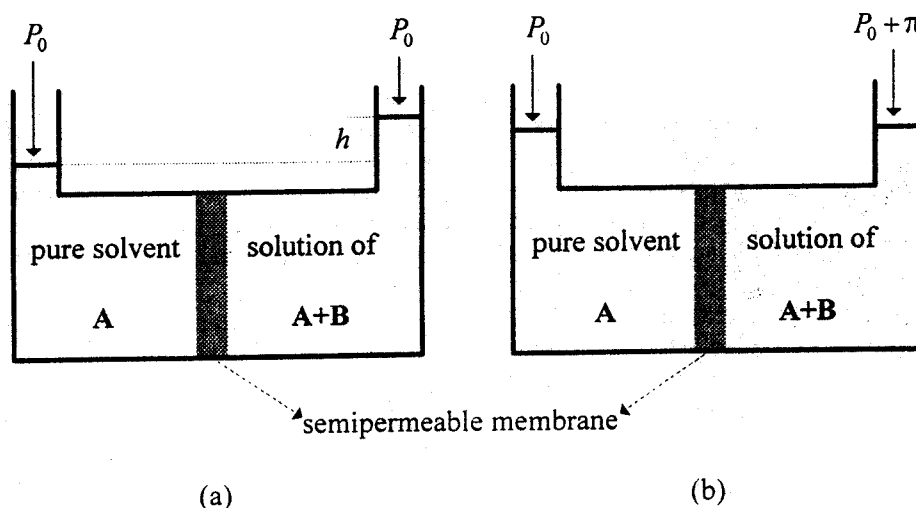


Figure 1. Osmotic pressure in an open system. (a) The hydrostatic pressure ρgh is exactly equal to the osmotic pressure. (b) Additional mechanical pressure π on the right side, which prevents the transfer of matter, is the osmotic pressure.

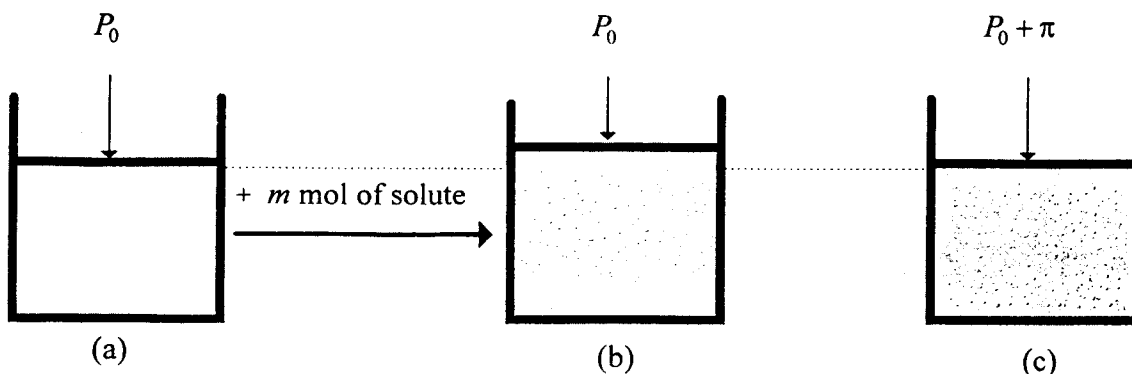


Figure 2. Definition of osmotic pressure in a closed system at constant T . (a) 1 kg. of solvent under pressure P_0 and volume V_A^* . (b) Solving m mole of solute with volume V' under the previous pressure. (c) m molal solution with volume $V=V_A^*$ under pressure $P_0+\pi(V'>V_A^*)$.

volume of the solution is the same as that of the pure solvent, namely:

$$V(T, P_0 + \pi, x_A) = V_A^*(T, P_0) \quad (3)$$

According to these two assumptions, the osmotic pressure can be viewed as the pressure needed to insert the solute molecules among solvent molecules without any change in volume [Figure (2.c)].

4. Calculation of Osmotic Pressure in the Closed System Model Using an Equation of State

Now, we calculate the osmotic pressure by using an appropriate equation of state (EOS) for the closed system model [Figure (2)]. Using a general potential function, Parsafar and Mason derived an EOS for compressed solids[2]. Recently, this EOS has been extended to pure dense fluids [3] and is called the equation of state for dense systems which is abbreviated as DSEOS. However, a small improvement in the temperature dependent parameters of the EOS is made. The general form of this EOS is as follows:

$$P/\rho^2 = A_0 + A_1\rho + A_2\rho^2 \quad (4)$$

where P and ρ are pressure and molar density, respectively. This EOS is valid for densities greater than the Boyle density. The A_i coefficients depend on the kind of solution, temperature, and solvent mole fraction. It is shown that this equation can be applied to different pure dense fluids with satisfactory results[3]. Since our model system has high density, we can use DSEOS for such a model. Although DSEOS is derived for pure dense systems, we may expect that it can be used for dense mixtures too, according to the van der Waals one fluid

approximation[4,5,6]. In our interested systems, the variation of water mole fraction is small and therefore, we may ignore the composition dependencies of A_i coefficients.

In order to use Equation (4) for closed osmotic systems model based on Figure 2.c, we define the pressure and density as follows:

$$P = P_0 + \pi \quad (5)$$

$$\rho = (n+m)/V \quad (6)$$

where V is the volume of 1 kg of pure solvent at constant T [see assumption (ii), the basis of Equation (3)].

5. Calculation of the Osmotic Pressure of Solution Using DSEOS

In order to find the coefficients of the DSEOS, we have used the experimental PVT data of pure water [7] and aqueous sucrose[8] to plot P/ρ^2 with respect to ρ , for which the results are shown in Figure 3 at 298 K, which has been fitted very well by a quadratic function with $R^2=0.999995$ where R^2 is the coefficient of determination[9]. The coefficients of Equation (4) for the sucrose solution at 298 K are obtained as:

$$\begin{aligned} A_0 &= 1.347027 \text{ atm.lit}^2 \text{ mol}^{-2} \\ A_1 &= -0.056573 \text{ atm.lit}^3 \text{ mol}^{-3} \\ A_2 &= 5.824246 \times 10^{-4} \text{ atm.lit}^4 \text{ mol}^{-4} \end{aligned} \quad (7)$$

Using these coefficients and Equations (4) to (6), we are able to calculate the osmotic pressure at any concentration. Also, we have calculated ΔP which is equal to $|P_{\text{cal}} - P_{\text{exp}}|$, where P_{cal} and P_{exp} are the calculated and experimental osmotic pressure, respectively. Such calculations are also carried out for different sucrose solutions for some given isotherms. The results are

Table 1. The DSEOS coefficients for isotherms of aqueous sucrose solutions in the concentration range of 0.1-1 of molal (A_0, A_1, A_2), the coefficient of determination (R^2), the osmotic pressure range ($\Delta\pi$), and average absolute deviation from experimental values (ΔP^a) for the given solutions

$\frac{T}{K}$	$\frac{A_0}{\text{atm} \cdot \text{lit}^2 \cdot \text{mol}^{-2}}$	$\frac{A_1}{\text{atm} \cdot \text{lit}^3 \cdot \text{mol}^{-3}}$	$\frac{10^4 \times A_1}{\text{atm} \cdot \text{lit}^4 \cdot \text{mol}^{-4}}$	R^2	$\frac{\Delta\pi}{\text{atm}}$	$\frac{\Delta P^a}{\text{atm}}$
273	1.300748	-0.054017	5.510178	0.999997	2-25	0.01 (0.02)
278	1.263386	-0.052818	5.415255	0.999992	2-26	0.02 (0.03)
283	1.242050	-0.052208	5.374838	0.999997	2-26	0.01 (0.02)
288	1.274285	-0.053548	5.512533	0.999993	2-26	0.02 (0.03)
293	1.302068	-0.054745	5.639168	0.999995	2-27	0.01 (0.03)
298	1.347027	-0.056573	5.824246	0.999995	2-27	0.01 (0.03)
303	1.106468	-0.048172	5.093583	0.999996	2-27	0.02 (0.03)
313	0.489447	-0.026377	3.175360	0.999995	2-28	0.01 (0.03)
323	1.120209	-0.049463	5.294492	0.999996	2-28	0.01 (0.03)
333	0.818007	-0.038859	4.373683	0.999992	2-29	0.02 (0.04)

^aMaximum absolute deviations from experimental values are given in parentheses.

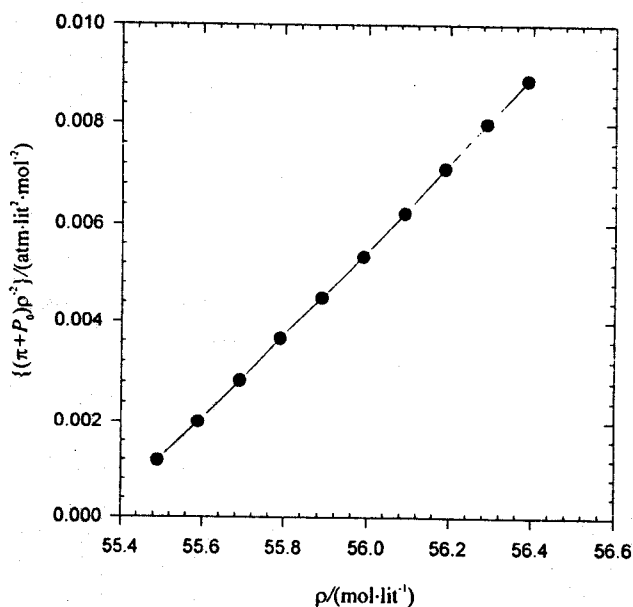


Figure 3. Evaluation of DSEOS for 298 K isotherm of sucrose solutions in the concentration interval of 0.1-1 molal.

tabulated in Table 1 [The experimental data is taken from reference 8]. Similar calculations were also done for solutions with smaller molecular weight for solute (i.e. glucose) and larger molecular weight (i.e. congo red with M.W. = 696 g/mol) than sucrose, for which the results are shown in Figures 4 and 5 [The experimental data is taken from reference 8].

In order to check the accuracy of predication of Equation (4) for electrolyte solutions, similar calculations were done for NaCl solutions, for which the calculated results are compared with the experimental data [10]. The results are summarized in Table 2. As shown in this table, the calculated results for the electrolyte solutions of NaCl are in very good agreement with the experiment.

6. Calculation of Solvent Activity Using DSEOS

Using the assumptions (i) and (ii), the van der Waals one fluid approximation, and the DSEOS for the calculation of osmotic pressure, we may expect that the solvent activity can be calculated (remember that the activity is a key function in solution thermodynamic). As we noted

Table 2. The same as Table 1 for aqueous sodium chloride in the concentration range of 0.05-6 molal

$\frac{T}{K}$	$\frac{A_0}{\text{atm} \cdot \text{lit}^2 \cdot \text{mol}^{-2}}$	$\frac{A_1}{\text{atm} \cdot \text{lit}^3 \cdot \text{mol}^{-3}}$	$\frac{10^4 \times A_1}{\text{atm} \cdot \text{lit}^4 \cdot \text{mol}^{-4}}$	R^2	$\frac{\Delta\pi}{\text{atm}}$	$\frac{\Delta P^a}{\text{atm}}$
298	1.334749	-0.061052	6.674328	0.999904	2-384	0.99 (1.66)
313	1.191008	-0.057228	6.464522	0.999951	2-400	0.74 (1.24)
333	1.016223	-0.052744	6.252166	0.999979	2-418	0.51 (0.83)
373	0.744397	-0.046453	6.100886	0.999993	2-442	0.31 (0.50)

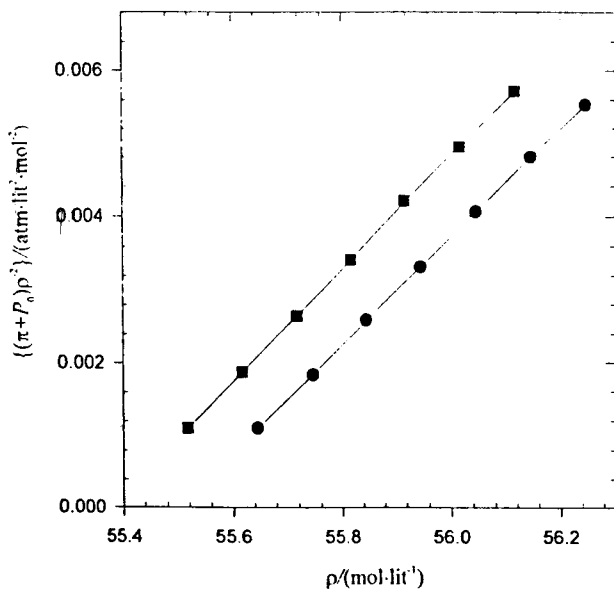


Figure 4. The same as Figure 3 for glucose solutions at (●) 273 and (■) 296K in the same concentration interval.

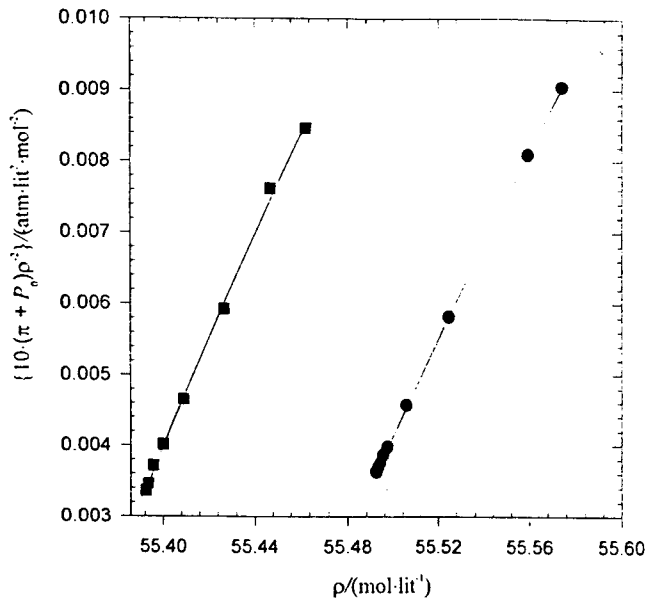


Figure 5. The same as Figure (3) for congo red solutions at (■) 290 K (in the concentration interval of 5-87 millimolal) and (●) 298 K (in the concentration interval of 1-71 millimolal).

before, the decrease in the solvent chemical potential by adding solute will be compensated by pressure increment [assumption (i)]. Therefore, the total chemical potential changes of the solvent must be zero.

$$d\mu_A = RTd\ln a_A(P_0) + \bar{V}_A dP = 0$$

or:

$$RTd\ln a_A(P_0) = -\bar{V}_A dP \quad (8)$$

where $a_A(P_0)$ denotes the activity of the solvent at pressure P_0 and \bar{V}_A is partial molar volume of A which is defined as:

$$\bar{V}_A = (\partial V / \partial n)_{P,T,m} \quad (9)$$

where V is the total volume of the system, whose variation is from V' in Figure (2.b) to $V = V^*$ in Figure (2.c). \bar{V}_A may be calculated by use of the DSEOS. First, we obtained dP at constant T from Equation (4):

$$dP = (2A_0\rho + 3A_1\rho^2 + 4A_2\rho^3)d\rho \quad (10)$$

Also, at constant m and T we have:

$$d\rho = d((n+m)/V) = (dn - \rho dV)/V \quad (11)$$

At constant P , from Equations (10) and (11) we have:

$$(2A_0\rho + 3A_1\rho^2 + 4A_2\rho^3)(dn - \rho dV)/V = 0 \quad (12)$$

The general solution to Equation (12) is,

$$dn = \rho dV \quad (13)$$

which may be written as:

$$1/\rho = \bar{V}_A = (\partial V / \partial n)_{P,T,m} \quad (14)$$

Therefore Equation (8) can be written as:

$$\rho RT d\ln a_A(P_0) = -dP \quad (15)$$

Taking $a \equiv a_A(P_0)$, the combination of Equations (10) and (15) gives:

$$\rho RT d\ln a = -(2A_0\rho + 3A_1\rho^2 + 4A_2\rho^3)d\rho \quad (16)$$

The integration of Equation (16) at constant temperature leads to,

$$\ln a = B_0 + B_1\rho + B_2\rho^2 + B_3\rho^3 \quad (17)$$

where:

$$B_{i+1} = -(i+2)A_i/RT(i+1), i = 0,1,2 \quad (18)$$

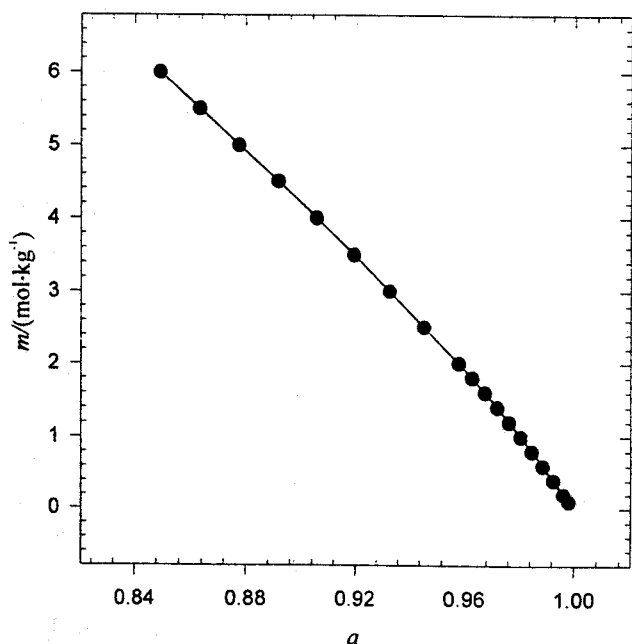


Figure 6. The calculated activity for water (solid curve) in aqueous sucrose solution, using Equation (17) and the experimental data (points) at 298 K.

where B_0 is an integration constant. To evaluate the final result, Equation (17), we may compare the calculated activities with those of the experiment. The calculation was made for the aqueous sucrose at 298 K in which its good agreement with the experimental data is shown in Figure 6.

Similar calculations are carried out for the electrolyte solution of NaCl, for which the calculated results are compared with the experimental data in Table 3. As

Table 3. The calculated activity of solvent at 298 K in aqueous solution of sodium chloride at different concentrations (a_{cal}) and its comparison with the experimental value (a_{exp}), and absolute percent error for the solvent activity (E%)

$\frac{m}{\text{mol.kg}^{-1}}$	a_{exp}	a_{cal}	E%
0.1	0.996649	0.996434	0.02
0.2	0.993366	0.993277	0.01
0.4	0.986835	0.986882	0.00
0.6	0.980261	0.980375	0.01
0.8	0.973605	0.973756	0.02
1.0	0.966883	0.967022	0.01
1.2	0.960089	0.960172	0.01
1.4	0.953186	0.953205	0.00
2.0	0.931650	0.931584	0.01
2.4	0.916689	0.916563	0.01
3.0	0.893247	0.893111	0.02
3.4	0.876977	0.876863	0.01
4.0	0.851569	0.851581	0.00
4.4	0.834049	0.834130	0.01
5.0	0.806954	0.807089	0.02
5.4	0.788414	0.788509	0.01
6.0	0.759990	0.759857	0.02

shown in this table, up to the concentration of six molal (which experimental data exists), the present error is less than 0.02%. The same calculations have been made for other electrolytes; specifically CaCl_2 , KCl , H_2SO_4 (using experimental data of reference 11), alkaline metal nitrates,[12] and aqueous glycine [13]. The results are summarized in Table 4.

Table 4. The coefficients of Equation 17 (B_0, B_1, B_2, B_3), and coefficient of determination (R^2), the concentration range (Δm), and the average absolute percent deviation of solvent activity (E%) for given solutions at 298 K

	$\frac{\Delta m}{\text{mol.kg}^{-1}}$	B_0	$\frac{B_1}{\text{lit.mol}^{-1}}$	$\frac{10^3 \times B_2}{\text{lit}^2.\text{mol}^{-2}}$	$\frac{10^3 \times B_3}{\text{lit}^3.\text{mol}^{-3}}$	R^2	*E%
NaCl	0.1-6	13.314	-0.760	14.982	-0.101	0.999998	0.01 (0.02)
KCl	0.1-4	12.458	-0.641	11.534	-0.073	0.999999	0.00 (0.01)
KNO_2	0.001-34	3.099	-0.084	0.578	-0.001	0.999973	0.08 (0.72)
RbNO_2	0.001-62	3.095	-0.088	0.710	-0.002	0.999728	0.45 (2.36)
CsNO_2	0.001-36	2.387	-0.050	0.075	0.001	0.999981	0.09 (0.47)
LiNO_2	0.001-20	-25.52	1.267	-20.178	0.102	0.999997	0.05 (0.18)
NaNO_2	0.001-12	-2.829	0.191	-3.548	0.018	0.999993	0.03 (0.07)
Sucrose.	0.1-6	-25.25	1.272	-20.91	0.112	0.999999	0.00 (0.01)
Glycine	0.1-3.3	-35.690	1.937	-34.741	0.206	0.999773	0.02 (0.07)

*Maximum absolute deviations from experimental values are given in parentheses.

7. Conclusion

In contrast to pure fluids, when the osmotic pressure varies in the closed system, the composition of the system will change and therefore the nature of the intermolecular forces will also be changed (due to the arrangement of hydrogen bonding between different species and hydration of dissolved particles). Therefore, we may expect that the temperature dependent coefficients A_i (of DSEOS) will be more complex than those for the pure systems. Due to the dependency of these coefficients on the system composition, we may not expect that such coefficients simply obey; $A_i = a_i + b_i T + c_i T^2 + d_i T \ln T$ (see reference 3), the irregularity of the tabulated values of A_i , given in Tables 2 and 3, verifies the complexity of these coefficients with temperature. We have assumed that these coefficients are composition independent and we have also assumed that the volume of solution in the closed system under osmotic pressure is equal to that of the pure solvent under atmospheric pressure. In other words, we assume that the osmotic pressure is the needed pressure to insert solute molecules among solvent molecules without any volume change. These two assumptions are valid independently only in dilute solutions. However, the results of Table 4 show that Equation (17) is also valid for concentrated solutions. Therefore it appears that these two assumptions compensate each other.

In this work, we proposed a closed system model with two fundamental assumptions [(i) and (ii)] in order to be able to use an appropriate EOS. The results in Table 1 to 3 and Figures 3 to 5 show that the DSEOS can be used to calculate the osmotic pressure accurately. It is interesting to note that the Van't Hoff equation $PV = mRT$ can predict only the osmotic pressure of dilute solutions, whereas, our approach is applicable for all concentrated solutions. The

results of our approach are compared with those given by the Van't Hoff equation in Table 5. As shown in this table, the Van't Hoff equation works for the solution in which its concentration is less than one molal, whereas our approach shows little deviation from the experimental data [14] even at high concentrations. The fact that our approach is capable of calculating the osmotic pressure accurately, allows us to use such a result to calculate the solvent activity which is a key function in solution thermodynamics. Tables 3 and 4 and Figure 6 show that the calculated activities are in good agreement with those of experiment. For example, for six molal aqueous solutions of sodium chloride, the maximum deviation is about 0.02 percent. The final and perhaps the most important conclusion in our approach is that in the calculation of the osmotic pressure and activity of electrolyte solutions there is no need for the effective particle number (i.e. Van't Hoff coefficient).

Acknowledgements

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Table 5. The experimental osmotic pressure at 298 K (P_{exp}), the calculated osmotic pressure from DSEOS and Van't Hoff equation at the same temperature (P_{cal}), and average absolute deviation from experimental values (ΔP) for aqueous sucrose solution at the given concentrations

m mol.kg ⁻¹	P_{exp} atm	P_{cal}^a atm	ΔP^a atm	P_{cal}^b atm	ΔP^b atm
0.1	2.25	2.07	0.18	2.24	0.01
0.3	6.91	6.86	0.05	6.71	0.20
0.6	14.22	14.36	0.14	13.43	0.79
1.0	24.76	25.00	0.24	22.38	2.38
2.0	54.90	54.88	0.02	44.76	10.14
3.0	90.00	89.71	0.29	67.15	22.85
4.0	129.70	129.85	0.15	89.53	40.17

^aFrom the DSEOS

^bFrom Van't Hoff equation

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