

Raoult's Law: A Reinterpretation for Concentrated Strong 1:1 Electrolyte Solutions

Kevin C de Berg

Department of Chemistry, Avondale College, PO Box 19, Cooranbong, NSW 2265 Email: kdeberg@avondale.edu.au

Abstract

Chemistry textbooks typically mention that Raoult's Law is strictly applicable only for ideal solutions which usually also means very dilute solutions. Non-ideal behaviour for electrolytes is normally accounted for using activity coefficient data. It has recently been shown that for strong 1:1 electrolytes departure from ideal behaviour is best interpreted through the Arrhenius model of partial dissociation and the Armstrong model of ionic hydration. The new model of strong electrolytes, first proposed by Raja Heyrovská, distinguishes between free and bound molecules of water at the surface and bulk of a solution and involves the calculation of fractional dissociation values (α) and hydration numbers (n_s , n_b) for solute species at the surface and bulk of a solution. Raoult's Law is shown to apply to concentrated strong 1:1 electrolytes if it is reinterpreted in terms of the Heyrovská model of an electrolyte solution. Examples are discussed here for the alkali chlorides with some important implications for the teaching of thermodynamics.

Introduction:

Raoult's Law was first proposed by the French chemist Francois Marie Raoult (1886) in papers published between 1886 and 1888. The law is commonly featured in physical chemistry and general chemistry textbooks in the section dealing with the properties of solutions. The law can be applied to mixtures of volatile solvents and to non-volatile solutes dissolved in volatile solvents. This paper focuses on solutions of the latter category and in particular to 1:1 salts dissolved in water. There are at least four different ways in which the law is typically presented as shown below for 1:1 salts dissolved in water.

- (i) p_w is proportional to x_{water} , where p_w represents the equilibrium water vapour pressure above the solution and x_{water} represents the mole fraction of water in the solution.
- (ii) $(p^\circ - p_w)$ is proportional to x_{salt} , where p° represents the equilibrium water vapour pressure above pure liquid water and x_{salt} represents the mole fraction of salt dissolved in the solution. $(p^\circ - p_w)$ represents the water vapour pressure lowering due to the dissolved salt in the solution.
- (iii) $(p^\circ - p_w)/p^\circ = 2x_{salt}$, where $(p^\circ - p_w)/p^\circ$ represents the relative water vapour pressure lowering. The factor, '2', is consistent with the Arrhenius idea (1887) of the electrolytic dissociation of a 1:1 salt into two ions (de Berg, 2003). Raoult (1891, p.297) agreed with this assessment when he noted that, "The exceptions in aqueous (salt) solutions (compared with non-electrolytes) are explained by the theory of electrolytic dissociation".
- (iv) $(p^\circ - p_w)/mp^\circ = \text{a constant}$, regardless of concentration and the 1:1 salt dissolved in water. Each solvent has a characteristic value for this constant and in the case of water the constant has a value around 3.4×10^{-2} for 1:1 salts. In the expression, $(p^\circ - p_w)/mp^\circ$, m is the molality and the expression thus refers to the relative molal water vapour pressure lowering.

What is limiting about Raoult's Law is that the four relationships outlined above only strictly apply to very dilute solutions. In the case of more concentrated solutions deviations from the so-called ideal behaviour represented in the previous four equations have been typically accounted for by the use of activity coefficients whose values are dependent on the concept of ionic strength through a range of equations developed initially by Debye, Huckel, and Onsager. In addition, electrolytes like NaCl in water are considered to be completely dissociated into its ions, a condition Arrhenius always believed was only achieved at infinite dilution. In the 1990's the Debye-Huckel-Onsager approach, including the large range of equations subsequently developed for determining activity coefficients, was severely criticised (Darvell & Leung, 1991; Franks, 1991; Wright, 1991) because the expressions containing correction coefficients were becoming so complicated that they lacked any physical significance as far as the molecular properties of a solution were concerned. For example, Hamer and Wu (1972, p.1050) give the following expression for the activity coefficient, γ :

$$\log \gamma = -|z_+ z_-| A \sqrt{I} / (1 + B^* \sqrt{I}) + \beta I + CI^2 + DI^3 + \dots$$

where z_+ and z_- are charge numbers on the cation and anion respectively, I is the ionic strength, A is a constant for a particular medium, and B^* , β , C and D are empirical correction factors. These authors comment that, "The constants C , D , etc as well as B^* and β are taken as empirical and are not considered to have physical significance....". Heyrovská (1991, 2006) responded to the criticisms referring to the lack of physical significance of the parameters in the various equations by suggesting that the properties of over one hundred strong electrolytes are better described by using the original Arrhenius concept of partial dissociation and the concept of ionic hydration. No theoretical or empirical correction coefficients were required under these conditions. A deeper physical

understanding of the molecular properties of the solution was thus possible. In this paper we wish to focus on Raoult's Law and how the Heyrovská model enhances the significance of this law and other thermodynamic properties for 1:1 concentrated alkali chloride solutions.

Principle of the Heyrovská Technique

The Heyrovská technique revolves around six equations which can be used to treat published osmotic coefficient data (Robinson & Stokes, 2002, p.476; Hamer & Wu, 1972, pp.1047-1099) in order to determine hydration numbers in the bulk (n_b) and surface (n_s) of the solution and the degree of dissociation (α) of the salt into its ions. The osmotic coefficient, φ , functions like the activity coefficient in that it is a correction factor accounting for non-ideal solution behaviour. The hydration numbers give one some idea as to how many water molecules are bound to the cation and anion in a way which prevents them from behaving freely as in pure water. The hydration numbers and the degree of dissociation of the salt enable one to then calculate the mole fraction of water molecules that are free at the surface, N_{Afs} , as opposed to the bulk of the solution and it is this property that, according to Heyrovská, will determine the vapour pressure of water above the surface. The six equations, shown in Box 1, and their derivations, where applicable, are discussed in some detail in Heyrovská (1997). See the Appendix for an

$$a_A = \exp(-2m\varphi/55.51) \quad (1)$$

$$N_{Afs} = n_{Afs}/(n_{Afs} + im) \quad (2)$$

$$-a_A \ln a_A/(1-a_A) = n_{Afs}/n_{Afb} = R_{Af} \quad (3)$$

$$n_{Afs} = (55.51 - mn_s) \quad (4)$$

$$n_{Afb} = (55.51 - mn_b) \quad (5)$$

$$i = 2\varphi n_{Afb}/55.51 \quad (6)$$

where a_A = activity of water

N_{Afs} = mole fraction of free water molecules at the surface

m = molality of the NaCl solution

φ = osmotic coefficient

n_{Afb} , n_{Afs} = molalities of free water in the bulk and at the surface respectively

55.51 = moles of water in 1 kg

n_b , n_s = hydration numbers in the bulk and at the surface respectively

$i = (1 + \alpha)$ where α is the degree of dissociation

= number of NaCl ion pairs, Na^+ and Cl^- ions, per molal of NaCl dissolved

Box 1. The six Heyrovská equations used to describe the properties of electrolytes.

example of how the six equations can be applied to NaCl data. Spreadsheet calculations for all the alkali metal chlorides can be obtained on request from the author. Data for the alkali chlorides from 0.001 molal

up to saturation or near saturation show conclusively that water vapour partial pressure (p_w) is directly proportional to the mole fraction of free water molecules at the surface (N_{Afs}). For the 1:1 alkali chlorides it is now possible to replace the four equations for Raoult's Law described in the introduction and applicable only for very dilute solutions with the following four equations applicable up to saturation or near saturation.

- (i) p_w is proportional to N_{Afs} , the mole fraction of free water molecules at the surface of the solution.
- (ii) $(p^\circ - p_w)$ is proportional to N_{salt} , the mole fraction of salt particles at the surface of the solution.
- (iii) $(p^\circ - p_w)/p^\circ = N_{salt}$
- (iv) $(p^\circ - p_w)/mp^\circ = 0.03356$

This is truly a remarkable advance for Raoult's Law made possible by focusing on the properties of the solution's surface, the hydration of the ions, and the partial dissociation of the salt in solution.

Significance for Chemistry Educators

The quantities calculated by the Heyrovská approach and used to reinterpret Raoult's Law for concentrated 1:1 salt solutions have a great applicability in enhancing one's understanding of the thermodynamics of such solutions. Calculated data for the alkali chlorides are shown in Table 1. Equilibrium water vapour partial pressures (p_w) were obtained from Hamer and Wu (1972, pp.1047-1099); the hydration numbers at the surface of the solution (n_s), the molality of free water molecules at the surface (n_{Afs}), and the degrees of dissociation (α) were calculated using the Heyrovská equations (1997) and data from Hamer and Wu (1972). The ΔH° and S° values for the processes shown were calculated using the data from Aylward and Findlay (2008).

Table 1. Thermodynamic trends for the series of alkali chlorides, LiCl to CsCl at 25°C. p° (equilibrium vapour pressure for pure water) is 23.753 mm Hg.

p_w = equilibrium water vapour partial pressure; n_s = hydration number at the solution surface; n_{Afs} = molality of free water molecules at the solution surface; α = degree of dissociation of the salt in an aqueous solution of the salt; ΔH° = standard enthalpy of hydration of the alkali cation; S° = standard entropy of the alkali metal cation in aqueous solution.

	LiCl	NaCl	KCl	RbCl	CsCl
p_w (1.0 molal) in mm Hg	22.8959	22.9653	22.9968	23.0067	23.0275
n_s	6.12	3.35	1.99	1.75	1.71
n_{Afs} (1.0 molal)	49.39	52.16	53.52	53.76	53.8
α (1.0 molal)	0.8489	0.7890	0.7598	0.7437	0.6947
ΔH° [$\text{M}^+(\text{g}) \rightarrow \text{M}^+(\text{aq})$] in kJ mol^{-1}	-519	-406	-322	-301	-276
S° [$\text{M}^+(\text{aq})$] in $\text{J K}^{-1}\text{mol}^{-1}$	12	58	101	122	132

The data in Table 1 are very informative as far as the molecular properties of solutions are concerned. The surface hydration number (n_s) is a measure of the average number of water molecules attracted and bound to an alkali metal ion and a chloride ion at the surface of

the solution. A naked lithium ion, Li^+ , is smaller than a corresponding caesium ion, Cs^+ , and therefore the electric field around Li^+ is stronger than around Cs^+ . It is no surprise therefore that the surface hydration number (n_s) increases from CsCl to LiCl (1.71 to 6.12). This means, as one might now expect, that the molality of free water molecules at the surface (n_{Afs}) decreases from CsCl to LiCl (53.8 to 49.39) with the natural result that the partial pressure of water vapour (mm Hg) also decreases from CsCl to LiCl (23.03 to 22.90). The stronger interaction between a smaller cation and surrounding water molecules compared to a larger cation also leads to an increasing negative enthalpy (kJ mol^{-1}) of solution $[\text{M}^+(\text{g}) \rightarrow \text{M}^+(\text{aq})]$ from CsCl to LiCl (-276 to -519). The entropy ($\text{J K}^{-1} \text{mol}^{-1}$) of the aqueous cation decreases from CsCl to LiCl (132 to 12) due to the stronger hydration. Another way of looking at the entropy changes is that as the number of free water molecules increases from LiCl to CsCl so does the entropy (12 to 132 $\text{J K}^{-1} \text{mol}^{-1}$). Such deductions as these were not possible with the traditional form of Raoult's Law.

Traditionally all the alkali chlorides would have been regarded as 100% dissociated into their ions. In the technique reported here the salts are only partially dissociated as shown by the α values in Table 1. One way of interpreting the trend in the α values is that ion-pairing is more likely to occur with a less hydrated metal ion leading to a smaller α value which is the case with CsCl (0.6947) compared to LiCl (0.8489) in Table 1. Ohtaki and Fukushima (1992) detected ion-pairs in concentrated NaCl and KCl solutions using X-Ray diffraction so the notion of ion-pairing (or conversely, partial dissociation) in alkali chlorides has some experimental support in addition to its theoretical value.

It is interesting that in the Heyrovská approach to Raoult's Law, the insights of two bitter enemies of 19th century/20th century chemistry have been united. The two insights are those of Svante Arrhenius' partial dissociation model of electrolytes and Henry Armstrong's emphasis on the role of the solvent in the properties of solutions and in particular his suggesting (1978) that water vapour pressure was related to the number of free 'hydrone' (H_2O) molecules present. The scientific controversy between Arrhenius (salts dissociate in water) and Armstrong (salts associate with water) has been elaborated elsewhere (de Berg, 2003; Brock, 1992) and it has been shown (de Berg, 2006) how the two ideas, dissociation and association, can be used to introduce students to the importance of argument and counter argument in scientific epistemology. What is an amazing feature in the study

elaborated in this article is how two seemingly antagonistic ideas came to serve one another in providing a new insight into Raoult's Law and ultimately the properties of electrolytes.

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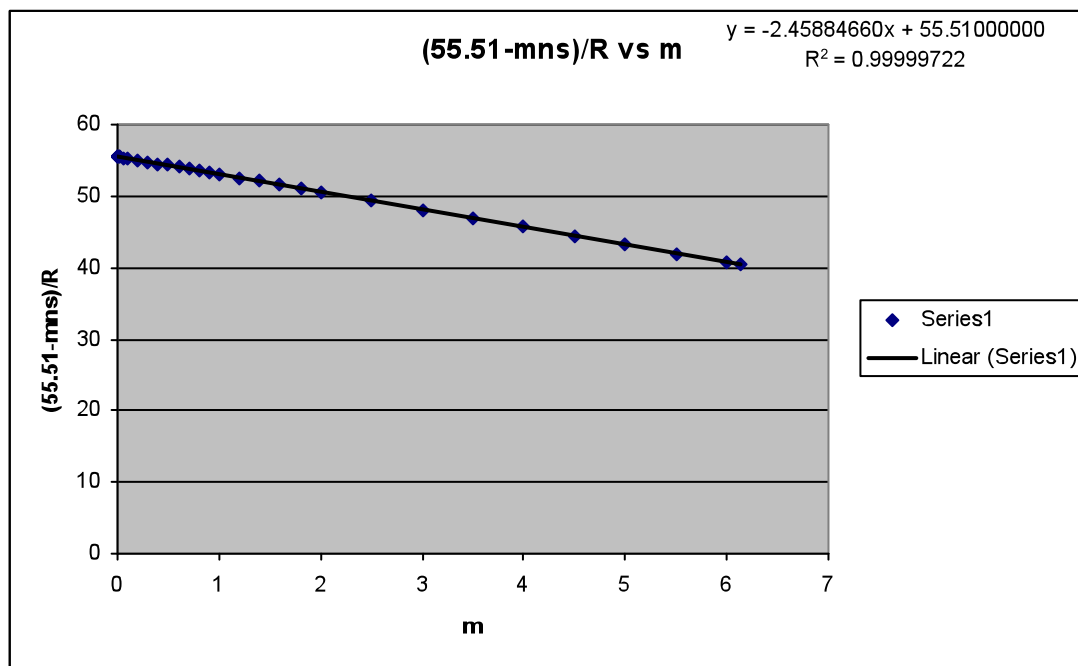
APPENDIX-NaCl EXAMPLE

Molality (m) and Osmotic Coefficient Data (ϕ) for NaCl are given on page 1067 of Hamer and Wu (1972). The following steps are now followed.

Step 1: Calculation of the activity of water (a_A) using equation (1) in Box 1.

Step 2: Calculation of R_{Af} from a_A using equation (3) in Box 1.

Step 3: It follows from equations (3), (4), and (5) in Box 1 that $(55.51-mn_s)/R_{Af}$ should equal $(55.51-mn_b)$, the equation of a straight line. So $(55.51-mn_s)/R_{Af}$ is plotted against m , and the value of n_s changed until a straight line with the highest correlation coefficient is obtained. The plot below shows the result for NaCl for which the hydration numbers, $n_s = 3.35$ and $n_b = 2.46$, apply.



Step 4: Having obtained n_s and n_b from Step 3, n_{Afs} , n_{Afb} , i (and α from $i = 1 + \alpha$), and N_{Afs} can now be calculated from equations (4), (5), (6), and (2), from Box 1.

Step 5: Water vapour partial pressures can be obtained by multiplying the equilibrium vapour pressure for pure water at 25°C (23.753 mm Hg) by a_A , the activity of water.

The following table shows five entries for the important variables in Box 1 for NaCl.

m	ϕ	a_A	R_{Af}	n_{Afs}	n_{Afb}	i	α	N_{Afs}	$p/\text{mm Hg}$
0.01	0.968	0.999651	0.999826	55.4765	55.4854	1.9351	0.9351	0.99965	23.745
0.05	0.944	0.998301	0.99915	55.3425	55.387	1.8838	0.8838	0.99830	23.713
0.1	0.933	0.996644	0.99832	55.175	55.264	1.8577	0.8577	0.99664	23.673
0.5	0.921	0.983545	0.991727	53.835	54.28	1.8012	0.8012	0.98355	23.362
1.0	0.936	0.966839	0.983233	52.16	53.05	1.7890	0.7890	0.9668	22.965