Communication

Dissociation Must Be Taken into Account in Raoult's Law

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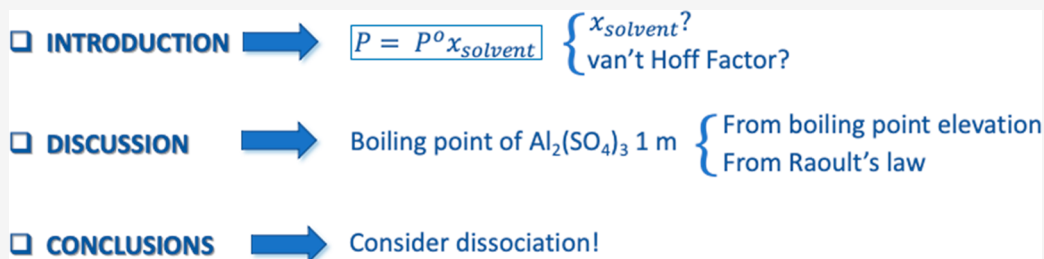
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ABSTRACT: This communication shows that although some textbooks do not discuss how to apply Raoult's law to electrolyte solutions, we should not ignore dissociation, and the van't Hoff factor must be considered.

KEYWORDS: *Introductory Chemistry, Misconceptions, Solution, Raoult's Law, Electrolytes*

INTRODUCTION

Raoult's law states that at a temperature T, the solvent vapor pressure, P, of an ideal solution is the product of the mole fraction of solvent, $x_{solvent}$, and the vapor pressure of pure solvent at the same temperature, $P°$:

$$P = x_{solvent}P° \qquad (1)$$

There are many scientific papers focusing on how Raoult's law should be explained or applied to aqueous salt solutions.[1−7] Some authors have stated that it should not be included in the introductory chemistry curriculum.[8,9] This has been the subject of controversy,[1,4,6,8−10] and papers have been published focusing on the application of thermodynamic principles[10−12] or on how to calculate the mole fraction of the solvent.[1,5−7,13] In this context, there is no doubt that the effect of solute dissociation, which can be accounted for by the van't Hoff factor, i, defined as the ratio of moles of particles formed by the solute in solution to moles of dissolved solute, must be considered. Even the need to take into account the concept of "free water", i.e., the total amount of water (in moles) minus any amount bound to solutes, and the actual number of particles formed per mole of solute to evaluate the solvent concentration has been pointed out.[1−3,5−7,13] However, the fact that most general chemistry textbooks explicitly include the effect of dissociation in the calculation of the other colligative properties but not for vapor pressure depression may lead to a misunderstanding at the introductory levels of chemistry, with the consequence that the same expression for vapor pressure is used for aqueous salt solutions as for ideal solutions, without considering dissociation.

In this regard, although there are general chemistry textbooks that explicitly state that dissociation must be considered,[14−18] some of them[19−22] include the van't Hoff factor in equations for other colligative properties but do not mention how to perform the vapor pressure calculation for solutions of electrolytes. In other cases,[23−25] although the explicit equation for the vapor pressure lowering in electrolyte solutions is not given or suggested, the reader can infer that dissociation is required for this calculation. On the other hand, in some books, the discussion of vapor pressure depression when considering colligative properties is excluded[26−28] or only briefly mentioned.[29,30] It is possible that these different approaches contribute to the misinterpretation mentioned above. Some literature on student or teacher misconceptions about colligative properties also does not consider the case of vapor pressure of electrolyte solutions.[31,32] Therefore, the aim here is to highlight that the lack of explicit expressions for calculating the vapor pressure of electrolyte solutions may lead to misunderstanding by some readers and to suggest a very simple exercise to demonstrate the need to consider dissociation.

DISCUSSION

When Raoult's law is applied to aqueous salt solutions, it is clear that the actual mole fraction of water available for evaporation must be taken into account. However, calculating

the relative amount of free water per mole of solute added and the actual number of entities formed in solution per mole of solute, which may differ from the stoichiometric values if the salt is not completely dissociated or if there is association between particles from the solute, is beyond the scope of the introductory chemistry courses. Nevertheless, at such levels, the van't Hoff factor must be considered when Raoult's law is applied to electrolyte solutions. A simple exercise can be performed to demonstrate this easily: consider an aqueous solution of a salt such as aluminum sulfate, $Al_2(SO_4)_3$, at a concentration of 1 molal (342.1 g of solute/kg of solvent). To solve the exercise, the contribution of water molecules bound to the solute is assumed to be negligible, complete dissociation of the solute is assumed, and the possibility of ion association is ignored. Although these approximations may result in some deviation from the actual boiling point temperature, and $Al_2(SO_4)_3$ aqueous solutions can be highly nonideal, they allow comparisons to be made and are certainly preferable to ignoring dissociation.

The vapor pressure of pure water, $P°$, as a function of the temperature, T, can be calculated using the Antoine equation, taken from the ChemCAD 8.0.2 database:[33]

$$\ln P° \text{ (mmHg)} = 18.304 - 3816.4/[T \text{ (K)} - 46.13] \quad (2)$$

According to eq 2, the calculated vapor pressure of pure water at 25 °C is 23.59 mmHg. The complete dissociation of $Al_2(SO_4)_3$ gives 5 moles of ions per mole of dissolved salt. Then the van't Hoff's factor, with the assumed simplifications, is $i = 5$. The solvent mole fraction, ignoring dissociation, for a 1 molal solution, which contains 1 mol of solute per 1 kg of water, i.e., per 55.5 mol of water, is

$$x_w = \frac{55.5 \text{ mol of water}}{55.5 \text{ mol of water} + 1 \text{ mol of solute}} = 0.9823 \quad (3)$$

In contrast, the solvent mole fraction considering $i = 5$ is

$$x_w = \frac{55.5 \text{ mol of water}}{55.5 \text{ mol of water} + \frac{5 \text{ mol of particles}}{1 \text{ mol of solute}} \cdot 1 \text{ mol of solute}}$$
$$= 0.9173 \quad (4)$$

The corresponding solvent vapor pressures calculated by applying eq 1 are 23.17 mmHg without considering the van't Hoff factor and 21.64 mmHg considering $i = 5$. If there is any doubt as to which result is closest to the actual (i.e., experimentally measured) value, the boiling point of this solution can be calculated by using two different approaches: (1) by using the colligative property of the boiling point elevation for an electrolyte solution and (2) by finding the temperature at which the vapor pressure of the solution, calculated using Raoult's law, is equal to atmospheric pressure. The comparison of the results obtained by the two procedures will help us to choose between the two values 23.17 and 21.64 mmHg.

(1) By applying the colligative property of boiling point elevation, $\Delta T = iK_e m$, where K_e is the ebullioscopic constant for the solvent (0.52 °C kg/mol in the case of water) and m is the molality ($m = 1$ mol/kg), we find that

$$\Delta T = \left(\frac{5 \text{ mol of particles}}{1 \text{ mol of solute}}\right) \cdot \left(\frac{0.52 \text{ °C kg of solvent}}{\text{mol of particles}}\right) \cdot$$
$$\left(\frac{1 \text{ mol of solute}}{1 \text{ kg of solvent}}\right) = 2.6 \text{ °C} \quad (5)$$

Since the boiling temperature of water at atmospheric pressure is 100 °C, the boiling temperature of this solution would be 100 + 2.6 = 102.6 °C, which is taken as the correct value. The actual boiling temperature of this solution may differ from this value if there is significant bound water and/or ion pair formation and should be determined experimentally. Nevertheless, the calculated value is taken as correct for comparison purposes only.

(2) The normal boiling temperature of an aqueous salt solution can be obtained by finding the temperature at which the solvent vapor pressure, P, calculated using Raoult's law (eq 1), is equal to the atmospheric pressure of 760 mmHg:

$$760 = x_w e^{18.304 - \frac{3816.4}{T \text{ (K)} - 46.13}} \quad (6)$$

In eq 6, the vapor pressure of pure water is calculated with the Antoine equation (eq 2). The results obtained are $T = 100.5$ °C when x_w is calculated with $i = 1$ (eq 3) and 102.4 °C when x_w is calculated with $i = 5$ (eq 4). Therefore, upon comparison of these results with those obtained from the boiling point elevation, it is clear that the solvent vapor pressure calculation requires the application of Raoult's law taking into account dissociation.

■ CONCLUSIONS

Although not all introductory chemistry textbooks include an explicit description of how to calculate the vapor pressure of electrolyte solutions, dissociation must be considered if Raoult's law is to be applied in early-level chemistry courses.

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Notes

The authors declare no competing financial interest.

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