A Simple Apparatus for the Measurement of Colligative Properties in Aqueous Electrolyte Systems: An Educational Approach

S. P. Pinho[1,2], **E. A. Macedo**[1,*]

[1] *LSRE – Laboratory of Separation & Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, e-mail: eamacedo@fe.up.pt*

[2] *Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, Campus de Santa Apolónia, Apartado 1134, 5301-867 Bragança, Portugal, e-mail: spinho@ipb.pt*

ABSTRACT

The importance of systems with electrolytes is well known nowadays, and many examples can be given about their industrial applications. However, at undergraduate level the properties of electrolyte solutions are neither theoretically nor experimentally focused in accordance to the role they play in chemical industry.

In this work a simple equipment for the measurement of freezing point depression due to the presence of strong electrolytes in water is introduced. A study with the salts NaCl and KCl in the molality range up to 4 molal is suggested. In this way, the students may gain some insight on the physical-chemistry of aqueous electrolyte solutions.

The experimental data are compared with the values obtained from available models to calculate the activity coefficients of the salts and water activities, mainly those concerned with the Debye-Hückel equation and its empirical extensions. It is also suggested to use those equations and the data to model the freezing point depression at high electrolyte concentrations.

INTRODUCTION

Electrolyte solutions can be found in many natural and industrial processes. Some examples are the absorption of acid gases such as carbon dioxide, for their removal from effluent gas streams, avoiding atmospheric pollution [1], the fractional crystallization processes, in which several salts are separated as pure phases from a multicomponent mixture, for the production of fertilizers like ammonium phosphate, ammonium nitrate or potassium sulphate [2], the extractive distillation using salt as extractive agent [3], and precipitation of globular proteins from an aqueous solution by addition of salts [4].

Therefore, it is not surprising that during the last few decades much attention has been devoted to experimental and theoretical studies in this area. However, at undergraduate level the thermodynamics of electrolyte solutions is usually ignored, not giving to the students enough insight for the big differences when compared to the non-electrolyte thermodynamics. Nevertheless, several authors have recognized this gap and the most recent editions of the books by Prausnitz et al. [5] and Tester and Modell [6] include a chapter totally dedicated to the thermodynamics of electrolyte solutions.

---

[*] author to whom correspondence should be addressed

In this work a simple experiment for the freezing point depression measurement in aqueous electrolyte solutions is suggested. The data is analysed using simple activity coefficients models for the electrolyte systems and comparisons are made with the same colligative property for non-electrolyte systems. In this way, the students are able to better understand the physical-chemistry of electrolyte solutions.

THEORETICAL BACKGROUND

Colligative properties, like the freezing point depression, depend on the concentration of the solute but not on its nature. In this section, using concepts of classical thermodynamics that are usually taught to the undergraduate students, the basic equations for the calculation of the freezing point depression are presented, focusing on the differences between non-electrolyte and electrolyte solutions.

Consider a solution of a solvent *1*, in which a solute *A* is dissolved. If the temperature of the solution is lowered, a temperature T_f is reached at which the pure solvent begins to separate out as a solid. This temperature is lower than the melting point of the pure solvent, T_m. The interest is to estimate the freezing point depression of the solvent, $\Delta T = T_m - T_f$, due to the addition of the solute.

If it is assumed that only pure solid *1* freezes out of the solution when it is cooled to the freezing point, the equilibrium condition when the first crystal of pure solvent forms is:

$$f_1^s(T_f,P) = x_1\gamma_1(T_f,P,\underline{x})f_1^l(T_f,P) \qquad (1)$$

where x_1 is the original liquid solution mole fraction of component *1*, γ_1 is its activity coefficient, *P* is the pressure, and f_1 is the fugacity of species *1* in pure solid (*s*) or liquid (*l*) states. In equation (1) it is considered that the composition of the liquid phase is not significantly changed by the appearance of a very small amount of the solid phase.

In order to obtain an expression for $f_1^s(T_f,P)/f_1^l(T_f,P)$, a thermodynamic cycle is idealized between the pure solid and liquid salt phase states which, after some assumptions, leads to the following expression [7]:

$$\ln\gamma_1 x_1 = \frac{\Delta H_f(T_m)}{R}\left(\frac{1}{T_m}-\frac{1}{T_f}\right)+\frac{\Delta C_P}{R}\left(\frac{T_m}{T_f}-1+\ln\frac{T_f}{T_m}\right) \qquad (2)$$

In equation (2), ΔH_f is the enthalpy of fusion at T_m, $\Delta C_P = C_P^l - C_P^s$ is the change of heat capacity upon fusion, and *R* is the ideal gas constant.

Frequently, T_f and T_m are sufficiently close to simplify equation (2) to:

$$\ln\gamma_1 x_1 = \frac{\Delta H_f(T_m)}{R}\left(\frac{1}{T_m}-\frac{1}{T_f}\right)=\frac{\Delta H_f(T_m)}{RT_m^2}\left(T_f - T_m\right) \qquad (3)$$

At infinite dilution, for which $\gamma_1 \cong 1$, and $\ln x_1 = \ln(1-x_A) \cong -x_A$, the simplest equation for the freezing point depression can be obtained and may be written as:

$$\Delta T = T_m - T_f = \frac{RT_m^2}{\Delta H_f(T_m)}x_A \qquad (4)$$

As can be seen, equation (4) indicates that ΔT depends on the concentration of the solute, but not on its nature. However, inversely to what happens in non-electrolyte solutions, even in very dilute solutions, the long-range nature of the electrostatic forces between the ions is responsible for the strong deviation from the ideal behaviour. Thus, while equation (4) has been widely applied for non-electrolyte solutions, for the electrolyte ones it cannot give reliable results since an electrolyte solution only becomes ideal at concentrations too low to produce a measurable ΔT.

The different performance, using equation (4), in the calculation of ΔT for non-electrolyte and electrolyte solutions can be readily compared. Figure 1 plots the relative percent deviations obtained for the representation of freezing point depression of aqueous solutions of fructose, ethanol and NaCl. Despite that the maximum mole fraction is around 0.01, for the NaCl solution the deviations are much more pronounced than for the other systems, showing errors higher than 4% at very low concentrations. It should be mentioned that for those calculations $\Delta H_f(T_m) = 6009.5$ J·mol^{-1} and $T_m = 273.15$ K were used [8].

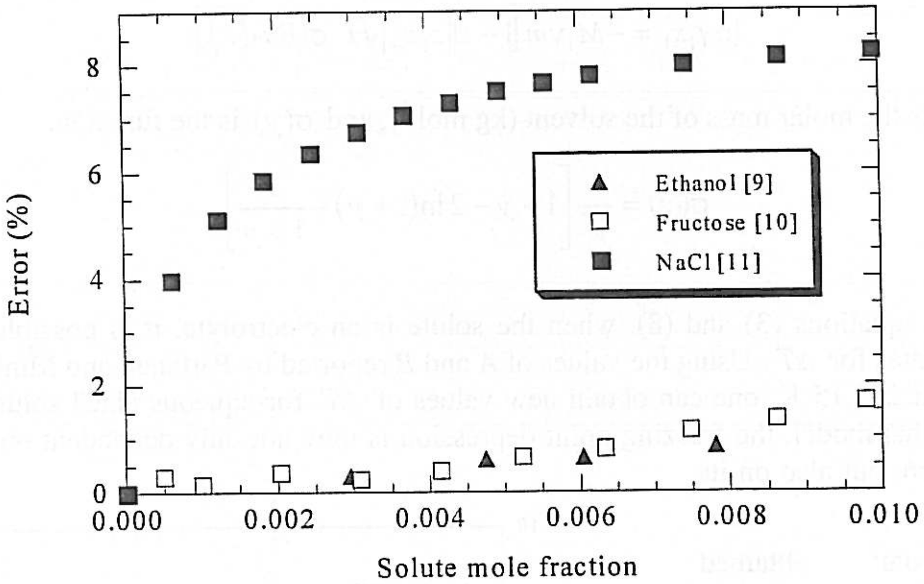

Figure 1. Comparison of the relative percentage deviations in the calculation of the ideal freezing point depression for aqueous non-electrolyte and electrolyte solutions.

Figure 1 is a very interesting way of showing to the students the different behaviour of electrolyte and non-electrolyte solutions at high dilution. Another important feature that arises in the electrolyte thermodynamics concerns the concentration scales used. In fact, it is common to use the molality scale instead of the mole fraction one. Moreover, in order to properly account the dissociation of the electrolyte, the mole fraction of solute A, used in equation (4), should be calculated as:

$$x_A = \frac{\nu n_A}{\nu n_A + n_1} \tag{5}$$

where n_A and n_1 are, respectively, the solute and solvent mole numbers, and ν is the sum of the stoichiometric coefficients of the anion and the cation.

So far, the students have learned that, for electrolyte solutions, to obtain trustworthy values of ΔT, the solvent activity coefficient should be retained in equation (3). Taking only into account the electrostatic forces and using well-established concepts from classical electrostatics, Peter Debye and Erich Hückel [12] derived the following expression for the mean ionic molal activity coefficient of an electrolyte ($\gamma^*_\pm$):

$$\ln \gamma^*_\pm = -\frac{A|z_+z_-|\sqrt{I}}{1+Ba\sqrt{I}} \qquad (6)$$

In equation (6) A and B are parameters related to the properties of the solvent, and a is the so-called distance of closest approach between ions (usually taken as 4 Å), z_+ and z_- are the charges of the cation and the anion, respectively, and finally I is the ionic strength defined by:

$$I = 0.5\sum_{i=1}^{N_{ions}} m_i z_i^2 \qquad (7)$$

From equation (6), and taking into consideration the Gibbs-Duhem equation, the activity of the solvent can be calculates as:

$$\ln \gamma_1 x_1 = -M_1 \nu m \left[1 - A|z_+z_-|\sqrt{I}\ \sigma\left(Ba\sqrt{I}\right)\right] \qquad (8)$$

where M_1 is the molar mass of the solvent (kg·mol^{-1}), and $\sigma(y)$ is the function:

$$\sigma(y) = \frac{1}{y^3}\left[1 + y - 2\ln(1+y) - \frac{1}{1+y}\right] \qquad (9)$$

Combining equations (3) and (8), when the solute is an electrolyte, it is possible to obtain better estimates for ΔT. Using the values of A and B reported by Partanen and Minkkinen [8], calculated at 273.15 K, one can obtain new values of ΔT for aqueous NaCl solutions. Note that, using this model, the freezing point depression is now not only dependent on the solute concentration, but also on its charges.

The errors obtained assuming ideal behaviour and using the Debye-Hückel equation are compared in figure 2. Using this new methodology the calculated values of ΔT only present deviations higher than 4% for x_1 around 0.05. This brief discussion alerts the students to understand the changes that must be taken into account when studying, in general, the description of electrolyte systems.

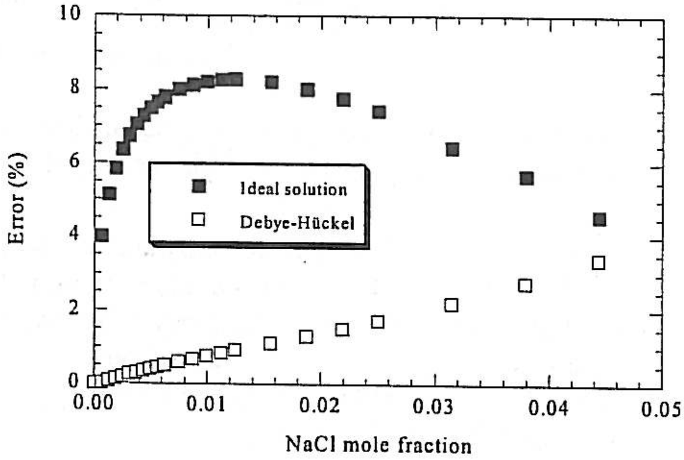

Figure 2. Comparison of the relative percentage deviations in the calculation of the freezing point depression: ideal behaviour and the Debye-Hückel equation. NaCl/water system [11].

EXPERIMENTAL

In this section the experiments are described. It is a simple adaptation of the experimental work proposed by Shoemaker et al. [13], but with the purpose of illustrating the importance of a Debye-Hückel type limiting law for the description of electrolyte solutions.

The solutions to be studied are aqueous solutions of NaCl at the concentrations 0.25 and 1 molal. Approximately 150 cm^3 of each solution are prepared by weighing the proper amounts of NaCl and distilled water. The solutions are placed in a glass flask packed in crushed ice. The NaCl should be dried in an oven before use.

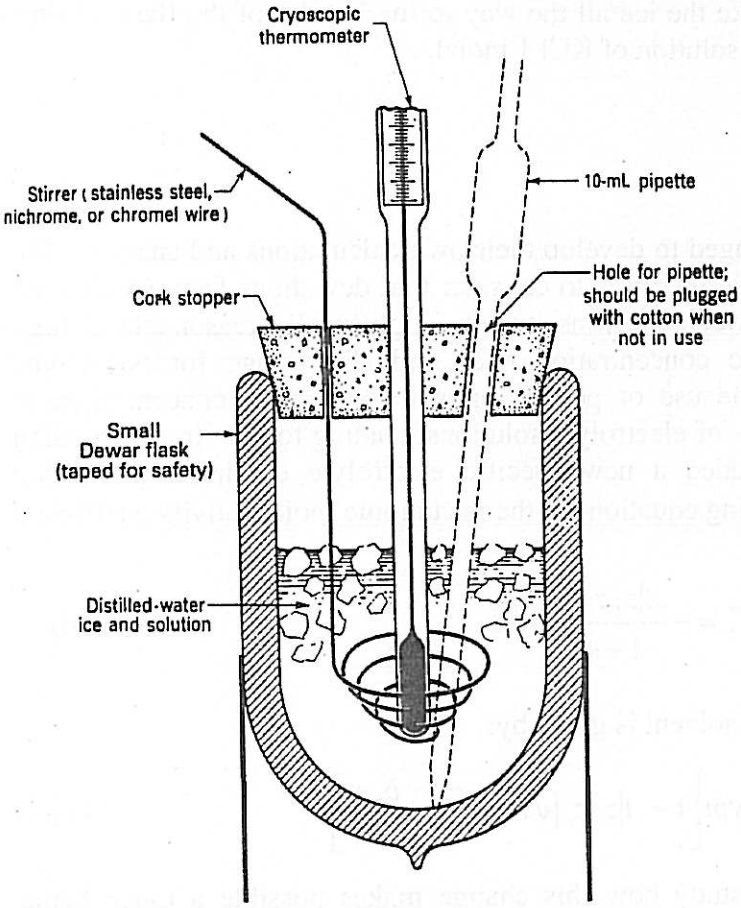

Figure 3. Apparatus for measuring the freezing point of aqueous solutions.

The apparatus to be used in this experiment is shown in figure 3. It is constituted by a Dewar flask with a cork stopper with holes for the stirrer, the cryoscopic or resistance thermometer, and for the sampling process with a pipette. The flask should be taped for safety and to isolate it thermically.

The main objective of the experimental work is not to measure the freezing point of the aqueous electrolyte solutions, but instead the difference to the freezing point of pure water. Thus, the melting point of pure water is measured first. The procedure follows the sequence: about 300 cm^3 of crushed, distilled--water ice is washed with several amounts of chilled distilled water. The Dewar flask is filled (about one-third) with this washed ice and about 100 cm^3 of chilled distilled water is added to the Dewar. Then, the apparatus is assembled, as shown in figure 3, and the mixture stirred well to achieve equilibrium. It must not be assumed that equilibrium has been obtained until the temperature shown in the thermometer has become quite stationary, and does not change when the stirring is stopped or when its strength is changed. If that is the case the temperature of melting T_m is recorded.

A second run is now carried out after using 100 cm^3 of chilled 0.25 m NaCl solution instead of pure water. After stirring to achieve the equilibrium, as described before, the temperature is recorded and two samples are withdrawn (around 10 cm^3 each) from the solution to measure the concentration in the final solution by gravimetry [14]. The pipette must be quickly introduced, while blowing a gentle stream of air through it until it touches the bottom.

In this way, the risk of dragging small particles of ice from the solutions is prevented. After, the solution is stirred again vigorously for about 5 minutes, and then another temperature is registered and two samples are taken, to obtain the concentration. It should be mentioned that the temperatures and concentrations of the two samples may differ slightly, owing to some melting of the ice. However, the differences should be consistent. If they are not consistent, at least one of the aliquots was not withdrawn at equilibrium.

Then the experiment is repeated with the NaCl solution 1 molal, already prepared.

Finally, it should be stressed out that the most difficult part of the experimental technique is the achievement of thorough mixing. The stirring must therefore be vigorous and prolonged. A good technique is to work the stirrer frequently above the mass of the ice and with a vigorous downward movement to take the ice all the way to the bottom of the flask. If time permits, a run should be made with a solution of KCl 1 molal.

DISCUSSION

At this point, the students are challenged to develop their own calculations and analysis. The main assumption of the Debye-Hückel theory is to consider that deviations from ideality are only due to electrostatic forces between the ions, which is physically reasonable at high dilution, but unreal when the ionic concentration rises and short-range forces become dominant. Guggenheim suggested the use of power series in electrolyte concentration to better describe the physical chemistry of electrolyte solutions, leading to the virial expansion models. To do so, Guggenheim added a new specific electrolyte empirical interaction parameter ($b_\pm$), proposing the following equation for the mean ionic molal activity coefficient [15]:

$$\ln \gamma_\pm^* = -\frac{A|z_+z_-|\sqrt{I}}{1+\sqrt{I}} + b_\pm I \tag{10}$$

From equation (10) the activity of the solvent is given by:

$$\ln \gamma_1 x_1 = -M_1 \nu m \left[1 - A|z_+z_-|\sqrt{I}\,\sigma\left(\sqrt{I}\right) + \frac{b_\pm m}{2} \right] \tag{11}$$

It is interesting for the students to study how this change makes possible a much better quantitative description of the freezing point depression at high concentrations. Thus, using the experimental value of the freezing temperature determined at 1 molal, it is possible to obtain a value for the empirical parameter $b_\pm$. For instance, the experimental value for an aqueous NaCl solution is $T_f = 269.8$ K: from this $b_\pm = 0.0807$ kg·mol^{-1} can be calculated. Now, combining equations (3) and (11) makes possible to study the usefulness of the equation proposed by Guggenheim for the calculation of the freezing point depression.

Figure 4 presents a comparison between the Debye-Hückel and Guggenheim equations for the estimation of ΔT in aqueous NaCl solutions to concentrations up to 4 molal. It can be easily observed that the use of the Guggenheim equation, with a new empirical parameter regressed from a unique experimental freezing point measurement, introduces a big improvement in the representation of ΔT. Applying this equation, the relative percentage deviations only attains 4% for $x_1 > 0.12$.

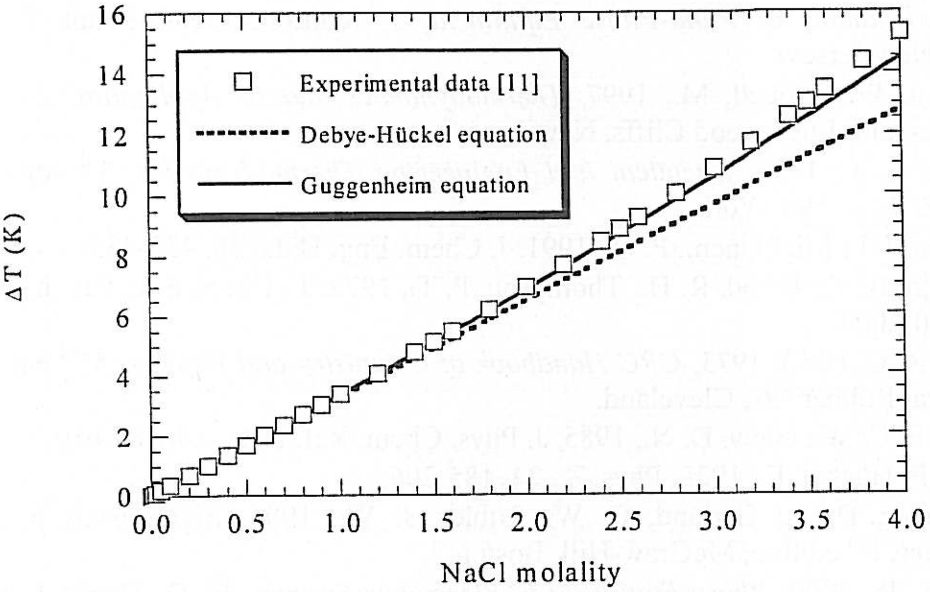

Figure 4. Comparison of the Debye-Hückel and Guggenheim equations for the calculation of the freezing point depression of NaCl aqueous solutions.

Since colligative properties depend upon the number of particles in solution, the freezing point data should be analysed in terms of the physical chemistry of the electrolyte solutions. That is, it might give indications about the degree of dissociation, solvation, and ion-pairing. Finally, the students are also suggested to observe other hypothesis made that can be improved in the development proposed.

CONCLUSIONS

In this work relevance is given to the differences to be taken into account when studying aqueous electrolyte systems. Specifically, it is shown the need, even at very high dilutions, of a Debye-Hückel type limiting law to properly represent the freezing point depression. A simple experimental work is proposed for the measurement of this colligative property. In this way, the students can compare the experimental data with values assuming the ideal behaviour and using the Debye-Hückel equation. Finally, the students are also challenged to understand the need of more elaborated expressions for the representation of that property at high concentrations. Therefore, it is possible to show that the extension of a thermodynamic framework for non-electrolytes to electrolytes it is not a straightforward task.

REFERENCES

[1] Maurer, G., 1983, Fluid Phase Equilibria, **13**, 269-296.

[2] Thomsen, K., 1997, *Aqueous Electrolytes: Model Parameters and Process Simulation*, Ph.D. Thesis, Department of Chemical Engineering, Technical University of Denmark, Lyngby.

[3] Furter, W. F., 1992, Chem. Eng. Comm., **116**, 35-40.

[4] Prausnitz, J. M., 1995, Fluid Phase Equilibria, **104**, 1-20.

[5] Prausnitz, J. M.; Lichenthaler, R. N.; de Azevedo, E. G., 1998, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd edition, Prentice-Hall, Englewood Cliffs, New Jersey.

[6] Tester, J. W.; Modell, M., 1997, *Thermodynamics and Its Applications*, 3rd edition, Prentice-Hall, Englewood Cliffs, New Jersey.

[7] Sandler, S. I., 1999, *Chemical and Engineering Thermodynamics*, 3rd edition, John Wiley & Sons, New York.

[8] Partanen, J. I.; Minkkinen., P. O., 1991, J. Chem. Eng. Data, **36**, 432-435.

[9] Okamoto, B. Y.; Wood, R. H.; Thompson, P. T., 1978, J . Chem. Soc. Faraday Trans. 1, **74**, 1990-2007.

[10] Weast, R. C. (Ed.), 1973, *CRC Handbook of Chemistry and Physics*, 53rd edition, The Chemical Rubber Co., Cleveland.

[11] Clarke, E. C. W.; Glew, D. N., 1985, J. Phys. Chem. Ref. Data, **14**, 489-610.

[12] Debye, P; Hückel, E., 1923, Phys. Z., **24**, 185-206.

[13] Shoemaker, D. P.; Garland, C. W.; Nibler, J. W., 1996, *Experiments in Physical Chemistry*, 6th edition, McGraw-Hill, Boston.

[14] Pinho, S. P., 2000, *Phase Equilibria in Electrolyte Systems*, Ph.D. Thesis, Department of Chemical Engineering, FEUP, Porto.

[15] Zemaitis, J. F., Jr.; Clark, D. M.; Rafal, M.; Scrivner, N. C., 1986, *Handbook of Aqueous Electrolyte Thermodynamics. Theory & Application*, AIChE, New York.

LIST OF SYMBOLS

a	distance of closest approach, m
A	constant in equation 6, $kg^{0.5}\cdot mol^{-0.5}$
A	solute
B	constant in equation 6, $kg^{0.5}\cdot mol^{-0.5}\cdot m^{-1}$
$b_{\pm}$	parameter in equation 10, $kg\cdot mol^{-1}$
C_P	heat capacity, $J\cdot mol^{-1}\cdot K^{-1}$
f	fugacity
I	ionic strength, $mol\cdot kg^{-1}$
m	molality, $mol\cdot kg^{-1}$
M	molecular weight, $kg\cdot mol^{-1}$
n	mole number
N_{ions}	total number of ions
P	pressure
R	ideal gas constant, $J\cdot mol^{-1}\cdot K^{-1}$
T	temperature, K
x	mole fraction
z	ionic charge
1	solvent

GREEK LETTERS	
γ	molal activity coefficient
Δ	property difference
ΔH_f	enthalpy of fusion, $J\cdot mol^{-1}$
ν	sum of the stoichiometric coefficients
σ	function according equation 9
SUBSCRIPTS	
A	solute
f	freezing
i	ions
m	melting
1	solvent
$+$	cation
$-$	anion
$\pm$	mean ionic property
SUPERSCRIPTS	
l	liquid phase
s	solid phase
$*$	unsymmetric