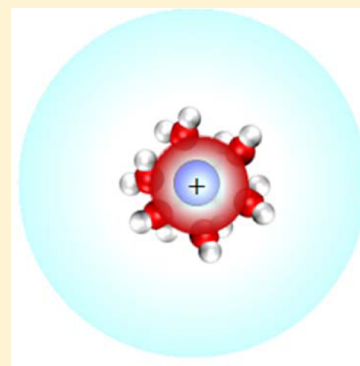


A Priori Prediction of Thermodynamic Properties of Electrolytes in Mixed Aqueous–Organic Solvents to Extreme Temperatures

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ABSTRACT: The unified theory of electrolytes (*J. Phys. Chem. B* **2009**, *113*, 2398–2404) for predicting the standard state thermodynamic properties of aqueous electrolytes has been extended to include mixed solvent systems. The solubility of solid sodium chloride in mixed solvents (methanol/water concentration up to 75% w/w) was also measured up to 466 K and pressures near 7 MPa. The present model, together with a simple modification of Pitzer's thermodynamic treatment of aqueous solutions, allows a priori prediction of solubility of electrolytes in aqueous/organic systems to extreme temperatures and pressures. Solubility is predicted for sodium chloride and potassium chloride in mixed solvents (methanol/water, ethanol/water) over a wide range of temperatures and compositions from the extension of the unified theory of electrolytes to mixed solvents. Comparisons indicate good agreement in all cases to well within the uncertainties of the experimental data. The stoichiometric activity coefficients of saturated solution of sodium chloride in methanol/water mixed solvents were calculated up to 473.15 K. The stoichiometric activity coefficients, as a function of temperature at all concentrations ($0 \leq m \leq m_{\text{sat}}$) and the entire range of mole fraction of methanol, were also calculated up to 473.15 K. The novelty of the present approach is that no additional parameters are required to account for the medium effect.



INTRODUCTION

The thermodynamic properties of electrolyte solutions at high temperatures and pressures are of theoretical and significant economic importance in mineral, oil, and other industries. Despite an increase in recent years of the experimental data available on the thermodynamic properties of aqueous electrolytes at high temperatures and pressures, the corresponding data for other solvents, especially mixed solvents at high temperatures, are sparse. Although the semiempirical models developed in aqueous solutions^{1–6} can in principle be extended to include mixed solvents, this extension is not possible (especially at higher temperatures) due to the scarcity of the experimental data necessary for estimation of the characteristic model parameters. In the literature, there are some semiempirical models for mixed solvents near 298.15 K;^{7–10} however, the extensions of these models to higher temperatures, again, are limited by the lack of availability of the required input data. Because of these limitations, a new approach is needed that requires as input a very limited set of data that are either available or can be obtained/estimated with the least amount of effort.

Recently, a unified theory for the Gibbs free energy of hydration in aqueous solutions was reported¹¹ for prediction of the standard state thermodynamic properties of electrolytes to extreme temperatures and pressures. The theory requires two constants for each electrolyte, and once these two constants are fixed from low temperature experimental data, the model can then be used to predict the standard state partial molar Gibbs free energies of electrolytes up to 1273 K.^{12–15} The objective of the present investigation is to extend the usefulness of the

unified theory to the thermodynamic properties of electrolytes in mixed solvent systems and especially for the situations in which only data at the reference temperature (298.15 K) is available.

An empirical relationship for calculation of the values for the activity coefficients of electrolytes in mixed solvents is also reported. This empirical model for estimation of the values of the activity coefficients allows, together with the present extension of the unified theory of electrolytes, a priori prediction of the solubility of electrolytes in mixed solvent systems to extreme temperatures and pressures. A number of examples are presented to illustrate the application of this extension of the theory. Solubility is predicted for a variety of simple (NaCl, KCl) electrolytes in mixed solvents (methanol/water, ethanol/water) over a wide range of temperatures and compositions, and the results are compared with the available experimental solubility data. Values for the activity coefficients of the saturated solution of sodium chloride and potassium chloride in methanol/water and ethanol/water mixed solvent systems are also calculated.

In this communication, we also report the experimental solubility of NaCl(cr) in mixed solvent systems (methanol/water up to 0.75 weight fraction of methanol (w/w)), temperature up to 466 K and pressure near 7 MPa. Large quantities of hydrate inhibitors, such as methanol and ethanol, are used to prevent gas hydrate formation during production

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from a gas/oil well. Due to environmental and economic concerns, these hydrate inhibitors are often recovered via a thermal vacuum distillation process and these hydrate inhibitors adversely enhance scale formation. The impact of temperature and concentration on mineral scale formation during inhibitor regeneration is largely unknown. The solubility data in aqueous/organic mixed solvent systems are needed to evaluate the impact of high temperature on mineral scale formation in hydrate inhibitor/brine solutions. Furthermore, from a theoretical standpoint, the infinite miscibility of a cosolvent such as methanol and ethanol with water provides an opportunity to study the transfer properties of an electrolyte between two solvents over the entire composition range, from one solvent, through solvent mixtures, to the other solvent.

2. EXPERIMENTAL SECTION

2.1. Materials. Reagent grade solid sodium chloride from Sigma-Aldrich and HPLC grade methanol from Fisher Scientific were used.

2.2. Apparatus and Procedures. Solubility was measured with a column flow through apparatus. The schematic diagram for the apparatus is given in Figure 1. All tubings, valves, and

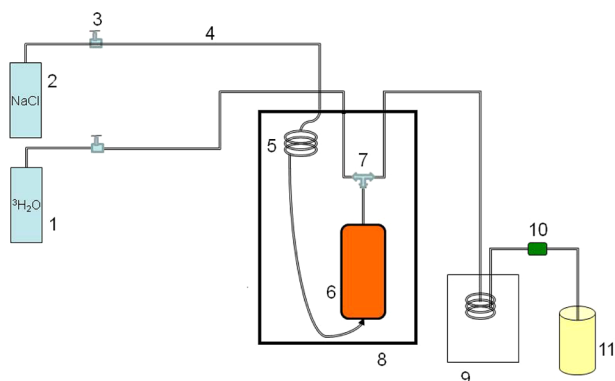


Figure 1. The schematic diagram of the apparatus: 1, syringe pump ($^3\text{H}_2\text{O}$); 2, syringe pump (NaCl solution); 3, valve; 4, Hastelloy C tubing; 5, preheating coil; 6, NaCl-packed column; 7, three-way valve; 8, oven; 9, cooling bath; 10, back pressure valve; 11, effluent collection vial.

connections were made of Hastelloy C alloy except for the reactor, which is made of 316 stainless steel. A saturated solution of sodium chloride was prepared in water at room temperature, mixed with various proportions of methanol, and used as feed solution. A 150 mL sample cylinder was filled with 160 g of reagent grade solid sodium chloride. The NaCl-packed column was placed in an oven for temperature control. A NaCl solution was pumped into the reactor by a high pressure syringe pump (Teledyne ISCO) at a steady flow rate of 0.2 mL/min. Also enclosed in the oven was a preheating coil that connected the pump to the column to heat the feed solution to the desired temperature prior to its contact with the NaCl salt. A $^3\text{H}_2\text{O}$ solution was injected via a tee into the end of the reactor at the same flow rate using a second syringe pump (Teledyne ISCO) to prevent precipitation of NaCl as the solution cooled and the pressure dropped. The radioactivity of the nonreactive tracer ($^3\text{H}_2\text{O}$) in the effluent was measured by scintillation counting to precisely determine the dilution factor. Sufficient residence time is allowed to ensure that the dissolution experiment reached equilibrium. The effluent from the back pressure valve

was collected at room temperature and one atmosphere for ion concentration analysis. Sodium concentration in the effluents was measured using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer 4300DV). The chloride ion concentration in the effluents was measured by $\text{Hg}(\text{NO}_3)_2$ titration. Excellent agreement between the measured Na^+ ion and Cl^- ion values was observed. The difference between concentrations of Na^+ and Cl^- was within 5% for most tests. At each experimental condition, four effluents were sampled consecutively. All measurements were based upon sample mass, and concentrations were expressed in mole per kg of solvent.

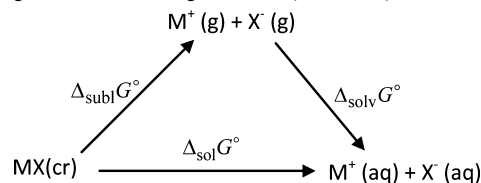
3. CALCULATIONS AND RESULTS

The solubility of solid sodium chloride in mixed solvents (methanol/water concentration up to 75% w/w) was measured up to 466 K and pressure near 7 MPa and is given in Table 1. The experimental solubility values for sodium chloride in methanol/water are compared with the corresponding values predicted from an extension of the unified theory of electrolytes to mixed solvents as follows. For a given temperature T and pressure p , at the equilibrium of a solid with its saturated solution, the solubility (m_{sat}) is related to the standard state Gibbs free energy of the solution of the electrolyte, $\Delta_{\text{sol}}G^\circ(T, p)$:

$$\begin{aligned}\Delta_{\text{sol}}G^\circ(T, p) &= G_2^\circ(T, p) - G^\circ(\text{cr}, T, p) \\ &= -\nu RT \ln(\gamma_{\text{sat}}(T, p; m_{\text{sat}}) \cdot m_{\text{sat}}(T, p))\end{aligned}\quad (1)$$

where $G_2^\circ(T, p) \equiv \mu_2^\circ(T, p)$ is the standard state partial molar Gibbs free energy (the chemical potential) of the solute electrolyte, $G^\circ(\text{cr}, T, p)$ is the molar Gibbs free energy of the solid, ν is the stoichiometric number of ions in the solute, R is the ideal gas constant, and γ_{sat} and m_{sat} (mol of solute/kg of solvent) are the stoichiometric mean molal activity coefficient and the solubility, respectively, of the solid-saturated solution at temperature T and pressure p .

The standard state Gibbs free energy of the solution, $\Delta_{\text{sol}}G^\circ(T, p)$, of an electrolyte at any temperature and pressure is in turn related to the standard state Gibbs free energy of solvation, $\Delta_{\text{solv}}G^\circ(T, p)$, and the standard state Gibbs free energy of sublimation, $\Delta_{\text{subl}}G^\circ(T, p)$, at the same T and p according to the following thermodynamic cycle



from which

$$\Delta_{\text{sol}}G^\circ(T, p) = \Delta_{\text{solv}}G^\circ(T, p) + \Delta_{\text{subl}}G^\circ(T, p) \quad (2)$$

The values for $\Delta_{\text{subl}}G^\circ(T, p)$ are calculated from the Gibbs free energies of formation from standard reference tables:^{16,17}

$$\begin{aligned}\Delta_{\text{subl}}G^\circ(T, p) &= \Delta_f G^\circ(\text{M}^+\text{X}^-(\text{g}), T, p) \\ &\quad - \Delta_f G^\circ(\text{MX}(\text{cr}), T, p)\end{aligned}\quad (3)$$

The values for $\Delta_{\text{solv}}G^\circ(T, p)$ are calculated from the unified theory of electrolytes,¹¹ which is summarized in Table 1. In the unified theory of electrolytes,¹¹ the standard state Gibbs free

Table 1. Unified Theory Equations for the Thermodynamic Properties of Electrolytes^a

$$\Delta_{\text{solv}} G^*(T, p) = [\Delta_{\text{solv}} G^*(T_r, p) + C_S T_r - C_H] F_1(D) - C_S T + C_H \quad (12a)$$

$$\Delta_{\text{solv}} G^* = \Delta_{\text{solv}} G^\circ - \Delta_{\text{ss}} G^\circ = \Delta_{\text{solv}} G^\circ - \nu RT \ln \left(\frac{m^\circ d^\circ RT}{1000 p^\circ} \right) \quad (12b)$$

$$F_1(D) = \left[\frac{D(T, p) - 1}{D(T_r, p) - 1} \right] \left[\frac{D(T_r, p)}{D(T, p)} \right] \quad (12c, 4c)$$

$$S_2^\circ(T, p) = -(\Delta_{\text{solv}} G^*(T_r, p) + C_S T_r - C_H) F_2(D) - C_S + \nu S^\circ(g) + \Delta_{\text{ss}} S^\circ \quad (13a)$$

$$F_2(D) = \left[\frac{D(T_r, p)}{D(T, p) - 1} \right] \left[\frac{1}{D(T, p)^2} \right] \left(\frac{\partial D}{\partial T} \right)_p \quad (13b)$$

$$\Delta_{\text{ss}} S^\circ = -\nu R \left[\ln(RT d^\circ) + T \left(\frac{\partial \ln d^\circ}{\partial T} \right)_T + 1 \right] \quad (13c)$$

$$V_2^\circ(T, p) = \{V_2^\circ(T_r, p) - (\Delta_{\text{h}} G^*(T_r, p) + C_S T_r - C_H) F_3(T_r, p)\} F_1(T, p) \\ + (\Delta_{\text{h}} G^*(T_r, p) + C_S T_r - C_H) F_3(T, p) \\ + [\Delta_{\text{ss}} V^\circ(T, p) - \Delta_{\text{ss}} V^\circ(T_r, p) F_1(T, p)] \quad (14a)$$

$$F_3(D) = \left[\frac{D(T_r, p)}{D(T, p) - 1} \right] \left[\frac{1}{D(T, p)^2} \right] \left(\frac{\partial D}{\partial p} \right)_T \quad (14b)$$

$$\Delta_{\text{ss}} V^\circ = \nu RT \left(\frac{\partial \ln(d^\circ)}{\partial p} \right)_T \quad (14c)$$

$$C_{p,2}^\circ(T, p) = -T(\Delta_{\text{solv}} G^*(T_r, p) + C_S T_r - C_H) F_4(D) + \nu C_p^\circ(g) + \Delta_{\text{ss}} C_p^\circ \quad (15a)$$

$$F_4(D) = \left(\frac{D(T_r, p)}{D(T, p) - 1} \right) \left(\frac{1}{D(T, p)^2} \right) \left[\left(\frac{\partial^2 D}{\partial T^2} \right)_p - \frac{2}{D(T, p)} \left(\frac{\partial D}{\partial T} \right)_p \right] \quad (15b)$$

$$\Delta_{\text{ss}} C_p^\circ = -\nu R \left[1 - 2T\alpha^\circ - T^2 \left(\frac{\partial \alpha^\circ}{\partial T} \right)_p \right] \quad (15c)$$

$$\alpha^\circ = -\frac{1}{d^\circ} \left(\frac{\partial d^\circ}{\partial T} \right)_p \quad (15d)$$

^aDefinition of symbols: D is the bulk dielectric constant of the solvent; C_S and C_H solute specific model constants; ν , stoichiometric number of ions in the solute; m° is equal to 1 mol/kg; d° is the density of the pure solvent in g/cm³; p° is equal to 0.1 MPa; α° is the coefficient of thermal expansion of solvent, $S_p^\circ(g)$ and $C_p^\circ(g)$ are the molar entropies and molar heat capacities of the gaseous ions; $\Delta_{\text{ss}} X^\circ$, $X = V, C, S, G$, are the standard state correction terms.

energies of solvation are calculated from the electrostatic and nonelectrostatic contribution to the solvation process.

From eq 2, after substitution of the Gibbs free energy of solvation (eq 12 in Table 1), the unified model for the calculation of the standard state Gibbs free energies of solution at temperature T and pressure p relative to reference temperature T_r is given by

$$\Delta_{\text{sol}} [G^\circ(T, p) - G^\circ(T_r, p)] \\ = \Delta_{\text{subl}} [G^\circ(T, p) - F_1(D) G^\circ(T_r, p)] \\ + [\Delta_{\text{sol}} G^\bullet(T_r, p) + C_S T_r] [F_1(D) - 1] - C_S \Delta T \\ + \nu R \ln [(RdT/1000)^T / (RdT_r/1000)^{F_1(D)T_r}] \quad (4a)$$

and

$$\Delta_{\text{sol}} G^\bullet(T_r, p) = \Delta_{\text{sol}} G^\circ(T_r, p) - C_H \quad (4b)$$

where d is the density of the solvent in g/cm³, d_r is the density of the solvent at the reference temperature 298.15 K, and $F_1(D)$ is a function of dielectric constant, D , of the solvent

$$F_1(D) = \frac{D(T_r, p) \cdot [D(T, p) - 1]}{D(T, p) \cdot [D(T_r, p) - 1]} \quad (4c)$$

The model constants, C_H and C_S , are related to short-range ion solvent interactions and further compensate for the errors in the electrostatic representation of the nearest solvent molecules in the primary solvation shell (the coordination shell). It was observed¹¹ that C_H and C_S define a constant radius, R_B (an effective electrostatic radius):

$$-Ne^2/2R_B = \frac{(\Delta_{\text{solv}} G^*(T, p) + C_S T - C_H)}{(1 - 1/D(T, p))} \quad (5)$$

where N is Avogadro's number, e is the value of the electronic charge, and $\Delta_{\text{solv}} G^*(T, p)$ is the standard state corrected Gibbs free energy of solvation for the hypothetically ideal 0.1 MPa gaseous ions being solvated to the hypothetically ideal 1 m (mol/kg) aqueous solution. Outside of R_B , the long-range electrostatic contribution to the Gibbs free energy of solvation is given by the Born equation.¹⁸ These constants, C_H and C_S , represent the enthalpy and entropy loss of the solvent molecules in the primary solvation shell (inside the effective electrostatic radius). The model constants, C_H and C_S , are solute specific and are fixed from experimental data; they have been shown to be independent of T and p ^{11–15} and are known^{11,19} for most solutes of interest (fixed from experimental data in aqueous solutions) and/or can be calculated from the

available low temperature data ($T < 373$ K).²⁰ The detailed development of the unified model was given previously.¹¹ The required value for $\Delta_{\text{sol}}G^\circ(T_r, p)$ in aqueous solutions is calculated from eq 6:

$$\Delta_{\text{sol}}G^\circ(T_r, p) = \Delta_{\text{sol}}G^\circ(T_r, p_r) + \int_{p_r}^p \Delta_{\text{sol}}V^\circ(T_r, p) dp \quad (6a)$$

and

$$\Delta_{\text{sol}}V^\circ(T_r, p) = V_2^\circ(T_r, p) - V^\circ(T_r, p) \quad (6b)$$

where p_r is the reference pressure 0.1 MPa, values for $\Delta_{\text{sol}}G^\circ(T_r, p_r)$ are from NBS tables,¹⁶ V_2° is the standard state partial molar volume,²¹ and V° is the molar volume of the solid calculated from available density at 298.15 K,²² assuming the pressure effect on the molar volume of the solid is negligible.

Given the Gibbs free energies of solution at 298.15 K, the dielectric constant and density of the pure solvent (solute free) as a function of temperature and pressure, the values of $\Delta_{\text{sol}}G^\circ(T, p)$ can be calculated from the present model (eq 4) up to the highest temperature that the dielectric constant and density are provided. It is important to note that eq 4 formally applies to any solvent including mixed solvents. One very important part of the present extension of the unified theory of electrolytes to mixed aqueous/organic solvent systems is to assume that the model constants (C_H and C_S) are also independent of the cosolvent. Accordingly, once the values for the constants (C_H and C_S) are fixed from experimental Gibbs free energies for a specific solute in a specific solvent (such as water), the same values for the unified model constants (C_H and C_S) can then be used for the same solute, to calculate the corresponding Gibbs free energies as a function of temperature and pressure, in any mixed solvent (for example, aqueous/organic). With this assumption, the $\Delta_{\text{sol}}G^\circ(T, p)$ value for an electrolyte in a mixed aqueous/organic solvent can now be predicted from eq 4. Furthermore, other thermodynamic properties (see Table 1) can also be predicted for the electrolyte in the mixed solvent, provided that the auxiliary data for temperature and pressure dependence of dielectric constant and density of the pure mixed solvent are available.^{11,19}

As an example of the application of the unified theory to mixed solvent systems, solubility of sodium chloride in methanol/water is predicted. From rearrangement of eq 1

$$m_{\text{sat}} = \exp[-\Delta_{\text{sol}}G^\circ(T, p)/(\nu RT)]/\gamma_{\text{sat}} \quad (7)$$

For prediction of solubility from eq 7, the value for the corresponding stoichiometric activity coefficient of the solid saturated solution in the mixed solvent systems, $\gamma_{\text{sat}}(T, p; m_{\text{sat}})$, is required. Unfortunately, at present, there are no experimental values for the required activity coefficient of electrolytes in mixed solvents, $\gamma_{\text{sat}}(T, p; m_{\text{sat}})$, above 298.15 K. A simple model for estimation of the values for the activity coefficients of a solute electrolyte in a mixed solvent at a given T , p and concentration m_{sat} (solubility in the mixed solvent) is reported below. The value for the activity coefficient of a solute in a mixed solvent, $\gamma_{\text{sat}}(T, p; m_{\text{sat}})$, is estimated from the corresponding value for the activity coefficient in aqueous solution, $\gamma_{\text{sat}}^{\text{aq}}(T, p; m_{\text{sat}})$, at the same T , p , and m_{sat} . Using a Pitzer model²³ for the functional form of the activity coefficient of a single 1:1 electrolyte, the present assumption gives

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{\text{aq}} + A_{\phi} |Z_+ Z_-| f^{\gamma} (1 - g^{\gamma}) + \Delta_m B \cdot m \quad (8a)$$

with

$$f^{\gamma} = \frac{I^{1/2}}{1 + 1.2I^{1/2}} + (2/1.2) \ln(1 + 1.2I^{1/2}) \quad (8b)$$

and

$$g^{\gamma} = [(d/w)(d)(D/sD)^3]^{1/2} \quad (8c)$$

where the subscripts s and w are for mixed solvent and pure water, respectively. I is the ionic strength, $1/2 \sum_i m_i Z_i^2$, Z is the ionic charge, A_{ϕ} is the limiting slope for the osmotic function (pure water),²⁴ and $\Delta_m B$ represents the differences in short-range interactions in pure water and in mixed solvent. In general, B has a complex form related to short-range interactions between ions and solvent molecules²³ and in practice is empirically fitted to experimental data. Equation 8 is a general equation applicable to any 1–1 electrolyte in aqueous/organic mixed solvent systems. In eq 8, the second term in the right-hand side corrects for the differences in the long-range interionic forces between the ions in methanol/water and in pure water as solvent. Due to the lack of available data for activity coefficients of electrolytes in mixed solvent systems at temperatures above 298 K and as a first approximation for calculation of the values of activity coefficients of NaCl in methanol/water mixed solvent systems, it is assumed that the short-range interactions between the ions in methanol/water are the same as that in pure water as the solvent.

The solubility was measured for solid sodium chloride in methanol/water mixed solvent systems up to 0.744 weight fraction of methanol and up to 466 K; the values are listed in Table 2. The predicted solubility of sodium chloride in methanol/water mixed solvent systems up to 473 K at steam saturation pressure, p_{sat} , and the entire concentration range of

Table 2. Experimental Solubility of Sodium Chloride in Methanol/Water Mixed Solvent Systems^a

T (K)	p (MPa)	w^b	x_2^c	$m_{\text{Na}^+}^d$	$m_{\text{Cl}^-}^d$	$m_{\text{NaCl}}^{d,e}$
298.15	0.10	0.000	0.000	6.107	6.009	6.058
298.15	6.04	0.000	0.000	6.334	5.959	6.144
378.15	6.36	0.000	0.000	6.552	6.574	6.563
466.15	6.44	0.000	0.000	7.748	7.539	7.643
298.15	0.10	0.249	0.157	3.666	3.610	3.638
297.15	6.41	0.249	0.157	3.730	3.600	3.664
356.95	6.61	0.249	0.157	4.364	4.116	4.238
402.15	6.83	0.249	0.157	4.548	4.430	4.489
465.15	7.24	0.249	0.157	4.882	4.748	4.815
298.15	0.10	0.500	0.360	1.908	1.834	1.871
297.15	7.21	0.500	0.360	1.781	1.728	1.754
353.15	7.33	0.500	0.360	2.141	2.048	2.094
404.15	7.31	0.500	0.360	2.377	2.270	2.323
468.15	7.34	0.500	0.360	2.370	2.233	2.300
298.15	0.10	0.750	0.628	0.763	0.727	0.745
297.15	6.82	0.750	0.628	0.798	0.774	0.786
345.15	6.89	0.750	0.628	1.002	0.963	0.982
390.15	7.23	0.750	0.628	1.060	1.001	1.030
464.15	7.26	0.750	0.628	0.848	0.847	0.847

^aFor the reaction $\text{NaCl}(\text{cr}) = \text{Na}^+(\text{mix. solvt.}) + \text{Cl}^-(\text{mix. solvt.})$.

^bWeight fraction of cosolvent. ^cMole fraction of cosolvent. ^dmol/kg of solvent. ^e $m_{\text{NaCl}} = (m_{\text{Na}^+} m_{\text{Cl}^-})^{1/2}$.

the mixed solvent are compared with the available experimental values from this study (Table 2) and the solubility values from the literature^{25,26} in Figure 2a. Neglecting the pressure

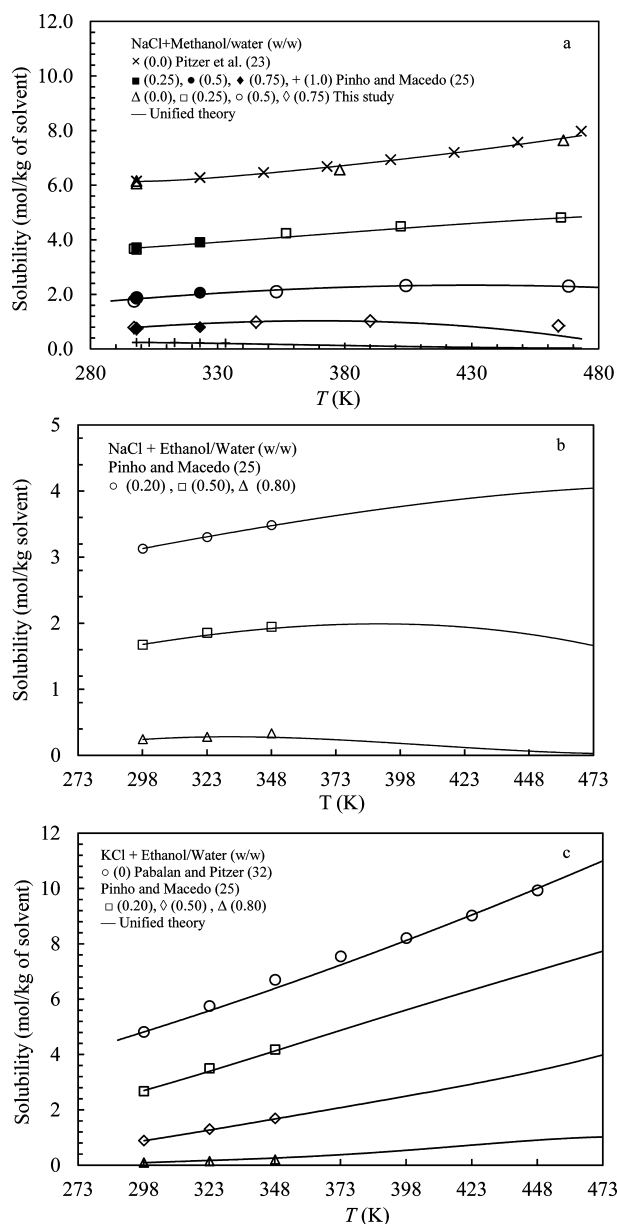


Figure 2. Comparison of experimental and predicted (eqs 4, 7, 8) values for the solubility of NaCl and KCl in aqueous/organic mixed solvent systems. The values in parentheses are the weight fraction of methanol: (a) NaCl + methanol + water; (b) NaCl + ethanol + water; (c) KCl + ethanol + water.

corrections from 7 MPa to p_{sat} results in less than 2% estimated uncertainties in the values of the solubility at the highest experimental temperature, 466 K, well within the uncertainties of the solubility data. The required auxiliary data for density and dielectric constant of methanol/water mixed solvents (see eq 4) are available in the literature. Xiao et al.²⁷ measured the density of methanol/water mixed solvents up to a temperature of 573.15 K, at pressures 7 and 13 MPa, and up to a mole fraction of 0.9 of cosolvent. The liquid density of pure methanol up to 490 K is also reported in the literature.²⁸ Akerlof²⁹ measured values for the dielectric constant of

methanol/water mixed solvents from 293.15 to 333.15 K and at mole fractions up to 1 of the cosolvent. Akerlof²⁹ fitted his experimental dielectric constants to a simple mathematical functional form:

$$\log D = a - b(T - 293.15) \quad (9)$$

A simple straight line relation (eq 9) of this kind can be used for extrapolation to higher temperatures. Using eq 9, values for the dielectric constants of methanol/water mixed solvents were calculated up to 473 K. Travers and Douzol³⁰ measured the dielectric constant of methanol/water mixed solvent systems up to 0.80 weight fraction of methanol in the temperature range 173–293 K. Their results confirmed extrapolation of the Akerlof²⁹ model to low temperatures. Furthermore, a similar fit (eq 9) to Archer and Wang²⁴ values for the dielectric constant of pure water up to $T \leq 348$ K reproduced the dielectric constant of pure water up to a temperature of 473 K with less than 1% error, well within the uncertainty of the best available dielectric constant values at such a high temperature. Franck and Deul³¹ reported dielectric constants of pure methanol at temperatures up to 525 K and pressures up to 200 MPa.

Similarly, the values for the solubility of sodium chloride and potassium chloride in ethanol/water mixed solvent systems at p_{sat} up to 0.8 weight fraction of ethanol and up to 473 K were also predicted from the unified model and compared with the available experimental values^{25,26,32} in Figure 2b and c, respectively. Comparison indicates good agreement in all cases to well within the combined uncertainties of the experimental data and uncertainties arising from errors in estimated activity coefficient, and dielectric constants of mixed solvents at higher temperatures. The values for dielectric constants of ethanol/water mixed solvents at lower temperatures ($T \leq 343.15$ K)^{29,33} were similarly extrapolated to 473.15 K using the procedure described above for methanol/water mixed solvents. The required density for ethanol/water mixed solvents is available in the literature.³⁴ The values for the unified model constants, C_H and C_S , for NaCl and KCl are listed in Table 3. The uncertainties of unified model prediction

Table 3. Unified Model Constants^a

electrolyte	solvent	cosolvent	$-C_S$ (J mol ⁻¹ K ⁻¹)	C_H (kJ mol ⁻¹)
NaCl	water	methanol	70.52	66.720
NaCl	water	ethanol	70.52	66.720
KCl	water	methanol	40.88	152.726
KCl	water	ethanol	40.88	152.726
NaCl	methanol		87.52	66.720
NaCl	ethanol		50.88	66.720
KCl	ethanol		87.52	152.726
KCl	methanol		50.88	152.726

^aEquation 4.

to higher temperatures due to uncertainty of the input data at the reference temperature 298.15 K are indicated in Figure 3 for the solubility of sodium chloride in 50% (w/w) methanol/water.

Solubility of sodium chloride in pure methanol up to 333.15 K is also available in the literature.^{25,26,35} These values were extended to 473 K using the unified model and plotted in Figure 4. However, since the coordination shell of sodium chloride in pure methanol is expected to be different from that in pure water, for prediction of high temperature thermodynamic properties of sodium chloride in pure methanol (as

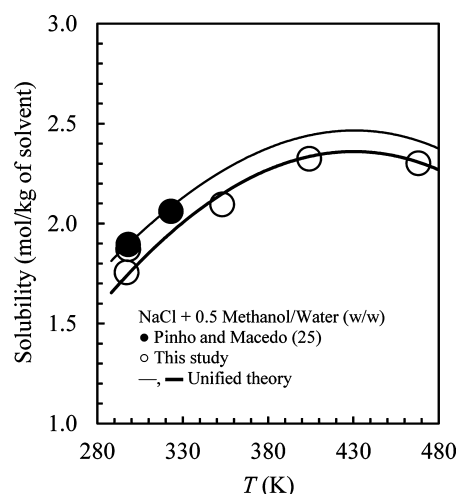


Figure 3. Differences in predicted solubility from unified theory at higher temperatures due to the differences in the values of solubility at the reference temperature.

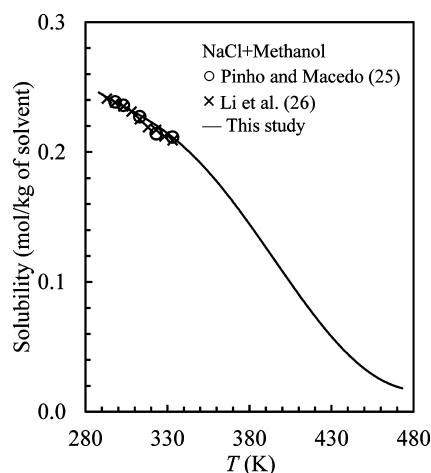


Figure 4. Comparison of experimental and predicted solubility of sodium chloride in pure methanol.

solvent) from the unified theory, a new set of values for the model constants (C_S and C_H) is required. The value for C_H in pure methanol was assumed to be the same as the corresponding value in pure water as solvent, and the C_S value was fixed using Pinho and Macedos²⁵ data at 323.15 K.

The solubility of sodium chloride at 466.15 K over the entire range of concentration of the methanol/water mixed solvent systems is compared with the corresponding values calculated from extension of the unified model to mixed solvents in Figure 5a. The values for the Gibbs free energies of transfer of sodium chloride from pure water (as solvent) to methanol/water mixed solvents at the reference temperatures 298.15 and 467.15 K over the entire range of mole fraction of methanol are also summarized in Figure 5b. The Gibbs free energies of transfer of NaCl at 298.15 K from this study are compared with the best available corresponding values selected by Heffer et al.³⁶ in Figure 5b. The comparison indicates a good agreement between the two sets of data to well within combined uncertainties.

The stoichiometric activity coefficients of sodium chloride in methanol/water mixed solvent systems at the solid-saturated solution, $\gamma_{\text{sat}}(T, p; m_{\text{sat}})$, up to 473.15 K and as a function of

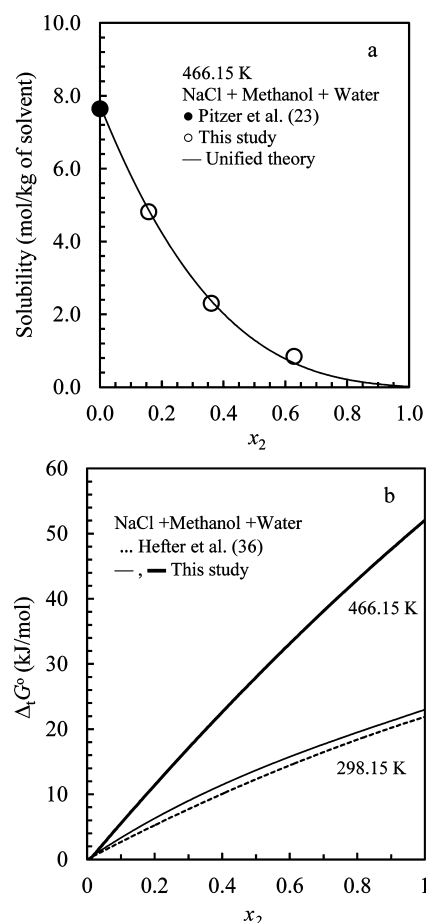


Figure 5. Experimental and predicted solubility of sodium chloride in methanol/water mixed solvent systems at 466.15 K (a) and Gibbs free energy of transfer from water to methanol/water mixed solvents at 298.15 and 466.15 K (b).

mole fraction of methanol calculated from eqs 4 and 8 are summarized in Figure 6a. In Figure 6b, the stoichiometric activity coefficients of sodium chloride in (0.5 w/w) methanol/water and potassium chloride in (0.5 w/w) ethanol/water mixed solvent systems are plotted as a function of temperature. These $\gamma_{\text{sat}}(T, p; m_{\text{sat}})$ values can be extended to all concentrations using eq 8. The calculated activity coefficients of sodium chloride in (0.5 w/w) methanol/water mixed solvent systems at all concentrations ($0 \leq m \leq m_{\text{sat}}$) are given in Figure 6c. The stoichiometric activity coefficients of NaCl in methanol/water mixed solvents at 298.15 K are compared with the available literature data^{37–41} in Figure 7. The values for activity coefficients of NaCl in pure methanol at 298.15 K from this study (eq 8) disagree with the corresponding values reported by Kamps,⁴¹ and both sets of data disagree with the activity coefficient data of Gladden and Fanning⁴⁰ at higher concentrations (Figure 7d). For calculation of the values for activity coefficient of NaCl in pure methanol from eq 8, it was assumed that the short-range contribution to the values of activity coefficient of NaCl in pure methanol is the same as that of pure water as solvent. Perhaps the disagreement of the values for activity coefficients of NaCl in pure methanol from this study (eq 8) with the corresponding experimental values of Gladden and Fanning⁴⁰ is the result of this assumption. However, Kamps⁴¹ used an extension of Pitzer's equation for the excess Gibbs energy of aqueous electrolyte solutions,

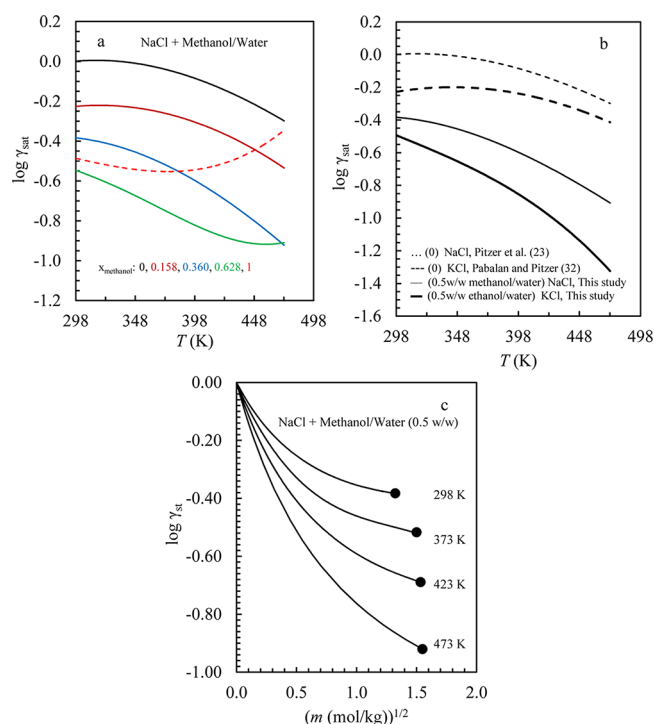


Figure 6. Stoichiometric activity coefficients of sodium chloride in methanol/water: (a) at solid saturation as a function of temperature and mole fraction of methanol; (b) sodium chloride in 0.5 w/w methanol/water and potassium chloride in 0.5 w/w ethanol/water mixed solvent systems as functions of temperature; (c) stoichiometric activity coefficients of sodium chloride in 0.5 w/w methanol/water mixed solvent systems at all concentrations ($0 \leq m \leq m_{\text{sat}}$) calculated from eq 8 up to 473.15 K.

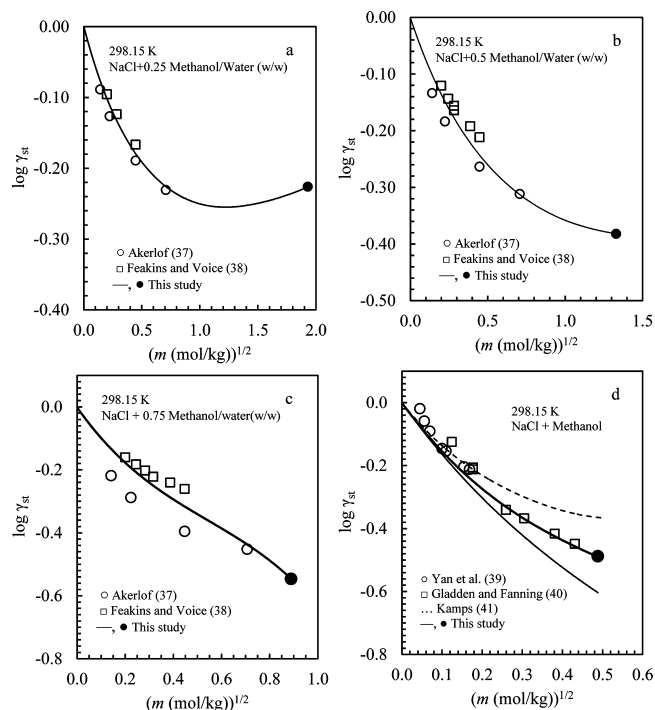


Figure 7. Comparison of the calculated and experimental activity coefficients of sodium chloride in methanol/water mixed solvent systems at 298.15 K: (a) 0.25 w/w; (b) 0.50 w/w; (c) 0.75 w/w; (d) 1 w/w (see text).

parameters for which were fitted to the experimental data for the osmotic coefficient which in turn were calculated from vapor pressure measurements ($0.04 < m < 0.22$). Calculation of activity coefficients requires osmotic coefficients that are known to very low concentrations (Gibbs–Duhem relationship); however, accurate determination of osmotic coefficients from vapor pressure measurements is difficult at low concentration due to very small differences in solvent activities between a dilute solution and the pure solvent.

As a second approach, the activity coefficient of NaCl at solid saturation, γ_{sat} in pure methanol at 298 K was calculated from the experimental solubility²⁵ and the Gibbs free energy of solution of NaCl in pure methanol at 298.15 K³⁶ using eq 1. The new value for the activity coefficient of NaCl at solid saturation, γ_{sat} in pure methanol at 298.15 K was (0.075) different than the one originally calculated from eq 8 (assuming $\Delta B = 0$). At other concentrations (and temperatures), this constant difference (adjusted for concentration) was then added to the values for the activity coefficients of NaCl in pure methanol from eq 8 and the results were then compared with the available experimental values at 298 K. The comparison indicates good agreement at all concentrations (the thick solid line in Figure 7d). The close agreement of the values for activity coefficients of NaCl in methanol/water mixed solvent systems, calculated from eq 8, with the corresponding experimental values from the literature (Figure 7a–c) supports the assumption that ΔB in eq 8 is close to zero for the systems under consideration. The activity coefficients of KCl in the 0.2 (w/w) ethanol/water mixed solvent system at 298.15 K from this study (eq 8) are compared with experimental literature data⁴² in Figure 8a, and the values for activity coefficients of

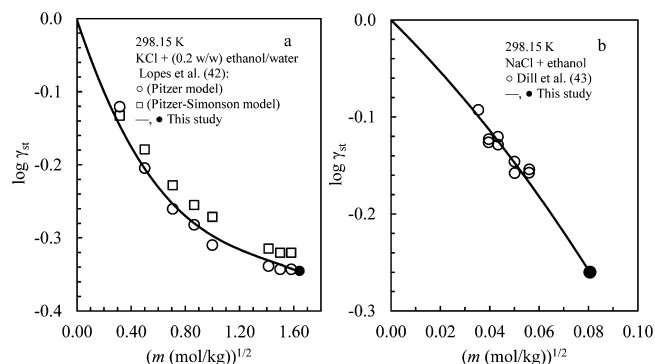


Figure 8. Comparison of experimental and calculated (eq 8) stoichiometric activity coefficients of KCl in the 0.2 w/w ethanol/water mixed solvent system (a) and NaCl in pure ethanol (b) at 298.15 K.

NaCl in pure ethanol are also compared with the corresponding experimental literature data⁴³ in Figure 8b. The comparison, again, indicates a good agreement at all concentrations.

Solubility of ionic salts is generally determined by the degree of solvation of the ions by solvent molecules (see eqs 1 and 2). Solubility as a function of T and mole fraction (x_2) of the cosolvent has a complex relationship with the solvent properties. Experimental observations of the solubility of NaCl in methanol/water mixed solvent systems indicate that the mole fraction of methanol has an inverse relationship with the driving force for the process of the solution of sodium chloride in methanol/water mixed solvent systems. This relationship at 298.15 K is summarized in Figure 9a. From

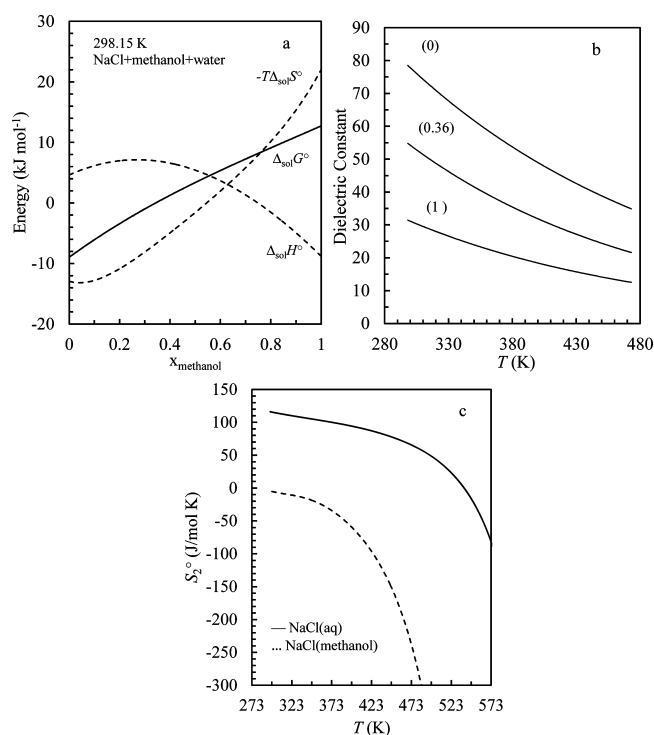


Figure 9. (a) The values for $\Delta_{\text{sol}}G^\circ$, $\Delta_{\text{sol}}H^\circ$, and $T\Delta_{\text{sol}}S^\circ$ of NaCl in methanol/water mixed solvent systems as a function of mole fraction of methanol, x_2 , at 298.15 K. (b) Dielectric constant of water/methanol mixed solvent systems as a function of T and x_2 . (c) Comparison of the values of standard state partial molar entropy of NaCl in pure water and pure methanol.

Figure 9a, the magnitude of the driving force is the result of enthalpy–entropy compensation, mainly entropy driven. This effect is reflected on the solubility of NaCl in the methanol/water mixed solvent systems; an increase in the mole fraction of methanol results in a decrease in the solubility of NaCl. As the temperature and/or x_2 of methanol increases and as a result the number of hydrogen bonds in the solvent decreases, it becomes easier for an ion to influence surrounding solvent molecules. Furthermore, the reduction in dielectric constant (Figure 9b) of the solvent at higher temperature and/or x_2 enables the electric field surrounding an ion to extend further into the bulk solvent and influence more solvent molecules. As temperature and/or x_2 increases, both of these effects enable the electric field surrounding an ion to reduce the degrees of freedom of more and more solvent molecules, resulting in increasingly negative contributions to the standard state partial molar heat capacity of the solute. A comparison of the effect of the standard state partial molar heat capacity of sodium chloride, $C_{p,2}^\circ$, on the standard state partial molar entropy, S_2° , of sodium chloride in pure water and pure methanol as solvent is given in Figure 9c. The values for S_2° NaCl (aq) are from Djamaali and Cobble,¹³ and those in pure methanol were calculated from eq 10:

$$S_2^\circ(T) = S_2^\circ(298.15 \text{ K}) + \int_{T_r}^T C_{p,2}^\circ(T) d \ln T \quad (10)$$

where the value for the standard state partial molar entropy for NaCl in pure methanol at 298.15 K is from Heffer et al.³⁶ and $C_{p,2}^\circ$ of NaCl in pure methanol as a function of temperature are estimated from Lankford and Criss⁴⁴ data.

The rate of the change of solubility, dm_{sat}/dT , of NaCl in methanol/water mixed solvent systems as a function of T and

x_2 is plotted in Figure 10a. The plot shows a gradual reversal of the sign for dm_{sat}/dT and that the temperature at which this

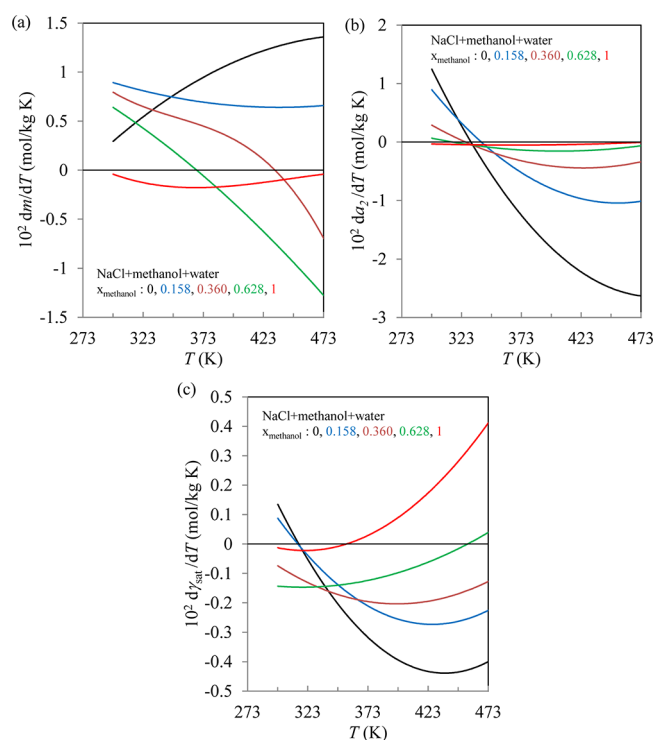


Figure 10. The rate of change of (a) solubility, (b) activity, and (c) activity coefficient of NaCl in a methanol/water mixed solvent system as a function of T and x_2 .

sign change occurs decreases with an increase in the mole fraction of methanol. The change in solubility of an electrolyte as a function of T and x_2 , in general, is related to the change in activity, a_{sat} (i.e., the driving force for the process of solution) (Figure 10b), as follows:

$$dm_{\text{sat}}/dT = 1/\gamma_{\text{sat}}(da_{\text{sat}}/dT - m_{\text{sat}}d\gamma_{\text{sat}}/dT) \quad (11)$$

For example, for a solution of NaCl in a water/methanol mixed solvent system, the solubility decreases with an increase in temperature and x_2 when $d\gamma_{\text{sat}}/dT \geq 0$. For $d\gamma_{\text{sat}}/dT < 0$, the sign of dm_{sat}/dT is determined by the difference between the first and the second term on the rhs of eq 11. The magnitude of the activity coefficient is in turn the resultant of opposing forces: the net effect of interionic attractions and repulsions which tend to decrease the free energy of the solute and hence decrease the activity coefficient, while the forces between ions and solvent dipoles will tend to increase the activity coefficients of the electrolyte (Figure 10c).

The effective electrostatic radius, R_B , for NaCl in a methanol/water mixed solvent system as a function of mole fraction of methanol, x_2 , is calculated from eq 5 and plotted in Figure 11. The effective electrostatic radius for NaCl increases smoothly with x_2 ; however, in the limit as x_2 approaches 1, a sudden decrease in the magnitude of R_B is detected. This sudden decrease in the value of R_B for sodium chloride, for the process of transfer from methanol/water mixed solvents to pure methanol as the solvent, is interpreted here as due to a sudden change in the environment near the ions in the two different solutions. This sudden change in R_B is perhaps an indication that the ions are preferentially hydrated by water molecules. For

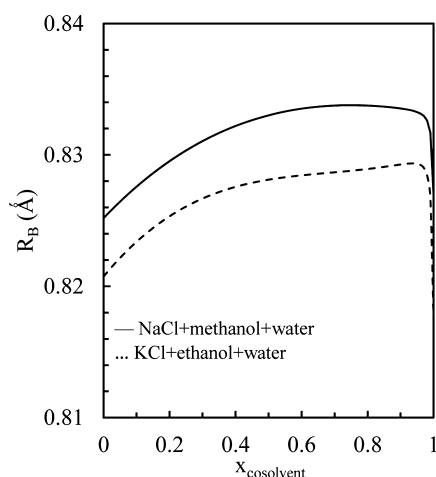


Figure 11. The effective electrostatic radius, R_B , for NaCl in a methanol/water and for KCl in an ethanol/water mixed solvent systems as a function of mole fraction of the cosolvent (eq 5).

sodium chloride in methanol/water mixed solvent systems, spectroscopic studies⁴⁵ indicate that sodium ion is preferentially hydrated and that chloride ion is preferentially solvated by methanol. However, it should be noted that the R_B values for NaCl from this study pertain to the neutral electrolyte not the ions. Further, from analysis of thermodynamic properties of transfer of NaCl from water to water/methanol mixed solvent systems, Cox and Waghorne⁴⁶ concluded that there is no preferential solvation of NaCl. Cox and Waghorne⁴⁶ propose that the absence of preferential solvation in methanol/water mixed solvent systems may be the result of the averaging of the acidity and basicity of the constituent solvents over the entire solvent molecules through intermolecular hydrogen bonding. From Figure 11, a similar conclusion can also be reached regarding preferential hydration of KCl in ethanol/water mixed solvent systems.

4. CONCLUSION

Solubility is predicted for sodium chloride and potassium chloride in mixed solvents (methanol/water, ethanol/water) over a wide range of temperatures and compositions from an extension of the unified theory of electrolytes to include mixed solvents. Comparisons indicate good agreement in all cases to well within the combined uncertainties of the experimental data and uncertainties arising from errors in estimated dielectric constants and densities at higher temperatures. The stoichiometric activity coefficients of a saturated solution of sodium chloride in methanol/water mixed solvents were calculated up to 473.15 K. The stoichiometric activity coefficients, as a function of temperature at all concentrations ($0 \leq m \leq m_{\text{sat}}$) and the entire range of mole fraction of methanol, were also calculated up to 473.15 K. Comparison of the activity coefficients in mixed solvents from this study with the available literature data (mainly at 298.15 K) indicates good agreement. The novelty of the present extension of the unified theory to mixed solvents is that no additional parameters are required to account for the medium effect.

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Notes

The authors declare no competing financial interest.

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