



# Investigating thermodynamic properties of LiCl in amide–water mixtures with $\epsilon$ -increasing and $\epsilon$ -decreasing solvent at 298.15 K

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## ABSTRACT

This article deals with the mean activity coefficients of LiCl in amide–water mixtures with both  $\epsilon$ -increasing co-solvent (urea–water, *N*-methylformamide–water), and  $\epsilon$ -decreasing co-solvent (*N,N*-dimethylformamide–water, *N,N*-dimethylacetamide–water) systems at 298.15 K by potentiometric method. Meanwhile, thermodynamic properties including the osmotic coefficients, the excess Gibbs free energy, the standard solubility product, the primary LiCl hydration number and the standard free energy of transference from water to the mixtures were also calculated. The nonideal behavior of these systems has been discussed in terms of the Pitzer, the Modified Pitzer and the extended Debye–Hückel equations parameters.

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## 1. Introduction

As the lightest metal element in the nature, lithium has high specific heat and conductivity [1]. Thus, it was widely used in industry, such as secondary batteries storage technologies with high energy density [2]. Research on electrolytes used in lithium-ion batteries, including conducting lithium salt, organic solvent and additives, is important [3]. Therefore, it is necessary for many practical purposes to know the thermodynamic properties of electrolytes in water and water–organic mixers. For instance, the thermodynamic properties of systems LiCl + KCl + NH<sub>4</sub>Cl + H<sub>2</sub>O [4] and CsCl + LiCl/NaCl + H<sub>2</sub>O [5] were determined by hygrometric method. Ternary system LiCl + SrCl<sub>2</sub> + H<sub>2</sub>O and its sub-binary systems were studied using the isopiestic method [6]. Moreover, vapor pressures and osmotic coefficients of LiCl/LiBr + *N,N*-dimethylacetamide at different temperatures were studied by Karamat and Roland [7]. With the rapid development of ion-selective electrode (ISE), potentiometric method was widely used to determine the thermodynamic properties of electrolyte solutions. For example, Hernandez-Luis et al. reported the activity coefficient of LiCl + PEG 4000/ethanol + water systems [8,9]. In addition, the research of lithium salt in ionic liquids LiBr/LiCl + 1,3-dimethylimidazolium chloride + H<sub>2</sub>O, LiBr/LiCl + 1,3-dimethylimidazolium tetrafluoroborate + H<sub>2</sub>O [10] and molten salt Li<sub>2</sub>O + LiCl + KCl [11] were also paid close attention to. As a kind of

solvent, amide was widely used in industry and laboratory, however, the thermodynamic properties of LiCl in amide–water mixed solvent systems was not studied systemically.

Thus, in this work, the thermodynamic properties for LiCl in amide–water mixtures both with  $\epsilon$ -increasing co-solvent (urea–H<sub>2</sub>O and *N*-methylformamide–H<sub>2</sub>O) and  $\epsilon$ -decreasing co-solvent (*N,N*-dimethylformamide–H<sub>2</sub>O and *N,N*-dimethylacetamide–H<sub>2</sub>O) at  $T = 298.15$  K were determined by potentiometric method. The experimental data were well fitted to the Pitzer, the Modified Pitzer and the extended Debye–Hückel equations.

## 2. Experimental

### 2.1. Materials and apparatus

Information about the studied substances is listed in Table 1. Urea was crystallized from ethanol and dried under vacuum. Other reagents were used without further purification. The concentration of lithium chloride was analyzed by Mohr method [12], titrated with silver nitrate solution using potassium chromate as indicator. The specific conductance of double distilled–deionized water used in this experiments was approximately  $(1.0$  to  $1.2) \times 10^{-4} \text{ S m}^{-1}$ .

BI-870 Dielectric Constant Meter (Brookhaven Instruments Corporation, USA) equipped with stainless steel probe was used to measure the relative permittivity of the mixed solvents at  $298.15 \pm 0.02$  K. The dielectric constant of the liquid sample is determined by measuring the current between the outer and inner

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## Nomenclature

### List of symbols

|                            |   |
|----------------------------|---|
| $a$                        | ion size parameter of the Debye–Hückel equation                       |
| $c, d$                     | ion interaction parameter of the Debye–Hückel equation                |
| $A, B$                     | Debye–Hückel equation constants                                       |
| $A_\varphi$                | Debye–Hückel constant for the osmotic coefficients in Pitzer equation |
| $b$                        | constant of the Pitzer equation                                       |
| $\beta^{(0)}, \beta^{(1)}$ | solute-specific interaction parameters of the Pitzer equation         |
| $C^\gamma$                 | triple-ion interaction parameter of the Pitzer equation               |
| $E$                        | electromotive force   |
| $E^\circ$                  | standard electromotive force  |
| $E^*$                      | apparent standard electromotive force                                 |
| $\gamma_\pm$               | mean activity coefficient   |
| $\Phi$                     | osmotic coefficient   |
| $G^E$                      | excess Gibbs free energy  |
| $\Delta G_t^\circ$         | standard free energy of transference                                  |
| $K_{sp, m}^\circ$          | standard solubility product   |
| $F$                        | Faraday constant  |
| $I$                        | ionic strength  |
| ISE                        | ion-selective electrode   |
| $k$                        | Nernst's theoretical slope  |
| $M$                        | average molecular mass of mixed solvent                               |
| $m$                        | molality  |
| $n_{hydr}$                 | primary hydration number  |
| $R$                        | gas constant  |
| $T$                        | absolute temperature  |
| $w$                        | mass fraction of water in the mixture                                 |
| $\rho$                     | density   |
| $SD$                       | standard deviation  |
| $D$                        | dielectric constant   |
| $\varepsilon$              | relative dielectric constant  |
| $\varphi_w$                | volume fraction of the water in the mixed solvent                     |

### Subscripts

|     |               |
|-----|---------------|
| $m$ | mixed solvent |
| $t$ | transfer      |
| $w$ | water         |

cylinders of the probe with absolute accuracy of  $\pm 2\%$ . The density of the mixture has been measured by density meter (Anton Paar DMA 4500). Before the measurement, twice distilled water and air were used as reference substances to calibrate the instruments under atmospheric pressure. A more detailed description of experiment instrument and equipments has already been reported in our previous work [13,14].

## 2.2. Procedure

The preparation technique of the Li ion-selective electrode and Ag–AgCl electrode was described by Wu [15]. Ag–AgCl electrode

**Table 1**

The source, purity and purifying method of chemicals.

| Chemical name         | Source                               | Mass fraction purity | Purification method |
|-----------------------|--------------------------------------|----------------------|---------------------|
| LiCl·H <sub>2</sub> O | Sinopharm Chemical Reagent Co., Ltd. | $\geq 99.0\%$        | None                |
| Urea                  | Sinopharm Chemical Reagent Co., Ltd. | $\geq 99.0\%$        | Recrystallization   |
| N-Methylformamide     | Aladdin reagent, Shanghai.           | $\geq 99.0\%$        | None                |
| N,N-Dimethylformamide | Sinopharm Chemical Reagent Co., Ltd. | $\geq 99.5\%$        | None                |
| N,N-Dimethylacetamide | Sinopharm Chemical Reagent Co., Ltd. | $\geq 99.5\%$        | None                |

was conditioned overnight in 0.1 mol L<sup>-1</sup> HCl solution. Both the electrodes need to be calibrated and present a good Nernst response before the experiment. The cell vessel is a double-walled glass and its temperature was controlled to 298.15 K (within an uncertainty of  $\pm 0.2$  K) with circulating water. All the samples weighed on an analytical balance (Mettler Toledo-AL204, Switzerland) with an accuracy of  $\pm 0.0001$  g. Voltage readings were achieved on a pH/mV meter (Orion-868, America), and the uncertainty of the value of potential in the experiment is  $\pm 0.1$  mV. The whole experiment process was maintained within 2 h.

## 3. Theoretical model

The application of the Pitzer model, the modified Pitzer model and the extended Debye–Hückel equation in organic–water mixed systems was found to be successful in many previous studies on thermodynamics properties.

The Pitzer model [16,17] is used widely to describe thermodynamics of electrolyte solution. The mean activity coefficient ( $\gamma_\pm$ ) of 1–1 type electrolytes can be written as

$$\ln \gamma_\pm = f^\gamma + mB^\gamma + m^2C^\gamma \quad (1)$$

where

$$f^\gamma = -A_\varphi \left[ \frac{I^{1/2}}{(1 + bI^{1/2})} + \left( \frac{2}{b} \right) \ln (1 + bI^{1/2}) \right] \quad (1a)$$

$$B^\gamma = 2\beta^{(0)} + 2\beta^{(1)} \left\{ \frac{[1 - \exp(-aI^{1/2})(1 + aI^{1/2} - a^2I/2)]}{(a^2I)} \right\} \quad (1b)$$

$$C^\gamma = 1.5C^\varphi \quad (1c)$$

In the equations,  $a$  and  $b$  are assumed to be constant with values of (2.0 and 1.2) kg<sup>1/2</sup> mol<sup>-1/2</sup>, respectively.  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^\varphi$  are the parameters of the Pitzer equation, which can be obtained by fitting the experimental data. It is known that the term  $C^\varphi$  makes a considerable contribution only at high concentrations of the electrolyte [18]. Hence, we assumed  $C^\varphi = 0$ .  $A_\varphi$  is the Debye–Hückel constant for the osmotic coefficient defined by

$$A_\varphi = 1.4006 \times 10^6 \rho^{1/2} (DT)^{3/2} \text{ kg}^{1/2} \text{ mol}^{-1/2} \quad (2)$$

The osmotic coefficient ( $\Phi$ ) is expressed by

$$\Phi - 1 = f^\varphi + mB^\varphi + m^2C^\varphi \quad (3)$$

with

$$f^\varphi = -A_\varphi \left( \frac{I^{1/2}}{(1 + bI^{1/2})} \right) \quad (3a)$$

$$B^\varphi = \beta^{(0)} + \beta^{(1)} \exp(-aI^{1/2}) \quad (3b)$$

The excess Gibbs free energy ( $G^E$ ) represents the nonideality in the behavior of the studied systems and informs us about fundamental interactions between solute and solvent [19,20]. The excess Gibbs free energy ( $G^E$ ) can be written as follows:

$$G^E = 2RTI(1 - \Phi + \ln \gamma_\pm) \quad (4)$$

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