



An investigation of ion-pairing of alkali metal halides in aqueous solutions using the electrical conductivity and the Monte Carlo computer simulation methods



Jure Gujt, Marija Bešter-Rogač*, Barbara Hribar-Lee**

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 23 August 2013

Accepted 28 September 2013

Available online 29 October 2013

Keywords:

Alkali halides aqueous solutions

Electric conductivity

Association constant

Monte Carlo computer simulations

Water structure

ABSTRACT

The ion pairing is, in very dilute aqueous solutions, of rather small importance for solution properties, which renders its precise quantification quite a laborious task. Here, we studied the ion pairing of alkali halides in water by using the precise electric conductivity measurements in dilute solutions, and in a wide temperature range. The low-concentration chemical model was used to analyze the experimental data, and to estimate the association constant of different alkali halide salts. It has been shown that the association constant is related to the solubility of salts in water and produces a 'volcano relationship', when plotted against the difference between the free energy of hydration of the corresponding individual ions. The computer simulation, using the simple MB + dipole water model, was used to interpret the results, to find a microscopic basis for Collins' law of matching water affinities.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Aqueous solutions of salts are ubiquitous, and solvated ions greatly influence many naturally occurring processes, such as the protein folding and the conformational changes of nucleic acids [1], the permeability, conductance, and electrostatic potential of cell membranes [2,3], the micellization of surfactants and hydrophobic effect (also Hofmeister effects) [4,5], enzymes, or have some other properties (e.g. acid–base properties), that influence activity of biomolecules [1]. Charged species also affect the mechanism, and thus kinetics, of chemical reactions [6,7]; the mechanism of ion-exchange [8]; the sol–gel transition [9]; and many other phenomena. Solvated ions were, thus not surprisingly, subject of many experimental [10–16] and theoretical [17–37] studies.

In this work, we are particularly interested in systematic investigation of the interactions between oppositely charged ions in aqueous solutions of simple alkali halide salts. These salts have been extensively studied in the past, experimentally [11,12,14–16] as well as theoretically [27–29,31–37]. Properties, such as osmotic coefficients and enthalpies of dilution, of these solutions show a strong correlation with the chaotropic or kosmotropic character of the ions [38,39]. The osmotic coefficient of aqueous solutions of salts with kosmotropic cation (such as sodium or potassium) increases with increasing anion size, whereas for salts with chaotropic cation like cesium, this order is reversed. On the other hand, for salts with common anion, osmotic coefficient of their aqueous

solutions decreases with increasing cation chaotropicity [40]. Enthalpies of dilution of salts with common small ion (e.g. sodium salts or chlorides) do not change much with increasing chaotropicity of counterion, whereas for salts with common larger ion (e.g. cesium salts or iodides) the dilution becomes more endothermic with increasing the size of the counterion [39]. The property that was of particular interest for us was the solubility of these salts. It is well known, that certain salts, such as LiF, which involve two small ions, are poorly soluble in water. Salts such as CsI, which involve both a large anion and cation, also have limited solubilities. However, in contrast, salts like CsF, in which one ion is large and the other is small, are highly soluble in water [41]. Interestingly, if plotted against the difference of the Gibbs free enthalpy of hydration between cation and anion, the results for the solubility show the inverse Collins' pyramid-like correlation [42], as it is presented in Fig. 1.

It has been already shown theoretically [36,37], that these differences can be explained following the idea of Collins' matching water affinities [42], with different ion-pairing tendency. However, due to the lack of appropriate experimental data and inconsistencies within different force field models a thorough analysis is still lacking.

Experimental quantification of weak association is not a trivial task. It has been reported, that even the conductivity measurements, as one of the most established techniques, yields only a rough estimation for the association constant, $K_A \leq 10$ [44]. Despite the fact that there is plenty of precise conductivity data for alkali metal halides in water [45–51], they are, in general, limited to 298.15 K and do not cover the diluted solutions in sufficient detail. The appropriate analysis of existing diluted conductivity data is therefore not reliable.

Here we decided to carry out precise conductometric measurements on diluted aqueous solutions ($c \sim <0.005 \text{ mol} \cdot \text{L}^{-1}$) of all alkali metal

* Corresponding author. Tel.: +386 12419410.

** Corresponding author. Tel.: +386 12419416.

E-mail addresses: jure.gujt@fkkt.uni-lj.si (J. Gujt), marija.bester@fkkt.uni-lj.si (M. Bešter-Rogač), barbara.hribar@fkkt.uni-lj.si (B. Hribar-Lee).

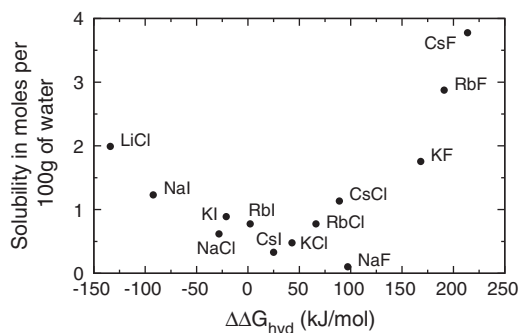


Fig. 1. The solubility of alkali halides at 25 °C [41] as a function of the difference between Gibbs' free enthalpies of hydration of single ions [43].

chlorides and three iodides (NaI, KI, and CsI) over the broad temperature range. To obtain the association constants, $K_A(T)$, and limiting molar conductivities at infinite dilution, $\Lambda^\infty(T)$, the experimental data were analyzed using Barthel's low-concentration chemical model (lcCM) [52]. Due to the hydrolysis of fluoride ion in water, fluoride salts were not included in our investigation.

To explain the obtained results of K_A on a microscopic scale, we used a simple 2D water model, that was parameterized to qualitatively reproduce the association tendency.

The paper is organized as follows. After this brief introduction, the experimental method is outlined, followed by the description of the model used to analyze the results. Next, the results are summarized and discussed; the conclusions are given at the end.

2. Experimental

2.1. Materials

Lithium chloride (LiCl, Merck, Darmstadt, Germany, Suprapur), potassium chloride (KCl, Aldrich, USA, 99.999%), rubidium chloride (RbCl, Merck, Darmstadt, Germany, Suprapur), cesium chloride (CsCl, Aldrich, USA, 99.999% (sample I) and CsCl, Sigma-Aldrich, USA, 99.9% (sample II)), sodium iodide (NaI, Aldrich, 99.999%), potassium iodide (KI, Aldrich, 9.999%) and cesium iodide (CsI, Aldrich, 99.999%) were used as received. All salts were dried for 24 h at $T \approx 400$ K with a vacuum line ($p < 0.01$ Pa) and stored in a desiccator over P_2O_5 before use.

Stock solutions were prepared by mass from the pure compounds and demineralized distilled water. Demineralized water was distilled two times in a quartz bidistillation apparatus (Destamat Bi 18E, Heraeus). The final product with specific conductivity $\kappa < 6 \cdot 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ was distilled into a flask permitting storage and transfer of water into the measuring cell under an atmosphere of nitrogen.

2.2. Conductivity measurements

Conductivity measurements were performed with a three-electrode flow cell (cell constant $C = 0.81143 \pm 0.00005 \text{ cm}^{-1}$ at 298.15 K) connected to a mixing chamber and mounted in a lid for immersion in a temperature bath [53,54]. The cell was calibrated with potassium chloride solutions [55]. The computer-controlled measurement system, based on a high-precision thermostat (Lauda UB 40J, WK 1400) and an impedance analyzer (Agilent 4284A), was described previously [56]. This system allows automatic setting of each temperature between $T = 278.15$ K and 313.15 K, with a reproducibility better than 0.005 K.

At the beginning of each measurement cycle, the cell was filled under nitrogen atmosphere with a known mass of water. After measurement of the water conductivity, $\kappa'(\nu)$, as a function of frequency, ν , in the range of 200 to 10,000 Hz in steps of 200 Hz for all chosen temperatures of the program, known masses of stock solution were

subsequently added with a gas-tight syringe and the temperature program repeated.

Conductivity of KI solutions was measured at 298.15 K only, because it turned out to be unstable in a longer time period as it is usually demanded for covering whole temperature range. We also encountered unexpected problems when investigating CsCl in extremely diluted solutions ($c \sim < 0.002 \text{ mol} \cdot \text{L}^{-1}$), so measurements done on CsCl solutions were repeated with different sample. Results are presented in the SI in Fig. S6.

The measurement procedure, which included correction for lead resistance and extrapolation of the recorded frequency-dependent conductivities, $\kappa'(\nu)$, to $1/\nu = 0$ in order to eliminate electrode polarization effects, was described in detail elsewhere [56]. The corrected conductivities, $\kappa = \lim_{1/\nu \rightarrow 0} \kappa'(\nu)$, of all investigated systems, converted to molar conductivities, $\Lambda = \kappa/c$, are given in Table S4 in the SI as a function of electrolyte molality, m . The latter relates to the corresponding (temperature-dependent) molar concentration, c , via $c = md/(1 + M_2m)$ where M_2 is the molar mass of the salt and d is the density of solution.

A linear change of density with temperature, T , was observed, $d = d_s + b \cdot m$, where d_s is the density of water at the given temperature, taken from the literature (see Table S3 in the SI). The density coefficients b were determined from density measurements of the stock solution and the final solution in the conductivity cell by the method of Kratky et al. [57] using Anton Paar density meter DMA 5000 (Anton Paar, Graz, Austria) with a declared precision of the measurements $\pm 0.01 \text{ kg m}^{-3}$. They are assumed to be independent of temperature and are included in the Table S4 in the SI.

Taking into account the sources of error (calibration, measurements, and impurities) the values of κ and Λ are certain within 0.05%.

2.3. Data analysis

The presented molar conductivities, $\Lambda(c)$ (Table S4 in the SI, Figs. 2 and 3), were analyzed in the framework of the low-concentration chemical model (lcCM) of Barthel [52]. This approach uses the set of equations

$$\frac{\Lambda}{\alpha} = \Lambda^\infty - S\sqrt{\alpha c} + E\alpha c \ln(\alpha c) + J_1\alpha c - J_2(\alpha c)^{\frac{3}{2}} \quad (1)$$

$$K_A^\circ = \frac{1-\alpha}{\alpha^2 c (y'_\pm)^2}; \quad y'_\pm = \exp\left(-\frac{\kappa_D q}{1 + \kappa_D R}\right); \quad \kappa_D^2 = 16\pi N_A q \alpha c; \quad q = \frac{e^2}{8\pi\epsilon\epsilon_0 k_B T} \quad (2)$$

and

$$K_A^\circ = 4\pi N_A \int_a^R r^2 \exp\left[\frac{2q W_\pm^*}{r k_B T}\right] dr \quad (3)$$

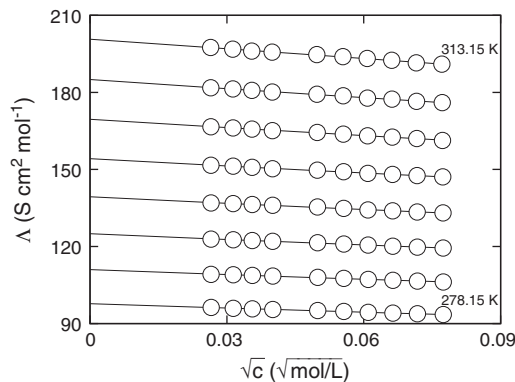


Fig. 2. Molar conductivities, Λ , of RbCl in water from $T = 278.15$ to 313.15 K in steps of 5 K and in the concentration range $0.7 \cdot 10^{-3} < c/\text{mol} \cdot \text{L}^{-1} < 0.006$. Lines show the results of the lcCM calculations.

Download English Version:

<https://daneshyari.com/en/article/5411677>

Download Persian Version:

<https://daneshyari.com/article/5411677>

[Daneshyari.com](https://daneshyari.com)