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Investigation of ion-pairing phenomenon in BaF_2 aqueous solution: Experimental and theoretical studies

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ABSTRACT

The ion-pair association constant values, related to the reaction $Ba^{2+} + F^- \leftrightarrows [BaF]^+$, are determined by means of NMR spectroscopy. The values for thermodynamic functions of the ion-pairing process are calculated on the basis of the NMR results. In addition, the association entropy has been found to be dependent on temperature. Comparing the experimental data and Fuoss theory, it is found that $[BaF]^+$ contact ion-pair is formed in the BaF_2 aqueous solution. Also, hydration of barium-fluoride ion-pair is investigated by the DFT method. The hydration number of barium-fluoride ion-pair is determined by comparing the experimental and theoretical results. The effect of number of water molecules on the properties of ion-pairs is investigated by determining NQR and NMR parameters. Also, the relation between the chemical shifts and the energy gap between the highest occupied molecular orbital (HOMO) and low-lying virtual molecular orbital (LUMO) is investigated.

1. Introduction

In the Debye–Hückel theory, it is assumed that strong electrolytes completely dissociate in aqueous solution [1]. However, there is also much evidence to show that cations and anions in solution can associate to form ion-pairs, as a result of strong electrostatic attraction. In ionic compounds, the separation to ions is complete. However, if ions associate in solution, the dissociation is not complete. Small ion dimensions, high ion valence, and small solvent dielectric constants are conducive to ion-pair formation.

Hydration of ion-pairs is an essential process in the solvation of ionic crystals into water, chemical reactions in aqueous solution, and stability and functionality of biological systems [2–4]. Solvation effects can profoundly alter chemical and physical interactions.

The investigations show that dissolved ions in water have “structure making” or “structure breaking” effects on water, depending on the ionic size and whether they are cations or anions [5]. For example, halide ions larger than Cl^-, i.e. Br^- and I^-, are regarded as water structure breakers, while smaller ions such as F^- are regarded as water structure makers. Yet it could equally be argued that a smaller ion, with its much greater local charge density, would be more likely to pull the water away from its hydrogen bonded configuration in the liquid than a larger ion, thus breaking the water structure [6,7]. Hribar et al. concluded that “small ions have high charge densities, so they cause strong electrostatic ordering of nearby water molecules, breaking hydrogen bonds” [7]. In other words, an ion which breaks water hydrogen bonds is regarded as a structure maker.

The ion-pairs were classified on the basis of mutual geometry of the ions and the solvent according to: (1) solvent-separated ion-pairs, (2) solvent-shared ion-pairs and (3) contact ion-pairs [8].

Several methods of studying ion-pairing including conductivity methods [9–15], ion-selective electrode potentiometry [16], gravimetric, solvent evaporation [17], NMR spectroscopy [18–22], and theoretical modeling [23–26] have been used to probe the phenomenon of ion association in both aqueous and non-aqueous solvents. Theoretical methods like DFT assume some structures in the solution and only a correct assumption leads to a theoretical result that agrees with experimental results. Thus, such agreement indicates indirectly the structure of the molecules. For example, the experimental and theoretical studies have been shown that Mg^{2+} is coordinated by six water molecules in an octahedral arrangement [27]. Also, the DFT and experimental ^{19}F NMR chemical shifts for sulfur-containing compounds have been shown

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that the fluorine atom is attached to a four and a six-coordinated sulfur atom [28]. Also, the experimental methods as extended-X-ray adsorption fine structure spectroscopy and large-angle X-ray scattering and theoretical methods such as molecular dynamic method have been used for determining of hydration number of Ca^{2+} in dilute $CaCl_2$ solution [29,30].

The phenomenon of ion association from the various aspects, e.g. plating and holding of tertiary structure of enzymes and proteins [31], maintaining the micelle stability [32], lowering the electric conductivity in Li-ion battery electrolytes, is of great interest.

Since careful analysis of NMR spectra for a nucleus exchanging among different environments yields information about the exchange process [33,34], for processes involving ion solvation, one can investigate the NMR spectroscopy of the solvent such as water [35]. But NMR investigation of the ion also provides direct evidence of exchange. ^{19}F NMR studies of aqueous salt solutions at room temperature show a significant variation in the NMR chemical shifts with concentration.

Choppin and Majer previously calculated thermodynamic parameters of the alkaline earth monofluorides in ionic strength 1 M. The investigations showed that the formation constant of ion-pair is small in high ionic strength [36,37].

In this study, we report the temperature and concentration dependence of ^{19}F NMR shifts of BaF_2 solutions, from which we have determined equilibrium constants as a function of temperature, the free energy, enthalpy and entropy of formation of the ion-pair in aqueous solution.

We studied the hydration process of $[BaF]^+$ in water by ab initio method and compared the results of theory and experiment to determine hydration number of $[BaF]^+$. Also, we investigated the effect of the number of water molecules present on the ion-pair properties by determining the NQR and NMR parameters.

2. Results and discussion

2.1. Ion-pairing in aqueous solution of BaF_2

Using NMR spectroscopy, we focused on the following ion-pairing:

$$Ba^{2+} + F^- \leftrightarrows [BaF]^+ : \quad K = \frac{a_{[BaF]^+}}{a_{Ba^{2+}} a_{F^-}} \tag{1}$$

Careful analysis of NMR spectra for a nucleus exchanging among different environments yields information about the exchange process. For process involving ion solvation, one can investigate the NMR spectroscopy of the solvent such as water [18]. In addition, comparing experimental data to Fuoss theory leads to evaluate ion association phenomenon and the type of ion-pair [1,8].

NMR investigation of the ion provides direct evidence of exchange ^{19}F. Also, NMR studies of the aqueous salt solutions at room temperature show a significant variation in the NMR chemical shifts with concentration. In this study, we report the temperature and concentration dependence of ^{19}F NMR shifts of BaF_2 solutions from which we determined equilibrium constants of formation of $[BaF]^+$ as a function of temperature, and then we calculated the enthalpy and the entropy of ion-pair formation in aqueous solution.

The NMR spectra of the fluoride ion in BaF_2 solution at different concentrations and temperatures consist of a single sharp resonance. Fig. 1 shows that chemical shift is strongly temperature-dependent at constant concentration. The NMR method enables us to study the phenomenon of ion-pairing. When the exchange of the F^- ion between the free state and ion-pair state (according to reaction 1) is fast, dependence of chemical shifts on the concentration of the F^- ion can be treated as follows [18–20,38]:

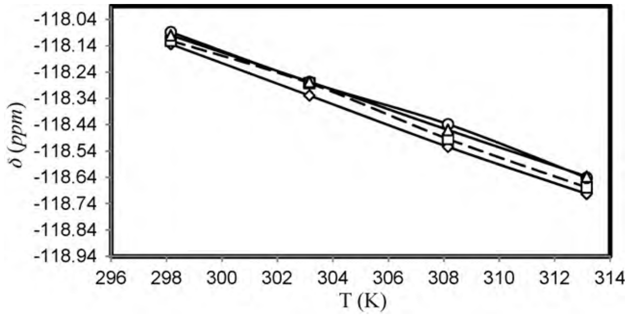

Fig. 1. Variation in chemical shift as a function of temperature at constant concentration: 0.0018 (◇), 0.0035 (△), 0.0038(○), 0.0043 (□). All concentrations are in mol L^{-1}.

$$\delta = \alpha\delta_{free} + (1-\alpha)\delta_{ion-pair} \tag{2}$$

where δ_{free} and $\delta_{ion-pair}$ are the chemical shifts of the F^- ion in the free and ion-pair states, respectively, and α is the fraction of the total F^- ions that are free in solution. The inverse of the exchange rate, τ, (mean lifetime) is given by [18]:

$$\tau = \frac{\tau_{free}\tau_{ion-pair}}{\tau_{free} + \tau_{ion-pair}} \tag{3}$$

where τ_{free} and $\tau_{ion-pair}$ are the lifetimes of the F^- ion in the free and ion-pair states, respectively.

It is obvious that there is a critical total concentration, M^*, below which ($\alpha = 1$) the ion-pair, $[BaF]^+$, is not formed, while above it ($\alpha < 1$), it is formed. Thus as an approximation, we may assume that:

$$\alpha = \frac{M^*}{M_{tot}} \tag{4}$$

where M_{tot} represents the total concentration (in mol L^{-1}) of BaF_2 in solution. Substituting Eq. (4) into Eq. (2) gives:

$$\delta = \left(\frac{M^*}{M_{tot}}\right)\delta_{free} + \left(1 - \frac{M^*}{M_{tot}}\right)\delta_{ion-pair} \tag{5}$$

or

$$\delta = \delta_{ion-pair} + \frac{M^*}{M_{tot}}(\delta_{free} - \delta_{ion-pair}) \tag{6}$$

Therefore, if $M_{tot} \le M^*$, then $\delta = \delta_{free}$ and $\alpha = 1$, but if $M_{tot} > M^*$, then $\delta = \delta_{ion-pair}$ (neglecting the second term in Eq. (6)) and $\alpha < 1$.

The overall plots of Eqs. (5) and (6) against the inverse of total concentration, M_{tot}^{-1}, of BaF_2 at a constant temperature gives two straight lines; one is horizontal, corresponding to the condition of $M_{tot} < M^*$ ($\delta = \delta_{free}$), and the other is sloped, corresponding to $M_{tot} > M^*$ (Fig. 2), while the intercept of the plot gives $\delta_{ion-pair}$. $\delta_{ion-pair}$ was determined using curve fitting the plot of δ versus M_{tot}^{-1} to linear equation and determining intercept of equation. It is clear that $\delta = \delta_{free}$, if the observed chemical shift is independent of M_{tot}.

Determining δ_{free} and $\delta_{ion-pair}$ by the procedure mentioned and substituting them into Eq. (2) yields the value of α. Thus we may calculate the stability constant for formation of $[BaF]^+$, as follows:

$$\begin{array}{l} Ba^{2+}_{(aq)} + F^- \leftrightarrows [BaF]^+ : \quad K' = \dfrac{[BaF^+]}{\left[Ba^{2+}\right][F^-]} \\ M_{tot}(2\alpha - 1) \quad 2M_{tot}\alpha \quad 2M_{tot}(1-\alpha) \\ K' = \dfrac{(1-\alpha)}{M_{tot}(2\alpha^2 - \alpha)} \end{array} \tag{7}$$

$$K = \frac{a_{BaF^+}}{a_{Ba^{2+}} a_{F^-}} \tag{8}$$