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Thermodynamic Study of Ion pairing in Aqueous Solution of BaF_2 by ^{19}F -NMR

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ABSTRACT

The ion- pair association constant values, related to the reaction $Ba^{2+} + F^{-} \leftrightarrows [BaF]^{+}$, were determined by means of the NMR spectroscopy. The values of the thermodynamic functions of the ion pairing process were calculated on the basis of the NMR results. In addition, the association entropy was found to be dependent on the temperature. Comparing the experimental data and the Fuoss theory it is found that BaF^{+} ion- pair is formed in the BaF_2 aqueous solution.

Keywords: ion- pair; ion association; association constant; NMR spectroscopy

INTRODUCTION

In the Debye- Hückel theory, it is assumed that strong electrolytes dissociate completely in aqueous solution. 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 dimentions, high ion valence and small solvent dielectric constants are conductive to ion pair formation.

In the Debye- Hückel model of strong electrolyte solutions, the electric potential, ψ , at a point distant r from the central ion and the average charge density, ρ, at this point are related through the Poisson's equation [1]

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\rho\frac{4\pi}{D} \qquad (1)$$

where D is the dielectric constant. The charge density at the given point is given by the Boltzmann distribution law as

$$\rho = \Sigma N_i^* Z_i e.\exp\left(\frac{-Ze\psi}{kT}\right) \qquad (2)$$

where N_i is the number of ions of charge $Z_i e$ in unit volume, $Ze\psi$ is the electrical work required to bring an ion of charge Ze to this point from infinity and k is the Boltzmann constant.

These two equation could be combined to eliminate ρ and yield an equation between ψ and r from which all ionic atmosphere effects could be evaluated. The rigorous solution of this combination is difficult, but if we assume $Ze\psi/kT \ll 1$, then $\exp(-Ze\psi/kT) \approx 1 - Ze\psi/kT$, so, the solution will be straightforward. However, the result, and the Debye- Hückel equation, will be valid for large values of r compared to the distance

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of the closest approach between ions specially for multiply charged ions, it will be possible for ions to approach one another sufficiently closely for there to be a region in which the approximation is not valid, and then the effects of inter- ionic attraction are not fully covered by the Debye- Hückel model. This problem has been discussed by Müler [2], Gronwall and La Mer [3], Bjerrum [4] and Guggenheim [5].

Bjerrum's approach yields for small values of r (small compared with the mean distance separating ions in solution), the probability, w, of finding an ion of the ith kind at a distance between r and r + dr from the central ion (of the kth kind) is

$$w = \frac{NM_i}{1000} 4\pi r^2 dr \exp(\varphi / kT) \qquad (3)$$

where Mi is the molar concentration of the considered ion and φ is the work of separation of the two ions; this is given, according to Coulomb's law, by

$$\varphi = - Z_i Z_j e^2 / Dr \qquad (4)$$

For oppositely charged ions, the probability tends to infinitely large values as the distance between the charges diminishes. The plot of equation (3) against r yields a curve with a minimum at point q, given by

$$q = Z_i Z_j e^2 / 2DkT \qquad (5)$$

(this distance is about 3.5 °A for univalent ions in water at 25 °C). At this point, the work of separation the ions is equal to 2 kT- that is, to four times the mean kinetic energy per degree of freedom- and Bjerrum proposed that ions separated by a distance smaller than q should be treated as ion pairs. So, all other ions could be considered free, and for these more distant ions the Debye- Hückel treatment will be a good approximation. He then developed formulae describing the degree of ion-association and the ion pair stability constant, K,

$$K = \frac{4\pi a^3}{1000} b^3 \int_2^b x^{-4} e^x dx \qquad (6)$$

where N is the Avogadro constant and b and x given by

$$b = \frac{|Z_i Z_j| e^2}{aDkT} ; \; x = \frac{Z^2 e^2}{rDkT} \qquad (7)$$

Parameter a represents the closest of approach of ions, and has to be determined experimentally for a given ion pair. Equation (6) does however show the influence of various factors (ionic valances, temperature and properties of the solvent) on association. For water at 298 K, $D = 78.30$, $e^2 / DkT = 0.7157\,\text{nm}$ and $q = 3.57 |Z_i Z_j|$ °A

Several methods of studying ion- pairing, including conductivity methods [6-12], ion-selective electrode potentiometry [13], gravimetric and solvent evaporation [14], and NMR spectroscopy [15,16,17] and theoretical modeling [18,26], have been used to probe the phenomenon of ion association in both aqueous and non aqueous solvents.

The phenomenon of ion association from the various aspects, e.g. plating and holding of tertiary structure of enzymes and proteins [19], maintaining the micelle stability [20], lowering the electric conductivity in Li-ion battery electrolytes, is of great interest.

Ion-pairing in aqueous solution of BaF_2

Using NMR spectroscopy, we focus on the following ion- pairing

$$Ba^{+}_{(aq)} + F^{-}_{(aq)} \leftrightarrows [BaF]^{+}_{(aq)} : K = \frac{a_{BaF^+}}{a_{Ba^{2+}} a_{F^-}} \qquad (8)$$

The phenomenon can be studied by determining the self- diffusion coefficient by using the PFG-NMR method [21,22].

Careful analysis of NMR spectra of 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 [15]. In addition, comparing experimental data to Fuoss theory leads to evaluate ion-association phenomenon.

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

EXPERIMENTAL

BaF_2 was purchased from Merck Company and used without further purification. For determining solubility of BaF_2, the saturated solution of BaF_2 was prepared (using deionized water). Then solutions of BaF_2 (at different concentration) were prepared by making of stock solution (to 0.00559 M). Then from this solution were prepared other solutions by dilution with deionized water.

We add to samples a few D_2O, because when chemical shifts were measured, the magnetic field was "locked" to the ${}^2H$ signal of the heavy water used as a solvent. For the purpose of the line width determination, special attention was paid to optimize the homogeneity of the magnetic field.

A Bruker advanced 500 MHz spectrometer was used to obtain ${}^{19}F$ NMR spectra at 470.59 MHz at temperatures between 298.15K and 313.15K.

As an external reference to calibrate the chemical shift scale, we used $CFCl_3$ in different temperatures were recorded.

The 90^{o}- pulse width was 26.5 μs and the relaxation delay was 1 s. Typically, signal averaging of 128 scans gave spectra with acceptable signal- to- noise ratios for all samples down 0.0015 M. All shifts are accurate to ± 0.1 ppm. Temperature was measured to a precision of ± 1 K.

RESULT AND DISCUSSION

The NMR spectrum of the fluoride ion in BaF_2 solution at different concentrations and temperatures as we investigated consists of a single sharp resonance. Figure I 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 the reaction 8) is fast the dependence of chemical shifts on the concentration of the F^- ion can be treated as follow [15,16,17,23]

$$\delta = \alpha\delta_{free} + (1-\alpha)\delta_{ion-pair} \qquad (9)$$

where δ_{free} and $\delta_{ion-pair}$ are the chemical shifts of the F^- ion in the free and ion- pair, $[BaF]^+$, 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 [15]

$$\tau = \frac{\tau_{free}\tau_{ion-pair}}{\tau_{free} + \tau_{ion-pair}} \qquad (10)$$

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^*, of BaF_2, bellow which the ion- pair, $[BaF]^+$, doesn't form $(\alpha = 1)$, while above it does form $(\alpha < 1)$. Thus, as an approximation we may assume

$$\alpha = \frac{M^*}{M_{tot}} \qquad (11)$$

where M_{tot} represents the total concentration (in mol L^{-1}) of BaF_2 in solution. Substituting eq. (11) into eq. (9) gives

$$\delta = \left(\frac{M^*}{M_{tot}}\right)\delta_{free} + \left(1 - \frac{M^*}{M_{tot}}\right)\delta_{ion-pair} \qquad (12)$$

or

$$\delta = \delta_{ion-pair} + \frac{M^*}{M_{tot}}(\delta_{free} - \delta_{ion-pair}) \qquad (13)$$

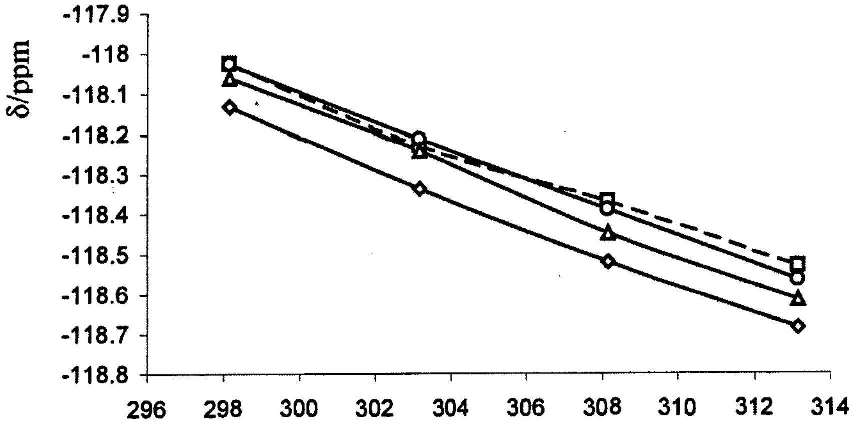

Fig 1. Variation of chemical shift as a function of temperature at constant concentration; $0.0043\,mol\,L^{-1}$ (□), $0.0038\,mol\,L^{-1}$ (O), $0.0035\,mol\,L^{-1}$ (Δ) and $0.0018\,mol\,L^{-1}$ (◇).

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 13) and $\alpha<1$

The overall plot of equations (12) and (13) 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 $M_{tot} > M^*$ (figure 2), while the intercept of the plot gives $\delta_{ion-pair}$. 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 mentioned procedure and substituting them into eq. (9) yields the value of α. Thus, we may calculate the stability constant of formation of $[BaF_2]^+$ as follow:

$$\underset{M(2\alpha-1)}{Ba^{2+}_{(aq)}} + \underset{2M\alpha}{F^-_{(aq)}} \leftrightharpoons \underset{2M(1-\alpha)}{BaF^+} \quad ;K'_c=\frac{[BaF^+]}{[Ba^{2+}][F^-]}$$

or

$$K'_c=\frac{(1-\alpha)}{M_{tot}(2\alpha^2-\alpha)} \qquad (14)$$

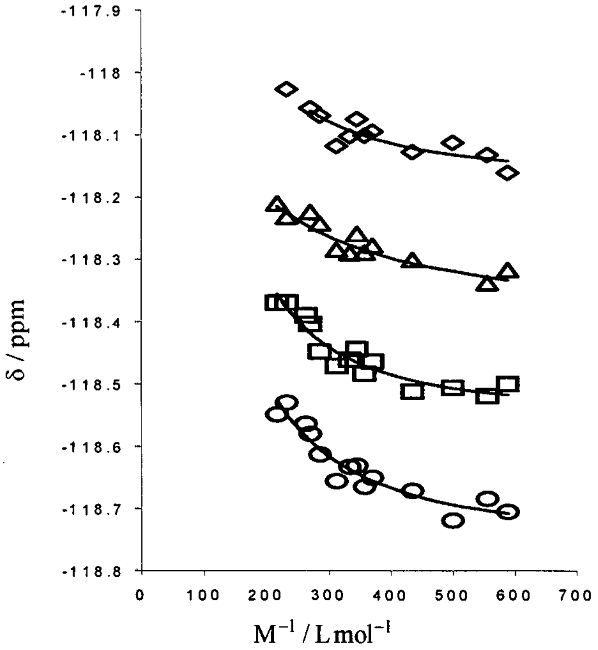

Fig 2. Variation of the ^{19}F NMR shift as a function of the inverse of total concentration of BaF_2 at 298.15 K (◇), 303.15K (△), 308.15K (□) and 313.15K (○).

We should express the stability constant of formation of BaF_2 in term of activities. So

$$K'_a=\frac{a_{BaF^+}}{a_{Ba^{2+}}a_{F^-}} \qquad (15)$$

where

$a_{BaF^+}=[BaF^+]f_{ion-pair}$; $a_{Ba^{2+}}=[Ba^{2+}]f_+$; $a_{F^-}=[F^-]f_-$

and f represent activity coefficients respectively.

Individual ion activity can be calculated by use of the extended Debye- Hückel equation

$$\log f_i=-AZ_i^2\left\{\sqrt{I}/(1+Ba\sqrt{I})\right\} \qquad (16)$$

Table 1. A and B constants for water at various temperatures

Table 1. A and B constants for water at various temperatures

Temperature (°C)	A	B×10^{-8}(cgs)
25	0.5115	0.3291
30	0.5161	0.3301
35	0.5206	0.3312
40	0.5262	0.3323

As equations (14) and (15) show, the association constants are concentration dependent. But the standard association constant, K, related to the ion- pair BaF^+ can be determined at intended temperature by the following linear extrapolation

$$\log K'=\log K-bI \qquad (17)$$

where I is the total effective ionic strength in term of mol L^{-1} and b is an empirical parameter. The values of log K obtained by this approach are listed in table 2.

On the other hand, one can estimate the association constant for various ion- pairs, on the basis of Fuoss theory [21], in dilute electrolyte solutions, as

$$\ln K_f=\ln\left(4\pi a^3N/3000\right)+|Z_+Z_-|e^2/aDkT \qquad (18)$$

where N is the Avogadro constant, k is the Boltzmann constant, e is the elementary charge and a is the distance of the closest approach between two ions. The values of $\log K_f$ calculated from equation (18) are also listed in table2. The concordance between the experimental and estimated values of log K is satisfactory.

Table 2. Experimental and estimated (on the basis of Fuoss theory) values of logK

Temperature (°C)	D^1	$LogK_f$	LogK	D^2	LogK
25	78.54	2.38	2.50	76.48	2.37
30	76.76	2.40	2.48	75.54	2.40
35	75.03	2.43	2.44	74.95	2.44
40	73.34	2.47	2.40	74.39	2.46

Regarding the NMR results and Fuoss model, one can conclude that the degree of dissociation and association constants of ion- pairing are temperature and dielectric constant dependent. Our experimental results show that $\ln K$ is a linear function of 1/DT

$$\ln K = A + B/DT \qquad (19)$$

where K represents the association constant of formation of $[BaF]^+$.

Our results were fitted by the table curve software on the basis of eq. (19) and obtained, A = -62.9988 and $B = 1.5954 \times 10^6 K^{-1}$, with a coefficient of correspondence $r = 0.947$

DETERMINATION OF THERMODYNAMIC FUNCTIONS

The standard molar thermodynamic functions $\Delta G^o_m, \Delta H^o_m$ and ΔS^o_m related to equation (8) were determinated as follow [25]:

$$\Delta G^o_m = -RT(A + B/DT) \qquad (20)$$

$$\Delta S^o_m = R[A - (B/D^2)(\partial D/\partial T)_P] \qquad (21)$$

$$\Delta H^o{}_m = -(RB/D)[1 + (T/D)(\partial D/\partial T)_P] \qquad (22)$$

The results are listed in table 3 and can be interpreted as follows:

$$Ba^{2+}(H_2O)_x + F^-(H_2O)_y \leftrightarrows [BaF]^+(H_2O)_Z + (x + y - z)H_2O \qquad (23)$$

1) A new bond is formed between Ba^{2+} and F^- ions
2) The water molecules are liberated from the hydration spheres
3) The liberated water molecules become bound to bulk water.

For the first and third steps, ΔH^o_m and ΔS^o_m are both expected to be negative. For the second step, ΔH^o_m and ΔS^o_m are both positive because in this step bond is lost. The experimental association entropy is the sum of the three step and its values increase with increasing temperature. The experimental enthalpy is positive and varies moderately with temperature. These considerations appear that electrostatic interaction is essential in the ion association process. However, when $\Delta G^o_m < 0$, the ion association reaction can occur spontaneously under the condition of constant temperature and pressure.

Table 3. Thermodynamic functions of formation of ion-pair $[BAF]^+$

Temperature (°C)	ΔG^o_m ($kJmol^{-1}$)	ΔS^o_m ($Jmol^{-1}K^{-1}$)	ΔH^o_m ($kJmol^{-1}$)
25	-13.53	76.84	9.38
30	-13.93	79.32	10.12
35	-14.34	81.97	10.92
40	-14.76	91.22	13.81

CONCLUSION

The subject of ion association was applied to specific case where electrostatic interactions are chemically more significant than structural considerations. The nonideality of aqueous electrolyte solutions was viewed as having physical (activity coefficient) and chemical (ion-pairing) components, whose contributions depend on the magnitudes of ionic charges, concentrations and dielectric constants.

In this work, the effect of these factors on thermodynamic values of solubility product and stability constant of formation of ion-pair is investigated. Our NMR results provide an interesting insight into the ion-pairing process in aqueous solution. At finite concentrations there is a measurable fraction of fluoride ions in solution that exists as the complex. At temperatures near to 313.15 K, $[BaF]^+$ becomes more stable than the separately hydrated Ba^{2+} and F^- ions in solution. This observation suggests that the effect of increasing the temperature is to weaken the bonding of water in the hydration sphere of the aquated ions, allowing the two ions to approach each other more easily through their electrostatic interaction to from the ion-pair.

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