
Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 2 (3)
(2005)

Science and Research Campus
ISSN: 1735-2126

**Thermodynamics of Non-Ideality and Ion-Association
in Saturated Aqueous Solution of Barium Nitrate at 25 °C**

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ABSTRACT

Using Solvent Evaporating and Atomic Emission Spectrophotometric methods, the solubility of Ba(NO₃)₂ in water at 25.0 °C was determined. Activity coefficients, f_+ and f_- of Ba_(aq)²⁺ and NO_{3(aq)}⁻ ions in the saturated solution at 25.0 °C were estimated upon the extended Debye-Hückel theory and then, the constant $K'_{sp} = [Ba^{2+}]f_+ [NO_3^-]^2 f_-^2$ was evaluated. Comparing the value of thermodynamic solubility product constant, $K_{sp(th)}$, of Barium Nitrate, $K_{sp(th)} = \exp(-\Delta G_{diss}^\circ / RT)$, to the value of K'_{sp} revealed a great difference.

The difference has satisfactorily been explained using a combination of Debye-Hückel theory and ion-association theory.

Keywords: Barium Nitrate; Solubility product; Ion-association; Activity coefficient

INTRODUCTION

The major studies of physico-chemical behaviors of aqueous electrolyte solutions almost require consideration of non-ideality and ion-association phenomenon [1-3]. It is very worthwhile, therefore, to regard these phenomena when interpreting the related experimental data. A strong electrolyte solution deviates, partly by non-ideal behavior of ions in the solution and partly by ion-association from ideality. The first contribution could be evaluated by the values of activity coefficients of considered ions which can be estimated upon some theoretical models [4-6]. On the other hand, the ion-association contribution, in turn, can

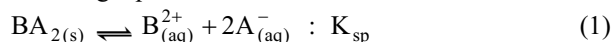
be studied both theoretically and experimentally [7-15].

In very dilute ionic solutions, the ions are sufficiently far apart that ionic interactions between them are negligible. Therefore, under these circumstance, one can expect the ideal behavior for the ionic solution of interest. In contrast, in an ionic solution that is not sufficiently dilute the ionic interactions are noticeable, so the solution exhibits the non-ideal behavior. The effect of non-ideality can be studied from the way in which certain properties of the solution, such as its molar conductivity, vary with concentration. Furthermore, when the electrolyte solutions are not very dilute the ion-association phenomenon takes place and contributes a more non-ideality to the solution compartment.

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BACKGROUND

Consider an ionic compound as BA_2 which is composed of B^{2+} and A^- ions and assume that its solubility in water at room temperature is fairly small. In saturated solution of BA_2 , one can consider following equilibrium:



$$K_{sp} = a_{B^{2+}} a_{A^-}^2 = [B^{2+}][A^-]^2 f_+ f_-^2 \quad (2)$$

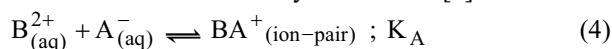
Neglecting the ion-association, at the first approximation, in the solution, one can calculate the solubility product constant, K'_{sp} , of BA_2 by measuring the solubility, $s/\text{mol L}^{-1}$, of BA_2 and estimating the activity coefficients, f_+ and f_- based on a suitable model and inserting them into the eq.(2). On the other hand, the thermodynamic solubility product constant, $K_{sp(th)}$, of the same salt can be calculated from ΔG° of equilibrium (1)

$$K_{sp(th)} = e^{-\Delta G_{diss}^\circ / RT}$$

$$\Delta G_{diss}^\circ = (\Delta G_{f(B^{2+})}^\circ + 2\Delta G_{f(A^-)}^\circ) - \Delta G_{f(BA_2)}^\circ \quad (3)$$

For many ionic compounds, it has been seen that there is a great difference between K'_{sp} and $K_{sp(th)}$ and almost always K'_{sp} is greater than $K_{sp(th)}$ [3, 16].

To explain the difference, we should also consider the ion-association phenomenon in electrolyte solutions. For many decades ion-association in electrolyte solutions has been an area of active research interest [7-20]. Bjerrum theoretical approach provides following results for association constant, K_A , of ion-pair formation in dilute electrolytic solutions [9]



$$K_A = \frac{4\pi N a^3 b^3}{1000} Q_{(b)} \quad (5)$$

$$Q_{(b)} = \int_2^b e^{x} x^{-4} dx \quad (6)$$

$$b = \frac{|z_+ z_-| e^2}{a\epsilon\kappa T} ; x = \frac{|z_+ z_-|}{r\epsilon\kappa T} \quad (7)$$

where, N is Avogadro constant, a is the closest of approach of ions, ϵ represents the dielectric constant, κ is Boltzmann constant, T denotes temperature in Kelvin and BA^+ refers to the respective ion-pair which is composed of B^{2+} and A^- ions. On the other hand, Fuoss theoretical approach leads to the contact ion-pair and the following expression for K_A [7, 12]

$$K_A = ca^3 e^{c'z^2/a\epsilon T} \quad (8)$$

where a is parameter of the closest approach of ions in cm, $c = 2.522 \times 10^{21}$ and $c' = 1.674 \times 10^{-3}$

EXPERIMENTAL

$Ba(NO_3)_2$ and other chemicals were purchased from Merck Company and used without further purification. The saturated solution of $Ba(NO_3)_2$ in deionized water was prepared at $25.0^\circ C$, and then the solubility of $Ba(NO_3)_2$ in water was determined using Solvent Evaporating and Atomic Emission Spectrophotometric methods. Our experimental results are given in table 1.

Table 1. Solubility, s , (mol L^{-1}) of $Ba(NO_3)_2$ at $25.0^\circ C$ (using solvent evaporating method)

| Iteration | Solubility/ mol L^{-1} |
|-----------|---------------------------------|
| 1 | 0.400 |
| 2 | 0.391 |
| 3 | 0.410 |
| 4 | 0.400 |
| 5 | 0.409 |
| 6 | 0.415 |
| 7 | 0.416 |

Average: $0.406 \pm 0.007 \text{ mol L}^{-1}$

The result obtained from Atomic Emission Spectrophotometric method is 0.414 mol L^{-1} .

DISCUSSION

The solubility product constant, K'_{sp} , of $Ba(NO_3)_2$ at $25.0^\circ C$, on the basis of this work and estimated mean activity coefficient, f_{\pm} , upon extended Debye- Hückel theory:

$$\log f_{\pm} = -A |Z_+ Z_-| \sqrt{I} / (1 + Ba \sqrt{I}) \quad (9)$$

is:

$$\begin{aligned} K'_{sp} &= [Ba^{2+}][NO_3^-]^2 f_{\pm}^3 \\ &= 4s^3 f_{\pm}^3 \\ &= 4(0.406)^3 (0.3476)^3 = 1.124 \times 10^{-2} \text{ mol}^3 \text{ L}^{-3} \end{aligned}$$

while, to use the Debye – Hückel equation, we have taken

$$A = 0.509, B = 0.328 \text{ } ^\circ A^{-1} ,$$

$$a = (a_+ + a_-)/2 = (5 + 3)/2 = 4^\circ A$$

On the other hand, using thermodynamic functions given in table 2, one can calculate the thermodynamic solubility constant, $K_{sp(th)}$, of $Ba(NO_3)_2$ at the same conditions:

$$\begin{aligned}\Delta G_{\text{diss}}^{\circ} &= \Delta H_{\text{diss}}^{\circ} - T\Delta S_{\text{diss}}^{\circ} \\ &= 2\Delta G_{\text{f}(\text{NO}_3^-)}^{\circ} + \Delta G_{\text{f}(\text{Ba}^{2+})}^{\circ} - \Delta G_{\text{f}(\text{Ba}(\text{NO}_3)_2)}^{\circ} \\ &= 2(-110.6) - 560.7 - (-795) = 13.1 \text{ kJmol}^{-1}\end{aligned}$$

Or

$$K_{\text{sp}(\text{th})} = e^{-\Delta G_{\text{diss}}^{\circ}/RT} = 5.05 \times 10^{-3}$$

Table 2. Thermodynamic functions of $\text{Ba}_{(\text{aq})}^{2+}$ and $\text{NO}_{3(\text{aq})}^-$ ions and $\text{Ba}(\text{NO}_3)_2(\text{s})$ salt at 298 K [21]

| Species | $\Delta H_{\text{f}}^{\circ}/\text{kJmol}^{-1}$ | $\Delta G_{\text{f}}^{\circ}/\text{kJmol}^{-1}$ |
|--------------------------------------|---|---|
| $\text{Ba}_{(\text{aq})}^{2+}$ | -538.3 | -560.7 |
| $\text{NO}_{3(\text{aq})}^-$ | -206.6 | -110.6 |
| $\text{Ba}(\text{NO}_3)_2(\text{s})$ | -992 | -795 |

Comparing the values of K'_{sp} and $K_{\text{sp}(\text{th})}$ reveals that the difference between them is large. The difference may be attributed to the formation of BaNO_3^+ ion- pair at the first approximation. If x denotes the concentration (in mol L^{-1}) of BaNO_3^+ ion- pair in the saturated aqueous solution of $\text{Ba}(\text{NO}_3)_2$ at 25.0°C , then $(s-x)$ and $(2s-x)$ will represent the molarities of $\text{Ba}_{(\text{aq})}^{2+}$ and $\text{NO}_{3(\text{aq})}^-$ ions in the free state in the saturated solution at the same temperature respectively. So, $K_{\text{sp}(\text{th})}$ may be adapted as:

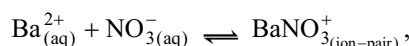
$$\begin{aligned}K_{\text{sp}(\text{th})} &= a_{\text{Ba}^{2+}, \text{free}} a_{\text{NO}_3^-, \text{free}}^2 \\ &= [\text{Ba}^{2+}]_{\text{free}} [\text{NO}_3^-]_{\text{free}}^2 f_{\pm}^3 \\ &= (s-x)(2s-x)^2 f_{\pm}^3 \\ &= (-x^3 + 5sx^2 - 8s^2x + 4s^3) f_{\pm}^3\end{aligned}\quad (10)$$

Now we assume that the extended Debye- Hückel law: $\log_{10} f_{\pm} = -0.509|Z_+Z_-|\sqrt{I}/(1+a_{\pm}B\sqrt{I})$ is a good approximation for estimating f_{\pm} . Therefore, the value of x can be resulted from solving the equation (10). In order to calculate f_{\pm} we assume $I = 3s$ at the first approximation and then calculate an approximate value of x after eq. (10). Then, iterating the calculation, but taking $I = 3s - 2x$, we will obtain a more precise value of x progressively (Table 3).

Table 3. Five successive calculation in order to achieve a reasonable value of $[\text{BaNO}_3^+]_{\text{ion-pair}}$

| Iteration | $I/\text{mol L}^{-1}$ | $x = [\text{BaNO}_3^+]/\text{mol L}^{-1}$ |
|-----------|-----------------------|---|
| 1 | 1.218 | 0.1396 |
| 2 | 0.9388 | 0.1644 |
| 3 | 0.8892 | 0.1692 |
| 4 | 0.8796 | 0.1701 |
| 5 | 0.8778 | 0.1701 |

Regarding the results of iterating calculation, we may assume $[\text{BaNO}_3^+] = 0.170$, $[\text{Ba}^{2+}]_{\text{free}} = 0.236$ and $[\text{NO}_3^-]_{\text{free}} = 0.642 \text{ mol L}^{-1}$ in saturated aqueous solution of $\text{Ba}(\text{NO}_3)_2$ at 25.0°C . So, the equilibrium constant, K_A , for the reaction of ion- pair formation:



at the same conditions is:

$$\begin{aligned}K_A &= \frac{a_{\text{i-p}}}{a_+ a_-} = \frac{[\text{BaNO}_3^+] f_{\text{i-p}}}{[\text{Ba}^{2+}] [\text{NO}_3^-] f_{\pm}^2} \\ &= \frac{0.170 \times 0.728}{0.236 \times 0.642 (0.3733)^2} = 5.86\end{aligned}\quad (11)$$

and

$$\Delta G_{\text{i-p}}^{\circ} = -RT \ln K_A = -4381 \text{ Jmol}^{-1}\quad (12)$$

Now, estimating the value of K_A from eq. (8) and taking $a = 4.0 \times 10^{-8} \text{ cm}$ and $z = |z_+ z_-| = 2$, we obtain

$$\begin{aligned}K_A &= 2.552 \times 10^{21} \times (4.0 \times 10^{-8})^3 e^{2 \times 1.674 \times 10^{-3} / 4.0 \times 10^{-8} \times 78.54 \times 298} \\ &= 5.74\end{aligned}$$

As we can see, the concord between estimated and experimental values of K_A is excellent.

CONCLUSION

Saturated aqueous solution of $\text{Ba}(\text{NO}_3)_2$ is far from ideality. The non- ideality of the solution may be interpreted as due partly to physical (activity coefficients) and partly to chemical (ion- association) factors. These contributions do predict a concordant fit of experimental data. On the other hand, the solubility of $\text{Ba}(\text{NO}_3)_2$ could be divided in three contributions; one, $\sqrt[3]{K_{\text{sp}(\text{th})/4}} = 0.108$, the other, $[\text{BaNO}_3^+]_{\text{i-p}} = 0.170$ and the third, activity coefficient contributions = 0.128 mol L^{-1}

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