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Non- Ideality and Ion-Pairing in Saturated Aqueous Solution of Lithium Carbonate at 25°C

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ABSTRACT

Using Solvent Evaporating and Atomic Emission Spectrophotometric methods, the solubility of Li_2CO_3 in water at 25°C was determined. Comparing the value of thermodynamic solubility product constant, Ksp(th), $(K_{sp(th)} = \exp(-\Delta G^{\circ}_{diss}/RT))$ of the mentioned salt to the value which is obtained from the observed solubility, **s/molL^{-1}**, and activity coefficients, f_+ and f_-, which are estimated upon the extended Debye- Hückel law, $K'_{sp} = [Li^+]^2[CO3^{-2}]f_+^2 f_-$, revealed a great difference. The difference has satisfactorily been explained using a combination of Debye-Hückel law and Ion-Association Theory.

Keywords: Solubility product; Ion-association; Ion-pair; Activity coefficient; Non ideality

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INTRODUCTION

Comparative studies of aqueous electrolyte solutions generally always require consideration of non-ideality and ion-association. It is vital, therefore, that one regards these phenomena in order to interpret the related experimental data. A strong electrolyte solution deviate, Partly by non-ideality (physical factor) or activity coeficients and partly by ion- association(chemical factor) from ideality. The non- ideality contribution could be evaluated by activity coefficients which can be estimated upon some theoretical models [1-5]. The ion-association contribution, in turn, can be studied both theoretically and experimentally by using several approahes [6-14].

When the concentration of an electrolyte solution tends toward zero, the ions are sufficiently far apart that coulombic interactions between them are negligible. Under these circumstance the ions behaviour is independent from each other and the electrolyte behaves as an ideal solution. As the concentration increases, the average distance between the ions decreases,so interactions between them become considerable and the solution becomes progressively less ideal. In addition, the ion-solvent interactions that are present even in the ideal solution also become increasingly modified as the concentration increases, again making a progressively increasing contribution to non- ideality. The solvent- solvent interactions become also modified- a further contribution to non-ideality. The effects of non- ideality and ion-association can be observed from the way in which certain properties of the solution, such as its molar conductivity, vapour pressure,… vary with concentration.

BACKGROUND

Consider an ionic compound as B_2A which is composed of $2B^+$ and A^{2-} ions and assume that its solubility in water at room temperature is fairly small. Therefore in saturated solution of ionic compound B_2A, one can consider following equilibrium

$$B_2A_{(s)} \rightleftharpoons 2B^+_{(aq)} + A^{2-}_{(aq)} : K_{sp} \quad (1)$$

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

Neglecting the ion-association, at the first approximation, in the solution, one can calculate the solubility product constant, K'_{sp}, of B_2A by measuring its solubility, s/molL^{-1}, and estimating the activity coefficients, f_+ and f_-, based on a suitable model and inserting them into 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)

$$K_{sp(th)} = e^{-\Delta G^\circ_{diss}/RT} \; ; \quad (3)$$
$$\Delta G^\circ_{diss} = (2\Delta G^\circ_{f(B^+)} + \Delta G^\circ_{f(A^{2-})}) - \Delta G^\circ_{f(B_2A)}$$

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 $K_{sp(th)}$ [15,16].

One way of explaining the difference, is to consider the ion-association phenomenon in electrolyte solutions. For many decades ion-association in electrolyte solutions has been an area of active research interest [6-20]. Bjerrum theoretical approach provides following results for association constant, K_A, of ion-pair formation in dilute solutions of electrolyts with B A formula. [6]

$$B^+_{(aq)} + A^-_{(aq)} \rightleftharpoons B^+A^-_{(ion-pair)} \; ; K_A \quad (4)$$

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

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

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

where, N is Avogadro constant, a is the closest of approach of ions, ε represents the dielectric constant, K is Boltzmann constant, T denotes temperature in Kelvin and B^+A^- refers to the respective ion-pair. On the other hand, Fuoss theoretical approach leads to the contact ion-pair and the following expression for K_A [6,11]

$$K_A = ca^3 e^{c'/a\varepsilon T} \qquad (8)$$

where a is the parameter of the closest approach of ions in cm, $c=2.522\times 10^{21}$ and $c'=1.66\times 10^{-3}$

EXPERIMENTAL

Li_2CO_3 and other chemicals were purchased from Merck Company and used without further purification. The saturated solution of Li_2CO_3 in deionized water was prepared at 25.0°C, and then the solubility of Li_2CO_3 in water was determined using Solvent Evaporating and Atomic Emission Spectrophotometric methods. Our experimental results are given in table 1.

At the first approximation, if we assume the ideal behavior for the Li^+ and CO_3^{2-} ions in solution and neglect the ion association in Li_2CO_3 solution, we can present the concentration solubility product, Ksp(c), of Li_2CO_3 in term of its solubility, s/molL^{-1}, as follow:

$$Li_2CO_{3(s)} \rightleftharpoons 2Li^+_{aq} + CO^{2-}_{3aq} : Ksp(c)$$

$$\begin{aligned} Ksp(c) &= [Li^+]^2[CO_3^{2-}] \\ &= (2s)^2(s) \\ &= 4s^3 \end{aligned} \qquad (9)$$

Regarding the value of experimental solubility of lithium carbonate, 0.169 molL^{-1} (table 1), we obtain the value of 0.0193 mol^3 L^{-3} for the concentration solubility product, Ksp(c) $=4s^3$, of Li_2CO_3. This value is considerably greater than thermodynamic solubility product, Ksp(th) $=9.278\times10^{-4}$ which is calculated upon eq.(3) and using the data of table 2.

Table 1. Solubility (mol L^{-1}) of Li_2CO_3, in water at 25.0° C (using solvent evaporating method)

Iteration	Solubility, s,/mol L^{-1}
1	0.170
2	0.169
3	0.171
4	0.166

Average: 0.169 ± 0.002 mol L^{-1}

The result obtained from Atomic Emission Spectrophotometric method is 0.168 molL^{-1}.

DISCUSSION

At the second approximation, the more rigorous solubility product constant, K'_{sp}, of Li_2CO_3 in water at 25.0°C, can be obtained on the basis of eq (2). So, estimating the mean activity coefficient, $f_\pm$, upon extended Debye-HÜckel Law, $\log f_\pm = -A|z_+z_-|\sqrt{I}/1+Ba\sqrt{I}$, and exerting it along with the experimental value of s into the eq.(2) we obtain the value of 2.037×10^{-3} for K'_{sp} as follow:

$$Li_2CO_{3(s)} \rightleftharpoons 2Li^+_{(aq)} + CO^{2-}_{3(aq)} : K'_{sp}$$

$$\begin{aligned} K'_{sp} &= [Li^+]^2[CO_3^{2-}]f_\pm^3 \\ &= 4s^3 f_\pm^3 \\ &= 4(0.169)^3(0.4725)^3 = 2.037\times10^{-3} mol^3L^{-3} \end{aligned} \qquad (10)$$

Comparing this value of K'_{sp} with the value of $K_{sp(th)} = 9.278\times10^{-4}$ that is calculated on the basis of data given in table 2 and the relation $K_{sp(th)} = \exp(-\Delta G^0_{diss}/RT)$ reveals a great difference.

One reasonable way to explain this difference is to consider the ion associaon phenomenon as mentioned before. The ions in a given electrolytic solution may be associate to form ion pairs, ion triplets and ion clusters. Now, it is worthwhile to denote that the ΔG^0_{diss} is related to the following equilibrium:

$$Li_2CO_{3(s)} \rightleftharpoons 2Li^+_{(aq)} + CO^{2-}_{3(aq)} : K'_{sp}$$

$$\begin{aligned} \Delta G^0{}_{diss} &= (2\Delta G^0_{f(Li^+)} + \Delta G^0_{f(CO_3^{2-})}] - [\Delta G^0_{f(Li_2CO_3)}] \\ &= [(2\times-293.8) - 528.1] - [-1133] \\ &= 17.3kJ \end{aligned}$$

Table 2. Thermodynamic functions of $Li^{+}_{(aq)}$, $CO_3^{2-}{}_{(aq)}$ and $Li_2CO_{3\,(s)}$ at 298K

Species	$\Delta H_f^o / kJmol^{-1}$	$S^0 / JK^{-1}mol^{-1}$	$\Delta G_f^0 / kJmol^{-1}$	Ref.
Li^+(aq)	-278.5	13.4	-293.8	[21,23]
$CO_3^{2-}(aq)$	-676.2	-56.9	-528.1	[21,23]
Li_2CO_3 (s)	-1216.0	90.4	-1133.0	[23]

Generally, in a given dilute aqueous electrolyte solution, the ion pair formation relative to other kinds of ion association is predominant. So we may focus our attention on the ion pairing in the saturated aqueous solution, of Li_2CO_3.

Now if x denotes the concentration (in $molL^{-1}$) of $Li^+CO_3^{2-}$ ion pair in the saturated solution of Li_2CO_3 at 25.0 °C , then (s-x) will represent the concentration of CO_3^{2-} ions and (2s-x) of Li^+ions in the free state in the considered solution respectively (neglecting the other kind, except the ion – pairing, of ion association). So,$K_{sp(th)}$ of Li_2CO_3 may be equally presented as follow:

$$K_{sp(th)} = (\exp(-\Delta G^0_{diss} / RT) = a_{Li^+,Free}\, a_{CO_3^{2-},free}$$
$$= f_\pm^3 [Li^+]^2_{free} [CO_3^{2-}]_{free}$$
$$= f_\pm^3 (2s-x)^2 (s-x) \qquad (11)$$

were s is solubility (in $molL^{-1}$) of Li_2CO_3 in aqueous solution at 25.0 °C. An alternative from of eq .(11)is:

$$-x^3 + 5sx^2 - 8s^2x + (4s^3 - (K_{sp(th)} / f_\pm^3)) = 0 \qquad (12)$$

Now we assume that the extended Debye-Hückel law

$$\log_{10} f_\pm = -0.509 | z_+ z_- | \sqrt{I}/1 + a_\pm B\sqrt{I} \qquad (13)$$

is a good approximation for estimating $f_\pm$ of Li_2CO_3 in saturated aqueous solution. Therefore, the value of x can be resulted from $f_\pm$, calculated $K_{sp(th)}$=exp(-17300/8.314×298) = 9.278×10^{-4}) and experimental solubility, s,(eq.12).

To calculate $f_\pm$, we need the value of ionic strength, I,. We take I = 3s at the first approximation and calculate an approximate value of x naming x_1. Then, iterating the calculation, but taking $I = (3s - 2.5x_1)$, we will obtain a more precise value of x naming x_2. We iterate the procedure until the difference between two successive x becomes less than %1. So the final value of x will reasonably represent the concentration of $Li^+CO_3^{2-}$ ion-pair in saturated aqueous solution of Li_2CO_3 at 25.0 °C (table3).

Table 3. six successive calculations in order to achieve a reasonable value of $[Li^+CO_3^{2-}]$

Iteration	$I/molL^{-1}$	$f_\pm$ *	$x = [Li^+CO_3^{2-}] / molL^{-1}$
1	0.507	0.4725	0.0573
2	0.3637	0.4998	0.0675
3	0.3383	0.5060	0.0690
4	03330	0.5074	0.0701
5	0.3318	0.5077	0.0702
6	0.3316	o.5078	0.0702

*Regarding eq.(13) to calculate $f_\pm$ we used the following approximation:

$$a_{\pm} = (a_{+} + a_{-})/2 = (6\ {}^{\circ}A + 4\ {}^{\circ}A)/2 = 5.25\ {}^{\circ}A$$

and $Ba_{\pm} = 0.328 \times 5.25 = 1.722$ [22].

As a result of previous calculation, we may assume $[Li^{+}CO_3^{2-}]$=0.0702molL^{-1} and $[Li^{+}]_{free} = 0.2678$ *and* $[CO_3^{2-}]_{free} = 0.0988 molL^{-1}$ in saturated aqueous solution of Li_2CO_3 at $25.0^{\circ}C$. So , K_A for the reaction $Li^{+}_{(aq)}$+ $Li^{+}_{(aq)} + CO_3^{2-}{}_{(aq)}\ \square\ Li^{+}CO_3^{2-}{}_{(ion-pair)}$ is:

$$K_A = \frac{a_{i-p}}{a_{+}a_{-}} = \frac{[Li^{+}CO_3^{2-}]f_{-}}{[Li^{+}][CO_3^{2-}]f_{\pm}^{2}}$$

$$= \frac{0.0702 \times 0.7975}{(0.2678 \times 0.0988)\ (0.5078)^{2}} = 8.206\,Lmol$$

CONCLUSION

Saturated aqueous solution of Li_2CO_3 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 and these contributions do predict a concordant fit of experimental data. The solubility of Li_2CO_3 could be divided in three contributions; one, $\sqrt[3]{K_{sp(th)}/4} = 0.06144 molL^{-1}$, the other, $[Li^{+}CO_3^{2-}]_{i-p} = 0.0702 molL^{-1}$ and the physical factor contribution = 0.03735molL^{-1}. The Percentage of each contribution is 36.4% , 41.5% and 22.1% respectively .

REFERENCES

[1] P. Debye, E. Hückel, Zur theorie der electrolyte, Physik. Zeitschrift 24(1923)185-206 , 305-325.

[2] C. W. Davies, J. Chem. Soc. (1938) 2093.

[3] H.S. Harned, B.B. Owen, Physical Chemistry of Electrolytic Solutions, Third Edition (1958) P. 697.

[4] Van Rysselberghe,p.Eisenberg,P.J.Am.(Chem.,Soc-61(1939)3030.

[5] Margaret , R.W.Lain,L.J.P . Kenneth , D.m.H.J.Chem.Ed.75/3(1998)352.

[6] R.M.,Fuoss, J.Amer. Chem. Soc . 80(1958)5059.

[7] W.,Eblig, Z.physik. Chem..(Leipzig),238(1968)400.

[8] N. Bjerrum, K.Danske Vidensk. Selsk (Math. fys.) Medd. , 7(1926) No.9.

[9] H. Yokoyama, H. Yamatera, Bull. Chem. Soc. Jpn. 48(1975) 1770.

[10] V.S.K. Nair, G.H. Nancollas, J.Chem. Soc. (1958) 3706.

[11] Yu. Ya. Fialkov, V.Yu. Gorbachev, Journal of Molecular Liquids 102/1-3 (2003)277.

[12] T. Takayanagi, Analytical Science February 2004, Vol. 20, The Japan Society for Analytical Chemistry.

[13] S. Kalhori, R. Thomas, A. Al- Khalili, A. Ehlerding, F. Hellberg, A. Neau, M. Larsson, Physical Review, A 69 (2004) 022713, The American Physical Society.

[14] Z. Zhigang, D. Zhenhao, Chemical Physics 297 (2004) 221.

[15] O. Steven Russo, I. George, H. Hanania, J. Chem. Educ. 66 (2) (1989)148.

[16] H. Aghaie, M. Aghaie, Journal of Science, University for Teacher Education, Iran, Vol. 5, No. 1,2 (1993) 25.

[17] R.M. Fuoss, L. Onsager, J. Phys. Chem. 61 (1957) 668, 62 (1958) 1339.

[18] G. Atkinson, S. Petrucci, J. Phys. Chem. 67 (1963) 337.

[19] A.A. Ansari, M.R. Islam, Can. J. Chem. 66 (1988) 1720.

[20] J. Wang, A.D.J. Haymet, J.Chem. Phys. 100 (1994) 3767.

[21] P.N. Atkins, Physical Chemistry, 4 th Edition, table 2.10 (1990).

[22] Fundamental of Analytical Chemistry, by Skoog,D.A.andWest,D.M.,Third Ed.(1976)

[23] Chemistry Data Book, by Stark,J.G.and Wallace,H.G.,2nd.Ed.(1990)p.62.