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The effect of dielectric constant and ionic strength on the solubility of lithium carbonate at 25.0 ^{0}C in thermodynamic view

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ABSTRACT

Using the Solvent Evaporating and Atomic Emission Spectrophotometric methods, the solubilities of Li_2CO_3 were determined in various mixed- solvent "water + ethanol" with various mass percent of ethanol, and in the presence of $NaNO_3$ in various molarities at 25.0°C . The results were interpreted in terms of mean ionic activity coefficient and ion association phenomenon.

Keywords: Dielectric constant; Ionic strength; Thermodynamic solubility product, Ion association

1. INTRODUCTION

The major physico- chemical properties of solutions are influenced by the solvent's dielectric constant. Indeed, in the context of solution chemistry, solvent polarity and solvent dielectric constant are of great interest as a measure of the solvent's ability to stabilize charges or dipoles. As an example, the dissolution of an ionic salt in a solvent depends on the dielectric constant and the polarity of the solvent and on the lattice energy. Of the many theories that have been applied to predict changes in solubility with variation of solvent, the majority is dependent upon changes in the electrostatic properties of the solvent. Numerous relations between solubility of electrolytes and various functions of the dielectric constant,D , of the solvent have appeared in the literature. One of them commonly used is

$$\log s = A_1 + \frac{A_2}{D} \tag{1}$$

where s is the solubility and A_1 and A_2 are constants [1].

Nevertheless, it is easy to find many exceptions to the rule (1). For instance, the solubility of NaF in water, methanol and ethanol at $25.0^{\circ}C$ are 0.973, 0.16 and 0.04 mol kg^{-1}, respectively, while their dielectric constants are 78.54, 32.6 and 24.3, respectively [1,2]. It is apparent, however, that the dielectric constant is not the main determinant of solubility, but rather ion solvation, which depends on the solvent's base strength of the hydrogen- bonding capability. Hence, any improvement should be based on free energy calculation.

Moreover, the solubility of an ionic compound is greatly influenced by the ionic strength of the medium. It is quite obvious that the following equilibrium should be exist in the saturated solution of an ionic compound such as B_2A

$$B_2A_{(s)} \rightleftharpoons 2B^{+}_{(soln)} + A^{2-}_{(soln)} \tag{2}$$

$$K_a = a^2_{B^+}\, a_{A^{2-}} \tag{3}$$

$$K_a = e^{-\Delta G^{\circ}_{diss}/RT} \tag{4}$$

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$$\Delta G^{\circ}_{diss} = (2\Delta G^{\circ}_{f\,(B^{+}_{,so\ln})} + \Delta G^{\circ}_{f\,(A^{2-}_{,so\ln})}) - \Delta G^{\circ}_{f\,(B_2A,s)} \quad (5)$$

So, knowing the standard Gibbs free energy of dissolution, ΔG°_{diss}, then the estimation of Ka is quite straight forward or vice versa.

It is worthwhile to consider the fact that the non- ideality of electrolyte solutions is due partly to the activity coefficient of ions in the solution and partly to the ion- association phenomenon [3-10]. Indeed, when two ions of opposite charges approach enough one another, an ion-pair species may be formed due to the Coulombic interactions [11-18]

$$B^{+}_{(so\ln)} + A^{2-}_{(so\ln)} \rightleftharpoons BA^{-}(ionpair);\ K_A \quad (6)$$

$$K_A = \frac{a_{ip}}{a^{+}a^{-}} \quad (7)$$

where K_A is the association constant for reaction (6) and a_i is respective activity. Attempts have been made to relate association constants to properties of the solvent and the solute, but all are limited in their application and can be used under restricted conditions if the results shall have any meaning [19,20].

The ion- pair concept was introduced by Bjerrum when he considered the probability of finding two ions of opposite charges at a distance, r, from each other [11]. The resulting distribution function has a minimum at a characteristic distance, q,

$$q = \frac{|z_{+}z_{-}|e^2}{2DkT} \quad (8)$$

where D, k and e are the dielectric constant, the Boltzmann constant and the charge of electron, respectively. Bjerrum proposed that an ion located at a distance r < q from the reference ion of opposite charge tends to form an ion pair, whereas any other one outside a sphere of radius q would be considered as being free. Then, the association constant was obtained from the calculation fraction of paired ions

$$K_A = \frac{4\pi N}{1000}\left(\frac{z^2e^2}{DkT}\right)^3 Q(b) \quad (9)$$

where Q(b) is a function that has been computed by Bjerrum for 1<b<15

$$Q(b) = \int_2^b e^x x^{-4} dx \quad (10)$$

$$b = z^2e^2/aDkT;\quad x = z^2e^2/rDkT \quad (11)$$

where a is the distance of closest approach, or mean ionic diameter.

A different approach has been proposed by Fuoss [20]. He obtained the following expression for the association constant of the contact ion pair

$$K_A = \frac{4\pi Na^3}{3000} e^{z^2e^2/DakT}$$

$$= 2.522\times10^{21} a^3 e^{1.674\times10^{-3}z^2/aDT} \quad (12)$$

where D is the dielectric constant, T is temperature, and a is the size parameter in cm.

It is useful to consider the definition of ion-pairs as given by Griffiths and Symons:

1. Complexes; two or more ions held in contact by covalent bonds.
2. Contact ion pairs; ions in contact that do not present any covalent bonding.
3. Solvent- shared ion pairs; pairs of ions linked electrostatically by a single oriented solvent molecule.
4. Solvent- separated ion pair; pairs of ions linked electrostatically but separated by more than one solvent molecule.

2. Experimental

Li_2CO_3 and other chemicals were purchased from Merck Company with high degree of purity and used without further purification. The mixed solvent "water + ethanol" at various mass percents of ethanol (9.897%, 14.856%, 19.962%, 25.171%, 30.392%, 39.542% and 49.084%) and in the presence of $NaNO_3$ salt at various molarities respectively (0.40, 0.35, 0.30, 0.25, 0.20, 0.15 and 0.10) were prepared. Then, the solubility of Li_2CO_3 in each mixture (mixed-solvent with the respective ionic strength due to the presence of $NaNO_3$) was determined at $25.0^{\circ}C$ by the Solvent Evaporating and Atomic Emission Spectrophotometric methods, Table 1.

Table 1. Solubility, s, mol L^{-1}, of Li_2CO_3 in mixed- solvent with respective ionic strength at $25.0^{\circ}C$

Mass percent of C_2H_5OH	Ionic strength / mol L^{1-} of $NaNO_3$	Solubility, s, mol L^{1-}	
		Evaporating method	Emission method
9.897	0.40	0.0964	0.1186
14.856	0.35	0.0792	0.0881
19.962	0.30	0.0563	0.0634
25.171	0.25	0.0435	0.0466
30.392	0.20	0.0331	0.0324
39.542	0.15	0.0202	0.0199
49.084	0.10	0.0118	0.0132

3. Discussion

Regarding the solubility given in Table 1, one may conclude that, the extended Debye-Hückel law (equation 13) is an appropriate approximation for estimating the activity coefficient of ions Li^+ and CO_3^{2-} in the studied solutions

$$\ln\gamma_i = -\frac{Cz_i^2 I_M^{1/2}}{1+Ba_i I_M^{1/2}} \tag{13}$$

where,

$$C = (2\pi N_A)^{1/2}\left(\frac{e^2}{4\pi\varepsilon_\circ DkT}\right)^{3/2} \tag{14}$$

$$B = e\left(\frac{2N_A}{\varepsilon_\circ DkT}\right)^{1/2} \tag{15}$$

$$I_M = \frac{1}{2}\sum_i M_i Z_i^2 \tag{16}$$

In these equations, which are written in SI units, γ_i is the molarity- scale activity coefficient of ion i, Z_i is the elementary charge of ion i, I_M is the ionic strength of solution on the molarity- scale, a_i is the ionic diameter, N_A is the Avogadro constant, k is the Boltzmann constant, e is the proton charge, $\varepsilon_\circ$ is the permittivity of vacuum, D is the medium dielectric constant.

Although the Debye-Hückel law gives γ of each ion, we can not measure γ_+ or γ_- individually. Hence, we should express the law in term of the mean ionic activity coefficient, $\gamma_\pm$, as follow:

$$\ln\gamma_\pm = -\frac{-A\,|z_+z_-|\,I_M^{1/2}}{1+Ba_\pm I_M^{1/2}} \tag{17}$$

Using the SI values of considered parameters and dividing C by 2.3026 to convert to based 10 logs, we get for the mixed solvent (water + ethanol) at $25.0^{\circ}C$:

$$A = \frac{C}{2.3026} = \frac{354}{D^{3/2}}(L/mol)^{1/2} \tag{18}$$

$$B/A^{\circ} = \left(\frac{2.9}{D^{1/2}}\right)(L/mol)^{1/2} \tag{19}$$

Using looyenga equation [21], we have evaluated the dielectric constant of mixed-solvent at various percentage of ethanol (Table2)

$$D_{\text{mixedsolvent}} \approx [(D_E^{1/3} - D_W^{1/3})\phi_E + D_W^{1/3}]^3$$

"looyenga equation" (20)

where, ϕ_E represents the volume fraction of ethanol.

Table 2. Dielectric constant of "water + ethanol" mixtures in term of volume percent of ethanol at $25.0^{\circ}C$

mass percent of ethanol	volume fraction of ethanol	dielectric constant of the mixed-solvent
4.994	0.0623	73.741
9.986	0.1230	69.403
15.018	0.1825	65.31
19.994	0.2400	61.519
24.966	0.2960	57.828
30.024	0.3516	54.584
39.941	0.4566	48.548
49.998	0.5582	43.152

$D_{H_2O} = 78.5$; $D_{C_2H_5OH} = 24.3$ at $25.0^{\circ}C$

Based on Eq. (12), one can estimate the value of K$_A$ for the following ion- pair formation respect to each saturated solution given in table 1:

$$Li^{+}_{(aq)} + CO^{2-}_{3(aq)} \rightleftharpoons Li^{+}CO_3^{2-} \ ; \ K_A \qquad (21)$$

Or

$$K_A = \frac{[Li^{+}CO_3^{2-}]f_{ip}}{[Li^{+}]\,[CO_3^{2-}]f_{\pm}^{2}} \qquad (22)$$

So

$$[Li^{+}CO_3^{2-}] = (f_{\pm}^{2}/f_{ip})K_A[Li^{+}]_{free}[CO_3^{2-}]_{free} \qquad (23)$$

Denoting $[Li^{+}CO_3^{2-}] = x\ mol\ L^{-1}$,

$[Li^{+}]_{free} = (2s - x)\,mol\ L^{-1}$

$[CO_3^{2-}]_{free} = (s - x)\,mol\ L^{-1}$ and then, inserting them into Eq. (22), we get

$$x^2 - (3s + \frac{f_{ip}}{K_A f_{\pm}^{2}})x + 2s^2 = 0 \qquad (24)$$

where K$_A$ is the equilibrium constant for ion-pair formation and should be estimated upon Eq. (12) (Table 3), f$_{ip}$ and $f_{\pm}$ are activity coefficient of ion- pair and mean ionic activity coefficient of ions Li$^+$ and CO_3^{2-} in solution; f$_{ip}$ and $f_{\pm}$ should be estimated upon Eq. (17) (Table 3).

Solving Eq. (24), we get the value of x for each saturated solution given in Table 1.

In order to evaluate f$_{ip}$ and $f_{\pm}$ (Eq. 17), we choose $a_{\pm} = (4.5\,\mathring{A} + 6\mathring{A})/2$,[2] and $I_M = M_{KNO_3} + 3s - 2x$. Moreover, respect to Eq. (12), we took $z^2 = z_{\pm}^{2} = |z_+ z_-|$, or, $z_{\pm} = 1.4142$

Table 3. Some calculated values that we need to solve equations (17) and (12)

mass percent of ethanol	s/ mol L^{-1}	D	A/ (L/ mol)$^{1/2}$	B/ $\mathring{A}$ (L/ mol) $^{1/2}$	K$_A$
4.994	---	73.741	0.559	0.338	6.646
9.986	0.03822	69.406	0.612	0.348	7.967
15.018	0.03259	65.310	0.671	0.359	9.660
19.994	0.02238	61.519	0.734	0.3697	11.829
24.966	0.01667	57.828	0.805	0.381	14.770
30.024	0.01253	54.584	0.878	0.393	18.408
39.941	0.00721	48.548	1.047	0.416	29.963
49.998	0.00382	43.152	1.249	0.442	51.995

A and B are related to Eq. (17).

Table 4. Ion- pair concentration, x, and thermodynamic solubility product, K$_{SP\ (th)}$, respect to each given saturated solution at $25.0^{\circ}C$

mass percent of ethanol	$f_{\pm}$	f_{ip}	$s\ /\ mol\ L^{-1}$	$[Li^{+}CO_3^{2-}] = x\ /\ mol\ L^{-1}$	$10^5 K_{SP(th)}$
4.994	---	---	---	---	---
9.986	0.4184	0.6469	0.03822	0.0051	1.174
15.018	0.4023	0.6343	0.03259	0.0043	0.6847
19.994	0.3913	0.6255	0.02238	0.0025	0.2139
24.966	0.3805	0.6168	0.01667	0.00165	0.08306
30.024	0.3748	0.6122	0.01253	0.00115	0.03426
39.941	0.351	0.600	0.00721	0.000507	0.00561
49.998	0.3394	0.5826	0.00382	0.000269	0.000754

4. Conclusion

The solubility of Li_2CO_3 in the mixed solvent "water + ethanol" at constant temperature decreases when increasing the mass percent of ethanol. The trend is along with decreasing dielectric constant of the mixed solvent. The total solubility of lithium carbonate can be considered as the sum of two contributions; one corresponding to the free ions in the saturated solution and the other to the ion association.

The formation constant of $Li^+CO_3^{2-}$ ion pair can be estimated with the help of Bjerrum or Fuoss models and then, the evaluation of the free ions and ion - association contributions to the total solubility of lithium carbonate will be quite straightforward. In addition, the thermodynamic solubility product constant, $K_{sp\,(th)}$, and ΔG°_{diss} of an ionic salt in mixed solvent can be evaluated upon the discussed approach. As we have seen, the estimated value of K_A increases as decreasing dielectric constant of the mixed solvent and the trend is along with Eq. (12). On the other hand, the value of $K_{sp\,(th)}$ related to the mixed solvent decreases with decreasing dielectric constant, D, and solubility, s, of Li_2CO_3 in the mixed solvent.

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