Solubility and Solvation Parameters of Calcium Carbonate in Mixed Ethanol-water Mixtures at 301.15 K

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Abstract The molar solubility of calcium carbonate (CC) in mixed ethanol (ETOH)-water solvents was measured at 301.15 K. From the molar solubilities, the solvation parameters, activity coefficients, solubility products, free energies of solvation and transfer free energies for interaction of (CC) from water as reference solvent to mixed (EtOH-H2O) solvents were evaluated. All the salvation parameters were discussed.

Keywords Molar Solubility, Calcium Carbonate, Free Energies of Solvation, Water, Ethanol

1. Introduction

The solubility of solutes in mixed solvents is of great practical importance since many industrial process as well as laboratory procedures call for the use of solvent mixtures. The solubility of solutes in mixed solvents depends primarily on the solvation of solutes or their constituent ions by the components of solvent mixtures[1]. Studying the thermodynamics of different salts, is important for evaluating the single ion thermodynamic parameters which help in explain the preferential solvation of the ions[2].

Removal of heavy elements and sulphate ions from an alkaline medium using solvent extraction was very important to get rid of these hard ions[3].

2. Experimental

The used calcium carbonate (CC) and ethanol (EtOH) were supplied from Merck Co. The saturated solution of calcium carbonate (CC) was prepared by dissolving little solid amount in closed test tubes containing different EtOH-H2O mixtures. The mixtures were then saturated with nitrogen gas as inert atmosphere. The tubes were placed in a shaking thermostat (Model GEL) for a period of one week till equilibrium reached.

The solubility of CC in each mixture were measured conductometrically exactly (three times minimum) by using conductometer of the type YSI model-35 and it was connected with an ultra-thermostat of the type Kottermann-4130. All conductance were measured at 301.15 K. The accuracy of the solubility data is in average of third number after coma, as in previous work[4].

3. Results and Discussion

The molar solubility for calcium carbonate (CC) at 301.15 K were measured conductometrically and the – log S values are cited in Table 1, in water, ethanol (EtOH) and their mixtures. The solubility of (CC) in water agreed well with that in literature[5].

The activity coefficients were calculated by the use of Debye-Hückel equation[6].

log \( \gamma \pm = -0.5062x(S)^{0.5} \) (1)

Where S is the molar solubility. Their data were tabulated also in Table 1. The solubility product was calculated by the use of equation 2[2].

\[ pK_{sp} = [-2 \log S + 2 (\log \gamma \pm)] \] (2)

| Xs (mole fraction) ethanol | - log S | log \( \gamma \pm \) | pK_{sp} | \( \Delta G \) k J/mole | \( \Delta G \) k J/mole |
|---------------------------|---------|-----------------|--------|-----------------|-----------------|
| 0                          | 4.2097  | -0.00347        | 8.4116 | 48.5026         | 0               |
| 0.031                     | 4.3519  | -0.00337        | 8.6976 | 50.1486         | 1.6460          |
| 0.072                     | 4.4087  | -0.00316        | 8.8107 | 50.8044         | 2.3018          |
| 0.110                     | 4.5648  | -0.00236        | 9.1243 | 52.6121         | 4.1095          |
| 0.171                     | 4.6594  | -0.00196        | 9.3141 | 53.7066         | 5.2040          |
| 0.231                     | 4.8249  | -0.00156        | 9.6459 | 55.6198         | 7.1172          |
| 0.310                     | 5.0236  | -0.00113        | 10.0441| 57.9159         | 9.41330         |
| 0.553                     | 5.2980  | -0.00075        | 10.5937| 61.0849         | 12.5823         |
| 0.735                     | 5.6528  | -0.00055        | 11.3042| 65.1818         | 16.6792         |
| 1.0                       | 6.1495  | -0.00042        | 12.29908| 70.9185        | 22.4158         |

Where S is the molar solubility of (CC) in mixed EtOH-H2O solvents. pK_{sp} data are given in Table 1. From these solubility products the Gibbs free energies of solvation...
and the transfer Gibbs free energies from water to mixed solvents were calculated by using the following equations[4] and[5]. Their values are tabulated also in Table (1).

\[ \Delta G = 2.303 \frac{RT}{p} K_{sp} \]  

(3)

\[ \Delta G_t = \Delta G_s - \Delta G_w \]  

(4)

It was concluded that the Gibbs free energies of transfer \( \Delta G_t \) increase in positivity by increasing the mole fraction of ethanol in the mixtures. This is due to more difficult solvation in the mixed solvents than that of water. Polar solvents like \( \text{H}_2\text{O} \) or \( \text{EtOH} \) or their mixtures cannot penetrate (CC) lattice due to the very high heats of formation, free energy, entropy and heat capacity for (CC) salts[7], calcite and aragonite.

### Table 2. Molar thermodynamic properties of pure (CC) solid

|          | \( \Delta H_f \) | \( \Delta G_f \) | S | Cp |
|----------|-----------------|-----------------|---|----|
|          | kJ/mol          | kJ/mol          | J/K.mol | J/K.mol |
| (CC)     |                 |                 |     |     |
| calcite  | -1206.92        | -1128.79        | 92.9 | 81.88 |
| aragonite| -1207.13        | -1127.75        | 88.7 | 81.25 |

Ethanol is much less polar than water. Since (CC) is insoluble in water. Therefore (CC) would be even less soluble in ethanol.

According to this small solubility, applying some thermodynamic model was done to explain the precipitation of some insoluble salts[8].

### Table 3. Molar (VM), van der (VW) and electrostriction volumes (Ve) for (CC) in mixed EtOH-H\(_2\)O solvents at 301.15 K (in cm\(^3\)/mol)

| X\(_s\) (EtOH) | \( V_M \) | \( V_W \) | \( V_e \) |
|---------------|-----------|-----------|-----------|
| 0             | 100.089   | 66.158    | -33.931   |
| 0.03          | 107.864   | 71.298    | -36.566   |
| 0.07          | 111.017   | 73.383    | -37.634   |
| 0.11          | 111.452   | 73.669    | -37.783   |
| 0.17          | 111.561   | 73.742    | -37.818   |
| 0.231         | 111.800   | 73.899    | -37.901   |
| 0.310         | 112.107   | 74.1027   | -38.004   |
| 0.553         | 120.825   | 79.865    | -40.960   |
| 0.735         | 121.999   | 80.641    | -41.358   |
| 0.900         | 140.571   | 92.917    | -47.674   |

The molar volumes (\( V_M \)) for (CC) in mixed EtOH-H\(_2\)O were calculated by dividing the molecular weight by the exact solution densities and their values are tabulated in Table (3). The packing density (P) as explained by Kim (in ref. 6), i.e., the relation between Van der Waals volume (\( V_w \)) and the molar volume (\( V_M \)) for relatively large molecules was found to be constant and equal 0.661.

\[ P = \frac{V_w}{V_M} = 0.661 \pm 0.017 \]  

(5)

The electrostriction volumes (\( V_e \)) which is the volume compressed by the solvent can be calculated by using equation (6) as follows:

\[ V_e = (V_M - V_w) \]  

(6)

All the different volumes for (CC) in mixed EtOH-H\(_2\)O solvents were represented in Table (3). The data in Table (3) indicate that the volumes increase by more adding alcohol favoring more energy required for salvation, i.e., less salvation process.

### REFERENCES

[1] Yizhak Marcus, "Solubility and solvation in mixed solvent systems", Pure and Applied Chem., 62 (1990) 2069-2076

[2] Esam A. Gomaa, "Single ion free energies of some ion and the hydrophobic interactions of Ph\(_4\)AsBPh\(_4\) and Ph\(_4\)SbBPh\(_4\) in mixed ethanol-water solvents", Thermochimica Acta, 156 (1989) 91-99

[3] Cleophase Ngoie Mpinga, "Removal of aluminium and sulphate ions from alkaline medium using solvent extraction", Master of Technology, Faculty of Engineering, Cape Peninsula University of Technology (2009)

[4] E. A. Gomaa, "Solvation parameters of lead acetate in mixed water-N, N-Dimethylformamide mixtures at 298.15 K ". Analele Universităţii din București, 19,1 (2010) 45-48

[5] Perry's "Chemical Engineering Handbook, Section 2, Physical and Chemical data, 8th Edition, McGraw Hill., USA (2008)

[6] A. A. El-Khouly, Esam A. Gomaa and S Abou El-Leaf, "Conductometry and solubility study of Cd\(^{2+}\) Kryptofix-221 complexes in various hydroorganic solvents", Bulletin of Electrochemistry, 19(4), (2003) 153-164

[7] Jim Plambec la @ Malberta. Ca

[8] L. Vicum, M. Hazzotti and J. Baldyga, "Applying a thermodynamic model to the non-stoichiometric precipitation of barium sulphate", Chemical Engineering and Technology, 26(2003) 352-333