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-H$_2$O) 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-H$_2$O 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 conductmetrically exactly (three times minimum) by using conductmeter 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 conductmetrically 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].

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

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].

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

Table 1. Molar solubilities (S), activity coefficient ($\gamma \pm$), solubility products (pk$_{sp}$) and salvation free energies (ΔG, ΔG_t) for molar solubilities, and free energies CaCO$_3$ (CC) in different ethanol-water mixtures at 301.15 K

Xs (mole fraction) ethanol	- log S	log $\gamma \pm$	pK$_{sp}$	ΔG k J/mole	ΔG_t k J/mole
0	4.2097	- 0.00347	8.4116	48.5026	0
0.031	4.3519	- 0.00337	8.69706	50.1486	1.6460
0.072	4.4087	- 0.00316	8.81073	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-H$_2$O 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).

$$\Delta G = 2.303\,RTpK_{sp} \tag{3}$$

$$\Delta G_t = \Delta G_S - \Delta G_W \tag{4}$$

It was concluded that the Gibbs free energies of transfer ΔG_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 H_2O or 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

	ΔH°_f	ΔG°_f	S°	Cp°
	k.J/mol	k J/mol	J/K.mol	J/K.mol
CaCO$_3$(calcite)	-1206.92	-1128.79	92.9	81.88
CaCO$_3$(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 cm3/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	111.0174	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
1.0	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.

$$P = \frac{V_W}{V_M} = 0.661 \pm 0.017 \tag{5}$$

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

$$V_e = (V_W - V_M) \tag{6}$$

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.

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