



SOLVATION PARAMETERS FOR SODIUM OXALATE IN MIXED ETHANOL-WATER SOLVENTS AT 301.15 K

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The molar solubility of sodium oxalate (Na_2Ox) in mixed ethanol (EtOH) – water solvent mixtures were measured at 301.15 K. From the molar solubilities, the activity coefficients, solubility products, free energies of solvation and the transfer free energies for the interaction of (Na_2Ox) in mixed (EtOH- H_2O) solvents were evaluated.

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Introduction

The solubility of solutes in mixed solvents is of great practical importance since many industrial processes as well as laboratory procedures need the use of solvent mixtures.

We know that, the solubility of solutes in mixed solvents depends primarily on the solvation of solutes or their constituent ions by the components of solvent mixture.¹

Sodium oxalate, like citrate, can be used to remove calcium ions from blood plasma. This salt prevents blood clotting. Sodium oxalate can be responsible for the impairment of brain function, and deposit calcium oxalate in the kidneys.² Solvation processes are also important to apply for (Na_2Ox) to understand its behaviour in solutions.³

Experimental

Sodium oxalate (Na_2Ox) and ethanol (EtOH) were supplied from Merck Co. Saturated solutions of (Na_2Ox) were prepared by dissolving different amounts in closed test tubes containing different EtOH- H_2O mixtures. These mixtures were then saturated with nitrogen gas as an inert atmosphere. The tubes were placed in a shaking thermostat (Model GEL) for a period of four days till equilibrium reached.

The solubility of (Na_2Ox) in each mixture was measured conductometrically (three times measurements for each) by using conductometer YSI Model-35 which connected with ultra thermostat of the type Kottermann-4130.

All the measurements were done at 301.15 K with the accuracy of the solubility in the average of the second number after comma as given in previous work.⁴

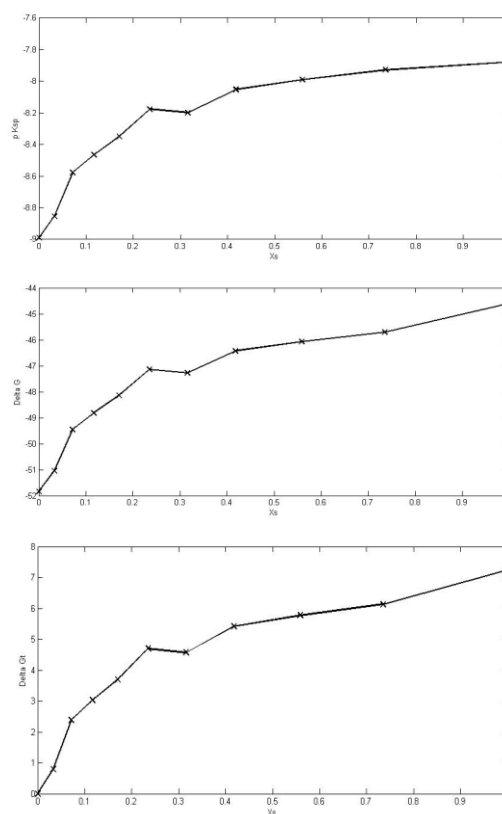


Figure 1. Solubility product (pK_{sp}), ΔG (Gibbs free energy) and ΔG_{t} (Gibbs transfer free energy) for Na_2Ox in mixed EtOH- H_2O solvents at 301.15 K.

Results and Discussion

The molar solubility (S) for (Na_2Ox) at 301.15 K were measured conductometrically in water, ethanol (EtOH) and their mixtures. The S values are cited in Table 1. The solubility of (Na_2Ox) in water agreed well with that in Literature values.⁵ The activity coefficients were calculated by the use of Debye-Hückel equation.⁶

$$\log \gamma_{\pm} = -0.5062S^{0.5} \quad (1)$$

Table 1. Molar solubilities (S), log activity coefficients (γ_{\pm}), solubility products (pK_{sp}) and free energies of solvation (ΔG and ΔG_t) for (Na_2Ox) in different ethanol-water solvents at 301.15 K.

X_s , mole fraction of ethanol)	S , g.mol ⁻¹	$\log \gamma_{\pm}$	pK_{sp}	ΔG , kJ mol ⁻¹	ΔG_t , kJ mol ⁻¹
0	7.91	-1.4236	-8.9909	-51.8433	0
0.0330	7.65	-1.4001	-8.8530	-51.0484	0.7949
0.0715	7.16	-1.3535	-8.5780	-49.4624	2.3809
0.1166	6.45	-1.3344	-8.4656	-48.814	3.0297
0.1703	6.750	-1.3151	-8.3503	-48.1495	3.6938
0.2355	6.61	-1.3014	-8.1764	-47.1467	4.6966
0.3159	6.493	-1.2898	-8.1985	-47.274	4.5693
0.4181	6.250	-1.2655	-8.0517	-46.428	5.4153
0.5591	6.150	-1.2553	-7.9898	-46.0707	5.7726
0.7349	6.051	-1.2451	-7.9279	-45.7138	6.1295
1.0	5.97	-1.2368	-7.8771	-44.600	7.243

where S is the molar solubility. Their data ($\log \gamma_{\pm}$) were tabulated also in Table 1. The solubility product was calculated by the use of equation 2.³

$$pK_{sp} = -\lg 4S^3 + 4(\log \gamma_{\pm})^3 \quad (2)$$

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 solvent were calculated by using equation (3) and (4). Their values are tabulated also in table (1).

$$\Delta G = 2.303 RT pK_{sp} \quad (3)$$

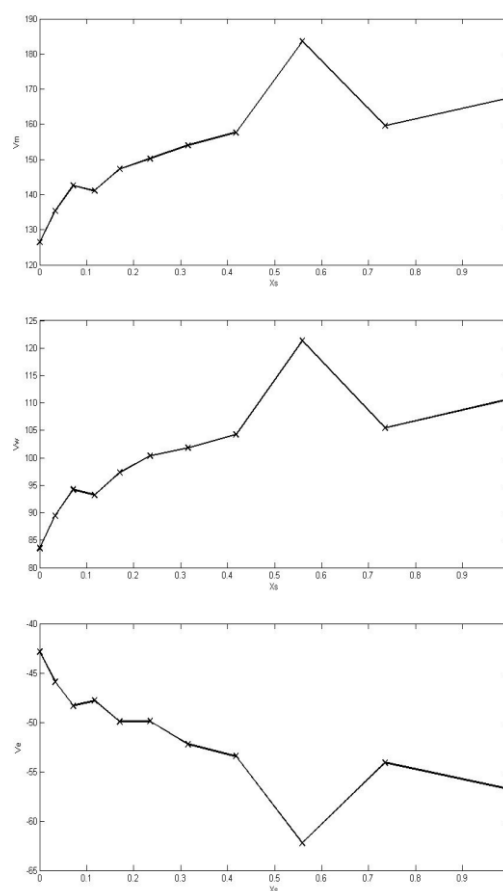
$$\Delta G_t = \Delta G_s - \Delta G_w \quad (4)$$

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 less solvation behaviour in the mixed solvents than that of water.

Table 2. Molar (V_M), Van der Waals (V_W) and electrostriction volumes (V_e) for (Na_2Ox) in mixed EtOH-H₂O solvents at 301.15 K (in cm³ mol⁻¹).

X_s , EtOH	V_M	V_W	V_e
0	126.4151	83.5604	-42.8547
0.033	135.3535	89.4686	-45.8848
0.0715	142.5532	94.2276	-48.3255
0.1166	141.0526	93.2358	-47.8168
0.1703	147.2527	97.3340	-49.9186
0.2355	150.2327	100.3340	-49.8986
0.3159	154.0224	101.8091	-52.2138
0.4181	157.6471	104.2047	-53.4423
0.5591	183.5616	121.3342	-62.2274
0.7349	159.5238	105.4452	-54.0786
1.0	167.500	110.7175	-56.7825

The molar volumes (V_m) for (Na_2Ox) in mixed EtOH-H₂O were calculated by dividing the molecular weight of (Na_2Ox) by the exact solvation densities, the values are given in Table 2.

**Figure 2.** Different volumes, molar (V_M), Van der Waals (V_W) and electrostriction volumes (V_e) for Na_2Ox saturated solutions in mixed EtOH-H₂O solvents.

The packing density (p) as explained in reference 6, i.e., the relation between Van der Waals volume (V_W) and the molar volume (V_M) for relatively large molecules ($M.W. > 40$) was found to be constant and equal to 0.661.

$$P = \frac{V_W}{V_M} = 0.661 \pm 0.017 \quad (5)$$

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

$$V_e = V_W - V_M \quad (6)$$

All the different volumes for (Na_2Ox) in mixed EtOH- H_2O solvents are represented in Table 2. The data in Table 2 indicate that the (Na_2Ox) volumes increase by adding more ethanol favouring more energy required for solvation, i.e. less solvation process.

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