Thermochimica Acta, 219 (1993) 65–72
Elsevier Science Publishers B.V., Amsterdam

Thermodynamic parameters of transfer and solution of oxalic acid in dimethylsulphoxide–water media

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(Received 26 August 1992; accepted 9 September 1992)

Abstract

The solubility measurements for oxalic acid in DMSO–H_2O mixtures have been performed at four temperatures (298.15, 303.15, 308.15 and 313.15 K) to calculate the thermodynamic parameters of solution and transfer of oxalic acid from water, as reference solvent, to DMSO–H_2O mixed solvent. The solubility data have been discussed in terms of the solubility parameters. A multiple linear regression method, known as the extended Hansen solubility approach, has been used to estimate the partial and total solubility parameters for oxalic acid. The activity coefficients of oxalic acid in water and mixed solvents have been calculated theoretically and found to be unity. The thermodynamic parameters of transfer of oxalic acid have been found to increase with increasing mole fraction of DMSO. The electrostatic parts of the standard free energies of transfer for oxalic acid have been calculated theoretically. These values increase with increasing DMSO content.

INTRODUCTION

Many applications for solubility measurements are well known [1]. Obtaining thermodynamic data, especially the Gibbs free energy of transfer, by measuring solubilities is a rather interesting topic. Moreover, the entropy of transfer of uncharged species may act as a structural probe for different solvent systems [2]. The solubilities of benzoic acid and its amino-derivatives in different solvents have been reported [2–5]. These solutes comprise hydrophobic and hydrophilic parts and their solubilities have been discussed from the point of view that the hydrophobicity of the aromatic nucleus is the key to the understanding of the driving force for their solubilities [6, 7]. Therefore, an analysis of solute containing no hydrophobic group seems desirable and important. This led us to investigate the thermodynamic parameters of transfer and dissolution of

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oxalic acid in dimethylsulphoxide–water mixtures, using solubility measurements to elucidate the different types of interaction between solute and solvent.

EXPERIMENTAL

Oxalic acid (OXA) of pure grade (Merck) and dimethylsulphoxide (DMSO) (Spectrosol BDH) were used without further purification. Free carbonate–NaOH (Merck) solution was prepared and standardized according to normal procedures [8]. Deionized water (specific conductance <1 μmho) was used for preparing all solvent mixtures.

Saturated solutions of OXA in DMSO–H_2O mixtures were prepared by dissolving the required amount in the corresponding solvent mixture using closed test-tubes saturated with purified nitrogen gas. The solutions were vigorously shaken for one week in a water bath thermostated at the desired temperature, followed by another day without shaking to reach the necessary equilibrium condition.

The solubility of OXA in each mixture was determined by taking and weighing 10 ml of the saturated solution, and dissolving it in 100 ml H_2O; then 10 ml of this solution were titrated with standard NaOH solution. $KMnO_4$ cannot be used as titrant in these media because it displays an oxidation character with DMSO [9]. The experimental values reported here are the average of more than three separate determinations. There is a good agreement between the results obtained within 0.5% error.

The dielectric constant values were taken from the data given by Kim and Gomaa [10].

RESULTS AND DISCUSSION

The solubility values for OXA in different percentages of DMSO over the range 298.15–313.15 K are listed in Table 1 and presented graphically in Fig. 1. These values increase with increasing temperature. This indicates that OXA absorbs heat (endothermic process) when it dissolves. This was confirmed by the positive values of the enthalpy of solution as shown in Table 1.

The solubility parameters δ, which express the cohesion between like molecules and serve as a measure of the internal pressure of the solvent and the solute in non-ideal solutions, were calculated using the equation [11]

$$\delta = \left(\frac{\Delta_v E}{V_e}\right)^{1/2} = \left(\frac{\Delta_v H - RT}{V_e}\right)^{1/2} \tag{1}$$

where $\Delta_v E$ is the molar energy of vaporization, $\Delta_v H$ is the heat of vaporization, V_e is the molar volume of the liquid compound at the desired temperature, R is the gas constant and T is the absolute temperature. The

TABLE 1

Solubility of oxalic acid in dimethylsulphoxide water mixtures at different temperatures and the thermodynamic parameters of solution of oxalic acid

DMSO (vol.%)	Solubility (S) (mol l^{-1})				Free energy of solution $-\Delta_s G^{\ominus}$ (kJ mol^{-1})				Enthalpy of solution	Entropy of solution
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	$\Delta_s H^{\ominus}$ (kJ mol^{-1})	$\Delta_s S^{\ominus}$ (J K^{-1} mol^{-1})
0	1.3183	1.6596	2.042	2.6320	0.69	1.28	1.83	2.52	35.29	120.6
10	1.6218	1.9771	2.2910	2.7670	1.20	1.72	2.12	2.65	27.09	95.0
20	1.9055	2.3440	2.5711	3.2512	1.60	2.15	2.42	3.07	26.21	93.5
30	2.2911	2.8121	3.1622	3.6903	2.06	2.61	2.95	3.40	23.97	87.7
40	2.8180	3.2362	3.4673	4.1691	2.57	2.96	3.19	3.72	19.22	93.2
50	3.4672	3.9811	4.3152	4.7862	3.08	3.48	3.75	4.08	16.23	65.0
60	4.1691	4.5712	5.0121	5.4953	3.54	3.83	4.13	4.44	14.26	59.7
70	4.8483	5.4576	5.9813	6.4572	3.91	4.28	4.58	4.86	14.71	62.6
80	6.9982	6.1659	6.6102	7.3909	4.44	4.59	4.84	5.21	10.76	50.6
90	6.6069	7.9794	7.3282	7.8341	4.68	4.93	5.10	5.36	8.45	44.2
100	7.5161	7.9431	8.2601	9.0240	5.00	5.22	5.41	5.73	9.04	47.1

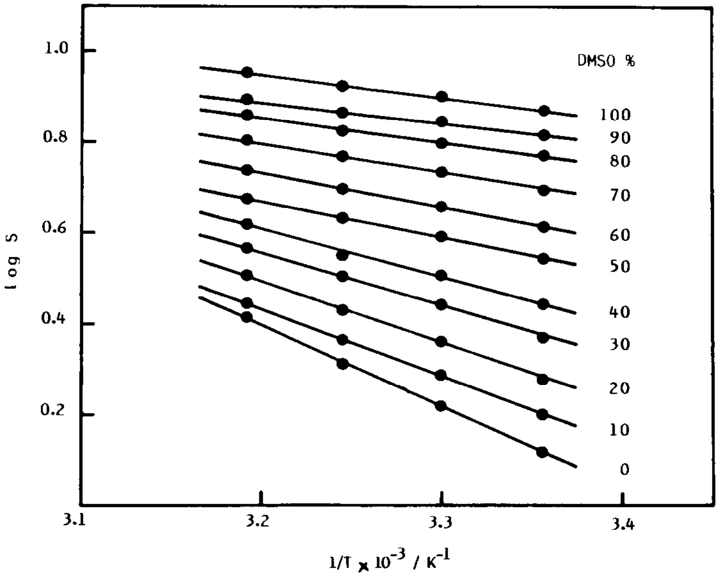

Fig. 1. Temperature dependence of solubility: plots of $\log S$ of oxalic acid in various percentages of DMSO versus $1/T$.

square of δ is called the cohesive energy density. Following a proposal by Crowley et al. [12], Hansen and Beerbour [13, 14] assumed that the cohesive energy is an additive quantity and consists of a term for non-polar or London dispersion forces ΔE_d, a second for polar forces ΔE_p, and a third for hydrogen bonding ΔE_h, i.e.

$$\frac{\Delta E}{V_e} = \frac{\Delta E_d}{V_e} + \frac{\Delta E_p}{V_e} + \frac{\Delta E_h}{V_e} \tag{2}$$

or

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{3}$$

where δ^2 is the total cohesive energy density. Therefore, the solubility parameter for OXA was found to be 15.2, after Hansen and Beerbour [13, 14].

From δ_1 and δ_2 (the solubility parameters of solvent and solute respectively), one can accurately predict the solubility using eqn. (4) according to Hildebrand et al. [15]

$$-\ln X_2 = \frac{\Delta_{fus}H}{R}\left[\frac{T_m - T}{T_m T}\right] + \frac{V_2 \phi_1^2 (\delta_1 - \delta_2)^2}{RT} \tag{4}$$

in which X_2 is the mole fraction solubility of the crystalline OXA, $\Delta_{fus}H$ is the heat of fusion of OXA, T_m is the melting point, V_2 is the molar volume of OXA and ϕ_1 is the volume fraction of the pure or mixed solvent.

The first term on the right-hand side of eqn. (4) represents the negative logarithm of the ideal solubility ($-\ln X_2^i$). The second term represents the

TABLE 2

Calculation of the activity coefficient of oxalic acid in dimethylsulphoxide–water mixtures at 298.15 K

DMSO (vol.%)	DMSO (wt.%)	X_2 [a]	δ_m [b]	X_1' [c]	V_1 [d]	ϕ_1 [e]	v_2 [f]
0	0	0.0000	23.45	0.977	18.00	0.0176	1.003
10	10.88	0.0273	23.16	0.969	19.36	0.0188	1.004
20	21.55	0.0595	22.83	0.961	21.18	0.0203	1.006
30	32.01	0.0978	22.43	0.948	22.92	0.0217	1.007
40	42.27	0.1443	21.94	0.930	25.23	0.0235	1.008
50	52.35	0.2371	20.97	0.905	27.95	0.0253	1.007
60	62.23	0.3272	20.03	0.874	31.69	0.0277	1.007
70	71.94	0.4330	18.93	0.836	36.77	0.0308	1.007
80	81.45	0.5042	18.18	0.776	43.91	0.0341	1.007
90	90.81	0.6961	16.18	0.717	54.42	0.0390	1.005
100	100.00	1.0000	13.00	0.630	71.30	0.0449	1.001

[a] X_2, mole fraction of the solvent. [b] δ_m, solubility parameter of the mixed solvent. [c] X_1', mole fraction of the solvent in the saturated solution of OXA. [d] V_1, molar volume of the mixed solvent. [e] ϕ_1, volume fraction of the solvent. [f] v_2, activity coefficient of OXA.

contribution of the heat of mixing which is equal to logarithmic solute (OXA) activity coefficient, i.e.

$$\ln \gamma_2 = (\delta_1 - \delta_2)^2 \frac{V_2 \phi_1^2}{RT} \tag{5}$$

Thus, the activity coefficient values of OXA in different solvents have been calculated according to eqn. (5) and recorded in Table 2. These values have been found to be unity, so that there is no need for activity coefficient correction. Similar results have been obtained for benzoic acid in mixed solvents [3, 4].

Inspection of Table 1 reveals that the experimental solubility of oxalic acid increases with increasing concentration of DMSO. This can be explained in terms of the solubility parameter [16], where the more alike the δ values of the two components, the greater the mutual solubility of the pair. Oxalic acid ($\delta = 15.2$) is more soluble in DMSO ($\delta = 13$) than in H_2O ($\delta = 23.4$). From Table 2, it can be seen that the solubility parameter of mixed DMSO–H_2O solvent decreases with the addition of DMSO, bringing it close to the solubility parameter for oxalic acid and enhancing its solubility.

The free energies of solution of OXA, $\Delta_s G^\ominus$, were calculated from the solubility values using

$$\Delta_s G^\ominus = -2.303 RT \log S \tag{6}$$

where S is the solubility of OXA expressed in molar units.

Assuming that the enthalpy of solution of OXA, $\Delta_s H^\ominus$, remains unchanged in the temperature range 298.15–313.15 K, one can evaluate $\Delta_s H^\ominus$ values from the slope of the plot of $\log S$ versus the reciprocal of the absolute temperature. In addition, the entropy of solution $\Delta_s S^\ominus$ was obtained from the well known relationship

$$\Delta_s G^\ominus = \Delta_s H^\ominus - T\Delta_s S^\ominus \qquad (7)$$

All the above calculated thermodynamic parameters of solution of OXA in DMSO–H_2O mixtures are recorded in Table 1.

The transfer free energies of OXA from water (w) to mixed solvents (s), $\Delta_w^s G_{OXA}$, were calculated from its solubilities or solubility products according to the equation [17]

$$\Delta_w^s G_{OXA} = 2.303RT\ \Delta pK_{sp} = 2.303RT \log\left[\frac{S_{OXA}(w)}{S_{OXA}(s)}\right] \qquad (8)$$

where ΔpK_{sp} is the difference between the solubility products of OXA in the organic solvent and water.

The transfer free energies of OXA from water to mixed DMSO–H_2O give negative values, because OXA is more bonded to water in pure water than in mixed solvents. This is due to the decrease in the charges in the mixed solvents resulting from the interaction between DMSO and H_2O forming complex compounds in the ratio 1:2 (DMSO:H_2O) [9]. Moreover, these transfer free energy values, as shown in Table 3, are exothermic with further addition of DMSO to the mixed DMSO/H_2O solvents. This may be due to the presence of a highly polar, highly crowded single oxygen, carrying a much greater negative charge density in the dimethylsulphoxide.

The electrostatic free energies ΔG_{el} of oxalic acid in mixed DMSO–H_2O

TABLE 3

Thermodynamics of transfer of neutral oxalic acid from water to dimethylsulphoxide–water mixtures at 303.15 K

DMSO (vol.%)	$-\Delta_w^s G$ (kJ mol^{-1})	$-\Delta_w^s H$ (kJ mol^{-1})	$\Delta_w^s S$ (J K^{-1} mol^{-1})
10	0.44	8.20	25.6
20	0.87	9.08	27.1
30	1.33	11.32	32.9
40	1.68	16.07	47.4
50	2.21	19.06	55.6
60	2.55	21.03	60.9
70	3.00	20.58	58.0
80	3.31	24.53	70.0
90	3.66	26.84	76.4
100	3.95	26.25	73.5

TABLE 4

Solvated radii r and electrostatic free energy of transfer ΔG_{el} of oxalic acid in mixed DMSO–H_2O at 298.15 K

DMSO (vol.%)	DMSO (wt.%)	r_s (Å)	ε	r (Å)	$-\Delta G_{el}$ (kJ mol^{-1})
0	0	1.365	78.5	6.965	0
10	10.87	1.523	76.6	7.123	0.13
20	21.55	1.658	74.2	7.258	0.29
30	31.99	1.782	70.7	7.382	0.55
40	42.33	1.897	67.7	7.497	0.85
50	52.33	2.002	63.3	7.602	1.17
60	62.21	2.097	59.2	7.697	1.57
70	71.92	2.185	55.6	7.785	1.96
80	81.45	2.264	51.9	7.864	2.41
90	90.81	2.335	49.2	7.935	2.77
100	100.00	2.404	46.4	8.004	3.20

solvents were calculated theoretically using the Born equation [18]

$$\Delta G_{el} = -\frac{694.1}{r}\left(\frac{1}{\varepsilon} - 0.0127\right) \tag{9}$$

where r is the solvated radius of oxalic acid and ε is the dielectric constant of the solvent. The solvated radii were estimated by adding the mixed solvent radii r_s to the van der Waals radius r_W of oxalic acid. The radius of the mixed solvents used were estimated from the treatment of the data in ref. 10. A polynomial regression was applied

$$Y = 2.754 + 2.764X - 0.7206X^2$$

where X is the mole fraction of DMSO and Y is the diameter of DMSO–H_2O mixtures. The r_W of the dihydrated oxalic acid was calculated using the Bondi [19] model and was found to be 5.6 Å. ΔG_{el} values for oxalic acid in mixed DMSO–H_2O solvents are listed in Table 4. It was noted from this table that the electrostatic free energy values increase with increasing DMSO content due to the increase in the dipole moment of the mixed solvent [10]. However, by increasing the mole fraction of DMSO, increases in $\Delta_w^s G_{OXA}$, $\Delta_w^s H_{OXA}$ and $\Delta_w^s S_{OXA}$ were observed (Table 3). This behaviour is due to the interaction between the localized charge of oxalic acid and DMSO resulting in an increase of the Born electrostatic term.

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