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Thermodynamics of Transfer Processes, 1. Solubility of Hydrophilic Solutes in Dioxane-Water Mixtures

I. Shehatta*, A. H. El-Askalany, E. R. Hassan, and **M. N. H. Moussa**

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Summary. The solubility profiles of oxalic and malonic acid in various dioxane-water mixtures are reported. These values are analyzed in terms of dipole moment and solubility parameter using the *Hildebrand* treatment for regular solutions. The effect of temperature upon the solubility values was investigated and thus the thermodynamic parameters of the solutions were derived. The thermodynamic transfer functions of oxalic and malonic acid from water to aquo-dioxane mixtures were also calculated and analyzed in terms of solute-solvent interactions.

Keywords. Thermodynamics of transfer; Oxalic acid; Malonic acid; Solubility; Dioxane-water mixtures.

Thermodynamik von Transferprozessen, 1. Mitt. Löslichkeit hydrophiler Verbindungen in Dioxan-Wasser-Mischungen

Zusammenfassung. Das Löslichkeitsverhalten von Oxalsäure und Malonsäure in verschiedenen Dioxan-Wasser-Mischungen wurde untersucht. Die erhaltenen Werte werden im Hinblick auf Dipolmoment und Löslichkeitsparameter unter Verwendung der *Hildebrand*schen Beziehung für reguläre Lösungen diskutiert. Aus der Temperaturabhängigkeit der Löslichkeit wurden die thermodynamischen Parameter der Lösungen abgeleitet. Die thermodynamischen Transferfunktionen für Oxalsäure und Malonsäure zwischen Wasser und Wasser-Dioxan-Mischungen wurden ebenfalls berechnet und werden im Zusammenhang mit Wechselwirkungen zwischen Lösungsmittel und gelöster Substanz diskutiert.

Introduction

Dioxane-water mixtures have been extensively used for the study of electrolytic solutions owing to the wide range of dielectric constants that can be achieved by them. Inspite of the low dielectric constant and dipole moment of dioxane, it interacts strongly with water and other molecules due to its high quadrupole moment. Several solubility measurements of acids consisting of hydrophobic and hydrophilic parts have been reported [1–4]. Their solubilities were discussed in terms of hydrophobic interaction. Thus, it seems desirable and important to study solutes containing no hydrophobic group such as oxalic and malonic acid where the CH_2 group in the latter is acidic and interacts through hydrogen bonds with hydrogen accepter molecules. Therefore, and in continuation of our previous work [5], the present article deals with the measurement of the solubility of oxalic and malonic acid in dioxane-water mixtures at 298.15, 303.15, 308.15, and 313.15 K. The thermodynamic parameters of solution and transfer are calculated and discussed.

Results and Discussion

In Figs. 1 and 2, the solubility values of oxalic and malonic acids in 0–100% (v/v) dioxane-water mixtures at 298.15, 303.15, 308.15, and 313.15 K are plotted against the mole fraction of dioxane.

The solubility of oxalic acid increases with increasing dioxane content. Plotting the solubility values of oxalic acid *vs.* percent dioxane (Fig. 1) yields a broken line consisting of two segments. The slope of the first segment is larger than that of the second. The break occurs at 70% (v/v) dioxane. This may be due to interactions between dioxane and water [7], where 70% (v/v) dioxane corresponds approximately to $x_{\text{dioxane}} \simeq 0.33$. Moreover, the average solubility parameter of oxalic acid, as

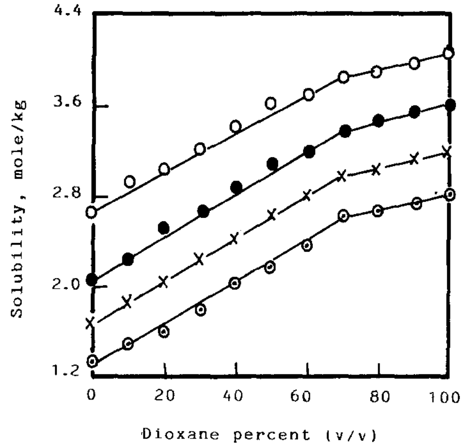


Fig. 1. Solubility of oxalic acid in dioxane-water mixtures at 298.15 (⊙), 303.15 (×), 308.15 (●), and 313.15 K (○)

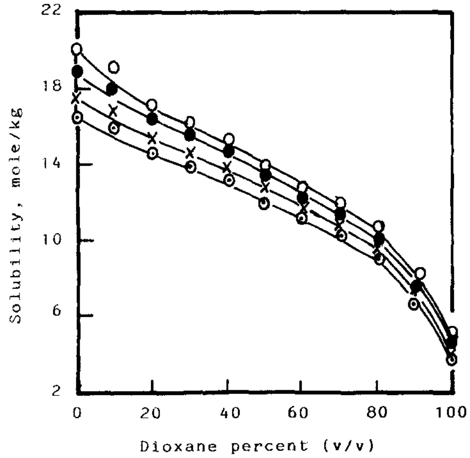
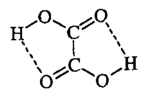


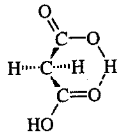
Fig. 2. Solubility of malonic acid in dioxane-water mixtures at 298.15 (⊙), 303.15 (×), 308.15 (●), and 313.15 K (○)

calculated by *Small* [8], *Hoy* [9], and *Fedors* [10], is 14.88 $(\text{cal/ml})^{1/2}$ which is close to the solubility parameter of 70% (v/v) dioxane-water as a solvent [14.04 $(\text{cal/ml})^{1/2}$]. This will be discussed in more detail later.

Contrary to oxalic acid, the solubility of malonic acid decreases with increasing dioxane content. This may be interpreted in terms of the dipole moment. The dipole moment of dioxane-water mixtures decreases with increasing dioxane content (the dipole moments of water and dioxane are 1.8 and 0.4 Debye, respectively). Moreover, the dipole moment of malonic acid is larger than that of oxalic acid.



Oxalic acid
dipole moment = 0



Malonic acid
dipole moment > 0

Table 1. Thermodynamic parameters of solution of oxalic and malonic acid in dioxane-water mixtures

Dioxane (Vol%)	δ_1^a	$-\Delta G_{sol}$ (kJ·mol^{-1}) 298.15 K	303.15 K	308.15 K	313.15 K	ΔH_{sol} (kJ·mol^{-1})	ΔS_{sol} (J·K^{-1}mol^{-1})
Oxalic acid							
0	23.45	0.69	1.28	1.83	2.52	35.29	120.6
10	22.11	0.96	1.59	2.16	2.79	35.11	121.1
20	20.76	1.18	1.77	2.33	2.92	31.70	112.8
30	19.42	1.47	2.02	2.51	3.03	29.34	103.4
40	18.07	1.75	2.24	2.68	3.18	26.39	94.5
50	16.73	1.92	2.44	2.87	3.33	25.89	93.4
60	15.39	2.13	2.57	2.98	3.39	22.80	83.7
70	14.04	2.34	2.75	3.11	3.50	21.64	80.7
80	12.70	2.41	2.78	3.18	3.52	19.91	74.9
90	11.35	2.47	2.84	3.23	3.59	19.70	74.3
100	10.01	2.56	2.92	3.28	3.63	18.74	71.5
Malonic acid							
0	23.45	6.93	7.20	7.51	7.84	11.23	60.9
10	22.11	6.85	7.11	7.37	7.67	9.43	54.6
20	20.76	6.63	6.88	7.15	7.38	8.55	50.9
30	19.42	6.51	6.74	7.03	7.25	8.59	50.6
40	18.07	6.40	6.66	6.95	7.12	8.40	49.7
50	16.73	6.16	6.49	6.65	6.85	7.13	44.7
60	15.39	6.02	6.24	6.48	6.68	7.07	43.9
70	14.04	5.85	6.03	6.28	6.50	6.96	43.0
80	12.70	5.57	5.82	6.02	6.23	7.46	43.7
90	11.35	4.80	5.06	5.24	5.50	8.94	46.1
100	10.01	3.53	3.73	3.99	4.26	11.01	49.0

[a] solubility parameter of solvent

These values increase with increasing temperature suggesting an endothermic nature for the dissolution process as shown by the positive value of the enthalpies of solution (Table 1) which reveal that such solutions are not ideal (the heat produced by mixing a solute and a solvent in an ideal solution is zero). Consequently, *Hildebrand* [11] introduced the concept of a regular solution for mixtures which are not ideal.

In a regular solution, the molecules of the solvent mix with those of the solute with maximum randomness and the heat of solution is positive. For such solutions, the solubility equation for crystalline solutes takes the following form [12]:

$$-\ln x_2 = \frac{\Delta H_{\text{fus}}}{RT} \cdot \left(\frac{T_{\text{m}} - T}{T_{\text{m}}} \right) + \frac{V_2 \phi_1^2 (\delta_1 - \delta_2)^2}{RT} \qquad 1$$

Here x_2 represents the mole fraction solubility of the solute; the other symbols have their usual meanings [4].

The first term on the right-hand side of equation 1 represents the logarithm of the ideal solubility ($-\ln x_2^{\text{i}}$). The second term, introduced by *Hildebrand*, represents the contribution of the heat of mixing which is equal to the logarithmic solute activity coefficient ($\ln \alpha_2$), *i.e.*

$$\ln \alpha_2 = (\delta_1 - \delta_2)^2 \cdot \frac{V_2 \phi_1}{RT} \qquad 2$$

Thus, the activity coefficient values of the dicarboxylic acids in different solvent blends have been calculated and found to be close to unity so that there is no need for activity coefficient correction. Similar results have been obtained for oxalic acid in *DMSO*-H_2O mixtures [5] and benzoic acid in alcohol-water [2, 3].

The solubility parameter δ_1 for the various compositions of the dioxane (d)–water (w) mixtures are calculated using equation 3 and are given in Table 1:

$$\delta_1 = \frac{\delta_{\text{w}} \phi_{\text{w}} + \delta_{\text{d}} \phi_{\text{d}}}{\phi_{\text{w}} + \phi_{\text{d}}} \qquad 3$$

$\phi_1 = \phi_{\text{w}} + \phi_{\text{d}}$ is the total volume fraction of the two solvents calculated using equation 4 where x_2 is the mole fraction solubility of the solute in the mixed solvent and V_1 the mean molar volume of the binary mixture.

$$\phi_1 = \frac{(1 - x_2) V_1}{(1 - x_2) V_1 + x_2 V_2} \qquad 4$$

The molar volumes of the solutes were calculated using the functional group contribution method of *Fedors* [10] and were verified using the data of molecular weights and densities cited in the literature.

The process of removing a molecule (oxalic or malonic) from the solute phase and depositing it in the solvent occurs in three steps [13]:

1. Removal of a molecule from the solute phase at a definite temperature into the vapour state. This requires a rupture of bonds between adjacent molecules.
2. Creation of a cavity in the solvent to accept the solute molecule. This means a rupture of hydrogen bonds.

3. Placement of the solute into the solvent hole. This involves formation of a solute-solvent bond.

The first and second step are accompanied by positive ΔH_{sol} and ΔS_{sol} values, whereas negative values are expected with the third one. Therefore, all steps contribute to the total enthalpy and entropy of dissolution.

The thermodynamic parameters of solution (ΔG_{sol}, ΔH_{sol}, and ΔS_{sol}) of oxalic and malonic acid were calculated according to well-known relationships [5] and are listed in Table 1. An inspection reveals that the dissolution process of oxalic and malonic acids in aqueous dioxane mixtures is spontaneous, endothermic, and entropically favourable.

As mentioned above, the solubility of oxalic acid increases as the proportion of dioxane increases in accordance with (a) the formation of an increasing number of holes in the solvent and (b) the formation of new bonds between solute and solvent. Therefore, the decrease in both ΔH_{sol} and ΔS_{sol} values of oxalic acid with increasing dioxane content may be due to the predominance of (b) over (a). For malonic acid, the corresponding values decrease up to 70% (v/v) dioxane and thereafter increase with increasing dioxane mole fraction. This may be due to the predominance of (a) over (b).

Thermodynamics of transfer processes

The free energy changes of transfer, $\Delta_w^m G$, of oxalic or malonic acid from water (*w*) as a reference solvent to aqueous dioxane (*m*) were calculated from the following relationship:

$$\Delta_w^m G = \Delta G_{sol}(\text{mixed solvent}) - \Delta G_{sol}\,(\text{water}) \qquad 5$$

The corresponding enthalpy and entropy changes of transfer ($\Delta_w^m H$ and $\Delta_w^m S$) were estimated by a procedure similar to that used for the free energy of transfer (equation 5). These functions are presented graphically *vs.* the dioxane mole fraction in Figs. 3 and 4. The following conclusions can be drawn:

i) The observed negative values of $\Delta_w^m G$ for oxalic acid suggest that the process is spontaneous and support the view that water is less basic than the mixed aquo-dioxane mixtures. Each carboxyl group in oxalic acid can form three hydrogen bonds with solvent molecules by its two oxygens and the hydrogen atom. The hydrogen bond formed by the basic carbonyl oxygen should be weakened as the solvent becomes more basic by the addition of dioxane, while the hydrogen bonds formed by the acidic oxygen and hydrogen atoms grow correspondingly stronger.

   Therefore, the total change in these hydrogen-bonding interactions may contribute to the decrease in $\Delta_w^m G$ values in dioxane-water mixtures. The opposite is the case for malonic acid. This may be due to the presence of the acidic $-CH_2-$ group which interacts through hydrogen bonds with hydrogen acceptor molecules.

ii) The enthalpy and entropy changes of transfer of malonic acid show a maximum in the region of $x_{dioxane} = 0.3–0.4$, whereas a change in behaviour other than that offered by the water-rich composition region (approximately constant values

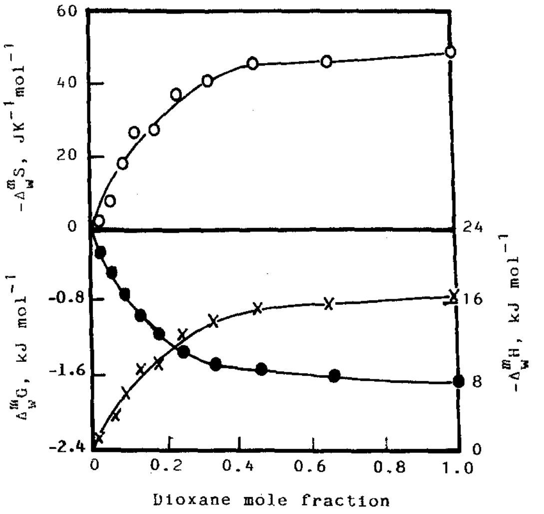


Fig. 3. Variation of $\Delta^m_w G$ (●), $\Delta^m_w H$ (×) and $\Delta^m_w S$ (○) of oxalic acid at 303.15 K with $x_{dioxane}$

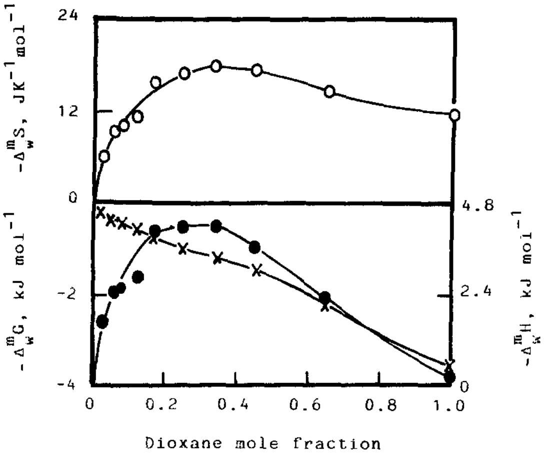


Fig. 4. Variation of $\Delta^m_w G$ (×), $\Delta^m_w H$ (●) and $\Delta^m_w S$ (○) of malonic acid at 303.15 K with $x_{dioxane}$

within experimental error) occurs thereafter in case of oxalic acid. This indicates maximum structure formation (solvent-solvent interactions) between dioxane and water at $x_{dioxane} \simeq 0.33$ as indicated from viscosity. density, and dielectric constant measurements [7].

In brief, the solubility parameter and the dipole moment have a considerable effect on the dissolution of oxalic and malonic acid in dioxane-water mixtures. The $\Delta^m_w G$ values serve as a measure of different interactions involving solute and solvent, whereas $\Delta^m_w H$ and $\Delta^m_w S$ provide information about the solvent structure. This is due to the transfer process which includes a number of changes connected with building up and breaking down the structure.

Experimental

Oxalic and malonic acid were used as received without further purification. A carbonate-free sodium hydroxide solution was used as a titrant and was standardized using A. R. potassium hydrogen phthalate. Dioxane was purified according to *Vogel* [6]. Deionized water was used for the preparation of the aquo-dioxane mixtures. The apparatus and the general conditions are the same as described previously [5]. The temperature was adjusted to ±0.05 °C using a shaking water bath (Precision, Chicago, USA). Three separate solubility determinations agree within 0.5%; the average value is reported.

References

[1] Das K., Das A. K., Kundu K. K. (1978) J. Phys. Chem. **82**: 1242

[2] Pal A., Lahiri S. C. (1989) Indian J. Chem. **28A**: 276

[3] Pal A., Lahiri S. C. (1986) Indian J. Chem. **25A**: 26

[4] Mousa M. A., Ahmed M. M. A. (1988) Thermochim. Acta **136**: 23

[5] Shehatta I., El-Askalany A. H., Gomaa E. A. (1993) Thermochim. Acta **219**: 65

[6] Vogel A. I. (1978) Textbook of quantitative Inorganic Analysis, 4th ed. Longmans, London

[7] Shehatta I., Hassan E. R., Moussa M. N. H. (1994) (unpublished work)

[8] Small P. A. (1953) J. Appl Chem. **3**: 71

[9] Hoy K. L. (1970) J. Paint Technol. **42**: 76

[10] Fedors R. F. (1974) Polym. Eng. Sci., **14**: 147

[11] Hildebrand J. H. (1929) J. Am. Chem. Soc. **51**: 66

[12] Hildebrand J. H., Praunitz J. M., Scott R. L. (1970) Regular and Related Solutions. Von Nostrand Reinhold, New York

[13] Martin A., Bustamante P., Chun A. H. C. (1993) Physical Pharmacy, 4th ed. Lea & Febiger, Philadelphia

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