M-2461

J. Chem. Thermodynamics **1990**, 22, 289–292

Solubility of suberic, azelaic, levulinic, glycolic, and diglycolic acids in water from 278.25 K to 361.35 K

ALEXANDER APELBLAT[a] and EMANUEL MANZUROLA

Department of Chemical Engineering,
Ben Gurion University of the Negev,
Beer Sheva, Israel

(Received 21 December 1989)

Solubilities of suberic, azelaic, levulinic, glycolic, and diglycolic acids in water were determined in the 278.25 to 361.35 K temperature range. The apparent molar enthalpies of solution at 298.15 K were derived: $\Delta_{sol}H_m(m = 0.0139\ mol \cdot kg^{-1}) = 37\ kJ \cdot mol^{-1}$ for suberic acid; $\Delta_{sol}H_m(m = 0.00946\ mol \cdot kg^{-1}) = 41\ kJ \cdot mol^{-1}$ for azelaic acid; $\Delta_{sol}H_m(m = 45.1\ mol \cdot kg^{-1}) = 47\ kJ \cdot mol^{-1}$ for levulinic acid; $\Delta_{sol}H_m(m = 32.54\ mol \cdot kg^{-1}) = 11\ kJ \cdot mol^{-1}$ for glycolic acid, and $\Delta_{sol}H_m(m = 5.30\ mol \cdot kg^{-1}) = 29\ kJ \cdot mol^{-1}$ for diglycolic acid.

1. Introduction

In a number of our earlier studies, the physicochemical properties of (an organic acid + water) were considered: molar enthalpies of solution,[1,2] solubilities,[3,4] and apparent molar volumes.[5] In this work the solubilities of five organic acids in water as a function of temperature are reported. With the exception of suberic and azelaic acids, for which the solubilities were measured by Lamouroux[6] in 1899, the determined solubilities are new.

2. Experimental

Suberic acid, $HO_2C(CH_2)_6CO_2H$, >98.0 mass per cent, $M = 174.196\ g \cdot mol^{-1}$ and azelaic acid, $HO_2C(CH_2)_7CO_2H$, >99.0 mass per cent, $M = 188.223\ g \cdot mol^{-1}$ were from Aldrich. Glycolic acid, CH_3OCO_2H, >99.0 mass per cent, $M = 76.052\ g \cdot mol^{-1}$; diglycolic acid, $HO_2CCH_2OCH_2CO_2H$, >99.0 mass per cent, $M = 134.086\ g \cdot mol^{-1}$, and levulinic acid, $CH_3COCH_2CH_2CO_2H$, >99.0 mass per cent, $M = 116.116\ g \cdot mol^{-1}$ were supplied by Merck. All reagents were used without further purification. Solubility measurements were performed as described elsewhere.[3]

[a] To whom correspondence should be addressed.

0021-9614/90/030289+04 $02.00/0

3. Results and discussion

The solubilities, expressed as mole fractions x, of organic acids in water as a function of temperature are presented in table 1. At equilibrium, if the solid phase contains unhydrated acids, the solubility (temperature) relation takes the form:[7]

$$\{\partial \ln m/\partial(1/T)\}(1+\partial \ln \gamma/\partial \ln m) = -\Delta_{sol}H_m/R, \quad (1)$$

where $\Delta_{sol}H_m$ is the molar enthalpy of solution, R is the gas constant, and m and γ are the molality of the saturated solution and the activity coefficient of the acid. Since values of activity coefficients are unknown, only the apparent enthalpies of solution at 298.15 K can be evaluated from equation (1), by neglecting the activity-coefficient term. Over the studied temperature range, the solubilities of suberic and azelaic acids in water are extremely small. Up to about 293 K, our results for suberic acid are in a reasonable agreement with those determined by Lamouroux[6] in 1899, but at higher temperatures the presented solubilities are systematically lower. Lamouroux[6] measured also the solubility of azelaic acid in water; however, the results presented by him are incorrect, probably because he considered the acid as monobasic. This is evident when the correspondingly corrected solubilities, his original solubilities, and our results are plotted together (figure 1). As can be seen, the corrected and our solubilities form the same $x(T)$ curve. Determined from equation (1), the apparent

TABLE 1. Mole-fraction solubilities of organic acids in water as a function of temperature

T/K	x	T/K	x	T/K	x	T/K	x	T/K	x
Suberic acid, $C_8H_{14}O_4$									
280.15	0.0000955	298.15	0.0002504	313.15	0.0004203	325.85	0.0006400	343.25	0.001494
285.85	0.0001279	305.65	0.0003414	317.65	0.0004851	334.65	0.001009	349.65	0.002123
291.85	0.0001765	307.65	0.0003695	323.35	0.0005789	337.15	0.001169		
Azelaic acid, $C_9H_{16}O_4$									
280.15	0.0000594	298.15	0.0001706	325.75	0.0004815	338.15	0.001281	353.05	0.001914
285.85	0.0000813	307.85	0.0002868	330.15	0.0006996	344.15	0.001324	357.65	0.001728
291.85	0.0001167	316.15	0.0003357	334.65	0.0009313	347.65	0.001528		
Levulinic acid, $C_5H_8O_3$									
280.15	0.1804	287.65	0.2782	298.15	0.4484				
283.15	0.2136	293.95	0.3737	303.25	0.5190				
Glycolic acid, $C_2H_4O_3$									
280.15	0.2038	298.15	0.3695	321.15	0.4375	337.65	0.4802	357.65	0.5163
284.05	0.2624	303.25	0.3881	322.15	0.4380	343.15	0.4900	361.25	0.5212
298.15	0.3155	309.15	0.4046	328.15	0.4557	348.15	0.5014		
293.85	0.3556	313.15	0.4186	332.65	0.4661	353.05	0.5076		
Diglycolic acid, $C_7H_6O_3$									
278.25	0.03655	296.65	0.08230	321.15	0.1605	338.15	0.2199	357.15	0.2845
284.15	0.04693	301.25	0.1038	323.15	0.1671	343.15	0.2391	361.35	0.2949
288.75	0.06859	310.65	0.1283	327.65	0.1882	348.15	0.2537		
293.75	0.07477	313.15	0.1390	332.65	0.2051	353.05	0.2680		

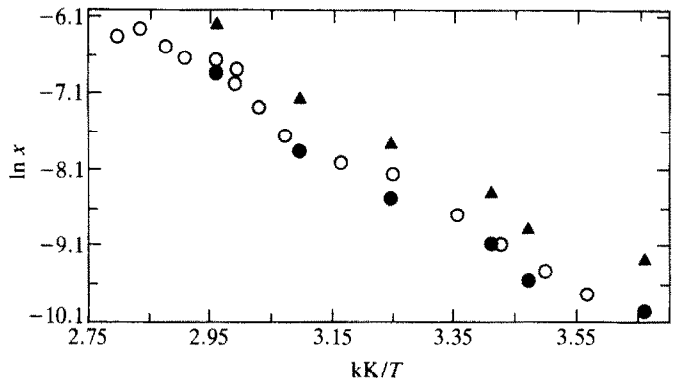

FIGURE 1. Solubility of azelaic acid in water as a function of temperature. ○, This work; ▲, reference 6; ●, reference 6, corrected results, see text.

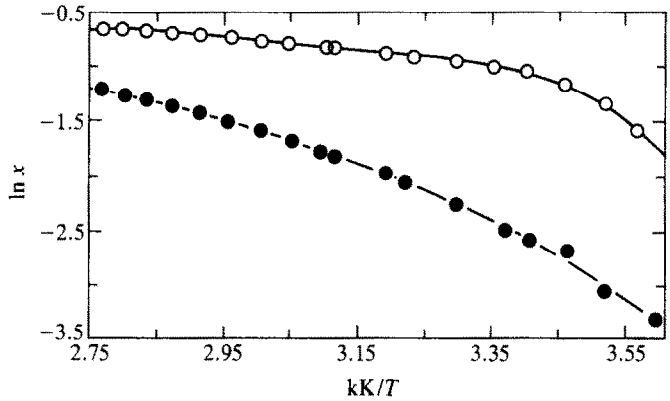

FIGURE 2. Solubility of glycolic and diglycolic acids in water as a function of temperature. ○, glycolic acid; ●, diglycolic acid.

molar enthalpies of solution at 298.15 K are: $\Delta_{sol}H_m(m = 0.0139\ mol \cdot kg^{-1}) = 37\ kJ \cdot mol^{-1}$ for suberic acid and $\Delta_{sol}H_m(m = 0.00946\ mol \cdot kg^{-1}) = 41\ kJ \cdot mol^{-1}$ for azelaic acid. Contrary to suberic and azelaic acids, levulinic, glycolic, and diglycolic acids are very soluble in water (table 1). No solubilities for these acids exist in the literature. For levulinic acid, the solubility depends strongly on temperature and the apparent molar enthalpy of solution at 298.15 K is: $\Delta_{sol}H_m(m = 45.1\ mol \cdot kg^{-1}) = 47\ kJ \cdot mol^{-1}$. In figure 2 are presented solubilities of glycolic and diglycolic acids over the studied temperature range. It is observed that for both acids, the solubility depends weakly on temperature and evidently the apparent molar enthalpies of solution at 298.15 K are rather low: $\Delta_{sol}H_m(m = 32.54\ mol \cdot kg^{-1}) = 11\ kJ \cdot mol^{-1}$ for glycolic acid and $\Delta_{sol}H_m(m = 5.30\ mol \cdot kg^{-1}) = 29\ kJ \cdot mol^{-1}$ for diglycolic acid.

The authors appreciate the technical assistance of Mr Kamran Golan.

REFERENCES

1. Apelblat, A. *J. Chem. Thermodynamics* **1986,** 18, 351.
2. Apelblat, A. *J. Chem. Thermodynamics* **1990,** 22, 253.
3. Apelblat, A.; Manzurola, E. *J. Chem. Thermodynamics* **1987,** 19, 317.
4. Apelblat, A.; Manzurola, E. *J. Chem. Thermodynamics* **1989,** 21, 1005
5. Manzurola, E.; Apelblat, A. *J. Chem. Thermodynamics* **1985,** 17, 579.
6. Lamouroux, F. *Compt. Rend.* **1899,** 128, 998.
7. Williamson, A. T. *Trans. Faraday Soc.* **1944,** 40, 421.