Entropy of Hydration and State of the Water in Organic Carboxylic Acid Hydrates

By D. H. FINE and P. GRAY

(*School of Chemistry, The University, Leeds*)

A NUMBER of carboxylic acids crystallize as hydrates. A thermodynamic study of the equilibrium between hydrated and anhydrous forms:

$$\underset{S^\circ_{\text{hyd}}}{\mathrm{O(H_2O)}_n\mathrm{(s)}} \rightleftharpoons \underset{S^\circ_{\text{anhyd}}}{\mathrm{O(s)}} + \underset{n\,S^\circ_{\text{gas}}}{n\,\mathrm{H_2O(g)}} \ldots n\,\Delta S^\circ_{\text{vap}}$$

by yielding information on the entropy change on dehydration and on the difference in entropy between the hydrated and anhydrous forms, can make possible a thermodynamic comparison between the states of hydrogen-bonded water in an organic hydrate and in crystalline ice,

$$\underset{S^\circ_{\text{ice}}}{\mathrm{H_2O(s)}} \rightleftharpoons \underset{S^\circ_{\text{vap}}}{\mathrm{H_2O(g)}} \ldots \Delta S^\circ_{\text{vap}}.$$

Such an analysis is possible when reliable vapour-pressure measurements are available over a range of temperatures, since

$$\Delta S^\circ_{\text{vap}} = \boldsymbol{R}T(\mathrm{d}\ln p/\mathrm{d}T) + \boldsymbol{R}\ln p.$$

Though many hydrates are known, such data are available only in a limited number of cases. A number of these are listed in the Table.

For citric acid monohydrate,[1] the standard entropy of vaporization is 33·6 cal. deg.$^{-1}$ (mole H_2O)$^{-1}$ and the difference in entropy between the crystalline monohydrate and the anhydrous form is 11·5 cal. deg.$^{-1}$ (mole H_2O)$^{-1}$; for oxalic acid dihydrate,[2] $\Delta S^\circ_{\text{vap}}$ is 34·6 cal. deg.$^{-1}$ (mole H_2O)$^{-1}$ and the difference, $S^\circ_{\text{hyd}} - S^\circ_{\text{anhyd}}$ is 10·5 cal. deg.$^{-1}$ (mole H_2O)$^{-1}$. These figures bear a striking resemblance to those for the sublimation of ice,[3] where $\Delta S^\circ_{\text{vap}} = 34$ cal. deg.$^{-1}$ mole^{-1} and $S^\circ_{\text{ice}} = 10{\cdot}6$ cal. deg.$^{-1}$ mole^{-1}. It may therefore be expected that the water molecule in these two hydrates has a similar environment, with a similar degree of randomness, to that of water in ice.

Recently, Ladd and Lee carried out calculations[4] which permit both the enthalpy of hydration and the entropy-difference between hydrated and anhydrous forms of a number of crystalline inorganic hydrates to be evaluated. For the octahydrates of eleven rare-earth sulphates an average entropy difference (per mole of water) *i.e.* $\frac{1}{8}$ ($S^\circ_{\text{hyd}} - S^\circ_{\text{anhyd}}$) of 10·9 ± 0·6 cal. deg.$^{-1}$ (mole H_2O)$^{-1}$ was obtained, similar to the figure for the organic hydrates and ice. The average enthalpy change for the dehydration $\frac{1}{8}\,M_2(SO_4)_3, 8\,H_2O \rightleftharpoons \frac{1}{8}\,M_2(SO_4)_3 + H_2O(g)$ implied by their calculations is 13·6 kcal. mole^{-1}, which is also near to the heat of sublimation of ice (12·0 kcal. mole^{-1}).

Similar conclusions may be drawn from an analysis of vapour-pressure data[5] for dilituric acid trihydrate, and from calorimetric data[6] for L-asparagine monohydrate (though these are not

TABLE

Thermodynamic data for organic hydrates

(Referring to 1 mole of H_2O)

Compound and degree of hydration	$\Delta H^\circ_{\text{dehyd}}$ kcal. (mole H_2O)$^{-1}$	$\Delta G^\circ_{\text{dehyd}}$ kcal. (mole H_2O)$^{-1}$	$\Delta S^\circ_{\text{dehyd}}$ cal. deg.$^{-1}$ (mole H_2O)$^{-1}$	$S^\circ_{\text{hyd}} - S^\circ_{\text{anhyd}}$ cal. deg.$^{-1}$ (mole H_2O)$^{-1}$
Ice	12·0	2·0	33·7	10·6
Citric acid, $1H_2O$	12·3	2·3	33·6	11·5
Oxalic acid, $2H_2O$	13·7	3·4	34·6	10·5
Dilituric acid, $3H_2O$	13·2	2·9	34·8	10·6
L-Asparagine, $1H_2O$	—	—	35·8	9·3
Eleven rare-earth sulphate octahydrates	13·6 (average)	—	—	10·9 (average)

---

[1] J. L. Marshall, *J. Proc. Austral. Chem. Inst.*, 1938, **5**, 383.

[2] R. S. Bradley and S. Cotson, *J. Chem. Soc.*, 1953, 1684.

[3] "Selected Values of Chemical Thermodynamic Properties" (Nat. Bur. Stand., circ. 500, Washington, 1952).

[4] M. F. C. Ladd and W. H. Lee, *J. Phys. Chem.*, 1965, **69**, 1840.

[5] M. C. Loeffler and W. J. Moore, *J. Amer. Chem. Soc.*, 1948, **70**, 3650.

[6] H. M. Huffman and H. Borsook, *J. Amer. Chem. Soc.*, 1932, **54**, 4297.

carboxylic acid hydrates). There would not seem to be reliable data for any other organic systems. The recent study[7,8] of the dissociation pressures of citric acid monohydrate was carried out at temperatures above its transition point, and the measurements thus refer to the system (anhydrous citric acid plus solution). Although (±)-tartaric acid forms a monohydrate, the only vapour-pressure data[9] yield such a markedly curved graph of log p *versus* $1/T$, that the measurements cannot be relied on. Until further determinations have been made, any limitations on the above generalization are not established. Where, however, experimental data lead to values for these entropy changes that are very discordant with those reported here, their reliability may be suspect.

(*Received, November 1st*, 1965; *Com.* 689.)

---

[7] T. P. Melia, *Trans. Faraday Soc.*, 1964, **60**, 1286.
[8] T. P. Melia, *Trans. Faraday Soc.*, 1965, **61**, 594.
[9] J. R. Partington, *J. Chem. Soc.*, 1911, **99**, 466.