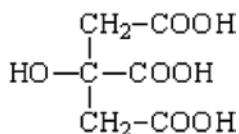


Chapter 2

Properties of Citric Acid and Its Solutions

2.1 Physicochemical Properties of Citric Acid in the Solid State

Citric acid - 2-hydroxy-1,2,3-tricarboxylic acid, $C_6H_8O_7 \equiv H_3Cit$, molar mass $192.12 \text{ g mol}^{-1}$. CAS registry [77-92-9], E 330



Sometimes, also the notation H_4Cit is used for it in the literature, when the hydrogen atom from hydroxyl group is involved in complexation reactions. There are no asymmetric carbon atoms in citric acid or in its anions, i.e. they are optically inactive. However, it is possible to make them asymmetrical by substitution of one of the hydrogen atoms in the methylene groups by another atom or group (the central carbon atom is prochiral).

Citric acid is a natural constituent of many plants, animal tissues and physiological fluids. In trace amounts it appears in a variety of fruits and vegetables, but macroscopic quantities are present in citrus fruits notably lemons and limes. Fruits having above 1 % (on the dry weight basis) are: lemons 4.0–8.0 %, black currents 1.5–3.0 %, grapefruits 1.2–2.1 %, oranges, tangerines, red currents, raspberries and strawberries contain citric acid in the 0.6–1.3 % range. Some typical values for a human body are: blood 10–25 ppm, bones 7500 ppm, semen 2000–4000 ppm, thyroid gland 750–900 ppm, mammary gland 3000 ppm, human milk 500–1250 ppm and urine 100–750 ppm [1].

At first, the crystal structure of anhydrous citric acid was established by Bennett and Yuill [2] in 1935 and later refined by others [3, 4] with an indication of the hydrogen bonding in the crystal. The crystal structure of citric acid monohydrate was reported by Burns and Iball [5] and Roelofsen and Kanters [6]. According to Nordman et al. [3], anhydrous citric acid is monoclinic, crystallizes in the space group $P2_{1/a}$ and citric acid monohydrate is orthorhombic and belongs to the space

group P2₁2₁2₁, both crystals have four molecules in the unit cell. Bennett and Yuill also found that the transition from citric acid monohydrate to anhydrous citric acid occurs between 36.15 and 36.45 °C with the mean value of 36.3 °C. The Marshall results [7] are slightly higher, from 36.35 to 36.6 °C and he proposed the transition temperature of 36.5 °C when De Kruif et al. [8] gave the value of 36.0 ± 0.5 °C based on the X-ray powder diffraction patterns. Oechler [9] based on solubility and vapour pressure measurements reported the value of 36.7 °C. From solubility determinations Dalman [10] and Slobodin and Novotelnova [11] estimated the transition temperature as 35.8 and 36.6 °C respectively. Using dynamic vapour sorption (DVS) and discontinuous isoperibolic thermal analysis (DITA) techniques Lafontaine et al. [12] gave 37.0 ± 1.0 °C result. Lower values about 34.5 °C, were reported by Nývlt [13] and Helmdach et al. [14] from solubility, ultrasound and turbidity studies.

The used by Bennett and Yuill crystals of anhydrous citric acid had density of $d = 1.665 \text{ g cm}^{-3}$ at 18 °C and the melting point was 156–157 °C. The density of citric acid monohydrate as reported by Laguerie et al. [15] was $d = 1.542 \text{ g cm}^{-3}$ at 25 °C. Wilhoit and Shiao [16] measured, from 20 to 80 °C, the specific volumes of the solid citric acid by using a glass dilatometer and expressed their results by the following quadratic equation

$$\begin{aligned} v/\text{cm}^3 \cdot \text{g}^{-1} &= 0.6415 - 4.770 \cdot 10^{-5} \theta + 2.363 \cdot 10^{-6} \theta^2 \\ \theta &= (T / \text{K} - 273.15) \end{aligned} \quad (2.1)$$

The volume expansion and the inner energy coefficients at 25 °C were also determined: $(\partial V / \partial T)_p / \text{cm}^3 \text{ g}^{-1} \text{ K}^{-1} = 0.704 \cdot 10^{-4}$ and $(\partial U / \partial P)_T / \text{J} \cdot \text{g}^{-1} \cdot \text{atm}^{-1} = -2.134 \cdot 10^{-3}$ with 1 atm = 101.325 kPa. They observed that citric acid decomposes in the 152.9–155 °C temperature region. The elastic and thermoelastic properties of anhydrous and monohydrate citric acid crystals were studied by Khan and Narasimhamurty [17] and Haussuehl and Wang [18].

Citric acid crystallizes from hot aqueous solutions in the anhydrous form as colorless transparent crystals or white crystalline powders. Citric acid monohydrate crystallizes from cold solutions and the crystals lose their hydration water if gently heated at 70–75 °C and melt in the range of 135–152 °C. Fast heating leads to dehydration at about 100 °C, melting at 153 °C and decomposition above 175 °C. Citric acid is deliquescent in wet air. Considering the importance of industrial aspects of crystallization from aqueous solutions, a number of studies of supersaturated or nearly saturated citric acid solutions were performed. It was demonstrated that the structure of these solutions and impurities have a great influence on nucleation kinetics and crystal formation and growth of citric acid crystals [19–32].

Utilization of citric acid in solid dispersions to increase the dissolution and oral absorption of sparingly soluble drugs was first suggested by Chiou and Riegelman [33] in the case of a water-insoluble antifungal antibiotic griseofulvin. A number of other pharmaceutical preparations (e.g. phenobarbital and hexobarbital) in the form of glass dispersions mixtures which include citric acid, were also investigated by various experimental techniques [34–43]. The melted highly viscous citric acid can be drawn into threads or sheets and after standing at 37 °C for a few days into a

hard, brittle and transparent glass. This glassy state is transformed into a crystalline state after months of standing at room temperature [44]. Thus, a physiologically acceptable and easily soluble carrier and poorly water-soluble drug are melted together and later solidified by cooling to room temperature. The formed glassy solid mixture when exposed to water or gastrointestinal fluids will dissolve rapidly the carrier and disperse drug particles. The competition during a rapid cooling between crystallization and glass formation determines whether a crystal or glass transition occurs. The glass–liquid transition is the reversible transition in amorphous or semi-crystalline materials which is accompanied by changes in physical properties (specific heat capacity and viscosity).

The glass transition temperatures T_g and corresponding changes in physical properties were determined for investigated solid mixtures but also for pure citric acid. Simmer and Enever [35] reported $T_g = -23^\circ\text{C}$ for citric acid monohydrate, but this result was in conflict with the Timko and Lordi [36] findings for anhydrous citric acid. The glass transition for bulk-prepared citric acid glass was $T_g = 13.2^\circ\text{C}$ and for the *in situ* conditions $T_g = 10.2^\circ\text{C}$. Repeated determination by Simmer and Enever [37] showed $T_g = 7.0^\circ\text{C}$ and that water present in citric acid monohydrate strongly reduces the glass temperature. Thermal citric acid studies of Timko and Lordi also indicated that the bulk-prepared melt (an amorphous + crystalline citric acid) exhibits a broad exothermic transition about -80°C which is followed by an endothermal effect. On contrary, the *in situ* did not exhibit an exothermic transition. Timko and Lordi [38] also investigated the effect of impurities and thermal history on the value of T_g and found that the lowering of glass transition temperatures is associated with a higher temperature of the melt preparation and with a longer exposure at this temperature. Decrease in T_g is accompanied by a progressive discoloration of the molten citric acid from a clear transparent liquid to a yellowish brown liquid. The effect of impurities was simulated by adding acotinic acid, a dehydration decomposition product of citric acid, which degrades upon melting. With increasing quantities of acotinic acid in the mixture it was observed that the glass transition temperature strongly decreases. A more systematic study of the properties of citric acid at its glass transition in a dry and hydrated states was performed by Lu and Zografu [39]. Their values for anhydrous citric acid are: $T_g = (10.2 \pm 0.2)^\circ\text{C}$; $\Delta C_p = (0.83 \pm 0.04) \text{ J g}^{-1} \text{ K}^{-1}$ and $\Delta H_\eta^* = 733 \text{ kJ mol}^{-1}$ (the activation energy for viscous flow at T_g) and for citric acid monohydrate are: $T_g = (10.7 \pm 1.0)^\circ\text{C}$; $\Delta C_p = (0.81 \pm 0.05) \text{ J g}^{-1} \text{ K}^{-1}$ and $\Delta H_\eta^* = 410 \text{ kJ mol}^{-1}$. These values are consistent with the Hoppu et al. [42] results: $T_g = (11.7 \pm 0.9)^\circ\text{C}$; $\Delta C_p = (0.82 \pm 0.03) \text{ J g}^{-1} \text{ K}^{-1}$; $\eta = 2.6 \cdot 10^{10} \text{ Pas}$ and $\Delta E_\eta^* = 156 \text{ kJ mol}^{-1}$ (flow activation energy at T_g). In the case of amorphous citric acid which contains 8.6 w/w% of residual water (the equimolar composition) the glass transition temperature has the value of $T_g = -25^\circ\text{C}$ and $\Delta C_p = (0.92 \pm 0.02) \text{ J g}^{-1} \text{ K}^{-1}$ which is similar to the Simmer and Enever value [35]. The glass transition of frozen solution of citric acid was estimated to be $T_g = -50^\circ\text{C}$ [39] which is in an agreement with the Kodoya et al. result $T_g = -55.1^\circ\text{C}$ as determined in the freeze-drying process study [40]. Lu and Zografu claimed that the relatively low values of T_g are responsible for difficulty to prepare and maintain a large quantity of pure citric acid in the amorphous state without significant crystallization. Evidently, besides drug + citric acid solid dispersions, the values of glass transition temperatures

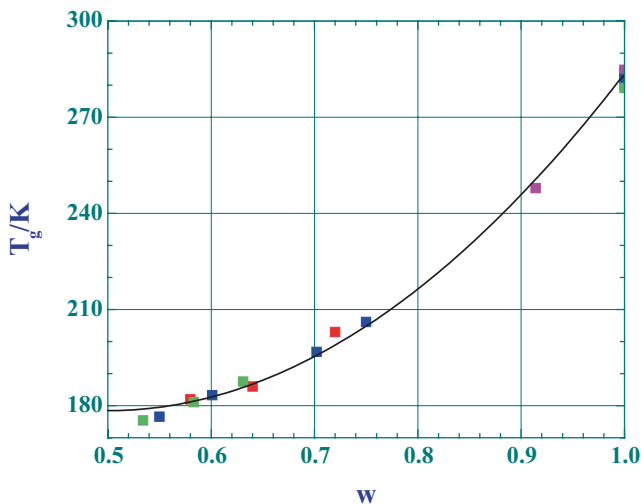


Fig. 2.1 The glass transition temperature T_g as a function of weight fraction of citric acid w in the citric acid + water mixtures. ■ - [35–39, 42]; ■ - [43]; ■ - [45]; ■ - [46]; continuous line is calculated using Eq. (2.2)

in the citric acid + water system, are also of great interest in meteorological investigations. Systematic measurements of T_g as a function of added water to citric acid were performed by Lienhard et al. [43], Maltini et al. [45], and Murray [46]. Moreira [47] determined T_g values in the $0.4 < w < 0.8$ concentration range, but unfortunately they are given only in graphical form. All available in the literature T_g values are plotted in Fig. 2.1 and they can be correlated by the following equation

$$T_g / K = 283.15 - 419.36w + 419.89w^2 \quad (2.2)$$

where w is the weight fraction of citric acid in the mixture. This and other fitting equations were evaluated by using an unweighted multivariate least-squares method.

Aerosols in upper troposphere often contain a substantial and variable fraction of organic compounds (ranging from 10 to 70% of the total dry aerosol mass). They are mixed with inorganic material, usually with ammonium sulfate. Water-soluble organic components of aerosols effect the hygroscopicity, phase transition, light scattering, formation and properties of cloud droplets. Under upper tropospheric conditions, droplets containing dissolved organic substances in aqueous solutions can become glassy. Thus, the impact of organic compounds on the cloud forming and ice cloud nucleation has been widely investigated [46, 48–56]. In this context, citric acid which was identified in aerosol particles, was frequently used as a model substance for atmospheric experiments. Citric acid as well other organic acids received much attention because they are able to absorb water and alter the radiation balance and finally the climate. It is worthwhile also to note that citric acid solutions, as was observed by Corley and Killoy [57], are stable with regards

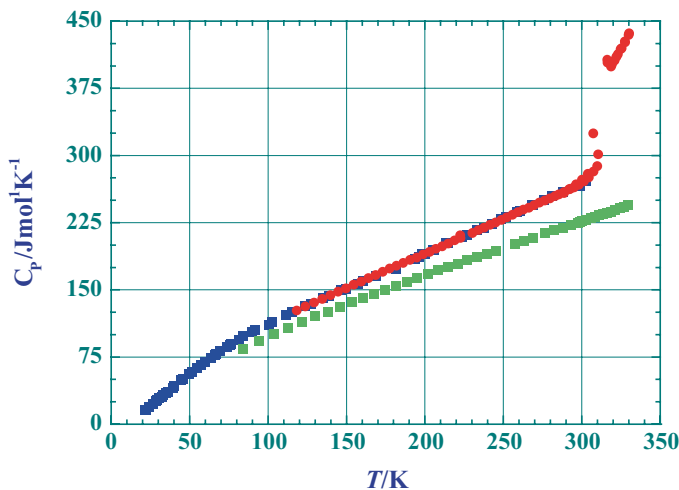


Fig. 2.2 The molar heat capacity of anhydrous and monohydrate citric acid as a function of temperature. Anhydrous citric acid ■ - [8]; citric acid monohydrate ■ - [58]; ● - [8]

to time, light and air exposure. The studies of the water-citric acid-electrolyte aerosols in atmosphere are also important because they provide significant information about activities, solubilities, surface tension and other properties of aqueous solutions of citric acid [46, 49–51, 53–56].

From thermodynamic properties of solid citric acid monohydrate, the heat capacities, enthalpies and entropies were determined by Evans et al. [58] in the 20–300 K temperature range. De Kruif et al. [8] reported the heat capacities, enthalpies, entropies and the Gibbs free energies from 120 to 300 K for monohydrate, and the corresponding values of the thermodynamic functions from 90 to 330 K for anhydrous citric acid. They observed a slightly superheated large transition at 312.1 K and above this transition, a very large molar heat capacities with a significant temperature dependence (Fig. 2.2). This temperature is higher than that mentioned above from the literature ~ 309.7 K but probably it indicates that the formation of the monohydrate from the high-temperature solid phase was not complete [8]. As can be seen in Fig. 2.2, both sets of molar heat capacities of citric acid monohydrate agree well and they can be represented by the polynomial expression for $20\text{ K} < T < 305\text{ K}$

$$C_p(\text{H}_3\text{Cit} \cdot \text{H}_2\text{O}) / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 27.324 + 2.1259(T / \text{K}) - 1.0333 \cdot 10^{-2}(T / \text{K})^2 + 3.3504 \cdot 10^{-5}(T / \text{K})^3 - 3.9008 \cdot 10^{-8}(T / \text{K})^4 \quad (2.3)$$

For temperatures below 22 K, Evans et al. [58] obtained the molar heat capacities using the Debye function with $T_D = 150$ K. In the case of anhydrous citric acid, in the $84\text{ K} < T < 330\text{ K}$ temperature interval, the molar heat capacities can be expressed by

$$C_p(\text{H}_3\text{Cit}) / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -6.7603 + 1.3632(T / \text{K}) - 4.1314 \cdot 10^{-3}(T / \text{K})^2 + 1.0096 \cdot 10^{-5}(T / \text{K})^3 - 9.4236 \cdot 10^{-9}(T / \text{K})^4 \quad (2.4)$$

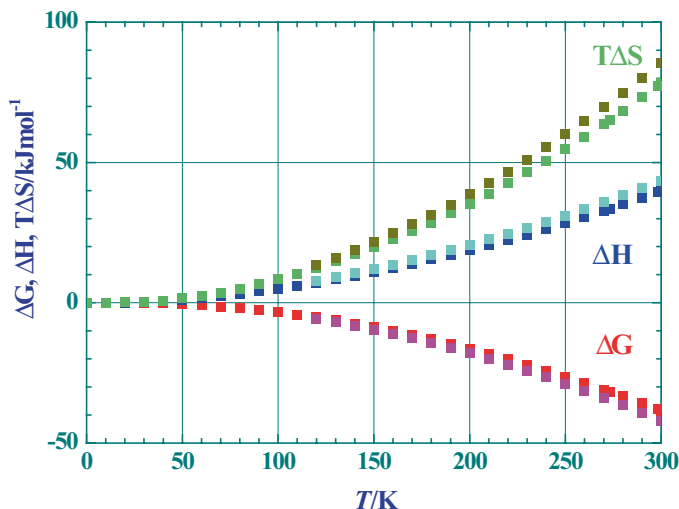


Fig. 2.3 Thermodynamic functions ΔG , ΔH and $T \cdot \Delta S$ of citric acid monohydrate as a function of temperature. \blacksquare , \blacksquare , \blacksquare - [8]; \blacksquare , \blacksquare , \blacksquare - [58]

Thermodynamic functions ΔG , ΔH and $T \cdot \Delta S$ of citric acid monohydrate as a function of temperature were determined by Evans et al. [58] and De Kruif et al. [8] and they are plotted in Fig. 2.3. De Kruif et al. used in calculations of thermodynamic functions the absolute entropy and enthalpy reported by Evans et al. at 120 K. The functions ΔG , ΔH and $T \cdot \Delta S$ are consistent in both investigations but there is a noticeable difference between them (Fig. 2.3). As can be observed, the Gibbs free energy is negative $\Delta G < 0$ and the enthalpy and entropy are positive and they have similar values with $\Delta H < T \cdot \Delta S$. The absolute values of all thermodynamic functions increase with increasing of temperature T . Using the Evans et al. [58] results which cover a more extended temperature range $0 < T < 300$ K, the thermodynamic functions of citric acid monohydrate are

$$\begin{aligned}
 \Delta G(\text{H}_3\text{Cit} \cdot \text{H}_2\text{O}) / \text{kJ mol}^{-1} &= 1.6377 \cdot 10^{-2} (T / \text{K}) - 5.1776 \cdot 10^{-4} (T / \text{K})^2 \\
 &\quad + 1.2185 \cdot 10^{-7} (T / \text{K})^3 \\
 \Delta H(\text{H}_3\text{Cit} \cdot \text{H}_2\text{O}) / \text{kJ mol}^{-1} &= -2.7307 \cdot 10^{-3} (T / \text{K}) + 5.5329 \cdot 10^{-4} (T / \text{K})^2 \\
 &\quad - 3.4548 \cdot 10^{-7} (T / \text{K})^3 \\
 T \Delta S(\text{H}_3\text{Cit} \cdot \text{H}_2\text{O}) / \text{kJ mol}^{-1} &= -1.9108 \cdot 10^{-2} (T / \text{K}) + 1.0710 \cdot 10^{-3} (T / \text{K})^2 \\
 &\quad - 4.6733 \cdot 10^{-7} (T / \text{K})^3
 \end{aligned} \tag{2.5}$$

The enthalpy, entropy and the Gibbs free energy of formation of crystalline monohydrate at 298.15 K, as calculated from the values of constituent elements in their standard states are: $\Delta G_f(s, 298.15 \text{ K}) = -1472.8 \pm 1.3 \text{ kJ mol}^{-1}$, $\Delta H_f(s, 298.15 \text{ K}) = -1837.6 \pm 0.8 \text{ kJ mol}^{-1}$ and $\Delta S_f(s, 298.15 \text{ K}) = -1223.8 \pm 0.8 \text{ J mol}^{-1} \text{ K}^{-1}$ [58, 59] when Burton

[60] using the enzymatic equilibrium data, gives a slightly higher value for the Gibbs free energy of formation of the crystalline monohydrate $\Delta G_f(s, 298.15 \text{ K}) = -1168.8 \pm 6.3 \text{ kJ mol}^{-1}$. The Wilhoit and Shiao value $\Delta H_f(s, 298.15 \text{ K}) = -1543.9 \text{ kJ mol}^{-1}$ and the Korcherina et al. [61] value $\Delta H_f(s, 298.15 \text{ K}) = -1551.7 \pm 1.3 \text{ kJ mol}^{-1}$ for the enthalpy of formation are lower than these given above because they used in calculations the heat of formation of the standard substance for $\text{CO}_2(\text{gas})$ and not for $\text{C}(\text{graphite})$ as in [58, 59].

Thermodynamic data which exists for anhydrous citric acid is given in the form of relative values. De Kruif et al. [8] reported not absolute values of thermodynamic functions, but changes in the Gibbs free energy, enthalpy and entropy, $\Delta[G(T) - G(90 \text{ K})]$, $\Delta[H(T) - H(90 \text{ K})]$ and $\Delta[S(T) - S(90 \text{ K})]$. They can be represented in the $90 \text{ K} < T < 330 \text{ K}$ temperature range by the following polynomials

$$\begin{aligned}
 \Delta[G(T) - G(90 \text{ K})]/\text{kJ mol}^{-1} &= -8.3675 \cdot 10^{-4} \theta - 4.7714 \cdot 10^{-4} \theta^2 \\
 &\quad + 1.7331 \cdot 10^{-7} \theta^3 \\
 \Delta[H(T) - H(90 \text{ K})]/\text{kJ mol}^{-1} &= 9.1225 \cdot 10^{-2} \theta + 3.6364 \cdot 10^{-4} \theta^2 \\
 &\quad - 1.3423 \cdot 10^{-7} \theta^3 \\
 \Delta[S(T) - S(90 \text{ K})]/\text{J mol}^{-1} \text{ K}^{-1} &= 9.9208 \cdot 10^{-1} \theta - 9.90972 \cdot 10^{-4} \theta^2 \\
 &\quad + 1.1041 \cdot 10^{-6} \theta^3 \\
 \theta &= T / \text{K} - 90
 \end{aligned} \tag{2.6}$$

In order to convert the relative values of entropies of anhydrous citric acid in Eq. (2.6) to absolute values, they must be increased by $75 \text{ J mol}^{-1} \text{ K}^{-1}$, i.e. $S(s, 90 \text{ K}) = 75 \text{ J mol}^{-1} \text{ K}^{-1}$ and $S(s, 298.15 \text{ K}) = 252.1 \text{ J mol}^{-1} \text{ K}^{-1}$ [8]. Thermal effects associated with the citric acid monohydrate to anhydrous citric acid transition will be discussed later in the context of citric acid dissolution in water.

The Gibbs free energy of formation of citric acid in a saturated solution is given by Evans et al. [58] as $\Delta G_f(\text{sat. soln}, 298.15 \text{ K}) = -1235.0 \pm 1.3 \text{ kJ mol}^{-1}$. They reported also the corresponding value for the aqueous citrate ion formation in a solution of unit activity, $a=1$, as $\Delta G_f(\text{aq. soln}, 3 \text{ H}^+ + \text{Cit}^{3-}, 298.15 \text{ K}) = -1161.9 \pm 1.4 \text{ kJ mol}^{-1}$ (the Burton result is $\Delta G_f(\text{aq. soln}, \text{Cit}^{3-}, 298.15 \text{ K}) = -1165.5 \pm 0.2 \text{ kJ mol}^{-1}$ [60]). Kochergina et al. [61] performed a detailed calorimetric study of formation of citrate ions in water and KOH solutions. They presented the following enthalpies of formations $\Delta H_f(\text{aq. soln}, \text{Cit}^{3-}, 298.15 \text{ K}) = -1534.6 \pm 1.6 \text{ kJ mol}^{-1}$; $\Delta H_f(\text{aq. soln}, \text{HCit}^{2-}, 298.15 \text{ K}) = -1526.5 \pm 1.6 \text{ kJ mol}^{-1}$; $\Delta H_f(\text{aq. soln}, \text{H}_2\text{Cit}^-, 298.15 \text{ K}) = -1530.0 \pm 1.6 \text{ kJ mol}^{-1}$ and $\Delta H_f(\text{aq. soln}, \text{undiss. H}_3\text{Cit}, 298.15 \text{ K}) = -1528.5 \text{ kJ mol}^{-1}$.

The equilibrium vapour pressure over crystals of citric acid monohydrate (the decomposition pressure of the hydrate) was determined by Marshall [7] using the dynamic air current method [62, 63]. His results are in a reasonable agreement with those of De Kruif et al. [8]. They used the static method by employing a diaphragm manometer. Oechler [9] applying a direct manometric technique measured vapour pressure of water over solutions saturated with both, the monohydrate and anhydrous citric acid, and obtained practically the same results. These three sets

Table 2.1 Vapour pressures of water over solid citric acid monohydrate

$t/^{\circ}\text{C}$	p/kPa	$t/^{\circ}\text{C}$	p/kPa	$t/^{\circ}\text{C}$	p/kPa
10.0 [7]	0.669 ^a	20.1	1.367	30.1	2.788
13.1	0.809	25.0	1.961	30.2	2.898
13.1	0.895	25.0	1.928	35.0	3.890
13.1	0.852	25.0	1.970	35.0	3.790
13.1	0.852	25.0	1.845	35.0	3.834
15.0	0.964	25.1	1.968	35.0	3.980
20.0	1.377	25.1	1.978	35.0	4.008
20.1	1.384	30.0	2.770	35.05	3.913
20.1	1.367	30.1	2.810	36.50	4.293
4.95 [8]	0.325	24.52	1.748	33.02	3.399
9.73	0.521	25.27	1.760	33.27	3.373
15.96	0.893	28.84	2.332	35.81	3.902
19.97	1.212	30.08	2.582	35.91	3.906
20.60	1.213	33.00	3.240		
26.10 [9]	1.911	33.88	3.546		
31.15	2.836	37.78	4.666		

^a 1 kPa = 7.5006 mmHg

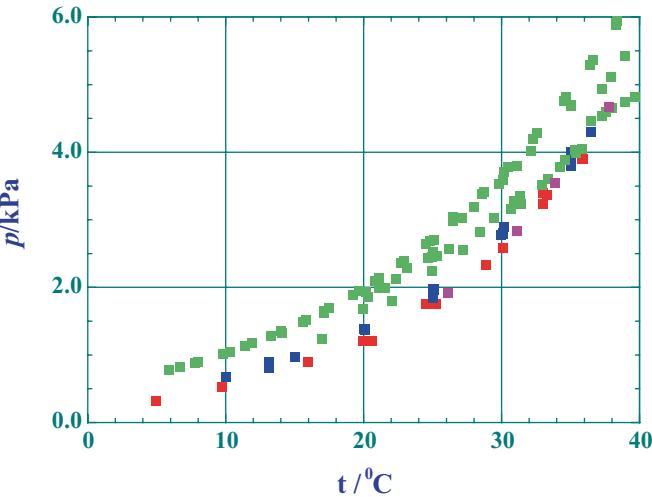


Fig. 2.4 Vapour pressure of water over solid citric acid monohydrate and over aqueous saturated solutions of citric acid as a function of temperature. Vapour–solid equilibrium ■ - [7]; ■ - [8]; ■ - [9, see text] and liquid–solid equilibrium ■

of experimental data are presented in Table 2.1 and plotted in Fig. 2.4. They are presented in the temperature range of citric acid monohydrate existence, together with vapour pressures over saturated solutions taken from the literature. As can be observed, especially at higher temperatures with approaching the transition point,

the scattering of the experimental points is large and the results are less certain. Melia [64, 65] erroneously claimed that he measured vapour pressures over citric acid monohydrate (above $T > 313$ K) but these vapour pressures are probably over the saturated solutions of citric acid.

The enthalpy change associated with dehydration process is determined from the Clausius–Clapeyron equation

$$\left(\frac{\partial \ln p(T)}{\partial (1/T)} \right)_{s \rightarrow g} = - \frac{\Delta H(T)}{R} \quad (2.7)$$

and by assuming that $\Delta H(T)$ linearly depends on temperature T , the integral form of Eq. (2.7) gives the temperature dependence of vapour pressures

$$\begin{aligned} \ln[p(T)/\text{kPa}] &= 241.82 - \frac{16262.7}{(T/\text{K})} - 32.757 \ln(T/\text{K}) \\ \Delta H(T)/\text{kJ mol}^{-1} &= 135.22 - 0.2724 (T/\text{K}) \end{aligned} \quad (2.8)$$

It follows from Eq. (2.8) that $\Delta H(298.15 \text{ K}) = 54.0 \text{ kJ mol}^{-1}$ when the De Kruif et al. [8] values are $\Delta H(298.15 \text{ K}) = 56.8 \pm 1.0 \text{ kJ mol}^{-1}$ and $\Delta H(309.5 \text{ K}) = 55.8 \pm 1.0 \text{ kJ mol}^{-1}$. Marshall [7] gives in the 288.15–308.15 K temperature range, the average enthalpy of hydration reaction as $\Delta H(T) = 51.6 \text{ kJ mol}^{-1}$.

2.2 Melting and Freezing Temperatures of Aqueous Solutions of Citric Acid

The complete phase diagram of the citric acid–water system in the 273–373 K temperature range which includes the liquid and solid phases is plotted in Fig. 2.5. The solid–liquid equilibrium is considered here and the vapour–liquid equilibrium will be discussed later. The temperature–composition curves (in Fig. 2.5, the composition of phases is expressed in the mass fractions of citric acid w) were constructed using experimental data available from the literature. They come from determinations of melting, freezing points, glass transitions and solubilities. The homogenous ice freezing temperatures and the glass transition temperatures were already discussed when other phase relations will be considered in a more detail below. The melting temperatures T_m (Fig. 2.6) and the homogenous ice freezing temperatures T_f are presented in Table 2.2.

Related to determinations of T_m temperatures are cryoscopic measurements where the freezing-point depressions of aqueous solutions of citric acid, $\theta(m) = T_{f,p}(\text{H}_2\text{O}) - T_{f,p}(m)$, are very accurately measured. This colligative property depends only on the solvent and not on the nature of the solute present in

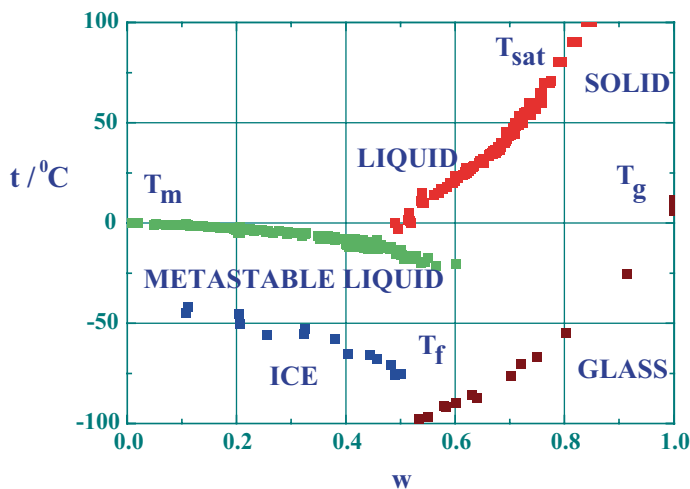


Fig. 2.5 Phase diagram of the citric acid–water system. ■ - liquid–solid equilibrium (the solubility curve); ■ - equilibrium melting curve; ■ - homogenous ice freezing temperature curve; ■ - the glass transition curve

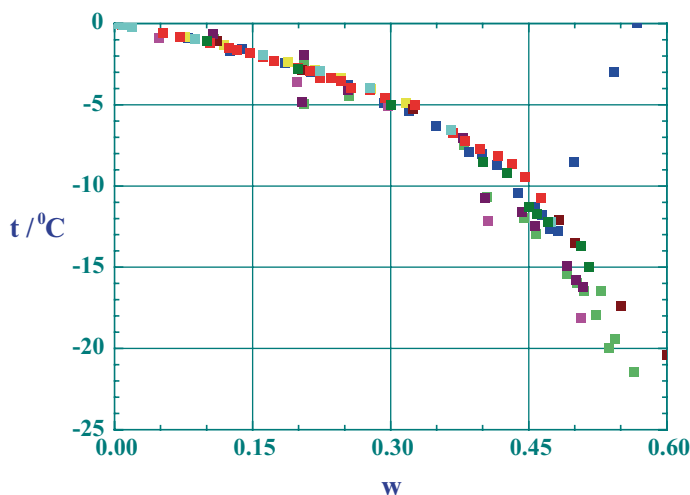


Fig. 2.6 The equilibrium melting-point curve of the citric acid–water system. ■ - [43]; ■ - [45]; ■ - [46]; ■ - [53]; ■ - [66]; ■ - [67]; ■ - [68]; ■ - [69]; ■ - [70]

the solution. Systematic measurements of $\theta(m)$ values for $m < 5.0 \text{ mol kg}^{-1}$ were performed by Apelblat and Manzurola [68], Kendall et al. [66] (in their study, the reported mole fractions are actually molarities of citric acid) and few additional points are given in International Critical Tables [67]. There is a very satisfactory agreement between these sets of data (Table 2.3). In CRC Handbook of Chemistry

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