

# Some Physicochemical Data on Monohydrate Citric Acid Solutions in Water: Solubility, Density, Viscosity, Diffusivity, pH of Standard Solution, and Refractive Index

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Six different series of data are given, relative to monohydrate citric acid concentrated solutions in water. Solubility, density, viscosity, pH of a standard solution, and refractive index are determined by the usual methods. Diffusivity is measured with a new type of porous diaphragm cell.

Physicochemical properties of concentrated aqueous solutions of citric acid are not well known. Data on solubility, density, viscosity, diffusivity, pH of a standard solution, and refractive index of monohydrate solutions are given.

## Solubility

Solubility in water has been determined by dissolving small quantities of solid acid (the purity of which is greater than 99.5%) in a given quantity of pure water, in a stirred vessel at controlled temperature. After dissolution has stopped, stirring is continued for 5–6 hr to ensure that equilibrium has been reached. Then the remaining solid is quickly filtrated and dried. The concentration of the solution is determined by weighing the solid (method 1) or titrating the liquid with sodium hydroxide (method 2). The results expressed in grams of monohydrate acid/100 g of pure water are presented in Table I. As shown in Figure 1, the agreement with Dalman's data (2) which are recommended by Mullin (11) and Nyvlt (13) is very good and also with the data given by Perry (14), Kirk and Othmer (6), and Stephen and Stephen (15). On the contrary, the difference is more important with Kremann and Eitel's data (7). Between 17° and 33°C, experimental results can be correlated in the form:

$$\log C_S = 5.634 - \frac{988}{T} \quad (1)$$

in which  $C_S$  is expressed in grams of hydrate/100 g of water and  $T$  in K. The mean deviation between experiments and correlation is 0.2%, and the maximum deviation is smaller than 0.5%.

For temperatures higher than 33°C, correlation (1) is no longer valid. This is probably due to the fact that this type of correlation is not the most adequate. Usually, concentration has to be expressed as the mole fraction of nonsolvated solute in the solution.

## Density

The density of the solution prepared by weight has been determined at 20° and 25°C by a pycnometer technique with an error smaller than 0.0005 g/cm<sup>3</sup>. The data are presented in Table II.

The variations of density with concentration are conveniently represented by the correlation:

$$\rho = \frac{C + 100}{\frac{C}{\rho_A} + \frac{100}{\rho_E}} \quad (2)$$

For example, at 20°C where  $\rho_A = 1.542$  g/cm<sup>3</sup> (6) and  $\rho_E = 0.9983$  g/cm<sup>3</sup> (14), and at 25°C where  $\rho_A = 1.542$  g/cm<sup>3</sup> and  $\rho_E = 0.9970$  g/cm<sup>3</sup> (14), the deviation between the experiments and the proposed correlation is less than 0.17%. This quite satisfactory agreement probably means that the dissolution of citric acid in water takes place at constant partial molecular volumes.

## Viscosity

The viscosity of solutions has been determined in a viscometer Rheomat 15, composed of two coaxial cylinders, the inner one rotating. The results obtained at 25°C are presented in Table III. The estimated precision is 2%.

Extrapolating a form of correlation valid for dilute electrolytic solutions (4), we have represented the data by

$$\mu - \mu_0 = 0.18 \sqrt{C} \exp(0.95 C) \quad (3)$$

in which  $C$  is expressed in moles of hydrate/l. of solution.

The mean deviation between experimental results and calculated values is 2.5%; the maximum deviation is 5%. For dilute solutions, the difference  $\mu - \mu_0$  is quite proportional to the square root of concentration.

## Diffusivity

The diffusivity of citric acid in water has been determined at 25°C, as a function of the concentration, by means of a porous diaphragm cell method similar to that proposed by Lozar (8, 9). The diaphragm used is a Millipore filter Microweb WS, 150 μm in thickness. The pore diameter is 3 μm, and the void fraction 45%. The two-cell compartments are filled with solutions at different concentrations, well stirred to prevent development of significant diffusional films on both sides of

Table I. Solubility of Monohydrate Citric Acid in Water

Method 1		Method 2	
Temp, °C	C, g of hydrate/100 g of water	Temp, °C	C, g of hydrate/100 g of water
17.2	172.0	17.2	170.5
20.2	183.5	19.8	183.0
22.5	195.0	22.9	196.5
25.1	208.0	25.3	208.5
27.0	220.0	27.6	221.0
28.6	227.0	30.7	239.5
30.5	240.0	33.7	261.0
31.8	247.5		
34.4	271.5		
35.4	283.5		

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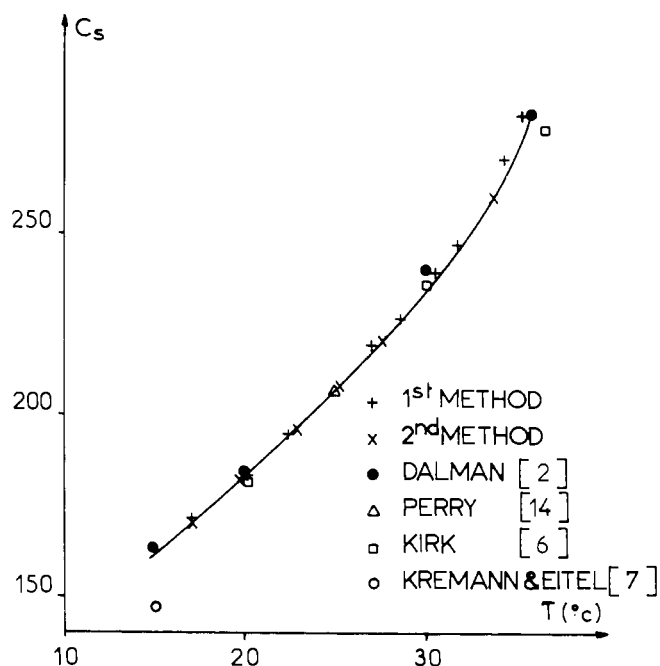


Figure 1. Solubility of monohydrate citric acid in water (grams of hydrate/100 g of water) vs. temperature in °C

Table II. Density of Monohydrate Citric Acid Aqueous Solutions

20°C		25°C	
C, g of hydrate/100 g of water	$\rho$ , cm <sup>-3</sup>	C, g of hydrate/100 g of water	$\rho$ , cm <sup>-3</sup>
8.3	1.0252	22.4	1.0651
29.0	1.0843	40.1	1.1012
43.2	1.1153	63.6	1.1579
55.1	1.1422	97.4	1.2118
70.8	1.1703	116.2	1.2319
87.1	1.1951	134.8	1.2539
109.6	1.2227	155.5	1.2703
120.7	1.2381	185.5	1.2924
136.6	1.2518	199.5	1.3006
167.4	1.2799	208.5	1.3094
188.5	1.2958	217.0	1.3102
223.8	1.3195	220.9	1.3151

Table III. Viscosity of Monohydrate Citric Acid Aqueous Solutions at 25°C

C, g of hydrate/100 g of water	C, mol l. <sup>-1</sup>	$\mu$ , cP
0	0	0.91
40.1	1.53	1.87
63.6	2.14	3.03
97.4	2.82	5.03
116.2	3.14	7.50
134.8	3.42	9.45
155.5	3.68	12.30
170.0	3.84	14.22
185.5	4.0	16.87
199.5	4.13	19.55
217.0	4.29	23.80

the diaphragm. The procedure and advantages of this type of equipment have been discussed elsewhere (9). The diffusivity  $D$  obtained is an integral value through the range of concentration  $[(C_{1i} + C_{2i})/2, (C_{1f} + C_{2f})/2]$ , and it is determined using the relation (8, 9, 11, 12, 16):

$$D = \frac{1}{\beta t} \ln \frac{C_{1i} - C_{2i}}{C_{1f} - C_{2f}} \quad (4)$$

The cell constant  $\beta$  is obtained after calibration of the equipment by use of aqueous solutions of potassium chloride, the diffusivity of which is well known (5). For all diaphragms used,  $\beta$  was almost constant between  $18.2 \cdot 10^4$  and  $18.5 \cdot 10^4$  m<sup>-2</sup>.

When the diffusivity varies linearly with concentration, Gordon (3) has shown that the mean value determined by Equation 4 is nothing but the differential coefficient at concentration

$$C_m = \frac{C_{1i} + C_{1f}}{2} + \frac{C_{2i} + C_{2f}}{2} \quad (5)$$

This hypothesis is more valid when the difference in concentration between both compartments of the cell is weaker; we selected low differences of the order of 10 g of hydrate/100 g of water, never exceeding 25 g/100 g. Table IV summarizes the obtained results, which are represented in Figure 2. The estimated precision is 8% (8).

Table IV. Diffusivity of Monohydrate Citric Acid in Aqueous Solutions at 25°C

$C_m$ , g of hydrate/100 g of water	19.5	44.8	68	115.5	180.7	181	213.7
$D$ , cm <sup>2</sup> sec <sup>-1</sup> · 10 <sup>6</sup>	7.0	5.1	3.7	3.4	4.0	4.2	4.3

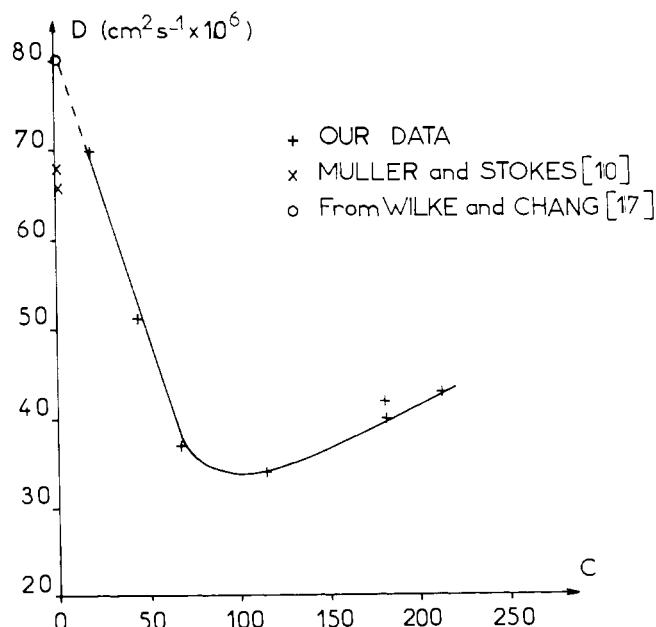


Figure 2. Diffusivity of monohydrate citric acid in aqueous solution (cm<sup>2</sup> sec<sup>-1</sup>) vs. concentration of solution (grams of hydrate/100 g of water) at 25°C

**Table V. pH of Standard Solution at 20°C**  
50 cm<sup>3</sup> of aqueous solution of Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O (M/4)  
5 cm<sup>3</sup> of aqueous solution of monohydrate citric acid

C, g of hydrate/100 g of water	pH
43.2	4.430
55.1	4.060
70.7	3.772
87.1	3.567
99.3	3.480
109.6	3.410
120.7	3.344
127.0	3.300
149.5	3.230
166.3	3.160
174.8	3.132
186.0	3.110
194.5	3.088
205.5	3.055
217.5	3.027
239.1	2.985

Diffusivity at zero concentration extrapolated from the results is 14% higher than that proposed by Muller and Stokes (10) who used an interferometric method, but it is in close agreement with the value obtained by Wilke and Chang's correlation (17).

#### pH of Standard Solution

Standard solutions can be used to determine rapidly the concentration of a given solution by means of a pH meter. For citric acid, Brunel (1) proposed different types of buffer solution composition (of Soerensen, McIlvaine, Kolthoff, Vleeschower, etc.). A standard solution derived from the buffer solution of McIlvaine is proposed here which is much more convenient for concentrated solutions. Its composition is 50 cm<sup>3</sup> of M/4 aqueous solution of sodium diphosphate Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O; 5 cm<sup>3</sup> of aqueous solution of monohydrate citric acid. The pH variations of this standard solution as a function of the concentration of the monohydrate citric acid aqueous solutions at 20°C are given in Table V.

#### Refractive Index

The refractive index of aqueous citric acid solutions prepared by weight has been determined at 25° ± 0.2°C by means of a refractometer. The results are presented in Table VI.

#### Conclusions

Six different series of data have been given for concentrated aqueous solutions of monohydrate citric acid. Knowledge of these physicochemical properties appears to be necessary for the treatment of mass-transfer phenomena, such as dissolution or crystallization, by chemical engineers.

#### Nomenclature

*C* = concentration, g of hydrate/100 g of water or moles of hydrate  
*C<sub>m</sub>* = mean concentration

**Table VI. Refractive Index of Aqueous Monohydrate Citric Acid Solutions at 25°C**

C, g of hydrate/100 g of water	η, refractive index
0	1.3324
20.0	1.3589
42.6	1.3764
68.5	1.3908
91.0	1.4009
96.6	1.4047
110.0	1.4101
124.5	1.4157
148.0	1.4209
161.3	1.4257
173.5	1.4272
177.1	1.4289
182.0	1.4298
201.0	1.4341
216.5	1.4375
236.2	1.4402

$\left. \begin{matrix} C_{1f} \\ C_{2f} \\ C_{1i} \\ C_{2i} \end{matrix} \right\} =$  initial and final concentrations in cell

*D* = diffusivity, cm<sup>2</sup> sec<sup>-1</sup>

*T* = temperature, K or °C

*t* = time, sec

*β* = constant of cell, cm<sup>-2</sup>

*η* = refractive index

*μ* = viscosity of the solution, cP

*μ<sub>0</sub>* = viscosity of water, cP

*ρ* = density of solution, g cm<sup>-3</sup>

*ρ<sub>A</sub>* = density of solid monohydrate citric acid, g cm<sup>-3</sup>

*ρ<sub>E</sub>* = density of water, g cm<sup>-3</sup>

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