[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BROOKLYN COLLEGE OF PHARMACY, LONG ISLAND UNIVERSITY]

The Solubility of Citric and Tartaric Acids in Water

BY LAWRENCE H. DALMAN

In a recent investigation[1] a few measurements were reported for the solubilities of citric and tartaric acids in water. A search of the literature reveals practically no data with which to compare the results obtained for citric acid. While Seidell[2] has reported an isolated solubility at 25° and Kremann and Eitel[3] have obtained some measurements at lower temperatures from freezing point data, no systematic investigation appears to have been made of the solubility of citric acid over the usual range of temperature from 0 to 100°.

The figures obtained for the solubility of tartaric acid were found to be about 1% lower than those given in "International Critical Tables"[4] and Seidell's Tables[5] which are both taken from the results originally reported at 5° intervals from 0 to 100° by Leidie.[6] It is not stated how these measurements were made except that they were obtained with the aid of two equations. When these values are plotted, the solubility curve appears to consist of two sections which intersect between 40 and 45°, although the saturating solid phase is reported to be anhydrous tartaric acid throughout the entire temperature range. The author does not offer an interpretation of this irregularity and it was therefore decided to repeat these measurements. The present investigation presents the results obtained for the solubility measurements of citric and tartaric acids at ten degree intervals from 0 to 100°.

Materials

Citric and Tartaric Acids.—The citric and tartaric acids were supplied by Charles Pfizer and Company. These acids were thrice recrystallized from water, dried and stored over sulfuric acid. Titration against sodium hydroxide gave results which agreed within 0.1% of their theoretical values.

Standard Sodium Hydroxide.—This solution was prepared and used according to accepted standards. It was preserved in a container protected against dust, carbon dioxide, etc., and standardized at regular intervals.

Procedure.—Solubilities were measured by analysis of the saturated solutions obtained by agitation of the acids in water enclosed in glass-stoppered tubes and rotated in an electrically controlled thermostat for at least six hours. This was found to be sufficient time to bring about equilibrium although the samples below 50° were rotated from eight to ten hours. The measurement at 0° was obtained in a well-stirred mixture of ice and water, while that at 100° was taken in boiling distilled water. The temperature control was ±0.02°, read directly from a thermometer standardized by the Bureau of Standards.

For analysis samples of the saturated solution were taken up in a pipet (warmed when necessary) and weighed in a small vial. To prevent ingress of solid material, the end of the pipet was protected by means of a piece of cloth held securely by thread. The acid content of the sample was determined by titration with standard sodium hydroxide using phenolphthalein as indicator. All determinations were made in triplicate and averaged. The data thus obtained have been expressed in weight per cent. and plotted in Fig. 1. It is believed that the measurements are precise within 0.1%, although it was found that they could be checked on the average within 0.06%.

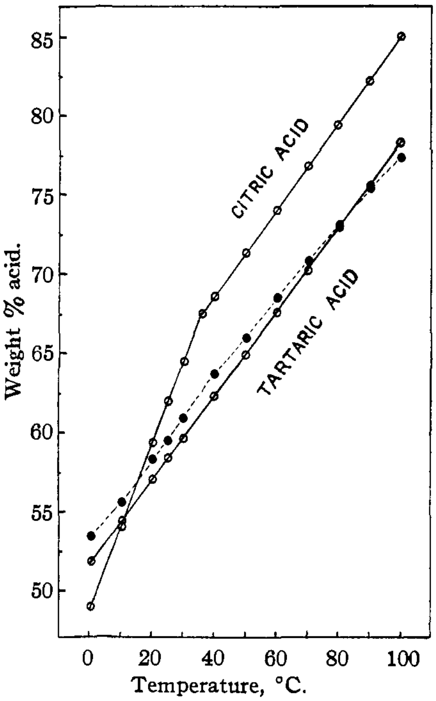

Fig. 1.—The solubilities of citric and tartaric acids in water: ●, Leidie's curve for tartaric acid.

Results

Citric Acid.—It will be seen from Fig. 1 that the solubility curve for citric acid consists of two straight lines which intersect at approximately

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(1) Dalman, THIS JOURNAL, **59**, 775 (1937).

(2) Seidell, *Bull. No.* **67**, *Hyg. Lab.*, 254, (1910).

(3) Kremann and Eitel, *Rec. trav. chim.*, **42**, 539 (1923).

(4) "I. C. T.," Vol. IV, p. 251.

(5) Seidell, "Solubilities," p. 710.

(6) Leidie, *Compt. rend.*, **95**, 87 (1882).

36°, thus indicating the existence of two solid phases. To determine the composition of these solid phases, the crystals from the sample tubes were well centrifuged, weighed and dried for moisture content after which their acid content was measured by titration with alkali. The results of these analyses showed that the solids corresponding to the curve above the break were practically pure citric acid, while those corresponding to the one below contained 91.1 to 91.4% acid which is approximately that required by the formula $H_3C_6H_5O_7 \cdot H_2O$. It is evident that the two solid phases existing in this system are citric acid monohydrate which is stable below the transition point and anhydrous citric acid which is stable above.

Attempts to determine this transition temperature accurately by means of cooling curves obtained from mixtures stirred in a Beckmann freezing-point tube repeatedly proved unsuccessful. The most probable explanations appear to be that either the transition occurs exceedingly slowly or that the heat change is too small to produce measurable results as read on a tenth degree thermometer. In view of this failure it was decided to determine the solubility curves to their point of intersection and to attempt by analysis of the solid phases to locate the point at which the change of phase occurs. The results show that this change occurs between 35.7 and 35.9°. A final sample determined at 35.8° gave crystals which contained 94.7% acid. This figure lies between that of the anhydrous and the hydrated acid which is 91.43%, thus indicating a mixture of the two solids. Since the composition of the solution showed no appreciable change after further rotation in the bath, it is evident that equilibrium had been attained and the transition temperature is therefore reported as 35.8°. The saturated solution at this temperature contains 67.61% acid. This figure agrees well with the computed value which is found to be 67.63% (average of values from the two equations).

The following equations for the solubilities of the hydrated and anhydrous citric acids expressed in percentages by weight have been obtained from the data by the method of least squares

$$\text{Monohydrated citric acid solubility} = 48.9559 + 0.5231t$$
$$\text{Anhydrous citric acid solubility} = 57.8564 + 0.2616t$$

The solubilities computed by these equations agree very well with the observed values, the average deviation being 0.027 and 0.025% while the maximum deviation is 0.08 and 0.05% for the anhydrous and hydrated acids, respectively.

The solubility of citric acid at 25° was found to be 62.07%. This is 0.36% higher than that reported by Seidell.[2] It is hardly feasible to make a comparison of these results with those obtained by Kremann and Eitel[3] at 0, 10 and 15° since their values appear to be much too high and do not show a consistent curve.

Tartaric Acid.—The results obtained for the solubility measurements of tartaric acid are represented graphically in Fig. 1. In contradistinction to the irregular curve obtained by Leidie,[6] it is apparent that the solubility curve for tartaric acid closely approximates a straight line. There is no evidence of a break near 45° and the saturating phase was found to be anhydrous tartaric acid throughout the entire range of temperature from 0 to 100°. It is of interest to note that while Leidie's curve (shown by the shaded circles in Fig. 1) lies about 1.5% above at 0° it crosses the author's curve at 90° and lies 0.2% below at 100°.

The solubility of tartaric acid at 25° was found to be 58.48%. Seidell's[2] figure for the corresponding solubility is given as 57.90%, while that reported by Leidie[6] is 59.79%. Perhaps the best check on the accuracy of these measurements is the agreement to be found between the observed values and those derived from the equation

$$\text{Tartaric acid solubility} = 51.8573 + 0.2643t$$

the constants having been derived by the method of least squares. The average deviation between the experimentally determined solubilities and those computed by this equation is 0.058%, while the maximum deviation is 0.1%.

It was suspected that the measurements at 90 and 100° might fall away somewhat from the straight line solubility curves, since these acids had been found to decompose in an oven at the same temperature. While no serious loss in weight is noted when these acids are heated at 75° for a week, or at 100° for a few hours, there are distinct signs of decomposition (browning) when they are heated for several days at 100°. It is quite probable that decomposition likewise occurs when solutions of these acids are subjected to the same conditions. However, since the 90 and 100° samples were rotated in the bath for at least six hours, it appears that solutions of citric and tartaric acids can be heated safely at 100° for a few hours without appreciable decomposition.

Summary

The solubilities of citric and tartaric acids in water have been determined at 10° intervals (including 25°) over the range of temperature 0–100°.

The solubility curve for citric acid consists of two straight line curves which intersect at 35.8°; below this transition temperature citric acid monohydrate exists, while above anhydrous citric acid is the stable phase.

The solubility curve for tartaric acid is a straight line representing solutions in equilibrium with the anhydrous form of the acid.

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The Partial Molal Volumes of Potassium Chloride, Potassium Bromide and Potassium Sulfate in Sodium Chloride Solutions

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Since the discovery by Masson[1] that the apparent molal volume of a dissolved salt is a linear function of the square root of the volume concentration, several investigators[2,3] have made exhaustive tests of the applicability of this relationship. It was found valid for a number of salts over a surprisingly large concentration range. Root[4] derived from Masson's rule a simple equation relating density and volume concentration which has found wide application.

Redlich and Rosenfeld[5] derived from the Debye–Hückel theory a linear relationship between the square root of the volume concentration and the partial molal volume of a dissolved salt. This gave a partial theoretical basis to Masson's rule as the apparent molal volume is closely related to the partial molal volume. The expression obtained was

$$\overline{V}_2 = \overline{V}_2^0 + q\omega^{3/2} c^{1/2} \qquad (1)$$

$\overline{V}_2$ is the partial molal volume of the salt in a solution of concentration c; $\overline{V}_2^0$ is the partial molal volume at infinite dilution; q is a complex factor involving the temperature, compressibility, the type of electrolyte, the dielectric constant and its change with pressure; and ω is one-half the summation of the number of ions times the square of the valence of the ion. When considering a solution containing two or more electrolytes the last term in Eq. 1 becomes $q'(\Sigma\omega c)^{1/2}$.

The factor $\Sigma\omega c$ corresponds to the ionic strength on a volume basis, so that the partial molal volume of a salt in solution should be a linear function of the square root of the volume ionic strength. This relationship was tested by determining the partial molal volumes of potassium chloride, potassium bromide and potassium sulfate in sodium chloride solutions of different concentrations.

Methods

Preparation of Solutions.—The salts used were either Baker Analyzed or Mallinckrodt Reagent quality and were not further purified. Salts to be weighed were dried at 350–400°. Solutions for the density determinations were prepared by adding a weighed amount of the dried salt (potassium chloride, potassium bromide or potassium sulfate) to a weighed amount of water or sodium chloride solution. The volume concentration of the added salt could then be calculated using the observed density. Enough sodium chloride solution for each series was prepared and its concentration determined from the density. This concentration was corrected for the change caused by the addition of another salt. The concentrations reported are expressed as moles per liter of solution.

The sodium chloride solutions used were approximately 0.04, 0.16, 0.36, 0.64 and 1.0 normal. To each of these solutions was added sufficient potassium chloride, potassium bromide or potassium sulfate to make the volume ionic strength of the added salt approximately 0.04, 0.16, 0.36 and 0.64. Solutions in water of the latter salts of volume ionic strength 0.04, 0.16, 0.36, 0.64 and 1.0 were also prepared.

Density Determination.—The density of each of the above solutions was determined by means of the sinker method. The solutions whose densities were to be measured were placed in heavily silver plated copper cans immersed in a thermostat at 25°. Metallic containers were used to decrease the time required to attain temperature equilibrium. The temperature was maintained constant to ±0.001°. The sinker was suspended in the solution by means of a fine platinum wire which was coated with platinum black where it passed through the liquid surface. This wire could be fastened to a pan of a balance which was supported over the thermostat.

Differences in density were calculated directly using the equation

$$d_3 - d_2 = (m_2 - m_3)/v \qquad (2)$$

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(1) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(2) Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

(3) Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

(4) Root, THIS JOURNAL, **55**, 850 (1933).

(5) Redlich and Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931).