Equilibria in the Oxalic Acid–Tartaric Acid–Water System

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Isothermal phase equilibria for the oxalic acid–tartaric acid–water system have been studied at 0°, 30°, 50°, and 70° C. (also partially at 60° C.), and the data are reported here.

Table I. Solubility Data

Complex, Wt. %		Saturated Solution, Wt. %		Wet Residue, Wt. %		
OA	TA[a]	OA	TA	OA	TA	Solid Phase
At 0° C.						
...	...	3.39	...	...	...	OA, $2H_2O$
5	20	2.12	21.10	54.65	4.64	OA, $2H_2O$
5	40	1.19	41.83	50.12	12.53	OA, $2H_2O$
4	55	1.05	51.45	21.87	52.18	OA, $2H_2O$ + TA
0.5	55	0.48	51.16	0.04	80.64	TA
...	...	...	51.83	...	...	TA
At 30° C.						
...	...	12.22	...	...	...	OA, $2H_2O$
15	5	11.00	5.70	54.67	1.03	OA, $2H_2O$
15	15	8.88	16.69	54.81	5.24	OA, $2H_2O$
10	30	6.90	31.02	53.92	8.20	OA, $2H_2O$
10	44	4.58	46.52	51.08	14.50	OA, $2H_2O$
7	50	3.77	52.60	46.86	19.00	OA, $2H_2O$
5	60	2.36	58.13	19.02	58.77	OA, $2H_2O$ + TA
1	65	1.04	58.53	0.15	79.65	TA
...	...	...	59.66	...	...	TA
At 50° C.						
...	...	24.11	...	...	...	OA, $2H_2O$
25	10	20.87	10.44	55.50	2.75	OA, $2H_2O$
25	25	14.04	31.60	49.50	12.80	OA, $2H_2O$
20	40	7.50	50.80	51.30	16.04	OA, $2H_2O$
10	54	4.70	59.30	51.25	17.80	OA, $2H_2O$
5	65	4.46	61.21	2.73	77.60	OA, $2H_2O$ + TA
2	66	1.87	62.90	0.85	78.27	TA
...	...	...	64.82	...	...	TA
At 60° C.						
15	53	9.88	58.28	50.55	19.60	OA, $2H_2O$
15	55	9.64	58.14	32.63	44.81	OA, $2H_2O$ + TA
10	62	9.63	58.53	7.06	76.20	OA, $2H_2O$+ TA
7.5	63	8.00	59.20	2.82	81.58	TA
At 70° C.						
...	...	38.06	...	...	...	OA, $2H_2O$
40	10	32.90	11.98	58.74	4.34	OA, $2H_2O$
40	15	28.18	20.85	56.75	6.62	OA, $2H_2O$
30	25	25.78	27.27	52.60	11.31	OA, $2H_2O$
30	30	22.24	36.20	53.31	13.84	OA, $2H_2O$
30	35	18.67	45.11	50.67	18.30	OA, $2H_2O$
25	45	15.62	55.13	48.80	21.95	OA, $2H_2O$
25	50	15.64	55.10	30.78	48.22	...
20	55	14.63	57.47	29.09	51.25	...
15	60	14.63	57.70	9.57	76.87	...
10	65	9.70	62.27	5.74	79.30	TA
5	70	4.70	65.82	2.11	83.43	TA
...	...	...	69.81	...	...	TA

[a] OA, oxalic acid; TA, tartaric acid.

TERNARY SOLID-LIQUID equilibrium data on water soluble organic substances are limited in the literature. Such data can be useful either for the primary separation or purification by recrystallization of these substances. While oxalic acid is much less soluble than tartaric acid at lower temperatures, the difference in their solubilities rapidly decreases with an increase in temperature. Phase equilibrium studies of the oxalic acid-tartaric acid-water system should help to ascertain the cumulative effects of these characteristics of the aqueous binaries.

Materials. The chemicals, purified by recrystallization, assayed more than 99.5%. Distilled water was used throughout the investigation.

Experimental Method. The solubilities were determined in a stirred borosilicate glass equilibrium cell, placed in a thermostatic water bath controlled to within ±0.1° C. For each run, 100 grams of a complex of known composition were used. Though good reproducibility indicated that 10 to 12 hours were sufficient for equilibration, more time was allowed in the normal course. For subsequent analysis, the clear saturated solution was sampled in a tared bottle. The wet residue was also sampled in another tared bottle, after complete decantation of the supernatant saturated solution from the borosilicate glass cell.

Analysis. Various feasible methods for analysis of equilibrated saturated solutions and wet residues were carefully considered. Measurement of total acidity, with either density or refractive index as the other property, was investigated for possible use. Similar physical properties are widely used in phase equilibria investigations, including solid-liquid systems (*1*). Density and refractive index of three-component unsaturated solutions of different concentrations were determined at 30° C. Total acidity (milliliters of normal NaOH per 100 grams of solution) was then plotted separately against density and refractive index, following the method of Othmer and coworkers (*2*). Both charts were checked for accuracy with solutions of known concentration. The density-total acidity chart gave better accuracy (about ±1%). Known weights of saturated solution and wet residue, from each equilibration run, were separately diluted to obtain unsaturated solutions below 30° C., and the weights were noted. Total acidity and density of the latter were determined, and the concentrations read from the chart. The compositions of the equilibrated phases were subsequently calculated from the dilution ratio. This analysis was checked from time to time by the total solids method carried out with appropriate precautions recommended for organic substances (*4*).

Experimental Results. Table I summarizes the results at the various temperatures studied. The relevant isotherms

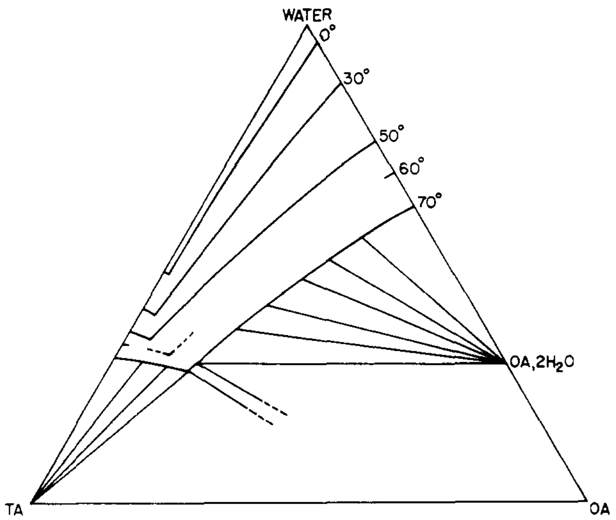

Figure 1. Solubilities at 0°, 30°, 50°, 60° (partially), and 70° C.

are shown in a consolidated form in Figure 1. Solubilities of pure compounds in water reported in the literature (*3*) were satisfactorily reproducible in the present investigations.

Discussion. The different isotherms show that the system exhibits a simple phase behavior involving neither solid solution nor double salt formation up to 60° C. The solid phases, determined by geometric extrapolation of tie-lines, show that they are pure substances up to 60° C.—hydrated in the case of oxalic acid. The 60° C. isotherm was partially established to delineate the temperature range where the change in phase behavior starts, though the true invariant point has not been determined. At 70° C., the phase behavior tends to change as evidenced by the composition of saturated solutions and the corresponding wet residues. Solid phases in this region could not be properly identified owing to the highly viscous nature of the adhering mother liquor.

The isothermal phase diagrams show that separation of the two acids is rendered practical by a judicious combination of cooling and evaporation of solutions, likely to be obtained in some cases. This is particularly true because of significant shifts of isothermal invariant compositions at increasing temperatures.

LITERATURE CITED

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Variation of Dielectric Constant with Temperature for Some Five- and Six-Carbon Ketones

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The dielectric constant values for seven five- and six-carbon cyclic and acyclic ketones, liquid in the −30° to +20° C. range, were determined in a noninductive-type cell. The measured values increased as the temperature decreased, as would be expected from theory. However, these changes in values did not correlate with other physical data.

THE CHANGE in dielectric constant with temperature of ketones has received only limited study. White and Bishop (*8*) included a few ketones in their determinations of the dielectric constant of the liquid and solid phase at the transition temperature. Cole (*1*) studied changes of density and dielectric constant with temperature in the liquid phase for a series of ketones.

The purpose here was to study the effect of changes in temperature and frequency on dielectric constant values for a group of five- and six-carbon cyclic and acyclic ketones.

MATERIALS AND EQUIPMENT

Compounds. The dielectric constants were determined from −30° to +20° C. and at five different frequencies from 3 to 25 mc. The selection of ketones was limited to those five- and six-carbon ketones that remained liquid over this temperature range.

Purification. Two physical constants, refractive index and boiling point, were used as a means of checking the purity of the compounds. The ketones and the other compounds that

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