temperature and pressure. Due to the limited amount of data, the compressibilities can be determined presently with an accuracy only on the order of 10%. Other uncertainties related to temperature or pressure measurement and liquid level measurements are considered to be insignificant compared to the errors described above. Finally, adverse interactions between the melt and the crucible can lead to anomalous liquid level measurements. However, this problem is basically eliminated by the appropriate selection of materials.

The *PvT* trends observed in the results obtained here are the same as those generally observed for organic liquids. For example, the compressibility decreases quickly with increasing pressures, making the isobar lines much more linear than the isotherms. Also, the slopes of the molar volume vs temperature lines (at constant pressure) decrease with increasing pressure, and the liquids are generally more compressible at higher temperatures.

List of Symbols

a,b	Atmospheric molar volume parameters
β	Compressibility
B,C	Constants in Tait equation
ϵ	Linear coefficient of thermal expansion
P	Pressure
T	Temperature
v	Molar volume

Registry No. Mercury, 7439-97-6; tin, 7440-31-5; lead, 7439-92-1; bismuth, 7440-69-9.

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Solubility and Heat of Solution of Potassium Dihydrogen Citrate

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The aqueous solubility of potassium dihydrogen citrate from 15 to 55 °C has been determined. From these data the heat of solution has been calculated to be 8.10 kcal/mol. The densities of saturated solutions of potassium dihydrogen citrate from 15 to 55 °C are also reported. A previously unreported dihydrate—$KH_2C_6H_5O_7\cdot 2H_2O$—has been discovered. Potassium dihydrogen citrate readily tends to form supersaturated solutions, which are sometimes stable for weeks.

Introduction

Bielig (*1*) measured the solubility of potassium dihydrogen citrate in concentrated sugar solution (65° Brix). These are reported as follows:

20 °C = ca. 260 g
10 °C = ca. 150 g
2 °C = ca. 85 g

The volume of these solutions was not reported, but probably was 1000 mL. Kimball (*2*) used these values to estimate the heat of solution to be 8.065 kcal/mol. I have measured the solubility of potassium dihydrogen citrate in pure water form 15 to 55 °C.

Experimental Section

Potassium dihydrogen citrate is not commercially available, so it was prepared by the stoichiometric reaction of 1 mol of tripotassium citrate (Fisher Certified ACS grade) with 2 mol of citric acid (Fisher Certified ACS grade) in distilled water. This produced a crystalline mass of long needles, which was removed by vacuum filtration. Second crops were obtained by cooling the filtrate in a refrigerator. The crystals were dried at room temperature in a strong flow of air. Sometimes crystallization did not begin for several days without the aid of a seed crystal.

Saturated solutions were prepared by heating water to about 5 °C above the target temperature and adding potassium dihydrogen citrate slowly with stirring. When salt remained after a considerable time, the flask was stoppered and placed in a thermostated water bath. Temperatures were set by using an NBS certified thermometer and were held to within 0.1 °C. The solutions were allowed to equilibrate for at least 3 days.

*1. **Solubilities.*** Concentrations were determined by titration and by gravimetry.

*a. **Titrimetric Method.*** Aliquots (10.0 mL) were taken with a calibrated pipet, weighed into 100-mL volumetric flasks, and then diluted. The solutions were titrated with 0.1 N sodium hydroxide solution to a phenolphthalein end point.

*b. **Gravimetric Method.*** Aliquots (10.0 mL) were taken from the thermostated solution with a calibrated pipet and placed in tared weighing dishes. The solutions were evaporated in a strong air flow until weights were nearly constant. Drying to constant weight was finished in a desiccator with Drierite.

*2. **Densities.*** Densities were determined by weighing 10-mL samples of the saturated solutions held at target temperature. Volumes (10.0 mL) were measured with either a "to deliver" pipet, a graduated pipet, or a calibrated volumetric flask.

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Table I. Concentrations and Densities of Saturated Aqueous Solutions of Potassium Dihydrogen Citrate from 15 to 55 °C

	concentrations				densities[a]				
temp, °C	mean concn, mol/L	std dev (absolute)	N^b	method[c]	mean density	std dev (absolute)	N^b	method[c]	av of all methods
15	0.6156	0.0019	2	G	1.071	0.000	3	G	1.07
25	0.9391	0.0014	4	T	1.109	0.004	3	T	1.11
35	1.6042	0.0048	3	G	1.168	0.000	3	G	
35	1.4904	0.0064	3	T	1.179	0.002	3	T	1.17
45	2.4247	0.0076	3	T	1.272	0.001	3	T	1.27
55	3.3893	0.0495	3	G	1.321	0.015	3	G	
55	3.3838	0.0610	6	T	1.361	0.129	6	T	1.35
55					1.374	0.004	3	V	

[a] All samples were 10.0 mL. [b] Number of measurements. [c] Methods: G = volume measured by graduated pipet; T = volume measured by "to deliver" pipet; V = volume measured to volumetric flask.

Table II. Elemental Analyses[a] and Equivalent Weights[b]

	C, %	H, %	O, %	K, %	equivalent weight	water content, wt %
calcd for $KH_2C_6H_5O_7$	31.30	3.07	48.65	16.98	115.11	0
calcd for $KH_2C_6H_5O_7{\cdot}H_2O$	29.03	3.65	51.56	15.75	124.12	7.26
calcd for $KH_2C_6H_5O_7{\cdot}2H_2O$	27.07	4.16	54.08	14.69	133.12	13.53
found—air-dried needles	27.07	4.20			133.25	
found—vacuum oven-dried powder	31.01	3.18			115.11	<0.3

[a] Elemental analyses were done by Galbraith Laboratories, Knoxville, TN. [b] By titration with 0.0988 N NaOH to a phenolphthalein end point. [c] $n = 3$; standard deviation = ±0.14.

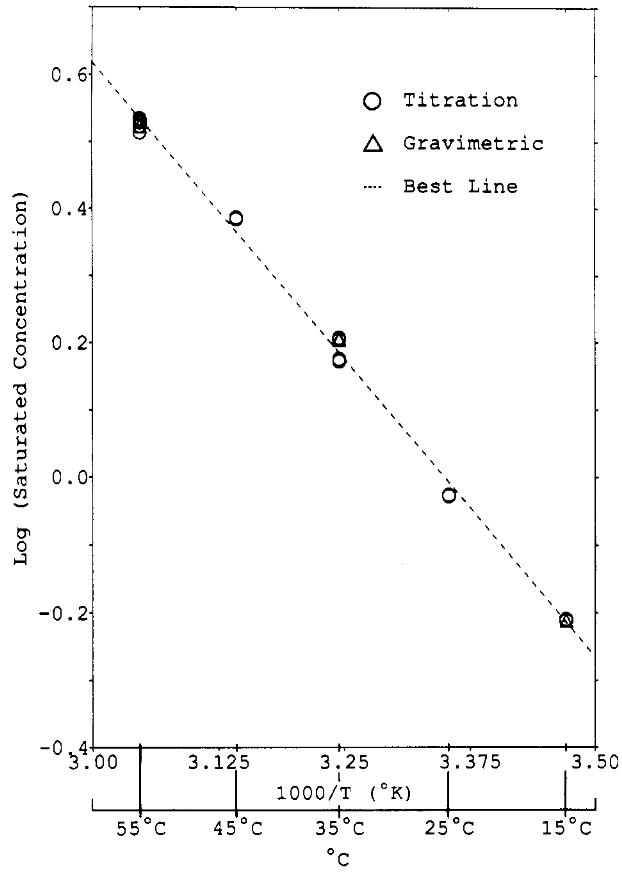

Figure 1. log S vs $1/T$.

Results and Discussion

Solubility. The solubilities determined by this study (Table I) range from 0.62 mol/L at 15 °C to 3.38 mol/L at 55 °C—an increase of 336% over a 40-deg range. A comparison with Bielig's results was made by calculating the expected solubilities using eq 1. Bielig's results show higher solubilities, presumably due to the concentrated sugar solution he worked in.

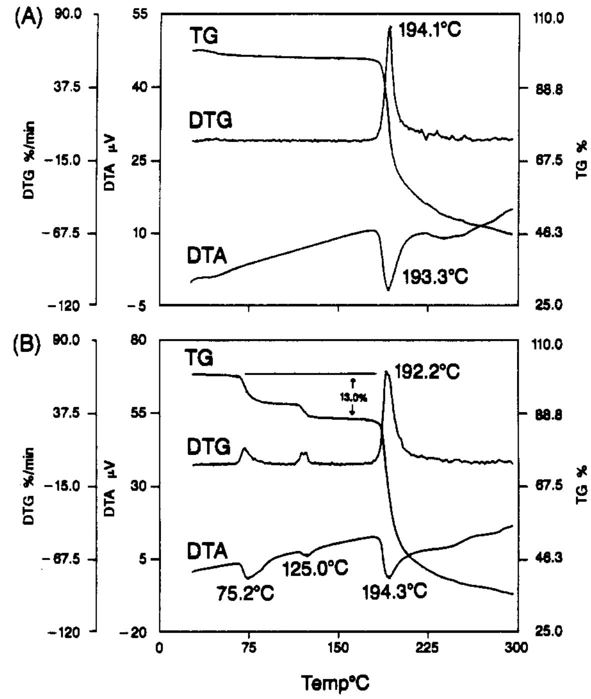

Figure 2. Thermal analyses of potassium dihydrogen citrate: (a) anhydrous; (b) dihydrate.

Heat of Solution. The heat of solution is related to solubility by Schröder's van't Hoff related equation (eq 1), where S is the solubility at saturation in g/L, ΔH_s is the heat of solution, R is the universal gas constant, T is the temperature in K, and C is a constant. The heat of solution was determined from the

$$\log S = -\Delta H_s/2.303RT + C \qquad (1)$$

slope of the fitted line in Figure 1. This slope is equal to $-\Delta H_s/2.303R$. The fitted line has a slope of -1769 ± 19 K, which gave $\Delta H_s = 8.10$ kcal/mol.

Kimball (*2*) calculated a value of 8.065 kcal/mol from Bielig's data (*1*). This suggests that the heat of solution is unchanged in sugar solution, but the total solubility is different.

***Densities of Saturated Solutions*.** The measured densities of saturated solutions of potassium dihydrogen citrate are shown in Table I. They reflect the solubilities of the salt, rising with increasing temperature from 1.07 g/mL at 15 °C to 1.37 g/mL at 55 °C.

***Hydrates*.** Blanco and Perninet (*3*) studied the ternary-phase systems of the sodium salts of citric acid in water and of the potassium salts of citric acid in water. They isolated hydrates of dipotassium hydrogen citrate and tripotassium citrate, but they only isolated anhydrous potassium dihydrogen citrate.

Potassium dihydrogen citrate crystallizes from water as the dihydrate (beautiful, long needles), which can be dried in air at 23–24 °C. Drying at 110 °C and ca. 250 Torr gives the anhydrous salt. These conclusions are supported by the elemental analyses and equivalent weights (Table II) and by thermal analyses (Table II and Figure 2). The dihydrate loses 2 equiv of water (13.0 wt %) in two steps below 125 °C. The thermogravimetric curve for potassium dihydrogen citrate published by Blanco and Perinet (*3*) showed a flat line until decomposition at ca. 160 °C. This is comparable to my findings for the anhydrous salt (Figure 2a). The decomposition temperature changes with heating rate and other factors and should not be used as a characteristic of the salt.

***Supersaturation*.** Blanco and Perninet (*3*) reported that potassium dihydrogen citrate readily forms supersaturated solutions. During this work, I have also observed the ready formation of supersaturated solutions. Some solutions remained supersaturated for at least 2 weeks without crystallization.

***Precision*.** The precision of this study below 55 °C is within 0.5% of the measured value. At 55 °C the precision is within 1.8% of the measured value. At 35 °C there is significant lack of agreement between the two methods of determining solubility, although each method shows internally consistent precision. Density measurements show good agreement at temperatures below 55 °C among the three methods used, and fair agreement at 55 °C among the three methods, but the precision of the "to deliver" pipet method is not good at 55 °C.

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