



Figure 3. Values of V_{\min}^E (minimum values of V^E in Table I) plotted against the number of carbon atoms n in the methyl n -alkyl ketones. The full drawn and dashed lines refer to the 1-chloronaphthalene and 1-methylnaphthalene systems, respectively. The dotted line refers to 1-chloronaphthalene + alkanes (5).

naphthalene substituted by CH_3 and Cl , decreasing for $n_c < 5$ and then increasing slowly for increased n_c .

Figure 3 shows the curve of V_{\min}^E against n_c for 1-chloronaphthalene + alkanes (5). In this case, increasing chain length is accompanied by increased V_{\min}^E with an asymptotic

trend toward large n . This behavior suggests that the carbonyl group of ketones with $n_c < 5$ interacts with aromatic substituted compounds differently than long chain ketones, with V_{\min}^E increasing independently of substituted groups for large n_c .

Registry No. 1-Chloronaphthalene, 90-13-1; 1-methylnaphthalene, 90-12-0; 2-propanone, 67-64-1; 2-butanone, 78-93-3; 2-pentanone, 107-67-9; 2-octanone, 111-13-7; 2-undecanone, 112-12-9.

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Received for review September 26, 1991. Revised January 22, 1992. Accepted March 8, 1992. This work is partly supported by CNR, Rome, Italy "Progetto finalizzato Chimica Fine II".

Solubility of *meso*-1,2,3,4-Butanetetracarboxylic Acid and Some of Its Salts in Water

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The solubility of *meso*-1,2,3,4-butanetetracarboxylic acid (BTCA) in water was determined at 5 and 25 °C. The solubilities of BTCA's ammonium, potassium, and sodium salts were determined at 25 °C. In terms of BTCA content in the saturated solutions, only the monobasic and the tetrabasic salts are more soluble than the free acid. Densities of the saturated solutions are reported.

Introduction

meso-1,2,3,4-Butanetetracarboxylic acid (BTCA) is a candidate to replace formaldehyde-based agents for cross-linking cotton fabrics to produce textiles with smooth-drying properties (1-3). Concentrated aqueous solutions of BTCA are desirable for application to fabric at low wet pickup and as a commercial product.

The little information in the literature about the solubility of BTCA in water is inconsistent. Auwers and Jacob (4) indicated that at 19 °C a saturated aqueous solution contains 21.46% BTCA. Rowland et al. reported that at unspecified temperatures they were unable to prepare solutions containing as much as 9.1 mass % (5) or 7.4% (6) BTCA, a commercial product of unknown purity, but that conversion to a partial sodium salt increased the acid's solubility. Recent research at the Southern Regional Research Center has shown that the solubility of BTCA in water can decrease with time, the decrease being attributed to solution-mediated phase transitions to progressively less soluble crystal forms of BTCA (7).

This paper compares the solubility of BTCA and its ammonium, potassium, and sodium salts at 25 °C and reports the solubility of the free acid at 5 °C.

Experimental Section

BTCA was obtained from Aldrich Chemical Co. Its claimed purity of 99% was verified by acidimetric titration. Deionized water was further purified by passage through a Milli-Q Plus system. Base solutions of known concentration were used to convert BTCA to the indicated salts: ammonium hydroxide, Baker Analyzed Reagent (tetraammonium salt) or Titrstar from EM Science (other ammonium salts); potassium hydroxide, standard solution prepared from J. T. Baker DILUT-IT volumetric concentrate (monopotassium salt) or Baker Analyzed Reagent (other potassium salts); and sodium hydroxide, Baker Analyzed Reagent—diluted when appropriate, analyzed by conventional acid-base titration (sodium salts). The formaldehyde solution was analytical reagent grade formalin from Mallinckrodt.

Mixtures of water and an excess of BTCA were equilibrated at 5 or 25 °C by stirring in stoppered flasks thermostated by circulating water. After varying periods, portions of the solutions were filtered through a 0.45- μm Durapore membrane. Measured volumes of the filtrates were weighed and analyzed for BTCA by conventional acid-base titration using phenolphthalein as indicator.

The monobasic, dibasic, tribasic, and tetrabasic potassium and sodium salts of BTCA were prepared by adding the calculated amounts of base solutions to BTCA-water mixtures with cooling to keep temperatures near ambient. The solubilities of the monobasic, dibasic, and tribasic salts were determined as described in the preceding paragraph. The solubilities of ammonium salts of BTCA were determined in a similar way by treating the aliquots of filtrate with formaldehyde to convert ammonium ions to hexamethylenetetramine prior to titration (8).

Table I. BTCA Contents and Densities ρ of Saturated Aqueous Solutions of BTCA and Its Salts at 25 °C

BTCA salt	mass % BTCA	ρ /(g cm ⁻³)
After Equilibration for 15 min		
free acid	20.00 ^a	1.074 ^a
K	24.62 ± 0.04	1.138 ± 0.008
After Equilibration for 5 h		
free acid	18.30 ± 0.10	1.067 ^a
NH ₄	21.19 ± 0.11	1.087 ^a
(NH ₄) ₂	5.99 ± 0.05	1.035 ^a
(NH ₄) ₃	16.01 ± 0.18	1.083 ± 0.000 ^b
(NH ₄) ₄	25.35 ± 0.41	1.138 ± 0.003
K	22.46 ± 0.78	1.092 ± 0.004
K ₂	3.72 ± 0.00	1.019 ± 0.005
K ₃	3.17 ± 0.02	1.179 ± 0.002
K ₄	>32.05 ^a	
Na	24.59 ± 0.04	1.128 ± 0.000 ^c
Na ₂	10.00 ± 0.04	1.070 ± 0.000 ^b
Na ₃	16.23 ± 0.42	1.191 ± 0.006 ^d
Na ₄	21.56 ± 0.02	1.227 ± 0.001 ^d
KNa	7.90 ± 0.08	1.050 ± 0.001 ^b
After Equilibration for 16 h		
free acid	18.28 ± 0.02	1.067 ± 0.000 ^b

^aNo replication. ^bDensity at 26 °C. ^cDensity at 24 °C. ^dDensity at 23 °C.

The weighed aliquot of tetrasodium salt solution, obtained as described for the other sodium salts, was dried in an oven at temperatures no higher than 40 °C and then kept in a vacuum desiccator until its weight became constant. The tetrasodium salt's solubility was calculated from the weight of this residue and its Karl-Fischer water content.

Except as otherwise noted, reported values are means of data from 2-4 replications.

Results and Discussion

The results of solubility determinations at 25 °C, expressed as mass percent BTCA (free acid) in the saturated solutions, are presented in Table I. The solubility data and the accompanying density data are given as means plus/minus standard errors. Because no solid remained in the tetrapotassium salt mixture after equilibration, only a minimum value for the solubility of this salt was calculated.

As discussed elsewhere (7), at this temperature the BTCA content of a saturated aqueous solution prepared from the anhydrous compound decreased from 20 mass % to less than 19 mass % within 3 h, remained almost constant for a time, and then decreased again. An equilibration time of 5 h, within

the period of constant BTCA solubility, was selected for the comparison of BTCA's solubility with the solubilities of its salts. Thus, the solubility reported for BTCA is not that of the form that is thermodynamically stable at 25 °C, and it is possible that this is true of the salts also. The observed decrease in the solubility of the monopotassium salt within 5 h is evidence that it, like the free acid, can undergo a transformation to a less soluble crystal form. The reported solubilities are minimums that can be expected within the given time. Therefore, they can serve as a basis for selecting salts to be tried as substitutes for the free acid in applications requiring a high solubility in water. Only the monobasic and the tetrabasic salts are more soluble than the free acid in terms of BTCA content in the saturated solutions.

The solubility of BTCA in water at 5 °C was found to be 7.50 ± 0.46 mass % after equilibration for 1 h and 7.20 ± 0.23 mass % after equilibration for 5 h. This decrease in solubility with time was not significant even at the 50% confidence level.

The solubility reported for BTCA at 19 °C by Auwers and Jacob (4) was substantially higher than would be expected from the data presented here; the reason for this difference is not evident. The low solubility for BTCA indicated in the reports by Rowland et al. (5, 6) may have been due to impurities in the commercial product they used and/or to the presence of BTCA monohydrate (7) in their solid phase.

Acknowledgment

I thank Sarah L. Batiste for technical assistance.

Registry No. BTCA, 4534-68-3; NH₄BTCA, 141411-71-4; (NH₄)₂BTCA, 141411-72-5; (NH₄)₃BTCA, 141411-73-6; (NH₄)₄BTCA, 141411-74-7; KBTCA, 141411-75-8; K₂BTCA, 141437-75-4; K₃BTCA, 141411-76-9; K₄BTCA, 141411-77-0; NaBTCA, 141411-78-1; Na₂BTCA, 141411-79-2; Na₃BTCA, 141411-80-5; Na₄BTCA, 141411-81-6; KNaBTCA, 141411-82-7.

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Received for review November 19, 1991. Accepted March 19, 1992.

Surface Tensions of Propylene Glycol + Water

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Surface tensions of propylene glycol + water have been measured using the maximum bubble pressure method from ambient temperature to the mixture boiling point at 1 atm of pressure. A correlation of the surface tensions as a function of temperature and composition is given.

Introduction

In an earlier paper by Hoke and Chen (1), surface tensions for mixtures of 2-propanol + water and ethylene glycol + water are reported. The maximum bubble pressure method described by Sugden (2) was used to measure the surface tension as a function of temperature and composition. In this paper, surface tension results for propylene glycol + water are reported. Propylene glycol, as received from Fisher Scientific, was used. A description of the experimental approach, apparatus, and

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