

Figure 4.  $\log K_A$  vs  $(1/D) \times 10^{-2}$  for salts:  $\text{Bu}_4\text{N}^+\text{Ph}_4\text{B}^-$  ( $\Delta$ ); potassium picrate ( $\circ$ ); KI ( $\square$ );  $\text{Bu}_4\text{N}^+\text{I}^-$  ( $\nabla$ );  $\text{Et}_4\text{N}^+\text{Br}^-$  ( $\times$ ); potassium salicylate ( $\diamond$ ); KBr ( $\blacksquare$ ).

picrate < KI < potassium salicylate, indicating that the ion-solvent electrostatic interaction is greater in the case of picrate ion as compared to salicylate ion (cation being common). This order is reversed in sulfolane + water mixtures.

The conventional  $\log K_A$  vs  $1/D$  graph given in Figure 4 never showed any linear variation for all the salts studied. This indicates that ion association may not be solely dependent on the dielectric constant of the medium; however, the other factors like shape, size, dipole moment, polarizability, and possibly other details of solvent molecules could also be taken into account for the rationalization of association constant values obtained in the present work.

The cosphere diameter ( $R$ ) values for all the salts under study in sulfolane and sulfolane + water mixtures are also portrayed in Tables IV and V, respectively. The  $R$  values were found to have a somewhat irregular trend in the solvents studied. As  $R$  is the measure of the extent of influence of ionic charge in the solvent and consequently the ionic association,  $R$  and  $K_A$  values are expected to increase with the decrease of the dielectric constant of the solvents, but no systematic trend in  $R$  values for all the salts studied has been observed in the given solvent mixture (sulfolane + water). Since the best fit conductance parameters are reproduced equally well over a wide range of arbitrarily chosen  $R$  values, a comprehensive correlation of the cosphere diameter of the respective system could not be made in the present instance.

Registry No. KI, 7681-11-0;  $\text{Bu}_4\text{N}^+\text{Ph}_4\text{B}^-$ , 15522-59-5;  $\text{Bu}_4\text{N}^+\text{I}^-$ , 311-28-4;  $\text{Et}_4\text{N}^+\text{Br}^-$ , 71-91-0; KBr, 7758-02-3; potassium picrate, 573-83-1; potassium, 578-36-9; sulfolane, 128-33-0.

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## Excess Molar Volumes of 1-Chloronaphthalene and 1-Methylnaphthalene + Five Methyl *n*-Alkyl Ketones at 298.15 K

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Excess molar volumes  $V^E$  of 1-chloronaphthalene and 1-methylnaphthalene + five methyl *n*-alkyl ketones have been determined from density measurements at 298.15 K and atmospheric pressure by means of an Anton Paar digital densimeter. Values of  $V^E$  are all negative ( $-0.9 \leq V^E_{\text{mix}}/(\text{cm}^3 \text{mol}^{-1}) \leq -0.7$ ). The variation of  $V^E$  with molecular size is discussed.

#### Introduction

In previous publications (1, 2), the excess molar enthalpies  $H^E$  of 1-chloronaphthalene and 1-methylnaphthalene + five methyl *n*-alkyl ketones were reported. This paper reports the excess molar volumes  $V^E$  of the same systems. These results provide more information about the thermodynamic properties of these mixtures.

Table I. Densities  $\rho$  of Pure Components at 298.15 K and Comparison with Literature Data

component	$\rho/(\text{g cm}^{-3})$	
	this paper	lit.
1-chloronaphthalene	1.188 093	1.188 11 (3)
1-methylnaphthalene	1.015 430	1.016 76 (1)
2-propanone	0.785 005	0.784 7 (4)
2-butanone	0.799 905	0.799 45 (2)
2-pentanone	0.801 400	0.801 5 (1)
2-octanone	0.814 359	0.814 3 (1)
2-undecanone	0.821 704	no lit. data at 298.15 K

#### Experimental Section

**Reagents.** 1-Chloronaphthalene and 1-methylnaphthalene, a Kodak and an Aldrich product, analytical grade 99% and 98%, respectively, were purified by two fractional distillations through a 120 theoretical plate column at the rate of 30 mL/h.

**Table II. Experimental Densities  $\rho$  and Excess Molar Volumes  $V^E$  for Binary Mixtures of 1-Chloronaphthalene and 1-Methylnaphthalene + Methyl *n*-Alkyl Ketones at 298.15 K**

$x_1$	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$	$x_1$	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$	$x_1$	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$
1-Chloronaphthalene (1) + 2-Propanone (2)								
0.0059	0.789 759	-0.362 23	0.2225	0.931 893	-0.650 96	0.4540	1.036 650	-0.738 13
0.0396	0.815 543	-0.186 84	0.2459	0.943 686	-0.668 44	0.5551	1.073 150	-0.702 54
0.0708	0.838 021	-0.298 79	0.2685	0.955 862	-0.702 24	0.6613	1.105 980	-0.556 55
0.1135	0.866 937	-0.443 21	0.3131	0.976 938	-0.723 78	0.7389	1.127 550	-0.445 81
0.1415	0.884 485	-0.498 21	0.3549	0.995 843	-0.730 65	0.8419	1.153 210	-0.256 04
0.1764	0.905 474	-0.574 82	0.3955	1.013 320	-0.742 90	0.8764	1.161 250	-0.196 94
0.2163	0.927 981	-0.636 03	0.4355	1.029 520	-0.741 58	0.9835	1.184 571	-0.019 15
1-Chloronaphthalene (1) + 2-Butanone (2)								
0.0081	0.805 118	-0.052 35	0.2179	0.921 437	-0.669 84	0.4506	1.022 360	-0.785 10
0.0257	0.816 012	-0.132 56	0.2603	0.941 624	-0.712 14	0.5248	1.049 850	-0.745 41
0.0508	0.831 223	-0.237 66	0.2830	0.952 227	-0.746 29	0.6085	1.078 580	-0.666 87
0.0884	0.853 056	-0.372 08	0.3118	0.965 229	-0.774 36	0.8289	1.144 460	-0.326 39
0.1166	0.868 880	-0.459 10	0.3193	0.968 555	-0.784 51	0.9390	1.173 140	-0.118 83
0.1864	0.905 801	-0.623 75	0.3405	0.977 774	-0.793 16	0.9868	1.184 810	-0.019 64
0.2055	0.915 809	-0.653 83	0.3983	1.001 830	-0.803 12			
1-Chloronaphthalene (1) + 2-Pentanone (2)								
0.0068	0.805 098	-0.049 04	0.2480	0.922 363	-0.822 84	0.5523	1.045 400	-0.876 95
0.0296	0.817 096	-0.164 07	0.2860	0.939 040	-0.869 98	0.6264	1.071 450	-0.794 59
0.0545	0.829 843	-0.263 19	0.3297	0.957 043	-0.917 54	0.7079	1.099 170	-0.674 01
0.0924	0.848 995	-0.420 66	0.3967	0.985 310	-0.930 38	0.7702	1.119 400	-0.555 19
0.1202	0.862 829	-0.513 53	0.4275	0.997 613	-0.934 40	0.8823	1.153 990	-0.340 97
0.2107	0.905 519	-0.756 21	0.4973	1.024 470	-0.898 08			
1-Chloronaphthalene (1) + 2-Octanone (2)								
0.0102	0.817 480	-0.033 11	0.3017	0.921 299	-0.805 43	0.6857	1.064 740	-0.767 05
0.0619	0.835 828	-0.224 32	0.3685	0.945 670	-0.880 84	0.7162	1.076 430	-0.714 48
0.1132	0.853 836	-0.391 40	0.4758	0.985 339	-0.925 74	0.7905	1.105 240	-0.575 56
0.1771	0.876 502	-0.567 90	0.4862	0.989 236	-0.925 08	0.8400	1.124 570	-0.459 39
0.2482	0.901 188	-0.708 57	0.5396	1.009 210	-0.909 54	0.8622	1.133 270	-0.402 66
0.2764	0.912 134	-0.768 16	0.6312	1.043 850	-0.836 19	0.9222	1.156 940	-0.238 76
1-Chloronaphthalene (1) + 2-Undecanone (2)								
0.0167	0.823 338	-0.041 00	0.3464	0.922 610	-0.777 55	0.7529	1.071 920	-0.639 52
0.0803	0.845 102	-0.252 84	0.3856	0.935 233	-0.816 83	0.8081	1.095 900	-0.532 63
0.1329	0.859 401	-0.394 53	0.4337	0.951 168	-0.847 51	0.8804	1.128 910	-0.360 37
0.1717	0.870 230	-0.482 53	0.4771	0.966 034	-0.861 68	0.9025	1.139 450	-0.310 51
0.2594	0.895 806	-0.659 02	0.6048	1.012 410	-0.825 13	0.9540	1.164 540	-0.146 51
0.2859	0.903 790	-0.700 72	0.6877	1.044 890	-0.740 22	0.9923	1.184 020	-0.024 72
1-Methylnaphthalene (1) + 2-Propanone (2)								
0.0361	0.801 875	-0.155 03	0.2794	0.889 278	-0.702 60	0.5760	0.957 010	-0.714 45
0.0502	0.808 102	-0.206 24	0.3009	0.895 292	-0.718 40	0.5817	0.958 073	-0.713 77
0.0931	0.826 063	-0.346 76	0.3366	0.904 908	-0.747 50	0.6468	0.969 151	-0.641 01
0.1230	0.837 683	-0.426 72	0.3815	0.916 181	-0.763 57	0.7174	0.980 156	-0.548 83
0.1611	0.851 743	-0.529 09	0.4289	0.927 264	-0.771 75	0.8774	1.001 460	-0.246 42
0.2131	0.869 151	-0.615 44	0.4695	0.936 086	-0.762 40	0.9771	1.012 95	-0.046 35
0.2414	0.877 995	-0.654 09	0.5231	0.947 052	-0.749 35			
1-Methylnaphthalene (1) + 2-Butanone (2)								
0.0074	0.802 732	-0.041 01	0.2764	0.886 078	-0.693 74	0.6255	0.960 877	-0.683 49
0.0409	0.814 758	-0.166 18	0.3496	0.904 318	-0.753 96	0.6823	0.970 554	-0.619 69
0.0725	0.825 665	-0.273 45	0.3979	0.915 548	-0.776 72	0.7833	0.986 383	-0.464 36
0.1069	0.836 964	-0.372 54	0.4448	0.925 896	-0.787 77	0.8451	0.995 320	-0.350 71
0.1561	0.852 394	-0.502 28	0.5258	0.942 393	-0.757 73	0.9785	1.012 830	-0.057 08
0.2160	0.869 816	-0.618 27	0.5448	0.946 072	-0.746 25	0.9861	1.013 760	-0.037 47
0.2469	0.878 247	-0.654 69						
1-Methylnaphthalene (1) + 2-Pentanone (2)								
0.0086	0.804 115	-0.045 04	0.2641	0.875 359	-0.763 66	0.5857	0.946 77	0.946 577
0.0321	0.811 297	-0.139 83	0.3230	0.889 783	-0.840 32	0.6470	0.958 237	-0.083 27
0.0407	0.813 911	-0.173 35	0.3591	0.898 273	-0.871 80	0.7750	0.980 352	-0.599 58
0.0928	0.829 261	-0.358 52	0.3762	0.902 247	-0.884 45	0.8399	0.991 469	-0.457 28
0.1407	0.842 804	-0.502 72	0.4555	0.919 894	-0.913 38	0.9252	1.004 610	-0.231 82
0.1426	0.843 395	-0.514 24	0.5187	0.933 186	-0.904 70	0.9866	1.013 540	-0.045 14
0.1772	0.852 771	-0.593 60	0.5675	0.943 013	-0.877 71			
1-Methylnaphthalene (1) + 2-Octanone (2)								
0.0132	0.817 062	-0.043 38	0.3977	0.893 580	-0.798 9	0.7931	0.973 660	-0.561 9
0.0455	0.823 388	-0.140 34	0.4364	0.901 305	-0.811 14	0.8218	0.979 492	-0.561 86
0.1033	0.834 753	-0.298 89	0.4685	0.907 796	-0.822 81	0.8645	0.988 140	-0.405 69
0.1788	0.849 658	-0.470 83	0.5246	0.919 148	-0.829 07	0.9098	0.997 291	-0.287 54
0.2642	0.866 716	-0.633 77	0.5942	0.933 206	-0.798 24	0.9541	1.006 230	-0.156 05
0.3046	0.874 785	-0.691 56	0.6497	0.944 573	-0.771 23	0.9855	1.010 290	-0.051 42
0.3709	0.888 109	-0.765 43	0.7460	0.964 071	-0.641 29			

Table II (Continued)

$x_1$	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$	$x_1$	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$	$x_1$	$\rho/(\text{g cm}^{-3})$	$V^E/(\text{cm}^3 \text{mol}^{-1})$
1-Methylnaphthalene (1) + 2-Undecanone (2)								
0.0173	0.826 603	-0.042 05	0.4694	0.899 449	-0.700 68	0.7472	0.955 244	-0.573 52
0.1109	0.840 136	-0.251 33	0.5169	0.908 807	-0.710 66	0.7835	0.963 289	-0.521 22
0.1917	0.852 442	-0.404 96	0.5245	0.909 770	-0.712 77	0.8366	0.975 401	-0.425 94
0.2621	0.863 649	-0.518 29	0.5763	0.919 864	-0.723 15	0.8973	0.989 764	-0.293 08
0.3156	0.872 472	-0.586 41	0.5942	0.923 327	-0.703 28	0.9401	1.000 250	-0.181 59
0.3663	0.881 093	-0.638 46	0.6428	0.933 092	-0.671 23	0.9919	1.013 340	-0.027 63
0.4184	0.890 223	-0.675 79	0.7226	0.949 889	-0.602 73			

Table III. Parameters  $a_k$  of Equation 1 and Standard Deviation  $\sigma(V^E)$  at 298.15 K

systems	$a_0$	$a_1$	$a_2$	$a_4$	$\sigma(V^E)/(\text{cm}^3 \text{mol}^{-1})$
1-chloronaphthalene (1) + 2-propanone (2)	-2.8762	1.0710	-0.2627	1.0158	0.0077
1-chloronaphthalene (1) + 2-butanone (2)	-3.0537	1.2237	-0.4248	0.4337	0.0070
1-chloronaphthalene (1) + 2-pentanone (2)	-3.6455	1.2379	-0.5249		0.0086
1-chloronaphthalene (1) + 2-octanone (2)	-3.6761	0.3498			0.0043
1-chloronaphthalene (1) + 2-undecanone (2)	-3.4408	-0.2114			0.0049
1-methylnaphthalene (1) + 2-propanone (2)	-3.0389	0.7635	-0.2137	0.6478	0.0037
1-methylnaphthalene (1) + 2-butanone (2)	-3.0789	0.7764	-0.3303		0.0050
1-methylnaphthalene (1) + 2-pentanone (2)	-3.6354	0.5169	-0.2809		0.0034
1-methylnaphthalene (1) + 2-octanone (2)	-3.3254	-0.1589			0.0043
1-methylnaphthalene (1) + 2-undecanone (2)	-2.8487	-0.3819			0.0041

2-Pentanone, a Fluka product, analytical grade 99%, and 2-octanone and 2-undecanone, both Aldrich products, analytical grade 98% and 99%, respectively, were purified by distilling the commercial samples through a 100 theoretical plate column at a reflux ratio of 100:1 at atmospheric pressure. 2-Propanone and 2-butanone, two Aldrich products, analytical grade 99.98% and 99.9%, were used without further purification.

Before use, all liquids were stored in dark bottles over molecular sieves (Union Carbide Type 4A,  $1/16$ -in. pellets).

**Density Measurements.** Densities  $\rho$  of pure components and samples of mixtures were measured by an Anton Paar DMA 60/602 digital densimeter. Table I shows the experimental values for the pure components at 298.15 K, compared with published values (3-7). The densimeter was calibrated with bidistilled and degassed water and dry air at atmospheric pressure. The procedure for the preparation of the samples of mixtures is described in ref 7, and we have used the same method. The temperature was measured with a digital thermometer (Anton Paar/DT 100-25), and the temperature was kept constant within less than 0.01 K with a Colora ultrathermostat bath circulator.

Measured densities have an uncertainty not exceeding  $3 \times 10^{-6} \text{ g cm}^{-3}$ , which leads to excess volumes with an accuracy of about  $3 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ .

## Results and Discussion

From the measured densities of the pure components and of the binary mixtures, the excess molar volumes  $V^E$  were calculated and then correlated by the polynomial function

$$V^E/(\text{cm}^3 \text{mol}^{-1}) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \quad (1)$$

where  $x_1$  and  $x_2$  are the mole fractions of components 1 and 2, respectively, and  $a_k$  are the parameters determined by the least-squares method with the minimized objective function

$$\phi = \sum_{k=1}^N \eta_k^2 \quad (2)$$

where  $N$  is the number of experimental points and  $\eta_k = V^E_{\text{calc}} - V^E$ , where  $V^E_{\text{calc}}$  has been determined from the right-hand side of eq 1.

Table III summarizes the values of parameters  $a_k$  together with their standard deviations  $\sigma(V^E)$  defined as

$$\sigma(V^E) = (\phi_{\text{min}}/(N - n))^{0.5} \quad (3)$$

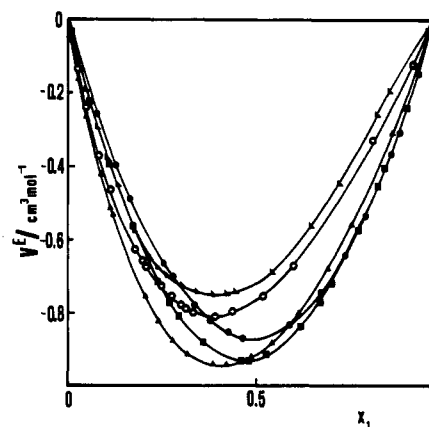


Figure 1. Excess molar volumes at 298.15 K for 1-chloronaphthalene + 2-propanone ( $\blacktriangledown$ ), + 2-butanone (O), + 2-pentanone ( $\blacktriangle$ ), + 2-octanone ( $\blacksquare$ ), and + 2-undecanone ( $\bullet$ ).

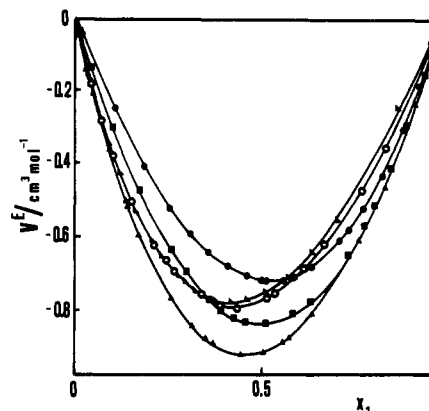


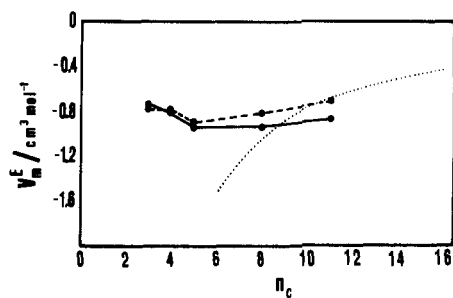
Figure 2. Excess molar volumes at 298.15 K for 1-methylnaphthalene + 2-propanone ( $\blacktriangledown$ ), + 2-butanone (O), + 2-pentanone ( $\blacktriangle$ ), + 2-octanone ( $\blacksquare$ ), and + 2-undecanone ( $\bullet$ ).

where  $n$  is the number of parameters.

Densities  $\rho$  and excess volumes  $V^E$  are shown in Table II. Figures 1 and 2 present graphically the  $V^E$  values for the 10 systems.

In all cases  $V^E$  is negative and the curves are mostly asymmetric.

Figure 3 shows the minimum values of  $V^E$  plotted against the number  $n_c$  of carbon atoms in the methyl  $n$ -alkyl ketones. From Figure 3, the trend of  $V^E_{\text{min}}$  against  $n$  is quite similar for



**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  $\text{CH}_3$  and  $\text{Cl}$ , 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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## 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- $\mu\text{m}$  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).