Tetrahexylammonium Benzoate, a Liquid Salt at 25°, a Solvent for Kinetics or Electrochemistry[1]

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Abstract: Tetrahexylammonium benzoate (THAB) is a liquid salt at 25°, miscible with most organic solvents but not with water. Its "solvent ionizing power" *Y*, based on rate of solvolysis of *t*-butyl chloride in THAB as solvent, is −0.39, intermediate between ethanol and water. Its ability to dissolve organic compounds, intrinsic conductance, and electrochemical inertness over a wide voltage range make it a suitable solvent for electrochemical studies. Half-wave potentials with a dropping mercury electrode in THAB are recorded for oxygen, fumaric acid, benzophenone, anthracene, and β-naphthol.

Tetra-*n*-hexylammonium benzoate (hereafter THAB) is a viscous liquid at 25°, miscible with benzene, toluene, or carbon tetrachloride, in contrast to tetrapentylammonium or tetrabutylammonium benzoate, which are solids, only slightly soluble in benzene. As a liquid salt, it constitutes an unusual kind of solvent for kinetics or electrochemistry. Its synthesis and properties are described in the Experimental Section.

Kinetics. Reactions in fused salts are receiving increasing attention.[2] THAB permits such studies at 25° or below. To determine whether THAB is better regarded as a polar solvent because of its ionic bonds or as a nonpolar solvent because most of its bulk consists of saturated alkyl groups which shield and sterically hinder approach to the ionic centers, we measured its solvent polarity *Y*. *Y* values are defined operationally[3] as log (k/k°), where k and k° are first-order rate constants for solvolysis of *t*-butyl chloride at 25° in any solvent and in the standard solvent, ethanol–water (80:20), respectively. From the measured rate constant of $3.8 \pm 0.2 \times 10^{-6}$ sec^{-1}, in THAB as solvent, its *Y* value is −0.39, of the same order as that for 80% ethanol, *i.e.*, fairly polar, more polar than ethanol (−2.03), but less polar than water (+3.49). Its remarkable balance of ionic and nonpolar characteristics thus permits a moderate rate of solvolysis of *t*-butyl chloride, easily measurable by conventional kinetic techniques.

Electrochemistry. Solubility and reduction potential are two important properties of tetra-*n*-alkylammonium salts when used as supporting electrolytes in electrochemical studies. Of the many available salts in the series, tetrabutylammonium perchlorate has gained wide acceptance because of its solubility in a wide variety of solvents and because it is not easily reduced, *e.g.*, in aqueous solutions not before −2. 6 v *vs.* the saturated calomel electrode. No significant increase in usable potential range results from further increases in alkyl chain length.

Current–voltage curves were obtained in THAB as solvent using both a dropping mercury electrode and a platinum microelectrode. Figures 1 and 2 illustrate typical results. Details are given in the Experimental Section. Relative to the silver chloride electrode, oxygen, fumaric acid, benzophenone, anthracene, and β-naphthol exhibited $E_{1/2}$ values at −0.37, −0.50, −1.42, −1.7, and −2.3 v with the dropping mercury electrode. Thus, THAB is usable as a solvent and advantageous because it is a good solvent for organic compounds, has adequate intrinsic conductance, and ions that are electrochemically inert over a wide range.

Experimental Section

Synthesis. Tetrahexylammonium iodide (Eastman White Label) was recrystallized three times from 3:1 acetone–ether solutions, mp 104–105°, or in later work used without purification without adverse effects. Freshly precipitated silver oxide (0.15 mole) was added in several portions with prolonged shaking to a solution of 25 g (0.052 mole) of the iodide in 150 ml of methanol–water (80:20). The residual iodide ion was negligible. Without isolation of the tetrahexylammonium hydroxide, the filtered solution was neutralized with reagent benzoic acid dissolved in 80% methanol to pH 7, using "pHydrion" pH 7–8 paper as an indicator. The volume of benzoic acid solution required agreed with that calculated. Solvent was evaporated at or below 25° in a rotary evaporator at 10^{-2} to 10^{-3} mm. The pale yellow oil obtained was dried in a vacuum desiccator under reduced pressure over P_2O_5 or $Mg(ClO_4)_2$ for a day; yield 20 g. Last traces of water are difficult to remove. Its analysis corresponds to a hemihydrate. *Anal.* Calcd for $C_{31}H_{57}NO_2$: C, 78.25; H, 12.08; N, 2.94. Calcd for $C_{31}H_{57}NO_2 \cdot 0.5\ H_2O$: C, 76.80; H, 12.06; N, 2.93. Found: C, 76.67; H, 11.84; N, 2.90. A sample heated for 10 min at 100° (25 mm) partially decomposed to a mixture analyzing 72.62% C and 11.94% H, indicating accumulation of benzoic acid. Further drying of another sample for 2 weeks at 25° (25 mm) over $Mg(ClO_4)_2$ also gave some decomposition (75.09% C and 11.71% H).

An alternate, less desirable procedure for the conversion of iodide to hydroxide involved ion exchange. The iodide (2 g) in 80% methanol was charged into 130 ml of Dowex I-X4 anion-exchange resin in hydroxide form in a 20-mm i.d. column, followed by elution with 600 ml of 80% methanol at the rate of 20 drops/min. There may be a possibility of contamination of the THAB by traces of amines derived from the resin in this procedure.

Properties, At 25° THAB has a viscosity similar to that of glycerol and a density of 0.90 g/ml. It does not have a liquid crystal state. It solidifies at Dry Ice temperature. Specific resistance was 18 kohm cm after several days in a vacuum desiccator at 25-mm pressure over $Mg(ClO_4)_2$. Some water was probably absorbed upon

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[2] B. R. Sundheim, "Fused Salts," McGraw-Hill Book Co., Inc., New York, N. Y., 1964; M. Blander, "Molten Salt Chemistry," Interscience Publishers, Inc., New York, N. Y., 1964; J. E. Gordon, *J. Am. Chem. Soc.*, **86**, 4492 (1964); **87**, 1499, 4347 (1965); *J. Org. Chem.*, **30** 2760, 4396 (1965).

[3] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

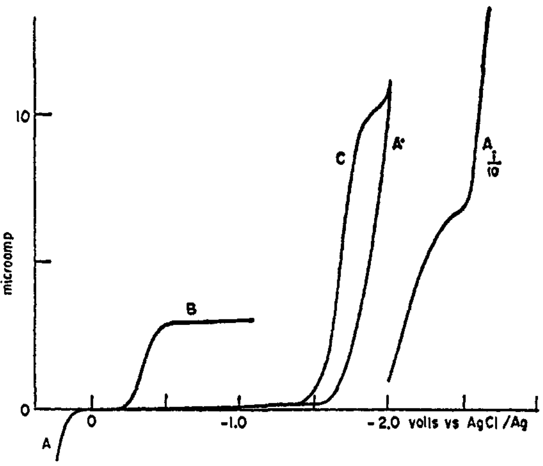

Figure 1. Tracings of peak currents of polarograms: curve A, residual current, beyond −2 v at one-tenth sensitivity; curve B, reduction of oxygen at saturation concentration; curve C, reduction of anthracene.

standing since the specific resistance decreased to 760 ohm cm on contact with the atmosphere, but increased to 1.6 kohm cm after a brief heating to 90° (25 m). Relatively little water is miscible with THAB; addition of 1% by volume of water results in a two-phase system.

Both toluene and carbon tetrachloride are miscible with THAB; a mixture of THAB-toluene (75:25) had a rather low specific resistance of 3.8 kohm cm. The mixtures are much less viscous than pure THAB, and therefore easier to use, especially in electrochemical cells where dissolved oxygen is removed by bubbling with nitrogen. Acetone also dissolves this salt and is useful for rinsing it off glassware and apparatus.

The light yellow-brown color is due to an unidentified impurity. From the voltammetric curves it is clear that the impurity is not iodine.

Proton nmr absorption in carbon tetrachloride with tetramethylsilane as internal standard had τ values (and integrated areas) of 6.88 (8), 8.80 (32), and 9.18 (12) ppm. Infrared absorption was noted at 650 (w), 715 (s), 815 (w), 850 (w), 925 (w), 1020 (w), 1050 (w), 1355 (s), 1465 (m), 1480 (m), 1570 (s), 1605 (s), 1620 (m), 2850 (s), 2870 (s), 2915 (vs), 2950 (vs), and 3050 cm^{-1} (w).

Kinetics. *t*-Butyl chloride was dried over Drierite (calcium sulfate) and distilled, bp 52°. A 0.1 *M* solution (10 ml) of *t*-butyl chloride in THAB was placed in a constant temperature bath at 25 ± 0.02°. At desired intervals, 1-ml aliquots were dissolved in 5 ml of benzene and shaken for 15 min with 10 ml of water to hydrolyze the *t*-butyl chloride remaining. The water layer (6 ml) was titrated by 0.01 *M* aqueous sodium hydroxide using phenolphthalein as an indicator. One-third of the benzoic acid is in the water layer. The acid titer decreased to zero by a first-order rate law.

Electrochemistry. Current-voltage curves were obtained with both a dropping mercury electrode and a platinum microelectrode. Figures 1 and 2 illustrate typical results. An aqueous AgCl(1 *M* NaCl)|Ag electrode was used as a reference. Contact was provided by a short piece of porous glass rod (Corning 7930). Characteristics of the DME at 0 v were $m = 6.10$ mg/sec, $t = 5.62$ sec/drop. A short piece of platinum wire was used as the counter electrode. The polarograph was a Heath EUW-401. Oxygen removal from the THAB solvent was accomplished by a nitrogen purge. All measurements were made at room temperature, 23 ± 3°. No correction was made for *iR* voltage drop in the cell. Although the polarograph is essentially a potentiostat, the potential is independent of current only if zero resistance exists between the reference and indicator electrodes. As noted above, THAB solutions have a rather high resistance and the cell used did not allow the two electrodes to be positioned close together.

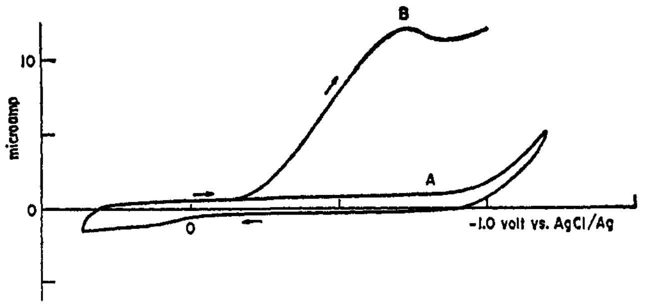

Figure 2. Scan rate 100 mv/sec: curve A, residual cyclic voltammogram of platinum microelectrode; curve B, reduction of oxygen.

From curve A in Figure 1, the anodic limit with a mercury electrode is +0.2 v (AgCl|Ag). The lack of an anodic wave at potentials negative to the reference suggests either that there is negligible iodide remaining in the salt or that mercurous(ic) iodide is soluble in THAB.

No significant concentrations of reducible impurities, including iodine, contributed to the cathodic current at potentials positive to −1.8 v, but a reduction wave was evident beyond this point. After a perceptible diffusion plateau of 80 μa at −2.5 v, the current increased sharply. The last current rise is undoubtedly the reduction of THA ion and the impurity wave was probably an alkali metal cation since $E_{1/2}$ was −2.09 v. Sodium or potassium ions at 0.01 *M* are not uncommon in reagents of the quality used in this synthesis. It is also possible that hydrogen ion reduction from traces of water may have contributed to the reduction wave, although this is not reported to be the case with neutral, aqueous solutions of tetraalkylammonium salts.

The point of zero charge of the mercury electrode was −0.25 v, based on observations of the shapes of the current-time curves of individual drops. The slope of the (peak) charging current-potential curve is very small so that the intersection on the potential axis (the point of zero charge) is difficult to determine. The change in shape of the charging current-time curves on either side of −0.25 v was very evident, however. Drop times changed rather markedly with potential beyond −1.5 v. At −1.7 v, the decrease was about 30% compared to the drop time at 0 v.

Oxygen is reduced in a single wave having $E_{1/2} = -0.37$ v. The diffusion current was 3.4 μa after prolonged contact with the atmosphere (curve B). Since the difference between the potentials at one-fourth and three-fourths of the diffusion current was 75 mv, the rising part of the wave was not related to a simple diffusion-controlled process but instead was activation controlled. Traces of water were undoubtedly present, so that reduction of oxygen to hydroxide ion was possible.

Reduction waves (and $E_{1/2}$ values) were observed for anthracene (−1.7), benzophenone (−1.42), fumaric acid (−0.50), and β-naphthol (−2.3). Curve C of Figure 1 shows a polarogram for anthracene added as a small crystal. In aqueous solution, anthracene is reduced at $E_{1/2} = -2.4$ v. Interference from the assumed alkali metal cation reduction prevented an assessment of the quarter-wave potential difference. The reduction of naphthalene was not observable over the accessible range to −2.6 v.

A platinum microelectrode in pure THAB exhibited an anodic limit at about +0.3 v, and at −1.2 v cathodic current became significant, as shown in Figure 2, curve A. Within this potential range, the current was essentially capacitive in that a first-power dependence on scan rate was observed. Oxygen reduction occurred as a drawn-out wave (curve B), rising from −0.2 v to a peak at −0.7 v when the scan rate was 100 mv/sec. The peak potential was very dependent upon scan rate. The addition of a small amount of water did not alter the residual curve, which suggests that traces of water were already present. A mixture of 25% by volume of toluene with THAB had essentially the same residual currents as the pure liquid.

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