Part II PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Densities of Some Molten Organic Quaternary Halides

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The buoyancy method was used to measure the densities of the following molten organic quaternary halides, tributylbenzylphosphonium chloride, tributyl-2:4-dichlorobenzylphosphonium chloride, tetra-*n*-butylammonium bromide, tetra-*n*-butylammonum iodide, and tetra-*n*-hexylammonium iodide. All salts were studied over the temperature range in which they were stable and the data was fitted to equations of the form $\rho = \alpha - \beta t$ by a least squares analysis. The standard deviation is also given.

THE DENSITIES of many organic liquids are well known but there appears to be no data recorded for the densities of organic salts that are stable upon melting. This information is necessary when such salts are used as spectroscopic solvents (*1*). In this work, a modification of an existing apparatus for density determinations (*2*) is described which allows accurate measurements to be made in small volumes of melt, and the densities of the following compounds are recorded: tributylbenzylphosphonium chloride, tributyl-2:4-dichlorobenzylphosphonium chloride, tetra-*n*-butylammonium bromide, tetra-*n*-butylammonium iodide, and tetra-*n*-hexylammonium iodide.

EXPERIMENTAL

Density Determinations. The densities were determined by the buoyancy method. A platinum bob of known weight was immersed in the molten salts and weighed, and the densities of the melts were calculated from the observed weight losses.

The apparatus used was that originally described by Smith and Petersen (*2*). However, they required a melt volume of about 40 ml. since the thermocouple was encased in a thin-walled, fused silica tube which also served as a stirring rod. As organic salts are often very expensive, the volume of the melt was reduced to about 12 ml. by using a tube of borosilicate glass of 22 mm. internal diameter as the melt container. A platinum wire stirrer was employed (wire diameter 2 mm.). The platinum bicone bob had a greatest diameter of 8 mm. and was always carefully aligned to be in the middle of the melt and the top of it 1 cm. or more below the surface of the melt (*2*). Under these conditions no surface tension effects were observed, nor was there any noticeable condensation upon the platinum wire supporting the bob.

The salts were heated in an electric tube furnace (*2*) which contained an aluminum block with one hole drilled in it to take the narrower glass tube and another for the thermocouple used for measuring the melt temperature. Thermal equilibrium thus took longer to reach but temperature fluctuations were minimized. The actual temperature measurements were found to have the same accuracy as the earlier work (*2*).

The apparatus was under a continual steady flow of high purity nitrogen to reduce any possible charring that might occur. The established technique of Smith and Petersen (*2*) was used for the density measurements. The validity of these modification was demonstrated by determining the density of a lithium-potassium nitrate eutectic; the results agreed with published results (*2*) within experimental error.

Materials. The tetraalkylammonium salts were obtained from Eastman Kodak and their purity and ability to remain undecomposed on melting, and also that of the phosphonium chlorides, was established in the following manner.

(a) After drying for 24 hr. or more at room temperature in a drying-pistol under high vacuum their melting points were taken; all recorded sharp melting points (Table I).

(b) Weighed samples were held molten at different temperatures under a slow flow of nitrogen for many hours, their percentage weight losses being regularly recorded.

Table I. Density Equations for Organic Melts

Salt	Melting Point (° C.)	$\rho = \alpha - \beta t$		Std. Dev. × 10^3 (G./Cc.)	Temperature Range (° C.)
		α (g./cc.)	$\beta \times 10^4$ (g./cc./° C.)		
Tributylbenzylphosphonium chloride	162–163	1.021	5.48	0.2	178–240
Tributyl-2:4-dichlorobenzylphosphonium chloride	117–118	1.165	6.90	1.1	155–221
Tetra-*n*-butylammonium bromide	109–110	1.086	6.87	0.7	123–146
Tetra-*n*-butylammonium iodide	143–144	1.187	6.60	0.2	149–169
Tetra-*n*-hexylammonium iodide	103.5–104.5	1.093	7.30	0.6	122–150

The phosphonium chlorides were the most stable, their percentage weight loss being <1% after 20 hr., while the alkylammonium halides began to lose weight after about 8 hr. The vapor pressures of the molten salts and the absence of a stationary atmosphere above the melts can explain the weight losses.

(c) Melting points of samples of the salts after prolonged melting, but prior to slight decomposition, agreed well with those of the pure salts.

(d) Infrared spectra of the phosphonium chlorides and tetra-*n*-butylammonium iodide before and after prolonged melting showed little evidence of subsequent decomposition.

RESULTS

The density data were fitted to the equation $\rho = \alpha - \beta t$ by the method of least squares. In this equation, ρ is the density, α and β are constants and t is the temperature in ° C. The results are given in Table I which lists the melting point of the pure component, α and β in the density equation, the standard deviation from the least squares fit, and the experimental range in ° C. Densities were determined at approximately 5° intervals.

The experimental temperature range was often limited in the case of the alkylammonium salts since they usually had low boiling points, whereupon data points were taken at more frequent intervals.

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Basicities of Alkylamines and Substituted Pyridines in Fifty Volume–Per Cent Dioxane–Water

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Acid dissociation constants for the protonated species of certain alkylamines and substituted pyridines in 50 volume–per cent dioxane–water are reported and trends within a series of similar compounds are discussed. Differences in the basicities of the aminopyridines are attributed to electromeric effects. The constants determined for these compounds in aqueous solution are included for comparative purposes.

MEASUREMENTS of the dissociation constants for the conjugate acids of many organic bases have been made in order to study their coordination tendencies with metal ions, using both aqueous and nonaqueous media as solvents. Of special interest as a solvent system is 50 volume–per cent dioxane–water, which is being used extensively for compounds that are somewhat insoluble in water. Since the properties of this mixed solvent differ from those of water, the basicities of water-soluble organic bases which have not been studied in this system were determined.

In this investigation apparent p*K* values for a series of alkylamines and substituted pyridines in 50 volume–per cent dioxane–water are reported and discussed. The values