SURFACE TENSION OF CAPILLARY-ACTIVE ORGANIC HALIDES[1]

A PRELIMINARY STUDY

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In recent years a number of organic compounds, generally termed cationic soaps, have found increasing application in the textile-finishing industry. These compounds owe their name to the fact that they exhibit properties similar to regular soaps,—i.e., they are strong depressors of surface tension,—but, contrary to the case of soaps, the surface-active group is the cation.

Of the many cationic compounds now available, cetylpyridinium bromide and cetyltrimethylammonium iodide are among the best known.

Besides their industrial value, these compounds seem to offer considerable interest from the point of view of surface chemistry, because by substituting different halides as the dissociatable anion, it should be possible to study the influence of the anion on the surface tension. Therefore, it was decided to prepare in the purest possible form the chlorides, bromides, and iodides of the above-mentioned organic compounds and to determine the surface tension of their solutions under comparable conditions by the pendant-drop method as developed by Andreas, Hauser, and Tucker (1).

METHOD OF PREPARATION OF COMPOUNDS

The reaction vessel used in the preparation of the following group of compounds consisted of a 2-liter, three-necked, Pyrex flask. The central neck was equipped with a mercury-sealed glass stirrer driven by an electric motor. One of the outside necks was equipped with a reflux condenser and the other with a thermometer. All heating was done on an oil bath to prevent local overheating.

Cetyl chloride

Commercial cetyl alcohol ($C_{16}H_{33}OH$) was reacted with phosphorus pentachloride in equimolecular quantities at a temperature of 135–136°C. for 5 hr. The resultant product was distilled at atmospheric pressure to remove all of the phosphorus oxychloride. The remaining residue was

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distilled under vacuum (aspirator water temperature 10.5°C.), all the distillate which came over between 193° and 197°C. being retained.

This distillate was dissolved in commercial ether, and the ethereal solution was washed with water, then with 5 per cent sodium hydroxide, and again with water. The ethereal layer was dried over anhydrous calcium chloride and the ether was then distilled off, leaving purified cetyl chloride, a clear, light-colored, oily liquid.

Cetyl iodide (6)

Commercial cetyl alcohol was reacted with iodine and yellow phosphorus in molecular proportions according to the following equation:

$$3C_{16}H_{33}OH + P + 1.5I_2 \rightarrow 3C_{16}H_{33}I + P(OH)_3$$

These were allowed to react for 5 hr. at 145–146°C. This reaction was also carried out using red phosphorus. This is the recommended procedure, as the reaction is much less violent than the one using yellow phosphorus.

The reaction mixture was dissolved in commercial ether; the ethereal solution was filtered to remove unreacted phosphorus, and was washed with water, then with 5 per cent sodium hydroxide, and finally with water. The ether layer was dried over anhydrous calcium chloride and the ether was distilled.

Cetyl bromide

Liquid bromine was slowly added from a separatory funnel to an ice-cooled flask containing red phosphorus. The product, phosphorus tribromide, was reacted with cetyl alcohol in molecular proportions at 135–140°C. for 6 hr. The reaction mixture was dissolved in ether, and the ethereal solution was washed, dried, and distilled as described above.

The yields of the cetyl halides were approximately 50 per cent, except in the case of the bromide where the yield was 90 per cent.

Cetylpyridinium halides (3, 4, 5)

Cetylpyridinium chloride, bromide, and iodide were made in the same apparatus as the cetyl halides. The cetyl halides were reacted with pyridine, the chloride at 120°C. for 8 hr. the bromide at 135–140°C. for 6 hr., and the iodide at 135–140°C. for 3.5 hr.

Trimethylamine

Trimethylamine for the preparation of the cetyltrimethylammonium halides was prepared by distilling the amine (b.p. 3.2–3.8°C.) from a commercially available aqueous solution and absorbing the gas in anhydrous alcohol. The resulting solution was titrated with hydrochloric acid, using methyl orange as an indicator, and the normality was determined.

Cetyltrimethylammonium halides (3, 5)

Because of the low boiling point of trimethylamine, the reaction between it and the cetyl halides could not easily be carried out in the apparatus used for the pyridinium salts except by using a condenser packed in dry ice. Since the standard-sized beer bottle is designed to withstand at least 3 atmospheres internal pressure, this container, with the cork wired in, was used for a reaction vessel with excellent results. However, the bottle must not be over half full and the oil-bath temperature must not be over 120°C.; otherwise there is serious danger of the bottle exploding.

The cetyltrimethylammonium halides were prepared by heating the cetyl halide and the alcoholic trimethylamine in equimolecular quantities, the chloride for 5 hr. at 110°C., the bromide for 6 hr. at 115°C., and the iodide for 5 hr. at 115–120°C.

PURIFICATION OF SALTS

Following the method of Knight and Shaw, the trimethylammonium halides and the pyridinium chloride and iodide were purified by recrystallizing three times from absolute ethyl alcohol and absolute ether. The salt was dissolved in the minimum amount of alcohol, diluted with absolute ether, and cooled on ice. This solution was vacuum filtered and air dried.

The cetylpyridinium bromide did not readily lend itself to this type of crystallization. It was found after several trials that the crude pyridinium bromide could easily be dissolved in the minimum amount of commercial dioxane, diluted with acetone, cooled on ice, vacuum filtered, and air dried. The product was washed with acetone while in the vacuum filter. The other salts may also be easily purified by this method and much more economically than with absolute alcohol and ether.

PROCEDURE AND RESULTS

Since we were primarily interested here in ascertaining if and to what extent the dissociatable anion influences the surface activity of the cation in surfaces aged for only a short time, no extensive surface aging tests are included in this work.[2] All drops were photographed 3 min. after formation.

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[2] N. K. Adam and H. L. Shute (Trans. Faraday Soc. **34**, 758 (1938)) applied the sessile-bubble method in their studies on the changes of surface tension with time and with concentration of solutions of the bromide compounds used for this investigation. They found that equilibrium is reached only after at least a week in the case of dilute solutions, although the drop in surface tension with time is most pronounced in the first stages of surface aging. This seems to be in general agreement with the slow attainment of surface-tension equilibrium for strong electrolytes, as reported by McBain and Wood (Proc. Roy. Soc. (London) **A174**, 287 (1940)) and Nutting, Long, and Hawkins (J. Am. Chem. Soc. **62**, 1496 (1940)).

The solutions of cetylpyridinium chloride and bromide and cetyltrimethylammonium chloride and bromide were made by the dilution of 0.001 *N* solutions of these salts, and those of the corresponding iodides by dilution of 0.0003 *N* solutions, which concentration represents approximately the limit of solubility of the iodides. The solutions were made with pure water having a known surface tension of 72 dynes per centimeter.

DISCUSSION OF RESULTS

The results of the surface-tension measurements are, for the purpose of clarity, depicted in graphical form in figures 1, 2, and 3. These show, first of all, the definite surface activity of these substances, with the pyridinium salt being somewhat more active than the corresponding trimethylammonium salt. Secondly, the surface tension is lowered in the periodic order of the halide anions: namely, chloride least, bromide intermediate, and iodide most.

For purposes of discussion only, we shall use cetylpyridinium chloride and cetylpyridinium iodide, but the arguments set forth for these salts will hold between the chloride and bromide as well as the bromide and iodide salts. Obviously, only solutions of the same concentration must be considered.

A further examination of figures 1, 2, and 3 shows that the magnitude of surface-tension lowering is of the same order for each pair of halide salts,—i.e., cetylpyridinium chloride and cetyltrimethylammonium chloride. This immediately suggests the conclusion that surface-tension lowering is not dependent only upon the cation, but that the anion determines its final degree.

This phenomenon can be explained about as follows: Born (2) has calculated the heats of hydration of the halide ions and found that they decrease in the order chloride, bromide, and iodide, thus giving us an indication of the relative degree of hydration of these ions.

To put this into colloid-chemical terms we can say that the chloride ion is more hydrophilic than the bromide and the latter more than the iodide. The pendant-drop method has already offered ample proof that the establishment of surface equilibrium of solutions containing capillary-active components is far more complex than has been originally thought. The final result will depend on the outcome of a war waged between the lyophobic and lyophilic groups of the solute, the first battle establishing the importance of the various types of lyophilic troops engaged therein.

In the present case the lyophobic hydrocarbon-chain cation is capable of lowering the surface tension to a definite extent for every concentration.

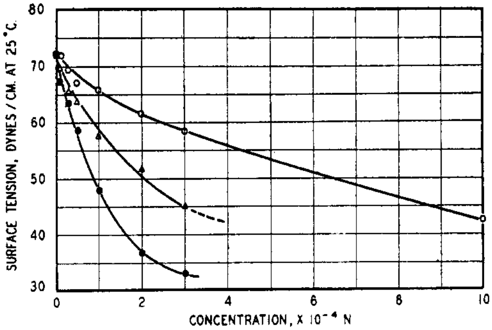

FIG. 1. Surface tension of solutions of cetylpyridinium salts: ○, cetylpyridinium chloride; △, cetylpyridinium bromide; ●, cetylpyridinium iodide.

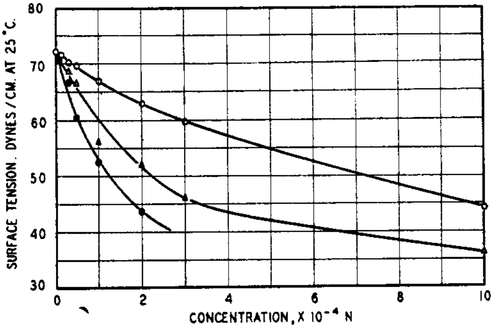

FIG. 2. Surface tension of solutions of cetyltrimethylammonium salts: ○, cetyltrimethylammonium chloride; △ cetyltrimethylammonium bromide; ●, cetyltrimethylammonium iodide.

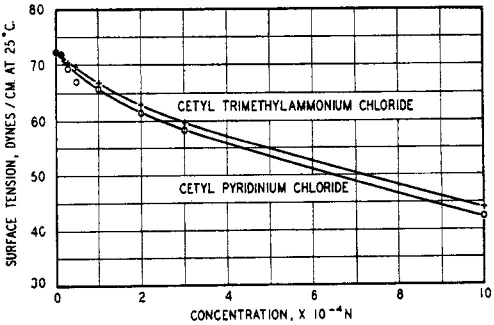

FIG. 3. Surface tension of solutions of cetyl salts

However, the actual depression obtained so far depends entirely on the extent to which the lyophilic anion compensates for this tendency. The results reported offer further proof for the importance of the lyotropic series of anions in colloidal systems. Further work on the aging of surfaces of the solutions discussed in this paper until equilibrium is established and an extension of this work to include soaps with varying anions will be reported on an early occasion.

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HEAT CAPACITY AND DENSITY OF AQUEOUS SOLUTIONS OF POTASSIUM IODATE, POTASSIUM ACID SULFATE, IODIC ACID, AND SULFURIC ACID AT 25°C.[1]

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The heat capacity of an ideal solution is, by definition, the sum of the heat capacities of the various constituents in their pure states at the same temperature and pressure. In any actual solution, this ideal heat capacity will be modified by the intermolecular and electrostatic effects which each constituent exerts upon the heat capacities of the other constituents. If a reaction,—for example, the dissociation of bisulfate ion into hydrogen and sulfate ions,—is more complete at a higher temperature than at a lower, then the heat corresponding to the additional fraction of bisulfate ion dissociated at the higher temperature will be measured as though it were a part of the heat capacity of the solution.

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[2] Present address: Shell Development Company, Emeryville, California.