[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

THE SOLUBILITIES OF LONG-CHAIN DIALKYLDIMETHYLAMMONIUM CHLORIDES IN ORGANIC SOLVENTS

A. W. RALSTON, R. A. RECK, H. J. HARWOOD, AND P. L. DUBROW

Received September 2, 1947

The fact that the quaternary ammonium halides are true salts has a decided influence on their solubilities in organic solvents. It has recently been shown (1) that dodecyl- and octadecyl-trimethylammonium chlorides possess limited solubilities in the non-polar and slightly polar organic solvents with the exception of carbon tetrachloride and chloroform, and that they are appreciably soluble in polar organic solvents. These solubility behaviors are explainable on the basis of their salt-like properties. The replacement of a methyl group in the alkyltrimethylammonium chlorides by a second long-chain radical should yield a series of compounds which possess interesting solubility characteristics. Although the higher dialkyldimethylammonium chlorides are salts, the presence of the two long chains should materially increase their solubilities in the non-polar and slightly polar organic solvents. In the present study we have determined the solubilities of dioctyl-, didecyl-, didodecyl-, ditetradecyl-, dihexadecyl-, and octyldodecyl-dimethylammonium chlorides in a variety of organic solvents of varying polarities. These observations have enabled us to formulate some generalizations regarding the solubilities of the higher alkyl quaternary ammonium chlorides.

EXPERIMENTAL

Preparation of dioctyl-, didecyl-, didodecyl-, ditetradecyl-, and dihexadecyl-dimethylammonium chlorides. All these quaternary ammonium salts were similarly prepared. The preparation of didodecyldimethylammonium chloride will be described in detail as an example of the procedure employed.

Predistilled dodecylamine was carefully fractionated through a Stedman-packed column. In a two-necked flask fitted with a mercury-sealed stirrer and an air condenser, 212 g. of this distilled amine (f.p. 28.26°) and 8.5 g. of 50% Raney nickel suspended in dodecylamine were heated with stirring at 200° for 2.5 hours. The resulting product was taken up in ethyl acetate, the Raney nickel removed by filtration, and the didodecylamine crystallized from the solvent.

To 77 g. of the recrystallized didodecylamine dissolved in 200 cc. of ethanol, 49 cc. of 85% formic acid was slowly added, the temperature being maintained at about 40°. After this addition, 46 cc. of a 36% aqueous formaldehyde solution was added and the temperature raised to 60°. After the evolution of carbon dioxide had subsided, the temperature was maintained at the reflux point of the solution for one-half hour. The solution was then neutralized with aqueous sodium hydroxide, and the top layer was drawn off, dried over anhydrous potassium carbonate, filtered, and distilled (b.p. 183° at 0.35 mm.). The didodecylmethylamine so obtained (f.p. 10.4°) was dissolved in ethyl acetate, methyl chloride was added, and the mixture was heated in a bomb at 80° for one hour. The didodecyldimethylammonium chloride was recrystallized twice from ethyl acetate to give a white, crystalline, hygroscopic product. Dioctyldimethyl- and didecyldimethyl-ammonium chlorides are extremely hygroscopic. This property was not observed with ditetradecyldimethyl- and dihexadecyldimethyl-ammonium chlorides.

Preparation of octyldodecyldimethylammonium chloride. To 102 g. of dodecyl chloride dissolved in 50 cc. of ethanol was added 38.7 g. of methylamine and the solution was heated in a bomb at 125° for eight hours. The contents of the bomb were neutralized with aqueous sodium hydroxide, the top layer dissolved in Skellysolve F, dried over anhydrous potassium carbonate, filtered, and the methyldodecylamine distilled. To 64 g. of distillate was added 56.3 g. of freshly distilled octyl bromide and the mixture was heated at 90° for five hours. One-half of the theoretical amount of aqueous sodium hydroxide required for complete neutralization was added at the end of 2.5 hours and the remainder added slowly during the last 2.5 hours. The top layer was extracted with Skellysolve F, dried over anhydrous potassium carbonate, filtered, and the octyldodecylmethylamine distilled (b.p. 170° at 0.25 mm.). This distillate was converted to the quaternary ammonium chloride by heating with methyl chloride in a bomb at 80° for one hour. The product was recrystallized twice from cold ethyl acetate. Octyldodecyldimethylammonium chloride is very hygroscopic.

The solubilities were determined in sealed tubes by the method and with the apparatus previously described (2, 3, 4).

RESULTS AND DISCUSSION

The solubility behavior of the higher dialkyldimethylammonium chlorides in the non-polar solvent hexane is extremely interesting. Dioctyl-, didecyl-, and octyldodecyl-dimethylammonium chlorides are essentially insoluble in this solvent and thus exhibit the solubility characteristics of salts. On the other hand, their higher homologs, didodecyl-, ditetradecyl-, and dihexadecyl-dimethylammonium chlorides function as typical organic non-electrolytes, their solubilities decreasing with increase in chain lengths. The solubilities in hexane increase rapidly over a small temperature range; for example, that of didodecyl- increases from 4.16 to 186 g. per 100 g. of solvent over the temperature interval 31° to 34°, ditetradecyl- from 3.1 to 150 g. between 42° and 44°, and dihexadecyldimethylammonium chloride from 5.2 to 108 g. between 52° and 54°.

The solubilities of the dialkyldimethylammonium chlorides in benzene do not exhibit the discontinuities encountered in hexane. The lower members, dioctyl-, didecyl-, and octyldodecyl-dimethylammonium chlorides are extremely soluble in benzene and could not be induced to crystallize below the freezing point of the solvent. The higher homologs are also appreciably soluble in benzene, the solubilities decreasing with increase in chain lengths. Some of the observed values are as follows: didodecyl-, 1.1 g. in 100 g. solvent at 5°, 39.5 g. at 10°; ditetradecyl-, 4.7 g. at 20°, 78.5 g. at 30°; dihexadecyl-, 1.0 g. at 30°, 85.5 g. at 40°. The solubilities of these compounds in benzene are, therefore, quite similar to those of the higher alkyl non-electrolytes and are in contrast to those of the higher alkyltrimethylammonium chlorides, which are only slightly soluble in this solvent.

The higher alkyltrimethylammonium chlorides have been shown (1) to be extremely soluble in the chlorinated solvents chloroform and carbon tetrachloride. The higher dialkyldimethylammonium chlorides are likewise very soluble in chloroform, and only didodecyl-, ditetradecyl-, and dihexadecyldimethylammonium chlorides give well-defined solubility curves, Fig. 1. Although the dialkyldimethylammonium chlorides are not so soluble in carbon

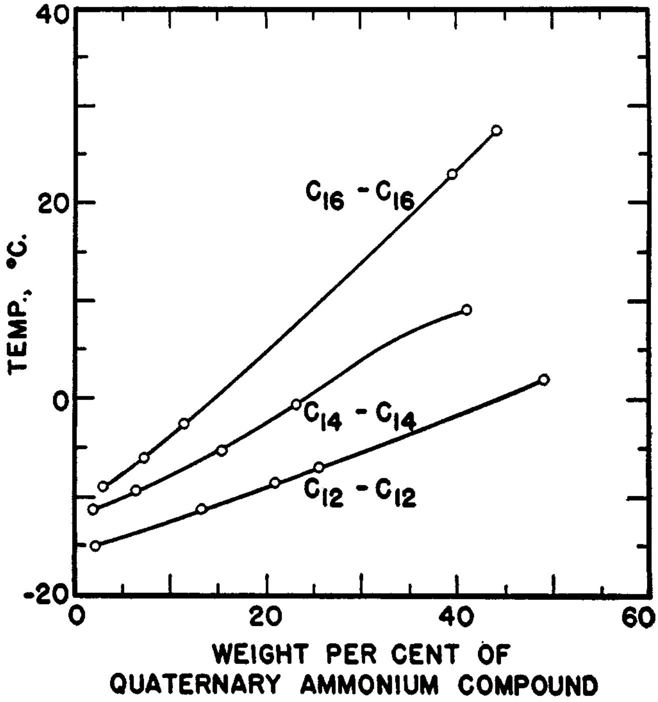

FIG. 1. SOLUBILITIES OF DIALKYLDIMETHYLAMMONIUM CHLORIDES IN CHLOROFORM

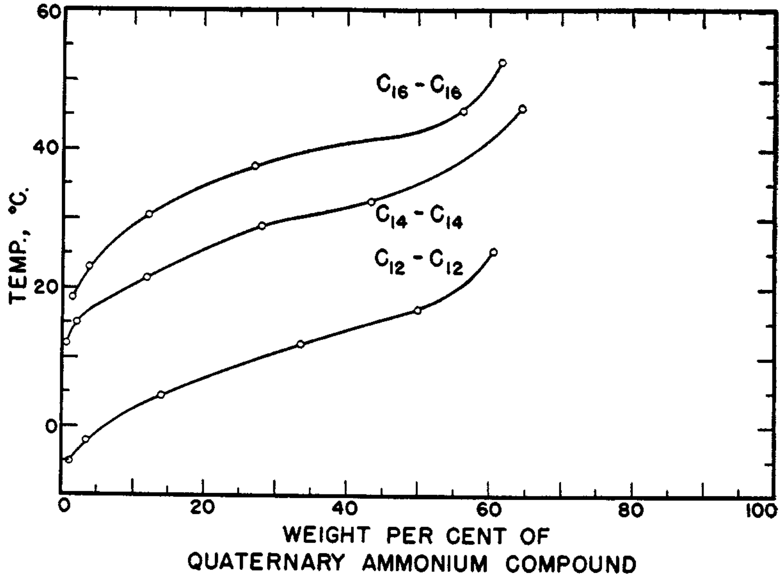

FIG. 2. SOLUBILITIES OF DIALKYLDIMETHYLAMMONIUM CHLORIDES IN CARBON TETRACHLORIDE

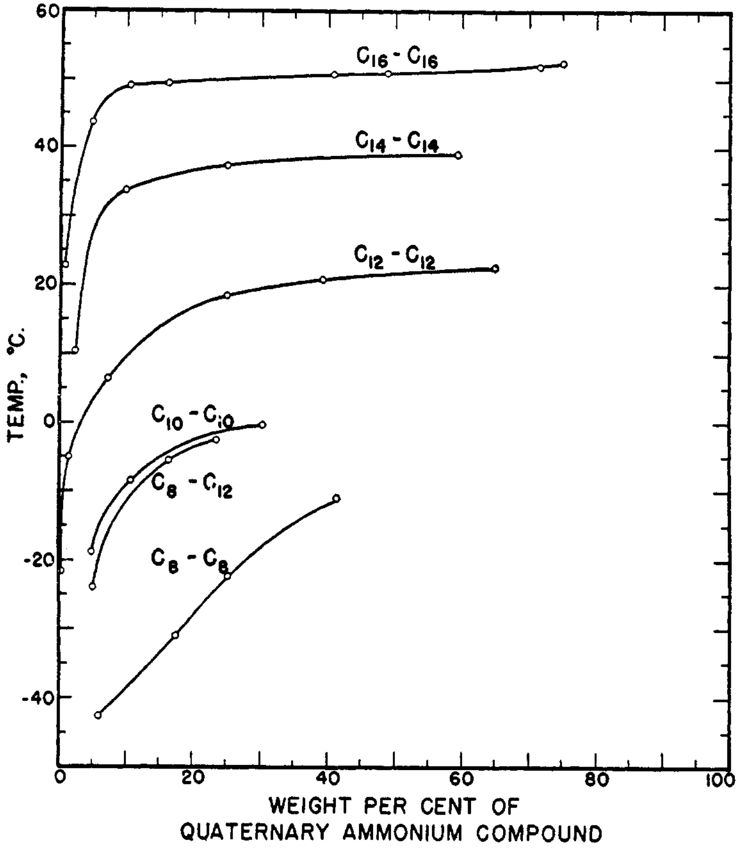

FIG. 3. SOLUBILITIES OF DIALKYLDIMETHYLAMMONIUM CHLORIDES IN ACETONITRILE

TABLE I

SOLUBILITIES OF DIALKYLDIMETHYLAMMONIUM CHLORIDES IN METHANOL AND ACETONE

SALT	SOLVENT	SOLUBILITY IN 100 G. OF SOLVENT
Didodecyl-	Methanol	$0.5^{-80\circ}$, $0.7^{-70\circ}$, $1.1^{-60\circ}$, $4.1^{-50\circ}$, $13.6^{-40\circ}$, $49.6^{-30\circ}$, $119.7^{-20\circ}$ 312.9^{-10}:
Ditetradecyl-	Methanol	$1.1^{-40\circ}$, $5.7^{-30\circ}$, $12.9^{-20\circ}$, $29.0^{-10\circ}$, $146.9^{0\circ}$, $257.1^{10\circ}$
Dihexadecyl-	Methanol	$3.6^{-10\circ}$, $10.4^{0\circ}$, $30.7^{10\circ}$, $163.2^{20\circ}$
Octyldodecyl-	Acetone	$4.8^{-10\circ}$, $17.8^{-3\circ}$
Didecyl-	Acetone	$4.7^{-10\circ}$, $17.6^{-3\circ}$
Didodecyl-	Acetone	$2.6^{10\circ}$,$55.0^{20\circ}$
Ditetradecyl-	Acetone	$3.6^{30\circ}$, $78.5^{40\circ}$
Dihexadecyl-	Acetone	$3.1^{40\circ}$, $92.3^{50\circ}$

tetrachloride, Fig. 2, as in chloroform the lower members could not be crystallized from this solvent.

All the higher alkyl quaternary ammonium chlorides investigated are extremely soluble in polar organic solvents. They are appreciably more soluble in methanol than in acetone, and the lower members could not be crystallized from the former solvent. Their solubilities in methanol and acetone are shown in Table I.

The higher dialkyldimethylammonium chlorides are appreciably less soluble in acetonitrile than in methanol, their solubilities decreasing greatly with increase in chain lengths. Their comparative solubilities in these two solvents are similar to those previously observed (1) for the alkyltrimethylammonium chlorides. The solubilities of the higher dialkyldimethylammonium chlorides in acetonitrile are shown in Fig. 3. It will be noted that the solubility of octyldodecyldimethylammonium chloride is quite similar to that of didecyldimethylammonium chloride and much greater than that of didodecyldimethylammonium chloride. This indicates that the solubility of these compounds is influenced more by the total number of carbon atoms in the two chains than by the length of the longest chain.

Few series of organic compounds show the wide range of solubilities which has been observed with the higher dialkyldimethylammonium chlorides. The fact that they are appreciably soluble in both polar and non-polar solvents is predictable from their structures.

SUMMARY

The solubilities of dioctyl-, didecyl-, didodecyl-, ditetradecyl-, dihexadecyl-, and octyldodecyl-dimethylammonium chlorides have been determined in hexane, benzene, chloroform, carbon tetrachloride, methanol, acetone, and acetonitrile.

Certain comparisons have been made between the solubilities of these compounds and those of the alkyltrimethylammonium chlorides.

Chicago 9, Ill.

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