Inclusion Compounds of Urea and Thiourea with Cationic Surfactants

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Abstract

Quaternary ammonium compounds, having at least one long aliphatic group, readily formed adducts with urea. These cationics also had structural features that allowed adduct formation with thiourea. IR analysis confirmed that these adducts were of the canal complex type of inclusion compound.

Introduction

BENGEN (1) DEMONSTRATED that urea adducts could be formed simply by mixing urea with a long chain component. Similar adduct formation, using thiourea, was shown by Angla (2). Compounds of this type fall into the category of inclusion compounds (Schlenk's "Einschlussverbindugen") (3), and arise from the ability of one compound to enclose another spatially. An excellent review on this subject was recently presented by Brown (4).

The principles of adduct formation have been utilized in many practical applications. A field of application apropos to this investigation was the preparation of urea-solidified nonionic surfactants (5). A solution of urea and liquid surface-active agents of the polyoxyethylene type solidified on standing at room temp.

Cationic surfactants are available not only as solids but also as sticky, semisolid materials. Quaternaries having at least one long aliphatic chain possess a necessary structural requirement for urea adduction, and in the case of a semisolid compound this could mean the preparation of a solid adduct. Quaternary ammonium compounds might also have structural features that allow adduct formation with thiourea. This investigation is concerned with the preparation and analysis of solid adducts formed when urea or thiourea is combined with various cationic surfactants.

Experimental

Materials. Reagent grade urea, thiourea and methanol were employed. The various cationic surfactants are listed in Table I. Many of these were available as concs, and, when necessary, the anhydrous or dry compounds were prepared by allowing the concs to remain in an oven at 70–80C until free of solvent.

Preparations of Urea Adducts. Method A. Dry quaternary compound (0.01 mole) was added to 80–100 ml of saturated solution of urea in methanol (2.83 M at 30C) and dissolved by gentle agitation. Precipitation of the adduct took place shortly after solution was complete, and the mixture was allowed to stand at 30C for 24 hr. The adduct was collected on a Buchner funnel by suction, carefully washed with cold isopropyl alcohol, and dried at 50–60C.

Method B. The procedure was essentially the same as described above except that modifications were necessary to induce adduct formation. A higher concn of anhydrous quaternary (0.03 mole/100 ml of methanolic urea) and longer standing (one week at room temp) were needed to prepare benzalkonium chloride and Atlas G-263 adducts. Triton X-400 (0.03 mole/100 ml methanolic urea) gave a very thick, gelatinous precipitate which was slurried with isopropyl alcohol before filtering. The Dynaltone Chloride adduct was prepared by dissolving 0.03 mole of dry quaternary in 100 ml of methanolic urea, adding 20 ml of an aqueous saturated urea solution (10 M at 30C) and refrigerating at 4C until precipitation occurred.

Preparation of Thiourea Adducts. Method A. Quaternary compound (0.005 mole) was dissolved in 5 ml of saturated solution of thiourea in methanol (0.99 M at 30C). Then 40 ml of freshly prepared saturated aqueous thiourea solution (1.67 M at 30C) was added and the solution allowed to stand 1 hr at 30C before placing in a refrigerator (4C) where precipitation took place within 1–8 hr. The product was collected on a Buchner funnel by suction, carefully washed with cold isopropyl alcohol, and dried at 60–70C.

Method B. Ten grams of the conc (form supplied) was dissolved in 10 ml of methanolic thiourea and 40 ml of freshly prepared aqueous thiourea added. This solution was allowed to stand at 30C for 1 hr and then refrigerated at 4C for 1–8 hr. For Triton X-400 it was necessary to dissolve 10 g of the conc in isopropyl alcohol with gentle heat and add 200 ml of aqueous thiourea solution. This solution was stored at 4C for 24 hr. The adducts prepared by this method were collected, washed and dried as described above.

Method of Assay. The titrimetric assay used to determine the amt of quaternary in an adduct was essentially that of Barr et al. (6) as modified by Auerbach (7). The adduct (100 mg) was dissolved in 100 ml of water and 1 ml of this solution placed in a 50-ml glass stoppered cylinder. The amounts of 5 ml of pH 9.5 phosphate buffer, 15 ml of 0.0001 *N* dioctyl sodium sulfosuccinate, 1 ml of bromphenol blue indicator and 5 ml chloroform were added. The excess anionic was titrated with a 0.0001 *N* cetyldimethylbenzylammonium chloride solution and the end point indicated by the appearance of a blue color in the chloroform layer. The assay results were used to calculate moles urea or thiourea/mole quaternary ratios which are shown in Table 1.

Infrared Analysis. IR spectra were made on a Perkin Elmer Infracord, Model 137. The crystalline quaternary-urea or thiourea adducts were examined as Nujol mulls. Spectra of the quaternary adducts were compared to literature spectra and to spectra of adducts prepared using compounds known to form urea or thiourea inclusion compounds readily. Dodecane and hexadecane adducts with urea were easily prepared by adding the hydrocarbons to saturated

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TABLE I

Adducts of Urea and Thiourea with Quaternary Ammonium Compounds

Quaternary Ammonium Compounds		Urea Adducts		Thiourea Adducts	
Common or trade name	Chemical name	Method	Moles urea / Mole quat	Method	Moles thio. / Mole quat
Ceepryn Chloride ® [a]	N-cetyl pyridinium chloride	A	14.9	A	10.9
Cetyl Zephiran ® [b]	N-cetyl-N,N-dimethyl-N-benzyl-ammonium chloride	A	22.0	A	11.5
C.T.A.B.[a]	N-cetyl-N,N,N-trimethylammonium bromide	A	20.8	A	8.0
Arquad 2HT ® [c]	N,N-distearyl-N,N-dimethyl-ammonium chloride	A	25.0	Many [i]	No adduct formed
Benzalkonium chloride [d]	N-alkyl(C_8-C_{18})-N,N-dimethyl-N-benzylammonium chloride	B	16.7	B	7.7
Dynaltone Chloride ® [e]	N-dodecyl-N,N-dimethyl-N-3,4 dichlorobenzylammonium chloride	B	19.4	B	10.0
Triton X-400 ® [f]	N-stearyl-N,N-dimethyl-N-benzyl-ammonium chloride	B	26.1	B	10.4
Atlas G-263 ® [g]	N-cetyl-N-ethylmorpholinium ethosulfate	B	19.1	Many [i]	No adduct formed
Hyamine 2389 ® [h]	N-alkyl(C_9-C_{15})tolylmethyl-N,N,N-trimethylammonium chloride(1 part) and N-alkyl-benzyl-N,N,N-trimethyl ammonium chloride(4 parts)	Many [i]	No adduct formed	Many [i]	No adduct formed

Samples supplied by (a) Eastman Organic Chem. as white crystals; (b) Sterling Wintrop Research Inst. as 93.4% white crystals; (c) Armour Ind. Chem. as 75% conc; (d) Sterling Winthrop Res. Inst. as 50% conc and (e) as 20.3% conc; (f) Rohm and Haas Co. as 25% conc; (g) Atlas Chem. Co. as anhydrous paste; (h) Rohm and Haas Co. as 50% conc.

(i) "Many" refers to Methods A and B as well as time and concentration modifications of these methods.

solutions of urea in methanol (8). Thiourea adducts of camphor and cyclohexane were prepared by adding these compounds to saturated methanolic solutions of thiourea (2,9).

Volume and Concentration of Urea Solution vs Adduct Formation. After preliminary experiments, it became apparent that adduct formation was dependent on the volume of saturated urea solution in contact with a fixed amt of quaternary compound. To illustrate the presence of an optimum yield volume, volume vs yield experiments were carried out as follows: Dry quaternary compound (0.005 mole) was dissolved by gentle shaking in various amts of saturated solution of urea in methanol (2.83 M at 30C). These solutions were allowed to stand at 30C ± 0.5C for 24 hr and the precipitated adduct collected on Buchner funnels and dried by suction. The adducts were not washed since even careful treatment caused decomposition of the complex. Additional drying was carried out at 60–70C before weighing. The percentage yield (based on the urea/quaternary mole ratios in Table I) vs. the volume of saturated methanolic urea solution is shown in Figure 1 for C.T.A.B., Arquad 2HT and Cetyl Zephiran.

To illustrate the dependency of adduct formation upon degree of saturation of urea in methanol, experiments were carried out as follows: Dry quaternary compound (0.005 mole) was dissolved in an exact amt of methanol (0–40 ml) and saturated solution of urea in methanol (2.83 M at 30C) added up to a predetermined standard volume. This standard volume was different for each quaternary studied and was the optimum yield volume obtained in the preceding experiments; i.e., C.T.A.B., 30 ml; Arquad 2HT, 100 ml; Cetyl Zephiran, 50 ml. The solutions were allowed to stand for 24 hr at 30C ± 0.5C and the adduct collected and dried as previously described. The percentage yield vs. degree of saturation of urea solutions is shown in Figure 2 for the above quaternaries.

Results and Discussion

Urea Adducts. The published theories (3, 8, 10, 11) of urea addition appear to apply to urea-quaternary adducts. In urea canal complexes, the molecules of $CO(NH_2)_2$ ("host" or occluding compound) are held together by hydrogen bonds between the nitrogen and oxygen atoms. These interconnected urea molecules form spirals composed of hexagonal units, and central channels are formed which accommodate "guest" molecules. It is necessary to have the guest molecule present to help the urea achieve this hexagonal lattice structure. It appears that the long hydrocarbon chains (such as C_{12}–C_{18} groups) on the quaternaries studied fit neatly into the channels resulting in solid adducts. In most cases the moles urea/mole quaternary ratios shown in Table I indicated quaternaries with the longer alkyl chains required more molecules of urea to form adducts than shorter chained compounds. Previous studies with urea adducts of straight-chain hydrocarbons and organic acids have shown that the moles urea/mole compound ratios increase with increasing chain length (8,9). The moles urea/mole compound ratios for quaternary adducts were greater than the reported ratios for hydrocarbons and acids having approx the same chain length.

Urea-quaternary adducts in Table I were white, crystalline solids. These adducts did not show well-defined melting points and, with the exception of Dynaltone Chloride, Atlas G-263 and Arquad 2HT adducts, had melting point ranges somewhere between 129–38C, approx the same as the host urea (mp 133–35C). (Fisher Johns block, uncorrected.) Schlenk (8) reported similar behavior in his studies with crystalline urea-aliphatic compounds. Dynaltone Chloride and Atlas G-263 had lower melting point ranges (115–23C and 122–25C, respectively) while Arquad 2HT-urea adduct demonstrated exceptional melting behavior having a melting point range of 141–44C. This higher melting point range might be attributed to the structure of Arquad 2HT. Instead of one long-chain alkyl group, as is the case with the other quaternaries studied, Arquad 2HT has two $C_{18}H_{37}$-groups. The presence of two long groups could allow the urea to form a very stable adduct having a lattice structure that is actually stronger than the host compound.

As seen in Figure 1, equal mole amts of the quaternaries studied displayed different behaviors for adduct formation when added to various amts of saturated urea solution. Each quaternary had a different optimum yield volume and the maximum

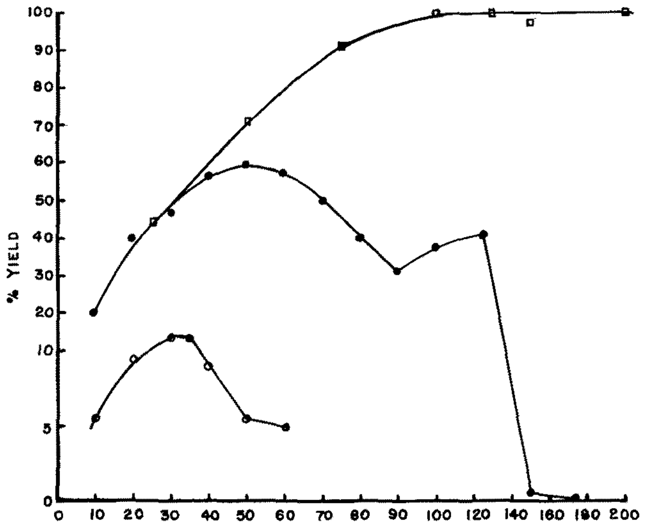

FIG. 1. Yield of adduct vs. volume of saturated urea in methanol for quaternary ammonium compounds (0.005 mole). Key: open square, Arquad 2HT; closed circle, Cetyl Zephiran; open circle, C.T.A.B.

yields varied from 100% for Arquad 2HT to 13.2% for C.T.A.B.

Figure 2 illustrates the dependency of adduct formation on the degree of saturation of the methanolic urea solution. A small decrease in concn of the urea solution greatly decreased the amt of adduct formed and precipitated from the reaction solution.

Of the cationics studied, Hyamine 2389 did not form urea adducts. Although this compound has a long hydrocarbon chain in its structure, its aliphatic group is not attached directly to the quaternary nitrogen as is the case with the other quaternaries studied. Hyamine 2389 has a benzyl or tolyl group between the long aliphatic group and nitrogen. It appears that this type of grouping interferes with adduct formation. Schiessler and Flitter reported that phenyl groups in unbranched aliphatics interfere with urea adduction (12).

A practical application of urea adduct formation with quaternary ammonium compounds can be the conversion of sticky, semisolid compounds into dry, easy-to-handle powders. With most cationic surfactants studied, solid adducts were prepared by adding urea to quaternary concs (2 to 3 parts urea to 1 part pure quaternary), preparing a solution with gentle heat, then allowing the preparation to remain at 70–80C until free of solvent.

Thiourea Adducts. In general, the theories of the formation of thiourea adducts are similar to those of urea (2,3,9,10,13). A main difference between urea and thiourea adducts is that the central channels formed by thiourea have larger diam than the urea channels. As a result, more bulky compounds such as branched aliphatic, cyclic, heterocyclic and aromatic compounds will form adducts with thiourea. Unbranched aliphatic compounds will not form adducts with thiourea since they are too slender to promote formation of the necessary lattice structure. From this information, it appears that the bulkier portions of the quaternary compounds (e.g., dimethylbenzyl, trimethyl, pyridinium) are responsible for thiourea adduction.

The thiourea adducts in Table I were white, crystalline solids, and the moles thiourea/mole quaternary ratios ranged from 7.7–11.5. These ratios agree with the thiourea ratios reported by Schlenk (9) for multiple branched aliphatic chains of similar chain length.

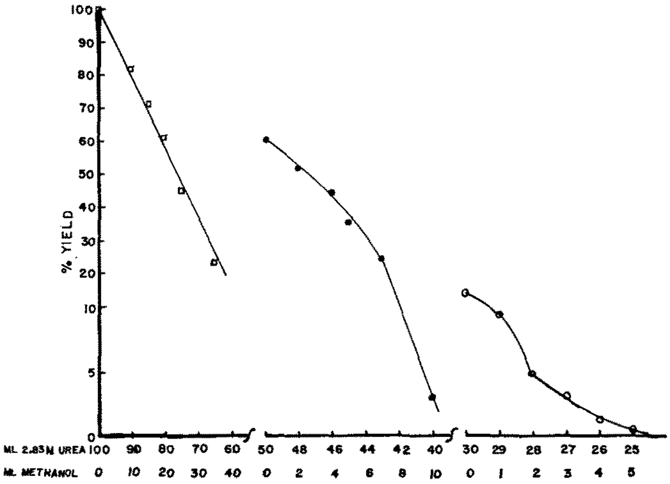

FIG. 2. Yield of adduct vs. degree of saturation of urea in methanol for quaternary ammonium compounds (0.005 mole). Key: open square, Arquad 2HT; closed circle, Cetyl Zephiran; open circle, C.T.A.B.

The thiourea adducts had poorly defined melting points. Triton X-400 and Ceepryn Chloride adducts had melting point ranges of 165–73C and 152–57C, respectively. The other thiourea adducts had a melting point range of 142 to 148C. It has been reported that long normal alkyl chains in compounds which have other groups suitable for thiourea adduction greatly reduce the stability of the complex (12). This could account for the breakdown of the thiourea-quaternary adducts at temps considerably lower than the melting point of the occluding compound.

In a previously mentioned report (12) it is stated that phenyl groups appear to interfere with thiourea as well as urea adduction. This could account for the unsuccessful attempts to prepare thiourea adducts with Hyamine 2389.

Infrared Analysis. Confirmation that the inclusion compounds of urea and thiourea with quaternary compounds were of the canal complex type was obtained by IR analysis. IR spectra of urea and thiourea adducts were compared to literature spectra (14,15), and all showed similar changes from the spectra of tetragonal urea or thiourea. The spectra of urea-quaternary adducts were similar to the spectra of urea adducts of dodecane and hexadecane. The spectra of thiourea-quaternary adducts were similar to spectra of thiourea adducts of cyclohexane and camphor.

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