Catalysis in Micellar and Macromolecular Systems

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Preface

Surfactants and macromolecules are increasingly being utilized as reaction media. Rates, products, and, in some cases, stereochemistry are affected. Analogies between structures of globular proteins and micelles as well as enzymatic, micellar, and macromolecular catalyses have been drawn. In some respects, these systems also provide models for membrane-mediated processes. Many of the affected reactions have potential industrial utility in such varied fields as pharmacy, photography, extraction, and polymerization.

The objective of this book is to provide a comprehensive monograph on the catalyses elicited by aqueous and nonaqueous micelles, synthetic and naturally occurring polymers, and phase–transfer catalysts. We have delineated the principles involved in designing appropriate catalytic systems throughout. Additionally, an attempt has been made to tabulate the available data, to June, 1974, exhaustively. The more recent research work, to December, 1974, is summarized in the Addendum. These data compilations should facilitate comparisons of the catalytic efficacy of the different systems. Details have been provided on the preparation and purification of surfactants (Chapter 1), on the physical and chemical properties of surfactants and micelles (Chapter 2), on solubilization in aqueous micellar systems (Chapter 3), and on the principles of micellar catalysis (Chapter 4). We felt that the availability of recently published books and reviews did not warrant equally detailed treatments of the physical–chemical properties of the different macromolecular systems. By no means should this be construed to mean that macromolecules are inferior to micelles as catalysts or indeed as model systems since in many cases they are not.

Our book is aimed at the industrial and academic researcher regardless of his arbitrarily defined subfield, be it organic, inorganic, biological, colloid, etc. The treatment provides guidance and stimulus to bioorganic, inorganic, pharmaceutical, colloid, physical, and polymer chemists as well as to those who seek novel and unique catalysts in industrial processes. It can also serve as the basis of a graduate course. Indeed, such courses have been given at several institutions in the United States and abroad.

We are grateful to the authors and publishers of books and journals for permission to reproduce original illustrations. Our sincere gratitude is extended to our colleagues for their invaluable comments, their constructive criticism, and their willingness to provide information and manuscripts prior to publication. To all of our co-workers who directly and indirectly contributed to this work we wish to express our sincere thanks. Credit is particularly due to Dr. Willie L. Hinze and Mr. Vernon Constien for their assistance in compiling some of the tables in Chapter 11 and to Dr. Willie L. Hinze and Mr. Pong-Su Sheih for assistance in proofreading the manuscript. Inevitably some of the work reported is our own. Without the generous support from the U.S. Atomic Energy Commission, the National Institutes of Health, the National Science Foundation, the National Aeronautics and Space Administration, and the Robert A. Welch Foundation, undoubtedly our progress would have been much slower. At last, but certainly not least, we sincerely thank Mrs. Grace R. Rufus for her superior competence in translating our almost illegible handwriting into a respectable manuscript.

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Contents

Chapter 1

Preparation and Purification of Synthetic and Naturally Occurring Surfactants

A. Synthetic Surfactants

Surfactants, surface active agents, or detergents are amphiphilic, organic, or organometallic compounds which form association colloids or micelles in solution. Amphiphilic substances, or amphiphiles, are molecules possessing distinct regions of hydrophobic (water-repelling) and hydrophilic (lipophilic or water-attracting) character. Since the polarity of the distinct regions of these substances varies greatly, these substances have also been referred to as amphipathic, heteropolar, or polar–nonpolar molecules.

Depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion, the surfactant may be classed as cationic, anionic, nonionic, or ampholytic (zwitterionic). Industrial preparations of cationic (Jungermann, 1970) and nonionic (Schick, 1967) detergents have been recently reviewed. Commercially available synthetic surfactants are often impure, containing either starting materials and/or mixtures of homologs often in unspecified proportions. Since accurate physical data on micellar properties and physiochemical data on micellar systems containing reactive and inert solutes are most reliable and comparable for highly purified surfactants, the following discussion will present illustrative examples of the preparation and purification of each type of amphiphile. Specific emphasis is placed on the surfactants which have been used most frequently in kinetic studies of micellar catalysis. Additionally, commercial sources (if available) and references to methods of preparation and purification are given in Table 1.I

TABLE I.I

Selected Surfactants

Surfactant	Structure	Commercial source	Comments	Ref. for preparation and/or purification
Cationic				
Decylammonium bromide	$CH_3(CH_2)_9N^+H_3Br^-$	Aldrich (*n*-decylamine)	Also Cl salt; C_{11} to *ca.* C_{18} compounds can be prepared similarly	Geer *et al.*, 1971; J. H. Fendler *et al.*, 1972
Decylmethylammonium bromide	$CH_3(CH_2)_9N^+H_2CH_3Br^-$		...so ethyl analog and Cl salt; C_{11} to *ca.* C_{18} compounds can be prepared similarly	Geer *et al.*, 1971
Decyldimethylammonium bromide	$CH_3(CH_2)_9N^+H(CH_3)_2Br^-$		Also ethyl analog and Cl salt; C_{11} to *ca.* C_{18} compounds can be prepared similarly	Geer *et al.*, 1971
Decyltrimethylammonium bromide	$CH_3(CH_2)_9N^+(CH_3)_3Br^-$	Chemical Procurement Labs; Eastman; Fisher		Geer *et al.*, 1971
Dodecylammonium chloride	$CH_3(CH_2)_{11}N^+H_3Cl^-$	Chem. Procurement Labs; Eastman; K & K Labs; Schwarz/Mann		Ralston and Eggenberger, 1948; Brown *et al.*, 1949
Dodecyltrimethylammonium chloride	$CH_3(CH_2)_{11}N^+(CH_3)_3Cl^-$	Eastman; K & K Labs	Hygroscopic; recrystallize from methanol–ether	Emerson and Holtzer, 1967
Dodecyltrimethylammonium bromide	$CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$	DuPont-Organic Chem. Dept., Eastman (*n*-dodecyl bromide)		Scott and Tartar, 1943; Bruning and Holtzer, 1961
Dodecyltrimethylammonium nitrate	$CH_3(CH_2)_{11}N^+(CH_3)_3NO_3^-$			Emerson and Holtzer, 1967
1-Dodecylpyridinium chloride	$CH_3(CH_2)_{11}N^+C_5H_5Cl^-$	Hooker; Matheson, Coleman and Bell; Milton Industrial Chemicals (U.K.)		Ray and Mukerjee, 1966
1-Dodecylpyridinium bromide	$CH_3(CH_2)_{11}N^+C_5H_5Cl^-$	City Chemical Corp. (tech.); K & K Labs		Adderson and Taylor, 1964; Ray and Mukerjee, 1966
1-Dodecylpyridinium iodide	$CH_3(CH_2)_{11}N^+C_5H_5I^-$			Kresheck *et al.*, 1966; Ray and Mukerjee, 1966; Bennion and Eyring, 1970
Dodecylbenzyldimethylammonium chloride	$CH_3(CH_2)_{11}C_6H_4CH_2N^+(CH_3)_2Cl^-$	I.C.I. Organics, Inc.	Also other homologs	Ledbetter and Bowen, 1969, 1971

2-(Dodecylammonio)ethanol bromide	$CH_3(CH_2)_{11}N^+H_2CH_2CH_2OH$ Br^-		Also chloride and iodide salts	Robins and Thomas, 1968
Tetradecyltrimethylammonium chloride	$CH_3(CH_2)_{10}N^-(CH_3)_3Cl^-$			Venable and Nauman, 1964
Tetradecyltrimethylammonium bromide	$CH_3(CH_2)_{13}N^+(CH_3)_3Br^-$	Columbia Organic Chem.; Chemical Procurement Labs		Venable and Nauman 1964
Hexadecyltrimethylammonium bromide (CTAB)	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$	J. T. Baker; Eastman; Fisher Matheson, Coleman and Bell; Sigma		Mukerjee and Mysels, 1955; Duynstee and Grunwald, 1959; Attwood *et al.*, 1970; Casilio *et al.*, 1971
1-Methylpyridinium iodide	$CH_3N^+C_5H_5I^-$	Eastman		Kosower, 1955; Ray and Mukerjee, 1966
Didodecyldimethylammonium chloride	$[CH_3(CH_2)_{11}]_2N^+(CH_3)_2Cl^-$	Eastman; Fisher (bromide)	Also other homologs	Ralston *et al.*, 1948
Octyldodecyldimethylammonium chloride	$[CH_3(CH_2)_7][CH_3(CH_2)_{11}]N^+(CH_3)_2Cl^-$			Ralston *et al.*, 1948
Phenothiazine hydrochlorides	$C_6H_4(S)(NR)C_6H_3R'$	May & Baker Ltd.; John Wyeth & Brother Ltd.; Sandoz Prod. Ltd.		Florence and Parfitt, 1971; Attwood *et al.*, 1974
Anionic				
Heptafluorobutyric acid	$CF_3(CF_2)_2COOH$	Pierce		Bailey and Cady, 1969
Sodium perfluorooctanoate	$CF_3(CF_2)_6COO^-Na^+$	K & K Labs; Pierce (perfluorooctanoic acid)	Also C_7 analog	Muller and Simsohn, 1971; for properties, also see Haque, 1968
Potassium perfluorooctyl sulfonate	$CF_3(CF_2)SO_3^-K^+$	Minn. Mining and Manuf. Co.	Also other fluorinated acids and metal salts	Shinoda *et al.*, 1972
Sodium 10,10,10-trifluorodecanoate	$CF_3(CH_2)_8COO^-Na^+$		Also C_8, C_{11}, and C_{12} analogs	Muller and Birkhahn, 1967; Muller and Johnson, 1969
Sodium decyl sulfate	$CH_3(CH_2)_9SO_4^-Na^+$			Kurz, 1962
Sodium decyl sulfonate	$CH_3(CH_2)_9SO_3^-Na^+$			Tartar and Lelong, 1955
Cobalt dodecanoate	$[CH_3(CH_2)_{10}COO^-]_2Co^{2+}$		Also C_{14}, C_{16}, and C_{18} homologs	Malik and Jain, 1967
Potassium dodecanoate	$CH_3(CH_2)_{10}COO^-K^+$	Eastman (lauric acid)		Kolthoff and Johnson, 1948
Silver dodecanoate	$CH_3(CH_2)_{10}COO^-Ag^+$	Eastman		Kolthoff and Johnson, 1948
Sodium dodecanoate	$CH_3(CH_2)_{10}COO^-Na^+$	Applied Science Labs. Eastman (also lauric acid)		
Sodium ethyl 2-sulfododecanoate	$CH_3(CH_2)_9CHCOOCH_2CH_3Na^+$ SO_3^-		Also other homologs	Stirton *et al.*, 1962
Aluminum dodecyl sulfate	$[CH_3(CH_2)_{11}SO_4^-]_3Al^{3+}$		Also Fe and Th salts	Miyamoto, 1960a
Copper(II) dodecyl sulfate	$[CH_3(CH_2)_{11}SO_4^-]_2Cu^{2+}$		Also Ba, Ca, Co, Mg, Mn, Pb, and Sr salts	Miyamoto, 1960b; Satake *et al.*, 1963
Potassium dodecyl sulfate	$CH_3(CH_2)_{11}SO_4^-K^+$	Sigma		Shirahama *et al.*, 1969

(*continued*)

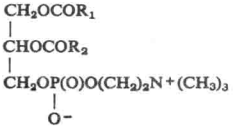
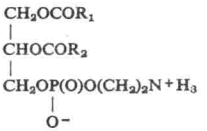
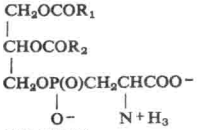
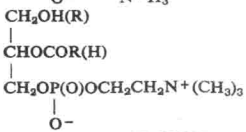
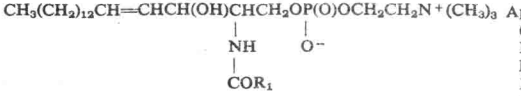
TABLE 1.I (*continued*)

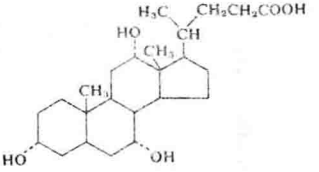
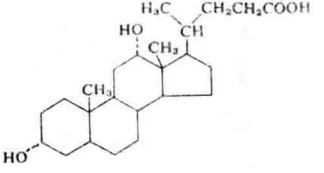
Surfactant	Structure	Commercial source	Comments	Ref. for preparation and/or purification
Silver dodecyl sulfate	$CH_3(CH_2)_{11}SO_4^- Ag^+$		Also Ca salt	Corkill and Goodman, 1962
Sodium dodecyl sulfate	$CH_3(CH_2)_{11}SO_4^- Na^+$	Applied Science Labs.; British Drug House; City Chemical Corp.; Eastman; Fisher; Nutritional Biochemicals; and others		Dreger *et al.*, 1944; Harrold, 1960; Corkill *et al.*, 1961; Kurz, 1962
Sodium 12,12,12-trifluorododecyl sulfate	$CF_3(CH_2)_{11}SO_4^- Na^+$			Muller and Johnson, 1969
Magnesium dodecyl sulfonate	$[CH_3(CH_2)_{11}SO_3^-]_2Mg^{2+}$		Also C_6, C_8, and C_{10} homologs	Lelong *et al.*, 1955
Sodium dodecyl sulfonate	$CH_3(CH_2)_{11}SO_3^- Na^+$		Also C_7, C_{10}, and C_{14} homologs	Reed and Tartar, 1935; Tartar and Wright, 1939; Tartar and Lelong, 1955
Sodium 1-hydroxydodecyl 2-sulfonate	$CH_3(CH_2)_9CHCH_2OH$ | $SO_3^- Na^+$		Also other homologs	Weil *et al.*, 1962, 1963
Sodium *p*-dodecylbenzene sulfonate	*p*-$CH_3(CH_2)_{11}C_6H_4SO_3^- Na^+$		Commercial products are often mixtures of isomers with branched chains, see refs. for ortho and meta isomers	Paquette *et al.*, 1943; Truce and Lyons, 1951; Gray *et al.*, 1955
Sodium hexadecanoate	$CH_3(CH_2)_{14}COO^- Na^+$	Applied Science Labs.; Fisher; Sigma (hexadecanoic acid)		
Sodium 2-sulfohexadecanoate	$CH_3(CH_2)_{14}CHCOO^- Na^+$ | $SO_3^- Na^+$		Also other homologs and salts	Weil *et al.*, 1953, 1955, 1957, 1960a,b, 1962; Weil and Stirton, 1956
Potassium hexadecyl sulfate	$CH_3(CH_2)_{15}SO_4^- K^+$			Shirahama *et al.*, 1969
Sodium hexadecyl sulfate	$CH_3(CH_2)_{15}SO_4^- Na^+$	K & K Labs		Kurz, 1962
Sodium 2-sulfohexadecyl sulfate	$CH_3(CH_2)_{13}CHCH_2SO_4^- Na^+$ | $SO_3^- Na^+$		Also other homologs	Stirton *et al.*, 1965
Sodium oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^- Na^+$	Applied Science Labs.; J. T. Baker; Fisher, Matheson, Coleman and Bell; Sigma (oleic acid)		
Sodium oleyl sulfate	$CH_3(CH_2)_7CH{=}CH(CH_2)_8SO_4^- Na^+$			Stirton *et al.*, 1952
Sodium linoleate	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COO^- Na^+$	Applied Science Labs.; Sigma (linoleic acid)		

Zwitterionic				
3-(Dimethyldodecylammonio)-propane-1-sulfonate	$CH_3(CH_2)_{11}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$	Aldrich (1,3-propane sultone); Pfaltz & Bauer (*N*,*N*-dimethyldodecylamine)		E. J. Fendler *et al.*, 1972
3-(Dodecylmethylammonio)-propane-1-sulfonate	$CH_3(CH_2)_{11}N^+H(CH_3)CH_2CH_2CH_2SO_3^-$	Aldrich (1,3-propane sultone); Lachat (*N*-methyldodecylamine)		E. J. Fendler and J. H. Fendler, unpublished results, 1972
3-(Dimethylhexadecylammonio)-propane-1-sulfonate	$CH_3(CH_2)_{15}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$	Aldrich (1,3-propane sultone); K. & K. Labs; Lachat (*N*,*N*-dimethylhexadecylamine)	Also C_{22} homolog	Clunie *et al.*, 1967
N-Dodecyl-*N*,*N*-dimethylglycine	$CH_3(CH_2)_{11}N^+(CH_3)_2CH_2COO^-$		Also C_6, C_8, C_{10}, C_{11}, C_{14}, and C_{16} homologs	Beckett and Woodward, 1963; Tori and Nakagawa, 1963b; Molyneux *et al.*, 1965
C-Dodecyl-*N*,*N*-dimethylglycine	$CH_3(CH_2)_{11}CHN^+(CH_3)_3$ COO^-		Also C_8 and C_{10} homologs	Tori and Nakagawa, 1963a,b,c; Tori *et al.*, 1963
N-Dodecyl-3-aminopropionic acid	$CH_3(CH_2)_{11}N^+H_2CH_2CH_2COO^-$	General Mills Chem. Div.		Tokiwa and Ohki, 1967
N-Dodecylaminobenzylphosphinic acid	$CH_3(CH_2)_{11}N^+H_2CH(C_6H_5CH_2)PO_2^-H$		Also other homologs	Linfield *et al.*, 1961
Nonionic				
Polyoxyethylene(3) decanol	$CH_3(CH_2)_9O(CH_2CH_2O)_3H$		Also C_6 and C_8 homologs	Corkill *et al.*, 1964
Polyoxyethylene(6) dodecanol	$CH_3(CH_2)_{11}O(CH_2CH_2O)_6H$			Corkill *et al.*, 1961; Attwood *et al.*, 1970
Polyoxyethylene(6) hexadecanol	$CH_3(CH_2)_{15}O(CH_2CH_2O)_6H$		Also C_4, C_8, C_{10} and C_{12} homologs	Corkill *et al.*, 1961, 1964
Polyoxyethylene(6) 8,8,8-trifluorooctanol	$CF_3(CH_2)_7O(CH_2CH_2O)_6H$			Muller and Platko, 1971
Polyoxyethylene(8) dodecanol	$CH_3(CH_2)_{11}O(CH_2CH_2O)_8H$	Nikko Chemicals. Co., Ltd	Homogeneous commercial product	Shinoda *et al.*, 1971
Polyoxyethylene(9) hexadecanol	$CH_3(CH_2)_{15}O(CH_2CH_2O)_9H$		Also polyoxyethylene (7) and (8) and C_8 and C_{10} homologs	Elworthy and Macfarlane, 1962; Corkill *et al.*, 1964; Elworthy and McDonald, 1964; Attwood *et al.*, 1970
N,*N*-Dimethyldodecylamine oxide	$CH_3(CH_2)_{11}N(CH_3)_2$ $\downarrow$ O	Armour Industrial Chemicals; Baird/Lonza; Continental Chem.	Also other homologs	Courchene, 1964; Tokiwa and Ohki, 1966, 1967
n-Octylsulfinylethanol	$CH_3(CH_2)_7SOCH_2CH_2OH$		Also other homologs	Corkill *et al.*, 1966
8,8,8-Trifluorooctyl methyl sulfoxide	$CF_3(CH_2)_7SOCH_3$			Muller and Platko, 1971

(*continued*)

TABLE I.1 (*continued*)

Surfactant	Structure	Commercial source	Comments	Ref. for preparation and/or purification
Lipids—Isolated				
Phosphatidylcholine (lecithin)		Applied Science Labs (bovine, egg, plant); Calbiochem. (DL); General Biochem. (beef, egg); Nutritional Biochem. [bovine (90%), egg, soy (refined), vegetable]; P-L Biochemicals (bovine, egg, plant); Pierce [L-α (egg)]; Sigma [L-α (egg, soybean)]		Elworthy and Saunders, 1957 Saunders, 1957; Robins and Thomas, 1963; Singleton *et al.*, 1965; Lundberg, 1973
Phosphatidylethanolamine		Applied Science Labs (bacterial, bovine, plant); Calbiochem. (bacterial, egg); General Biochem.; Nutritional Biochem.; P-L Biochemicals (bacterial, bovine, egg, plasmogen); Pierce (bacterial); Sigma (sheep brain)		Robins and Thomas, 1963
Phosphatidylserine		Applied Science Labs (bovine); Calbiochem. [L (bovine brain)]; General Biochem.; Nutritional Biochem. (L); P-L Biochemicals (bovine)		See refs. in text
Lysophosphatidylcholine		Applied Science Labs (egg); Calbiochem.; General Biochem.; Nutritional Biochem.; P-L Biochemicals (egg); Pierce; Sigma		Hamori and Michaels, 1971
Sphingomyelin		Applied Science Labs (bovine); General Biochem.; Nutritional Biochem.; P-L Biochemicals (bovine); Pierce (bovine brain); Sigma (bovine brain)		See refs. in text

Cholic acid		Applied Science Labs; Calbiochem.; General Biochem.; Nutritional Biochem.; P-L Biochemicals; Pierce; Sigma
Deoxycholic acid		Calbiochem.; Nutritional Biochem.; P-L Biochemicals; Sigma
Lipids—Synthetic		
β,γ-Dimyristoyl-L-α-phosphatidylcholine		Calbiochem.; Nutritional Biochem.; Sigma
β,γ-Dipalmitoyl-L-α-phosphatidylcholine		Applied Science Labs; Calbiochem.; General Biochem.; P-L Biochemicals
β,γ-Dipalmitoyl-DL-α-phosphatidylcholine		Nutritional Biochem.; Sigma
β,γ-Distearoyl-L-α-phosphatidylcholine		Calbiochem.; P-L Biochemicals
β,γ-Dioleoyl-L-α-phosphatidylcholine		Applied Science Labs.; P-L Biochemicals
α,γ-Lysophosphatidylcholine (lysolecithin)		Nutritional Biochem.
β,γ-Dipalmitoyl-L-phosphatidylethanolamine		Calbiochem.; Sigma (α)
β,γ-Distearoyl-L-phosphatidylserine		Calbiochem.

1. Cationic Surfactants

Cationic surfactants have the general formula of $R_nX^+Y^-$, where R represents one or more hydrophobic chains, X is an element capable of forming an "onium" structure, and Y is the counterion. In principle, X may be N, P, S, As, Te, Sb, Bi, and the halogens. Owing to the availability of long-chain alkyl amines and halides as starting materials as well as the relative ease of preparation and stability, nitrogen containing cationic surfactants ($R_4N^+X^-$) predominate over the more infrequently used sulfoxonium ($R_3S^+X^-$), sulfonium ($R_3S^+X^-$), and phosphonium ($R_4P^+X^-$) compounds. The hydrophobic alkyl or substituted alkyl group may be bonded directly to the positively charged atom, e.g., hexadecyltrimethylammonium bromide, or indirectly, e.g., *p*-octadecanoyl-*N*,*N*,*N*-trimethylanilinium bromide. Common bridging groups include benzyl, phenyl, pyridinyl, amido, and keto groups. Alternatively the quaternary nitrogen atom can be part of a saturated, unsaturated, or aromatic heterocyclic ring as in the case of alkyl pyridinium halides. The hydrophobic portion of the surfactant may be a straight or branched-chain alkyl or alkenyl group and may contain saturated and unsaturated cyclic systems.

Long-chain alkyl ammonium halides can be conveniently prepared in the laboratory by the reaction of stoichiometric quantities of a secondary or tertiary amine with a long-chain alkyl halide, usually in alcohol or diethyl ether. Thus, hexadecyltrimethylammonium bromide can be prepared by reacting equimolar quantities of trimethylamine and hexadecylbromide in ethanol at −3°C for 7 days (Attwood *et al.*, 1970). Decylmethyl-, decylethyl-, and decylpropylammonium chlorides and the corresponding bromides can be prepared similarly in diethyl ether using at least 2 moles per mole excess amine and quaternization with ammonium chloride or bromide, NH_4Cl or NH_4Br (Geer *et al.*, 1971). Quaternary *n*-alkylammonium chlorides and bromides of long-chain primary amines, e.g., dodecylammonium bromide, can be prepared analogously by reaction of the *n*-alkylamine with about 0.5 mole per mole excess of ammonium chloride or bromide (NH_4Cl or NH_4Br) in hot methanol solution (Geer *et al.*, 1971; J. H. Fendler *et al.*, 1972). Alternatively, the *n*-alkylamine can be converted to the corresponding alkyl ammonium bromide by the addition of concentrated hydrobromic acid and evaporation *in vacuo* (Lindman *et al.*, 1970). In order to obtain pure surfactants, it is often necessary to purify the starting amine by distillation or other techniques. The reaction mixture is preferably worked up in such a way as to remove all the unreacted bromides and amines; thorough triturating (washing) with anhydrous ether is often useful. Several recrystallizations are necessary to obtain the required high purity surfactant. Commercial practical-grade hexadecyltrimethylammonium bromide, for example, can be repeatedly

washed with anhydrous ether until no amine is detected in the eluant, recrystallized from methanol, and then recrystallized at least four times from methanol with the addition of anhydrous ether. After pulverization and drying *in vacuo* (P_2O_5), the purified material melts with decomposition at 237°–239°C (Casilio *et al.*, 1971; see also Mukerjee and Mysels, 1955; Duynstee and Grunwald, 1959).

Most simple long-chain ammonium halides can be satisfactorily purified analogously using mixtures of methanol, ethanol, or acetone and ether. Due to decomposition at high temperatures and in some cases low melting points, e.g., dodecylammonium alkanoates, removal of traces of water is preferably accomplished by pulverization of the recrystallized material and drying *in vacuo* over phosphorus pentoxide at room temperature.

Alkyl pyridinium halides can be prepared by reacting stoichiometric amounts of pyridine with a long-chain alkyl halide. Dodecylpyridinium iodide can be prepared, for example, by heating pyridine and dodecyl iodide in an evacuated and sealed tube at 80°C for 24 hr. Alternatively, it can be precipitated from dodecylpyridinium chloride solution by the addition of potassium iodide. In both cases, the crude product should be recrystallized several times either from alcohol–water or from water until the critical micelle concentration (CMC) remains constant and no minimum is observed in the surface tension–surfactant concentration plot (Ray and Mukerjee, 1966). See Chapter 2 for a definition and discussion of critical micelle concentration.

2. Anionic Surfactants

The most frequently used anionic surfactants are alkali or alkaline earth-metal salts of mono- or polybasic carboxylic (fatty) acids and of sulfuric, sulfonic, and phosphoric acids containing a saturated or unsaturated hydrocarbon substituent.

Carboxylate surfactants are manufactured via the hydrolysis of fats and oils followed by neutralization with the appropriate hydroxide when the salt is desired. Laboratory purification of the free fatty acids can be achieved by recrystallization from methanol or other polar solvents and thorough drying *in vacuo*. In the case of liquids, especially those with high boiling points, hydrogenation is often useful to remove unsaturated homologs from otherwise pure material (Almgren, 1972). The purity of the free acid, especially the absence of other fatty acids, can be established readily by gas liquid chromatography of the methyl or *n*-propyl ester (de Lindemann, 1970). Other analytical techniques, such as thin-layer, paper, and column chromatography can also be used (Ma, 1969).