FIG. 1. Log. molar concentration-surface tension for compounds 3(b-e).

insoluble of all five (high Krafft point), whereas the 3a is the most soluble (low Krafft point).

The after-treated fabric with 3e gave a satisfactory result in the washing fastness test.

All the compounds 3 except 3a show strong antimicrobial activity.

REFERENCES

1. Jungermann, E., in Cationic Surfactants, Marcel Dekker, New York, NY, 1969, Vol. 4., pp. 48, 492.
2. Chwala, A., and V. Anger, in Handbuch der Textilhilfsmittel, Verlag Chemie, Weinheim, NY, 1977, p. 3.
3. Puchta, R., J. Amer. Oil Chem. Soc. 61:367 (1984).
4. Tsatsaronis, G., and F. Effenberger, Chem. Ber. 94:2876 (1961).
5. Gawish, S.W., A.A.B. Hazzaa, Sh. Zourab and B. El-Din Gebril, J. Amer. Oil Chem. Soc. 58:757 (1981).
6. Borghetty, H.C., and C.A. Bergman, Ibid. 27:88 (1950).
7. Smith, F.D., and W.M. Linfield, Ibid. 55:741 (1978).
8. Jain, S.R., and A. Kar, Planta Med. 20:118 (1971).
9. Gawish, S.M., A.A.B. Hazzaa and B. El-Din Gebril, J. Amer. Oil Chem. Soc. 55:745 (1978).
10. Lange, H., Tenside Deterg. 12:27 (1975).

[Received December 13, 1985]

♣Counterion Effects on the Aqueous Solution Viscosity of Cationic Surfactants

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The effect of varying counterion structure on the aqueous solution viscosity of various cationic surfactants was systematically examined for compounds of the type: $CH_3(CH_2)_xN(CH_3)_3YAr$. Ar = functionally substituted aryl moieties and Y = carboxylate (CO_2^-), sulfinate (SO_2^-) or sulfonate (SO_3^-).

Aqueous solution viscosity, which is assumed to be a measure of ion pair stability, is clearly affected by anion and cation structure, temperature, concentration and stoichiometry. An ortho substituent to the anionic functionality, e.g. hydroxyl, substantially increases ion pair stabilization. Ion pair stability is also enhanced by increasing the solution concentration, decreasing temperature, increasing cation/anion ratio or by increasing the alkyl (x) chain length.

Unusual counterion effects have been reported for cationic surfactants of the quaternary ammonium and alkyl pyridinium type (1-5). For example, sodium salicylate exhibited unusually large viscosity effects with micellar solutions of cetyltrimethylammonium (CTA^+) which far exceeded those previously found for other CTA^+ salts (6). Substantial viscoelasticity and low critical micelle concentrations for the meta and para chlorobenzoate salts of CTA^+ also have been reported (2). However, most other substituted benzoic acids were found to have little or no unusual effect on surface or colloid properties when they were used as alternative counterions to bromide in CTAB.

Subsequent work by Gravsholt, Hyde and others has shown that the viscosity increases observed with salicylic acid/cationic surfactant complexes are actually due to concentration dependent anion/cation aggregate structures in solution (5,7). Work completed thus far suggests that there is a regular increase in solution order for ionic surfactants as follows: single ions, ion pairs, spherical micelles and rod shaped or lamellar micelles, leading finally to crystals. Such effects clearly have a direct bearing on the consistency and stability of formulated liquid cationic detergents.

A previous paper detailed the behavior of docosyltri-

methylammonium (DCTA+) bromide monolayers spread on subsolutions of a number of aromatic and aliphatic carboxylates and sulfonates, including some with hydroxyl and chloro substitution (8). In the present paper, the results of a systematic study performed to determine the effects of various factors on the anion/cation interaction in aqueous solution, as evidenced by viscosity measurements, are described. These factors include: anion structure, cationic alkyl chain length, temperature effects, concentration effects, anion/cation stoichiometry, and pH effects.

EXPERIMENTAL PROCEDURES

The solutions for viscosity measurements were prepared by adding an equivalent amount of an aqueous solution of the cationic material to the (neutralized if necessary) solution of the anionic material, followed by stirring to achieve homogeneity.

The viscosities of the aqueous solutions were determined at room temperature, unless otherwise specified, using Cannon-Fenske Viscometers—Numbers 74, 100, 200, 300, 400 or 500. In one set of experiments, a Brookfield Viscometer (Model HBT) was used with a #3 spindle. The measurements were taken at 50 rpm.

The Oswald viscosities of a 0.2 M solution of a 2/1 complex of N-tetradecyl-N,N-N-trimethyl ammonium chloride/4,4'-biphenyldisulfonic acid (dipotassium salt) were measured after repeated freeze-thaw cycling. The cycling process consisted of first measuring the viscosity at 25 C, then storing the solution in a freezer at −10 C for 16 hr. The solution was then allowed to thaw at 24 C for 7 hr, at which point the viscosity was measured again. This constitutes one freeze-thaw cycle. The process was repeated three times. The material utilized fell into two categories, laboratory synthesized and purchased.

Laboratory synthesized materials. The 2-hydroxybenzene sulfonic acid (sodium salt) was prepared by the method described by Losev et al. (10).

The sodium salts of n-butyl sulfonic acid and 1,4-butane disulfonic acid were prepared from the corresponding alkyl bromides by the Strecker reaction (11).

The 4,4'-biphenyldisulfonic acid (dipotassium salt) was prepared via an aqueous alkali hydrolysis of 4,4'-biphenyldisulfonyl chloride which was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin.

The N-butyl, hexyl, nonyl, myristyl, stearyl and eicosyl N,N,N-trimethylammonium bromides were prepared by the reaction of trimethylamine with the appropriate alkyl bromide. The quaternary ammonium salts were purified by recrystallization from methanol.

The N-methyl pyridinium iodide salts were prepared by reacting a methanol solution of pyridine or the appropriate pyridine derivative, e.g., 2-hydroxy-pyridine (all purchased from Aldrich Chemical Co., Milwaukee, Wisconsin), with an excess of methyl iodide at 0 C. After workup, the purity of the pyridinium salts was determined to be >99% by titrimetric analysis.

Purchased materials. Aldrich Chemical Co., Milwaukee, Wisconsin: Terephthalic acid, phthalic acid, isonicotinic acid, picolinic acid, di-pipecolinic acid, 2-pyra-

zine carboxylic acid, 2,6-dihydroxybenzoic acid, salicylic acid, isophthalic acid, adipic acid, anthranilic acid, thiosalicylic acid, hydroquinone sulfonic acid (potassium salt), and benzyl trimethylammonium bromide.

Pfaltz and Bauer, Flushing, New York: 3-Hydroxypicolinic acid, 2-aminobenzenesulfonic acid, 3-aminobenzenesulfonic acid, and 4-aminobenzenesulfonic acid.

Reilly Tar and Chemicals Co., Indianapolis, Indiana: 1-Carboxy-N-methyl-pyridinium chloride.

Eastman, Rochester, New York: 2,5-Dihydroxy-4-benzenedisulfonic acid (dipotassium salt), 2-naphthalene sulfonic acid, and benzene sulfonic acid.

K&K/ICN, Plainview, New York: 3-Benzenedisulfonic acid (disodium salt) and benzenesulfonic acid.

Witco Chemical Co., New York, New York: Sodium lauryl sulfonate.

RESULTS AND DISCUSSION

Increasing bulk solution viscosity has been shown to be due to increasing long-range order of surfactant aggregation in solution. This order, of course, may be enhanced by various molecular structural features which enhance the formation and stability of surfactant aggregates in solution, notably the polar and hydrophobic interactions. Therefore, for discussion purposes, we make the assumption that increasing bulk solution viscosity signifies increasing ion-pair stability.

The effect of varying aryl-carboxylate and -sulfonate structure on solution viscosity of N-myristyltrimethyl-

TABLE 1

Effect of Aryl Carboxylate and Sulfonate Counterion Structure on Viscosity of MTA+ Solutions (0.2M)

Carboxylate	n (cSt)
Benzoate	18.8
Isonicotinate	1.3
4-Hydroxybenzoate	1.3
2-Hydroxybenzoate	6275
2-Aminobenzoate	131
2-Mercaptobenzoate	111
Picolinate	1.3
2,4-Dihydroxybenzoate	84
2-Pyrazinecarboxylate	1.3
2,6-Dihydroxylbenzoate	coacervate
3-Hydroxypicolinate	28.2
Phthalate	1.8
Terephthalate	1.8
2,5-Dihydroxybenzoate	388
1-Carboxylate-N-methylpyridinium chloride	1.2

Sulfonate or Sulfinate	n (cSt)
Benzenesulfonate	287.0
4-Hydroxybenzenesulfonate	1.3
2-Hydroxybenzenesulfonate	precipitate
2-Aminobenzenesulfonate	4168
m-Benzenedisulfonate	594
2,5-Dihydroxy-4-benzenedisulfonate	520
Benzenesulfinate	107.7

ammonium (MTA)$^+$ cation is evident in the data of Table 1. The most significant viscosity enhancement was observed with ortho substituents, the order of increased ion-pair stabilization being: SH < NH$_2$ < OH. There is considerable evidence, especially in the case of cationic surfactants, that specific counterion binding plays an intimate role in determining the micellar structure which underlies these effects (12).

The results shown in Table 1 demonstrate that ion-pair stabilization is greater for the orthohydroxybenzene sulfonate ion than for the carboxylate analog when combined stoichiometrically with MTA$^+$. In the former case, this is evidenced by precipitation from solution, the final manifestation of structure. Interestingly, the presence of a second anionic group on the ring does not lead to as pronounced interactions. Evidently the resulting structure is not as favorable for interaction with the micellar array of cationic head groups.

Three different benzene functional anions were combined with MTA$^+$. The solution viscosities (not tabulated) indicated the following order of ion-pair stabilization: sulfonate > sulfinate > carboxylate. Interestingly, these stabilization effects are inversely proportional to the relative basicities of these anions (9).

The viscosities of 0.2M aqueous solutions of a number of N-alkyltrimethylammonium cations of varying chain length in the presence of equivalent amounts (i.e. 0.1M solutions) of two different disulfonate anions, viz. m-benzenedisulfonate and 4,4'-biphenyldisulfonate, were examined (Table 2). It can be inferred from the data that a significant viscosity increase, i.e., a value substantially above that of water (1 centistoke), occurs when the alkyl group exceeds a certain chain length. In both cases, when the alkyl chain length was C-22 the resulting complex precipitated. This demonstrates that the balance between stabilization of a water-soluble (e.g., micellar) state and an insoluble state (crystalline) is driven toward the latter when the interchain cohesion exceeds a critical value.

The results of varying temperature on the solution viscosity of MTA$^+$ and a 3,6-dihydroxydisulfonate dianion can be seen in Table 3. An exponential increase in viscosity with decreasing temperature was observed which reflects the increasing thermal stability of an ion-pair in aqueous solution at lower temperatures and consequent stabilization of anisometric micellar structures.

It is also possible for ion pair complexes to exhibit thermally dependent phase changes which are reversible. For example, at 20 C a 0.2M solution of a 2/1 complex of MTA$^+$ and the sodium salt of 2-naphthalenesulfonic acid forms a precipitate. If this solution is warmed to 30 C a coacervate results. However, continued heating to $\geqslant$40 C results in a clear homogeneous solution. These thermally dependent phase changes were found to be reversible and, as discussed above, are related to, and involve, the strength of the ion pair bond formed. However, this reversible behavior was not observed in every case where precipitation occurred, suggesting for different ion-pair complexes the existence of varying effects in the ion pair bonding in the different states. Again, the data obtained showed that the strength of ion-pair bond formation is directly related to the structure of the cationic and ionic moieties. Furthermore, in some situations when ion-pair formation is not spontaneous, it can be induced by freeze-thaw cycling (Table 4). The resulting ion pair complex appears to be stable even when warmed to room temperature, as evidenced by increased solution viscosity. Thus, another way to influence the balance of forces (interchain and head group) which govern the state of the surfactant in solution (viz. single ions, ion pairs, spherical micelle, rod or lamellar micelle, and ultimately crystal) is temperature adjustment. In the above case it is possible that long term time effects were involved, but these were not investigated.

Two other factors expected to influence the viscosity of ion-pair complex solutions are concentration and

TABLE 2

Viscosity of Alkyl Trimethylammonium Bromides (0.2M) in the Presence of Equivalent Amounts of Two Disulfonate Anions

N-alkyl Group	n (cSt)
Disodium m-benzenedisulfonate	
Butyl	1.1
Hexyl	1.1
Nonyl	1.1
Myristyl	594.4
Eicosyl	P/g[a,b]
Disodium 4,4'-Biphenyldisulfonate	
Butyl	1.1
Hexyl	1.2
Nonyl	1.1
Myristyl	1.1
Eicosyl	P[a]

[a]P, precipitate at room temperature.
[b]P/G, precipitate at room temperature, gel at temperature >60 C.

TABLE 3

Effect of Temperature on Viscosity of 0.2M Bis- 1,4-Tetradecyltrimethylammonium-3,6-Dihydroxy Disulfonate

Temperature (°C)	n (cSt)
51.5	19.5
38.5	91.8
22.1	720.0
10.0	8896.0

TABLE 4

Effect of Freeze-Thaw Cycles on Viscosity of Bis-4,4'-Tetradecyltrimethyl Ammonium 4,4'-Biphenyl Disulfonate (0.2M)

Number of Cycles	n (cSt)
0	1.1
1	9.7
2	12.4
3	12.2

ion-pair stoichiometry. To pursue the former factor the bulk solution viscosity of the stoichiometric MTA⁺ m-benzene disulfonate ion-pair complex was examined (Table 5). A strong dependence on the ion-pair complex concentration was found.

Table 6 provides a demonstration of the effect of varying the cation/anion ratio of the MTA⁺/salicylate complex. Higher solution viscosities were achieved with the cationic moiety in excess. In all previous cases in this paper, equal stoichiometric ratios of the cationic surfactant and anion were used.

In the work described above and in previous work (8), ortho hydroxy functionalization of an "aromatic" anionic group contributed the largest degree of stabilization during complexation with cationic quaternary ammonium halide. However, since the ortho hydroxyl functionality itself can be ionized at high pH's and since at low pH's there would be essentially no ionization of the acidic functionality, it would seem reasonable that the strength of ion pair interaction would be pH dependent. This idea was examined briefly by evaluating the solution properties of a 0.2M solution of a 1/1 molar complex of MTA⁺ and salicylic acid at the following

TABLE 5

Concentration Effects on Solution Viscosity

Concentration (mol/liter)	n (cSt)
0.2	594.4
0.17	410.0
0.14	245.2
0.11	51.7
0.09	52.4
0.077	24.8
0.066	16.4

TABLE 6

Effect of Stoichiometry on Viscosity

Ratio of N-tetradecyl-N,N,N-trimethylammonium bromide/ sodium salicylate	Total complex concentration	Brookfield viscosity (cps)
2/1	0.6	18,048
1/1	0.4	6,275
1/2	0.6	2,778

pH's: 0.43, 6.16, and 11.30. At a pH of 0.43 the salicylic acid is essentially un-ionized, at pH 6.16 only the carboxylic acid functionality is ionized and at pH 11.30 both the ortho hydroxy and the carboxylic acid functionality are ionized. The results of this study showed that the complex precipitated at both a pH of 0.43 and 6.16, whereas at pH 11.30 a solution viscosity of only 1.3 centistokes was obtained. This experiment further demonstrates ion pair stabilization by hydrogen bonding of these complexes.

All of the examples presented thus far have demonstrated that an ortho active hydrogen substituent to an anionic moiety, e.g., carboxylate or sulfonate, can cause substantial stabilization enhancement in complexation with a cationic quaternary ammonium halide derivative. It was therefore of interest to determine if an active hydrogen group ortho to the cationic moiety would allow a similar stabilization effect. To evaluate this, the viscosities of 0.2M solutions of 1/1 molar complexes of N-methylpyridinium, 2-hydroxy-N-methylpyridinium, and 4-hydroxy-N-methylpyridinium iodides with a sodium salt of tetradecylsulfonic acid were determined and found to be 1.43, 1.45 and 1.44 centistokes, respectively. Thus, none of these examples illustrate any active hydrogen (hydroxyl) stabilization of the pyridinium alkyl sulfonate ion pair. However, it would be interesting to evaluate a model system where hydrogen bond stabilization would be more sterically favorable, e.g., a 2-hydroxyl-N,N,N-trimethylanilinium halide.

REFERENCES

1. Wan, L.S.C., *J. Pharm. Sci. 55*:1395 (1966).
2. Gravsholt, S., *J. Colloid Interface Sci. 57*:575 (1976).
3. Gravsholt, S., *Ibid. 69*:358 (1979).
4. Gravsholt, S., *Rheol., Proc. 8th Int. Congr.* 1980, p. 629.
5. Hyde, A.J., D.J. Maguire and D.M. Stevenson, *Chem. Phys. Chem. Anwedungstech.* Grenzflaechenktiven Stoffe, Ber. Int. Kongr., 6th, Vol. 2, Teilz, 1973.
6. Gravsholt, S., in *Polym. Colloids 2, Proc. Symp. Phys. Chem. Prop. Colloid Port., 1978,* 1980, pp.405-417.
7. Ulmius, G., H. Wennerstrom, L.B.A. Johansson, G. Lindblom and S. Gravsholt, *J. Phys. Chem. 83*:2232 (1979).
8. Goddard, E.D., G.H. Matteson and G.E. Totten, *J. Colloid Interface Sci. 85*:19 (1982).
9. Eisenhardt, P.F., and S.G. Schillman, *Anal. Chim. Acta 84*:423 (1976).
10. Losev, I.P., A.S. Tevlina and E.G. Troseyanskaya, *Chem. Abstr. 52*:13677 (1958).
11. Reed, R.M., and H.V. Tartar, *J. Am. Chem. Soc. 57*:570 (1935).
12. Cohen, I., and T. Vassiliades, *J. Phys. Chem. 65*:1781 (1961).