Cationic Surfactants in Organic Solvents
III. Critical Micelle Concentration of Dodecylammonium Halides in Benzene and Toluene

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The behavior of primary, secondary, tertiary and quaternary dodecylammonium chloride and bromide in benzene and toluene was investigated by surface tension measurements, the dye-solubilization and iodine-complex formation method and vapor pressure osmometry at 37° and 50°C. The smooth continuity in the measured properties of these solutions as a function of concentration has been interpreted in terms of a progressive oligomerization of the cationic surfactants rather than in terms of a monomer $\leftrightarrows$ micelle equilibrium, familiar in aqueous solutions. No indication for the phenomenon of critical micelle concentration could be observed.

The process of aggregation of ionic surfactants in nonpolar, low-dielectric constant, nonionizing organic solvents has been discussed in previous reports from this laboratory (1–3). It has been emphasized that the behavior of such solutions differs from that of aqueous solutions of similar surfactants in many respects. Among the most significant characteristics of such organic solutions is the low average aggregation number of surfactants, and the absence of a distinct critical micelle concentration. The aggregation of various cationic surfactants in hydrocarbons has been shown to proceed via stepwise building up of the aggregates with increasing solute concentration, which can be represented by the equilibrium

$$S \rightleftarrows S_2 \rightleftarrows S_3 \rightleftarrows S_4 \rightleftarrows S_{n-1} \rightleftarrows S_n \quad [1]$$
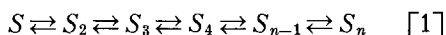
rather than by the mass-action equilibrium of micellization in aqueous solutions representing a monomer $\rightleftarrows$ micelle equilibrium

$$nS \rightleftarrows S_n. \quad [2]$$

It has been shown that the stepwise aggregation, represented by Eq. [1], results in a smooth continuity in many properties of hydrocarbon solutions with increasing concentration of the alkylammonium salts. This in contrast to the phenomenon of great sharpness of transition familiar in aqueous solutions of surfactants, commonly associated with the critical micelle concentration. It is indeed difficult to determine the clear transition region (CMC) when the aggregates formed contain a few molecules only, and should thus not be surprising that CMC is not really discernible in hydrocarbon solutions.

We have now investigated benzene and toluene solutions of primary, secondary, tertiary and quaternary dodecyl (lauryl) ammonium chlorides and (mainly) bromides by a number of conventional methods used for the determination of CMC in aqueous and organic solutions, and report here the results obtained by surface tension and vapor-pressure osmometry measurements, and by two spectrophotometric methods based on the formation of colored complexes. By none of these methods could the CMC of the surfactants be determined.

406

The new experimental evidence supports the mass-action law concept on a stepwise formation of aggregates in hydrocarbon solutions.

EXPERIMENTAL

n-Dodecylammonium chloride (m.p. 182°C) and bromide (m.p. 191°C), di-n-dodecyl-(m.p. 210°C), tri-n-dodecyl-(m.p. 87°C) and tetra-n-dodecylammonium bromide (m.p. 86°C) were prepared, purified and recrystallized by a standard procedure described previously (4, 5). All salts are white, crystalline, nonhygroscopic and stable. They were checked for purity by elemental analysis and acidimetric titration of their ethanolic solutions. None contained either free acid or base. For all measurements the anhydrous salts were dissolved in dry benzene or toluene. All solutions were made up by weight, freshly before use.

Thermoelectric differential vapor-pressure (osmometric) measurements were carried out on a Mechrolab Osmometer Model 301-A with thermistors designed to work at 37° and 50°C by a procedure previously reported (6, 7).

Surface tension measurements at the above temperatures were made by the ring and the drop-weight methods, with good agreement between the two. Mass changes were measured with an RG Cahn Automatic Electrobalance. The ring employed was made of platinum–iridium wire. Since the ring was enclosed, and readings were made within about 30 sec, no corrections were made to the evaporation effect. In the drop-weight measurements, the set-up consisted of a microburette and a low-speed motor. About 10–15 drops were weighed.

The measurements for the two spectrophotometric methods were made on a Beckman Model B spectrophotometer. The iodine method (8) is based on the color change of iodine that takes place when undissociated micelles are added to an iodine solution, and is claimed (discussion to Ref. (8)) to have been successfully used for organic solutions of alkylammonium salts. The position of the maximum absorption peak at 360 mμ does not vary from one solvent to another. The method

is believed (8) to be more reliable for the determination of CMC than the conventional dye-solubilization method because the former does not affect micelle formation. For the dye-solubilization method the freely soluble, purified and several times recrystallized Rhodamine B was employed, and the absorption reading taken at 560 mμ.

RESULTS

Surface Tension

This reliable tool for the determination of CMC of surfactants in aqueous solutions cannot detect the CMC in the systems under consideration. For comparison we have measured the variation of the surface tension with concentration of dodecylammonium chloride and bromide in water, 1:1 v/v of water–ethanol, and in anhydrous ethanol, and toluene.

In water and water–ethanol mixtures, the surface tension of the pure solvent is reduced on addition of the salt, and the CMC values evaluated from the apparent sharp break are in good agreement with literature data (9). On the other hand, in anhydrous organic solvents, as shown in Fig. 1 for toluene solutions, there is no measurable depression of the surface tension of the pure solvent. This is true even at very high concentrations, as shown for the tridodecylammonium bromide in toluene. The abrupt increase in the surface tension is due to the incipient coacervation rather than the formation of micelles. It should be emphasized that our measurements refer to the surface tension of freshly prepared solutions. Namely, it is known (10) that the changes observed by increasing concentration of the surfactant are frequently smaller than those caused by aging, small temperature differences or the experimental errors inherent in the experimental techniques employed.

Spectrophotometry

In all five systems investigated the optical density of the solutions in presence of iodine increases smoothly with the concentration of
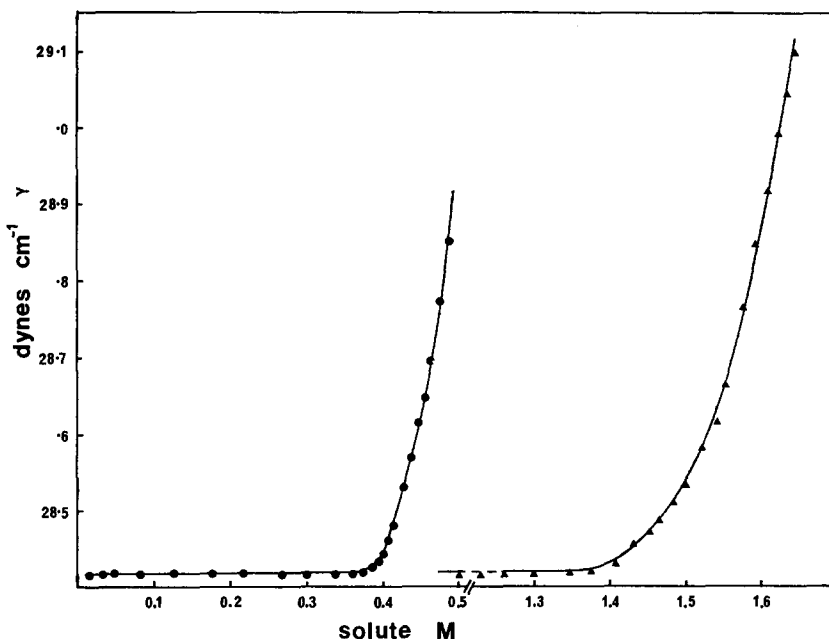
FIG. 1. Surface tension of toluene solutions of n-dodecylammonium chloride (●) and tri-n-dodecylammonium bromide (▲) as a function of concentration, 50°C.

the surfactant, as shown in Fig. 2 for tetra-dodecylammonium bromide in toluene. In no case is a break discernible.

The Rhodamine B solubilization method gives measurable optical density values only in the tridodecylammonium bromide-toluene system. The shape of the optical density curve is similar to that obtained for the iodine-complex absorbance shown in Fig. 2, increasing smoothly with concentration. In all other cases the changes in optical densities, compared to the blank, were too small for reproducible and reliable readings to be made.

Vapor-Pressure Osmometry

The vapor-pressure lowering of benzene and toluene solutions of dodecylammonium salts was interpreted in terms of the overall formation constants of the aggregates n

$$\beta_n = [S_n]/[S]^n \qquad [3]$$

where the best set of n and the corresponding β_n values were obtained by a computerized least-squares calculation procedure described

previously (1, 2, 6, 7). The results are compiled in Table I.

From this set of data the average aggregation number $\bar{n}$ was calculated using the relationship

$$\bar{n} = \sum_{1}^{N} n\beta_n[S]^n / \sum_{1}^{N} \beta_n[S]^n \qquad [4]$$

and the variation of $\bar{n}$ as a function of concentration for the five systems investigated is shown in Figs. 3 and 4. The number-average aggregation number of these surfactants does not exceed a few units in the concentration range up to 0.1 molar in benzene or toluene.

DISCUSSION

For most practical purposes it is sufficient for the determination of CMC in aqueous solutions to concentrate on the breaks in the property versus concentration curves, without necessarily analyzing the magnitude of the changes in the property. This is made possible by the appearance of *sharp* breaks between two lines, one representing a given colligative
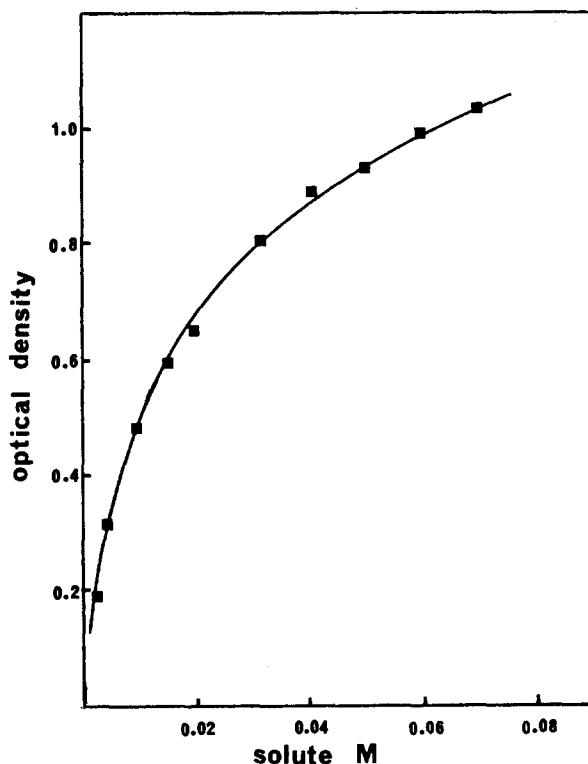
FIG. 2. Optical density (360 nm) of toluene solutions of tetra-n-dodecylammonium bromide in presence of iodine as a function of concentration, 50°C.

property of the surfactant when in molecular dispersion, and the other that of the completely, or nearly so, micellized solute. The smooth curvature of the plots rather than a sharp break in them, seems to be the characteristic feature of detergents in organic solvents, making thus the existence of CMC as conventionally defined, rather questionable.

Early work on micelle formation in organic solvents used the concepts originating from aqueous systems (1, 11). Thus, when molecules of amphiphiles in organic solvents aggregate to form the Hartley type "inverted micelle," the hydrocarbon chains occupy the surface to form a large sphere with the polar heads inside it. Such a concept, developed for aqueous solutions, is based on models which assume an equilibrium between monomers and micelles. This model does not provide for the possible existence of clusters of intermediate size,

TABLE I

AGGREGATION CONSTANTS OF DODECYLAMMONIUM HALIDES IN BENZENE AND TOULENE

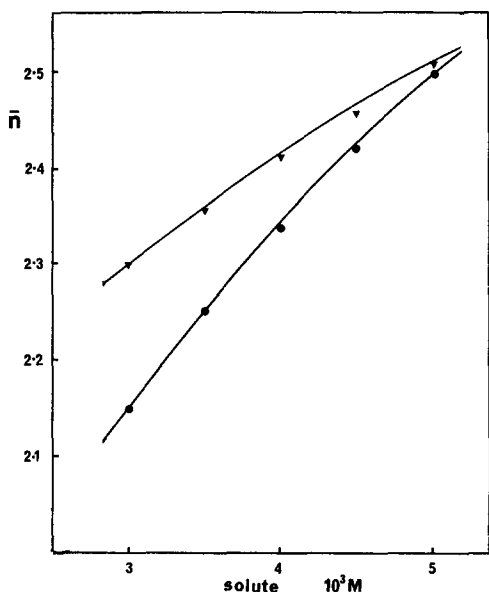| Surfactant	Solvent	Temperature °C	Concentration range $10^3 M$	p	$\log\beta_p$	q	$\log\beta_q$	r	$\log\beta_r$
$C_{12}H_{25}NH_3Cl$	Benzene	37	3–5	3	5.89 ± 0.04	5	11.79 ± 0.06		
$C_{12}H_{25}NH_3Br$	Benzene	37	3–5	3	6.59 ± 0.06	5	12.22 ± 0.07		
$(C_{12}H_{25})_2NH_2Br$	Toulene	50	3–30	2	3.42 ± 0.05	3	6.73 ± 0.08	5	11.10 ± 0.09
$(C_{12}H_{25})_3NHBr$	Toulene	50	5–50	2	1.96 ± 0.02				
$(C_{12}H_{25})_4NBr$	Toulene	50	5–50	3	5.98 ± 0.03	16	41.40 ± 0.09		

FIG. 3. Average aggregation number of n-dodecylammonium chloride (●) and bromide (▼) in benzene solutions as a function of concentration, 37°C.

smaller than the micelle, and requires that the activity of the monomer remains constant after the CMC.

The small micellar sizes, and the low overall aggregation numbers encountered in hydrocarbon solutions of surfactants suggest that the increase in the experimentally determined average aggregation number does not necessarily imply the growth of aggregated clusters. The increase in $\bar{n}$ with increasing solute concentration should be regarded as resulting from an increase in both the *extent* (number of aggregated units) and *degree* (size of aggregated units) of aggregation. With this modified concept which distinguishes between the extent and degree of aggregation in the type of systems under consideration, the conventional model for aqueous systems of monomer $\rightleftarrows$ micelle equilibrium becomes untenable. As a matter of fact, the two models are mutually exclusive. The extent-degree model is characterized by a stepwise formation of aggregates and the existence of a series of oligomers of nonuniform size which are in a dynamic equilibrium with the monomer and with each other. Equally important is the fact that this model makes it unreasonable to expect for the sur-
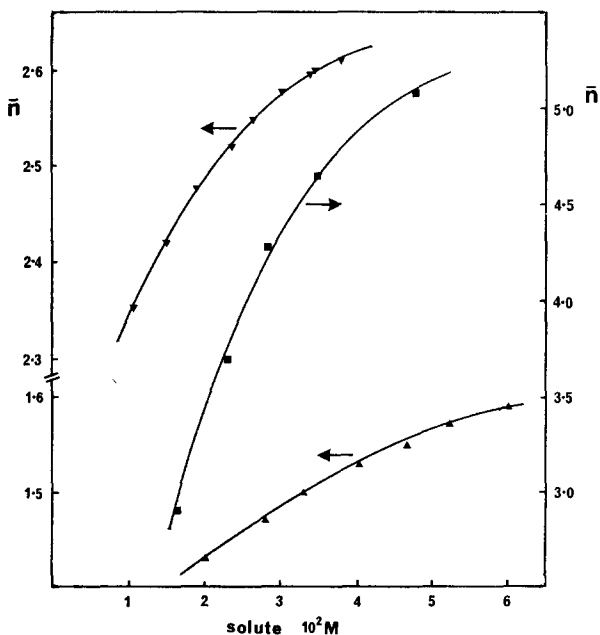

FIG. 4. Average aggregation number of di-n-dodecyl-(▼), tri-n-dodecyl-(▲) and tetra-n-dodecylammonium bromide (■) in toluene solutions as a function of concentration, 50°C.

factant to exhibit the phenomenon of critical micelle concentration.

Dipole–dipole type electrostatic interactions are primarily responsible for the formation of aggregates of highly polar ionpairs in hydrocarbon solutions (12). There is a decrease in free energy on aggregating a number of monomeric solute molecules, with a possible additional enhancement from intermolecular hydrogen bonds or coordination bonds (1). The reason for the stability of small aggregates in hydrocarbon solutions cannot be rationalized in simple terms. The size limiting factor is probably the balance between the cohesive, nonspecific dipole–dipole forces, and the entropy changes as the number of particles decreases in the system. Steric and geometrical considerations are certainly important factors preventing the indefinite growth of aggregates by restrictions on the packing of bulky hydrocarbon chains.

The factors affecting both the formation of the aggregate and its size will depend on the nature of the surfactant, its volume, geometry and dipole moment, and its concentration, the nature of the organic solvent, and temperature. Solvent is of course a very important factor. Its physical and chemical properties govern the extent of competition between solute–solute and solute–solvent interactions.

Finally, it should be emphasized that the mass-action law concept advocated here implies that the aggregates of the alkylammonium salts type cationic surfactants in organic solvents are formed reversibly from monomers by a progressive molecular association, and that different oligomers exist in equilibrium in accordance with the principle of the mass-action law. Such aggregates, some presumably present in undetectably small concentrations (1), should be regarded as having a statistical size, and they should not be regarded as persistent, long-life entities of well-defined aggregation number. Small aggregates, however, might have a pronounced stability.

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