

sulfonate was still slowly gaining in weight, the amount of water that had already been taken up was 3.42 molecules.

These data show that the sodium salts of the higher straight chain alkyl sulfonates form hydrates containing 3.5 molecules of water. No evidence for other hydrates was found, though the possibility was not eliminated.

In the solubility calculations no correction was made for the water present in the hydrate. As it was shown that these hydrates at room temperature have a vapor pressure close to that for water, in all probability they cease to exist at the higher temperatures encountered in most of these solubility determinations. For the low solubilities at the lower temperatures where hydrates do exist, the correction would be less than the experimental error.

### Summary

1. A method for testing the purity of the sodium salts of the higher alkyl sulfonates by precipitation and weighing as the corresponding barium salt has been described.

2. The solubility-temperature curves were determined for sodium decyl, dodecyl, tetradecyl, hexadecyl and octadecyl sulfonates. For each of these sulfonates at the lower temperatures, the solubility is a linear function. However, for each there exists a definite critical concentration after which the solubility loses its linearity and rises very sharply with temperature. The critical phenomenon is interpreted in terms of the ionic micelle concept.

3. These sulfonates were found to have hydrates of 3.5 molecules of water.

SEATTLE, WASHINGTON

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## Studies of Sulfonates. IV. Densities and Viscosities of Sodium Dodecyl Sulfonate Solutions in Relation to Micelle Formation

BY KENNETH A. WRIGHT<sup>1</sup> AND H. V. TARTAR

The study of the solubilities of the sodium salts of the higher alkyl sulfonates<sup>2</sup> indicated that micelles begin to form when a critical concentration of solute is reached. These earlier observations have been confirmed by a study of the densities and viscosities of sodium dodecyl sulfonate solutions over a series of concentrations and temperatures.

Grindley and Bury<sup>3</sup> from their study of the density-concentration curve for *n*-butyric acid solutions showed that the partial specific volume of the acid undergoes a decided change over a certain concentration range; they ascribed the change to the formation of micelles. Later Bury and co-workers extended their study to include solutions of potassium *n*-octoate<sup>4</sup> and potassium laurate<sup>5</sup>; the density-concentration curves for these solutions also exhibit an abrupt change in slope.

### Density Measurements

Since micelles begin to form at a rather dilute concentration, it was necessary to determine the densities to an ac-

curacy of 2 or 3 parts in 100,000 to demonstrate the existence of a break in the density curve. Figure 1 illustrates a densimeter designed to give this accuracy. With one filling and weighing, density determinations over a series of temperatures may be carried out by observing the rise of the meniscus in the calibrated capillary stem.

The capillary, selected for straightness and uniformity of bore, was marked in mm. divisions over a length of 15 cm. This was done by rotating the capillary against a diamond-point pencil fixed rigidly in a heavy vise. One end of the capillary tube rested against the carriage of a traveling microscope. After each mark was completed, the carriage was shifted 1 mm. for the next mark. The divisions were made to an accuracy of  $\pm 0.01$  mm.

The instrument was filled by drawing the solution up to the desired mark and closing the stopcock, which had been moistened with a little water for lubrication. At the end of the determination the plug of the stopcock was removed to allow this water to evaporate. The best means found for closing the orifice was by stretching a wide rubber band from it to a glass hook as shown in the diagram; tests showed that there was no leakage. The rubber band was reinforced by a vulcanized rubber patch to prevent puncturing. In slipping the band over the orifice, care was taken not to trap air bubbles.

The stopcock was then opened and the densimeter immersed to C in a thermostat. A finer capillary tube BC of radius 0.25 mm. joined the coarser capillary at B; the purpose of this constriction was to minimize the diffusion of hot water vapor from the calibrated to the cooler exposed part of the tube. The amount of water vaporizing

(1) Standard Oil Company of California Fellow, 1937-38.

(2) Tartar and Wright, *THIS JOURNAL*, **61**, 539 (1939).

(3) Grindley and Bury, *J. Chem. Soc.*, 679 (1929).

(4) Davies and Bury, *ibid.*, 2263 (1930).

(5) Bury and Parry, *ibid.*, 626 (1935).

from the solution into the capillary bore was shown, even at the higher temperatures, to affect the cathetometer reading to less than the experimental error; furthermore, since the instrument was calibrated with water, any small effect was compensated. During the determination, it was not necessary to close the stopcock; its main function was to facilitate the filling of the densimeter. The densimeter was calibrated by filling with freshly-boiled distilled water and noting the cathetometer readings as the temperature was increased by short intervals. From the weight of the water and the densities at the different temperatures, the volumes for the observed readings were calculated. The volumes for any other reading could then be obtained by interpolation.

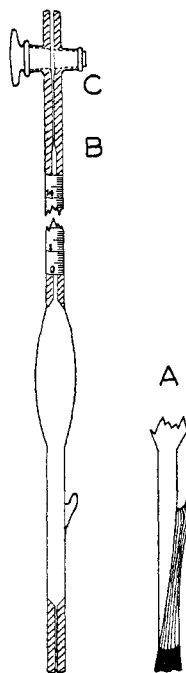


Fig. 1.—Design of densimeter. A shows method of closing orifice with rubber band.

The same thermostat and solutions were used for both the viscosity (*vide infra*) and density determinations which usually were run simultaneously.

The height of the meniscus in the capillary stem was determined with the aid of a cathetometer to  $\pm 0.01$  mm. Because of the sharp decrease in solubility of sodium dodecyl sulfonate<sup>2</sup> below  $36^\circ$ , it was necessary to fill the densimeter at this temperature, and the first cathetometer reading was taken at  $40^\circ$ . The tempera-

ture of the thermostat was then raised by  $10^\circ$  intervals and a reading taken at each temperature. Readings were not taken with decreasing temperature because of the drainage error resulting from the receding meniscus.

At the end of the series of readings, the densimeter was removed from the thermostat and allowed to stand, usually overnight, until the rubber band had come to equilibrium with the moisture of the air. The densimeter was examined for the presence of any gas bubbles; it was always necessary to bring the solution near to boiling for a short time just previous to the filling of the densimeter, because otherwise during the determinations at the higher temperatures of  $60^\circ$  and  $70^\circ$ , bubbles were produced from dissolved air.

The weighings were made to 0.1 mg. to obtain the desired accuracy. A tare of like dimension and shape was used to compensate for adsorbed moisture. The densimeter and tare were wiped with a slightly damp cloth just prior to weighing to avoid the influence of static electric charges. After weighing, the densimeter was inverted and the rubber band carefully removed. The orifice was constructed of fine capillary, radius 0.25 mm., to facilitate the removal of the band without

wetting with solution. The band was weighed immediately and the weight of the solution could then be determined by difference and corrected to vacuum.

From the calibration data, the volume corresponding to each cathetometer reading was obtained. The densities were finally calculated from the weight of the solution and its volume at a given temperature.

The volume for a given reading varies slightly with temperature because of the expansion of the glass. If the solution at a given temperature gave a reading differing from that of the water used in calibration, a small positive or negative correction was made. For a volume of 10 cc. the correction for the expansion of Pyrex glass amounts to 0.00010 cc. per degree or 1 part in 100,000 for the density determination.

The measurements were carried out with two densimeters. The data are presented in Table I.

### Discussion of Density Data

The density-concentration curves (*cf.* Fig. 2) show a definite break at a low concentration essentially the same as that found for the solubility curve. With rise in temperature, the critical concentration shifts to higher values.

Bury and Parry<sup>5</sup> determined the densities of potassium laurate solutions at  $25^\circ$  and  $35^\circ$  and stated that the critical concentration decreased with rise in temperature. In Fig. 3 their data have been plotted against volume normality (calculated from their weight concentrations). For each temperature, the curve consists of two straight lines intersecting at the critical concentration. From a large-scale graph it can be shown that the critical concentration is 0.032<sub>5</sub> *N* at  $25^\circ$  and 0.033<sub>0</sub> *N* at  $35^\circ$ , thus showing that it increases with rise in temperature. This is in accord with the observations reported herein for

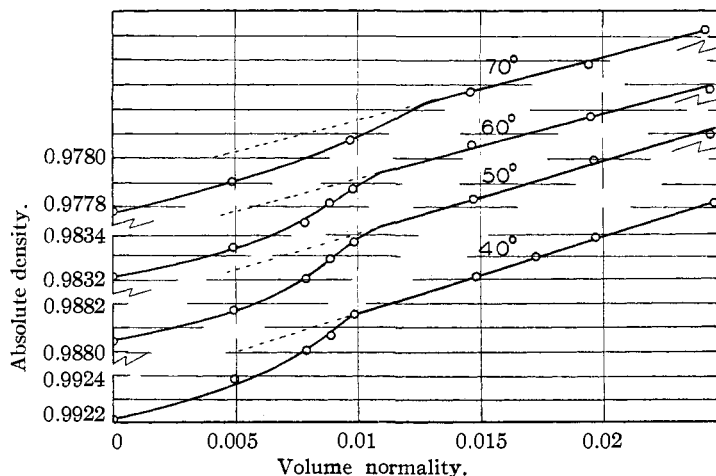


Fig. 2.—Density-concentration curves for aqueous solutions of sodium dodecyl sulfonate, showing the breaks at the critical concentrations,

sulfonates and is to be expected because of the disaggregating effect of thermal agitation on the micelle.

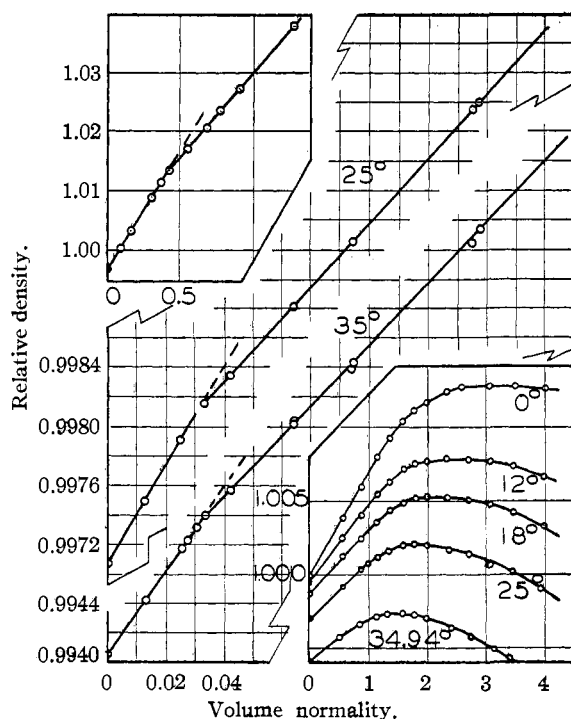


Fig. 3.—Density-concentration curves from data for potassium laurate (5) solutions. Upper inset, potassium octoate (4) solutions at 25°; lower inset, *n*-butyric acid (3) solutions.

The decided increase of critical concentration (0.033 *N*) of potassium laurate over that (0.01 *N*) for sodium dodecyl sulfonate cannot be ascribed wholly to the change in nature of the polar group since the former has a paraffin-chain length equivalent only to eleven carbon atoms, the twelfth being included in the polar carboxyl group. Substitution from sodium to potassium should have little effect on the critical concentration.<sup>6</sup>

The density curve for potassium *n*-octoate<sup>4</sup> solutions, shown in Fig. 3, has a definite break at 0.36 *N* concentration.

In Fig. 3, the density data of Grindley and Bury<sup>3</sup> for *n*-butyric acid solutions have been plotted against volume normality over the concentration range where they supposed micelles to form. The curves show smooth maxima which shift to lower concentrations with rise in temperature (propionic and acetic acid solutions also show maxima in their density curves). The

(6) Cf. data of Lottermoser and Puschel, *Kolloid Z.*, **63**, 175 (1933).

smooth curves hardly can be interpreted in terms of critical phenomena; until more definite information is forthcoming, it may reasonably be questioned whether micelles exist in *n*-butyric acid solutions.

TABLE I  
DENSITIES OF SODIUM DODECYL SULFONATE SOLUTIONS

Weight normality, $N_w$	Absolute Densities			
	40°	50°	60°	70°
0.005000	0.99238	0.98817	0.98333	0.97790
.008000	.99250	.98830	.98343	.....
.009000	.99256	.98838	.98351	.....
.01000	.99265	.98845	.98357	.97807
.01500	.99281	.98863	.98375	.97827
.02000	.99297	.98879	.98387	.97838
.02500	.99311	.98889	.98398	.97852
.05000	.99380	.98959	.98470	.97917
.1000	.99537	.99106	.98607	.98056

### Viscosity Measurements

Two Bingham-Green pressure viscometers<sup>7</sup> were used for measuring the viscosities. They were of similar dimensions, each having a capillary of length 10 cm. and radius of bore 0.10 mm.

A 70-liter steel tank, lagged for heat insulation, proved satisfactory to maintain constant pressure during a determination. The pressure was measured to an accuracy of  $\pm 0.1$  mm. by means of a mercury manometer and the time measurement to an accuracy of one-tenth second with a good stop watch. Since the time was rarely less than two hundred seconds and the pressure measurement seldom below 20 cm., the maximum error for the viscosity determination was 0.1%.

The instruments were calibrated<sup>7</sup> (p. 295) using dust-free water prepared by filtering through a Berkefeld filter and distilling in an all-glass still.

Because of the low solubility of sodium dodecyl sulfonate below 36°,<sup>2</sup> it was necessary to keep the solutions above this temperature. By the application of pressure, a solution was forced from its container through a fine-mesh Pyrex sintered-glass filter<sup>8</sup> into the viscometer.

The thermostat was designed to allow a rapid change of temperature and could be held constant to  $\pm 0.001^\circ$  at room temperature and to  $\pm 0.005$  at 70°. The temperature was actually measured to an accuracy of  $\pm 0.01^\circ$  by means of a Mueller bridge using a platinum resistance thermometer which had been checked at 10° intervals against a Bureau of Standards thermometer.

(7) Bingham, "Fluidity and Plasticity," McGraw-Hill Book Company, Inc., New York, 1922, p. 76.

(8) Kirk, Craig and Rosenfels, *Ind. Eng. Chem., Anal. Ed.*, **6**, 154 (1934).

The thermostat was always set at even values (40.00, 50.00°, etc.).

At higher temperatures, evaporation of water from the solution and condensation on the cooler connecting tubing may produce considerable change in concentration. This was overcome by using an overflow trap on the right arm of the viscometer similar to that on the left; during a run both traps were partially filled with solution to act as an evaporation buffer to protect the working solution from change. The effectiveness of this arrangement was demonstrated by filling with 0.1 *N* solution and quickly taking readings at 40, 60 and 80° and then refilling and taking readings at 5° intervals up to 80°. The viscosities checked to within the experimental error of 0.1%.

The solutions were made up by weight, corrected to vacuum, to predetermined weight normalities. The salt was prepared and tested for purity as described in the preceding paper.<sup>2</sup>

After each run, the viscometers were cleaned by allowing to stand filled with hot dilute cleaning solution free from dust particles. They were then rinsed eight times with dust-free water and dried in an oven in a current of filtered air.

#### Discussion of Viscosity Data

The viscosities, plotted in Fig. 4, show the same characteristic breaks in the curves as do the densities.

TABLE II

Weight normality, <i>N<sub>w</sub></i>	VISCOSITIES OF SODIUM DODECYL SULFONATE SOLUTIONS			
	40°	50°	60°	70°
	Centipoises			
0.005000	0.6582	0.5515	0.4698	0.4076
.01000	.6612	.5539	.4722	.4098
.01500	.6672	.5582	.4748	.4114
.01750	.6711	.5619	.4780	.4126
.02000	.6751	.5649	.4805	.4153
.02500	.6825	.5709	.4853	.4197
.05000	.7270	.6067	.5149	.4440
.1000	.8158	.6790	.5757	.4947
.2000	.9985	.8313	.7041	.6033
.4000	1.4331	1.1918	1.0083	.8648

**Test of the "Anionic Network" Theory.**—Howell and Robinson,<sup>9</sup> from a study of the conductivities of long-chain alkyl sulfate solutions, suggested that at the critical concentration "the anions are unable to pass one another owing to electrical repulsion and that on electrolysis they therefore move as a complete lattice-like loose network."

(9) Howell and Robinson, *Proc. Roy. Soc. (London)*, **155A**, 386 (1936).

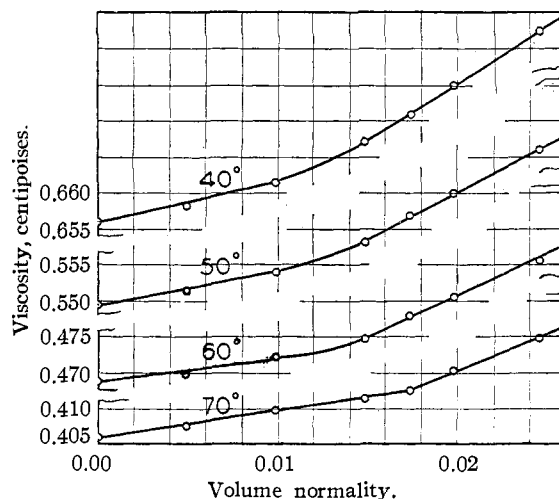


Fig. 4.—Viscosity-concentration curves for aqueous solutions of sodium dodecyl sulfonate.

It must be stressed that at the concentration at which the "anionic network" is supposed to form, the anions are still quite widely separated; for example, taking the data of Howell and Robinson for sodium dodecyl sulfate, the average distance between the anions is 47 Å., the length of the anion being 15 Å.

This wide separation precludes the possibility of a network in a mechanical sense, and consequently the density curve should show no irregularity as it passes through the critical concentration. The observed break in the density curve is, therefore, not in accord with this theory.

At the concentration for the minimum of the equivalent conductance curve, Howell and Robinson assume that the "network falls into micelle formation." Sodium dodecyl sulfonate solution at 60° has a minimum at a concentration of *ca.* 0.2 *N*.<sup>10</sup> From Fig. 5 it will be seen that the viscosity curve is quite linear over this range; it is difficult to see how so radical a transition in the structure of the solution as a change from a network arrangement to micelle formation could occur without having a profound influence on viscosity.

#### Discussion of Ionic Micelle

The experimental data so far presented establish definitely the existence of a critical concentration for the breaks in the property-concentration curves for these aqueous sulfonate solutions. The critical concentration is lowered with increase in chain length of the anion; rise in temperature has the opposite effect. It also has been

(10) Reed and Tartar, *THIS JOURNAL*, **58**, 322 (1936).

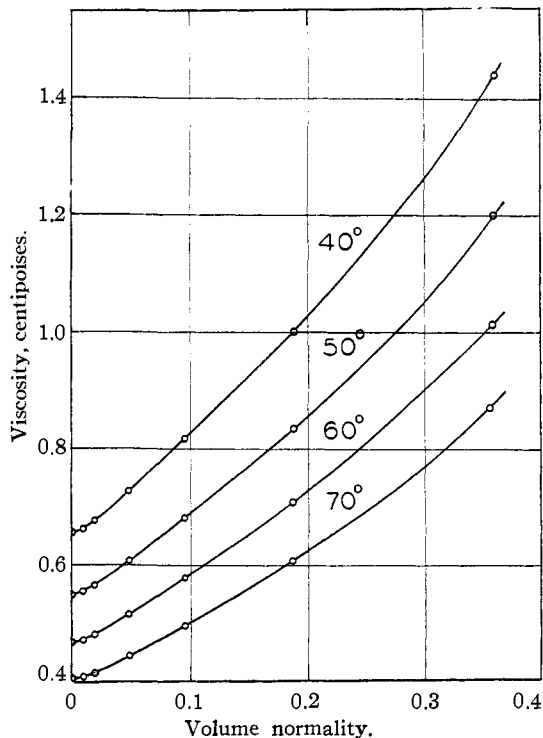


Fig. 5.—Viscosity-concentration curves over an extended range of concentrations for aqueous solutions of sodium dodecyl sulfonate.

shown that the property-concentration curves immediately beyond the breaks are surprisingly linear. These and other observations apparently can be most easily explained by assuming that ionic micelles of a quite definite size begin to form at the critical break in the property-concentration curve.

The equilibrium relationship between the micelle and its ions must follow directly from a consideration of its stability and how this is dependent on the ion concentrations. Before a discussion of this equilibrium can be made, it will be necessary to consider the forces that determine the stability of the micelle, and particularly how this stability is dependent on the sodium ion concentration and the degree of ionization of the micelle.

As a basis for explanation we may assume, as Hartley<sup>11</sup> does, that the ionic micelle consists of many anions (say 50 to 100) with polar groups outward. Because of the "attraction of a close atmosphere of oppositely charged ions toward the highly charged micelle and the consequent adherence of a large fraction of these to the

micelle," we may in a certain sense speak of it as having a definite degree of ionization.

The data presented in this series of papers do not give any indication as to the form of the micelle. Hartley<sup>11</sup> presents evidence to support the idea that the micelle is a "roughly spherical" aggregate without definite form. On the other hand, Krishnamurti<sup>12</sup> and Hess and Gundermann<sup>13</sup> show that with transparent sodium oleate solutions sufficiently concentrated to permit satisfactory X-ray examination, pronounced diffraction evidently is caused by crystalline micelles whose width is that of pairs of molecules laid end to end, the side spacing being equal to the thickness of the molecules.

The micellar stability will depend on the interplay of certain forces which are indirectly affected by the concentrations of the simple ions; one group of forces tends toward stability and the other toward disaggregation. To the first, belongs van der Waals attraction between hydrocarbon chains. This is comparatively weak and probably insufficient to produce aggregation were it not for the accompanying reduction in free energy from the decrease in hydrocarbon-water interface when the anions coalesce to form micelles.

The disaggregating effect of thermal agitation is evidenced by the shift of the critical concentration with rise in temperature. Possibly a more potent force tending toward disruption is the coulombic repulsion of the negatively charged polar ends of anions. If the charge on the surface were not partially neutralized by adhering gegenions, the micelle probably could not exist. The "degree of ionization" as determined by the sodium ion concentration must play a very important role for the micellar stability. Change from univalent to bivalent cation would undoubtedly result in a lower "degree of ionization," thus enhancing the stability and lowering the critical concentration; this effect was observed by Lottermoser and Puschel<sup>14</sup> for the higher alkyl sulfates.

The micelle represents the maximum in stability for the possible types of aggregation of the solute. As pictured by Hartley<sup>11</sup> it has a diameter roughly twice the length of the anion; any further increase in size would be improbable because this would necessitate the introduction of water molecules or polar groups into the interior with resultant increase in potential energy. Small-

(12) Krishnamurti, *Indian J. Phys.*, **3**, 307 (1919).

(13) Hess and Gundermann, *Ber.*, **70B**, 1800 (1937).

(14) Lottermoser and Puschel, *Kolloid.-Z.*, **63**, 175 (1933).

(11) Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie., Paris, 1936, pp. 32 and 43.

ler aggregates would be less stable because of their higher "degree of ionization" and would rapidly build up to the final form.

It is probable that both the mass and volume of the micelle will become greater with increase in the length of the aggregating anion. Undoubtedly, this would result in both a greater decrease in free energy and a lower "degree of ionization," the two effects contributing to enhanced stability. A marked lowering of the critical concentration is thus to be expected in going from a lower to a higher member in the paraffin-chain salt series.<sup>2,12</sup>

The equilibrium between the micelles and the simple ions with increasing concentration of sulfonate can be treated most easily for a condition of constant temperature. The concentration of the sulfonate anion remains always just sufficient to satisfy the requirements for the stability of the micelle, since any excess over this minimum results in the formation of additional micelles. As the solution becomes more concentrated the sodium ion concentration steadily increases with a resulting decrease in the "degree of ionization" of the micelle; the stability is thereby enhanced and the sulfonate ion concentration becomes less. The critical concentration must, therefore, represent the maximum for the sulfonate ion. Figure 6 depicts a general idea of the components at different concentrations of an aqueous solution of a sodium alkyl sulfonate. No pretense is made of representing quantitative relationships.

#### Summary

1. A densimeter has been described for meas-

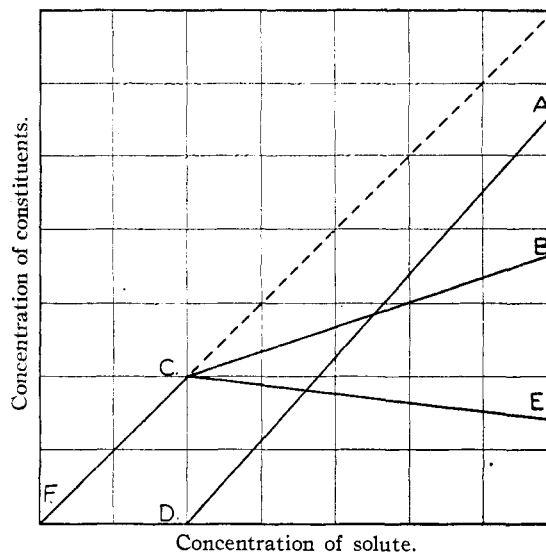


Fig. 6.—Generalized constitution diagram for aqueous solutions of the sodium salts of higher alkyl sulfonates. AD represents the concentration of solute in micelle form; FCB and FCE, the concentrations of sodium ion and alkyl sulfonate ion, respectively.

uring densities over a series of temperatures with only one filling and weighing required.

2. The densities and viscosities for dilute solutions of sodium dodecyl sulfonate have been determined at 40, 50, 60, and 70°. Breaks appear in the curves where ionic micelles are supposed to form.

3. The equilibrium between the ionic micelle and the sodium and alkyl sulfonate ions has been discussed in a qualitative manner.

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## Studies of Sulfonates. V. Electrical Conductance of Sodium Decyl, Dodecyl, and Hexadecyl Sulfonate Solutions at 40, 60 and 80°—Micelle Formation

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Previous studies<sup>2,3</sup> on solutions of these sulfonates definitely established the existence of critical concentrations at which certain property curves change abruptly, supposedly due to the formation of ionic micelles. The conductances have been determined by Reed and Tartar<sup>4</sup> at 25 and 60° but unfortunately their data are too

limited to determine the critical concentrations with certainty. The object of the present study was to investigate the conductance-concentration curve more carefully over this range and to determine the effect of temperature.

#### Experimental

The Leeds and Northrup Dike conductivity bridge<sup>5</sup> was calibrated with standard resistances. A Leeds and Northrup A. C. vacuum tube oscillator and amplifier were

(1) Standard Oil Company of California Fellow, 1937-38.

(2) Tartar and Wright, *THIS JOURNAL*, **61**, 539 (1939).

(3) Wright and Tartar, *ibid.*, **61**, 544 (1939).

(4) Reed and Tartar, *ibid.*, **58**, 322 (1936).

(5) Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).