[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

The Surface Tension of Aqueous Solutions of Some Paraffin Chain Colloidal Electrolytes, Including a Comparison of the Capillary Rise and Sessile Bubble Methods of Measurement

BY H. V. TARTAR, V. SIVERTZ AND R. E. REITMEIER

Numerous measurements have been made of the surface tensions of aqueous soap solutions; mostly by the drop weight and anchor ring methods. Some workers[1] have reported reproducible results, while others[2,3] have been unable to duplicate their findings. The lack of reproducibility has been attributed by Reed and Tartar[3] to the change of the surface tension with time. Bigelow and Washburn[4] have reported studies on systems of colloidal electrolytes which show similar changes. In such cases the same general type of behavior has been observed: namely, an initial higher value, followed by a more or less regular decrease to a final minimum value which was usually reached in a few hours. Bigelow and Washburn, as well as Reed and Tartar, concluded that the capillary rise method was the most suitable for observing such behavior because the necessary observations could be made without disturbing the surface.

Further information concerning the surface tension behavior of solutions of colloidal electrolytes is of both theoretical and practical importance. In this paper are reported the results of a study of the time changes and the final equilibrium values of the surface tensions of aqueous solutions of some monoethanolammonium soaps, sodium laurate and sodium alkyl sulfonates as obtained by the use of two static methods of measurement, the capillary rise and the sessile bubble methods. Since only the latter method gave reproducible and accurate results, the account of work using the former has been greatly abbreviated; results only sufficient for comparison are presented, tabulated data are omitted and the results are presented in graphical form. The findings afford the only data available for a comparison of the application of these methods to the study of solutions of colloidal electrolytes.

Surface Tension Measurement by the Capillary Rise Method.—The capillarimeters were of the design of Richards and his co-workers[5] and were made of Pyrex glass with tightly ground glass stoppers. The capillary tubes were carefully inspected for uniformity of bore, and the radii were determined by the method of Harkins and Brown.[6] These values checked with close agreement those found by determining the capillary rise of water at 20°. The capillarimeters were cleaned with chromic acid cleaning solution, well rinsed with distilled water, steamed out thoroughly and dried. The cathetometer could be read to 0.02 mm. and meniscus correction for the observed heights was made by the method of Richards and Coombs.[5] The measurements at 25° were made in a water-bath with temperature control to ±0.05°; for those at 40° and 60°, an air-bath held to ±0.03°.

The solutions were stored in glass-stoppered Pyrex bottles. It was found that monoethanolammonium soaps in solution readily undergo hydrolysis; to prevent this change, the solutions were buffered by using two equivalents of monoethanolamine for each equivalent of fatty acid. The excess of varying amounts of amine was found not to modify appreciably the surface tension of the unhydrolyzed soap solution. The surface tension of solutions of monoethanolamine with concentrations equivalent to those used in the soap solutions gave surface tensions differing but little from that of water alone.

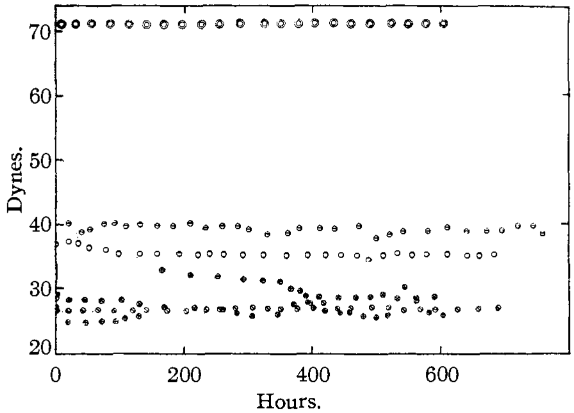

Fig. 1.—Surface tension of buffered monoethanolammonium oleate solutions at 25°: ⊗, 0.1 molal; ⦸, 0.01 molal; ⊕, 0.001 molal; ○, 0.0001 molal; ⊖, 0.00001 molal; ◉, 0.000001 molal.

The results presented in Fig. 1 show the variation of the surface tension of monoethanolamine solutions over a period of approximately seven hundred hours, during which time care was taken not to disturb the tubes. Repetition of the measurements with fresh solutions gave results qualitatively similar but not in quantitative agreement.

---

(1) Lottermoser and Stoll, *Kolloid Z.*, **63**, 49 (1933).

(2) Walker, *J. Chem. Soc.*, **119**, 1521 (1921).

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

(4) Bigelow and Washburn, *J. Phys. Chem.*, **32**, 321 (1928).

(5) Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915).

(6) Harkins and Brown, *ibid.*, **41**, 449 (1919).

That this lack of reproducibility was not due to dissolution of the glass was indicated by the constancy and reproducibility of solutions of the related compound ammonium acetate at 40°. The fluctuations shown by the monoethanolamine oleate solutions were evidently due to the colloidal nature of these systems.

Similar results were obtained with the oleate at 40 and 60° and with both monoethanolammonium laurate and nonylate solutions at 25 and 40°.

Since Adam and Shute[7] have stated that salts with long chain cations in dilute aqueous solutions do not wet glass properly and seem to become adsorbed on the glass which is negatively charged with respect to the solution, our assumption of zero contact angle was carefully checked although the solutions were salts with long chain anions which might possibly exhibit a different behavior. The angle was measured by the method of Bosanquet and Hartley[8] using all concentrations of the monoethanolammonium oleate and found in each case to be zero.

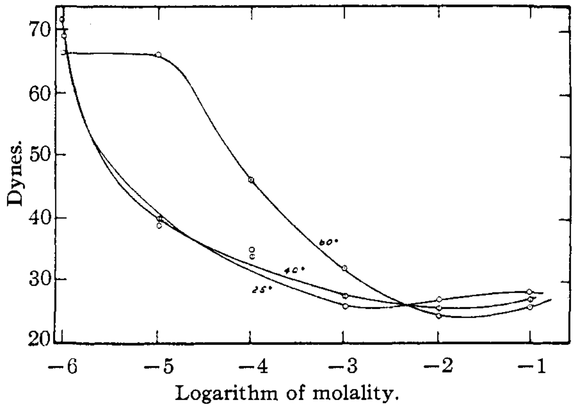

Fig. 2.—Surface tension of buffered monoethanolammonium oleate solutions.

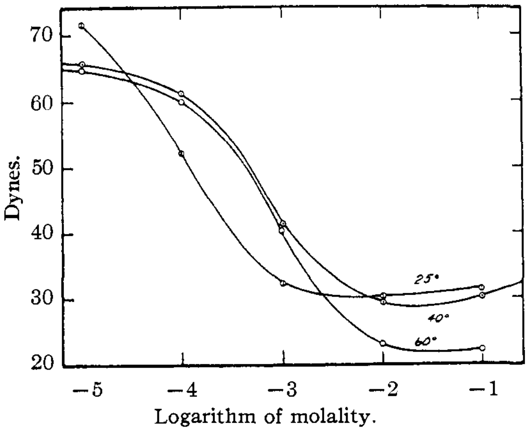

Fig. 3.—Surface tension of buffered monoethanolammonium laurate solutions.

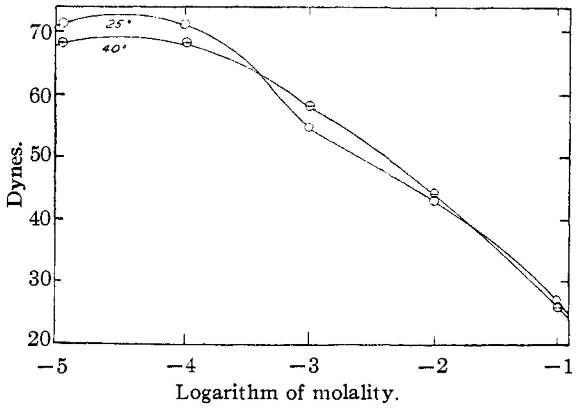

Fig. 4.—Surface tension of buffered monoethanolammonium nonylate solutions.

The best steady ("equilibrium") values for surface tension for the various solutions at the different temperatures when plotted against the logarithm of the concentrations afford the curves in Figs. 2, 3 and 4.

Measurements were made at 25, 40 and 60° to show the influence of temperature on surface tension.

The Sessile Bubble Method.—The measurement of surface tension by the use of a sessile bubble confined under a plate apparently affords the only reliable method available for the study of the changes occurring with the aging of the surface. It also gives results which are independent of contact angle, provided that the bubble is a true surface of revolution about a vertical axis, and it is not invalidated by any evaporation, or marked preferential adsorption, or other effects which may influence the capillary rise method.

It is unnecessary to give here a review of the literature on this sessile bubble method.[9]

Because of its possible greater use, however, in the study of the surface behavior of solutions of capillary active substances and of colloidal electrolytes in general and of the paucity of information given in the literature, the authors deem it advisable to give some details concerning the apparatus and the technique of its operation.

---

(7) Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

(8) Bosanquet and Hartley, *Phil. Mag.*, **42**, 456 (1912).

(9) Quincke, *Ann. phys.*, **105**, 38 (1858); Bashforth and Adams, "An Attempt to Test the Theories of Capillary Action," 1883; Magie, *Phil. Mag.*, [5] **26**, 162 (1888); Ferguson, *ibid.*, [6] **25**, 507 (1913); Porter, *ibid.*, [7] **15**, 163 (1938); Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1933).

Apparatus.—The Pyrex glass cell in which the bubble was produced and held is shown in Fig. 5.[10] It had two observation windows which were parallel and optically plane even close to the all-glass seal to a piece of tubing 50 mm. diam. and 60 mm. long. The top of the cell was constructed with a ground glass joint through which extended a capillary tube, 1 mm. inside diam. Affixed to the lower end of the capillary was a round, smooth, glass plate with a 1-mm. hole in the center which coincided with that of the tube. The upper end of the capillary could be closed with a stopcock. The capillary extended from the top of the cell through a ground glass joint into a reservoir. The lower part of the cell was provided with a stopcock.

The cell was held in a vertical position by means of a wooden framework mounted on leveling screws for adjustment to maintain the small circular plate horizontal. The framework was weighted heavily to prevent any vibration. The set-up was housed in a specially constructed air-bath at 40 ± 0.03°.

The small comparator for making measurements on the bubble was specially made by the Gaertner Scientific Corporation and consisted of a micrometer slide (M300), a measuring microscope (M103) and a leveling stand (5748). The instrument rested on a level, plate glass base. The micrometer head and eyepiece were calibrated by comparison with a standard scale. Measurements could be made directly to within 2.5 micron. The microscope objective extended through a small opening in the side of the air-bath.

Monochromatic light from a sodium vapor lamp was used for illuminating the bubble to avoid the dispersion of light at the edges. The light was made essentially parallel by bringing it to the cell through a small, level, wooden tube, 1.5 meters in length, 3.5 cm. in internal diameter, which extended through the wall of the air-bath and was blackened inside with lampblack to eliminate reflection. The bubble was illuminated on the side directly opposite the measuring instrument.

The air-bath and comparator were both mounted on a concrete pier which was especially free of vibration.

Technique.—The cell was cleaned with hot chromic acid cleaning solution, rinsed first with water and next with twice-distilled acetone, and finally dried in a current of filtered air. It was then filled to about an inch (2.5 cm.) above the horizontal plate with the solution which had been preheated to the temperature at which the surface tension measurement was to be made in order to eliminate difficulties due to the later liberation of dissolved air. The cell was then placed in approximate position in the air-bath where it remained for one hour to attain the desired temperature.

With the upper stopcock closed, the lower stopcock was opened long enough to allow as much solution to flow out as atmospheric pressure would permit. A bubble was formed beneath the plate by opening the upper stopcock and the plate leveled, using the bubble as an indicator. With the upper stopcock open, solution was released through the lower stopcock until the bubble attained the desired size, which was usually between 1 and 2 cm. diameter.

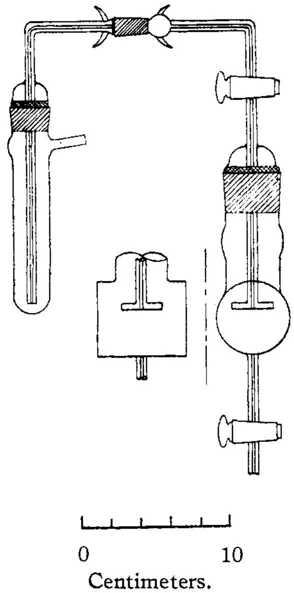

Fig. 5.—Sessile bubble apparatus.

The method requires only two measurements on the bubble, the maximum horizontal diameter and the distance from the equator to the vertex. When the bubble was illuminated with monochromatic light of proper intensity[11] practically all the light was reflected or refracted except that coming perpendicular to the line of maximum diameter; when viewed from the opposite side the result was a very dark, sharply-defined silhouette of the bubble with a short, centrally located, horizontal slit of light at the equator.

Measurements of the diameter of the bubble were made by means of the micrometer head and distance from the maximum diameter to the apex by the micrometer eyepiece. The surface tension was calculated from these measurements using the tables of Porter.[12] The accuracy was close to ±0.05 dyne per cm.

The Surface Tensions of Solutions of Monoethanolammonium Salts at 40° by the Sessile Bubble Method.—Series of aqueous solutions of monoethanolammonium laurate, myristate and oleate were prepared as previously described and their surface tensions determined. Figure 6, giving the results with the laurate solutions, shows the typical change of surface tension with time. The final equilibrium values are recorded in Table I and presented graphically in Fig. 7. The surface tension decreased rapidly and equilibrium was reached in a few hours, excepting the very dilute solutions. This result is in general agreement with the data obtained by Adam and Shute[9] on aqueous solutions of cetylpyridinium bromide, cetyltrimethylammonium bromide and sodium

---

(10) Grateful acknowledgment is made for useful information given by Professor F. E. Bartell of the University of Michigan concerning a set-up he has used in work of a different nature.

(11) The light was dimmed by interposing two or three thicknesses of yellow paper between the lamp and the tube.

(12) Porter, *Phil. Mag.*, [7] **15**, 163 (1933).

TABLE I

EQUILIBRIUM SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF MONOETHANOLAMMONIUM LAURATE, MYRISTATE AND OLEATE BUFFERED WITH EXCESS MONOETHANOLAMINE AT 40°

Laurate		Myristate		Oleate	
Concn., molal	Surf. tension, dynes per cm.	Concn., molal	Surf. tension, dynes per cm.	Concn., molal	Surf. tension, dynes per cm.
0.001232	41.40	0.0009992	39.60	0.0001019	35.49
.004424	25.63	.002560	29.17	.0005283	27.69
.008251	23.03	.004138	21.76	.001065	25.70
.01127	22.95	.005902	21.66	.001401	25.56
.01450	23.81	.007535	22.68	.003423	24.86
.01664	25.35	.01107	23.70	.008841	24.97
.01892	26.35	.01770	25.26	.02040	25.90
.03379	27.34			.02994	26.03
.03677	29.00			.03816	25.78
.05177	29.08				

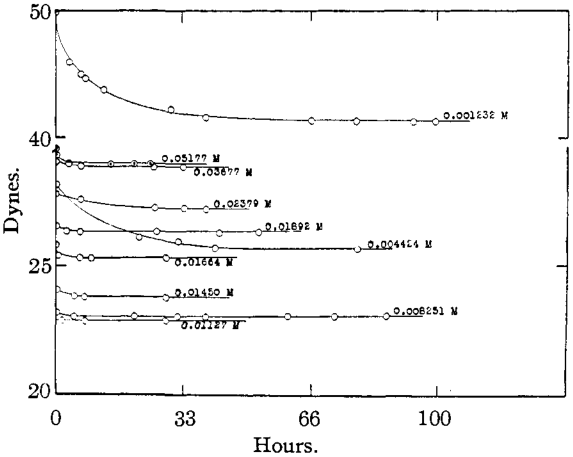

Fig. 6.—Surface tension of buffered monoethanolamine laurate solutions at 40° by the sessile bubble method.

dodecyl sulfate. The curves for equilibrium values show definite minima followed by first an increase in surface tension and then a small gradual decrease. Concentrations at which minima are obtained decrease with increase in chain length of the anion: laurate, 0.01 *M;* myristate, 0.005 *M;* and oleate, 0.005 *M.* The increase in surface tension following the minima also decreases with anion chain length: laurate, 6 dynes; myristate, 3.6 dynes; and oleate, 1.1 dyne.

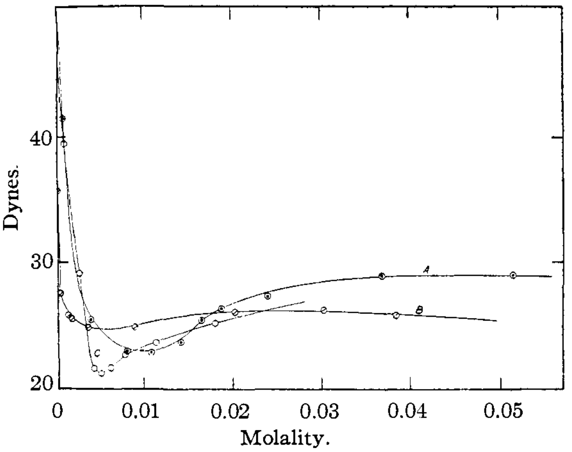

Fig. 7.—Surface tension of buffered monoethanolamine soap solutions at 40° by the sessile bubble method: A, laurate; B, oleate; C, myristate.

Surface Tensions of Sodium Laurate Solutions.—These solutions were buffered with 0.002 *M* sodium carbonate to prevent hydrolysis and the subsequent formation of acid soap. The results of the measurements are given in Table II and Figs. 8 and 9. So far as the writers are aware, these are the first data giving reliable values for the equilibrium surface tensions at a given temperature of solutions of a typical soap. The behavior is similar to that previously reported for the monoethanolammonium salts.

TABLE II

EQUILIBRIUM SURFACE TENSIONS OF SODIUM LAURATE SOLUTIONS BUFFERED WITH 0.002 *M* SODIUM CARBONATE AT 40°

Concn., molal	Surface tension, dynes
0.008901	34.03
.01592	28.60
.02061	27.29
.02291	27.96
.02531	28.98
.03727	29.77

Surface Tension of Solutions of Higher Alkyl Sulfonates at 40.°—Determinations by the sessile bubble method were made of the surface tensions of solutions of sodium decyl, dodecyl and tetradecyl sulfonates. These substances do not hydrolyze and their solutions are essentially neutral. Previous studies in this Laboratory[13] had established the critical concentrations at which micelles are formed and revealed variations in

---

[13] Tartar and co-workers, THIS JOURNAL, **61**, 539, 544, 549 (1939).

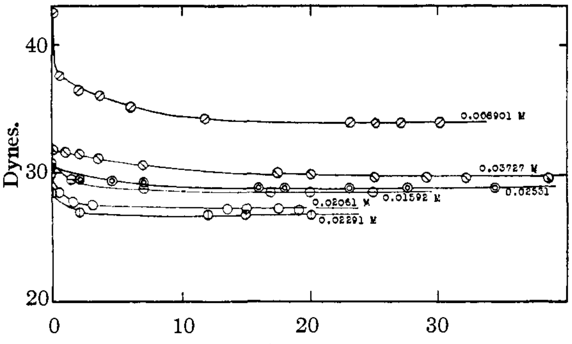

Fig. 8.—Surface tension of buffered sodium laurate solutions at 40° (sessile bubble method).

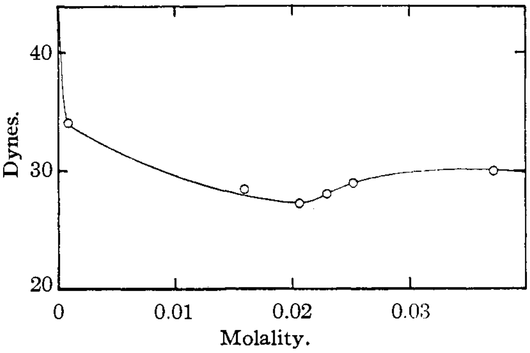

Fig. 9.—Surface tension of buffered sodium laurate solutions at 40° (sessile bubble method).

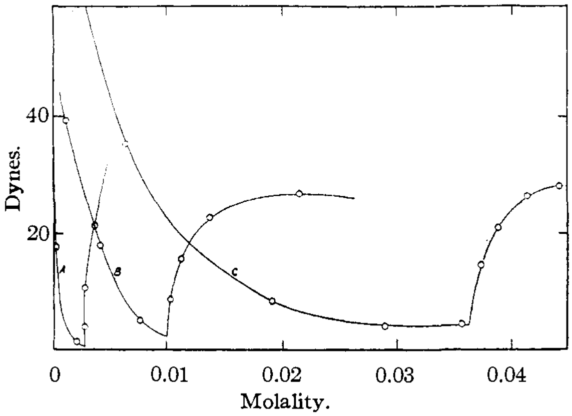

Fig. 10.—Surface tension of sodium alkyl sulfonate solutions at 40° by the sessile bubble method: A, sodium tetradecyl sulfonate; B, sodium dodecyl sulfonate; C, sodium decyl sulfonate.

surface tension at different concentrations as obtained by the capillary rise method.

The data obtained using the sessile bubble are presented in Table III and Fig. 10. The change of the surface tension of the decyl sulfonate solutions with time is shown in Fig. 11; this behavior is typical. No difficulty was experienced in obtaining reproducible equilibrium values. The time required to reach equilibrium was about ten to thirty hours; this period decreased with concentration up to the critical concentration for micelle formation; above that there was a small increase. The most striking result is the very abrupt rise in surface tension when the concentration exceeded the critical value. In fact, this abrupt change affords an excellent means for determining the critical concentration for micelle formation in the aqueous solutions of these substances.

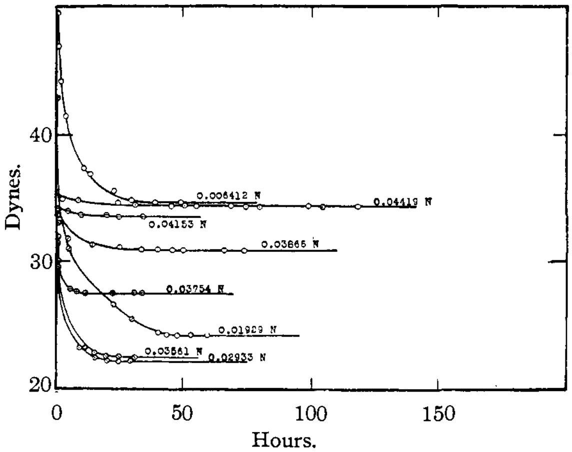

Fig. 11.—Surface tension of sodium decyl sulfonate solutions at 40° (sessile bubble method).

TABLE III

EQUILIBRIUM SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF SODIUM ALKYL SULFONATE SOLUTIONS AT 40°

Decyl sulfonate		Dodecyl sulfonate		Tetradecyl sulfonate	
Concn., normality	Surf. tension, dynes per cm.	Concn., normality	Surf. tension, dynes per cm.	Concn., normality	Surf. tension, dynes per cm.
0.006412	38.05	0.001209	39.75	0.00007859	58.25
.01929	24.19	.004003	34.95	.00009027	28.62
.02933	22.17	.007438	25.40	.001887	20.35
.03561	22.64	.01055	24.30	.002403	21.98
.03754	27.50	.01113	27.90	.002603	25.05
.03866	30.85	.01366	31.45	.003437	30.41
.04153	33.39	.02149	33.60		
.04419	34.20	.02569	29.00		

Discussion

A comparison of the results obtained using the capillary rise method with those obtained with the sessile bubble indicates that the mysterious fluctuations obtained by the former must be largely due to the method itself and are not characteristic of these solutions. The minimum surface tension values obtained by capillary rise are in qualitative agreement with those observed by the sessile bubble procedure. These minima in the surface tension–concentration curves appear to be characteristic of long chain colloidal electrolytes, having been found by less exact methods (than the sessile bubble) for solutions of soaps,[14] alkyl sulfates,[15] alkyl benzene sulfonates,[16] and lauryl sulfonic acid.[17,18]

The nature of the process by which the surface tension changes with the aging of the surface is not clarified by the experiments reported herein. The chain length of the anion at a given concentration was without marked effect. Below the critical concentration, equilibrium was reached more rapidly with increase in concentration.

The increase in surface tension with the formation of ionic micelles is difficult to explain satisfactorily. The decrease in surface tension at lower concentrations is undoubtedly due to adsorption into the surface of the paraffin chain anions, the surface probably becoming saturated when micelle formation begins. The micelles are exceedingly soluble and have polar groups on the outside; consequently they should be less adsorbed than paraffin chain anions. Murray[19] and also Wright and Tartar[20] have suggested that accompanying the increase in micelle concentration there is a gradual increase in cation and a corresponding decrease in anion concentration. This diminution of anions would decrease their adsorption in the surface but this change should be gradual, probably at a rate similar to their adsorption at lower concentrations. The abrupt change in surface tension with micelle formation, particularly in the case of the alkyl sulfonates, indicates that this explanation is inadequate. Furthermore, McBain and Wood[21] have recently presented data obtained by two different methods to show that throughout the analogous region of lauryl sulfonic acid solutions there is *positive* adsorption in the surface. Further study is necessary to account for the nature of this interesting phenomenon.

The results reported in this and previous papers from this Laboratory show that the surface behavior of aqueous solutions of paraffin chain colloidal electrolytes depends upon the concentration, length of carbon chain, age of surface and temperature.

Summary

1. A comparison has been made of the capillary rise and sessile bubble methods for the determination of the surface tension of solutions of some paraffin chain colloidal electrolytes; the latter method only gave reproducible and accurate results.

2. Data have been presented showing the type of time changes and the final equilibrium values of the surface tension of aqueous solutions of some monoethanolammonium soaps, sodium laurate and sodium alkyl sulfonates.

SEATTLE, WASHINGTON RECEIVED MARCH 5, 1940

---

[14] Lottermoser and Tesch, *Kolloid Beiheft.*, **34**, 339 (1931); Lottermoser and Baumgertel, *Trans. Faraday Soc.*, **31**, 200 (1935).

[15] Lottermoser and Puschel, *Kolloid Z.*, **63**, 174 (1933).

[16] Neville and Jeanson, *J. Phys. Chem.*, **37**, 1001 (1933).

[17] McBain, Vinograd and Wilson, THIS JOURNAL, **62**, 244 (1940).

[18] For additional references to surface tension measurements on related systems see McBain and Mills, *Reports on Progress in Physics*, **5**, 30 (1938).

[19] Murray, *Trans. Faraday Soc.*, **31**, 207 (1935).

[20] Wright and Tartar, THIS JOURNAL, **61**, 544 (1939).

[21] McBain and Wood, *Proc. Roy. Soc.* (London), **A174**, 286 (1940).