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

Studies of Sulfonates. III. Solubilities, Micelle Formation and Hydrates of the Sodium Salts of the Higher Alkyl Sulfonates

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This and the papers which immediately follow are a continuation of former work in this Laboratory.[2]

The investigation reported herein is largely a study of the solubility of the sodium salts of straight chain alkyl sulfonates of 10, 12, 14, 16 and 18 carbon atoms. The work was undertaken to obtain information relating to micelle formation in these solutions.

McBain and co-workers,[3] in their studies on the different soaps, have shown quite conclusively that the abnormal behavior of aqueous soap solutions is due to the presence of micelles. Although the existence of micelles has now become generally accepted, investigators are not in accord regarding their structure nor the concentration at which their formation becomes significant.

The equivalent conductance of sufficiently dilute aqueous solutions of long chain paraffin salts, such as soaps, sulfates and sulfonates[4–7] is quite normal, but with increasing concentration it diminishes extremely rapidly and may reach a minimum after which it actually increases slightly at higher concentration. McBain and his co-workers, using the earlier conductivity, freezing

point and vapor pressure data for solutions with concentrations not more dilute than 0.1 N, brought forth the view that the sudden drop in equivalent conductance was due to a rapid increase in the formation of undissociated molecules from ions, with the subsequent formation of neutral micelles and ionic micelles, the effect of the latter becoming predominant when the conductivity reaches a minimum.

Hartley and co-workers,[8] using conductivity and transference number data for dilute solutions and the modern theories of strong electrolytes, have simplified McBain's explanation by employing his ionic micelle concept only to account for the properties of solutions of these substances. Hartley offers some very plausible arguments in support of the hypothesis that the ionic micelle is formed directly from the paraffin chain ions at dilutions much greater than those formerly associated with the ionic micelle, that its formation begins to take place at a fairly definite concentration and that the sudden diminution in equivalent conductance is due largely to a decrease in the amount of ionization with the formation of gegenions. Applying the law of mass action, he shows that the formation of ionic micelles can explain this behavior quite satisfactorily. He also interprets, with less surety, the increase of equivalent conductance in the more concentrated solutions as being due to a loosening of the gegenions, a type of "retrograde" dissociation.

(1) Standard Oil Company of California Fellow, 1937–1938.

(2) Reed and Tartar, THIS JOURNAL, **57**, 570 (1935); **58**, 322 (1936); Houlton and Tartar, *ibid.*, **60**, 544 (1938).

(3) For numerous references see McBain and Betz, *ibid.*, **57**, 1905 (1935).

(4) McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1282 (1919).

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

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

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

(8) Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie., Paris, 1936.

Howell and Robinson[9] give evidence to support their view that the initial break in the conductivity curve is not due to micelle formation but to an anionic "network" and that the minimum is the point "at which the network falls into micelle formation."

The varying interpretations of the equivalent conductance behavior of these colloidal electrolytes indicate that further data from different methods of approach are desirable. The solubilities of the sulfonates were determined in the hope that the results would throw new light on the problem.

Experimental

Preparation of Salts.—The sodium salts of decyl, dodecyl, tetradecyl, hexadecyl and octadecyl sulfonic acids were prepared from the corresponding alcohols by the method outlined by Reed and Tartar.[2] The alcohols in fairly pure form were obtained through the courtesy of the Procter and Gamble Company, to whom we desire to express our gratitude. These materials were further purified by fractional distillation. Further purification was accomplished by the distillation of the alkyl halides prepared as an intermediate step.

In the preparation of lower homologs, sodium decyl and dodecyl sulfonates, the alkyl chloride was used instead of the bromide. This substitution was found to afford no advantage either in yield or in purity of product.

Analysis of Salts.—These substances adsorb moisture very rapidly. To obtain them in anhydrous form, the samples were placed in weighing bottles which could be closed easily and dried in a vacuum desiccator containing phosphorus pentoxide or magnesium perchlorate in an oven at 70°; a pressure less than 1 mm. of mercury was maintained during the drying period by a vacuum pump. The seal between the lid and the body of the desiccator was effected by means of a rubber gasket which projected a little beyond the edge to facilitate removal. After the desiccator was removed from the oven, dry air was permitted to pass in while cooling to room temperature for weighing.

Careful tests showed that the salts were entirely free of sulfites.

One test of the purity of sulfonates is the determination of sulfur[10,2] by oxidation of the sulfonate to sulfate followed by precipitation and weighing as barium sulfate. This procedure is tedious and the usual error of the determination disqualifies it as an exacting test for purity. Carbon, hydrogen or sodium determinations may be made but it is not always easy to obtain results within an error of 0.1%. It has been found more satisfactory with the sulfonates containing 12 or more carbon atoms to precipitate directly from aqueous solution as barium sulfonate and weigh. The use of the sulfonate instead of the sulfate of barium also affords a considerable increase in accuracy because of the more advantageous gravimetric factor.

(9) Howell and Robinson, *Proc. Roy. Soc.* (London), **A155**, 386 (1936).

(10) Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

The sample of sodium sulfonate was dissolved in hot water and 0.1 N barium chloride was added until definite flocculation occurred. The precipitate was digested on the steam-bath for an hour, transferred to a Gooch crucible prepared with an asbestos or hardened filter paper mat and washed with warm water. The crucible was then dried in a vacuum desiccator as described above.

The solubility of the barium salts increases with decreasing carbon chain length. To overcome this error the wash water for the hexadecyl, tetradecyl and dodecyl, barium sulfonates was saturated with the appropriate barium salt. With a correction of 0.15% for the solubility of the salt in the solution from which it was precipitated, the analyses checked the theoretical within 0.1%.

Sodium decyl sulfonate cannot be tested for purity by this method because the barium salt is too soluble.

The results of the analyses of the salts showed a purity of 100 ± 0.2%.

Solubility Determinations.—The solubility determinations were made in 30 × 2.5 cm. Pyrex test-tubes containing 40 cc. of water and sufficient sulfonate to give an excess of solid phase. Equilibrium was approached from both directions, from the unsaturated and supersaturated states. The tubes were closed with two-hole stoppers, kept in a thermostat to ±0.005°, the temperature being determined by a carefully calibrated platinum resistance thermometer.

The solutions in the tubes were stirred efficiently by raising and lowering, by means of a mechanical device, a stirring rod bent at the lower end into a transverse spiral. Equilibrium was approached very slowly, especially with the hexadecyl and octadecyl sulfonates. The solutions with suspended solid phase were sometimes stirred as long as one hundred hours. This mechanical agitation was required even though the solid was sufficiently finely divided to remain easily in suspension. It was found impractical to stir until perfect equilibrium was obtained as this in many cases would have required weeks of continuous stirring. The solubility as calculated from the determinations approaching equilibrium from the unsaturated state was always slightly lower than that calculated from the other approach. The amount of divergence depended upon the carbon chain length of the sulfonate. If the divergence was too great, the determination was repeated using a longer period of stirring. The solubility at any given temperature was taken as the mean of two determinations approaching equilibrium from opposite directions.

At the end of the determination the solution was permitted to stand until the suspended crystals had settled. By the application of pressure a portion (about 30 cc.) of the solution was forced through a conduit tube into a shallow weighing bottle. Any suspended crystals were filtered by a small filter paper fastened to the inlet end of the tube; adsorption of the solute by the paper was inconsequential. Precipitation of the sulfonate in the conduit tube due to cooling was prevented by a heating coil. During the transfer of the solution the weighing bottle was kept in an ice-bath and provided with a cover to prevent loss of water vapor. After evaporation of the water the salt was dried at 70°.

The solubilities were calculated as the number of grams of salt dissolved in 100 g. of water.

Discussion of Data

The experimental data for the solubilities (of the sodium salts of decyl, dodecyl, tetradecyl, hexadecyl and octadecyl sulfonates) are given in Table I.

TABLE I

SOLUBILITIES OF THE SODIUM SALTS OF THE HIGHER ALKYL SULFONATES

Temp., °C.	G./100 g. H₂O	Weight normality	Temp., °C.	G./100 g. H₂O	Weight normality

Temp., $°C.$	G./100 g. H_2O	Weight normality	Temp., $°C.$	G./100 g. H_2O	Weight normality
Sodium Decyl Sulfonate					
15.00	0.733	0.0300	29.00	11.02	0.451
17.00	.800	.0327	31.00	18.70	.766
20.00	.897	.0367	32.00	23.68	.969
23.00	1.04	.0426	34.00	36.70	1.503
24.00	1.22	.0499	36.00	53.5	2.19
25.00	1.93	.0791	36.86	62.3	2.55
27.38	6.43	.263			
Sodium Dodecyl Sulfonate					
20.00	0.134	0.0049	37.00	1.78	0.065
25.00	.191	.0070	38.00	2.97	.109
30.00	.248	.0091	40.00	6.54	.240
31.00	.260	.0096	41.00	9.60	.353
32.00	.277	.0102	43.00	18.20	.669
34.00	.360	.0132	45.00	31.46	1.155
35.00	.441	.0162	46.34	52.8	1.940
36.00	.950	.0349			
Sodium Tetradecyl Sulfonate					
25.00	0.040	0.00133	46.00	1.38	0.046
29.00	.052	.00173	47.00	2.20	.073
34.91	.068	.00227	48.00	3.28	.109
40.00	.087	.00290	49.00	5.08	.169
40.98	.106	.00353	50.00	8.20	.273
41.70	.129	.00429	51.00	12.3	.410
43.00	.270	.00900	53.00	22.4	.747
45.00	.700	.0233	54.02	32.9	1.095
Sodium Hexadecyl Sulfonate					
37.00	0.013	0.00040	55.00	0.88	0.027
41.00	.0205	.00062	56.50	1.60	.049
47.50	.0350	.00106	58.00	2.60	.079
48.25	.0462	.00141	60.00	6.00	.183
49.00	.0560	.00171	61.96	11.55	.352
50.00	.100	.00300	63.36	20.86	.635
53.00	.351	.0107			
Sodium Octadecyl Sulfonate					
47.50	0.0117	0.000329	61.50	0.177	0.00497
54.00	.0217	.000609	65.00	0.90	.0250
57.02	.0270	.000757	67.01	2.00	.0561
58.00	.0362	.001016	69.05	5.60	.157
59.00	.0620	.00174	70.23	11.5	.323
60.00	.0820	.00230			

Throughout the temperature range of the determinations for a given salt, the solid phase was always distinctly crystalline. Solubilities at higher temperatures were not attempted because the solution became so viscous that equilibrium was doubtful. Slightly above the highest temperature reported the crystalline solid changed to a translucent gel-like phase, which dissolved only very slowly.

Murray and Hartley[11] have given some solubility data for a number of salts of hexadecyl sulfonic acid. Their method of determination was simply to observe the clarification point upon slowly heating a known mixture of salt and water. Their curve for sodium hexadecyl sulfonate, which is reproduced in Fig. 2, is not in good agreement with the data of this investigation.

The only other work that seems to be available in the literature on the solubility of these salts is that by Reed and Tartar.[2] They present data for the calcium, magnesium and sodium salts of the higher alkyl sulfonates at 25 and 60°. A comparison of values for the sodium salts with those of this work shows theirs to be consistently higher. As their method of determination was simply to approach equilibrium from the supersaturated solution, with occasional shaking, this difference is not surprising in view of the difficulty of attaining equilibrium.
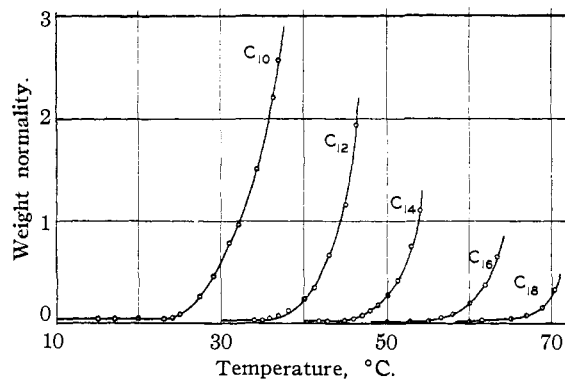

Fig. 1.—Solubilities of the sodium salts of the higher alkyl sulfonates: C_{10} refers to sodium decyl sulfonate, C_{12} to sodium dodecyl sulfonate, etc.

The solubilities calculated to weight normalities have been plotted in Fig. 1. The curves explain the difficulty met in purifying the salts by crystallization in the usual manner. Owing to the small solubilities of all the higher alkyl sulfonates at room temperature, removal of both lower and higher homologs as impurities can only be accomplished by crystallizing and filtering between definite temperature limits determined by the solubility behavior.

Figures 2 and 3, where the low solubilities are

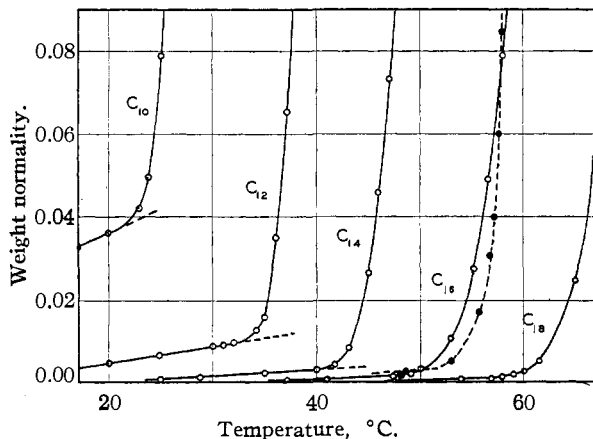(11) Murray and Hartley, *Trans. Faraday Soc.*, **31**, 183 (1935).

Fig. 2.—Solubilities of the sodium salts of the higher alkyl sulfonates showing the breaks in the curves for the lower members. Dashed curve represents Hartley's data for sodium hexadecyl sulfonate.

represented, reveal a phenomenon not evident in the more extended plot of Fig. 1. The solubilities increase as a linear function of the temperature until a critical concentration is reached. Immediately beyond this point the simple ionic species in solution must undergo some kind of aggregation, and since equilibrium must be maintained between the ionic species and the crystal phase, the effect is to increase the solubility enormously.

TABLE II

CRITICAL CONCENTRATIONS FOR SOLUBILITIES

Sodium salt of sulfonate	Crit. concn., N_w	Temp., °C.
C_{10}	0.040	22.5
C_{12}	.0098	31.5
C_{14}	.0027	39.5
C_{16}	.00105	47.5
C_{18}	.00075	57.0

In Table II the critical concentrations have been given with the corresponding temperatures. Lottermoser and Puschel[5] in their investigation of electrical conductance of solutions of the corresponding alkyl sulfates also found critical concentrations. Exact quantitative comparison cannot be made because they presented their data in the form of curves without the accompanying experimental values. An examination of the curves indicates that the breaks for the sulfates are at least approximately at the same concentrations as for the corresponding sulfonates. Their curves over a series of temperatures show that the breaks were shifted somewhat to higher concentrations with increase in temperature. They found that change in univalent cation, as
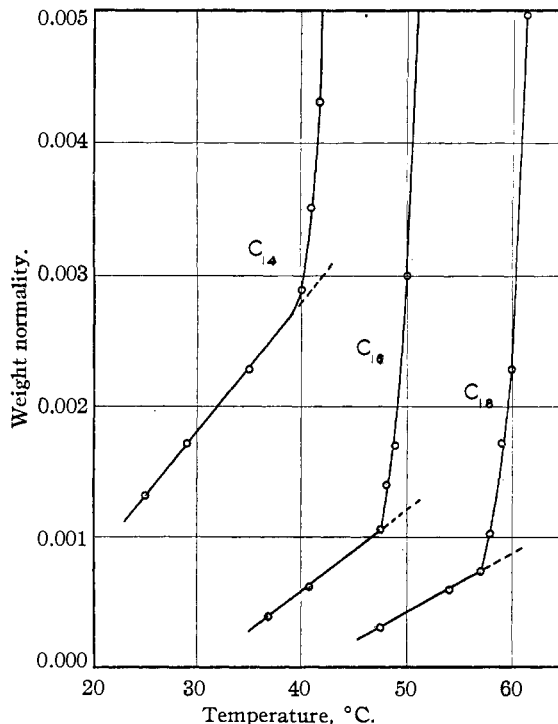

Fig. 3.—Solubilities of the sodium salts of the higher alkyl sulfonates showing the breaks in the curves for the higher members.

from sodium to silver, had no effect on the critical concentration, but that a change from univalent to bivalent cation lowered it markedly.

The sharpness of the breaks in the solubility curves is very significant in relation to the micelle theory. As they occur at critical concentrations essentially the same as for the corresponding alkyl sulfates, solutions of these two classes of salts must be similar in behavior, and any theory proposed for one should also explain the behavior of the other.

The "anionic network" theory of Howell and Robinson[9] does not offer an explanation for the solubility behavior of these sulfonates. At the dilute concentrations where the critical breaks occur, the anions are still too widely separated to have any profound influence on one another so as to affect the interchange of ions between the crystalline phase and the solution.

McBain's assumption that the solute undergoes a rapid decrease in ionization past the critical concentration is equally unsatisfactory as an explanation. Hartley[8] has in a discussion, too lengthy to be presented here, given very good reasons why the paraffin-chain salts are to be considered as strong electrolytes; at the dilution

involved here they must be practically completely ionized.

The solubility behavior can be explained most satisfactorily on the basis of micelle formation, as suggested by Hartley.[8] For the purpose of this discussion, it will be assumed the micelle consists of an aggregation of a large number of anions (say 50 to 100) with the polar ends outward in contact with the solution. Because of this envelope of hydrated polar groups the so-called solubility of the micelle is very great. Below the critical break, the solubility of the sulfonate is dependent only on the equilibrium between the simple ions and the crystalline phase, and is small as is to be expected because of the nonpolar character of the alkyl chain. The observed solubility above the critical concentration depends on the fraction of solute in micellar form, that is, on the equilibrium relationship between the micelles and the sodium and the alkyl sulfonate ions.

It will be noted from Hartley's curve for the solubility of sodium hexadecyl sulfonate given in Fig. 2 that he did not carry his solubility determinations to sufficient dilution to demonstrate the true critical break as shown in Fig. 3. From his data he concluded that "the solubility phenomenon is not so markedly critical as the conductivity break, but it emerges from the mass action calculations that this is only to be expected." In the light of the new data presented herein, it seems that certain of his conclusions will need revision. In particular, it may be reasonably questioned whether the mass action principle can be applied in its usual form to critical phenomena of the kind encountered in micelle formation.

Hydrates of Sodium Salts of the Higher Alkyl Sulfonates

These hydrates have a vapor pressure at room temperature very close to that of water and cannot be air dried without dissociation. With the exception of sodium decyl sulfonate, the hydrate crystals are small and have little mechanical strength so that they form a mushy paste with the adhering solution.

For these reasons the following method for the determination of the water of hydration was employed. A sample of the sulfonate in a shallow weighing bottle was dried in a vacuum desiccator at 70°. The open weighing bottle with the dried sample along with another bottle to serve as a tare was placed in a closed vessel, and air of a definite humidity was passed continuously over the sample until it ceased to take up water. The humidity of the air was controlled by passing it through sodium chloride solutions of the required concentration, a trap being used to catch any spray that might pass off from the solution.

The tests were conducted at room temperature (ca. 23°). Anhydrous sodium decyl sulfonate was found not to take up water of hydration at a relative humidity of 75% (corresponding to a saturated solution of sodium chloride). As there is every indication that the vapor pressure of the hydrates of the sulfonates increases for the higher members, the conclusion can be drawn that the vapor pressure for all the hydrates investigated must exceed 16 mm. of mercury.

Samples of anhydrous sodium decyl, dodecyl and tetradecyl sulfonate were subjected to air of 97% humidity and after a lapse of five days they had come to constant weight. The water gained by sodium decyl sulfonate corresponded to 3.56 molecules of water of hydration, by sodium dodecyl sulfonate to 3.45 molecules and by sodium tetradecyl sulfonate to 3.48 molecules; all three showed 3.5 molecules of water of hydration within experimental error.

To check the above results by approaching equilibrium from the opposite direction, sodium decyl sulfonate was crystallized from water in the form of well-defined crystals of the hydrate. They were drained as dry as possible, placed in a shallow weighing bottle and subjected to air of 97% humidity to remove the excess water. After constant weight was attained, the sulfonate was dried to the anhydrous state by heating in an air oven and then in a vacuum desiccator at 70°. The water of hydration thus determined corresponded to 3.50_7 molecules of water.

Samples of sodium hexadecyl and octadecyl sulfonates were tested with air of relative humidity of 97%. The former slowly gained weight over a period of three days but the latter did not. Only when air of 100% humidity was used did it begin to take up water and then only after an initial period of hysteresis of two days, showing that the presence of the hydrate phase accelerated further hydration. In ten days sodium hexadecyl sulfonate had come to constant weight, giving a value of 3.49 molecules of water. After a period of twenty-two days, sodium octadecyl

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.

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

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The study of the solubilities of the sodium salts of the higher alkyl sulfonates[2] 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[3] 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[4] and potassium laurate[5]; 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 ±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 reënforced 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

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(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).