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The Critical Concentration for Micelles in Solutions of Cetane Sulfonic Acid

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The existence of a fairly critical transition with change of concentration in solutions of some micelle-forming substances was first demonstrated by Bury and collaborators,[1] who explained the phenomenon by application of the mass-action law to the equilibrium between micelles and single ions or molecules. The critical phenomenon is strikingly apparent in the conductivity of unhydrolyzed higher paraffin chain salts, the equivalent conductivity showing a sudden fall when the concentration is increased beyond a certain value, as was first observed by Lottermoser and Püschel[2] in various salts of higher alkyl sulfuric acids and later by the author and collaborators in other salts.[3] Ekwall[4] found a sudden inflection in the equivalent conductivity–concentration curves for soaps in dilute solution, a phenomenon which has probably the same explanation, but is modified by the enhanced conductivity due to hydrolysis.[5] Murray and Hartley extended in some respects the theoretical treatment of Bury and applied it to the abnormal solubility–temperature curves of paraffin chain salts, and Murray[6] has also applied it to the surface tension data of Lottermoser and collaborators.

McBain's well-known theories of the constitution of soap solutions were based on data obtained at higher concentrations than those with which most of the work quoted above has been concerned. This work has necessitated a considerable modification of McBain's former conception of the nature of the dilute solutions, chiefly in that we now know colloidal aggregates to be formed in considerably lower concentrations than was previously thought to be the case. McBain and Betz,[7] in discussing their conductivity, f. p. and e. m. f. data on several paraffin sulfonic acids, have in part accepted the newer point of view, but they make no mention of the critical phenomenon, although such of their data as are given in detail are not inconsistent with its existence. McBain[8] now considers the "bulk of the transition from simple electrolyte to colloid" to take place between 0.05 and 0.15 N in the case of the C_{11} and C_{12} acids and at a still lower concentration in the C_{14} acid. From the results of earlier work on the C_{16} acid he previously concluded[9] that at so high a concentration as 0.1 N there was still less than 15% of the acid in colloidal form. The C_{16} acid is, however, almost certain to be more aggregated than the C_{14}.[10]

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[1] Jones and Bury, *Phil. Mag.*, **4**, 841 (1927); Grindley and Bury, *J. Chem. Soc.*, 679 (1929); Davies and Bury, *ibid.*, 2263 (1930).

[2] Lottermoser and Püschel, *Kolloid Z.*, **63**, 175 (1933).

[3] (a) Malsch and Hartley, *Z. physik. Chem.*, **170A**, 321 (1934); (b) Murray and Hartley, *Trans. Faraday Soc.*, **31**, 183 (1935); (c) Hartley, Collie and Samis, *ibid.*, **32**, 795 (1936).

[4] Ekwall, *Z. physik. Chem.*, **161**, 195 (1932).

[5] See Hartley, "Aqueous Solutions of Paraffin Chain Salts," Hermann, et Cie, Paris, France, 1936, p. 29.

[6] Murray, *Trans. Faraday Soc.*, **31**, 206 (1936).

[7] McBain and Betz, THIS JOURNAL, **57**, 1905, 1909, 1913 (1935).

[8] McBain, *ibid.*, p. 1916.

[9] See the diagrams in the "International Critical Tables," Vol. V, 1929, p. 448.

[10] Unless the difference is to be attributed to the effect of temperature, the diagram for the C_{16} acid being worked out from data at 90° and the recent work on the other acids referring to 0 and 25°. The influence of temperature is dealt with later in this paper.

The object of this paper is to present the results of a closer study than has previously been made of the conductivity in the immediate neighborhood of the critical concentration and of the influence on this concentration of changes of temperature and addition of other solutes. Since McBain (in a private communication) has suggested that the observations recorded on the critical phenomenon may have been due to incomplete solution at the higher concentrations, and Ekwall[4] made a similar suggestion with regard to his own work, particular attention has been paid to the question of reversibility.

Experimental

Cetane sulfonic acid was prepared by a modification of the method described by Murray.[11] Fifty grams of pure cetyl bromide[3c] was stirred for three hours at 60° with 1 liter of 0.5 *N* solution of caustic potash in 95% alcohol, previously saturated with hydrogen sulfide and kept saturated during the reaction. Sufficient strong hydrochloric acid was then added to drive off the hydrogen sulfide and solid iodine added till its color persisted in order to oxidize the mercaptan to the stable disulfide which is less soluble in alcohol. The mixture was cooled and filtered, the residue washed with hot water to remove salts and recrystallized from ethyl acetate, a yield of about 40 g. of disulfide melting at 54° being obtained. The disulfide was oxidized on the steam-bath with redistilled nitric acid and the product dried in a vacuum desiccator over solid caustic soda. The resulting solidified foam was recrystallized from redistilled (40–50°) petroleum. The warm solution (which goes brown if kept warm) deposits lustrous plates on cooling, but these are impossible to remove by filtration. Accordingly the warm solution was placed in warmed centrifuge cups and allowed to cool during centrifuging. A hard crust of crystals was obtained from which the mother liquor could be poured off fairly completely. The process was several times repeated, drying the product if necessary in between as it takes up water readily from the air and its solubility in petroleum ether may in consequence rise inconveniently high. The product, after drying *in vacuo* over anhydrous calcium chloride, was white in color and free from ash and from nitrate. It gave, however, a milky solution in hot water which became clear only if kept hot and concentrated for a long time. A clear solution, at temperatures above about 36°, was given more quickly by acid which had been fused and kept molten for some minutes, but the molten acid becomes rapidly brown.

A weighed sample of the product, which melted about 53–54°, was heated slowly in a high vacuum. It did not then melt till 74° and was found to have lost in weight by 5.8%. This is in good agreement with Noller and Gordon's[12] finding that the acids ordinarily obtained are monohydrates (theoretical loss on conversion to anhydrous form 5.5%). The fused anhydrous acid also went brown on continued heating, but without further loss of weight. Titration of a 0.01 *N* solution of the anhydrous acid with standard alkali, using brom cresol purple as indicator, gave the equivalent weight as 305 (theoretical 306). The anhydrous acid went into perfectly clear solution when kept at about 80° for three hours, initial opalescence gradually disappearing during this time, probably a similar phenomenon to that attributed by McBain and Betz to the slow solution of an anisotropic phase. Once the clear solution has been obtained, it may be allowed to form an opaque curd by cooling, but the curd, if stored in Pyrex or quartz vessels, will, no matter how old, always quickly become completely clear on warming. If stored in soft glass vessels, small crystals, presumably of alkali salt, are slowly produced and these require a higher temperature for solution. The color of the resulting solution at a concentration of *ca.* 0.3 *N* was about the same as that of *N*/300,000 methyl orange (alkaline).

As there seemed room for doubt, from the behavior described, about the purity of the resulting solution, stock solutions (*ca.* 0.01 *N*) were made up from the hydrated acid by four different methods. These stock solutions, all becoming clear above 35°, were standardized by titration with alkali and their conductivities were determined at different dilutions at 60°, the intrapolated values at two concentrations being given in Table I. Within experimental error the two different solutions gave the same results and we can conclude that no appreciable amounts of unstable impurities of a nature which might affect the conductivity are present. The concentrations as determined by titration with standard barium chloride solution (using the simultaneous disappearance of foaming power and coagulation of precipitate as end-point) agreed with those determined by alkali titration within the experimental error (±0.5%) of the former. The extrapolated value of the equivalent conductivity at infinite dilution was 543 ± 3, to which the hydrogen ion alone would, according to intrapolation of Johnston's[13] data, contribute 507. Johnston's figures however were calculated from conductivity data on the assumption that the potassium and chloride ions are equally mobile at higher temperatures. If the value of MacInnes and Longsworth[14] of 0.490 for the cation transport number in potassium chloride at 25° held good at 60°, we should have to reduce the hydrogen value to 504. The maximum probable value for the infinite dilution equivalent conductivity of the cetane sulfonate ion at 60° is thus seen to be 42. The value for the cetylpyridinium ion, which will have about the same mobility, was found[3a] to be 21 at 25°. Multiplying by the viscosity ratio, we should expect a value of 40 at 60°. There is therefore little room for the presence of other anions of higher mobility. The absence of

TABLE I

	Method of treatment of recrystallized acid	Equiv. cond. at 60° 0.0005 *N*	0.003 *N*
I	80° in air for 5 minutes	535.3	225.0
II	80° in air for 10 minutes	534.3	255.5
III	Concd. soln. at 90° for 48 hrs.	535.1	255.0
IV	Dehydrated and melted *in vacuo* at 74°	535.0	255.2

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(11) Murray, *J. Chem. Soc.*, 739 (1933).

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

(13) Johnston, *ibid.*, **31**, 1010 (1909).

(14) MacInnes and Longsworth, *Chem. Rev.*, **11**, 211 (1932).

sulfate, the most probable anion arising from oxidation of cetane sulfonic acid, was confirmed by addition of 0.1 *N* magnesium nitrate solution to an equal volume of 0.001 *N* cetane sulfonic acid, evaporation to 0.1 of the initial volume, cooling, filtering and testing the filtrate with barium chloride solution. No immediate precipitate resulted. A slight precipitate appeared slowly but similar behavior resulted when the magnesium cetane sulfonate on the filter was washed with *N* magnesium nitrate and was therefore considered due to the slight solubility of the magnesium cetane sulfonate itself. Addition of sulfate in amount equivalent to 0.3 equivalent % of the original sulfonate gave an immediate precipitate. It can be concluded that sulfate certainly is not present in greater amount than this.

Cetyl pyridinium chloride was prepared from the bromide[3c] by recrystallizing several times from hydrochloric acid and then drying the product *in vacuo* over solid caustic soda until a *ca.* 0.1 *N* solution was no longer appreciably acid to α-naphthylamine-azo-*p*-benzyltrimethylammonium nitrate[15] (*i. e.*, *p*H > 5). A 0.01 *N* solution was standardized by electrometric titration with standard silver nitrate solution (equivalent weight, found 359, calcd. for monohydrate 358).

Conductivity water, free from ammonia and collected in carbon dioxide-free air ($\kappa_{25°}$ 0.11–0.16 × 10^{-6} ohm^{-1} cm.$^{-1}$), was used throughout but no attempt was made to exclude atmospheric carbon dioxide from the conductivity cell as it is almost completely undissociated in the acid solutions examined.

Dilution was carried out by weight in a 250-cc. stoppered conical Pyrex flask. The densities of the solutions used are not appreciably different from that of water and no correction for this very small difference was made. Dilution was always made so as to have the flask nearly full and thus reduce the volume of froth formed on shaking, since otherwise considerable depletion of solute from the bulk of the solution was found to occur when dealing with very dilute solutions. All concentrations are expressed in gram equivalents per liter at the temperature studied, allowance being made for the expansion of water.

The conductivity cell used was of Jena 16 III glass, fitted with smooth platinum electrodes of about 1 cm. diameter, having a cell constant of 1.431 cm.$^{-1}$ and a capacity of about 25 cc. It was filled from the top by means of a pipet and closed by a ground stopper sunk within a protecting collar so that the cell could be placed in the thermostat with the ground neck below the level of the liquid without danger of contaminating the solution. At least three fillings at each concentration were measured and the solution heated above the temperature of the thermostat before filling to prevent formation of air bubbles on the electrodes. Water was used in all cases for the **thermostat** liquid, but for work at 60 and 80° was covered with a layer of paraffin oil.

Resistance measurements were made on a direct-reading Wheatstone bridge with 6-dial non-inductive decade resistance box and equal ratio, fed by a valve-oscillator giving three frequencies of about 1000, 1000 × $\sqrt{2}$ and 2000 cycles per second; detection being by tuned amplifier and telephones. The common point of the variable resistance and cell was directly earthed and error from capacitative coupling between oscillator and output coils was eliminated by commutating the leads from output coil to bridge, and taking the mean of the readings. Error due to non-ideal capacity between the leads to the cell was determined by calibration with a standard resistance box in the cell position. Error in measurement of high resistances due to resistance–capacity shunts in the cell was eliminated by extrapolation against square of frequency to zero frequency. Error due to polarization in measurement of low resistances was eliminated by extrapolation against inverse square of frequency to infinite frequency. Except for the polarization error, which amounted to only 0.3% in the lowest resistances measured, the error, for a given leads system, frequency and oscillator-bridge connection, is a single-valued function of the measured resistance and so, by previous calibration, the procedure was considerably simplified.

Results and Discussion

In order to decide whether cetane sulfonic acid is behaving as a strong electrolyte in dilute solution, it is necessary to know what fall of equivalent conductivity with concentration is to be expected. Owing to the absence of reliable data for the dielectric constant of water at higher temperatures, it is not possible to apply Onsager's equations directly. The behavior must therefore be compared with that of an acid known to be strong—*e. g.*, hydrochloric acid. Data for 100°

TABLE II

EQUIVALENT CONDUCTIVITIES AT 60° IN WATER

$C \times 10^3$	λ	$\lambda_0 - A\sqrt{C}$	Difference
	HCl, $A = 250$		
0.0000	640.0	640.0	0.0
.0939	637.4	637.6	+ .2
.2791	635.8	635.8	.0
.5708	633.8	634.0	+ .2
1.0870	631.5	631.7	+ .2
2.359	628.0	627.7	− .3
3.921	624.7	624.4	− .3
	$C_{16}H_{33}SO_3H$, $A = 230$		
0.0000	543.0	543.0	0.0
.0860	540.7	540.9	+ .2
.1132	540.5	540.6	+ .1
.1928	538.9	539.8	+ .9
.3187	538.2	538.9	+ .7
.5131	534.8	537.8	+ 3.0
.7410	526.4	536.7	+ 10.3
.831	512.6	536.4	+ 23.8
.8615	499.4	536.3	+ 36.9
.970	467.8	535.8	+ 68.0
1.184	416.2	535.1	+118.9
1.450	366.7	534.2	+167.5
1.899	315.2	533.0	+217.8
2.580	273.8	531.3	+257.5
3.098	251.3	530.2	+278.9

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(15) An indicator whose color change is associated with a change from a univalent to a divalent cation and is not therefore displaced by cationic paraffin chain salts; see Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

already available[13] show that the relative fall of equivalent conductivity with concentration is not much greater than at room temperature, but no accurate measurements were available on very dilute solutions at intermediate temperatures. Accordingly measurements were made at 60°. The results of these, and of the measurements on cetane sulfonic acid (solution IV) at this temperature, are given in Table II. C is the concentration in gram equivalents per liter and λ the equivalent conductivity. In the third column are given the values calculated from the equation $\lambda = \lambda_0 - A\sqrt{C}$, λ_0 being the infinite dilution value of λ and A a constant. In the fourth column the experimental values have been subtracted from the values given by this equation.

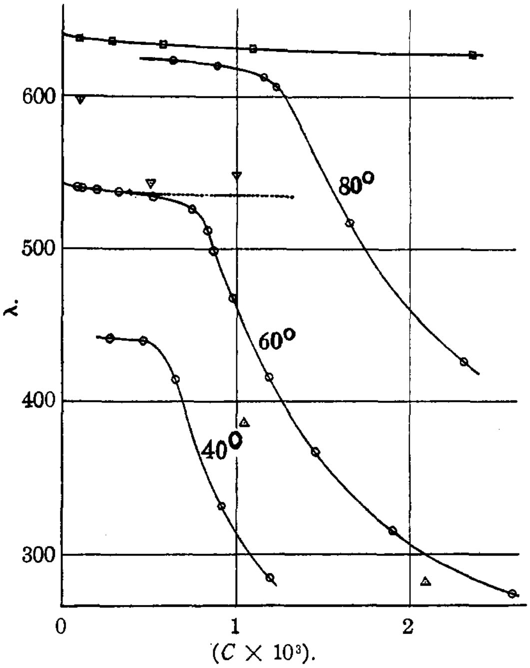

Fig. 1.—Equivalent conductivity of hydrochloric acid (□) at 60° and of cetane sulfonic acid (○) at 40, 60 and 80°. Dotted line represents approximate conductivity if cetane sulfonic acid behaved as a normal strong acid. (△), data of Reychler at 60°; (▽), data of McBain and Williams at 90°.

The data for hydrochloric acid are fitted, within the experimental error, by $\lambda_0 = 640.0$ and $A = 250$, except at the two highest concentrations. The value of λ_0 obtained by intrapolation of Johnston's[13] figures is 640.5. At 25°, where $\lambda_0 = 426$, Onsager's formulas give $A = 157$. A/λ_0 is thus, as expected, slightly greater at 60 than at 25°. It was assumed that the ratio of A for cetane sulfonic acid to A for hydrochloric acid would be the same at 60 as at 25°. Taking λ_0 for cetane sulfonic acid at 25° to be 371, we obtain $A = 144$, and therefore, at 60°, $A = 230$. Below 0.0003 N, the agreement is within the experimental error. At 0.0005 N the observed conductivity is appreciably smaller. At 0.00074 N the deviation amounts to 2% of the whole conductivity, increases to about 12% for a further increase of 30% in concentration, and is no less than 30% at twice this concentration. This behavior, almost equivalent to a sudden change of direction of the λ–c curve at about 0.0008 N, is to be expected if the deviation is due to the formation only of fairly large aggregates. That association is playing a considerable part in these low concentrations is now recognized by McBain, but his conclusion that, in sufficiently dilute solution, the behavior is that of a "simple partially dissociated electrolyte" could only be maintained if there were a range of concentration in which the deviation is proportional to concentration. The effect of aggregation extends to too low a concentration for it to be possible to separate a deviation proportional to the first power of concentration from that proportional (when small) to a much higher power. It is improbable that, in the lower sulfonic acids examined by McBain and Betz, it would be any more simple to separate these effects, because, although the region of great deviation is displaced to higher concentrations, it will also spread over a greater range of concentration, both absolutely, and, owing to the micelles being smaller, relatively. The experimental points of McBain and Betz are, in any case, insufficiently close together in the dilute solutions for this separation to be attempted.

That there is an appreciable formation of covalent acid, except in the aggregates, is extremely improbable from theoretical considerations[5] (p. 17). An experimental test was made by examining the behavior in a solvent appreciably less polar than water, namely, a mixture of glycerol and water. Simple dissociation will certainly be less complete than in water. Aggregation will probably also be less, since the solvent will have less tendency to expel the paraffin chains from solution. The conditions will therefore be more favorable for a separation of the two effects. It was found that the λ–C curve is of the same form as in water, but the critical concentration is increased some three times. Below

0.002 *N*, however, cetane sulfonic acid in the glycerol–water mixture is as strong as hydrochloric acid, *and apparently stronger than in water.* Since the solvent (water diluted to twice its volume at room temperature with ordinary "pure" glycerol, containing *ca.* 56.3% by weight of glycerol) had a considerable residual conductivity (17.1 ohm^{-1} cm.$^{-1}$ at 60°), the procedure adopted was to subtract the value of κ/C (*i. e.*, the equivalent conductivity without correction for solvent conductivity) for cetane sulfonic acid from that for hydrochloric acid at the same concentration. If the two acids have, at the same concentration, the same effect on the solvent conductivity,[16] this difference will be equal to that of the corrected λ values. The data are given in Table III and the difference plotted against concentration in Fig. 2.

TABLE III

EQUIVALENT CONDUCTIVITY OF CETANE SULFONIC ACID IN 56.3% GLYCEROL AT 60°

HCl		$C_{16}H_{33}SO_3H$			
C × 10³	κ/C	$C \times 10^3$	κ/C	κ/C for HCl	Diff.
5.615	180.8	5.886	96.6	181.4	84.8
5.590	180.9	5.870	96.8	181.4	84.6
3.460	182.4	4.490	112.7	181.7	69.0
2.150	183.9	3.394	132.6	182.4	49.8
1.374	186.4	2.964	142.3	182.9	40.6
1.135	187.8	2.486	151.6	183.3	31.7
0.422	202.4	1.800	156.1	183.8	27.7
.275	220.0	1.391	158.8	186.3	27.5
		0.665	166.7	194	27
		.332	182.9	210	27

Quite different is the effect of another nonelectrolyte, *n*-amyl alcohol, which, unlike glycerol, has a highly unsymmetrical distribution of affinity and will therefore tend to be sorbed by the aggregates and so, in sufficient concentration, will facilitate their formation. The concentration may be kept too low for there to be any possible effect on the unaggregated acid. In this case the additional solute was used at a constant concentration with respect to the cetane sulfonic acid, dilution being by addition of water only. The data are given in Table IV and plotted in Fig. 2. It will be seen that the effect is, as expected, to lower the critical concentration.[17]

The critical concentration is also lowered by the presence of another strong acid. In Table IV are given the results of measurements on a solution containing hydrochloric acid in about the same concentration as cetane sulfonic acid and on dilutions of this solution with water. From the observed conductivity was subtracted the product of the concentration of hydrochloric acid by its equivalent conductivity in a pure solution of concentration equal to the total acid concentration of the mixture. The quantity λ is the quotient of this difference by the cetane sulfonic acid concentration and is plotted in Fig. 2. The critical concentration of sulfonate[18] in this mixture is lower than in pure

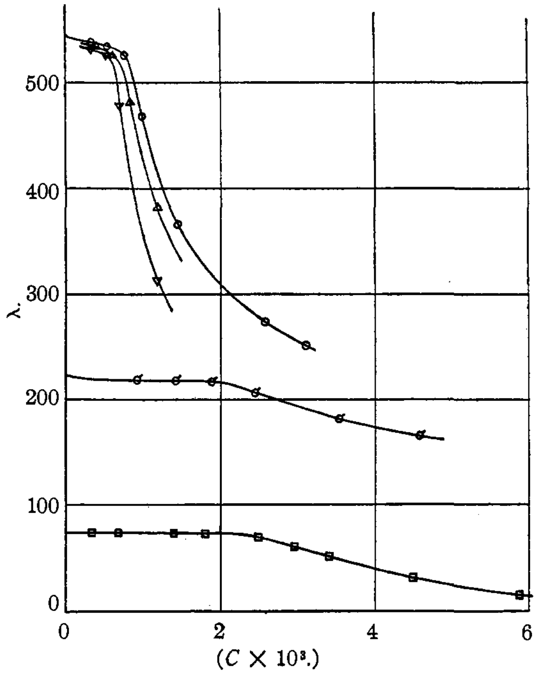

Fig. 2.—Equivalent conductivity of cetane sulfonic acid at 60°: (○), in water; (△), in dilute aqueous amyl alcohol; (▽), in dilute aqueous hydrochloric acid; (□), $\lambda_{C_{16}H_{33}SO_3H} - \lambda_{HCl} + 100$ in glycerol–water mixture. Also, (○-), equivalent conductivity of cetyl pyridinium chloride at 80° in water.

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[16] This is due *mainly* to a weak acid, as the λ values obtained by subtracting the whole conductivity of the solvent are too low in low concentrations, but not *entirely*, as κ/C curves sharply upward. The two acids will certainly have nearly the same effect below the critical concentration and above it the correction is in any case small.

[17] It is possibly this effect which may be responsible for the data obtained by Reychler [*Bull. soc. chim. Belg.*, **27**, 113 (1913)] being consistently lower than mine, as is seen in Fig. 1. Reychler's final stage of preparation was the evaporation of an alcoholic solution and his product (which was in any case only 90% pure) may have contained some ethyl ester, which, being far more absorbable than amyl alcohol, might have a profound influence on the conductivity when present in even small amount. The data for dilute solutions of McBain and Williams [THIS JOURNAL, **55**, 2250 (1933)] at 90° are also obviously not in agreement with mine, but their internal consistency is obviously not good. The neutralization by glass mentioned below may have played a part. The work here described was repeated on the other three solutions with results agreeing everywhere to within 0.5%. A measurement by Mr. C. S. Samis on solution III at a concentration of 0.02 *N* was in good agreement with McBain and Williams' data, if the latter's value at 0.047 *N* is set aside as being a misprint or otherwise in error.

[18] This result is not in conflict with that of McBain and Searles [*J. Phys. Chem.*, **40**, 493 (1936)], who found that the conductivity

cetane sulfonic acid solution, but that of total acid is greater, as is to be expected if the aggregates, primarily of cetane sulfonate ions, are partly neutralized by hydrogen ions, attached either electrostatically or by covalent linkage or even only forming a close "atmosphere."

TABLE IV

EQUIVALENT CONDUCTIVITY OF CETANE SULFONIC ACID AT 60° IN WATER IN PRESENCE OF HYDROCHLORIC ACID AND AMYL ALCOHOL

Concn. $C_5H_{11}OH$ = 8.4 × concn. $C_{16}H_{33}SO_3H$		Concn. HCl = 0.958 × concn. $C_{16}H_{33}SO_3H$			
$C \times 10^3$	λ	$C \times 10^3$	$\kappa \times 10^6$	λ_{HCl}	λ
0.000	543.0	0.000			543
.398	534.8	.306	348.7	636.6	532
.597	525.7	.511	577.8	631.8	526
.817	482.4	.680	735.2	630.7	478
1.180	382.6	1.172	1073.4	628.1	313

Measurements were also made on cetane sulfonic acid at 40 and 80° (Table V, Fig. 1) and on cetyl pyridinium chloride at 80° (Table V, Fig. 2). The curves for cetane sulfonic acid at the three temperatures are very similar. The critical concentration at 80° is about 1.5 times that at 60°, and that at 60° is 1.3 times that at 40°. The temperature coefficient of the critical concentration therefore increases with increasing temperature in this range and is about 2% per degree at 60°. This is more than twice as great as the coefficient for the higher alkyl sulfates obtained, though with less certainty, from the data of Lottermoser and Püschel.[2] That cetane sulfonic acid is at least not unique in having this high temperature coefficient is evident from the increase in the critical concentration of cetyl pyridinium chloride from 0.0009 at 25°[3a] to 0.0022 at 80°.

TABLE V

EQUIVALENT CONDUCTIVITIES AT OTHER TEMPERATURES

$C_{16}H_{33}SO_3H$ 40°		$C_{16}H_{33}SO_3H$ 80°		$C_{16}H_{33}NC_5H_5Cl$ 80°	
$C \times 10^3$	λ	$C \times 10^3$	λ	$C \times 10^3$	λ
0.263	440.9	0.628	623.4	0.906	218.8
.454	439.3	.884	620.2	1.411	217.9
.641	414.2	1.155	612.1	1.889	216.9
.902	331.5	1.224	606.6	2.455	206.1
1.178	283.6	1.647	517.7	3.536	182.1
		2.307	426.3	4.580	164.9

That the critical phenomenon is due either to supersaturation or to incomplete solution is extremely improbable since it is equally evident at 40, 60 and 80°, while the curd form of cetane sulfonic acid gives place to a perfectly clear solution some 4° below the lowest of these temperatures. Although the clear solution has not been examined in the ultramicroscope, that of cetyl pyridinium chloride, the macroscopic crystals of which dissolve at about 18°, showed no ultramicrons, yet it has a well-defined critical concentration, even at 80° (see Fig. 2).

In cetane sulfonic acid solutions, a slow increase of resistance of the solution in the glass cell was always found, greatest at the highest temperature and amounting in the most dilute solutions examined to some 3% in twenty-four hours. This drift was not peculiar to the colloidal electrolyte, being found to almost as great an extent in hydrochloric acid. It was undoubtedly due to slow neutralization of the acid by alkali from the glass, and, in the case of cetane sulfonic acid, minute crystals of the alkali salt became visible after about forty-eight hours at 60°. The solution attained a resistance, constant except for this steady drift, within ten minutes after introduction into the cell. All the results recorded were obtained from measurements made after this time, except in the work with glycerol, when twenty minutes was allowed. A sample of one solution, kept in a quartz vessel in the thermostat for twenty-four hours, had a resistance only 0.03% less than that of a sample freshly heated from room temperature.

In the case of the neutral salt, cetyl pyridinium chloride, the glass solubility introduces no disturbing effect, and a more satisfactory test of reversibility can therefore be made. A solution of concentration about 0.0014 *N* was cooled down slowly in the cell from 80°. At about 60° a fairly abrupt increase in the rate of change of conductivity with temperature indicated that below this temperature aggregates are formed. The bath was therefore kept constant at a somewhat lower temperature, 53.7°, where aggregated and unaggregated salt must exist in comparable amount, so that the resistance would be very sensitive to changes of aggregation. The cell was then maintained at 80° for half an hour, put back into the thermostat and the resistance measured at one-minute intervals. After eight minutes the resistance had reached a value which was constant to 1 part in 6000 for the next half hour. The cell was then cooled[19] to 20°, main-

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of soaps and a simple salt with common ion were approximately simply additive, because we are here dealing with the increased degree of aggregation of the partly aggregated acid, whereas McBain and Searles are dealing, in higher concentration, with an effect on the fully aggregated soap.

(19) The cell had been almost completely filled for this experiment, and the stopper was sealed with mercury before cooling, so that solution of air was prevented, a precaution rendered necessary because air bubbles, if formed, adhere very tenaciously to the electrodes in this solution.

tained at that temperature for half an hour, put back in the thermostat and resistance readings taken as before. In eleven minutes the resistance had fallen to identically the same steady value previously reached, and decreased by only 2 parts in 6000 during the next twenty-four hours.

The high temperature coefficient of the critical concentration in cetane sulfonic acid gives rise to the existence also of a fairly definite critical temperature at one concentration. In Fig. 3 is plotted the specific conductivity of a 0.00073 *N* solution as a function of temperature, obtained by allowing the bath in which the cell was contained to cool slowly (about 10° per hour). The temperature coefficient in the range AB is the normal one (*ca.* 0.7% per degree) for a fully dissociated acid, while in the range BC it is very much greater (*ca.* 1.7% per degree). At B, aggregation commences and increases as the solution is cooled further. Once in the AB range and once in the BC range the fall of temperature was arrested and in each case the conductivity remained constant, after a slight fall as the temperature of the cell, which was of course slightly higher than that of the bath during cooling, fell to bath temperature. Quite different is the behavior when the second break, at C, occurs. Here curd fibers form slowly in the supersaturated solution. By quick cooling, values irregularly spaced below the dotted extension of the BC curve were obtained, but these fell in about half an hour to approximately constant values lying on the full line CD. It is a discontinuity of this latter type, more pronounced in the higher concentrations examined, which has been described by Reychler[20] and by Laing and McBain.[21] It is quite distinct from the break at B, which is caused by the rapid reversible formation of amicroscopic aggregates.

The formation of large aggregates in equilibrium with the simple ions is the only satisfactory explanation[22] which has been advanced of the existence of a fairly well-defined critical concentration. I have in the foregoing avoided the use of the word "micelle" as it was presumably my previous use of this word which led McBain and Betz to consider that I regarded aggregates as containing paraffin chain ions only.[23] I do not identify the aggregates formed in these dilute solutions with either the "ionic micelle" or the "neutral colloid" of McBain, as I do not believe that the separate existence of these entities is established. Evidence of a more direct nature has been put forward elsewhere,[3,5] that, just above the critical concentration, what I have there called micelles do in fact exist, and their nature has also been discussed[5] as fully as our present knowledge permits.

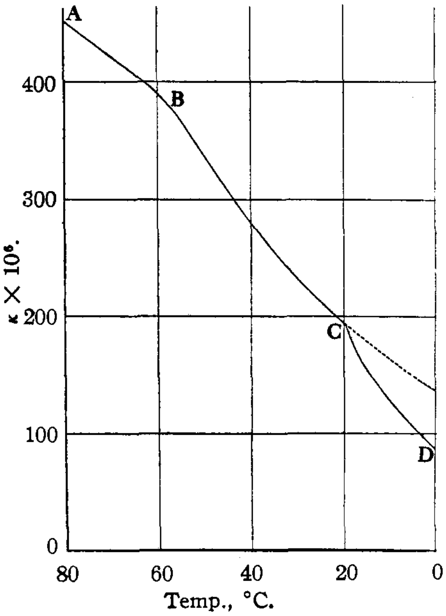

Fig. 3.—Specific conductivity of 0.00073 *N* cetane sulfonic acid on cooling.

It is reasonably certain that nearly all the paraffin chain ions in excess of the critical con-

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[20] Reychler, *Bull. soc. chim. Belg.*, **26**, 193 (1912); **27**, 113 (1913).

[21] Laing and McBain, *J. Chem. Soc.*, **117**, 1506 (1920).

[22] In a recent publication [*Proc. Roy. Soc.* (London), **155A**, 386 (1936)] Howell and Robinson have advanced an entirely different theory of the critical phenomenon. They believe that the paraffin chain ions, owing to their great "*rotational* volume," form a loose *network* which obstructs the passage of the small ions of opposite charge. They do not state how this theory can explain an *abrupt* change of properties, and the theory does not explain the observed increase of mobility of the paraffin chain ions when the critical concentration is exceeded,[3c] nor the increase of equivalent conductivity in high fields.[3c] Howell and Robinson's experimental data confirm the small temperature coefficient of the critical concentration in the case of the alkyl sulfates.

[23] McBain and Betz[7] (p. 1907) quote values for A in the equation $\lambda = \lambda_0 - A\sqrt{C}$ calculated by Mukherjee for uni-deci, and unicenti-valent electrolytes from Onsager's limiting formulas. They then combine these with the λ_0 value for the univalent acid and obtain λ values far lower than the experimental ones. They conclude that the ionic micelle does not behave as an "ordinary" polyvalent ion. Mukherjee's figures, however, were derived from formulas containing no term for the radius of the ion, and other simplifying approximations which made these formulas possible are certainly not applicable in solutions of very high-valent electrolytes in concentrations accessible to measurement. In an attempt, admittedly tentative, to estimate the real magnitude of effects of the Debye–Hückel type in colloidal electrolytes [*Trans. Faraday Soc.*, **31**, 55 (1935)], I concluded that the fall of conductivity in dilute solutions of paraffin chain salts could *not* be explained adequately in this way, and that the adherence of a considerable number of oppositely charged ions to the micelles must be assumed.

centration exist in micelles, and the concentration of single paraffin chain ions probably decreases absolutely.[24] By extrapolation of the figures given here, the critical concentration for cetane sulfonic acid at 90° will be about 0.0015 N. The aggregation will therefore be almost complete in a 0.01 N solution. According to McBain's diagram[9] it is only just appreciable at this concentration.

Summary

The critical fall of conductivity in dilute solutions of paraffin chain salts has been examined in considerable detail in the case of cetane sulfonic acid. A stable equilibrium has been shown to exist in the solution in the neighborhood of the critical concentration. The critical concentration, about 0.008 N in water at 60°, has been shown to increase with temperature by about 2% per degree. Addition of glycerol raises the critical concentration, while addition of amyl alcohol or hydrochloric acid lowers it.

The conductivity data lend no support to the belief that the acid is not a strong one in concentrations where it is not aggregated.

It is concluded that aggregation must be practically complete in a 0.01 N solution.

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[24] See refs. 3b, 5 (pp. 25–29), and, in particular, ref. 6.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Heat Capacities and Entropies of Organic Compounds. II. Thermal and Vapor Pressure Data for Tetramethylmethane from 13.22°K. to the Boiling Point. The Entropy from its Raman Spectrum

BY JOHN G. ASTON AND GEORGE H. MESSERLY[1]

The high symmetry of tetramethylmethane along with the absence of polarity makes this compound an inviting one for a comparison of the entropy calculated from its Raman spectrum and moments of inertia[2] and from calorimetric data using the third law of thermodynamics. In the present paper the necessary measurements are described and such a comparison is made.[3]

Tetramethylmethane.—The partially purified compound was kindly furnished by Dr. F. C. Whitmore and his students.[4] About 700 cc. was fractionally sublimed. The resulting material (freezing point about −23°) was twice distilled, at 370–400 mm., through an efficient glass fractionating column (packed with glass spirals) in which fractionation could be carried out in the absence of air in an all glass system.[5] The middle fraction was collected in a glass bulb. A 30-cc. middle portion was distilled from this fraction into a weighed 30-cc. sample bulb connected to the line by a ground glass joint. This sample was cooled to liquid air temperature and pumped out to less than 10^{-6} mm., melted, cooled again and repumped to remove the last traces of air.

The bulb was sealed off at a constriction below the ground glass joint and reweighed along with the joint. A correction to vacuum weights was made to ascertain the weight of tetramethylmethane. The sample bulb was equipped with a side arm closed by an inner-sealed capillary. For introduction into the calorimeter, the side arm was attached to the filling line which was evacuated to less than 10^{-5} mm. After cooling the tetramethylmethane to liquid air temperature the inner-sealed capillary was broken by a piece of iron sealed in glass and activated by a solenoid. The weight of sample was checked on removal from the apparatus. The impurity was 0.73 mole per cent. as estimated from the melting point range.

The Apparatus.—This was similar to that described by Giauque and Wiebe[6] except for details mentioned below. The calorimeter was made from 2.5-cm. copper tubing (0.025 cm. wall) and was 8 cm. long. Heat conduction was furnished by thirty-nine perforated disks (0.008 cm. thick) which made a spring fit with the walls and with a central tube, re-entrant from the bottom, which served as the well for the standard thermocouple.[7] The latter was fastened in with Wood's metal. A 3-mm. soft glass filling tube was sealed onto a short platinum tube brazed to the top. The whole was gold plated inside and out.

The calorimeter was wrapped with a gold resistance thermometer-heater (No. 40 B. and S. gage, double silk insulated annealed gold wire, containing 0.175% silver and drawn using only jewel dies). It was similar to that used by Giauque and Wiebe, except that a gap was left in the center in which a constantan resistance thermometer-heater for use below 25°K. was wound. It had a resistance at room temperature of 140 ohms, and 20 ohms at 25°K. The lower half, with a resistance of 81 ohms at room temperature, was used for heat of vaporization

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[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[2] (a) Kassel, *J. Chem. Phys.*, **3**, 115 (1935); (b) Eidinoff and Aston, *ibid.*, **3**, 379 (1935); (c) Kassel, *ibid.*, **4**, 276 (1936).

[3] For a report of the preliminary results of this comparison see Aston and Messerly, *ibid.*, **4**, 391 (1936).

[4] Whitmore and Fleming, THIS JOURNAL, **55**, 3803 (1933). These authors discuss the previous work on this compound.

[5] We wish to thank Professor J. H. Simons for the loan of the column and help in the purification.

[6] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

[7] Parks, *ibid.*, **47**, 338 (1925).