is approximately the magnitude of the two-dimensional heat of condensation.

When the transition is completed, the isosteric heat of adsorption of diborane shows a pronounced increase of 2700 cal./mole, between 94 and 100% surface coverage. The origin of this phenomenon is to be found in the chemistry of diborane, since it does not occur with xenon, methane or ethane on the same adsorbent. It can be interpreted as a surface reaction, such as polymerization, of the condensed surface layer, accompanied by an exothermic heat of reaction. The desorption hysteresis (Fig. 1) is evidently related to the surface reaction, since it occurs at the same degree of surface coverage. There is reversible adsorption–desorption equilibrium in the second layer (Fig. 1), which means that whatever the reaction taking place between the adsorbed molecules in the condensed surface phase of the first layer, it does not extend to the molecules of the second adsorbed layer. The same conclusion is also drawn from the decrease of the isosteric heats for second layer coverage ($\theta > 1$).

Exothermic polymerization of bulk diborane is not known, although molecular association in the liquid state has been reported.[12] It does not seem that the heat effect of molecular association would be marked. In the surface layer, however, the forces of molecular association would have better scope because of the enhanced availability of neighbors, and the heat effect magnified accordingly.

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Evidence for Micelle Formation in Aqueous Solutions of Sodium Salts of Benzene Sulfonic Acids Substituted in the Ring by Methyl Groups[1]

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The effects of sodium *p*-toluenesulfonate, sodium *p*-xylenesulfonate, sodium *m*-xylenesulfonate and sodium *p*-cymenesulfonate on the polarographic reduction of nitrobenzene were studied in three different buffer systems, and, in addition, the effect of sodium *p*-xylenesulfonate on the electrocapillary curve of mercury was determined in the same buffer systems. The polarographic effects observed were very similar to those which take place in the presence of colloidal electrolytes and, on the basis of this fact, it is suggested that these simple aromatic sulfonates form micellar aggregates in much the same manner as do long chain alkyl sulfonates and the more complex aromatic sulfonates. It is believed that the phenomena observed are caused by preferential adsorption of the negatively charged micelles on the surface of the dropping mercury electrode.

The sodium salts of simple substituted aromatic sulfonic acids, such as the sodium toluenesulfonates, have not usually been considered as colloidal electrolytes, although the sodium salts of the aromatic sulfonates substituted with long chain alkyl groups have definitely shown to exhibit the behavior of micellar colloidal electrolytes.[2,3] Sodium toluenesulfonate has been included in the class of substances called hydrotropes, a term which has been applied to any substance whose presence in aqueous solution enhances the solubility of another substance in the same solution. Since it was considered likely that salts such as sodium toluenesulfonate would show micellar behavior at concentrations somewhat greater than that at which conventional micelle formers show evidence of aggregation, this study was initiated in hope of obtaining polarographic evidence of such behavior.

L. Meites and T. Meites, and Colichman have shown[4,5] that critical micelle concentrations of colloidal electrolytes can be determined with the use of the polarograph by plotting the half-wave potential or diffusion current of a simple metal ion reduction against the concentration of colloidal electrolyte in solution. The pronounced discontinuities in such plots (polarographic micelle points) were shown to be comparable to critical micelle concentrations determined from surface tension data taken by the conventional DuNouy ring method. In addition, the critical micelle concentration of a colloid was shown to be identical to the maximum suppression point, the concentration of colloid which just suppressed the polarographic maximum.

In this research, polarographic micelle points, maximum suppression points and electrocapillary curve changes were measured for the polarographic reduction of nitrobenzene in aqueous solutions of sodium *p*-toluenesulfonate, sodium *p*-xylenesulfonate, sodium *m*-xylenesulfonate and sodium *p*-cymenesulfonate. The measurements were made in well-buffered solutions at three *p*H values, and the concentration of the sulfonate salt was varied over a rather wide range while the concentration of nitrobenzene was held constant at 6×10^{-4} mole per liter.

Experimental

A Sargent Model XXI polarograph was employed for all of the polarographic measurements. All initial potential and span settings were checked with an auxiliary potentiometer circuit. The cell used was a modified H-type cell described by Lingane and Laitinen[6] with a saturated calomel half-cell anode. Oxygen was removed from the test solution by the passing of oxygen-free nitrogen. All measurements were carried out at 25 ± 0.2°. A Beckman model G *p*H meter was used for all *p*H measurements.

The commercial sulfonate salts obtained from Eastman Kodak were dissolved in distilled water, the water-insoluble impurities filtered off, and the clear solutions evaporated to dryness. These products were recrystallized twice from

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[1] Taken from the Ph.D. thesis of Harold M. Hubbard, September, 1951.

[2] R. G. Paquette, E. C. Lingafelter and H. V. Tartar, THIS JOURNAL, **65**, 686 (1943).

[3] G. R. Shuck and E. C. Lingafelter, *ibid.*, **71**, 1325 (1949).

[4] L. Meites and T. Meites, *ibid.*, **73**, 177 (1951).

[5] E. L. Colichman, *ibid.*, **72**, 4036 (1950).

[6] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

absolute ethanol and dried at 110°. The Eastman nitrobenzene was distilled in a packed fractionating column, and the fraction boiling at 210–212° was collected. All the mercury used for the polarographic measurements was first sprayed through two towers, one containing a 10% sodium hydroxide solution, and the other a dilute nitric acid solution; this treatment was followed by filtration through a Bethlehem type-F mercury filter and by distillation in an all-glass mercury still.

The following buffer solutions made with reagent grade chemicals were employed: *p*H 2.5, 10 ml. of 0.4 *M* potassium dihydrogen phosphate and 15 ml. of 0.2 *M* citric acid; *p*H 7.2, 15 ml. of 0.2 *M* sodium hydroxide and 10 ml. of 0.4 *M* potassium dihydrogen phosphate; *p*H 11.0, 10 ml. of 0.2 *M* sodium hydroxide and 15 ml. of 0.4 *M* disodium hydrogen phosphate.

When a series of samples was required in order to run a concentration study, all the samples in the series were made up at the same time, and the polarograms were obtained as closely together as possible. In addition, the *p*H of each sample was measured just before a polarogram was run.

Results

The results with *p*-xylenesulfonate have been chosen to illustrate the effects produced by the sulfonate salts on the polarographic wave of nitrobenzene. All the data given here are for the first reduction step of nitrobenzene. Although the second step is present in acid solution at all sulfonate concentrations, it is so poorly defined that it is not suitable for detailed study. Figure 1 shows the change in diffusion current for the nitrobenzene wave at a *p*H of 11.0 with increasing concentration of sodium *p*-xylenesulfonate. It can be seen from Fig. 1 that as the sulfonate concentration is increased up to 0.025 mole per liter the diffusion current is unaffected. At this point the current decreases markedly until a concentration of sulfonate of 0.040 mole per liter is reached. Any further increase in the sulfonate concentration has little effect and the diffusion current again becomes constant.

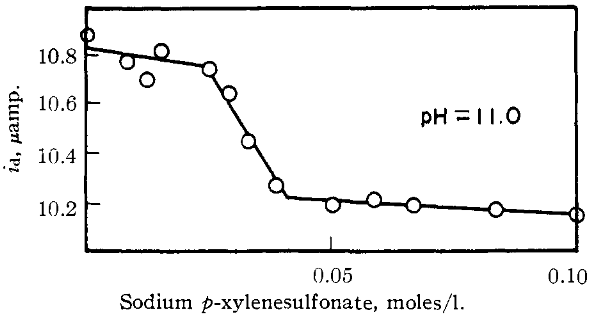

Fig. 1.—Effect of sodium *p*-xylenesulfonate on the diffusion current of nitrobenzene.

Also it was observed that the half-wave potential is dependent upon the concentration of the sulfonate salt. An inspection of Fig. 2 shows that as the concentration of sodium *p*-xylenesulfonate is increased there is a gradual shift of the half-wave potential to more negative values. A well-defined inflection point corresponding to a sulfonate concentration of 0.040 mole per liter is evident. All half-wave potentials were measured in solutions containing 0.005% gelatin, since the apparent half-wave potentials observed in the presence of a maximum have no meaning. It was previously determined, however, that the presence of 0.005% gelatin had no effect upon the value of the diffusion current for the first nitrobenzene wave, so it is believed that this constant amount of gelatin does not alter the significance of the results.

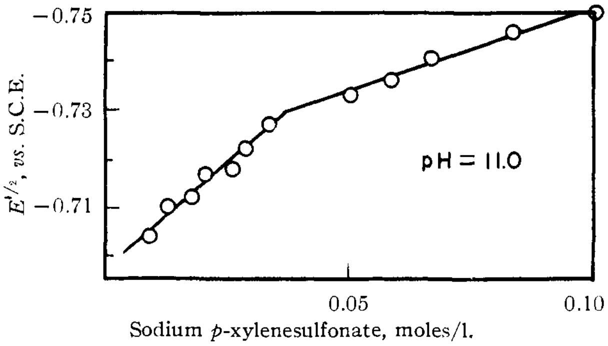

Fig. 2.—Effect of sodium *p*-xylenesulfonate on the half-wave potential of nitrobenzene.

Early in the course of this work it was noted that nitrobenzene gives no polarographic maximum in solutions containing a large excess of the sulfonate salt. Therefore, it was decided to determine the minimum concentration of sulfonate necessary to suppress the nitrobenzene maximum; this point is the maximum suppression point (M.S.P.) defined by Colichman.[5] In Fig. 3 the ratio of the maximum current to the diffusion current is plotted against the logarithm of the concentration of sodium *p*-xylenesulfonate. As the sulfonate concentration approaches the maximum suppression point, such a plot becomes linear, and the M.S.P. is determined by extrapolation to $i_m/i_d = 1$. A value of 0.028 mole per liter for the M.S.P. was determined for sodium *p*-xylenesulfonate at a *p*H of 11.0.

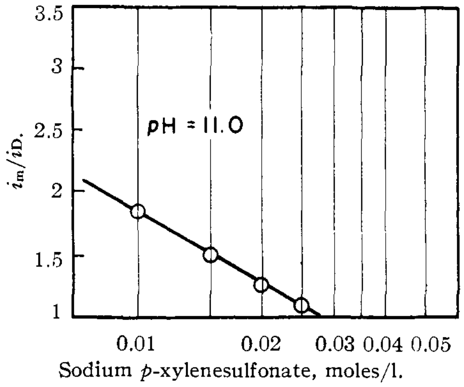

Fig. 3.—Effect of sodium *p*-xylenesulfonate on the nitrobenzene maximum.

Table I lists all the inflection points observed in the diffusion current and half-wave potential measurements with all four sulfonates in solutions buffered at three different *p*H values. Maximum suppression points are also contained in Table I. In the case of sodium *p*-cymenesulfonate no inflection point was observed in the half-wave potential–sulfonate concentration relationship in solutions of *p*H 7.2 and 11.0.

Because of the marked effect of the concentration of the sulfonate salts upon the drop time of the dropping mercury electrode, it seemed desirable to

Table I

Diffusion Current and Half-wave Potential Inflection Points and Maximum Suppression Points for Four Aromatic Sulfonates

*p*H	P.M.P.			M.S.P.
	(i_d)pt.		$(E_{1/2})$pt.	
	Sodium *p*-toluenesulfonate (moles/l.)			
2.5	0.032	0.062	0.033	0.056
7.2	.18	.22	.30	.21
11.0	.035	.070	.040	.065
	Sodium *p*-xylenesulfonate (moles/l.)			
2.5	0.030	0.045	0.06	0.055
7.2	.15	.17	.17	.16
11.0	.025	.040	.040	.028
	Sodium *m*-xylenesulfonate (moles/l.)			
2.5	0.040	0.050	0.045	0.055
7.2	.15	.30	.28	.27
11.0	.040	.060	.040	.050
	Sodium *p*-cymenesulfonate (mmoles/l.)			
2.5	0.019	0.025	0.03	0.025
7.2	1.5	1.9	[a]	1.9
11.1	0.62	0.75	[a]	0.65

[a] No inflection point was observed.

determine complete electrocapillary curves in solutions containing different amounts of sulfonate. Figure 4 shows the electrocapillary curve of mercury in solutions of *p*-xylenesulfonate buffered at a *p*H of 2.5. As would be expected, if a negatively charged particle were adsorbed on the mercury drop, the positive leg of the curve is the portion of the curve most affected by the increasing concentration of the sodium *p*-xylenesulfonate, and the electrocapillary maximum is shifted to a more negative value. The addition of 0.040 mole of sulfonate per liter materially lowers the electrocapillary curve, and for a solution which is 0.060 molar with respect to sulfonate, the curve is still lower. However, the continued addition of sulfonate has no effect, for the electrocapillary curve obtained for a solution which is 0.080 molar or above with respect to sulfonate is identical with that obtained for a 0.060 molar solution.

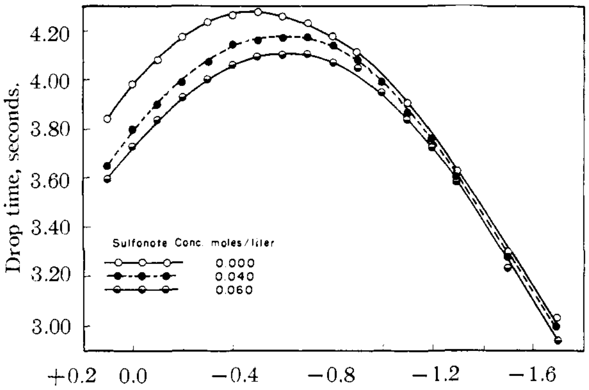

Fig. 4.—Effect of sodium *p*-xylenesulfonate on the electrocapillary curve of mercury at a *p*H of 2.5.

Discussion

In every case the values obtained for the maximum suppression points and the concentration at which discontinuities appear in the half-wave potential curves fall within or very close to the concentration range over which the decrease in diffusion current takes place. The behavior observed in the present investigation is very similar to that noted by Meites and Meites[4] and by Colichman[5] during investigations of the polarographic reduction of inorganic cations in the presence of colloidal electrolytes and non-electrolytes. For these compounds such phenomena serve to locate a point which is in good agreement with the critical micelle concentration as determined by conventional methods. It seems probable then that the effects of the simple substituted aromatic sulfonates used in this investigation on the polarographic wave of nitrobenzene are indicative of the formation of micellar aggregates by these same sulfonates. In other words, the maximum suppression point and the discontinuities which are observed in diffusion current and half-wave potential all serve to locate the same point, and that point is a critical micelle concentration of the sulfonate in question.

The initial break in the diffusion current seems to be the most reliable indication of the onset of aggregation for it is exceedingly well-defined in every case studied in the present investigation, and the point at which it occurs will be taken as the previously defined[4] P.M.P., polarographic micelle point. However, in some cases it is more satisfactory to consider the range of sulfonate concentrations bounded by the two discontinuities in diffusion current as the "critical micelle concentration range."

For some time it has been established that a great many of the more complicated aromatic sulfonates as well as many long chain sulfonates form micelles, and critical micelle concentrations have been determined for many of these compounds. McBain, Walter and Johnson[7] made conductivity, refractive index and density measurements on aqueous solutions of a homologous series of straight chain, sulfonic acids containing from 2 to 14 carbon atoms. Their data show a gradual transition from the behavior of fully dissociated electrolytes for the lowest homologs through the intermediate members to typical colloidal electrolyte behavior for the higher homologs. A similar transition might be expected in the case of an aromatic series. Lingafelter and co-workers[2,3] have obtained values for the critical micelle concentrations of sodium triisopropyl benzenesulfonate and sodium *n*-octyl benzenesulfonate in aqueous solutions of 0.063 and 0.013 molar, respectively. Since the sulfonates used in the present investigation were smaller molecules than these, the critical concentrations would be expected to be higher. The polarographic micelle points for the sodium salts of toluenesulfonic acid and xylenesulfonic acid in the buffer system corresponding to a *p*H of 7.2 are in line with this prediction since the average value obtained was about 0.16 molar. The results obtained in buffer systems corresponding to *p*H values of 2.5 and 11.0,

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[7] E. L. McBain, B. D. Walter and S. A. Johnson, This Journal, **61**, 3210 (1939).

however, are smaller than expected and are of the same order of magnitude as those quoted above for more complex sulfonates. Actually these results are not strictly comparable because the solutions used in the present investigation for the determination of the P.M.P. values contained a considerable amount of indifferent electrolytes whose presence would tend to decrease the critical concentration.

The results obtained with sodium *p*-cymenesulfonate are of an entirely different order of magnitude than those obtained with the other three sulfonate salts. It is true that the critical concentration of sodium *p*-cymenesulfonate should be lower than that of the toluene and xylenesulfonates, but the values obtained for the P.M.P. of this compound are even lower than would be reasonably expected. At *p*H values of 7.2 and 11.0, the P.M.P. values approach the critical concentrations obtained for sodium tetradecylsulfonate and sodium hexadecylsulfonate,[8] and the value obtained at a *p*H of 2.5 is even lower. However, it was checked several times in this Laboratory with the same result each time. The sodium *p*-cymenesulfonate used in this investigation was technical grade and considerable difficulty was experienced in purifying it. It may be that the P.M.P. values reported for this compound are lower than the true values because of the presence of impurities in the sample.

Throughout this paper it has been convenient to refer to the results as having been obtained at certain *p*H values, and the polarographic micelle points were observed to be much higher at a *p*H of 7.2 than at *p*H values of 2.5 and 11.0. This method of reference, although convenient, is misleading because the variable which determines the critical concentration is almost certainly not the *p*H value of the solution. Instead, the determining factors are the nature of the buffer system and the concentration of the gegen ion, that is, the ion of charge opposite to that of the micelle.

Merrill and Getty[9] have shown that at equal sodium ion concentrations, solutions of sodium chloride, sodium hydroxide, sodium ortho- or pyrophosphate, sodium tetraborate and sodium metasilicate lower the critical concentration for micelle formation in sodium laurate solutions to the same extent. This is conclusive evidence that in alkaline solutions with an anionic micelle the *p*H value does not appreciably affect the critical concentration. The effects of lanthanum chloride, barium chloride, and sodium chloride on cationic soaps such as dodecylamine hydrochloride were studied by Debye,[10] who found that the critical concentration and the micellar molecular weight were dependent only upon the concentration of chloride ion, and that the replacement of chloride ion by another univalent ion has no material effect on either the molecular weight or the critical concentration.

Both solutions used in the present investigation which were buffered at a *p*H of 7.2 contained 4 millimoles of potassium ion and 3 millimoles of sodium ion before any sulfonate was added. The solutions which were buffered at a *p*H of 11.0 contained 14 millimoles of sodium ion before the addition of any sulfonate. This difference in cation concentration is largely responsible for the differences which were observed in the critical concentrations.

It is more difficult to account for the fact that the P.M.P. value observed at a *p*H of 2.5 was lower than that observed at a *p*H of 7.2. Those solutions which were buffered at 2.5 contained only 4 millimoles of potassium ion, and 0.15 millimole of hydronium ion plus the sodium ion added with the sulfonate. Thus the acid solutions contained fewer millimoles of cation than the solutions of *p*H 7.2, and this should have had an effect on the P.M.P. opposite to that observed. It is true that in this case we are dealing with an anionic aggregate and therefore the hydronium ion concentration would be important in strongly acid solution, but the hydronium ion concentration at a *p*H of 2.5 is still comparatively small. A more promising explanation is the following. It has been shown[11] that in the presence of alcohols, critical micelle concentrations are greatly decreased. Apparently the alcohol molecules are incorporated in the micelle. It may be that something of this sort, involving a component of the buffer, citric acid, takes place here. If the citric acid molecule were oriented in the micelle in much the same way as the sulfonate ion, it should reduce the critical concentration.

It seems likely that the decrease in diffusion current and the maximum suppression effects are caused by the preferential adsorption of anionic micelles on the mercury drop. At low concentrations of sulfonate there are few micelles present in the solution and the reaction of the reducible substance at the electrode is uninhibited, but as the concentration of the sulfonate is increased, the number of micelles adsorbed on the surface of the electrode becomes appreciable, and the diffusion current decreases. Eventually a complete layer is formed around the drop, and the further addition of sulfonate has little effect on the reduction.

This explanation is strongly supported by the electrocapillary curves obtained in dilute solutions of sodium *p*-xylenesulfonate. In all three buffer systems which were employed, the positive leg of the electrocapillary curve was greatly affected by the addition of the sulfonate, and the electrocapillary maximum was shifted to more negative values. This is positive evidence of the adsorption of a negatively charged particle at the surface of the mercury drop. The addition of moderate amounts of sodium *p*-xylenesulfonate exerts a marked effect on the electrocapillary curve and, once the critical concentration is reached, additional amounts of sulfonate have no effect.

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[8] R. C. Merrill, *J. Chem. Ed.*, **27**, 312 (1950).

[9] R. C. Merrill and R. J. Getty, *J. Phys. Colloid Chem.*, **52**, 774 (1948).

[10] P. Debye, *ibid.*, **53**, 1 (1949).

[11] S. H. Herzfeld, M. L. Cohen and W. D. Harkins, *ibid.*, **54**, 271 (1950).