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ANALYSIS OF SOLUTIONS FOR SURFACE ACTIVE AGENTS

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ABSTRACT

The objective of this study was to obtain a better understanding of the behavior of surfactants in aqueous solutions at electrodes. With this understanding it should be possible to design electrochemical methods for the detection, identification, and quantitative determination of such substances. This study was concerned primarily with the influence of extraneous salts on the behavior of surface active agents when these are examined by the electrochemical technique known as tensammetry.

The tensammetric method consists essentially of the measurement of the electrical impedance of an electrochemical cell. This impedance is characteristically increased in the presence of surfactants at those potentials where the surfactants are absorbed on the electrode. At sufficiently negative and at sufficiently positive polarization, surfactants are absorbed, and at these absorption potentials, the impedance of the cell is decreased. Curves of admittance as a function of polarization of the electrode therefore usually show two tensammetric waves. The extent of surface activity is proportional to the separation between the two tensammetric waves, to the heights of these waves, and to the degree to which the impedance is increased at polarizations between the two waves.

Since tensammetric measurements can be made only in solutions of sufficiently high conductivity, the nature and effects of added salts on the result obtained is a considerable importance. In this study it was found that the salt effect is relatively unimportant when the salt concentration is not greater than approximately 0.1 m. This concentration might then be used as a standard condition for making measurements of the surfactant concentration in aqueous solution.

The applicability of the technique to the analysis of surface active agents under actual field conditions was not attempted.

KEY WORDS: Analytical techniques, tensammetry, pollutant identification, electrochemistry, surface active agents.

ANALYSIS OF SOLUTIONS FOR SURFACE ACTIVE AGENTS

RESEARCH OBJECTIVES

The following extracts from "A Ten-Year Program of Federal Water Resources Research" are relevant to the objectives of the work:

"Water Resources Research Categories

I. Nature of Water

- B. Aqueous solutions and suspensions - Study of the effects of various solutes on the properties of water; surface interactions; colloidal suspensions.

V. Water Quality Management and Protection

- A. Identification of pollutants - Techniques of identification of physical, chemical and biologic pollutants; rational measures of character and strength of wastes.

p. 27: Work reported by three agencies (Agricultural Research Service, Federal Water Pollution Control Administration, Geological Survey) is pointed to the same problem - development of satisfactory laboratory techniques for identifying pollutants in water - especially pesticides and other exotic substances present in very small amounts. Reliable methods for such analyses are urgently needed. Monitoring programs are useless if a compound cannot be reliably identified. Research on the movement of pollutants is limited without adequate means of quantitative measurement.

For each pollutant several possible analytical procedures exist. The problem is to find one which is reliable, reproducible in any laboratory, and sensitive enough to give needed quantitative results. It is almost essential that several laboratories investigate this problem, compare results and test each other's methods

p. 53: A clear necessity for proper management of water quality is the ability to detect and identify pollutants in water. Fairly adequate methods for laboratory analysis of most of the common pollutants are available, but today's technology is producing many new compounds which may find their way into streams in trace amounts. A continuing research program to develop analytical procedures for such compounds is necessary. Present research by the Agricultural Research Service, Geological Survey and the Federal Water Pollution Control Administration is directed particularly at organic pesticides, but as appropriate techniques for dealing with these compounds are found, it may be expected that new substances will have been developed. Other Federal Water Pollution Control Administration research is directed at identifying chemical, physical, and biological pollutants.

p. 65: The Federal Water Pollution Control Administration proposes to develop new methods for detecting and measuring pollutants; especially those resulting from new technology; and to develop automated instruments capable of continuously measuring a wide variety of pollutants".

Understanding of the behavior of surfactants at electrodes in aqueous solutions containing various other substances is not at present adequate for the rational design of electrochemical methods for the detection, identification, and quantitative determination of such substances; it was the objective of the present work to obtain such understanding.

It seemed likely that an electrochemical method could be advantageous. This results from the fact that substances with surface-active properties produce characteristic effects when examined by the electrochemical technique known as tensammetry,¹ and these effects are already qualitatively interpretable in terms of the extent of the surface-activity and to a certain degree in terms of the structure of the substance (e. g. , whether it is charged or uncharged, and whether it is aliphatic or aromatic in character). However, there is very little information available about the exact manner in which these effects are influenced by the presence of salts or of other surface-active substances; it is these latter effects that were to be investigated.

One of the potentially useful aspects of tensammetric-type methods is that they can be applied in ways that are either specific for a particular substance or non-specifically sensitive to the presence of any surface-active species present. Thus, monitoring of polluted waters by such a technique could show immediately whether any appreciable amount of any surface-active species is present. Moreover, successive stages of treatment of such waters could readily be monitored to show the extent to which the surface-activity

present had been decreased at each stage; in general, the method responds to the most active substance present, but techniques have been devised that point to the possibility of simultaneous determination of several surface-active substances².

It is worth noting that a great many substances are surface-active, not only in the detergents and soaps that immediately come to mind in this connection. In other words, the tensammetric method is obviously applicable where surfactants are to be determined, but it may also be applicable to the determination of other substances whose presence is undesirable for reasons other than their possibly surface-active properties. In addition, the instrumentation and technique of tensammetry is the same as that used for the analysis of oxidizable and/or reducible species by polarography with alternating currents,¹ and therefore one may envisage the possibility of a single instrument that is capable by a single technique of monitoring many of the constituents of aqueous samples. It is clearly desirable that the range of instruments required for any monitoring program be no greater than is absolutely necessary, and the principal investigator believes that the use of tensammetric-type instruments may be very useful in this connection.

PROCEDURE

The tensammetric method¹ consists essentially of the measurement of the electrical impedance of an electrochemical cell. This impedance is characteristically increased in the presence of surfactants at those potentials

where the latter are adsorbed on the electrode; at sufficiently negative and at sufficiently positive polarization, surfactants are desorbed, and at these desorption potentials, the impedance of the cell is decreased - curves of admittance as a function of polarization of the electrode therefore show usually two tensammetric waves. The extent of surface activity is proportional - though not linearly so - to the separation between the two tensammetric waves, to the heights of these waves, and to the degree to which the impedance is increased at polarizations between the two waves.

Quantitative theory of adsorption processes has considered only the interaction of surfactants with an electrode that is assumed to be clean; such theory is of very limited applicability in situations where more than a single substance is present, even though the substance be an inorganic salt that is not normally regarded as being strongly surface-active. Consequently, understanding of the behavior of surfactants in the presence of a range of other substances was best sought by a series of experiments.

It should be noted that tensammetric measurements can only be made with solutions of sufficiently high conductivity. Thus, salts may need to be added to samples that are to be analysed. The nature of salt effects is therefore of considerable importance, and formed the major aspect of the work undertaken.

RESULTS

Information was obtained about two aspects of salt effects: influence on the observed adsorptive behavior of the surfactants studied, and influence on the solubility of the surfactant since knowledge of the latter is needed for proper interpretation of adsorption parameters. Detailed results are reported below.

1. SOLUBILITY EFFECTS

Salting effects of sodium sulfate, potassium fluoride, potassium chloride, sodium perchlorate, and perchloric acid on cyclohexanol, 1-pentanol, and 1-butanol were determined by measuring the solubilities of the alcohols in the various electrolyte solutions. Solubilities were determined by color development and spectrophotometry. The relevant Setschenow parameters are reported. There was no apparent correlation between the salting effect and the dipole moment of the alcohol.

"Salting effect" refers to the increase or decrease in the activity coefficient of the alcohol in the presence of a salt; an increased coefficient corresponds to salting-out, a decreased coefficient to salting-in. The activity coefficients are related to the solubilities of the alcohol by

$$f S = f^{\circ} S^{\circ} \quad (1)$$

where S° and S are the solubilities of the alcohol in pure water and in the salt solution respectively, and f° and f are the corresponding activity coefficients. Taking the activity coefficient in pure water as unity, one obtains

$$f = S^{\circ}/S \quad (2)$$

Strictly speaking, the activity coefficient so defined refers only to a saturated solution of the alcohol. However, it is known that the variation of the activity coefficient of a nonelectrolyte with changing concentration of the nonelectrolyte is small compared to the salting effect, and consequently we shall refer to the coefficient defined by equation (2) as "the" activity coefficient of the alcohol in the relevant salt solution.

Solubility determinations and calculations according to equation (2) were performed for 1-butanol, 1-pentanol and cyclohexanol in solutions of potassium fluoride, potassium chloride, sodium sulfate, sodium perchlorate, and perchloric acid; the concentrations of the electrolytes ranged from 0.1 M to 1.4 M. Previous workers have generally found that the logarithm of the activity coefficient of the nonelectrolyte is a linear function of the electrolyte concentration, i. e. , where C_s is the electrolyte concentration and K,

$$\log f = KC_s \quad (3)$$

the Setschenow parameter, is a constant for a given alcohol and a given electrolyte. We found this relationship to hold for all systems studied. Values of the Setschenow parameters obtained are shown in Table I.

It can be seen that the salting effect of a given electrolyte is essentially the same toward 1-pentanol and cyclohexanol (except perhaps in perchlorate solutions), whereas there is an appreciable difference with 1-butanol. The molar solubilities of the alcohols in distilled water were found to be as follows: 1-pentanol, 0.243; cyclohexanol, 0.389; 1-butanol, 1.01.

TABLE I

Electrolyte in Solution	Alcohol		
	1-pentanol	cyclohexanol	1-butanol
Na_2SO_4	0.610#	0.596#	0.561
KF	0.301	0.319#	0.287
KCl	0.215	0.222	0.178
NaClO_4	0.14*	0.125*	0.084
HClO_4	-0.096*	-0.033*	-0.153

Three concentrations of electrolyte were used, except: *one concentration; #four concentrations.

Nonpolar nonelectrolytes have been used in recent studies of salting-out (and, more rarely, salting-in) effects. Examples are benzene³ and hydrogen⁴. However, dipole moments and salting effects observed in potassium-chloride solutions have been compared; it seemed that the extent of salting-out decreases with increasing dipole moment⁵. Apparently, no recent comparison has been made of the salting effects shown by various electrolytes toward nonelectrolytes which have large but similar dipole moments. In this respect, the values in Table 1 should be of interest: the alcohol dipole moments (in benzene, at 25°C) are:⁶ 1-butanol, $\mu = 1.63$ D; 1-pentanol, $\mu = 1.66$ D, cyclohexanol, $\mu = 1.9$ D; there is evidently no direct correlation between dipole moment and the salting effect in these systems.

EXPERIMENTAL DETAILS

Molar, 0.5 molar and 0.1 molar electrolyte solutions were saturated with an alcohol during thirty minutes of vigorous mechanical shaking with an excess of the alcohol. After shaking, the solutions were set aside for several hours (or until the aqueous layers became clear). During and after shaking the solutions remained in glass-stoppered flasks. The temperature of the solutions remained within the range (24-25°C).

Samples were prepared from the equilibrated solutions as follows:

(a) 1-pentanol (and cyclohexanol) solutions:

1 ml aliquots from 1-pentanol slns. (0.5 ml aliquots from cyclohexanol slns.) were diluted to 250 ml with distilled water. 1 ml portions of the diluted solutions were transferred to dry test tubes.

(b) 1-butanol solutions:

A microliter syringe was used to transfer 10 μ l aliquots from the saturated solutions into 1 ml volumes of distilled water in test tubes.

Precautions were taken to prevent undissolved alcohol from being transferred along with the aliquots taken from the saturated solutions.

Standard solutions of the alcohol in water were prepared volumetrically.

Samples were prepared from the standard solutions as described above.

Color was developed in each tube by a method similar to that described by Boruff⁷ for the spectrophotometric determination of fusel oil. It was necessary to modify the accepted method by lengthening the times allowed for the first two steps in the procedure, i. e., addition of the reagents to the samples. This was done in order to accommodate a large number of samples

and standards at one time. The reagents were those called for in the above reference: (I) a solution of p-dimethylaminobenzaldehyde (1 g/100 ml) in dilute (approximately 5%) sulfuric acid and (II) concentrated sulfuric acid; they were added to the tubes in the prescribed order and amounts. The p-dimethylaminobenzaldehyde was supplied by Eastman Organic Chemicals; reagent-grade sulfuric acid was used. The tubes were cooled in an ice bath before and during addition of the reagents. Color development was then accomplished by immersing each of the tubes in a boiling water bath for a timed interval (1-pentanol and cyclohexanol, 20 minutes; 1-butanol, 30 minutes). At the end of this period, each tube was transferred to an ice bath and, afterwards, returned to room temperature.

Percent transmittance of each developed solution was measured at 535 millimicrons, using a Spectronic 20 spectrophotometer. Preliminary tests indicated obedience to Beer's law despite the modifications already mentioned.

The percent transmittance values for standards were plotted on semi-log graph paper versus alcohol concentration. The line of best fit was drawn and the alcohol concentration in the saturated solutions was found by graphical interpolation.

Due to dilution of the electrolyte solutions by dissolved alcohol, it was necessary to correct the original values of the electrolyte molarity. Experiments with 1-butanol and cyclohexanol indicated that the solutions were

diluted by a volume approximately equal to the volume of alcohol dissolved. Exact dilution factors were not determined because saturation of the solutions could be obtained only after extensive shaking. Instead, the factor $(100-s)/100$, was multiplied by the original electrolyte concentrations, where s is the volume of alcohol dissolved in 100 ml of alcohol-electrolyte-water solution.

2. ADSORPTION MEASUREMENTS

In virtually all studies of the adsorption of surfactants at electrodes, attention has been focused on the properties of the surfactant itself. The process involved, however, is actually the displacement of water and of the ions of the background electrolyte, so that properties of the latter should be taken into account. The role of water has recently been emphasized by Bockris and his co-workers⁸. The influence of the supporting electrolyte has been briefly mentioned in a number of studies, but the only attempts at systematic investigation appear to be those of Breyer and Hacobian⁹ and of Damaskin et al.¹⁰. It soon became apparent that, before the competitive adsorption of surfactants and ions could be quantitatively investigated, it would be necessary to take into account the salting effect on the surfactant of the various electrolytes. Results illustrating this point are reported here.

Region of surfactant adsorption

Usually, the difference in potentials of the tensammetric waves - the wavespread - increases with increasing concentration of surfactant⁶. The wavespread might therefore be used as a measure of adsorbability in comparing different surfactants and supporting electrolytes. This procedure is more

advantageous than measuring changes in the peak potential of either wave, since the individual potentials are affected by the liquid-junction potentials. The utility of the wavespread as a criterion was investigated by examining the effects of various electrolytes, at different concentrations, on the behavior of n-amyyl alcohol (Table 2).

The wavespread was found to be unaffected by the frequency of the alternating current (40 Hz-4 kHz). The magnitude decreased as the electrolyte concentration (KF or KCl) increased, in accordance with the idea that electrolyte and surfactant are competitively adsorbed. However, in sodium sulfate solutions the opposite effect was observed in solutions not saturated with the alcohol. Clearly, two effects are present: salting out of the alcohol by the salt, and competitive adsorption of electrolyte and surfactant. The former effect outweighs the latter with sodium sulfate, but not with potassium chloride or fluoride.

TABLE II

TENSAMMETRIC WAVESPREAD AND CONCENTRATION OF AMYLL ALCOHOL

Concentration Salt Solution	Salt Soln.					
	KF		Na ₂ SO ₄		KCl	
	0.1M (mV)	1M	0.1M (mV)	1M	0.1M (mV)	1M
0.01	810	770	740	920	620	550
0.02	1033	954	903	1078	788	745
0.03	1100	1070	990	1170	900	860
0.04	1218	1154	1071	1211	950	902
0.05	1270	1210	1120	1220	1020	960
satd.	1577	1420	1436	1315	1463	1345

Results in Table II can be converted to results as constant activity of n-amyyl alcohol by using the ratio of alcohol concentration to the saturation concentration for each salt solution. Table III shows that the "anomaly" in sulfate solutions then disappears - the wavespread at constant activity of alcohol always decreases as the concentration of sulfate increases (changes in the activity coefficient of the alcohol with changing concentration of alcohol are neglected here; such changes are much less than the salting effects⁵).

TABLE III
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 TENSAMMETRIC WAVESPREAD AND ACTIVITY OF AMYLL ALCOHOL

Activity of alcohol	Salt soln.					
	KF		Na ₂ SO ₄		KCl	
	0.1M (mV)	1M	0.1M (mV)	1M	0.1M (mV)	1M
0.079	986	757	858	748	768	606
0.143	1132	914	988	876	908	748
0.224	1254	1038	1098	979	1020	862
0.316	1342	1132	1178	1056	1105	948
1.0	1577	1420	1436	1315	1463	1345

Measurements of the decrease in double-layer capacity near the point of zero charge showed that, in the systems studied, adsorption closely followed the Frumkin isotherm¹¹

$$B_c = \frac{\Theta}{1 - \Theta} \exp(-2a \Theta) \quad (4)$$

where B is an adsorption coefficient, c the concentration of surfactant in the solution, a an interaction parameter, and Θ the fraction of surface covered.

The latter was obtained by the approximation that

$$C_{dl} = (1 - \Theta) C_o + \Theta C_s \quad (5)$$

where C_{dl} is the observed capacity and C_o , C_s are the capacities for $\Theta = 0$ and $\Theta = 1$, respectively.

Values of B are shown in Table IV. Once again, there are anomalies in that B apparently increases as the electrolyte concentration increases. To allow for activity changes, one can use a different adsorption coefficient, B_a , defined by

$$B_a = \frac{S}{S_o} B \quad (6)$$

TABLE IV
ADSORPTION COEFFICIENTS OF AMYL ALCOHOL

Salt soln.	B(see eqn. (1)) ^a (1/mole ⁻¹)	B_a (see eqn. (3)) (1/mole ⁻¹)
0.1 M KF	37.0	34.3
1 M KF	60.9	30.1
0.1 M Na ₂ SO ₄	64.1	55.4
1 M Na ₂ SO ₄	147	35.5
0.1 M KCl	34.8	32.5
1 M KCl	18.9	11.5

^aAll values of B were obtained from measurements at -0.5 V vs. SCE. The qualitative trend was the same as at -0.45 V and at -0.55 V.

where S is the solubility of the alcohol in the given salt solution and S_0 its solubility in water. Results in Table IV show that B_a values decrease as the salt concentration increases, as would be expected.

Thus, apparently anomalous results are obtained when one seeks to compare the adsorptive effects of amyl alcohol and of various electrolytes, if allowance is not made for salting effects. The corrected data do not, however, provide a straightforward measure of adsorbability; for instance, the largest wavespread (0.1 M KF, Table III) is not found in the same system as the largest value of the adsorption coefficient (in 0.1 M Na_2SO_4 , Table IV). Indeed, one would not expect otherwise in view of the change of specific adsorbability of anions with changes in the electrode potential.

CONCLUSIONS

Salt effects are relatively unimportant when the salt concentration is $\sim 0.1\text{M}$. Such a concentration still is sufficiently highly conductive for tensammetric measurements, and therefore a technique for determining surfactants in aqueous solution might well use as standard conditions, making the sample 0.1 M in a particular salt before the measurement is made.

The applicability of the technique now needs to be assessed by field work, using samples that are known to - and others that may or may not - contain surface-active constituents.

Fundamental work is also needed to establish guidelines for situations where several surfactants are present simultaneously.

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