

strongly for the unimolecularity of the decomposition,⁷ especially in light of the large differences in the fate of the *t*-butoxy radicals. There is a slight trend of *k* with concentration (Table II), but this variation is no greater than that exhibited by the decomposition of nitrogen pentoxide in carbon tetrachloride.⁸

TABLE II

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE IN CUMENE
Temp. 135.0 ± 0.1 °

Initial concentration (moles/kg. soln.)	<i>k</i> × 10 ^{3a} (sec. ⁻¹)
0.455	4.9 ± 0.4
0.799	5.2 ± .1
1.62	5.0 ± .2
2.35	5.7 ± .4

^a Calculated from data for the first 50% decomposition.

The regular behavior in tri-*n*-butylamine is especially interesting in view of Nozaki and Bartlett's^{3,9} finding of explosive reactions of benzoyl peroxide in nitrogen-containing solvents. Di-*t*-butyl peroxide does not behave as an oxidizing agent in the usual sense of the expression.

(7) For comparison with the thermal decomposition of N₂O₅ in various solvents, see F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, pp. 100-107.

(8) Eyring and Daniels, *THIS JOURNAL*, **52**, 1472 (1930).

(9) Also private communication from Dr. Nozaki.

The trends in the stoichiometries enable one to calculate roughly the differences in the activation energies of the steps 2 and 3a. The values of ($E_{3a} - E_2$) are *ca.* 16 kcal. for cumene and 11 for *t*-butylbenzene. It should be mentioned that calculation shows that step 3a is endothermic to the extent of *ca.* 5 kcal.

Acknowledgment.—The authors wish to thank Mr. William R. Harp and Dr. Robert S. Rasmussen of the Spectroscopic Department of this Company for their extensive coöperation, without which the analytical procedures would have been far more complicated and less accurate. Thanks are also due Mr. Charles E. Fuller and Miss Betty J. Benell for their assistance.

Summary

The small variation in the first order rates of decomposition of di-*t*-butyl peroxide in cumene, *t*-butylbenzene and tri-*n*-butylamine solution and in the vapor state is strong evidence that the same process is rate-determining in all cases. This is thought to be unimolecular scission of the peroxy-oxygen linkage. With increasing temperature the *t*-butoxy radicals become more subject to loss of methyl rather than abstraction of hydrogen from solvent molecules.

EMERYVILLE 8, CALIFORNIA RECEIVED OCTOBER 6, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Effect of Salts on the Solubilization of Insoluble Organic Liquids by Cetylpyridinium Chloride

BY PAUL H. RICHARDS AND JAMES W. MCBAIN

Solutions of colloidal electrolytes and of similar non-electrolytic detergents have the power of dissolving otherwise insoluble substances by putting them into or upon the colloidal micelles of the detergent. Salts promote the formation of colloidal micelles of the detergent. Salts promote the formation of colloidal micelles and probably change even their sizes and relative proportions. Therefore they also affect solubilization. Heretofore¹⁻⁶ salts have always been reported to enhance solubilization, as well as produce it in solutions of detergents otherwise too dilute to contain colloidal particles.

Materials.—The detergents used in these experiments were cetylpyridinium chloride, obtained in very pure form through the courtesy of Wm. S. Merrell Company, Emulsol 607L (Emulsol Corporation), and Triton X-100 (Röhm

and Haas); compare previous publications using these detergents.^{3,5,7} The relative effects of a number of detergents with a series of insoluble organic liquids has already been reported.⁷

The organic compounds used were benzene (Kahlbaum "K," thiophene free), *n*-octane (Eastman Kodak Co.) and *n*-octyl alcohol (Eastman Kodak), as well as others previously referred to.⁷ The salts employed in the investigation were Kahlbaum sodium and potassium chloride "zur Analyse."

Method.—The method of determining the solubilization of the organic compound by the detergent has been fully described.⁷ The turbidimeter was used to detect the saturation or inflection point where solubilization in the clear solution was complete, and any excess of organic liquid began to appear as emulsified droplets. The solutions were shaken in a thermostat maintained at 25° for from ten to twenty hours before readings were taken. The solutions of the detergent and of the salts were prepared at double the desired concentration and 5 cc. of each solution was pipetted

(1) Hartley, *J. Chem. Soc.*, 1968 (1938).

(2) McBain, Merrell and Vinograd, *THIS JOURNAL*, **63**, 675 (1941).

(3) McBain and Merrill, *Ind. Eng. Chem.*, **34**, 915 (1942).

(4) McBain, in "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, pp. 129, 131.

(5) McBain and Green, *THIS JOURNAL*, **68**, 1731 (1946).

(6) McBain, Wilder and Merrill, *J. Phys. Chem.*, **52**, 12 (1948).

(7) McBain and Richards, *Ind. Eng. Chem.*, **38**, 642 (1946).

into the reacting bottle to make up a 10 cc. solution of the desired concentration.

As in the previous work, the results were expressed in terms of mole to mole ratio, that is, moles of the organic material solubilized per mole of detergent. The sources of error were the same as previously described. All normalities are volume normalities, N_v .

Results

The initial experiment was to prepare a solution that was 0.1 N in respect to the detergent and 1 N in respect to sodium chloride. It was found that in a few minutes the detergent was precipitated from the solution. This "salting out" of the detergent did not occur when dilute solutions of the salt were used; it began between 0.25 N and 0.5 N sodium chloride with 0.1 N cetylpyridinium chloride. Salting out of detergent depends on its concentration as well as upon that of the salt.⁸ Instead of discarding this precipitated solution (1 N sodium chloride, 0.1 N cetylpyridinium chloride), a few drops of benzene were added and the solution was shaken overnight. It was found that the solution had become clear. The turbidimeter reading of this solution was identical with the reading of a 0.1 N detergent solution. This phenomenon is similar to that observed by Lawrence,⁹ who found that small amounts of water-insoluble materials cleared up cloudy soap solutions. He called the phenomenon "peptization." However, it is observed that what happens is the spontaneous formation of stable colloidal particles of detergent solubilizing the insoluble benzene, a process that proceeds with positive affinity, that is, diminution of free energy. The benzene promotes the formation of these colloidal particles of detergent which otherwise could not have gone into solution in the presence of the salt. Peptization is merely the separation and protection of aggregates of previously existing particles.

The following results all refer to the solubility of benzene in 100 cc. of aqueous solution. In 0.1 N cetylpyridinium chloride it is 1.88; this includes the small amount, 0.08 cc., molecularly dissolved, but the greater portion of the benzene, 1.8 cc., is solubilized by the detergent. In the same solution, but containing 1 N sodium chloride, 2.5 cc. was dissolved and solubilized. (However, only 0.18 cc. was required to bring the detergent into solution in this mixture. Even the filtrate from a mixture of 1 N sodium chloride and 0.1 N detergent without benzene possesses some solubilizing action because the total solubility of benzene therein was 0.26 cc.)

From the above data it is seen that once the detergent is brought back into solution by the benzene the solubilizing power of the solution with salt, 2.5 cc., exceeds that of the original solution without salt, 1.88 cc.

Table I presents the data for the solubilization

(8) McBain and Field, *J. Phys. Chem.*, **30**, 1545 (1930).

(9) Lawrence, *Trans. Faraday Soc.*, **33**, 325 (1937).

of the aliphatic hydrocarbon octane, the aromatic hydrocarbon benzene, and the polar compound octyl alcohol, with and without various additions of sodium and potassium chloride. All results for solubilization in this paper are corrected for the solubility of benzene in pure water (see Table I of ref. 7). For benzene this may be an over-correction in dilute solution because it makes the ratio moles liquid/moles detergent appear to pass through a minimum. The results of Table I are graphically presented in Fig. 1. From the figure it is seen that potassium chloride has the larger effect on the solubilization of benzene in dilute solutions of detergent, and sodium chloride at higher concentrations, but the curves cross at 0.19 N where they are therefore equal. The results also clearly show that the addition of salts increases the solubility of the hydrocarbons, but that it equally definitely, and quite strongly, depresses the solubilization of the octyl alcohol. However, in the case of benzene above a certain concentration of added salt the solubilization begins to be again depressed and there is a slight indication that a similar result might occur with octane in

TABLE I

EFFECT OF VARYING SALT CONCENTRATION ON SOLUBILIZATION OF BENZENE, OCTANE AND OCTYL ALCOHOL BY 0.1 N CETYLPYRIDINIUM CHLORIDE. N_v EQUALS VOLUME NORMALITY

N_v of salt	NaCl		KCl	
	Total in solution cc./100 cc.	Ratio mole/mole solubilized	Total in solution cc./100 cc.	Ratio mole/mole solubilized
Benzene				
0	1.88	2.03	1.88	2.03
0.0156	2.25	2.40	2.30	2.50
.03125	2.45	2.67	2.50	2.71
.0625	2.65	2.89	2.80	3.06
.125	3.05	3.34	3.40	3.74
.25	3.90	4.29	3.30	3.62
.50	3.50	3.85	2.30	2.49
1.00	2.50	2.72	2.20	2.38
Octane				
0	0.40	0.242	0.40	0.242
0.0156	.43	.261	.44	.267
.03125	.50	.304	.50	.304
.0625	.55	.335	.60	.366
.125	.63	.383	.65	.396
.25	.75	.458	.70	.427
.50	1.00	.60	.80	.488
.75	1.05	.64
1.00	1.00	.60	1.00	.60
Octyl Alcohol				
0	1.10	0.652	1.10	0.652
0.0156	1.08	.639	1.05	.619
.03125	1.06	.628	0.98	.575
.0625	0.97	.569	.90	.525
.125	.90	.515	.85	.493
.25	.80	.462	.75	.429
.50	.60	.335	.60	.335
1.00	.55	.310	.40	.208

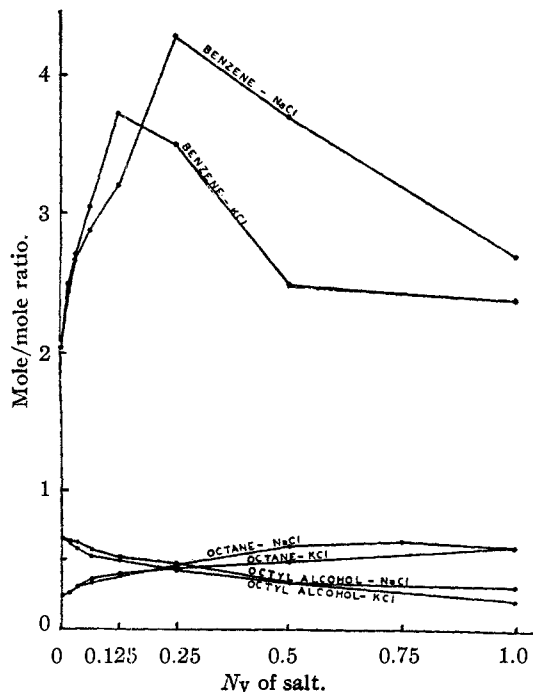


Fig. 1.—Effect of varying salt concentration on solubilization of benzene, octane and octyl alcohol by 0.1 *N* cetylpyridinium chloride.

much higher concentrations of salt, although actually only enhancement was observed.

TABLE II

EFFECT OF VARYING CONCENTRATION OF SODIUM CHLORIDE AND CETYLPYRIDINIUM CHLORIDE ON THE SOLUBILIZATION OF BENZENE, OCTANE AND OCTYL ALCOHOL

<i>N_v</i> cetyl pyr. chl.	No salt		0.125 NaCl		0.5 NaCl	
	Total in solution cc./100 cc.	Mole/ mole solubil- ized	Total in solution cc./100 cc.	Mole/ mole solubil- ized	Total in solution cc./100 cc.	Mole/ mole solubil- ized
Benzene						
0.00625	0.28	3.6		..		
.0125	.40	2.9	0.48	3.6	0.56	4.3
.025	.60	2.3	0.80	3.2	1.00	4.1
.05	.96	2.0	1.50	3.2	1.80	3.8
.1	1.88	2.0	3.05	3.2	3.50	3.7
.2	3.70	2.0	6.00	3.3	7.40	4.2
.4	8.50	2.4				
Octane						
0.0125	0.02	0.08	0.05	0.23	0.07	0.33
.025	.08	.19	.12	.29	.16	.38
.05	.20	.21	.30	.36	.40	.48
.1	.40	.24	.63	.38	1.00	.60
.2	1.00	.31	1.50	.45	1.90	.67
.4	2.50	.38				
Octyl Alcohol						
0.0125	0.18	0.56	0.12	0.26	0.08	0.04
.025	.30	.58	.26	.40	.12	.12
.05	.50	.61	.40	.42	.30	.29
.1	1.10	.65	.90	.52	.60	.34
.2	2.30	.70	1.70	.54	1.20	.37
.4	3.60	.56				

In Table II the concentration of cetylpyridinium chloride is varied and two concentrations of sodium chloride are added, and again the same effects of enhancing solubilization of the hydrocar-

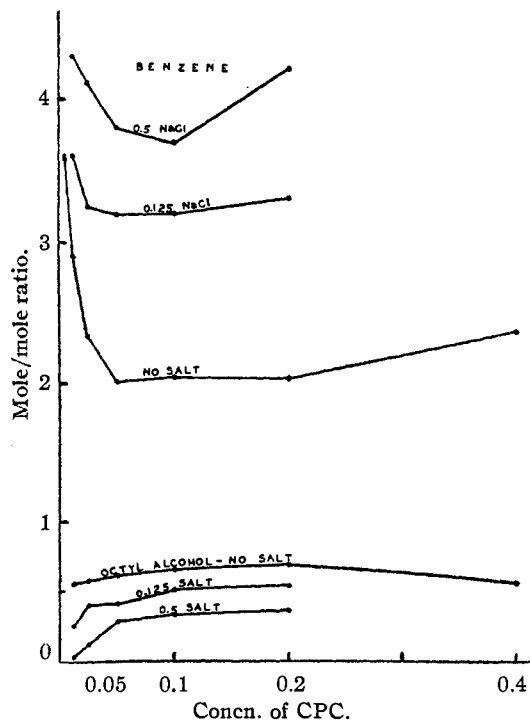


Fig. 2.—Effect of varying concentration of sodium chloride and of cetylpyridinium chloride on the solubilization of benzene and octyl alcohol.

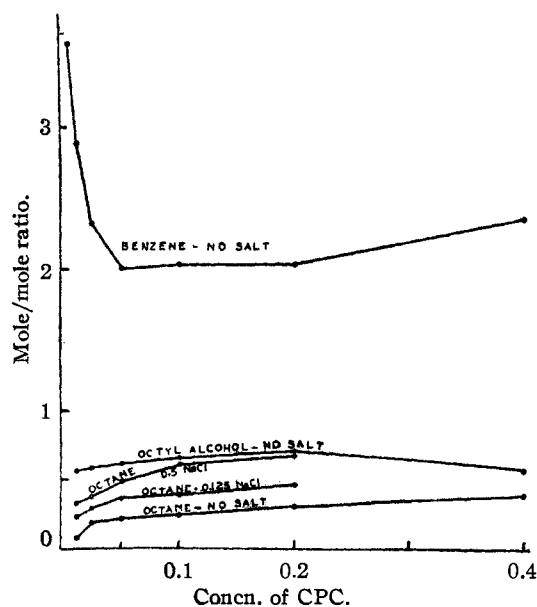


Fig. 3.—Effect of varying concentration of sodium chloride and of cetylpyridinium chloride on the solubilization of octane. Two curves from Fig. 2 are repeated for comparison.

bons, benzene and octane, but of lowering that of octyl alcohol, are noted in all cases, as appears in Figs. 2 and 3.

Discussion

In a dilute solution of detergent one can readily understand favorable effects of added salt because the salt increases the amount of colloid present, as is also shown by the decrease of the osmotic coefficient of the detergent.¹⁰ However, even in dilute solution of detergent the reduction of solubilization of octyl alcohol by added salt is in the opposite direction. It is a requirement of the mass law that in more concentrated solution practically all of the detergent (apart from Gegenions) is already in colloidal form, and the osmotic coefficient is rather increased than decreased. Hence it is clear that the added salt has changed the micelles.

One of us (J. W. M.) has long maintained that many kinds, shapes and sizes of colloidal micelles must occur simultaneously in a soap solution, the relative amounts being determined by such factors as concentration, temperature and presence of added salts or solubilized or other matter. Any manner in which ions, ion pairs or molecules of detergents can associate with a diminution of free energy (including such factors as surface energy, hydrogen bonding or cybotaxis of the solvent), will produce a micelle in competition with all other conceivable micelles of greater and less free energy. Hence, in any given solution all types and sizes of micelles must be present, their relative amounts being determined by the conditions just indicated. Hess and collaborators and McBain have elsewhere given diagrammatic sketches of numerous kinds of small micelles, including the McBain ionic micelle, which may, and probably do, occur.

In most cases of solubilization, the amount solubilized per unit amount of detergent increases from zero at zero concentration of detergent, quite appreciably before the so-called critical concentration is reached; and it rapidly grows to an approximately constant value, but finally increases rapidly again in more concentrated solution where the detergent micelles are evidently more effective solubilizers. In all examples hitherto published, salt has increased the solubilization, first in dilute solutions by producing colloid with which to solubilize, and in more concentrated solutions by promoting or stabilizing those sizes and kinds of micelles which are most effective. Wherever tested, the well known X-ray evidence has indicated that the solubilized material expands the micelles, and in the case of lamellar X-ray micelles much of the solubilized material lies between the hydrocarbon layers, completely shut away from the solvent. This is the only way in which the observed increase in long spacing has been explained.

Now, however, we have a clear case in octyl alcohol where the salts, in all concentrations of de-

tergent and of salt, *lower* the solubilization. We therefore suggest that with this polar compound, the solubilization occurs on or between the *polar* ends of the micelles that are exposed to the water. Hence the salt is now in competition with the solubilized material at the polar ends of the detergent molecules and interferes with its solubilization. Salt itself is sorbed by the micelles.¹¹

Benzaldehyde gives results similar to octyl alcohol. With 0.1 *N* cetylpyridinium chloride alone, the mole:mole ratio is 1.94, but in the presence of 0.5 *N* sodium chloride the solubilization is lowered to a mole:mole ratio of only 0.61.

Some Solubilization Data for Detergents without Salt.—The results set forth in Tables III and IV supplement (and in a few instances repeat) those previously reported.⁷ In the former investigation thirty-five organic liquids were solubilized by dodecylamine hydrochloride, sodium

TABLE III
SOLUBILIZATION BY 0.1 *N* CETYLPYRIDINIUM CHLORIDE AT 25°

Material	Total in 100 cc. solution	G. solubilized	Mole/mole ratio
Oleic acid ^a	0.22	0.19	0.065
<i>n</i> -Decane	.25	.19	.14
Octane	.4	.28	.24
<i>n</i> -Hexane	.66	.42	.49
Cyclohexane	.75	.55	.66
Xylenol	.88	.60	.49
<i>m</i> -Cresol	.96	.64	.59
<i>n</i> -Octyl alcohol	1.10	.86	.66
<i>p</i> -Xylene	1.2	1.02	.97
Ethylbenzene	1.3	1.11	1.05
Toluene ^b	1.6	1.33	1.45
Benzene ^b	1.83	1.57	2.03
Octylamine ^a	2.6	2.0	1.55
Benzaldehyde	2.24	2.06	1.94
Methyl isobutyl ketone	4.8	2.02	2.02
Methyl <i>t</i> -butyl ether	9.6	2.04	2.31

^a Reaction with octylamine observed to occur with color change; oleic acid might also react with the detergent. ^b The much lower results for benzene and toluene previously published were subsequently found to be in error owing to a wrong factor of calibration being used for the micro pipet.

TABLE IV
SOLUBILIZATION BY 0.0733 *M* TRITON X-100 AT 25° (MOLECULAR WT. 600)

Material	Total in 100 cc. solution	G. solubilized	Mole/mole ratio
<i>n</i> -Decane	0.02	0.015	0.015
Oleic acid	.04	.034	.016
Toluene	.14	.058	.086
Benzene	.16	.07	.123
<i>n</i> -Hexane	.14	.09	.14
Xylenol ^a	.16	.166	.185
<i>n</i> -Octyl alcohol	.36	.238	.245
<i>m</i> -Cresol ^a	.26	.269	.340

^a Impure, containing water.

(10) McBain and Brady, *THIS JOURNAL*, **65**, 2072 (1943).

(11) Tartar and Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).

oleate and potassium laurate, and seven of the thirty-five were solubilized by Emulsol 607L and cetylpyridinium chloride. Tables III and IV of the present paper also include solubilization of 8 additional organic liquids by a non-ionic detergent, Triton X-100. Not shown in the tables are the results of solubilization of amyl valerate and of 1-chloronitropropane by decinormal Emulsol 607L at 25°, namely: 0.44 and 1.14 cc. total in 100 cc. solution, or 0.39 and 1.40 g. solubilized, or 0.25 and 1.14 mole ratio, respectively.

The order of solubilization by the six detergents of this and the previous study is maintained for most of the forty-three organic liquids tested, with comparatively minor exceptions or specificities. The non-ionic detergent Triton X-100 is the poorest solubilizer. Next comes potassium laurate. Then come, near together, sodium oleate and Emulsol 607L (one anionic and the other cationic). Much the best are the cationic dodecylamine hydrochloride and cetylpyridinium chloride.

It may have been over-emphasized in the previous publication⁷ that high molecular weight of compounds undergoing solubilization hinders their solubilization. This is very true within any one homologous series, and it is emphasized when the volume or percentage solubilized is calculated in mole ratios. However, high molecular weight may be offset for such compounds as oleic acid by their belonging to an homologous series that is especially readily solubilized. Thus, although the mole ratio may be very small the actual volume or weight percentage solubilized may be quite comparable with that of such substances as *n*-decane.

Warren W. Woods and Dr. J. V. Robinson (Stanford Laboratories, unpublished) have found that castor oil is appreciably solubilized in lubricating oil by Aerosol OT, and similarly, sulfonated castor oil was solubilized in lubricating oil by Lead Aerosol OT.

Summary

1. Solubilization of organic liquids in solutions of the cationic detergents cetylpyridinium chloride and Emulsol 607L, and the non-ionizing Triton X-100 have been determined. The results, in general, follow the same order for different liquids as was previously described for three other detergents, dodecylamine hydrochloride, sodium oleate and potassium laurate. The non-ionic detergent Triton X-100 was the poorest solubilizer, and the best were the cationic cetylpyridinium chloride and dodecylamine hydrochloride.

2. Whereas all previous studies have shown that added salts greatly enhance solubility, and this is confirmed for the solubilization of benzene and octane by cetylpyridinium chloride, it is found that the solubilization of the polar compounds octyl alcohol and benzaldehyde is greatly depressed by the addition of sodium or potassium chloride. It is suggested that whereas with hydrocarbons and many other organic liquids solubilization occurs in the hydrocarbon portion of the micelles, with these polar compounds the solubilization occurs at the polar ends of the detergent molecules in the micelles.

STANFORD UNIVERSITY, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

The Polarographic Reduction of Gadolinium

BY SHERMAN W. RABIDEAU AND GEORGE GLOCKLER

On the basis of a dual wave obtained in the polarographic reduction of 0.01 *M* solutions of scandium, yttrium, and the rare earth sulfates without supporting electrolyte, Noddack and Brukl¹ concluded that the reduction proceeded first to the bivalent state and then to the metal. Leach and Terrey² observed a single wave in solutions of scandium chloride with 0.1 *N* potassium chloride as the supporting electrolyte. With additions of 1/6 *N* hydrochloric acid, the single wave gradually separated into two waves. The first wave was found to be due to the reduction of hydrogen ions while the second was attributed to the deposition of scandium.

Kolthoff and Lingane³ expressed doubt that the

double wave observed by Noddack and Brukl¹ corresponded in each case to the bivalent state, and suggested that it may have been caused by the discharge of hydrogen from the hydrolyzed solutions. This study was undertaken in an attempt to establish the half-wave potentials of gadolinium and to investigate polarographically the possibility of the existence of a bivalent state for this rare earth.

Experimental Procedure

The Sargent Model XX visible recording polarograph, the characteristics of which have been previously described by Lingane,⁴ was used to record the current-voltage curves. The initial and span potentials were determined potentiometrically since the voltmeters supplied with the instrument are not of the requisite accuracy. All polarograms were recorded for uniformity with the damping control in position 5. An Erlenmeyer type flask served as the electrolysis vessel when the mercury pool anode was used. An H-cell of the design described by

(1) W. Noddack and A. Brukl, *Angew. Chem.*, **50**, 362 (1937).

(2) R. H. Leach and H. Terrey, *Trans. Faraday Soc.*, **33**, 480 (1937).

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(4) Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).