[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Solubilization and the Colloidal Micelles in Soap Solution

BY J. W. MCBAIN AND K. E. JOHNSON

Solubilization is the power which even dilute aqueous solutions of soaps, detergents and other colloidal electrolytes possess of bringing into thermodynamically stable[1] colloidal solution hydrocarbons, dyes and other substances insoluble in water. The commercial importance of this phenomenon has long been known, but it is only recently that its mechanism has been established as consisting of sorption upon and incorporation within colloidal micelles.[2,3,4]

Conversely, a study of solubilization may now be utilized to throw light upon the nature of the micelles and solutions of colloidal electrolytes. The results here to be presented show that solubilization cannot be accounted for by solution in the hydrocarbon portion of the micelles, and they therefore show that assumed structures such as spherical micelles, in which this is the only mechanism so far proposed, are wholly inadequate. On the other hand, they lend further support to the conception that the solubilized material is placed in layers within the lamellar micelles.

Materials and Method

The dye and methods used were the same as those described in references 3 and 4, namely, 1-*o*-tolylazo-2-naphthol; F. D. and C. orange no. 2; Orange OT, in the form of well-developed crystals. The potassium soaps were prepared by neutralization of Kahlbaum purest fatty acids with Kahlbaum, washed, carbonate-free potassium hydroxide. These were made up in boiled-out distilled water and contained 0.4 equivalent per cent. excess of potassium hydroxide to suppress hydrolysis. Dye was added in only slight excess and the mixture was gently agitated in closed containers in a thermostat until equilibrium was reached. This required at least sixteen to twenty-four hours for more dilute solutions and from seven to ten days for more concentrated solutions of soap. When approaching equilibrium from supersaturation, much longer times were required, presumably on account of the effect of protective action upon the dye separating out. The liquid was then kept motionless in a thermostat for twenty-four hours, or until examination in a strong light showed that all dye particles had settled. Analysis was made by diluting a portion of the liquid with a mixture of acetone and water in such proportion as to keep the dye in solution, and measuring in a Klett–Summerson photoelectric colorimeter with a B-420 blue filter, calibrated against known benzene solutions of dye. The latter gave similar results to dye solubilized in aqueous Aerosol OT.

Some Results with Commercial Detergents

Data for many detergents have been published in reference 4. We may supplement these by the results in Table I.

TABLE I

THE SOLUBILIZATION IN MILLIGRAMS OF DYE PER HUNDRED CC. OF SOLUTION, MADE BY TAKING ONE GRAM OF COMMERCIAL DETERGENT IN ONE HUNDRED CC. OF WATER

Detergent	Mg. of dye	Type of detergent	Manufacturer
Aerosol 18	2.60	Disodium monosulfostearylsuccinamide, 35%, + 65% water and slight turbid impurities	American Cyanamide and Chemical Co.
Aerosol OS	3.65	Sodium isopropyl naphthalene sulfonate, 95% active alkyl naphthalene sulfonate—fairly pure	Same
Ammonium salt of Aerosol OT	1.44	Ammonium salt of dioctyl (2 ethyl hexanol) ester of sodium sulfosuccinic acid	Same
Zinc salt of Aerosol OT	6.56	Zinc salt of above	Same
Alronol (100%)	3.00	Non-electrolytic detergent with trivalent nitrogen	Alrose Chemical Co.
Alronol (90%)	3.4		Same
Nacconol NRSF	3.23	Sodium alkyl aryl sulfonate, not a sulfated fatty alcohol	National Aniline and Chemical Co.
Nopco 1067	1.17	An alkyl aromatic sulfonate	National Oil Products Co.
Nopco 1086-C	0.44	Same	Same
Orvus W. A. Flakes	3.70	Sodium lauryl sulfate	Procter and Gamble
Orvus W. A. Paste	1.85	Same	Same
Santomerse 1	1.25	Belongs to a homologous series of substituted aromatic sodium sulfonates (alkylated aryl sulfonate)	Monsanto Chemical Co.
Santomerse S	0.95	Same	Same
Sodium tetradecyl sulfate	0.13	Specially purified	E. I. du Pont de Nemours Co.
Triton W-30	0.57	A sulfonated aromatic ether alcohol	Röhm and Haas

The Solubilization of Dye in a Homologous Series of Pure Potassium Soaps Containing from Eight to Fourteen Carbon Atoms.—The lowest members of the homologous series of potassium salts of fatty acids, such as potassium acetate, propionate and butyrate, are ordinary strong electrolytes, whereas colloid appears in con-

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[1] J. W. McBain and M. E. L. McBain, THIS JOURNAL, 58, 2610 (1936).

[2] J. W. McBain, "Solubilization and other Factors in Detergent Action," Advances in Colloid Science I, 99–142, Interscience Publishers Company, Inc., New York, 1942.

[3] R. C. Merrill, Jr., and J. W. McBain, *J. Phys. Chem.*, 46, 10 (1942).

[4] J. W. McBain and R. C. Merril l Jr., *Ind. Eng. Chem.*, 34, 915 (1942).

centrated solutions of potassium hexoate, and in progressively less concentrated solutions of the higher soaps. Since solubilization of dye is a manifestation of the presence of micelles, it is of great interest to compare the solubilization of dye by various concentrations of typical homologs both to show in how far these are colloidal electrolytes, and also to throw light upon the nature of the colloidal micelles present in different concentrations of different homologs.

Measurements are therefore presented in Tables II, III, IV and V for the solubilization of Orange OT in potassium octoate, decylate, dodecylate and tetradecylate containing the added alkali sufficient to suppress hydrolysis. The results are also shown graphically in Fig. 1. To ensure attainment of the reversible equilibrium from both sides, the measurements with laurate and with myristate are approached from the side of undersaturation and also, by first heating the solution to cause more dye to dissolve, from the side of supersaturation. It is seen from the graphs how closely the corresponding values came together in the time allotted. We may therefore be sure that the true solubilization was actually measured.

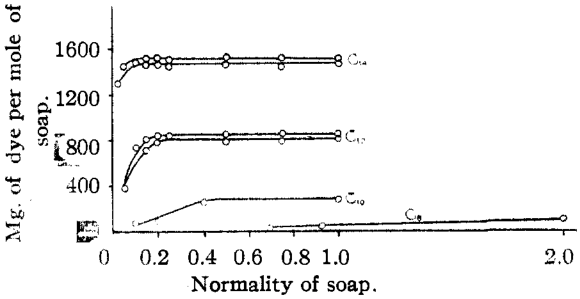

Fig. 1.—The solubility of orange OT in various molalities of aqueous solutions of a homologous series of pure potassium soaps at 25°.

TABLE II

THE SOLUBILITY OF ORANGE OT IN VARIOUS MOLALITIES OF AQUEOUS SOLUTIONS OF POTASSIUM CAPRYLATE (KC$_8$) AT 25°

	From undersaturation		From oversaturation	
m soap	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_8$	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_8$
0.700	2.73	39.0	3.18	45.4
0.924	4.90	53.0	..	..
2.00	23.0	115.2	26.7	133.7

TABLE III

THE SOLUBILITY OF ORANGE OT IN VARIOUS MOLALITIES OF AQUEOUS SOLUTIONS OF POTASSIUM CAPRATE (KC$_{10}$) AT 25°

	From undersaturation		From oversaturation	
m soap	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_{10}$	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_{10}$
0.1	1.81	181	1.49	149
.2	3.72	186	...	...
.4	10.33	258	11.26	282
1.0	29.21	292	28.98	290

TABLE IV

THE SOLUBILITY OF ORANGE OT IN VARIOUS MOLALITIES OF AQUEOUS SOLUTIONS OF POTASSIUM LAURATE (KC$_{12}$) AT 25°

	From undersaturation		From oversaturation	
m soap	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_{12}$	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_{12}$
0.05	1.94	388.0	1.95	390
.10	6.90	690	7.43	743
.15	10.74	716	12.16	811
.20	15.65	782	16.79	840
.25	20.87	835	21.03	841
.50	39.54	791	42.77	855
.75	59.59	795	65.10	868
1.00	83.15	832	85.44	854
2.00	164.5	822		

TABLE V

THE SOLUBILITY OF ORANGE OT IN VARIOUS MOLALITIES OF AQUEOUS SOLUTIONS OF POTASSIUM MYRISTATE (KC$_{14}$) AT 25°

m soap	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_{14}$	Mg. dye/ 100 cc.	Mg. dye/ mole KC$_{12}$
0.025	3.26	1306	...	..
.05	7.23	1445	7.24	1448
.10	14.87	1487	15.17	1517
.15	22.03	1468	22.73	1515
.20	29.27	1463	30.39	1520
.25	36.20	1448	37.76	1510
.50	73.09	1462	76.04	1521
.75	108.4	1445	114.1	1521
1.00	147.4	1474	152.3	1523

It will be seen from the tables and Fig. 1 that the amount of dye solubilized by one mole of each of these four successive homologs of even carbon number stand in the proportions of 1 to 2.34 to 6.77 to 12.04, when the concentration is sufficiently high to ensure full colloidality of the soap. In other words, the solubilizing power per soap molecule in a micelle increases enormously with relatively small increase in the number of carbon atoms in the molecule.

Nevertheless, the soap solutions are strictly comparable because, as Brady has shown,[5] the osmotic coefficients of all straight chain colloidal electrolytes actually coincide when they are plotted on a diagram in which the unit of concentration is in each case taken as the molality at which the osmotic coefficient, *g*, equals 0.5. The significance of these data will be discussed in a later section.

Next of interest was to ascertain the solubilizing power of equimolar solutions of laurate and myristate. The data given in Table VI and Fig. 2 show that the solubilizing power of the mixture lies not quite midway between that for the two pure soaps separately, namely, 9.09 times the solubilizing power of the caprylate.

In addition to these data for 25°, measurements at 50°, given in Table VII and plotted in Fig. 2, show the very high temperature coefficient of solubilization.

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[5] J. W. McBain and A. P. Brady, This Journal, **65**, 2072 (1943).

TABLE VI

THE SOLUBILITY OF ORANGE OT IN VARIOUS MOLALITIES OF AN EQUIMOLAR MIXTURE OF POTASSIUM LAURATE AND POTASSIUM MYRISTATE AT 25°

	From undersaturation		From oversaturation	
m soap	Mg. dye/ 100 cc.	Mg. dye/ mole soap	Mg. dye/ 100 cc.	Mg. dye/ mole soap
0.05	5.10	1019	5.17	1370
.10	10.58	1058	10.89	1519
.15	16.91	1127	17.14	1657
.20	22.58	1129	22.99	1741
.25	27.61	1105	29.21	1764
.50	55.07	1102	57.17	1746
.75	82.92	1106	84.83	1759
1.00	112.3	1123	114.2	1751

TABLE VII

SOLUBILITY OF ORANGE OT IN VARIOUS MOLALITIES OF SOAPS AT 50°

	Mg. dye/100 cc. soln.			Mg. dye/mole soap		
m soap	C_{12}	C_{12} + C_{14}	C_{14}	C_{12}	C_{12} + C_{14}	C_{14}
0.025	...	...	4.94	..	..	1796
.05	5.27	6.85	10.93	1054	1370	2185
.10	11.82	15.19	23.37	1182	1519	2337
.15	...	24.86	34.47	..	1657	2298
.20	...	34.81	46.34	..	1741	2319
.25	33.30	44.10	58.59	1332	1764	2344
.50	66.76	87.30	117.3	1335	1746	2346
.75	...	131.9	173.0	..	1759	2307
1.00	132.7	175.1	232.9	1327	1751	2329

The solubility has therefore increased between 25 and 50° to an extent corresponding to a negative heat of solubilization amounting to −3830, 3460 and 3830 calories per mole of soap for laurate, for mixture of laurate with myristate, and for myristate, respectively. These are similar to the values calculated from previous work.[3] They have the same order of magnitude as heats of solution or as heats of sorption of the van der Waals type.

The increase in temperature also has a marked effect on the concentration of soap at which the concentration necessary for full colloidality is higher at 50 than at 25°.

Solubilization and the Nature of Micelles.—Solubilization has been shown to be a property of the micelles in solutions of colloidal electrolytes. Conversely, solubilization can throw light upon the nature of these micelles.

The first micelles proposed were the spherical micelles of Reychler, McBain, and later Adam and Hartley. The radius of the spherical micelle is limited by the length of the hydrocarbon chain which is expelled from contact with the water as far as possible. Nevertheless, as Ward[6] points out, seven-tenths of the surface of a spherical micelle containing 50 soap ions of 12 carbon atoms is still hydrocarbon, even if it is assumed possible so to pack the short, thick rods, each length 15 Å., cross section 20–25 sq. Å., without interspaces.

It is an obvious suggestion that the solubilized dye merely dissolves in the hydrocarbon interior of the micelle. This accords well with the positive temperature coefficient of solubilization, and it has been adopted by Hartley in spite of some large numerical discrepancies between the amounts of dyes solubilized and their solubilities in a similar weight of hydrocarbon.

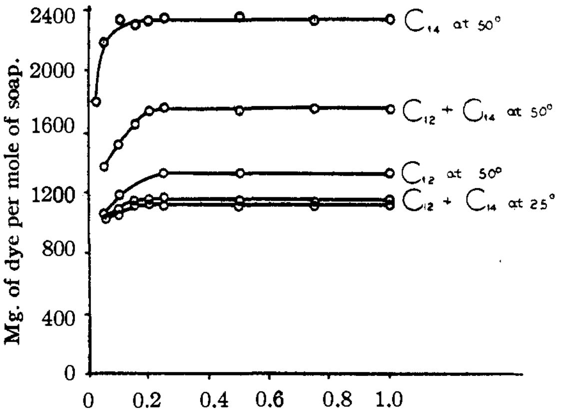

Fig. 2.—The solubility of orange OT in pure potassium soap solutions at 50° and in an equimolar mixture of potassium laurate and myristate at 25°.

The main result of the present communication is to show that the solubilization of the same dye by a homologous series of soaps changes with molecular weight in a manner which does not support the hypothesis that solubilization is solution in the hydrocarbon part of the soap. The results are expressed in milligrams of dye solubilized per mole of soap, because this allows of direct comparison with the number of CH_2 groups per molecule of soap.

The results show that for soaps containing 8, 10, 12 and 14 carbon atoms, respectively, the solubilizations are in the proportions 1:2.34:6.77:12.04.

Thus, for increases of 25, 20 and 16.7% in length of carbon chain, the increases in dye solubilized are 143.5, 190 and 79.5%, respectively. For an increase of 50% in carbon atoms from caprylate to laurate, the solubilization has increased 6.77-fold. The increments of these numbers are, in the same units, 1.34, 4.43 and 5.27 for each added pair of CH_2 groups, instead of being constant. It should be recalled that these numbers were strictly comparable because they refer to concentrations sufficiently high to ensure full colloidality in each case; likewise the numbers were constant for each soap as soon as full colloidality was reached. They are solubilization per molecule in the fully formed micelles.

The only form of micelle for which there is direct evidence is the lamellar micelle, first proposed by McBain. Several investigators[7] have

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(6) A. F. H. Ward, *Proc. Roy. Soc.* (London), **A176**, 420 (1940).

(7) P. Krishnamurti, *Indian J. Phys.*, **3**, 307 (1929); K. Hess, H. Kiessig and W. Philippoff, *Naturwissenschaften*, **26**, 184 (1938); K. Hess, W. Philippoff and H. Kiessig, *Kolloid-Z.*, **88**, 40 (1939b); H. Kiessig, *ibid.*, **98**, 213 (1942); H. Kiessig and W. Philippoff, *Naturwissenschaften*, **27**, 593 (1939); W. Philippoff and K. Hess, *Ber.*, **70**, 1808 (1937); J. Stauff, *Naturwissenschaften*, **27**, 213 (1939a); J. Stauff, *Kolloid-Z.*, **89**, 224 (1939b).

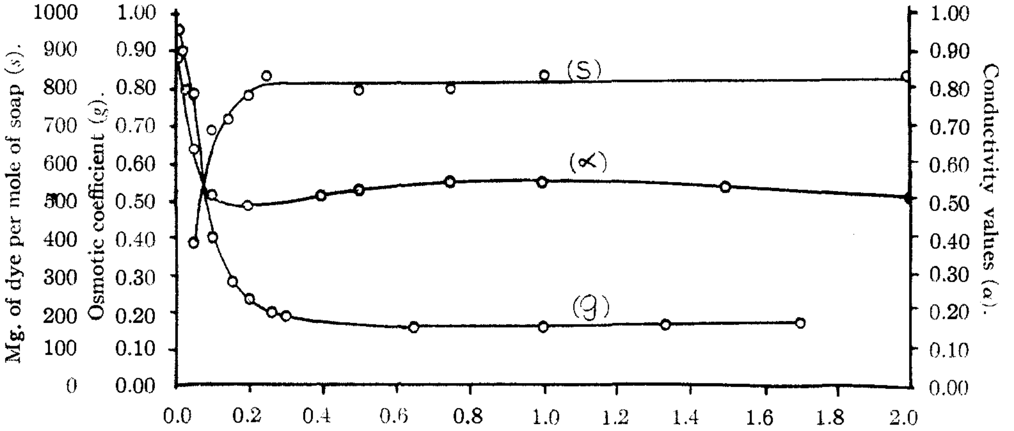

Fig. 3.—Comparison of the solubilization curve (*s*), the osmotic coefficient curve (*g*), and the conductivity curve (α) for potassium laurate.

found that the micelles in soaps and synthetic detergent solutions give an X-ray diffraction pattern corresponding to lamellar micelles in which molecules are packed side by side and layer to layer. According to Hess and his collaborators, when benzene is solubilized by the soap solution, spaces between the lamellar planes increase correspondingly. This mechanism, perhaps supplemented by sorption on the exterior of the micelles, would best accord with the present data.

It is of interest to compare the curve of solubilization by the typical soap, potassium laurate, with the corresponding curves for its osmotic coefficient, *g*, and conductivity ratio, α. This is done in Fig. 3. It is seen that solubilization attains its constant value at 0.25 *m*, while the osmotic coefficient is still definitely falling; whereas the conductivity has already reached its minimum value at 0.2 *m* and is on its way to the much higher value at 0.75 *m*. The changes in the micelles indicated by conductivity and osmotic activity are not reflected by any further change in solubilization. Most authors now agree that there are many sizes of micelles in different concentrations of the same colloidal electrolyte, ranging from "small micelles" or "ionic micelles" that raise the conductivity to larger lamellar micelles that greatly lower it.

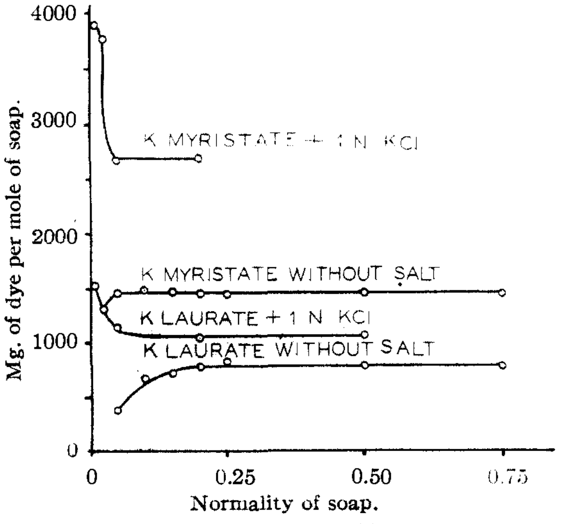

Fig. 4.—The solubility of orange OT at 25° in solutions of potassium laurate and potassium myristate with and without the presence of 1 *m* potassium chloride.

A comparison of the relevant data for lauryl sulfonic acid is given in reference 2.

Effect of Added Salts on Solubilization.—McBain and Merrill[3,4] advanced the plausible hypothesis that addition of a salt to a colloidal electrolyte having a common ion would favor formation of micelles in the dilute region where they were not already formed and tend to salt out dye in higher concentrations where the micelles were already completely formed. This they found to be true for solutions of sodium desoxycholate.

Table VIII gives the data for the solubilization of two potassium soaps as affected by the presence of molal potassium chloride in each case, and the results are plotted in Fig. 4. Solutions of 1 *m* myristate and 1 *m* and 0.5 *m* laurate could not be measured, since the dye particles would not settle in such viscous or jelly-like systems.

Table VIII

Solubility of Orange OT in Various Molalities of Potassium Laurate and Potassium Myristate at 25° in the Presence of 1 *m* Potassium Chloride

	Laurate		Myristate	
m	Mg. dye/ 100 cc. soln.	Mg. dye/ mole soap	Mg. dye/ 100 cc. soln.	Mg. dye/ mole soap
0.010	1.53	1530	3.895	3895
.025	2.70	1080	9.44	3776
.050	5.66	1132	13.39	2678
.200	20.72	1036	54.01	2700
.500	53.66	1073		

It is seen at once that the potassium chloride does greatly enhance the solubilization in dilute solutions, where but little micelle was previously present. Indeed, the micelle so formed appears to have a greatly increased solubilizing power, not only over the ordinary micelle of the same soap, but even over the same micelle in higher concentrations in the presence of the potassium chloride. Furthermore, even in the concentrated solutions, the potassium chloride has increased the solubilization. This is the opposite of the expected salting out effect. Neither can it be reconciled with the hypothesis of solution in the hydrocarbon, which must be unaffected since it is in equilibrium in all cases with solid crystals of dye. We have no adequate explanation either for the improved solubilizing power in concentrated solutions or for its still greater enhancement in dilute solutions. However, a similar effect in dilute solutions was indicated in Hartley's data for cetylpyridinium chloride with sufficient addition of sodium chloride (see reference 2, page 129). Likewise, Merrill found similar effects with pure *n*-(lauryl colamino formyl-methyl)-pyridinium chloride, commercially known as Catol 607, to which potassium chloride was added.

On the other hand, Dr. R. B. Dean in unpublished demonstrations in this Laboratory has shown that potassium chloride reduces the solubilizing power of 0.2 *m* potassium laurate for capryl alcohol. Addition of this chloride to a clear saturated solution of capryl alcohol in 0.2 *m* laurate produces a very evident turbidity, which is cleared by heating or by further addition of potassium laurate solution free from capryl alcohol.

Summary

1. The solubilization of water insoluble dye by four potassium soaps has been measured for equilibrium conditions over a range of concentrations.

2. The solubilization increases so rapidly with the higher soaps as to cast doubt upon the suggestion that it is solution in the hydrocarbon fraction of the molecule, but rather to favor its incorporation between the layers of lamellar micelles.

3. Potassium chloride not only greatly increases the solubilizing power of fully formed micelles, but it produces in dilute solution micelles of still higher solubilizing power.

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The Ionization of Strong Electrolytes. II. Ionization, Raman Spectrum and Vibrations of Perchloric Acid

BY O. REDLICH, E. K. HOLT AND J. BIGELEISEN[1]

As discussed in the first paper of this series,[2] the Raman spectrum furnishes a fairly general and unambiguous criterion of the existence of molecules. This criterion, in addition, is cogent if one retains the historical concept of the molecule which characterizes the molecule as a mechanical unit without referring to the nature of the intramolecular forces. The principle of determining the degree of ionization by means of Raman spectra, its history, and some experimental details have also been discussed previously. In the present paper, a refinement of the experimental method and measurements on perchloric acid are reported.

In a check of the Raman frequencies of anhydrous perchloric acid, a previously missing line was discovered by resolution of a doublet. Since this line completes the spectrum of the simplified model, our results for the frequencies of perchloric acid and the perchlorate ion, and an assignment of the frequencies to the vibration forms are included.

The Experimental Method

The spectrograph and the general equipment have been described previously.[2,3] Cells of the smaller type (18 ml.) were used. The front face of the cells was ground and polished. The perchlorate line 931 cm.$^{-1}$, excited by the blue mercury line was used. Because of the instability of the acid, the violet and ultraviolet light was filtered out by a sodium nitrite solution. Exposure times ranged from three minutes with Eastman Kodak Co. plates 103a-O and a slit width of 0.10 mm. to twenty-four minutes with plates II-O and 0.25 mm.

Like the nitrate line, the perchlorate line is fairly sharp and narrow in solutions of sodium perchlorate and in the practically completely ionized acid solutions of moderate concentrations, but considerably broader in concentrated solutions of the acid. Several attempts were made to diminish the error involved in the photographic comparison of the intensity of lines which appreciably differ in width.

For convenience, the usual way of comparing the areas under the microphotometric curves will be called the first method. This method can be considered to be based on two assumptions: (a) that under appropriate experimental conditions, the microphotometric curves of two lines are equal only if the total intensities striking the plate are equal, and (b) that a microphotometric curve is sufficiently characterized by its area.

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[1] Present address: Department of Chemistry, Columbia University, New York, N. Y.

[2] O. Redlich and J. Bigeleisen, THIS JOURNAL, **65**, 1883 (1943).

[3] O. Redlich and L. E. Nielsen, *ibid.*, **65**, 654 (1943).