in the time allowed for the reaction. The *p*-aminobenzoic acid derivative (I, R = *p*-COOH) could not be quantitatively brominated.

Some attempts to determine zinc quantitatively by bromination of its 7-(α-anilinobenzyl)-8-quinolinol derivative were made, but, although complete precipitation of zinc was obtained, the necessary use of excess reagent caused coprecipitation of reagent, leading to results that were high.

Experimental

Preparation of Reagents.—7-(α-Anilinobenzyl)-8-quinolinol and 7-[α-(*o*-carboxyanilino)-benzyl]-8-quinolinol were prepared by published methods.[9] Titration of 7-(α-anilinobenzyl)-8-quinolinol in glacial acetic acid with 0.1 *N* perchloric acid using a glass electrode gave a molecular weight of 325.4, assuming the compound is dibasic; calculated molecular weight is 326.4. Since similar titration of the anthranilic acid derivative did not give a satisfactory end-point, its molecular weight was obtained by the spectrophotometric picrate[10] method, giving for the molecular weight of the picrate 601; calcd., 599.

7-[α-(*o*-Carbethoxyanilino)-benzyl]-8-quinolinol was prepared by mixing 16.5 g. (0.1 mole) of ethyl anthranilate, 10.6 g. (0.1 mole) of benzaldehyde and 14.5 g. (0.1 mole) of 8-quinolinol in about 75 ml. of ethanol. After the stoppered flask had been standing for two days a white precipitate began to form which was filtered off after ten days and recrystallized from ethanol; yield 22 g. (55%); m.p. 135°.

Anal. Calcd. for $C_{25}H_{22}N_2O_3$: N, 7.03. Found: N, 7.08.

7-[α-(*p*-Carboxyanilino)-benzyl]-8-quinolinol was similarly obtained after 35 days from a mixture of 13.7 g. (0.1 mole) of *p*-aminobenzoic acid, 10.6 g. of benzaldehyde and 14.5 g. of 8-quinolinol in 300 ml. of ethanol. A cream-colored product, recrystallized from ethanol, was obtained; yield 16 g. (43%); m.p. 122°.

Anal. Calcd. for $C_{23}H_{18}N_2O_3$: N, 7.56. Found: N, 7.63.

Preparation of the Metal Chelate Compounds.—Approximately 0.01 molar solutions of the following ions in dilute acid were prepared from the pure metals or solid salts: Be^{+2}, Mg^{+2}, Ca^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, Pd^{+2}, Ba^{+2}, Pb^{+2}, UO_2^{+2}, Al^{+3}, Sc^{+3}, Fe^{+3}, Ga^{+3}, Y^{+3}, In^{+3}, La^{+3}, Ce^{+3}, Nd^{+3}, Sm^{+3}, Bi^{+3} and Th^{+4}.

Approximately 0.2-g. samples of each metal chelate compound were prepared from these solutions by adding the calculated amount of 7-(α-anilinobenzyl)-8-quinolinol (or derivative) in ethanol to a diluted solution of the metal ion, followed by addition of ammonium acetate, sodium acetate or ammonia as necessary to produce complete precipitation. The *p*H conditions used for 8-quinolinol precipitations generally sufficed, except that some of the 7-[α-(*o*-carboxyanilino)-benzyl]-8-quinolinol salts tended to redissolve in excess ammonia. After filtration the precipitates were washed thoroughly with water and generally given a final washing with a small portion of ethanol. Cerous and ferrous chelate compounds could not be satisfactorily prepared because the reagents oxidized these ions in nearly neutral solutions; compounds of 7-(α-anilinobenzyl)-8-quinolinol with cobalt, bismuth, lead, neodymium and samarium were prepared but not analyzed. Use of even a slight excess of reagent in these preparations was unsatisfactory because of its extreme insolubility in water.

Analyses.—For analysis of the metal compounds by the ignition method the entire 0.2-g. sample after drying at room temperature was ashed over a low flame and the oxide residue weighed after ignition under the usual conditions for the particular oxide. For the bromometric analyses 50-mg. samples were dissolved in 4 *N* hydrochloric acid by gentle heating for about five minutes. The solution was then cooled and diluted to about 100 ml. and an excess of 1–10 ml. of standard 0.1 *N* bromate–bromide solution added from a buret. The stoppered flask was allowed to stand for five minutes and then 0.5 g. of potassium iodide was added and the liberated iodine titrated after an additional five minutes with 0.05 *N* sodium thiosulfate to a starch–iodide end-point. A white precipitate of 2,4,6-tribromoaniline generally formed during the bromination and in one instance (titration of pure 7-(α-anilinobenzyl)-8-quinolinol) was filtered off, dried, and the m.p. determined to be 118°; reported m.p. of 2,4,6-tribromoaniline is 119°.

When analysis by both the ignition and bromination methods was desired, separately prepared samples of the metal compounds were used. In calculating the analytical results the possible presence of water of crystallization in some of the samples was not considered, because one or two molecules of water would have an almost negligible effect on the metal content owing to the large molecular weights of the metal compounds.

Sensitivity Tests.—These were performed by the method of Irving, Butler and Ring[11] using Al^{+3}, Fe^{+3}, Cu^{+2} and Ni^{+2} as representative ions. The sensitivities with 7-(α-anilinobenzyl)-8-quinolinol, expressed in micrograms per ml. were: Al^{+3}, 0.7; Fe^{+3}, 0.5; Cu^{+2}, 0.6 and Ni^{+2}, 0.3; with 7-[α-(*o*-carboxyanilino)-benzyl]-8-quinolinol, Al^{+3}, 1.5; Fe^{+3}, 0.5; Cu^{+2}, 0.1 and Ni^{+2}, 0.2.

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Studies on the Chemistry of Halogens and of Polyhalides. VI. Electrical Conductance of Polyhalogen Complexes in Ethylene Dichloride

BY ALEXANDER I. POPOV AND NORMAN E. SKELLY[1]

RECEIVED JUNE 27, 1955

Introduction.—Electrical conductance of several polyhalogen complexes has been recently determined in acetonitrile solutions.[2] The results obtained indicated that these complexes are strong electrolytes at least in solutions which are $\leqslant 10^{-1}\,M$. The work is now extended to ethylene dichloride solutions in order to see how the change in the dielectric constant of the solvent affects the conductance of these complexes. Ethylene dichloride was chosen because of its relatively low dielectric constant (10.23 *vs.* 36.5 for acetonitrile at 25°) and its ability to dissolve sufficient amounts of polyhalogen complexes for the conductance studies.

Experimental Part

Apparatus and Procedure.—The apparatus and the experimental procedure used in this investigation to obtain conductance measurements were discussed in an earlier paper.[2]

Polyhalogen Complexes.—Polyhalogen complexes studied in this work were tetramethylammonium iodobromochloride, tetrapropylammonium iododibromide, tetrabutylammonium iododichloride and the tetrabutylammonium tribromide. With the exception of the first compound it was found impossible to use the corresponding tetramethylammonium complexes because of their limited solubility in ethylene dichloride.

The first three compounds were prepared by the methods of Chattaway and Hoyle.[3] The tetrabutylammonium tribromide was supplied by Mr. L. Harris of this Laboratory. The purity of the compounds was checked by iodometric titration and found to be of the order of 98–99%. The

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[1] Du Pont pre-doctoral fellow 1953–1954.

[2] A. I. Popov and N. E. Skelly, THIS JOURNAL, **76**, 5309 (1954).

[3] F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923).

melting point of these preparations checked to within 0.1° with the literature values.

Solvents and Solutions.—Ethylene dichloride was purified by a previously described method.[4] The boiling point of the purified solvent was 83° at 750 mm. pressure. The specific conductance of the solvent was found to be less than 10^{-9} ohm $^{-1}$ cm.$^{-1}$ and was too low to necessitate any corrections even for the most dilute solutions.

Approximately 10^{-2} M stock solutions were prepared by dissolving a weighed amount of solute in an appropriate amount of solvent. Dilutions were made by the addition of a known amount of the stock solution from a weight buret to the solvent. This technique was found to be more accurate than the usual dilution method since solutions down to 10^{-5} M had to be prepared. All of the solutions were found to be stable for at least 24 hours, but the measurements were made on the solutions prepared on the same day.

Results and Discussion.—Equivalent conductances obtained for the polyhalide solutions are tabulated in Table I where a typical series of measurements are given. Several runs were made on different sets of solutions, but the results agreed within experimental error.

TABLE I

EQUIVALENT CONDUCTANCES OF POLYHALOGEN COMPLEXES IN ETHYLENE DICHLORIDE AT 25°

$c \times 10^4$	Λ	$c \times 10^4$	Λ
$(CH_3)_4NIBrCl$		$(n\text{-}C_3H_7)_4NIBr_2$	
0.6074	53.00	0.5185	56.20
1.367	43.88	1.306	48.86
2.217	38.27	2.242	44.12
5.727	28.41	2.972	41.45
7.582	25.93	3.720	39.35
9.277	24.24	7.258	33.30
27.02	20.74	9.013	31.64
$(n\text{-}C_4H_9)_4NBr_3$		$(n\text{-}C_4H_9)_4NICl_2$	
0.3689	52.70	0.1651	58.98
0.9208	47.20	1.199	47.68
1.667	42.54	2.717	40.59
2.566	38.69	4.467	36.22
3.614	35.76	7.132	32.22
8.513	28.59	14.49	26.79
17.99	23.23		

Plots of $\sqrt{c}$ *vs.* Λ deviated considerably from straight lines showing appreciable ion-pair association especially in the more concentrated solutions.

The data were treated by the method of Fuoss and Kraus.[5] The F/Λ *vs.* $c\Lambda f^2/F$ plots gave in each case satisfactory straight lines. The intercepts of the lines yield $1/\Lambda_0$ and the slopes $1/K\Lambda_0^2$. The calculated values of the limiting conductance and of the ion-pair dissociation constants are given in Table II.

TABLE II

CONDUCTANCE DATA IN ETHYLENE DICHLORIDE

Complex	Λ_0	$\lambda_0^{+\,a}$	λ_0^-	$K \times 10^4$
$(CH_3)_4NIBrCl$	81.6	42.6	39.0	0.68
$(n\text{-}C_3H_7)_4NIBr_2$	68.3	31.5	36.8	2.11
$(n\text{-}C_4H_9)_4NBr_3$	62.2	26.2	36.0	2.05
$(n\text{-}C_4H_9)_4NICl_2$	64.5	26.2	38.3	2.27

[a] Reference 6.

Since the limiting conductances of the tetramethylammonium, *n*-tetrapropylammonium and *n*-tetrabutylammonium cations in ethylene dichloride at 25° have been determined by Tucker and Kraus,[6] it is possible to calculate the limiting equivalent conductances of the polyhalogen ions used in this investigation.

The results are likewise given in Table II. As ionic mobilities are equal to $\lambda^{\pm}/F$, the mobilities of the polyhalogen ions come in the following sequence, $IBrCl^- > ICl_2^- > IBr_2^- > Br_3^-$ but the actual differences are rather small, which indicates that the ions are of approximately the same size.

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[5] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476 (1933); R. M. Fuoss, *ibid.*, **57**, 488 (1935).

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The Lowering of the Freezing Point of Sodium Hydroxide on Addition of Salts

BY R. P. SEWARD

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From calorimetric measurements, Douglas and Dever[1] have found the heat of fusion of sodium hydroxide to be 1520 ± 5% cal. per mole. These authors suggest that the figure of 1670 cal. per mole, calculated by the writer[2] from freezing points in the $NaOH-Na_2CO_3$ system, is in error because the effective molecular weight of Na_2CO_3 in solution may deviate from its formula weight. As the value from the freezing point measurements was calculated from temperatures determined to the nearest degree and the greatest lowering employed was 13°, it is quite probable that the discrepancy is due to the lack of precision in the freezing point data.

Subsequent to the observations on the $NaOH-Na_2CO_3$ system, the writer determined the lowering of the freezing point of sodium hydroxide on addition of NaBr, KBr, K_2CO_3 and again Na_2CO_3. While these measurements too are not of sufficient precision to define the heat of fusion accurately, it is thought that they may be of interest for their bearing on the extent of dissociation and ideal behavior in fused salt solutions.

The data on the lowering of the freezing point of sodium hydroxide are tabulated below. ΔT is the observed lowering, N is the ratio of the number of formula weights of solute to total formula weights, and i is the ratio of the observed lowering to $460N$. The mole fraction freezing point lowering constant, $RT^2/\Delta H_F$, using 1520 cal. per mole for ΔH_F, has a value of 460.

Within the precision of the measurements, it appears that the above data are consistent with complete dissociation of solute and solvent and ideal behavior; one formula weight of solute contributing one mole of solute ion in the case of Na_2CO_3 and NaBr, two moles of solute ion with KBr, and three with K_2CO_3. In view of the possibilities of solid solution formation, it is remarkable that the

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