[CONTRIBUTION NO. 374 FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Solubility of Silver Bromate in Mixtures of Alcohols and Water

BY EDWARD W. NEUMAN

The object of this investigation was to measure exactly the solubility at 25° of silver bromate in mixtures of methanol, ethanol, *n*-propanol and isopropanol with water with the purpose of testing the applicability of the simple electrostatic formula, first given by Born,[1] to solubility phenomena effects in different media. Since the experimental work was completed, a very similar research has been published by Owen.[2] It seems worth while nevertheless to record briefly the results of this investigation, which afford a confirmation, and to some extent an extension, of those of Owen.

The formula of Born expresses the amount of work necessary to carry a charged particle of a given radius from a medium having a certain dielectric constant to a medium having a different dielectric constant. It had been written by Scatchard[3] in a form suitable for solubility study as follows

$$\log S_1/S_2 = (0.4343\ e^2/2rkT)\ (1/D_2 - 1/D_1) \quad (1)$$

Here S is the solubility of a given electrolyte in a medium with a dielectric constant D, and r is taken as the mean radius of the ions of the electrolyte. The quantities e, k and T have their usual significance.

The method used for the solubility measurements was essentially that employed by Dalton, Pomeroy and Weymouth[4] in this Laboratory. The saturated solutions, however, were analyzed for silver by electrometric titration with potassium bromide using a cell of this type

$$\text{Cu-AgarAgar } Ba(NO_3)_2 - (Ag^+Br^-)Ag$$

The silver bromate was prepared by adding slowly a dilute solution of potassium bromate to a dilute solution of silver nitrate. The precipitate was washed several times by decantation, filtered out, and finally suspended in water for several days at a time to remove traces of potassium nitrate and silver nitrate. Preparations from cold solutions were considered preferable since Reedy[5] states that a more soluble form is precipitated from hot solutions. The crystals prepared in the cold were examined under a microscope and they were found to be uniformly tetragonal. None of the "hair-shaped" type described by Reedy as the higher form were found to be present.

The solubility data found when methanol, ethanol and *n*-propanol with water were used as solvents are in good agreement with the results on these mixtures that were obtained by Owen. The values for the solubilities in mixtures of isopropanol and water fall between the values found in ethanol- and those found in *n*-propanol-water mixtures.

The solubility in water at 25° was found to be 0.008131 mole liter as compared with the value of 0.00812 mole liter reported by Owen, and the value 0.00827 mole liter reported by Hill[6] and by Reedy.[5]

The Born formula as given above was found to be incompatible with the data when a constant value for r, and the dielectric constant values

TABLE I

SOLUBILITY OF SILVER BROMATE IN MIXTURES OF ALCOHOLS AND WATER

Methanol			Ethanol		
P	*S*	*r*	*P*	*S*	*r*
3.62	70.0	0.461	3.62	70.0	0.632
7.31	60.5	.494	7.30	60.6	.665
11.08	52.2	.522	11.06	52.7	.714
14.92	45.0	.560	14.89	45.5	.742
18.84	39.4	.603	18.84	39.7	.790
22.83	34.0	.635	22.80	34.6	.839
26.91	29.2	.663	30.79	26.3	.929
31.08	25.3	.694	35.29	22.3	.976
35.33	21.7	.720	39.62	19.4	1.039
39.67	18.4	.747	44.06	16.5	1.095
44.11	15.8	.781	48.59	14.0	1.169
48.63	13.1	.800			

n-Propanol			Isopropanol		
P	*S*	*r*	*P*	*S*	*r*
3.67	71.4	0.896	3.64	70.0	0.811
11.27	56.2	1.029	7.34	60.7	.861
15.16	49.9	1.10	11.12	52.9	.936
19.13	44.9	1.19	14.97	46.1	.992
23.17	40.5	1.29	18.90	40.6	1.061
31.49	32.1	1.48	22.90	36.0	1.15
40.13	24.3	1.66	26.99	31.8	1.24
49.13	17.0	1.81	31.16	28.1	1.34
63.28	8.6	2.01	39.77	21.0	1.59
			48.74	15.3	1.72

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[1] Born, *Z. Physik*, **1**, 45 (1900).

[2] Owen, THIS JOURNAL, **55**, 1922 (1933).

[3] Scatchard, *ibid.*, **47**, 2098 (1925); *Chem. Rev.*, **3**, 383 (1927).

[4] Dalton, Pomeroy and Weymouth, THIS JOURNAL, **46**, 60 (1924).

[5] Reedy, *ibid.*, **43**, 1440 (1921).

[6] Hill, *ibid.*, **39**, 218 (1917).

given by Åkerlöf[7] were used. Values of r based on Åkerlöf's constants and the experimental data seem to be a linear function of the mole fraction of the non-electrolyte in the solution. This function may be expressed by $r = a + bN$. The constants a and b vary from alcohol to alcohol, whereas a at least would be expected to be the same for all of the non-electrolytes involved.

The experimental results and the values of r calculated on the basis of Åkerlöf's dielectric constants are given in the Table. S denotes the solubility in millimoles per liter, and P denotes the weight per cent. of the alcohol.

Summary

The solubility of silver bromate in mixtures of methanol, ethanol, n-propanol and isopropanol with water was determined at 25°. The data were found to be incompatible with the Born electrostatic formula.

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[7] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

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Some Reactions of Anhydrous Thorium Tetrabromide with Organic Liquids

BY RALPH C. YOUNG

As the first step in the study of reactions of metals on non-aqueous solutions of thorium tetrabromide, experiments were carried out to find the results of the action of thorium tetrabromide alone on certain organic liquids.[1] With ethyl alcohol, ethyl acetate, methyl cyanide and pyridine at temperatures as high as the boiling points of the respective solutions, molecular compounds were formed having the formulas, $ThBr_4 \cdot 4C_2H_5OH$, $ThBr_4 \cdot 2CH_3COOC_2H_5$, $ThBr_4 \cdot 4CH_3CN$, $ThBr_4 \cdot 3C_5H_5N$. At room temperature $ThBr_4 \cdot 4C_6H_5NH_2$ was formed but at the boiling point of the solution of thorium tetrabromide in aniline other reactions occurred. Matthews has reported the formation of $ThBr_4 \cdot C_5H_5N$ and $ThBr_4 \cdot 4C_6H_5NH_2$ both in ether solution.[3]

The molecular compounds $ThBr_4 \cdot 3C_6H_5COOC_2H_5$, $2ThBr_4 \cdot 7C_6H_5COCH_3$ and $ThBr_4 \cdot 4C_6H_5CHO$ were obtained in the reaction of thorium tetrabromide with ethyl benzoate, acetophenone and benzaldehyde at room temperature, while at their respective boiling points, thorium tetrabromide reacted rapidly as follows with these liquids; ethyl bromide and thorium benzoate were formed from the reaction of the halide with the ester, and the hydrated thoryl bromide organic complexes, $ThOBr_2 \cdot 0.5C_6H_5COCH_3 \cdot H_2O$ and $ThOBr_2 \cdot 2C_6H_5CHO \cdot H_2O$ were precipitated when solutions of the tetrabromide in these other solvents were boiled; an equivalent amount of hydrogen bromide was eliminated and water was also formed by condensation reactions of the solvents. The tendency of thorium to retain two of its bromine atoms is also shown in reaction with propiophenone, in which case, $ThOBr_2 \cdot 0.5C_6H_5COC_2H_5 \cdot 2H_2O$ precipitated from the boiling solution. Continued heating of these reaction mixtures, accompanied by a slow distillation of the solvents, caused a further removal of the bromine only at a very slow rate.

Rosenheim, Santer and Davidson[4] report that benzaldehyde and thorium tetrachloride when heated together react, hydrogen bromide being evolved, and they suggest a formula, $ThCl_2(C_6H_5CO)_2$, for the resulting product, which formula they say "must be taken with reserve" as there was no analysis made for the organic residue and that for thorium failed to check well the above formula. With thorium tetrabromide it has been found that if oxygen was not carefully excluded in its reaction with benzaldehyde or if the benzaldehyde was not free from benzoic acid, the bromine was partially displaced by the benzoic acid radical, hydrogen bromide being evolved, and there was formed a product, insoluble in benzaldehyde, of composition, $ThBr_2(C_6H_5COO)_2 \cdot 3C_6H_5CHO$.

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[1] Comparison of the stabilities toward heat of the lower anhydrous bromides of titanium and zirconium[2] indicates that at only relatively low temperatures would a lower valence bromide of thorium be stable. Anhydrous titanous bromide has been produced by the action of mercury or silver on titanium tetrabromide in benzene solution.[2]

[2] Young with Schumb, THIS JOURNAL, **52**, 4233 (1930); Young, *ibid.*, **53**, 2148 (1931).

[3] Matthews, *ibid.*, **20**, 839 (1898).

[4] Rosenheim, Santer and Davidson, *Z. anorg. Chem.*, **35**, 424 (1903).