interpolated values of $m\varphi$ = 0.0, 0.1, 0.2, etc. The slope ($\partial\ 1/m\ \partial X_{HTol}$) was measured at X_{HTol} = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 for each value of $m\varphi$. These data allowed the calculations of ln (γ_1/γ_2) from equation 8. Ln γ_1 was next obtained from equation 5. Values of γ_1 and γ_2 as a function of m and X_{HTol} were next calculated and are presented in Tables I and II.

TABLE I

ACTIVITY COEFFICIENTS OF *p*-TOLUENESULFONIC ACID

m = X_{acid},	0.0	0.2	0.4	0.6	0.8	1.0
0.1	0.775	0.769	0.762	0.760	0.759	0.759
.2	.740	.723	.713	.710	.706	.703
.3	.720	.697	.679	.668	.662	.660
.4	.706	.680	.655	.642	.635	.630
.5	.697	.662	.633	.620	.612	.608
.6	.690	.650	.617	.601	.593	.589
.7	.684	.640	.602	.586	.578	.573
.8	.678	.630	.590	.574	.565	.559
.9	.671	.620	.576	.562	.553	.546
1.0	.666	.610	.563	.550	.542	.535
1.2	.653	.593	.541	.527	.520	.515
1.4	.642	.576	.521	.509	.502	.498
1.6	.630	.560	.503	.493	.485	.483
1.8	.620	.544	.487	.478	.471	.469
2.0	.613	.530	.472	.464	.459	.459
2.5	.597	.508	.446	.440	.438	.439
3.0	.589	.490	.428	.423	.423	.427
3.5	.585	.478	.417	.417	.419	.425

TABLE II

ACTIVITY COEFFICIENTS OF SODIUM *p*-TOLUENESULFONATE

m = X_{acid},	0.0	0.2	0.4	0.6	0.8	1.0
0.1	0.765	0.766	0.767	0.767	0.768	0.768
.2	.709	.718	.724	.726	.729	.731
.3	.674	.685	.690	.695	.698	.699
.4	.648	.659	.665	.669	.671	.673
.5	.627	.638	.645	.651	.654	.656
.6	.609	.623	.631	.636	.640	.642
.7	.593	.608	.618	.623	.629	.631
.8	.579	.595	.606	.612	.618	.621
.9	.566	.583	.595	.603	.608	.612
1.0	.554	.576	.584	.594	.600	.604
1.2	.532	.548	.563	.575	.584	.589
1.4	.511	.528	.543	.557	.568	.574
1.6	.493	.508	.524	.540	.553	.560
1.8	.476	.492	.509	.525	.539	.546
2.0	.460	.477	.495	.511	.526	.534
2.5	.427	.446	.465	.482	.498	.508
3.0	.402	.422	.442	.462	.479	.490
3.5	.383	.405	.429	.450	.469	.482

It was to be expected that these mixed solutions would exhibit unusual behavior because of the behavior of solutions of the two pure components. It has been found,[3] for example, that the osmotic coefficient of the sodium salt is greater than that of the acid in relatively dilute solutions ($m < 1.4$) and less than that of the acid in more concentrated solutions. In dilute mixed solutions $1/m$ initially increases with increasing percentages of acid at constant water activity, reaches a maximum at $X_{acid} \cong 0.3$, and then decreases. In concentrated solutions $1/m$ increases regularly with increasing percentages of acid at constant water activity. This behavior results in positive values of ln ($\gamma_{acid}/\gamma_{salt}$) for solutions containing large molar fractions of salt and negative values for this quantity for solutions containing large molar fractions of acid over the concentration range 0–3.5 m.

The variation of γ_{acid} with composition at constant ionic strength is also of interest. In dilute solutions this activity coefficient decreases with increasing acid concentration. In concentrated solutions the activity coefficient has a minimum value for solutions of intermediate composition and is higher in both pure solutions.

It may be observed that neither solute obeys, Harned's rule as to the linear variation of the logarithm of the activity coefficient with composition at constant total molality.

COLUMBIA, S. C.

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[3] O. D. Bonner, G. D. Easterling, D. L. West and V. F. Holland, THIS JOURNAL, **77**, 242 (1955).

[CONTRIBUTION NO. 685 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Physical Chemical Studies of Solutions in Anhydrous Ethylenediamine. II. Conductances and Viscosities of Solutions of Mercuric Bromide, Iodide and Cyanide

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The solubilities of mercuric bromide, iodide and cyanide in ethylenediamine at 25° have been found to be approximately 26, 300 and 113 g./100 g. solvent (0.61, 4.18 and 3.25 *M*), respectively. Conductances of solutions of these salts have been measured at 25° over the available range of concentrations. The plots of equivalent conductance against concentration for HgI_2 and $Hg(CN)_2$ show minima and maxima. The plot for $HgBr_2$ shows only a minimum since the more concentrated solutions proved to be unstable and were not suitable for conductance measurements. The maxima in the conductance curves are probably due to the formation of triple ions or, perhaps, to formation of complex ions of HgX_4^{--} ($X = Br^-$, I^- or CN^-) at moderate concentrations followed by a rapid drop in conductance at higher concentrations due to the large increase in viscosity observed in this region. The exceptionally high solubility of the iodide is typical of the behavior of iodides in ethylenediamine and other amine solvents. It is tentatively suggested that this is due to the solvation of the iodide through the expansion of the outer valency shell of the iodine.

Introduction

During an investigation of the solubility of certain salts in ethylenediamine,[2] it was found that while mercuric chloride is only slightly soluble,[3] and reacts with the solvent, mercuric iodide is exceedingly soluble, dissolving with the evolution of considerable heat to form yellow, viscous, conducting solutions, the color of which deepens with increasing

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[1] (a) Post-Doctoral Fellow, 1953–1954. (b) Address correspondence to F.C.S.

[2] B. B. Hibbard and F. C. Schmidt, THIS JOURNAL, **77**, 225 (1955).

[3] H. S. Isbin and K. A. Kobe, *ibid.*, **67**, 464 (1945).

concentration. Later investigations have shown that other mercuric salts behave similarly. This report presents the results of conductance and viscosity measurements on solutions of mercuric bromide, iodide and cyanide in ethylenediamine over the range of available concentrations at 25°. The composition of the solid phase in equilibrium with the saturated solution of the iodide has been found to be $HgI_2 \cdot 2en$. This information together with the shape of the conductance curves is used to interpret the nature of the species present in the concentrated solutions of HgI_2 and the other salts.

Experimental

Materials.—Anhydrous ethylenediamine was prepared from 98% material supplied by Eastman Kodak, by the method described by Hibbard and Schmidt.[2] The final product was fractionated through a 3 × 60 cm. helix-packed column and the distillate was collected in a receiver fitted with a magnetically controlled outlet. At slow rates of distillation, ethylenediamine of specific conductivity $\sim 5 \times 10^{-7}$ mho could be produced. Most of the determinations of conductance were made in a product of specific conductance 1 to 3×10^{-6} mho. Mercuric salts of reagent grade quality were used without further purification after drying at 110° *in vacuo*. The dilute solutions of the iodide used in the conductance measurements were made up from material sublimed from the original salt at ~150°. No difference could be detected between solutions prepared from sublimed and unsublimed salt in the more concentrated regions.

Apparatus and Procedure.—Conductances were measured with the apparatus described by Hibbard and Schmidt.[2] The more dilute solutions (10^{-3} to 10^{-1} *M*) were made up by the concentration method described by them; the more concentrated solutions were made by direct weighing of salt and solvent. Two cells with cell constants 1.136 and 2.529 were used. One of these was later reconstructed so that solution could be transferred from the concentration part of the cell to the conductance part merely by tilting the cell. Dissolution of the salt in the more concentrated solutions was aided by magnetic stirring.

Viscosities were measured in calibrated Ostwald viscometers. Several were constructed with different capillary diameters so that the time of flow was never less than 100 sec. Water and CO_2 absorbing tubes were fitted to the arms of the viscometers. Measurements were made in a glass-windowed thermostat of conventional design and kept at 25° ± 0.01°. Duplicate determinations at each concentration were made. Densities were measured at 25 ± 0.01° in 25-ml. density bottles.

Solid $HgI_2 \cdot 2en$.—The yellow plates were washed with alcohol and ether and then dried *in vacuo*. The analysis of the solid compound ($HgI_2 \cdot 2en.$) in equilibrium with the saturated solution is as follows: Calcd. for $HgI_2 \cdot 2(NH_2CH_2CH_2NH_2)$: C, 7.35; N, 9.75; Hg, 34.91. Found: C, 7.23; N, 8.01; Hg, 34.70. The reason for the low values of the carbon and nitrogen is that the mercury caused incomplete combustion.

Results

In Tables I and II are collected the conductance and viscosity data for the three salt solutions. The conductance data have been corrected for the conductance of the solvent by subtracting the measured conductance of the pure solvent from the values obtained for the solutions. The solvent correction is insignificant above 0.1 *M*. Some reduction of the mercuric bromide appeared to take place in the more concentrated solutions so values for these latter solutions are placed in parentheses. Plots of Λ against the molar concentration, shown in Fig. 1, display maxima and minima for the salts in question.

Density data needed to convert molalities to concentrations and to calculate viscosities have been interpolated from smoothed plots of density against mole fraction of salt, as these are practically linear. Conductance data at low concentrations are not numerous enough to permit the calculation of Λ_0 and *K* values by the method of Fuoss; however, Hibbard and Schmidt[2] found in their study that

TABLE I

CONDUCTANCES OF $HgBr_2$, HgI_2 AND $Hg(CN)_2$ IN ETHYLENEDIAMINE AT 25°

Concn., mole/l.	Specific cond. $k' \times 10^5$, ohm^{-1} cm.$^{-1}$	Equiv. cond., Λ ohm^{-1} cm.^{2} equiv.$^{-1}$	Concn., mole/l.	Specific cond. $k' \times 10^5$, ohm^{-1} cm.$^{-1}$	Equiv. cond., Λ ohm^{-1} cm.^{2} equiv.$^{-1}$
		$HgBr_2$			
4.349×10^{-4}	1.58	18.12	0.1765	62.8	1.78
3.732×10^{-3}	4.18	5.62	.3223	127.0	1.97
4.100×10^{-2}	16.4	2.00	(.5)	(220)	(2.2)
0.1121	35.2	1.58	(.6)	(270)	(2.25)
		HgI_2			
2.19×10^{-4}	0.93	21.23	1.620	375.2	1.16
1.39×10^{-3}	1.72	6.18	1.760	369.7	1.04
4.062×10^{-3}	3.74	4.60	1.895	356.3	0.94
8.421×10^{-3}	4.29	2.55	2.102	345.8	.82
0.1439	37.4	1.30	2.155	326.1	.75
.2115	57.7	1.36	2.585	273.9	.53
.4689	139.8	1.49	2.727	243.6	.49
.7665	235.7	1.54	2.775	235.9	.42
.9336	284.5	1.52	2.855	222.9	.39
1.233	351.5	1.42	3.360	171.8	.26
1.336	363.4	1.36	3.655	130.0	.18
1.494	365.2	1.22	4.184	81	.10
		$Hg(CN)_2$			
2.044×10^{-3}	0.05	0.122	0.9415	17.4	0.093
1.123×10^{-2}	0.18	.080	1.607	34.0	.106
0.0968	1.12	.052	2.121	38.8	.091
.2509	3.00	.060	2.554	40.4	.079
.4424	6.31	.072	3.249	31.9	.049

TABLE II

RELATIVE VISCOSITIES OF SOLUTIONS OF $HgBr_2$, HgI_2 AND $Hg(CN)_2$ IN ANHYDROUS ETHYLENEDIAMINE[a] AT 25°

Concn., mol./l.	η/η_0
$HgBr_2$	
0.1765	1.301
.3223	1.551
(.56)	(2.44)
HgI_2	
0.0635	1.19
.3351	1.70
.6257	2.90
1.50	4.21
1.71	5.14
2.28	6.98
2.36	7.77
2.53	9.60
2.72	11.65
3.36	18.87
3.58	21.10
3.83	26.90
$Hg(CN)_2$	
0.4424	1.251
0.9415	1.682
1.607	2.744
2.554	5.970
3.249	11.920

[a] Viscosity of pure ethylenediamine = 0.0154 poise.[4]

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[4] A. E. Dunsten, T. P. Hilditch and F. B. Thole, *J. Chem. Soc.*, 103, 133 (1913).

estimates of Λ_0 from plots of $1/\Lambda$ *vs.* M differed by only a small amount from the final values obtained by using the Fuoss treatment.

Values of Λ_0 and K obtained from the $1/\Lambda$ *vs.* M plots for mercuric bromide and iodide are given in Table III. The data for mercuric cyanide cannot be treated in this way, as the extrapolation is too uncertain. If we assume that Λ_0 for mercuric cyanide is of the same order as the values for the bromide and iodide, the value of K can be obtained.

Discussion

Qualitatively, the conductances and viscosities reported here are typical of salts in solvents of low dielectric constant. The values of Λ_0 are much lower than those which would be found for the same salts in water (for HgI_2, calculated from ionic mobilities, $\Lambda_0 = 110$), while the slopes of the Λ *vs.* concentration plots are much steeper than those calculated from the Onsager equations. Viscosities of simple salt solutions in water usually show only a slight increase with concentration and may even show a slight decrease. In the present systems the increase of viscosity with concentration is very marked as shown in Table II. The final decrease of equivalent conductance in the high concentration region in the cyanide and iodide solutions must be due mainly to this viscosity increase, but no satisfactory relation between the two properties is known with which to test this accurately. The product of the conductance and viscosity, $\Lambda\eta$, is not constant but increases in the region of higher concentration, *i.e.*, the viscosity increase is greater than the corresponding conductance decrease.

TABLE III

LIMITING EQUIVALENT CONDUCTANCES, Λ_0, AND DISSOCIATION CONSTANTS, K, IN ETHYLENEDIAMINE AT 25°

	Λ_0, ohm^{-1} cm.^{2} equiv.$^{-1}$	K
$HgBr_2$	80	1.8×10^{-5}
HgI_2	60	1.7×10^{-5}
$Hg(CN)_2$	..	(5×10^{-9})

All three salts are covalent in the gas phase and in solution in such solvents as benzene and ethyl acetate. The bromide is partially ionic in the solid state, but the iodide and cyanide are covalent. It is interesting to compare the behavior of the three salts toward water and ethylenediamine. The bromide and iodide are insoluble in water, but the cyanide is unusual in that it is soluble in water but un-ionized. All three salts dissolve in ethylenediamine with considerable evolution of heat (the addition of excess salt to 25 ml. of solvent will cause it to boil vigorously), but while the bromide and iodide give moderately high conducting solutions, the cyanide, though more soluble than the bromide, is a much poorer conductor. Conductance measurements alone cannot distinguish between uncharged covalent molecules and uncharged ion pairs, but since it is reasonable to assume that ion pair formation would take place to the same extent in similar solutions of all three salts, any large difference in conducting power of these salts must be due to differing extents of ionization.

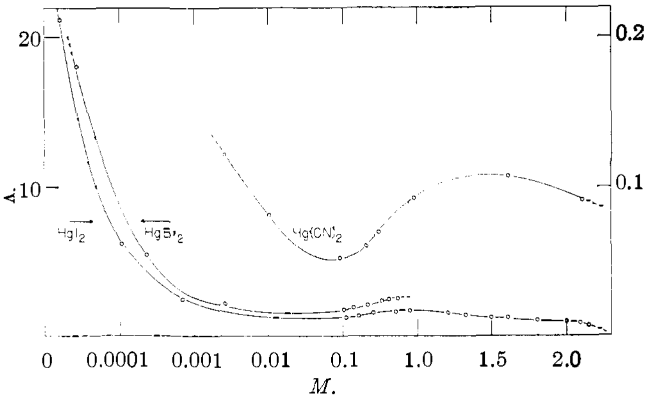

Fig. 1.—Curves showing change in conductance with molarity of some mercury salts in anhydrous ethylenediamine.

Information about the species present in the solutions can be obtained from the plots of equivalent conductance against concentration. These show marked maxima and minima as the concentration is increased. Most solutions of electrolytes in solvents of low dielectric constant show minima in these plots, but maxima would also be observed if the salts were soluble enough, as is the case with the salts in the present work. Fuoss and Kraus[5] have shown that the increase in conductance past the minimum may be due to the formation of triple ions held together by Coulombic forces. The final decrease in conductance as the concentration increases may then be due to the increasing viscosity of the solvent and/or to increasing association of the triple ions. In the case of solutions of salts of a metal ion capable of forming coördination complexes, the form of the conductance curve may also be explained as being due to the formation of "autocomplex" ions which form as the concentration increases and which are held together by coördination forces and not merely by Coulombic forces.

Consideration of the conductance data shows that $Hg(CN)_2$ is almost un-ionized in ethylenediamine, as in water, and that its heat of solution is then almost entirely a heat of coördination of the un-ionized covalent salt with ethylenediamine. The coördination number (C.N.) of mercury is usually 4, but some complexes with a C.N. of 6 are known,[6] and there is no reason to doubt that in pure ethylenediamine the C.N. of 6 can be attained. The principal species present in the $Hg(CN)_2$ solution is therefore probably uncharged $Hg(CN)_2en_2$, *i.e.*, a true "inner complex" salt. The increase in equivalent conductance past the first minimum in the curve of Λ *vs.* concentration of $Hg(CN)_2$ cannot be due to triple ion formation in this case, since relatively few ions would be present in the solution in equilibrium with the stable, uncharged "inner complex." Rather, the increase in conductance may be attributed to the formation of small amounts of "auto-complex" ions, probably of the "polymerization isomer" type, *i.e.*, $2Hg(CN)_2en_2 \rightleftarrows Hg(CN)_4en^{--} + Hg\ en_3^{++}$.

The situation with HgI_2 and $HgBr_2$ solutions is not so clearcut. Ionization takes place to a much

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[5] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476, 2390 (1933).

[6] C. Gensch, *Z. anal. Chem.*, **131**, 89 (1950).

greater extent than with the $Hg(CN)_2$ solutions raising the possibility that either the inner complex, HgX_2en_2, is much less stable in the case of bromide and iodide, or else that other ionized species are present with considerable ion-pair formation.

Solutions of $Hg(CN)_2$ and dilute solutions of HgI_2 in ethylenediamine are colorless, but the more concentrated iodide solutions are yellow, which is also the color characteristic of aqueous solutions of mercuric iodide in the presence of excess iodide ion which causes formation of HgI_4^{--}. This is taken as evidence that the species HgI_4^{--} may also be present in ethylenediamine. Moreover, the yellow solid phase in equilibrium with saturated HgI_2 solution in ethylenediamine has the empirical formula Hg·2I·2en. If this composition is indicative of the composition of the species in the solution, three possibilities exist for the solute species: (1) an uncharged inner complex salt, HgI_2en_2; (2) the ion pairs of a simple solvated salt, $Hgen_2^{++} + 2I^-$; (3) the complex ionic "polymerization isomer," $Hgen_3^{++} + HgI_4en^{--}$.

In dilute solutions of HgI_2, the data do not provide any basis for choosing between the soluble "inner complex" salt (not as stable as the cyanide) or the ion pairs formed by the interaction of solvated ions of the simple salt as the solute species; both would be expected to show a decrease in equivalent conductance with increasing concentration. In the more concentrated solutions, however, the yellow color of the solution indicates that the solvated ion HgI_4^{--} is present, so that the species in solution must be $Hgen_3^{++}$ and HgI_4en^{--}. Increasing formation of the yellow complex species from the un-ionized inner complex molecules can account for the increasing conductance at moderate concentrations as well as can the formation of triple ions.

With $HgBr_2$ solutions the situation might be expected to be about the same as with the iodide. However, since complexes between Hg^{++} and Br^- are known to be considerably weaker than between Hg^{++} and I^- (see below), the inner complex, $HgBr_2en_2$, and complex "polymerization isomer," $Hgen_3^{++} + HgBr_4en^{--}$, would both be less stable than the corresponding iodide and therefore would be less likely to be formed in as large amounts in solution. Thus, it seems probable that the simple solvated ions of the dissolved salt are important solute species in the bromide solutions and may be the explanation for the somewhat higher conductance of the bromide solutions. In this case, therefore, the increasing conductance at moderate concentrations may be due mainly to triple-ion formations. Since mercuric bromide is not as soluble in ethylenediamine as is the iodide or cyanide and, moreover, the more concentrated solutions of $HgBr_2$ become cloudy and apparently are not stable, conductance data could not be obtained over a concentration range large enough to show whether or not a maximum occurs in this case.

Since no data are available on relative stabilities of mercuric halides and cyanide in ethylenediamine as a solvent, it is of interest to compare the stabilities of the aqueous complexes.[7] The logarithms of the over-all formation constants (log $k_1k_2k_3k_4$) of HgX_4^{--} where $X = CN^-, I^-, Br^-$ and Cl^- are 41.4, 30.3, 21.6 and 16.0, respectively. For comparison, log k_1k_2 of the aqueous ethylenediamine complex, $Hgen_2^{++}$, is 23.4. Since the bonding between the mercury and the coördinating group is essentially covalent with all these groups, and not ionic, it seems reasonable that changing the solvent from water to ethylenediamine (dielectric constant = 12.9) would not alter the *order* of the stabilities of the halide and cyanide complexes. Of course, all such complexes would be much less stable in ethylenediamine as a solvent than in water, since the solvent molecules compete for the mercury cations. Comparison of the stability constants of the halide and cyanide complexes with that of the ethylenediamine complex leads one to predict that cyanide and iodide complexes would be stable in ethylenediamine as a solvent whereas bromide complexes would be weak, if formed at all, and chloride complexes would probably not exist. The chemical behavior, solubilities and conductances of the substances in ethylenediamine are not out of line with these predictions.

The possible formation of complexes between covalent compounds of iodine or the iodide ion and electron donors does not seem to have been investigated. The appearance of intense charge-transfer bands in the near ultraviolet would demonstrate the presence of complexing convincingly. Attempts were made in the present work to investigate the ultraviolet spectrum of the mercuric iodide solutions, but even in the narrowest cells available (0.1 mm.) the ethylenediamine itself strongly absorbs at about 260 mμ, thus masking any possible effect of solvation.

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[7] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 57, 518.