oxygen. The reaction is auto-inhibited by the nitrite, a "steady state" being established when only a very small quantity of nitrate has been decomposed.

2. Aqueous potassium nitrite solutions are stable in ultraviolet light.
3. The addition of potassium nitrite to a solution of potassium nitrate inhibits partially or completely the photolysis of the nitrate solution.
4. Hydroxides increase the rate of photolysis, and displace the "steady state" towards the nitrite, possibly due to the formation of a peroxide.
5. Acids decrease the rate of decomposition, but do not displace the "steady state."
6. Potassium nitrate solutions obey Beer's law, as a result of which the nitrate-nitrite equilibria in a stirred and unstirred solution are quite different, the disparity depending on the concentration of the solution.
7. The nitrate-nitrite equilibrium in an unstirred solution is entirely dependent on the size of the surface exposed to the light source, and on the concentration and thickness of the solution.
8. The rate of reaction is accelerated by heat, but complications make the determination of a temperature coefficient impracticable.
9. Warburg's calculations of quanta are shown to be untenable.

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A STUDY OF THE VISCOSITIES OF SOLUTIONS CONTAINING MIXTURES OF MERCURIC, CUPRIC AND COBALTOUS CHLORIDES WITH OTHER CHLORIDES FOR THE PURPOSE OF FINDING THE COMPOSITION OF THE COMPLEX IONS FORMED

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Introduction

It has been known for a very long time that certain properties of the solution undergo a change with the change in constitution of the solute, and some of these properties have been utilized in investigating the formation and composition of the complex compounds so formed in the solution. Sidgwick and Tizard,[1] for example, have investigated the composition of the complex compounds formed in the cases of cobalt and copper salts by studying the colors of their solutions at different concentrations.

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[1] Sidgwick and Tizard, *J. Chem. Soc.*, **93**, 187 (1908).

Moreover, according to the theory of Donnan and Bassett, the complex anions formed, in the cases of the concentrated solutions of copper and cobalt chlorides or in the cases of mixtures of these chlorides with other chlorides should have the composition $[M^{II}Cl_4]^{--}$ where M stands for Co or Cu. The work of LeBlanc and Noyes on mercuric chloride also indicates the formation of a similar complex anion in the cases of concentrated solutions of mercuric chloride or its mixtures with hydrochloric acid.

Viscosity, as is well known, is also a constitutive property, to a great extent, and it is rather strange that this property has been so little utilized for investigating the formation of complexes in solutions. It was felt that by viscosity measurements, it might be possible to determine the constitution of the much disputed compounds formed in the cases of the concentrated solutions of cobalt, cupric and mercuric chlorides and their mixtures in different proportions with other chlorides, and it was with this object in view that the present investigation was undertaken.

I have assumed as valid for electrolytic solutions the cube root equation, $\eta = x\eta_1^{\frac{1}{3}} + (1 - x)\eta_2^{\frac{1}{3}}$ (where x is the molecular fraction of one substance of η_1 viscosity while η and η_2 are the viscosities of the mixture and the second constituents, respectively) proposed by Kendall,[2] which is found to give satisfactory results when applied to ideal mixtures of various electrolytes.

The divergences between the observed and calculated values of the viscosities of mixture can be rightly considered to be due to the formation of the complex ions in such mixtures, and the data so obtained can be utilized for determining the composition of the complex ions so formed.

Experimental Part

The viscosimeter used in the present investigation was the modified form of the Ostwald viscosimeter used by Applebey[3] and by Washburn and Williams[4] in their works on aqueous solutions. This form of apparatus is now commonly used because it may be handled easily and because it obeys the Poiseuille law, if its tube and bulb are of the required dimensions. The formula for the viscosity resolves itself into $\eta \equiv Kdt - (Bd/t)$, where K and B are constants for the apparatus and d and t are the density and time of flow of the liquid. This can be simplified to $\eta \equiv Kdt$ by decreasing the bore of the capillary tubing and thus increasing the time of flow, as in such a case Bd/t will become negligibly small. The constant K for the apparatus was determined by observing the times of flow of four liquids of different densities (ethyl alcohol, carbon tetrachloride, benzene and water) and by taking the values for their viscosities from the standard

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[2] Kendall, THIS JOURNAL, **39**, 1790 (1917).

[3] Applebey, *J. Chem. Soc.*, **97**, 2000 (1910).

[4] Washburn and Williams, THIS JOURNAL, **35**, 737 (1913).

data. These values, divided by the respective products of density and time of flow, gave the constant of the apparatus; it was found that the value of the constant so obtained was practically uniform.

Pure liquid	Density d_4^{25}	Absolute viscosity	Constant of the apparatus $K \times 10^6$
Water	0.99706	0.00893	103.4
Ethyl alcohol	0.7853	.01004	103.3
Carbon tetrachloride	1.5822	.00905	103.4
Benzene	0.8739	.00605	104.7

As in the present work we are concerned only with the viscosities of aqueous solutions, and as the relative viscosities have been determined with respect to water, the constant K for the apparatus was taken as 103.4×10^{-6}.

Care was taken to purify thoroughly the various chemicals, using the standard methods of purification, and the solutions required were prepared with conductivity water. The viscosimeter was kept in a thermostat, the temperature of which was carefully regulated by a thermoregulator, and the observations were carried on in the usual way.

The viscosities of the single solutions of the different chlorides were observed at different concentrations and the results so obtained were utilized for calculating the viscosities of the mixtures of copper, cobalt and mercury chlorides with other chlorides in two different proportions, by using the Kendall equation; these calculated results were then compared with the actual experimental data for the same mixtures. The results of such comparisons were then utilized for deciding between the possibilities of the composition of the complex anion, represented either as MCl_3^+ or as MCl_4^{++} (where M stands for mercury, copper or cobalt).

TABLE I

DATA

Temperature 25°. Viscosity of water = 1

Molecular proportions	Volumes in liters	Density	Viscosity obs.	Viscosity calc.	Diff.
		MERCURIC CHLORIDE			
$HgCl_2 + 2HCl$	4	1.0641	1.0444	1.0574	0.0130
	8	1.0320	1.0249	1.0281	.0032
	16	1.0163	1.0140	1.0139	.0001
	32	1.0085	1.0062	0.9983	.0079
$HgCl_2 + HCl$	4	1.0598	1.0304	1.0365	.0061
	8	1.0295	1.0117	1.0130	.0013
	16	1.0148	1.0065	1.0058	.0007
		COBALTOUS CHLORIDE			
$CoCl_2 + 2HCl$	1	1.1284	1.4735	1.4225	.0509
	2	1.0677	1.2973	1.2662	.0311
	4	1.0355	1.1349	1.1253	.0096
	8	1.0163	1.0557	1.0529	.0028
	16	1.0090	1.0336	1.0213	.0123
$CoCl_2 + 2NaCl$	1	1.1792	1.5562	1.5059	.0503
	2	1.0814	1.3261	1.2972	.0289

TABLE I (*Continued*)

Molecular proportion	Volumes in liters	Density	Viscosity obs.	Viscosity calc.	Diff.
	4	1.0409	1.1647	1.1459	.0188
	8	1.0200	1.0821	1.0723	.0098
	16	1.0120	1.0341	1.0333	.0008
$CoCl_2 + 2KCl$	1	1.1856	1.3013	1.2856	.0657
	2	1.0930	1.1917	1.1822	.0095
	4	1.0471	1.0925	1.0835	.0090
	8	1.0236	1.0397	1.0379	.0020
	16	1.0120	1.0164	1.0155	.0009
$CoCl_2 + 2LiCl$	1	1.1471	1.7375	1.6907	.0468
	2	1.0745	1.3965	1.3689	.0276
	4	1.0400	1.1860	1.1706	.0154
	8	1.0194	1.0893	1.0800	.0093
	16	1.0098	1.0345	1.0355	.0010
$CoCl_2 + MgCl_2$	1	1.1784	1.8323	1.7894	.0429
	2	1.0894	1.3402	1.3205	.0197
	4	1.0450	1.2097	1.1993	.0044
	8	1.0194	1.0893	1.0800	.0093
	16	1.0098	1.0345	1.0355	.0010
$CoCl_2 + HCl$	1	1.1272	1.3937	1.3580	.0356
	2	1.0631	1.2308	1.2284	.0024
	4	1.0316	1.1336	1.1031	.0305
	8	1.0150	1.0561	1.0447	.0114
	16	1.0082	1.0248	1.0231	.0017
$CoCl_2 + NaCl$	1	1.1497	1.4143	1.3914	.0229
	2	1.0751	1.2632	1.2509	.0123
	4	1.0370	1.1283	1.1234	.0049
	8	1.0182	1.0593	1.0569	.0024
	16	1.0093	1.0257	1.0261	.0004
$CoCl_2 + KCl$	1	1.1449	1.2783	1.2680	.0103
	2	1.0768	1.1894	1.1827	.0067
	4	1.0390	1.0795	1.0872	.0077
	8	1.0193	1.0352	1.0387	.0035
$CoCl_2 + 2MgCl_2$	1	1.1478	1.5835	1.5447	.0388
	2	1.0740	1.3285	1.3092	.0193
	4	1.0386	1.1520	1.1461	.0059
	8	1.0185	1.0683	1.0691	.0008
$CoCl_2 + LiCl$	1	1.1345	1.5012	1.4682	.0330
	2	1.0674	1.2950	1.2778	.0172
	4	1.0339	1.1421	1.1315	.0106
	8	1.0169	1.0475	1.0487	.0012
		CUPRIC CHLORIDE			
$CuCl_2 + 2HCl$	1	1.1536	1.5373	1.4841	.0532
	2	1.0770	1.3014	1.2873	.0141
	4	1.0390	1.1409	1.1317	.0092
	8	1.0200	1.0621	1.0539	.0082
	16	1.0099	1.0258	1.0236	.0022
$CuCl_2 + 2NaCl$	1	1.1948	1.6205	1.5710	.0495
	2	1.1000	1.3423	1.3185	.0235

TABLE I (*Concluded*)

Molecular proportions	Volumes in liters	Density	Viscosity obs.	Viscosity calc.	Diff.
	4	1.0506	1.1633	1.1525	.0108
	8	1.0254	1.0795	1.0733	.0062
	16	1.0128	1.0379	1.0356	.0023
$CuCl_2 + 2KCl$	1	1.2045	1.3763	1.3413	.0350
	2	1.1025	1.2268	1.2019	.0249
	4	1.0520	1.1092	1.0897	.0195
	8	1.0268	1.0536	1.0387	.0149
	16	1.0135	1.0251	1.0178	.0073
$CuCl_2 + 2LiCl$	1	1.1670	1.9147	1.8597	.0550
	2	1.0840	1.4157	1.3816	.0241
	4	1.0425	1.1836	1.1773	.0063
	8	1.0221	1.0893	1.0810	.0083
	16	1.0115	1.0395	1.0378	.0017
$CuCl_2 + MgCl_2$	1	1.1945	1.9143	1.8669	.0474
	2	1.0980	1.4931	1.4642	.0249
	4	1.0491	1.2341	1.2062	.0327
	8	1.0248	1.0985	1.0949	.0036
	16	1.0125	1.0463	1.0475	.0012
$CuCl_2 + HCl$	1	1.1371	1.4478	1.4169	.0309
	2	1.0690	1.2656	1.2488	.0168
	4	1.0347	1.1193	1.1095	.0098
	8	1.0176	1.0465	1.0457	.0008
	16	1.0080	1.0249	1.0254	.0005
$CuCl_2 + NaCl$	1	1.1595	1.4723	1.4516	.0207
	2	1.0800	1.2283	1.2117	.0166
	4	1.0401	1.1387	1.1299	.0088
	8	1.0201	1.0621	1.0579	.0042
	16	1.0102	1.0301	1.0294	.0007
$CuCl_2 + KCl$	1	1.1648	1.3421	1.3229	.0192
	2	1.0825	1.2051	1.2024	.0027
	4	1.0420	1.1021	1.0935	.0086
	8	1.0210	1.0405	1.0397	.0008
	16	1.0107	1.0243	1.0247	.0004
$CuCl_2 + LiCl$	1	1.1445	1.5531	1.5317	.0214
	2	1.0730	1.3144	1.2991	.0153
	4	1.0370	1.1453	1.1380	.0073
	8	1.0187	1.0613	1.0602	.0011
	16	1.0095	1.0385	1.0304	.0008
$CuCl_2 + {}^1/_2MgCl_2$	1	1.1576	1.6321	1.6116	.0205
	2	1.0790	1.501	1.3310	.0191
	4	1.0398	1.1583	1.1527	.0056
	8	1.0200	1.0761	1.0701	.0060
	16	1.0101	1.0381	1.0360	.0021

Discussion of the Results

Binary Mixtures of Mercuric Chloride with Hydrochloric Acid.—Inspection of the results shows that the values of the observed viscosities, in the case of mixtures having the proportion of $HgCl_2 : 2HCl$ are less than the values calculated by means of Kendall's cube root equation. If the mixtures had been ideal, and if no chemical reaction had taken place between the constituents, the observed values would have been practically the same as the calculated ones.

In the case of mixtures having the proportion $HgCl_2 : HCl$, there is a slight difference between the observed and the calculated values; but this difference even in the most concentrated solution is much less than the difference obtained in the case of the mixture $HgCl_2 : 2HCl$ at the same concentrations.

The difference between the calculated and the observed viscosity begins to disappear with the increase in dilution, except at a dilution of 32 liters in the case of mixtures of $HgCl_2 + 2HCl$, where an abnormal result is obtained.

The solubility of mercuric chloride increases in the presence of hydrochloric acid. This fact also clearly indicates the possibility of some chemical reaction taking place between the constituents of the solution.

All of these observations can be satisfactorily explained by assuming that a complex bivalent anion having the composition $HgCl_4^{--}$ is formed by the addition of hydrochloric acid to mercuric chloride. If this be the case the maximum deviation between the calculated and the observed values will be found in the concentrated solution having the proportion $HgCl_2 : 2HCl$, and as the anion probably breaks up into $HgCl_2 + 2Cl^-$ on dilution in solutions at lower concentration, the normal viscosity will be observed.

In the case of the solutions having the composition $HgCl_2 + HCl$ the deviation between the observed and the calculated values is less than in the previous case. This small deviation can be explained, by assuming the existence of the ions $HgCl_4^{--}$ to a small extent, which on dilution dissociate, as explained above.

Mixtures of Cobalt Chloride and Copper Chloride with Other Chlorides.—Similar results were obtained in the cases of the mixtures of cobalt and cupric chlorides with other chlorides, in the ratio of $CoCl_2 : M^ICl$, $CoCl_2 : 2M^ICl$ and $CuCl_2 : M^ICl$, $CuCl_2 : 2M^ICl$. These observations also can be explained in the same way by assuming the formation of complex anions, $CoCl_4^{--}$ and $CuCl_4^{--}$.

Inspection of the tables shows that in the cases of mixtures of cobalt and cupric chlorides with other chlorides (except in the cases of the mixtures $CoCl_2 : NaCl$ at a dilution of 16 liters, $CoCl_2 : KCl$ at a dilution of 8 liters and $CuCl_2 : KCl$ at a dilution of 16 liters), the observed values of the viscosity are higher than the calculated values. This can probably be explained by assuming that the newly formed anions $CoCl_4^{--}$ and $CuCl_4^{--}$ are less symmetrical; moreover, as they are greater in weight than the simple ones, and as the degree of hydration of simple ions changes when the complex ions are formed, the viscosity should also change.

The observations made with respect to the color changes associated with these solutions, lead us to similar conclusions regarding both single solutions and mixtures. In dilute solutions, the colors were like those of ordinary solutions of cupric and cobaltous chlorides, but at higher concentrations cupric chloride solution was green, while cobaltous chloride solution became blue very quickly. The change in color observed at the greater dilutions is due to the dissociation of $CoCl_4^{--}$ and $CuCl_4^{--}$ into (1) $CoCl_2$, $2Cl^-$ and (2) $CuCl_2$, $2Cl^-$. The change of the color of cobaltous and cupric chlorides by formation of different chlorides or because of concentration of the solutions on heating is definitely due to the following reactions: $CoCl_2 + 2Cl^- \rightleftharpoons CoCl_4^{--}$ (blue) $\rightleftharpoons [Co^{++}$ (pink) $+ 2Cl^-] + 2Cl^-$; $2CoCl_2 \rightleftharpoons 2(Co^{++}$ (pink) $+ 2Cl^-) \rightleftharpoons CoCl_4^{--}$ (blue) $+ Co^{++}$.

Hence, it is clear that the color changes are connected with the formation of complex compounds.

In the case of the binary mixture of cobaltous chloride and hydrochloric acid (1 : 1) it was noticed that the mixture became deep blue when it was warmed to 31.5°. When it was cooled it regained its pink tinge at 28.0°. The depth of color changed with the concentration of hydrochloric acid and was observed to be at a maximum when two molecules of hydrochloric acid were present to one of cobaltous chloride. This observation also strengthens the hypothesis that color changes are due to complex formation, during which heat is evolved, since the color deepens (that is, the complex-ion formation increases) as the solution is warmed.

Summary

An attempt has been made to determine the degree of formation of complex ions and the compositions of such ions in the cases of mixtures of mercuric, cobaltous and cupric chlorides with other chlorides, by a study of the observed viscosities of such binary mixtures and by the values calculated by means of Kendall's equation, which when applied to ideal mixtures is found to give satisfactory results.

The observations have also been carried on with respect to the color changes associated with the solutions of cobalt and cupric chlorides, at different concentrations and their mixtures with other chlorides.

As the result of the present investigation, it appears that in the cases of mixtures of mercuric chloride with hydrochloric acid, and cupric and cobaltous chlorides with other chlorides, the complex anions formed have the compositions $HgCl_4^{--}$, $CuCl_4^{--}$ and $CoCl_4^-$, respectively.

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