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The Vapor Pressures of Chromic Salt Solutions

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Progress in the theoretical treatment of solutions of polyvalent electrolytes will require more experimental data than are at present available, particularly for dilute solutions, but it is known that the higher valence types do not conform to the Debye–Hückel relations in any of their present forms. Vapor pressure measurements have been made by Robinson[1] on potassium ferrocyanide, aluminum sulfate and lanthanum chloride, and by Mason[2] on the chlorides of aluminum and the rare earths, and while the impossibility of obtaining data at low concentrations by this method prevents the accurate evaluation of activity coefficients, the work has shown the general trend of the values. It is the purpose of this paper to add to the available vapor pressure data on polyvalent electrolytes by presenting measurements for five chromic salts obtained by the isopiestic method. In addition to this the well-known isomerism of chromic salts has been implicated and it has been possible to show that the vapor pressures of solutions of the violet and green isomers of any one salt are different for freshly prepared solutions but become identical when aged sufficiently to be at inner equilibrium. That such should be the case is predicted by Werner's theory[3] but has never been demonstrated, although Marchetti[4] and others have found a difference in the freezing points of fresh solutions of the isomeric chlorides and there are some ill-defined data[5] in the literature on the colligative properties of other chromic salts.

Experimental

The technique of the isopiestic method is described elsewhere in the literature.[6,7] In the present work Merck Analyzed potassium chloride was used for reference solute after recrystallizing and drying at 200°. Four gold-plated sterling silver dishes were held in place on a copper block by a brass plate and the whole contained in a glass desiccator and rocked in a thermostat at 25 ± 0.03°. Several small depressions were bored in the brass plate and in these 0.5 g. of water was distributed prior to each run in order to replace water lost by evaporation during evacuation. The use of liquid to improve the thermal contact between the dishes and the block was found unnecessary. The success of the method depended largely upon the complete removal of air from the desiccator, but, in order to avoid spattering of the solutions during evacuation caused by the escape of dissolved air and the boiling of the solutions, the following procedure was necessary: After momentary evacuation to seal the desiccator the latter was chilled in running water for an hour with occasional rocking. Evacuation was then carried out at 10° for thirty minutes using a filter pump to reduce the possibility of boiling. Except when working with aged solutions, only water which had been freshly boiled to expel air was used in preparing the solutions in the dishes.

The vapor pressures of solutions at inner equilibrium, which will henceforth be referred to as equilibrated solutions, were first measured. For this purpose only solutions which had been stored in glass bottles for two or three months at 25° were used, although it became apparent later that two weeks of storage would have sufficed. The composition of these solutions was determined after storage by direct analysis for chromium. The latter was oxidized to chromate with peroxide and the chromate determined iodometrically. In agreement with previous workers it was not found possible to carry the measurements below tenth molal. As the salts reported are of higher valence type it is to be expected that the accuracy would be somewhat less than usual, but, notwithstanding, the agreement of the duplicates even in the most dilute solutions was usually within 0.5%. At higher concentrations the precision was, of course, far better than this. In most cases a separate stored solution was used for each determination.

Chromium Chloride.—The common green hexahydrate, prepared by reprecipitating the Baker Analyzed chemical from water with hydrogen chloride, was used in making the solutions for storage. The product, which upon analysis showed 59.30% $CrCl_3$ (calcd. for $CrCl_3\cdot 6H_2O$, 59.44%), was found to keep its theoretical composition indefinitely over 60% sulfuric acid. The violet chloride was prepared from the nitrate (Baker Analyzed) according to the method of Bjerrum[8] and preserved over concentrated sulfuric acid; analytical composition, 59.27% $CrCl_3$.

Chromium Sulfate.—The stored solutions were made from the violet form prepared according to the method of Richards and Bonnet.[9] Both chromium and sulfate analyses of this material (the latter in the presence of acetic acid)[10] showed 56.34% $Cr_2(SO_4)_3$, (calcd. for $Cr_2(SO_4)_3\cdot 17H_2O$, 56.15%). The normal green sulfate was prepared by heating the solid violet form at 90°. Its composition corresponded to that of the octohydrate.

Chromic Nitrate.—Recrystallized Baker Analyzed chemical, the composition agreeing with the theoretical value for the nonahydrate. The period of storage was dispensed with in the case of this salt.

Potassium Chrome Alum.—The solutions were prepared from British Drug Houses alum recrystallized from a temperature not above 60°. Its composition corresponded to theory. Attempts at recrystallization from higher temperatures gave a greenish solid, which, while it may have been an isomer, was not further examined.

Ammonium Chrome Alum.—Baker Analyzed product was recrystallized and found to have the theoretical composition. In the case of this salt the same stored solution was used for several points in the neighborhood of its original concentration.

Results and Discussion

The isopiestic molalities are given in Table 1. As potassium chloride was the only reference solid used the range of concentrations measured was limited by its solubility except in the case of the alums.

In connection with the results for chromic nitrate it is of interest to point out that a plot of

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[1] Robinson, THIS JOURNAL, **59**, 84 (1937); *Trans. Faraday Soc.*, **35**, 1229 (1939).

[2] Mason, THIS JOURNAL, **60**, 1638 (1938).

[3] Werner and Gubser, *Ber.*, **34**, 1579 (1901).

[4] Marchetti, *Gazz. chim. ital.*, **22**, 375 (1892).

[5] See, for example, Colson, *Compt. rend.*, **144**, 637 (1907), and Jones and Mackay, *Am. Chem. J.*, **19**, 83 (1897).

[6] Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

[7] Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934).

[8] Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

[9] Richards and Bonnet, *ibid.*, **47**, 29 (1904).

[10] Willard and Schneidewind, *Trans. Am. Electrochem. Soc.*, **56**, 333 (1929).

TABLE I

AGED SOLUTIONS

Chromic Chloride

m_{KCl}	m_{CrCl_3}
0.186	0.1046
.633	.3203
1.359	.590
1.629	.672
2.173	.829
3.174	1.087
4.111	1.322

Chromic sulfate

m_{KCl}	$m_{Cr_2(SO_4)_3}$
0.1270	0.1144
.2160	.1965
.2379	.2143
.4524	.3775
.796	.565
.962	.634
1.385	.779
1.764	.878
2.396	1.029
3.880	1.304

Chromic nitrate

m_{KCl}	$m_{Cr(NO_3)_3}$
0.0966	0.0564
.2098	.1202
.4043	.2208
.685	.3485
1.202	.552
1.740	.734
2.380	.926
3.263	1.164
4.385	1.443

Potassium chrome alum

m_{KCl}	$m_{KCr(SO_4)_2}$
0.1101	0.0974
.229	.207
.243	.220
.260	.238
.373	.351
.405	.386
.492	.471
.501	.481
.523	.502
.668	.644
.791	.751
1.233	1.095

Ammonium chrome alum

m_{KCl}	$m_{NH_4Cr(SO_4)_2}$
0.0608	0.0485
.1297	.1106
.1381	.1196
.1426	.1223
.1643	.1424
.1778	.1556
.2243	.2004
.2324	.2077
.2465	.2225
.2677	.2422
.3141	.2866
.3250	.2983
.3607	.3329
.3774	.3483
.3817	.3535
.3996	.3695
.4125	.3829
.4458	.4148
.4806	.4485
.4947	.4608
.5230	.4855
.5464	.5048
.5911	.5472
.6000	.5558
.609	.5639
.618	.5692
.632	.5808
.647	.5957
.745	.6807

[a] Oversaturated.

isopiestic molalities is a smooth curve even though the nitrate solutions were not aged. In the case of the other four salts a period of storage was necessary for such a result. This is no doubt related to the fact that the nitrate is not known in isomeric violet and green solid forms so that the usual inner equilibrium does not exist in its solutions. This has been substantiated by a recent determination of its solubility.[11] In the case of ammonium chrome alum a larger number of experimental points was obtained because it was actually the first of the five salts studied and a greater number of data would indicate better the regularity of the results to be expected.

The failure of the isopiestic method at concentrations lower than tenth molal in the case of these high valence types causes difficulty in the calculation of activities because of the uncertainty involved in the extrapolations to zero concentration. The activity coefficient at the lowest experimental concentration was tentatively evaluated using the familiar equation

$$\ln \gamma = \frac{K\sqrt{m}}{1 + b\sqrt{m}} + \int_0^m \frac{\delta\varphi}{m}\, dm + \delta\varphi$$

assigning values for the distance of closest ion approach of 6.3, 4.6, 5.6, 4.1 and 4.7 Å. for the chloride, sulfate, nitrate, potassium chrome and ammonium chrome alums, respectively. The activity coefficients at the other concentrations were measured relative to tenth molal by the method of Randall and White,[12] taking the osmotic coefficients (φ) for potassium chloride solutions from the paper of Scatchard[13] and using graphical integration between two finite concentrations. The activity coefficient ratios therefore are accurate but the absolute values are uncertain. Table II gives the values at rounded concentrations of the osmotic coefficient and the activity coefficient (γ) for the salts studied. The activity coefficient for chromic chloride may be estimated alternatively with the help of the data for lanthanum chloride given by Robinson[1] by assuming that the ratio of $\gamma_{LaCl_3}/k\gamma_{CrCl_3}$ approaches constancy with dilution, k being a proportionality constant. A value of $\gamma = 0.393$ for $m = 0.1$ was thus obtained.

It is of interest to calculate the vapor pressure lowerings for the alum solutions and compare them with those of the component sulfates. A similar procedure was adopted by Robinson[14] with double chlorides to determine the extent to which the component salts retain their identity in solutions of the mixed electrolytes. Unfortunately, in the case of ammonium chrome alum sufficiently accurate data for ammonium sulfate are not available, but in the case of the potassium chrome alum a comparison was possible with the assistance of Robinson's data for potassium sulfate[15] and potassium chloride.[7] The vapor pressure lowering in two-tenths molal alum is found to be 0.1718 mm. The contributions to this of potassium sulfate and chromic sulfate calculated on the basis of their behavior singly, but in solutions of the same ionic strength as two-tenths molal alum, should be 0.0862 and 0.0872 mm., respectively. The total contribution, 0.1734 mm., differs therefore from the experimental value only by about 1%. Apparently the component salts retain their individuality in the alum solution.

Experiments on Non-equilibrated Solutions

The chief disadvantage of the isopiestic method as applied to non-equilibrated solutions is in the necessity of waiting at least a day for external equilibrium to be established. In the meantime, of course, an internal change in the solutions has occurred. In spite of this it was possible to observe a small but definite difference between the vapor pressures of the equilibrated and non-equilibrated solutions, the difference becoming immeasurably small after the solutions had aged for a week.

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[11] Smith, THIS JOURNAL, **67**, 1228 (1945).

[12] Randall and White, *ibid.*, **48**, 2514 (1926).

[13] Scatchard, Hamer and Wood, *ibid.*, **60**, 3061 (1938).

[14] Robinson, *Trans. Faraday Soc.*, **41**, 752 (1945).

[15] Robinson, THIS JOURNAL, **63**, 1011 (1941).

TABLE II

m	$CrCl_3$	$Cr_2(SO_4)_3$	$Cr(NO_3)_3$	$KCr(SO_4)_2$	$NH_4Cr(SO_4)_2$
			Osmotic Coefficient		
0.1	0.815	0.412	0.793	0.525	0.549
.2	.838	.401	.816	.503	.509
.3	.879	.414	.859	.486	.493
.4	.930	.441	.905	.474	.485
.5	.991	.477	.955	.468	.483
.7	1.116	.586	1.057	.466 (m = 0.6)	.488 (m = 0.6)
1	1.323	.834	1.231	.476 (m = 0.8)	
1.2	1.446	1.039	1.349		
1.4	1.555	1.260	1.469		
1.5			1.524		
			Activity Coefficient		
0.1	(0.365)	(0.0458)	(0.339)	(0.1086)	(0.1207)
.2	.330	.0300	.302	.0758	.0836
.3	.324	.0239	.295	.0607	.0672
.4	.332	.0208	.297	.0518	.0576
.5	.350	.0191	.308	.0456	.0512
.7	.403	.0182	.341	.0414 (m = 0.6)	.0467 (m = 0.6)
1	.535	.0209	.427	.0360 (m = 0.8)	
1.2	.649	.0253	.506		
1.4	.783	.0323	.608		
1.5			.665		

Experimental

Non-equilibrated solutions were obtained by dissolving the solid violet and solid green (where possible) isomers and using the fresh solutions. Of the several green chlorides and sulfates which are known only one of each was used. In a few cases the runs were continued beyond the original point of displacement in order to show the approach to equilibrium and the approximate time required therefor. For the alums, the slowness with which the solid entered solution made it difficult to obtain data on fresh solutions in the neighborhood of saturation, for by the time the solid had dissolved such a solution had already aged considerably.

Results and Discussion

In the case of the chloride and sulfate the displacement of the equilibrium was in the expected direction, for the vapor pressures of fresh violet solutions were found to be less than those of fresh green solutions of the same concentration, the vapor pressures of the equilibrated solutions lying between the two. The fact that solutions originally displaced from equilibrium eventually reached the equilibrium line proves that the observed displacements were real, external equilibrium having already been established as shown by the agreement of the duplicates. The results for the alums were unexpected. Whitney[16] found that none of the sulfate is masked in a fresh solution of potassium chrome alum and the same is probably true for the ammonium alum. On aging half the sulfate becomes masked. The vapor pressures of fresh solutions of both alums, however, were found to be greater than those of the equilibrated solutions. One would expect the reverse if the fresh solutions contain the maximum number of ions, but hydrolysis may well account for this discrepancy.

Summary

1. The vapor pressures of aged aqueous solutions of chromic chloride, chromic sulfate, chromic nitrate, potassium chrome alum and ammonium chrome alum have been determined at 25° and the osmotic coefficient and solute activities calculated at round concentrations.

2. Fresh solutions of violet chromic chloride have lower vapor pressures and fresh solutions of green chromic chloride have higher vapor pressures than aged solutions of the same concentration.

3. Fresh solutions of violet chromic sulfate have lower vapor pressures and fresh solutions of normal green chromic sulfate have higher vapor pressures than aged solutions of the same concentration.

4. There is no evidence that inner equilibrium is reached slowly in aqueous chromic nitrate solution.

5. Fresh potassium chrome alum and ammonium chrome alum solutions have higher vapor pressures than aged solutions of the same concentration.

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[16] Whitney, THIS JOURNAL, **21**, 1075 (1899).