133. Physicochemical Studies of Complex Acids. Part XI. Vapour-pressure Measurements.

By Robert A. Robinson and Donald A. Sinclair.

In previous communications in this series the hypothesis has been advanced that acid solutions of alkali molybdates, tungstates, and vanadates consist of aggregated, charged, colloidal micelles. An accurate method of determining vapour pressures of solutions has now been applied to these substances and, although the molecular weights are too large to be computed with accuracy, conclusive evidence has been obtained that polymerisation occurs in the solutions; an estimate has been made of the degree of polymerisation in the vanadate solutions.

The method, already described in detail (*J. Physical Chem.*, **1933**, **37**, 495), consists in allowing solutions of, *e.g.*, sodium vanadate and potassium chloride to evaporate freely under reduced pressure until the vapour pressures of the two solutions are equal; from the known vapour pressure of the chloride solution, that of the vanadate solution can then be obtained. It is believed that the method has a high degree of accuracy.

Solutions were made of three salts of composition $1{\cdot}024Na_2O,V_2O_5$, Na_2O,WO_3, and

Na_2O,MoO_3 respectively; to these, various amounts of hydrochloric acid were added, corresponding to different stages in the acidification of these salts; and their vapour pressures were then determined. The solutions of the salt and potassium chloride were allowed to evaporate for 3 days, a time which proved sufficient to attain equilibrium. Gold-plated silver boxes, lightly coated inside with vaselin to prevent the reduction which otherwise occurred, were used. In Table I, cols. 1—4 give, respectively, the concentrations (atoms or mols./l.)

TABLE I.

Vanadate solution.					
Na.	V.	HCl.	Equiv. KCl.	$10^6 \times \Delta p/p_0$.	HCl/V.
0·2500	0·2442	0	0·1140	1548	0
0·3301	0·3225	0	0·1496	1526	0
0·2650	0·2589	0·0518	0·1496	1904	0·200
0·1768	0·1728	0·0424	0·1040	2001	0·245
0·2519	0·2462	0·0626	0·1496	2002	0·254
0·2351	0·2296	0·1017	0·1601	2298	0·443
0·1372	0·1341	0·0659	0·0994	2467	0·491
0·2116	0·2067	0·1098	0·1588	2531	0·531
0·0952	0·0931	0·0548	0·0739	2659	0·589
0·1771	0·1731	0·1332	0·1588	3022	0·769
0·1632	0·1594	0·1483	0·1588	3282	0·930
0·0744	0·0727	0·0714	0·0748	3447	0·982
0·1429	0·1396	0·1524	0·1601	3779	1·092

FIG. 1.

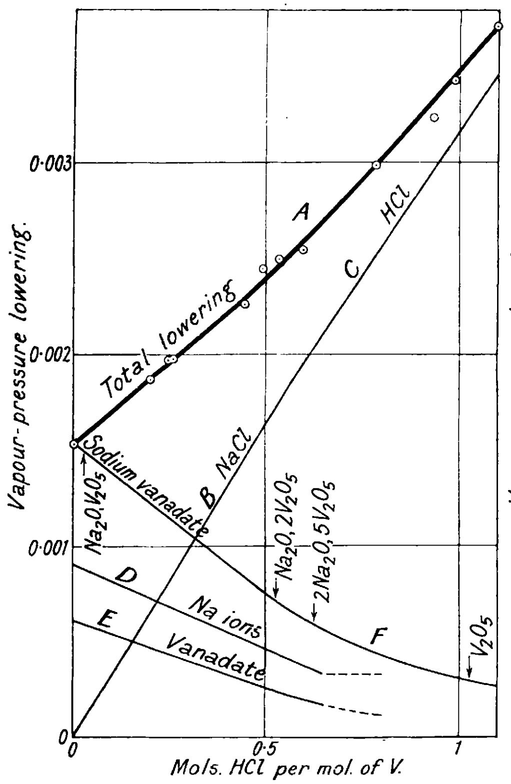
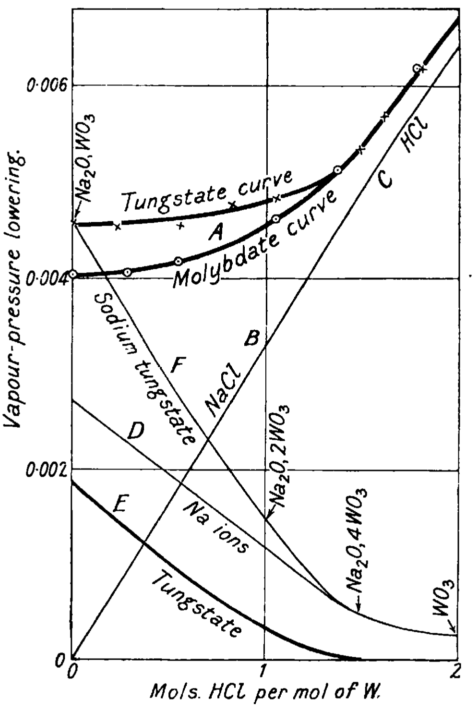


FIG. 2.



of sodium, vanadium, and hydrogen chloride in the one solution, and of potassium chloride in that of equal vapour pressure; col. 5 gives the vapour-pressure lowering of the former solution as derived from that of the latter solution (as the concentrations of the vanadate solutions are necessarily variable through evaporation in attaining equilibrium, all lowerings have been referred to solutions 0·1*M* with respect to vanadium by multiplying by 0·1 and dividing by the vanadium concentration given in col. 2); col. 6 gives the ratio HCl/V (mols. per atom).

These vapour-pressure lowerings are shown by the upper curve in Fig. 1. When 0·0024 mol. of acid has been added, 0·1*M*-sodium metavanadate is present along with 0·0024*M*-sodium chloride, and allowance being made for the vapour-pressure lowering of the latter, the lowering due to the vanadate is 0·001513; the vanadate, therefore, cannot be a simple molecule, for even an undissociated molecule would have given a lowering of 0·00180. If it is doubly polymerised the molar lowering is 0·03026, whence the van 't Hoff factor is 1·692. A triple polymerisation gives a molar lowering of 0·04539 and $i = 2{\cdot}522$, so the degree of dissociation is 0·51, which is a reasonable figure.

Now, it is known from previous experiments that acid acts on the metavanadate to yield a polyvanadate and sodium chloride until $2Na_2O,5V_2O_5$ is formed at 0·624 mol. of acid. During this reaction, therefore, allowance must be made for the sodium chloride formed; the lowering due to this is shown by curve B. Beyond this point the acid remains free, the vapour pressure due to it being shown by curve C. Subtracting these lowerings from the total lowering (curve A), we find the contribution of the vanadate in solution, this consisting of sodium ions and polymerised vanadate ions and molecules. Since the metavanadate is 51% dissociated, this solution contains 0·051*M*-$Na^{\cdot}$, 0·017*M*-V_3O_9''', and 0·0163*M*-$Na_3V_3O_9$, so the contribution of the sodium ion is 0·00918. When $2Na_2O,5V_2O_5$ is formed at 0·0624 mol. of acid, the conductivity data of Part II (J., 1930, 1261) justify the assumption that there is still 50% dissociation and therefore $[Na^{\cdot}] = 0{\cdot}02M$, the vapour-pressure lowering due to this ion being 0·00360. On further acidification, the sodium-ion concentration remains approximately constant, although the data in Part II show that in acid solutions some replacement of the sodium by hydrogen occurs and also some repression of the ionisation of the sodium salt. This will cause a small decrease in the contribution of the sodium ions which cannot be computed quantitatively. Consequently, the data for solutions more acid than $2Na_2O,5V_2O_5$ are only qualitative, especially as slight precipitation occurs with these acid solutions during the 3 days required for an experiment.

Subtraction of the sodium-ion contribution from curve F yields the contribution to be ascribed to the polymerised vanadate ions and molecules, shown by curve E. Since the molarity of the vanadium is $0{\cdot}1/n$, where n is the degree of polymerisation, then $n = 0{\cdot}0180 \times 0{\cdot}1$/observed lowering, 0·0180 being the molar lowering of the vapour pressure, whence the following values of n can be calculated:

Na/V	1	0·5	0·4	0·33	0·25
n	3	6	7	10	11

Although these figures would be altered if different assumptions were made as to the degree of dissociation of the vanadate, yet it is found that any value which is in reasonable agreement with the conductivity data of Part II leads to the same conclusion that the molecular weight of the complex must approach 1000 in the acid solutions. It is possible that polymerisation proceeds even further on the addition of more acid, but, as already pointed out, quantitative analysis of the data is not possible in this region.

TABLE II.

Solution.					
Na.	W (or Mo).	HCl.	Equiv. KCl.	$10^6 \times \Delta p/p_0$.	HCl/W (or Mo).
		Sodium tungstate.			
0·1942	0·0971	0	0·1360	4631	0
0·1720	0·0860	0	0·1201	4624	0
0·6080	0·3040	0	0·4233	4517	0
0·2020	0·1010	0·0246	0·1409	4605	0·244
0·1946	0·0973	0·0549	0·1360	4622	0·564
0·1728	0·0864	0·0487	0·1201	4604	0·564
0·1924	0·0962	0·0796	0·1409	4836	0·827
0·1634	0·0817	0·0870	0·1201	4870	1·065
0·1716	0·0858	0·1097	0·1304	5026	1·277
0·1664	0·0832	0·1247	0·1409	5592	1·499
0·1496	0·0748	0·1211	0·1304	5765	1·615
0·1346	0·0673	0·1088	0·1166	5744	1·617
0·1234	0·0617	0·1117	0·1166	6264	1·810
0·1376	0·0688	0·1246	0·1304	6282	1·811
		Sodium molybdate.			
0·3182	0·1591	0	0·2003	4126	0
0·3176	0·1588	0·0444	0·2003	4133	0·279
0·3094	0·1547	0·0823	0·2003	4243	0·532
0·2130	0·1065	0·1119	0·1509	4669	1·051
0·1912	0·0956	0·1305	0·1509	5201	1·365
0·1586	0·0793	0·1415	0·1509	6270	1·784

Table II gives the corresponding values obtained with solutions of sodium tungstate and molybdate. The data are shown graphically in Fig. 2, only the upper curve A being given in the case of the molybdate. It is evident that after the formation of a complex corresponding to $Na_2O,4MoO_3$ the curve for the molybdate is similar to that for the tungstate.

It is also clear that neither of the two original salts is polymerised in solution, the vapour-pressure lowerings corresponding to degrees of dissociation of 0·82 and 0·67 respectively. By calculations similar to those for the vanadate, the vapour-pressure lowerings contributed by the tungstate ion and the undissociated tungstate molecule are found (curve E). This curve shows that when the composition of the solution corresponds to $Na_2O,2WO_3$ the vapour-pressure lowering is very small and corresponds to a tungstate ion or molecule W_4O_{14}'''' or $Na_4W_4O_{14}$, whereas when the solution corresponds to $Na_2O,4WO_3$ the vapour-pressure lowering is too small to be detected by this method. It follows that the tungstate must be polymerised many times. The same holds true for the molybdate.

The authors thank Dr. H. T. S. Britton for his interest in this work.

UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND.

[*Received, December 11th,* 1933.]