properties of solutions of these "acids" in liquid ammonia. If the catalytic effect of the various ammonium salts were entirely dependent upon the concentration of ammonium ions, as calculated from physical data with the assumption that simple ionization is involved, one would expect the order to correspond to the anion series: $ClO_4^- > Br^- > Cl^- > C_6H_5COO^-$ (?).[5,6] For the ammonolysis of ethyl benzoate at 25° a comparison of the reaction velocity constants and half-reaction times indicates that the reverse order obtains.

Catalyst used	$C_6H_5COONH_4$	NH_4Cl	NH_4Br	NH_4ClO_4
K_c	0.00336	0.00272	0.00208	0.00155
Half-time in hours	206	252	333	447

Our experimental procedure did not permit an exact calculation of the normality of the solutions with respect to their ammonium salt content, since the solutions were made up to a volume of 25 ml. at the temperature of the solid carbon dioxide–acetone bath. For those solutions containing 0.00935 mole of ammonium salt it may be estimated that the solutions were better than 0.3 *N*. This concentration is higher than that used in most of Shatenshtein's experimental work. It lies, however, in the range where the catalytic activity of the ammonated proton is markedly influenced by the anion present. To quote Shatenshtein[2] (p. 433), "Assuming that the catalytic activity of the solvatized protons increases as the field of forces of the anions becomes stronger, one may expect that a series of acids placed in the ascending order of specific catalytic activity will be antibatic to a series of acids placed in the ascending order of electrical conductivity. . . ." Our experimental results may be regarded as confirmation of this statement. This hypothesis also is strengthened by a consideration of the properties of ammonia, which not only is a basic solvent of high proton affinity, but also one in which the effect of interionic forces is very pronounced, because of its low dielectric constant.

Summary

1. The ammonolysis of ethyl benzoate in the presence of various ammonium salts has been studied quantitatively at 0 and at 25°. The reaction has been found to be a pseudo first order reaction.

2. The catalytic effect of equivalent concentrations of various ammonium salts is given by the series

$C_6H_5COONH_4 > NH_4Cl > NH_4Br > NH_4ClO_4$

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(5) Shatenshtein and Uskova, *Acta Physicochim., U. S. S. R.*, **2**, 37 (1935).

(6) Gurjanova and Pleskov, *ibid.*, **5**, 509 (1936).

[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF MARYLAND]

Effect of Salts on the Acidity of Some Vanadium Pentoxide Sols[1]

BY M. M. HARING AND W. J. HART

Many studies have been made of the effect of salts on the *p*H of the intermicellar liquid of various hydrous oxide sols.[2] For the most part these studies have involved the positive sols. It was the purpose of this study to apply similar methods to the negative vanadium pentoxide sols.

Experimental

All reagents used were the purest grade obtainable and were subjected to no further purification.

Four sols were prepared, A and D by the method of Biltz[3] and B and C by the method of Müller.[4] In the case of B and C, the alternative method was used of pouring the molten oxide directly into water rather than quenching to a glass and then dispersing. No dialysis was employed with the pyrolytic sols, since the fusion at 700° for ten minutes certainly removed all volatile impurities derivable from ammonium vanadate and nitric acid. Sols A and D were both dialyzed, A for ten days with an eighteen-inch (46 cm.) length of one-inch (2.54-cm.) cellophane tubing, through which distilled water was passed at the rate of one drop per second, and D for eight days with a six-foot (1.8-meter) length of the same tub-

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(1) Abstracted from a thesis submitted by W. J. Hart to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) See Whitehead, *Chem. Rev.*, **21**, 113 (1937), for a fairly extensive bibliography.

(3) Biltz, *Ber.*, **37**, 1098 (1904).

(4) Müller, *Z. Chem. Ind. Kolloide*, **8**, 302 (1911).

ing at the same rate of flow. The dialysis was carried out at room temperature. All sols were tested for charge by cataphoresis and found to be negative.

The analyses of the sols are given in Table I.

TABLE I

Sol	% V_2O_5	NH_3 (parts/million)	Cl^-
A	0.068	28.7	Doubtful trace
B	0.308	....	....
C	0.110	....	....
D	0.078	22.6	No test

The vanadium pentoxide was determined as described by Scott.[5] The ammonia was estimated by the Kjeldahl method[6] and the chloride ion by the standard test. Incidentally the results of the analyses prove that the micelles must exist in equilibrium with vanadic acid in solution. The initial concentration of D in vanadium pentoxide was about eight times as great as that of A, yet the final concentrations were nearly the same. Ammonia and chlorine were only a little bit lower, although the ratio of the products (length of tubing by times of dialysis) in the two cases is 3.2.

Stock solutions of all salts were prepared of a concentration giving 0.1 mole per liter of the cation. This concentration expression will be denoted hereafter as cation-molarity (c-m). The various series of salted sols were prepared over the range 0.05 cation-molar to zero. To 10 ml. of the sol were added distilled water and stock salt solution, in the order given, to make 20 ml. of mixture of the desired concentration in salt. After shaking, the mixtures were allowed to stand for three days in glass-stoppered Pyrex flasks at room temperature. Prior to measurement all mixtures or other solutions were brought to 25 ± 0.03° in a water thermostat and measurements finally made in an air thermostat at 25 ± 0.01°. Zero points on all sols were obtained by mixing 10 ml. of sol with 10 ml. of water. These values are given in Table II.

TABLE II

Mixture	E, volts	pH
A + water (1:1)	0.2498	3.44
B + water (1:1)	.3027	2.55
C + water (1:1)	.2916	2.74
D + water (1:1)	.2638	3.21

All e. m. f. values were obtained with the glass electrode as neither the hydrogen nor the quinhydrone electrode can be used in the presence of vanadium pentoxide. The bulb type glass electrode was made of Corning 015 glass. A quinhydrone electrode immersed in 1.000 pH hydrochloric acid served as the internal electrode and a saturated calomel electrode, with a ground joint liquid junction, as the external electrode. Measurements were made with a Leeds and Northrup Type K potentiometer and Hellige vacuum tube galvanometer. The cell and measuring circuit were thoroughly shielded and equipotential. All measurements were corrected for asymmetry potentials. These were obtained by taking the difference between the potentials of the cells

Pt/Quinhydrone/HCl (1.000 pH)/Glass/HCl (1.000 pH)// Saturated calomel electrode

and

Pt/Quinhydrone/HCl (1.000 pH)//Saturated calomel electrode

The equation used to calculate the pH was

$$pH = (0.4534 - E)/0.0591$$

The equipment used was sufficiently sensitive to measure voltage to 0.01 millivolt. However, the reproducibility, as given by the average deviation, was ±0.8 millivolt or ±0.014 pH. This figure was consistent both for the identical points for each salt and sol mixture and for the fifteen or twenty values available for each zero point.

Data

In all, fourteen salts were studied with each of the four sols: primary and secondary potassium phosphate, potassium acetate and citrate, potassium and thallium sulfates, and lithium, sodium, potassium, cesium, silver, barium, magnesium and beryllium nitrates. The data for the first four salts are not given because buffer action was found to be so excessive as to mask the effect sought. The data for sodium nitrate do not appear since they are practically identical with those for potassium nitrate. For compactness, the data are given in Figs. 1–4. To avoid serious overlapping of points in the very dilute salt range, ΔE, rather than E or pH, is plotted against cation-molarity. ΔE is the measured potential minus the zero point potential for the particular sol (see Table II). If desired, the actual pH of any point is readily obtainable from Table II and the relation $\Delta\ pH = -\Delta E/59.1$. Each unit

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[5] Scott, "Standard Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 4th ed., 1925, p. 590.

[6] Courtesy of Mr. Daniel Ready, U. S. Department of Agriculture.

on the ΔE axis corresponds to 10 millivolts (approximately one-sixth of a pH unit). An increase in ΔE means, of course, an increase in acidity. Each plotted point represents the average of two or three independent observations.

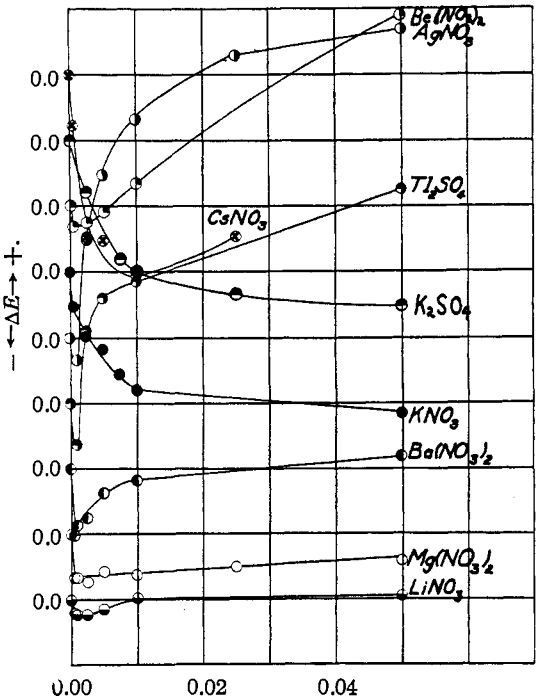

Fig. 1.—Sol A.

Discussion

Acidity changes in vanadium pentoxide sols on the addition of salts may be due to several factors. Assuming with Thomas[7] a large polyolated Werner complex, they may be listed as follows. (1) Anions may penetrate the ionic micelles, displacing hydroxo groups. This will lower the acidity. (2) Buffer action of the salts may modify the acidity, in general reducing it greatly. Vanadium pentoxide sols are quite acid, the pH ranging from 2.5 to 3.5. (3) The negative micelles are surrounded by an ionic atmosphere predominantly positive and consisting largely, at least in the case of the pyrolytic sols, of hydrogen ions. Replacement of any of these hydrogen ions by the cation of the salt will raise the acidity. (4) Such replacement may promote a change in the degree of dispersion. If this decreases, the extent of the ion atmosphere will likewise decrease with liberation of hydrogen ions. (5) If metathesis occurs between sol and salt, the equilibrium between micellar and intermicellar vanadic acid will be disturbed so as to increase the acidity. (6) The neutral salt effect also may raise the apparent acidity. This need not be considered here, since independent measurements on mineral acids at the acidities encountered and with the salt concentrations used showed it to be negligible.

That two or more of these factors must be operating is obvious from the shapes of the curves. With very few exceptions there is a minimum lying between zero and 0.01 cation-molar.

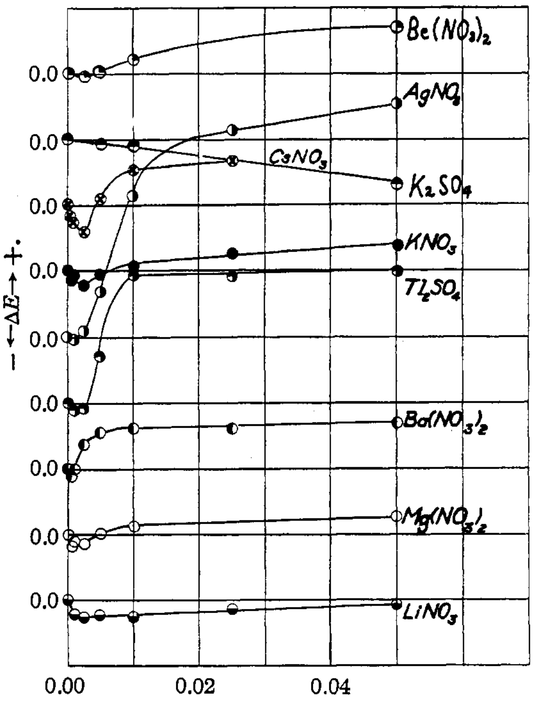

Fig. 2.—Sol B.

The most serious factor in proper interpretation of the data is possible buffer action. The acidity changes noted for salts, data for which are given in this paper, are usually a few tenths of a pH unit and in no case exceed one unit in either direction. However, for potassium primary and secondary phosphates, acetate and citrate the changes were large. In the order given, for 0.05 cation-molar mixtures, they amounted to 0.5, 4.0, 2.3 and 3.5 units, respectively. All these changes were in the direction of decreasing acidity, whereas changes for the other ten salts showed both increases and decreases for each salt. To investigate the extent of this buffer action, hy-

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[7] Thomas, "Colloid Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1934, p. 145 et seq.

drochloric and nitric acid solutions of nearly the same *p*H as sol A were treated with all the salts in exactly the same manner as the sol. For the four questionable salts the acidity changes noted were practically the same as with the sol. Absolute identity of results could not be expected since a very slightly soluble acid such as vanadic acid has some buffering capacity of its own. For eight of the remaining salts the buffering effect noted was negligible. For thallous sulfate and beryllium nitrate, the buffer change was small and, particularly noteworthy, opposite in sense to the acidity changes observed with the sol. For this reason data are included for these two salts. The buffer acidity change with the four questionable salts was so large that it was considered of little value to attempt to draw any conclusions from the data. However, some specific effect certainly exists since, in the case of the acetate and citrate, the brownish-red sol was decolorized and apparently peptized into the molecular state. This does not appear to be due to acidity level alone because secondary potassium phosphate produces greater decrease in acidity than either of these two salts yet does not disintegrate the sol.

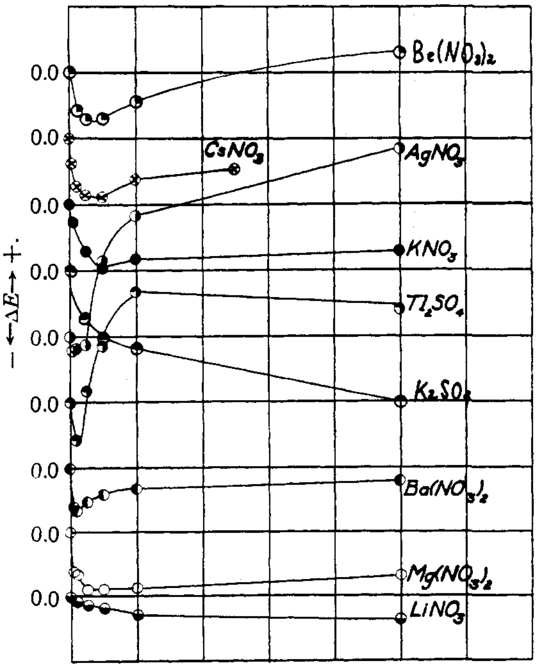

Fig. 3.—Sol C.

That penetration of the complex by the anion with displacement of hydroxo groups occurs is shown by the initial decrease in acidity noted with all salts. Only one comparison of penetrating power can be made from the data given. This is the case of potassium nitrate and sulfate. From our data the nitrate and sulfate ions cause nearly the same acidity decreases, the sulfate ion being very slightly more potent. With aluminum oxyiodide and chromic oxychloride sols Thomas[7] found the sulfate ion to be much more potent than the nitrate ion. These are both positive sols. It seems reasonable that a negative micelle will exert a repressant effect on penetration by a negative ion, and this effect should be greater the greater the valence of the ion. Hence the penetrating power should appear to be more nearly the same, as is the case.

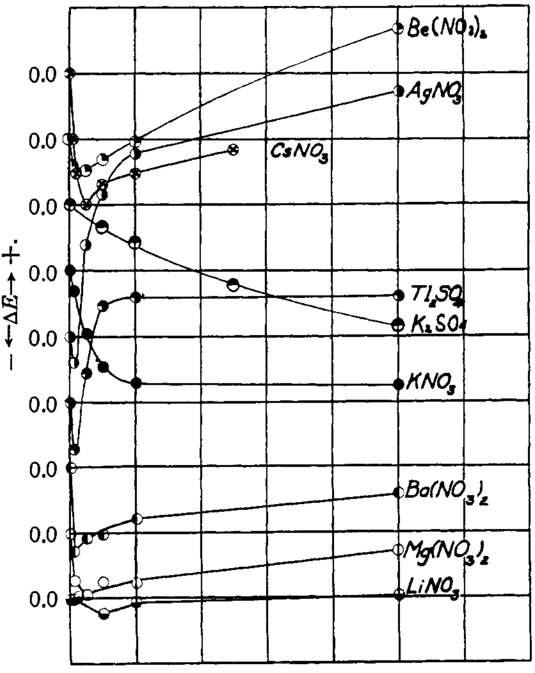

Fig. 4.—Sol D.

All the other factors mentioned will produce an increase in acidity, *i. e.*, an increase in ΔE. That factor (5), increase of acidity by metathesis, is appreciable in certain cases seems fairly certain. In the case of silver nitrate and thallous sulfate the sols were observed to change color from brownish-red to orange on the addition of the salt, especially at the higher concentrations. Both these elements yield insoluble metavanadates, whereas the other cations yield at least sparingly soluble metavanadates and, at the concentrations used, could scarcely have exceeded their solubility products. Actually these two salts do exhibit the greatest increase in acidity, as would be expected. Of course the color change may have been merely a change in degree of dispersion, which would also increase the acidity slightly, but this seems unlikely.

Lacking definite data on changes in degree of dispersity, it is impossible to distinguish between factors (3) and (4) . As a matter of fact the latter is secondary to the former. However, it seems reasonable to assume that the effect of replacing hydrogen ions of the micellar atmosphere with other cations will be considerably greater than the effect of merely reducing the degree of dispersion. Therefore the increase of acidity noted with cesium, barium, magnesium, lithium and beryllium nitrates may be ascribed to the effect of these ions on the micellar atmosphere. Potassium and sodium nitrates also exhibit an increase in ΔE, *i. e.*, rise in acidity, with the pyrolytic sols. Potassium sulfate exhibits no rise following the initial decrease. Apparently in this case the elimination of hydroxo groups from the micelle always transcends the replacement of hydrogen ion from the ionic atmosphere. The same thing must be true of sodium and potassium nitrates with the hydrolytic sols. If factor (3) is operating, the rise in acidity should be greater with polyvalent ions, and this is seen to be the case.

It should be pointed out that, with a positive sol, factors (3) and (4) will operate *with* factor (1), since anions will replace hydroxyl ions from the atmosphere. In fact, acidity changes with positive sols so far studied are considerably greater than those recorded in this paper. In general, the hydrolytic sols show greater effects on salt addition than do the pyrolytic sols. This may be due to their lower initial acidity and their lower concentration, which would produce lower buffer capacity, but more probably to a difference in micellar structure. Mellor[8] gives suggested structures for the two types of sols.

Other Observations

Although no special investigation was made, it was observed that very small amounts of any of the salts sufficed to cause the sols to set to gels. For univalent cations this occurred at about 0.01 cation-molar (average value), with potassium salts the least effective and thallous sulfate and silver nitrate the most effective. For bivalent cations the pectization occurred at 0.00075 cation-molar. All these gels were syneritic and those formed with potassium nitrate were thixotropic. The highest concentration of silver nitrate and thallous sulfate caused flocculation. No correlation could be made between the ΔE–concentration curves and these gelation values.

Some of these sols were stored for four or five months and acidity measurements were made at intervals. No change in acidity such as has been recorded in some other cases could be detected.

Sol C, a pyrolytic sol, and sol D, a hydrolytic sol, were boiled with refluxing for six and one-half hours. Measurements made after cooling showed no change in acidity. However, some change in structure must have occurred since both sols after boiling showed definitely greater acidity on treatment with either potassium or silver nitrate than the same sols, before boiling, showed with these salts.

Summary

1. The effect on the acidity of four different vanadium pentoxide sols with additions of fourteen different salts has been investigated.

2. Four salts were found to exert buffer action great enough to preclude analysis of the data. Such behavior probably will be encountered with other highly acid sols.

3. Ten salts were found to produce an initial decrease in acidity. This decrease can be accounted for in terms of a polyolated complex ion as suggested by Thomas and others.

4. Nine salts were found to produce a subsequent increase in acidity. To explain this the importance of the ionic atmosphere about the micelles is emphasized. This effect is apt to be more apparent with negative than with positive sols.

5. Factors that may modify the acidity of a sol on salt addition are discussed.

COLLEGE PARK, MD. RECEIVED SEPTEMBER 3, 1937

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[8] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., 1929, p. 751.