Using (12) and the slope of the straight line of Fig. 1—II, we obtain the same result for the parameter λa as was obtained using the slope of the limiting tangent to curve I. The difference between (2) and (10) is two-fold: the former represents a limiting law, while the latter is valid at finite concentrations and the former involves primarily only mathematical approximations while the latter involves in addition the physical approximation implied in (5).

It is interesting to note that it is impossible to treat the data for tri-isoamylammonium picrate by means of the equation deduced using two spherical ions in contact. At 5.5°, (13) gives

$$-\log k_i' = 4.605 + 0.2544b - 5.5 \log b \quad (14a)$$
$$= 4.605 + \log F(b) \quad (14b)$$

The function $\log F(b)$ defined in (14) has a minimum value of -2.96 where $b = 9.4$. If we substitute 0.105 in (14a) for k_i', we obtain $\log F(b) = -4.584$, which lies below the minimum. It follows, therefore, that there is no value of b, and hence of a, which will simultaneously satisfy both the data and (14). (If we had an explicit formula for k_i' instead of the asymptotic expansion, k_i' as a function of b would have no minimum, but values of b less than 10 would correspond to absurdly large a values in benzene.) As we might have expected from our notions of the chemical structure of $(C_5H_{11})_3HN\cdot OC_6H_2N_3O_6$, the ellip-

soidal model $(.\,.+-.\,.)$ is in much better agreement with experiment than the spherical $(-)\,(+)$.

In the case of salts with symmetrical ions of the type $R_4N\cdot X$, where the spherical model might be expected to apply, the osmotic deviations are large even at $0.001\ N$, and, consequently, in order to test the model, it would be necessary to have reliable data at lower concentrations. At present the only available data are at higher concentrations[9] where the apparent molecular weight is so much larger than the formula weight that none of our present equations apply. Further work on strong salts at lower concentration and in other solvents is in progress.

Summary

1. The hypothesis is made that ion pairs may, under suitable conditions, associate to groups containing four ions.

2. The osmotic properties of a very weak electrolyte, tri-i-amylammonium picrate in benzene, are shown to be in agreement with the hypothesis.

3. The molecular diameter, calculated from the data by proper application of Coulomb's law, is of the correct order of magnitude.

(9) Tetra-i-amylammonium nitrate in dioxane, Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934); silver perchlorate and tetra-i-amylammonium thiocyanate in benzene, Batson and Kraus, loc. cit.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Action of Acids upon Hydrous Alumina

BY ARTHUR W. THOMAS AND RICHARD D. VARTANIAN

Stiasny[1] has directed attention to the fact that the nature of the anions greatly influences the resistance of simple ol compounds of chromium to the action of acids. He has given the following order of anions with respect to their deolating tendency: nitrate < chloride < sulfate < formate < oxalate, which is the same as the order for their tendency to be coördinatively bound to the central atom.

In previous publications[2] from this Laboratory

it has been postulated that the micelles in aluminum oxysalt and chromium oxysalt[3] hydrosols are essentially polyolated structures. As a consequence of this viewpoint, acids producing anions which do not manifest a strong tendency to be coördinatively bound and therefore do not exert a deolating tendency should favor the formation of colloidal dispersions of the oxides. On the other hand, acids whose anions are strongly bound coördinatively to the central metallic atom should disrupt the ol linkages and as a consequence a colloidal dispersion should not be produced when such acids act upon a pure hydrous oxide which is not oxolated.
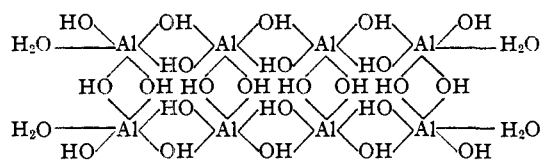
(1) E. Stiasny, "Gerbereichemie (Chromgerbung)," Verlag von Theodor Steinkopff, Leipzig, 1931, p. 351.

(2) (a) A. W. Thomas and T. H. Whitehead, J. Phys. Chem., **35**, 27 (1931); (b) A. W. Thomas and A. P. Tai, THIS JOURNAL, **54**, 841 (1932); (c) A. W. Thomas and F. C. von Wicklen, ibid., **56**, 794 (1934); (d) A. W. Thomas "Colloid Chemistry," McGraw-Hill Book Co., New York, 1934, Chapter VII.

(3) Such sols are generally denoted in the colloid literature as "aluminum oxide" and "chromium oxide."

Taking, for purposes of illustration, an end of a hypothetical two-dimensional picture of hy-

drous alumina,[4] a conception of the mechanism of the action of an acid might be as follows:

1. Hydrogen ions react with the hydroxo groups converting them to aquo groups and conferring one positive charge for each group thus converted.

2a. If the anion of the acid is a weak penetrator,[5] or displacer, then only a relatively small number of the anions may become coördinatively bound in the complex, effecting only a partial neutralization of the positive charges resulting under "1." Deolation may also occur to a small extent. The hydroxo groups thus formed may become in the main converted into aquo groups or be replaced to a minor extent by the anionic radical of the acid. Aluminum ionic micelles are formed when the ratio of charge to mass becomes sufficient.

2b. On the other hand, if the anion of the acid is a powerful displacer (or penetrator), a considerable number of the anions may displace aquo or hydroxo groups or both and become coördinatively bound in the complex, thus neutralizing the electrical effect produced by the hydrogen ions. If the ratio of acid to alumina is low, the result would be a disappearance of the acid from the solution, i. e., the hydrogen ions and anions would be said to have been adsorbed by the alumina.[6] At sufficiently large ratios of such acids to the alumina one would expect such complete deolation as to result in a crystalloid dispersion of the alumina[8] provided that the hydrous oxide is not oxolated.

(4) Ref. 2b, p. 853.

(5) The term "penetrator" has been applied to a radical which has the tendency to become coördinatively bound in Werner type complexes. This term is not without objections. The Editor of THIS JOURNAL has suggested the term "intruder" which in the process of its "intrusion" also acts as an "extruder" because aquo and hydroxo groups previously coördinately bound are displaced by the "penetrator" or "intruder." Inasmuch as the term "intruder" carries an unfortunate inference, the term "displacer" is suggested.

(6) The adsorption of anions from aqueous solution by hydrous alumina gel has been shown to be[7] SO₄ > Cl > NO₃ > I > CNS.

(7) D. Balarew and St. Krastew, Kolloid Z., 51, 329 (1930).

(8) In this connection it is interesting to note that the "solubility" of hydrous alumina in 0.2 N hydrochloric acid has been found to be increased by the addition of Na₂HPO₄, Na₂HAsO₄ and K₂SO₄.[9] This would be expected owing to the strong deolating tendency of the anions of these salts.

(9) H. V. Tartar, C. C. Bryan and H. Shinn, THIS JOURNAL, 55, 2266 (1933).

On the basis of the above mechanism, one would expect to obtain a peptization order of acids which would be the reverse of the displacement order of the anions of the acids.

Material and Procedure

Two specimens of pure hydrous alumina were prepared by the interaction of hot water and amalgamated aluminum.[10] After three and one-half hours of contact of amalgamated aluminum with agitated water at 95–100°, the resulting hydrous alumina (specimen "A") was filtered off, washed, air-dried and ground to pass through a 100-mesh screen. Its composition corresponded to $Al_2O_3 \cdot 2.90$ H_2O. The other specimen ("B") prepared in a similar manner but in which the amalgamated aluminum was allowed to react with the distilled water for eight hours had the composition $Al_2O_3 \cdot 2.39 H_2O$.

In all experiments the aqueous acid solutions were allowed to act upon the hydrous alumina in the proportion of one gram equivalent of acid to 30 gram equivalents of alumina in the following manner: 0.770 g. of specimen "A" or 0.725 g. of specimen "B" (0.005 g. mole) was added to 100 cc. of a 0.01 N acid solution in a 200-cc. resistance glass bottle and rotated at 25° at a rate of 7 r. p. m. At the expiration of a specified time interval, the mixture was centrifuged at 1550 r. p. m. (diameter = 42 cm.) for ten minutes.[11] The supernatant liquid was siphoned into a dry receptacle and submitted to analysis.

For the determination of the total aluminum content a portion of the liquid was evaporated to a small volume with concentrated hydrochloric acid until clear. The aluminum was precipitated as the hydroxide according to the method of Blum.[12] The precipitate was centrifuged, washed by decantation three times with 2% ammonium chloride solution, finally was washed onto an ash-free filter paper and ignited to constant weight in a covered platinum crucible at 1200°.

A slightly modified procedure was used when organic acids such as oxalic and tartaric were present. In these cases the liquid was evaporated to a small volume with alternate additions of concentrated sulfuric and nitric acids. Upon the complete oxidation of the organic acid, the aluminum content was determined as described above.

For the determination of the colloidally dispersed aluminum, a portion of the liquid was treated with a drop or two of a saturated aqueous solution of ammonium sulfate which precipitated all the colloidally dispersed aluminum. The precipitate was centrifuged, washed and ignited as described above.

The difference between the total Al_2O_3 and the colloidal Al_2O_3 was taken as the crystalloidal Al_2O_3. The latter, of course, is underestimated and the former overestimated owing to the entrainment of some of the crystalloidally dispersed aluminum in the precipitated colloid.[13]

(10) Aluminum having a specified purity of 99.94% was obtained from the Aluminum Company of America.

(11) A series of trials at differing intervals of centrifuging showed that the curve for concentration of dispersed alumina as a function of time flattened after eight minutes of centrifuging. For this reason the ten minute action of the centrifuge was adopted.

(12) W. Blum, THIS JOURNAL, 38, 1282 (1916).

(13) The following experiment was performed to test the validity of these methods: 2.9 g. of hydrous alumina ("B") was treated with

Results

Under the conditions described, the amounts of alumina dispersed to the colloidal and crystalloidal states are collected in Tables I and II. For convenience the data are expressed throughout in terms of mg. of Al_2O_3 per 100 cc. of liquid although in some instances much larger quantities were used, especially in the cases of the three last named acids in Table I, where 4.620 g. of the hydrous alumina was treated with 600 cc. of 0.01 N acid solutions. The ratio of acid solution to hydrous alumina, however, was the same.

TABLE I

ACTION OF ACIDS UPON HYDROUS ALUMINA (SPECIMEN "A")

Acid	Digestion time, hours	Mg. alumina dispersed Total	Col- loidal	Crystal- loidal	pH values Origi- nal	Final
Trichloroacetic	1	395	394	1	2.02	3.40
	24	416	409	7		3.78
Dichloroacetic	1	390	385	5	2.04	3.40
	24	412	407	5		3.81
Nitric	1	386	380	6	2.02	3.21
	6	398				
	24	398	394	4		3.92
Hydrobromic	1	378	373	5	2.02	3.40
	6	391				
	24	390	385	5		3.90
Hydrochloric	1	371	366	5	2.02	3.50
	6	382				
	24	384	378	6		3.90
Monochloro- acetic	1	318	312	6	2.40	3.51
	24	354	348	6		3.85
Formic	1	68	65	3	2.87	3.54
	6	93				
	24	101	96	5		4.20
Glycolic	1	43	42	1	2.86	3.41
	24	52	48	4		3.72
Acetic	1	34	32	2	3.37	4.08
	24	45	42	3		4.12
Oxalic	24	11.2	9.6	1.6	2.33	4.79
Tartaric	24	9.6	7.2	2.4	2.70	3.72
Sulfuric	24	4.8	1.2	3.6	2.04	4.04

400 cc. of 0.01 N hydrochloric acid solution for twenty-four hours as described under "Procedure." The supernatant liquid in the centrifuge tubes was then dialyzed in a nitrocellulose bag against frequently changed distilled water until no more aluminum ion could be detected in the diffusate. Fifty cc. portions of the contents of the bag were analyzed in duplicate for the total and colloidal aluminum content by the methods described. The results obtained were: total Al_2O_3 = 89.1 ± 0.2 mg. per 50 cc.; colloidal Al_2O_3 = 89.1 ± 0.1 mg. per 50 cc. In another experiment, aluminum chloride equivalent to 10 mg. of Al_2O_3 was added to 50-cc. portions of the above dialysate. The methods were again applied in duplicate with the results: total Al_2O_3 = 99.1 ± 0.0 mg.; colloidal Al_2O_3 = 90.2 ± 0.1 mg. These experiments show that precipitation by ammonium sulfate measures the same material which did not diffuse through a nitrocellulose bag and that under the conditions described 10% of the total of the added crystalloidal aluminum was carried down with the colloidal aluminum complex.

TABLE II

ACTION OF ACIDS UPON HYDROUS ALUMINA (SPECIMEN "B")

Acid	Digestion time, hours	Mg. alumina dispersed Total	Col- loidal	Crystal- loidal	pH values Origi- nal	Final
Trichloroacetic	1	327	321	6	2.02	2.77
	24	369	362	7		3.70
Dichloroacetic	1	322	315	7	2.04	2.72
	24	360	353	7		3.69
Nitric	1	316	311	5	2.02	2.89
	6	338				
	24	340	334	6		3.72
Hydrobromic	1	306	301	5	2.02	2.95
	6	335				
	24	336	330	6		3.79
Hydrochloric	1	304	296	8	2.02	2.91
	6	325				
	24	327	321	6		3.80
Monochloro- acetic	1	244	240	4	2.40	3.12
	24	296	288	6		3.72
Formic	1	70	66	4	2.87	3.80
	6	86				
	24	89	85	4		4.20
Glycolic	1	60	58	2	2.86	3.27
	24	70	66	4		3.64
Acetic	1	58	56	2	3.37	3.90
	24	69	66	3		4.12

The data in all cases represent the mean of three measurements. The precision of the measurements of dispersed alumina was ±0.5% for hydrochloric, hydrobromic, nitric and chloroacetic acids; ±1.0% for formic, acetic and glycolic acids and ±5.0% for oxalic, tartaric and sulfuric acids.

The pH columns give the pH values of the original acid solutions and of the liquid phase at the end of the specified digestion periods. It should be remarked that the precision of the pH measurements of the several chloroacetic acid systems, and especially of their neutral salt solutions which are not stable, was of a much lower order than that of the other acids and salts.

The peptizing order for the acids is seen to be: trichloroacetic > dichloroacetic > nitric > hydrobromic > hydrochloric > monochloroacetic > formic > glycolic > or = acetic > oxalic > tartaric > sulfuric.

Inasmuch as the tendency for anions to be coordinatively bound to the central atom is reflected in the property of neutral salts to raise the pH values of aluminum oxysalt and of chromium oxysalt hydrosols,[2] the above order of the acids should be just the reverse of the order of their neutral salts in raising the pH values of an alumi-

num oxysalt hydrosol. By means of a technique previously described[2b] an aluminum oxychloride sol[14] was treated with neutral salts and the pH values measured. The results are shown in Table III.

TABLE III

EFFECT OF POTASSIUM SALTS UPON THE pH VALUE OF AN ALUMINUM OXYCHLORIDE HYDROSOL

Salt	pH values of 0.1 N salt solutions	pH values of mixtures of hydrosol and salt solutions[15]
Trichloroacetate	6.40	5.55
Nitrate	6.38	5.58
Bromide	6.20	5.58
Chloride	6.35	5.67
Dichloroacetate	6.38	5.70
Monochloroacetate	6.25	6.08
Formate	6.52	6.40
Glycolate	6.23	6.50
Acetate	6.60	6.55
Sulfate	6.40	7.20
Tartrate	6.58	7.28
Oxalate	6.47	7.80

With the exception of dichloroacetate, sulfate and tartrate the order of these salts in raising the pH values (*i. e.*, their penetrating or displacing order) is the reverse of the order of the corresponding acids in peptizing hydrous alumina. The authors cannot account for the discrepancy in the case of the dichloroacetate. That sulfate and tartrate are not in accord with the expected order may be ascribed to the fact that whereas only the bivalent anions were present in the neutral salt solutions, the acid solutions contained the monovalent anions as well as the bivalent.

(14) This sol was prepared as follows: 0.05 N hydrochloric acid was allowed to act upon the hydrous alumina specimen in the proportion of 100 cc. to 7.70 g. of the latter for twenty-four hours at 25°. It was then dialyzed for twenty-four hours and centrifuged. The pH of the sol was 4.40. Its total Al and Cl contents were 300 and 3.2 milliequivalents per liter, respectively.

(15) Equal volumes of hydrosol and 0.1 N salt solutions were mixed and the pH values measured fifteen minutes later by means of a quinhydrone electrode at 25 ± 0.2°.

In 0.01 N solutions of these acids the ratios are approximately:

$$HSO_4^-/SO_4^- = 0.5$$
$$HC_4C_4O_6^-/C_4H_4O_6^- = 14$$
$$HC_2O_4^-/C_2O_4^- = 1000$$

Thus, a strict analogy between peptizing ability and the displacement order of the anions of their neutral salts cannot be drawn in the case of these three acids owing to the complications of kinds of anions present.

It is evident, however, that in general acids producing highly penetrating (or powerfully displacing) anions are poor peptizing agents for hydrous alumina and *vice versa*. Such acids are removed from solution as shown by the increase in pH value in the last two columns of Tables I and II. Their effect, however, in so far as they disperse the alumina, is to produce a high proportion of crystalloid aluminum compounds owing to the deolating effect of their anions.

Conclusion

The order of effectiveness of acids in dispersing hydrous alumina to the hydrosol state is, in general, inversely as the tendency of their corresponding neutral salts to raise the pH value of aluminum oxychloride hydrosols. Inasmuch as the ability of neutral salts to raise the pH value of such hydrosols is in the same order as the tendency for their anions to be coördinatively bound to the central metallic atom, one may be justified in making the following statement. Acids with anions which have a strong tendency to bind coördinatively to the central metallic atom are poor colloidal peptizers, while acids with weakly coördinative binding anions are excellent peptizers of hydrous alumina to the hydrosol state.