

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## The Activity Coefficient of Silver Acetate and Silver Monochloroacetate in the Presence of Electrolytes<sup>1</sup>

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This investigation was undertaken to determine the influence of ions of various valence types on the activity coefficient of uni-univalent electrolytes over a wider range of concentrations than is ordinarily encountered in the literature, and to compare the observed results with those computed on the basis of modern theories of electrolytic behavior. For this purpose the solubilities of silver acetate and silver monochloroacetate were determined at 25° in aqueous solutions of the nitrates of lithium, sodium, potassium, calcium, strontium, barium and lanthanum. These nitrates possess the advantage of a negligible degree of hydrolysis. The silver salts are, from a classical standpoint, strong electrolytes.<sup>2</sup> Their saturated solutions, while sufficiently concentrated for an accurate analysis, are nevertheless dilute enough to allow an extrapolation to zero ionic strength.

In an earlier work MacDougall<sup>3</sup> determined the activity coefficient of silver acetate in potassium nitrate solutions as concentrated as 3.014 molal, and showed that the Debye theory represents the experimental facts up to an ionic strength of unity. Larsson and Adell<sup>4</sup> later found equally good agreement with this theory for silver acetate in the presence of sodium nitrate, but poor agreement when sodium acetate is used as the solvent salt. It was considered unnecessary to repeat MacDougall's measurements in potassium nitrate solutions, but those of Larsson and Adell (which were made at 18°) were repeated for sodium nitrate solutions at 25° and were also extended to considerably higher concentrations. Our value for the composition of a saturated aqueous solution of silver acetate (11.06 g. per liter) is slightly less than the value (11.09) obtained by MacDougall.<sup>3</sup>

### Materials and Procedure

**Water.**—All solutions were prepared with "conductivity" water, obtained by the distillation of ordinary

(1) From a thesis submitted by John Rehner, Jr., to the Graduate Faculty of the University of Minnesota, June, 1933, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) S. Arrhenius, *Z. physik. Chem.*, **11**, 391 (1893).

(3) F. H. MacDougall, *THIS JOURNAL*, **52**, 1390 (1930).

(4) E. Larsson and B. Adell, *Z. anorg. allgem. Chem.*, **196**, 354 (1931).

distilled water over sodium hydroxide and potassium permanganate in a tin-lined vessel.

**Silver Salts.**—The acetate was from Eimer and Amend and from Merck. These were found upon analysis to contain 64.58 and 64.60% silver, respectively (compared with 64.64% theoretical), and were used without further purification. The monochloroacetate was prepared by the method of Hill and Simmons,<sup>5</sup> a solution of Kahlbaum monochloroacetic acid being neutralized with slightly less than an equivalent of de Haën sodium hydroxide, and the chilled solution precipitated by the dropwise addition of dilute silver nitrate. The product, after being thoroughly washed, was dried at 55° and was found to contain 53.23% silver (compared with 53.58% theoretical). It gave a negligible test for nitrate ion with diphenylamine reagent.

**Nitrates.**—The nitrates were of the best quality available and were recrystallized once, and in some cases twice, from conductivity water. They were then dehydrated. Anhydrous lanthanum nitrate was prepared from Eimer and Amend's chemically pure hexahydrate by the method of Frivold,<sup>6</sup> this procedure yielding a product free from basic nitrates.

All solutions were prepared by the addition of weighed amounts of the conductivity water and an excess of the silver salt. All weighings were corrected for buoyancy. The water-bath was kept at 25.00 ± 0.05° and the saturated solutions were sampled and analyzed gravimetrically in the manner already described by MacDougall.<sup>3</sup>

### Experimental Results and Calculations

In Tables I and II are recorded the solubilities at 25° of silver acetate and silver monochloroacetate, respectively, in aqueous solutions of the various nitrates used. We shall let  $m$ ,  $c$ , and  $x$  denote molality, molarity, and mole fraction, respectively,  $\gamma$ ,  $\gamma_c$  and  $f$  the activity coefficient on these three scales,  $d$  the density of the solution saturated with the silver salt,  $d_0$  the density of pure water at 25°, and  $\bar{X}$  the normalized mole fraction ( $\bar{X} = 55.51X$ ).

For a uni-univalent salt in aqueous solution at 25° the Debye theory gives

$$-\log f = \log \bar{X} - \log \bar{X}_0 = \frac{0.5045 S^{1/2}}{1 + 0.3283 \times 10^8 a S^{1/2}} = \frac{0.5045 S^{1/2}}{1 + 4.5 S^{1/2}} \quad (1)$$

in which  $\bar{X}_0$  is the normalized activity,  $\bar{X}$  is the normalized mole fraction (of either ion of the

(5) A. E. Hill and J. P. Simmons, *THIS JOURNAL*, **31**, 821 (1909).

(6) O. E. Frivold, *J. Phys. Chem.*, **30**, 1153 (1926).

silver salt, in our case) for an ionic strength  $S = \frac{1}{2}\sum c_i z_i^2$ , and  $a$  is the mean ionic diameter parameter. We shall compute  $S$  on the assumption of complete ionization. The two unknowns,  $\bar{X}_0$

.1002	1.0273	.08104	.05047	1.0228	.1034
.2009	1.0489	.08831	.1016	1.0389	.1304
.3014	1.0697	.09361	.2113	1.0715	.1746
.3500	1.0796	.09572	.3128	1.1000	.2077
.3902	1.0876	.09755	.3908	1.1210	.2315
			.4650	1.1410	.2545
			.5434	1.1613	.2771
			.7371	1.2110	.3313
			.9216	1.2558	.3856
			1.2013	1.3199	.4678
			1.3920	1.3618	.5269
			1.8568	1.4571	.6764
			2.3734	1.5532	.8682
			2.8185	1.6277	1.0487

TABLE I

SOLUBILITY AND ACTIVITY DATA FOR SILVER ACETATE IN AQUEOUS SOLUTIONS OF NITRATES AT 25°

(a) Lithium Nitrate			(b) Sodium Nitrate		
$m$	$d$	$m$	$m$	$d$	$m$
LiNO <sub>3</sub>	Satd. soln.	Ag <sup>+</sup>	NaNO <sub>3</sub>	Satd. soln.	Ag <sup>+</sup>
0	1.0050	0.06666	0	1.0050	0.06666
0.04817	1.0067	.07033	0.04776	1.0086	.07040
.09994	1.0097	.07280	.09648	1.0108	.07287
.1996	1.0143	.07799	.1914	1.0162	.07640
.2997	1.0185	.08198	.2868	1.0216	.08032
.4002	1.0226	.08490	.3840	1.0268	.08246
.5004	1.0269	.08765	.4767	1.0316	.08414
.6101	1.0314	.09033	.5743	1.0371	.08615
.8195	1.0395	.09491	.7631	1.0470	.08910
.9975	1.0461	.09819	.9533	1.0578	.09177
1.2636	1.0561	.1031	1.0504	1.0629	.09266
1.4997	1.0649	.1072	1.2398	1.0718	.09464
2.2835	1.0925	.1195	1.5325	1.0857	.09766
2.5193	1.1002	.1229	1.9108	1.1038	.09958
3.0305	1.1172	.1315	2.3884	1.1246	.1027
4.0221	1.1444	.1479	2.8723	1.1458	.1059
6.0125	1.2050	.1851	3.9954	1.1846	.1106
8.0153	1.2560	.2274	6.0191	1.2628	.1113
10.055	1.3007	.2768	8.0098	1.3212	.1123
			10.225	1.3753	.1109

(c) Calcium Nitrate			(d) Strontium Nitrate		
$m$	$d$	$m$	$m$	$d$	$m$
Ca(NO <sub>3</sub> ) <sub>2</sub>	Satd. soln.	Ag <sup>+</sup>	Sr(NO <sub>3</sub> ) <sub>2</sub>	Satd. soln.	Ag <sup>+</sup>
0	1.0050	0.06666	0	1.0050	0.06666
0.004993	1.0062	.06825	0.004967	1.0063	.06768
.009935	1.0071	.06920	.01001	1.0071	.06870
.01996	1.0084	.07187	.02002	1.0090	.07133
.04980	1.0126	.07691	.05038	1.0134	.07628
.09970	1.0191	.08365	.1008	1.0229	.08178
.1996	1.0318	.09311	.2009	1.0402	.08936
.2998	1.0441	.1007	.3016	1.0572	.09495
.3985	1.0560	.1067	.4022	1.0727	.1001
.4970	1.0673	.1118	.5023	1.0891	.1043
.5985	1.0792	.1170	.6036	1.1046	.1081
.7958	1.1010	.1269	.8040	1.1350	.1148
.9962	1.1225	.1363	1.0064	1.1645	.1218
1.2459	1.1485	.1477	1.2556	1.1997	.1291
1.4916	1.1726	.1588	1.5072	1.2338	.1354
2.0009	1.2199	.1813	2.0125	1.2988	.1488
2.4958	1.2634	.2034	2.5092	1.3575	.1588
2.9860	1.3026	.2259	3.0012	1.4110	.1632
3.9871	1.3766	.2759	3.4941	1.4605	.1632

(e) Barium Nitrate			(f) Lanthanum Nitrate		
$m$	$d$	$m$	$m$	$d$	$m$
Ba(NO <sub>3</sub> ) <sub>2</sub>	Satd. soln.	Ag <sup>+</sup>	La(NO <sub>3</sub> ) <sub>3</sub>	Satd. soln.	Ag <sup>+</sup>
0	1.0050	0.06666	0	1.0050	0.06666
0.005012	1.0064	.06796	0.001431	1.0060	.06809
.01001	1.0076	.06910	.004859	1.0073	.07109
.01998	1.0100	.07127	.008374	1.0085	.07407
.05025	1.0161	.07597	.01839	1.0122	.08231

TABLE II  
SOLUBILITY AND ACTIVITY DATA FOR SILVER MONOCHLOROACETATE IN AQUEOUS SOLUTIONS OF NITRATE AT 25°

(a) Lithium Nitrate			(b) Sodium Nitrate		
$m$	$d$	$m$	$m$	$d$	$m$
LiNO <sub>3</sub>	Satd. soln.	Ag <sup>+</sup>	NaNO <sub>3</sub>	Satd. soln.	Ag <sup>+</sup>
0	1.0097	0.07832	0	1.0097	0.07832
0.05039	1.0123	.08199	0.04979	1.0125	.08004
.1001	1.0145	.08489	.1000	1.0158	.08488
.2001	1.0191	.09026	.1994	1.0219	.08923
.2982	1.0234	.09380	.2998	1.0276	.09254
.4004	1.0277	.09772	.3990	1.0334	.09617
.5075	1.0318	.1009	.4992	1.0389	.09833
.6176	1.0363	.1034	.5988	1.0446	.1020
.8081	1.0440	.1081	.7975	1.0555	.1059
1.0065	1.0514	.1110	1.0008	1.0659	.1098
1.2710	1.0612	.1153	1.2496	1.0790	.1136
1.5025	1.0696	.1186	1.4930	1.0907	.1170
1.9967	1.0878	.1292	2.0028	1.1152	.1227
2.4908	1.1048	.1372	2.4863	1.1364	.1266
2.9908	1.1210	.1436	2.9847	1.1583	.1320
4.0011	1.1529	.1546	5.9807	1.2693	.1481
6.0071	1.2079	.1648	7.9772	1.3294	.1531
			9.9368	1.3798	.1568

(c) Potassium Nitrate			(d) Calcium Nitrate		
$m$	$d$	$m$	$m$	$d$	$m$
KNO <sub>3</sub>	Satd. soln.	Ag <sup>+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	Satd. soln.	Ag <sup>+</sup>
0	1.0097	0.07832	0	1.0097	0.07832
0.05005	1.0127	.08306	0.004993	1.0102	.08118
.1001	1.0161	.08641	.009935	1.0111	.08251
.1999	1.0229	.09112	.01996	1.0127	.08503
.3006	1.0291	.09466	.04974	1.0172	.09116
.3971	1.0353	.09825	.09970	1.0237	.09747
.4993	1.0416	.1011	.1996	1.0363	.1063
.5977	1.0479	.1045	.2998	1.0490	.1147
.7980	1.0598	.1087	.3985	1.0611	.1208
.9968	1.0712	.1139	.4970	1.0727	.1265
1.2464	1.0851	.1183	.5985	1.0840	.1318
1.4914	1.0984	.1233	.7958	1.1066	.1412
1.9923	1.1244	.1316	.9962	1.1280	.1510
2.4997	1.1499	.1393	1.2459	1.1542	.1628
2.9960	1.1728	.1440	1.4916	1.1782	.1728
			2.0009	1.2254	.1904
			2.4958	1.2683	.2073
			2.9860	1.3073	.2233
			3.9871	1.3786	.2550

TABLE II (Concluded)

(e) Strontium Nitrate			(g) Lanthanum Nitrate		
$m$	$d$	$m$	$m$	$d$	$m$
Sr(NO <sub>3</sub> ) <sub>2</sub>	Satd. soln.	Ag <sup>+</sup>	La(NO <sub>3</sub> ) <sub>3</sub>	Satd. soln.	Ag <sup>+</sup>
0	1.0097	0.07832	0	1.0097	0.07832
0.004978	1.0100	.08139	0.001431	1.0103	.08211
.009967	1.0112	.08272	.004859	1.0115	.08431
.01988	1.0133	.08466	.008374	1.0129	.08680
.05006	1.0189	.08982	.01839	1.0162	.09249
.09998	1.0279	.09524	.05047	1.0268	.1080
.1989	1.0452	.1044	.1016	1.0424	.1251
.2988	1.0619	.1111	.2113	1.0752	.1569
.3992	1.0786	.1175	.3128	1.1031	.1782
.4978	1.0943	.1224	.3908	1.1226	.1879
.6008	1.1103	.1274	.4650	1.1421	.2018
.7993	1.1407	.1362	.5434	1.1624	.2147
1.0002	1.1709	.1439	.7371	1.2098	.2441
1.2502	1.2052	.1522	.9216	1.2526	.2756
1.4977	1.2394	.1606	1.2013	1.3149	.3164
1.9918	1.3027	.1742	1.3920	1.3553	.3480
2.4953	1.3625	.1862	1.8568	1.4465	.4237
2.9985	1.4180	.1975	2.3734	1.5375	.5115
			2.8185	1.6080	.5939

(f) Barium Nitrate		
$m$	$d$	$m$
Ba(NO <sub>3</sub> ) <sub>2</sub>	Satd. soln.	Ag <sup>+</sup>
0	1.0097	0.07832
0.004930	1.0100	.07995
.009872	1.0114	.08180
.01990	1.0136	.08340
.05000	1.0207	.08878

and  $A$  (or  $a$ ), may be calculated from equation (1) by means of two sets of corresponding values of  $\bar{X}$  and  $S$ . Applying this method to the data for sodium nitrate in Table I, using in each case  $\bar{X}$  and  $S$  for which  $m$  (nitrate) = 0 combined successively with the corresponding values of the same quantities for each of the other solutions containing sodium nitrate as the solvent salt, we find that the first twelve values of  $A$  are practically constant, giving  $A$  (average) = 1.2877,  $a_1$  (average) =  $3.92 \times 10^8$  and  $\bar{X}_0$  (average) = 0.05312. This value  $\bar{X}_0$  may be compared with  $\bar{X}_0 = 0.05359$  obtained by MacDougall<sup>3</sup> by extrapolation from solutions of silver acetate containing potassium nitrate. The activity coefficients  $f$  for all the silver acetate solutions were then obtained by the relationship  $f = 0.05312/\bar{X}$ . From these values  $\gamma$  and  $\gamma_c$  were calculated by the formulas

$$\gamma = \frac{55.51 f}{55.51 + 2m_1 + \nu_2 m_2} \quad (2)$$

$$\gamma_c = \frac{(1000 + m_1 M_1 + m_2 M_2) d_0 \gamma}{1000 d}$$

in which subscripts 1 and 2 refer to the silver salt and the solvent nitrate salt, respectively,  $\nu_2$  is

the number of ions from one molecule of the nitrate, and  $M$  is the molecular weight. From the data for potassium nitrate in Table II we find that the first eight values of  $A$  are practically constant, giving  $A$  (average) = 1.0576,  $a_1 = 3.22 \times 10^8$ , and  $\bar{X}_0$  (average) = 0.06081. The values of  $f$  for the silver monochloroacetate solutions were then obtained from  $f = 0.06081/\bar{X}$ .

The quantity denoted in the tables by  $a_1$  is the mean ionic diameter calculated from the Debye equation, into which the observed values of  $f$  were substituted.

Gronwall, La Mer and Sandved<sup>7</sup> showed that a more complete analysis of the fundamental Poisson-Boltzmann equation yields

$$-\log f = 1.53636 \left( \frac{z^2}{10^8 a} \right) \frac{\kappa a}{1 + \kappa a}$$

$$- 0.15382 \left( \frac{z^2}{10^8 a} \right)^3 10^3 [1/2 X_3(\kappa a) - 2 Y_3(\kappa a)]$$

$$- 0.0770 \left( \frac{z^2}{10^8 a} \right)^5 10^6 [1/2 X_5(\kappa a) - 4 Y_5(\kappa a)] \quad (3)$$

This equation was deduced for aqueous solutions at 25° of symmetric electrolytes (in which  $Z_1 = -Z_2 = Z$ ;  $\nu_1 = \nu_2 = 1$ ), and  $\kappa$  is given by  $\kappa = 0.3283 \times 10^8 S^{1/2}$ . The treatment which gives equation (3) was carried out to the fifth approximation. Since this equation cannot be solved explicitly for  $a$ , it is necessary to evaluate this quantity by trial, the observed values of  $f$  being substituted into equation (3). Values of  $a$  were assumed, and the functions  $X$  and  $Y$  that correspond to the assumed value were obtained from the tables of Gronwall, La Mer, and Sandved.<sup>7</sup> This procedure was repeated until the correct value of  $a$  was obtained. We shall denote these values by  $a_5$ . It was not possible to test the third approximation equation obtained by La Mer, Gronwall and Greiff<sup>8</sup> for solutions containing unsymmetric electrolytes since the functions that occur in this case were not computed by those authors for values of  $a$  as large as those encountered in our data.

For our purpose the Hückel equation<sup>9</sup> may be written in the form

$$\log \bar{X} = \log \bar{X}_0 + \frac{0.5045 S^{1/2}}{1 + AS^{1/2}} + CS \quad (4)$$

in which the (practically) constant parameter  $C$  results from an attempt to take into account the variation in the dielectric constant of the solution

(7) T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

(8) V. K. La Mer, T. H. Gronwall and L. J. Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

(9) E. Hückel, *Physik. Z.*, **26**, 93 (1925).

with the ionic strength. The values of  $\bar{X}_0$ ,  $A$  and  $C$  were found for each silver salt-nitrate system by means of three experimentally determined values of  $\bar{X}$  and the corresponding  $S$ , the values used for this purpose being indicated in the table by parentheses. Equation (4) with the values of the constants given in Table III was found to represent the observed data satisfactorily up to an ionic strength of 1.5.

TABLE III  
VALUE OF THE HÜCKEL CONSTANTS

System	$\bar{X}_0$	$A$	$C$
CH <sub>3</sub> COOAg-LiNO <sub>3</sub>	0.05238	1.149	0.01736
CH <sub>3</sub> COOAg-NaNO <sub>3</sub>	.05309	1.241	-.004433
CH <sub>3</sub> COOAg-Ca(NO <sub>3</sub> ) <sub>2</sub>	.05262	1.153	.03457
CH <sub>3</sub> COOAg-Sr(NO <sub>3</sub> ) <sub>2</sub>	.05225	1.086	.01230
CH <sub>3</sub> COOAg-Ba(NO <sub>3</sub> ) <sub>2</sub>	.05280	1.220	.01394
CH <sub>3</sub> COOAg-La(NO <sub>3</sub> ) <sub>3</sub>	.04964	0.312	.1022
CH <sub>2</sub> ClCOOAg-LiNO <sub>3</sub>	0.06012	1.030	-0.03501
CH <sub>2</sub> ClCOOAg-NaNO <sub>3</sub>	.05839	0.913	-.01110
CH <sub>2</sub> ClCOOAg-KNO <sub>3</sub>	.06147	1.264	.02305
CH <sub>2</sub> ClCOOAg-Ca(NO <sub>3</sub> ) <sub>2</sub>	.06198	1.228	.02932
CH <sub>2</sub> ClCOOAg-Sr(NO <sub>3</sub> ) <sub>2</sub>	.06307	1.527	.03556
CH <sub>2</sub> ClCOOAg-Ba(NO <sub>3</sub> ) <sub>2</sub>	.06118	1.203	.01903
CH <sub>2</sub> ClCOOAg-La(NO <sub>3</sub> ) <sub>3</sub>	.06104	0.802	.06004

### Discussion

In the derivation of the Debye expression, equation (1), the parameter  $a$  is some sort of average ionic diameter depending (in its application to the experiments reported herein) on the closest distance of approach of all the ions of a solution to silver ions and acetate (or chloroacetate) ions. Even if the theory were perfectly adequate, we might expect a change in the value of  $a$  with changing ratios of solvent nitrate salt to dissolved silver acetate (or chloroacetate). The change in  $a$  might be marked when this ratio is low but should quickly become negligible for higher values of the ratio. A fairly constant value of  $a$  over a considerable range of concentrations of the solvent salt may therefore be taken as indicating that this value of  $a$  has substantially the meanings assigned to it by the Debye theory. On the other hand, failure of equation (1) to represent the observed facts may be due to a number of causes of which we may mention the following. (1) The Debye theory was developed for solutions of low ionic strength only. (2) The dielectric constant may change appreciably. (3) The ions may be hydrated and change their degree of hydration with change in concentration. (4) The salts may not be completely ionized, especially in the more concentrated solutions, and in the

case of electrolytes that are not of the simple uni-univalent type. The effects due to these various factors may, of course, happen to compensate one another but in general we should expect that they would exhibit themselves by a marked drift in the values of  $a$ . Unfortunately it is impossible at the present time to estimate with any precision the magnitude of the effects due to these several causes.

It was observed, on examining the values of  $a$ , that when the solvent salts are sodium nitrate and potassium nitrate and (to a lesser degree) lithium nitrate and barium nitrate, the  $a$  values are constant over a considerable range, indicating the approximate validity of equation (1) in these ranges. On the basis of the simple theory, we should expect differences in  $a$  for different solvent salts to be due entirely to the cation of the added nitrate. If we compare the values of  $a$  in the various cases at a given ionic strength (*e. g.*, 0.3 to 0.4), we find that we can arrange the cations in the following approximate order as regards their contributions to the magnitude of  $a$ , namely

K > Na > Ba > Li > Sr > Ca > La (Silver acetate)  
Na > Li > K > Ba > Sr > Ca > La (Silver chloroacetate)

In view of the uncertainties in the  $a$  values, perhaps all we are entitled to say is that the order is: alkali metals > alkaline earth metals > lanthanum.

If the ions are hydrated and if the water of hydration must be taken into account in assigning a diameter to an ion, we should expect an order which is almost the exact reverse of that given above for silver acetate solutions. On the other hand, the "radii" of the cationic ions in crystals according to Pauling<sup>10</sup> is as follows

Ba (1.35) > K (1.33) > La (1.15) > Sr (1.13) >  
Ca (0.99) > Na (0.93) > Li (0.60)

These considerations suggest that electrostatic hydration, if it is at all operative in the systems herein presented, is not the predominating factor. Data on the temperature coefficient of  $a$  lead to the same conclusion.<sup>11</sup>

A comparison of  $\bar{X}$  (Hückel), calculated by means of equation (4), with the observed values of  $\bar{X}$  does not indicate much more, probably, than that the Hückel equation is excellent for interpolation purposes.

The values of  $a_5$  calculated from equation (3) have been omitted from the tables. The follow-

(10) Pauling, *THIS JOURNAL*, **49**, 765 (1927).

(11) V. K. La Mer and W. G. Parks, *ibid.*, **53**, 2040 (1931); H. S. Harned and L. F. Nims, *ibid.*, **54**, 423 (1932).

ing values, taken from the data for silver acetate in the presence of lithium nitrate, may be regarded as typical

$m(\text{LiNO}_3)$	= 0.04817	0.5004	0.9975	2.5193
$S$	= 0.1175	0.5756	1.056	2.434
$10^3 a_1$	= 3.94	3.36	3.18	2.78
$10^3 a_3$	= 4.05	3.41	3.21	2.80

The values of  $a_3$  show that the Gronwall-La Mer-Sandved treatment yields a positive correction to

(3) that  $f$  for silver acetate in potassium nitrate solutions reaches a minimum at an ionic strength of approximately 2.5, its course of behavior being essentially the same as that represented by curve I, Fig. 1. It cannot be stated with certainty whether or not the remaining curves shown approach minima; that they may, however, would not be unexpected.

The experimental data presented seem to indicate that the purely physical aspect of inter-ionic attraction is superseded in importance by specific effects exhibited by the solvent salts at the concentrations under consideration. In solutions of these relatively high concentrations, it is questionable whether a quantitative application of Brönsted's principle of specific interaction<sup>12</sup> would have much significance. Whether the specificity referred to can be explained on the basis of a purely physical treatment of the variation of the dielectric constant or of incomplete ionization is still an open question.

#### Summary

The solubilities at 25° of silver acetate and silver monochloroacetate in aqueous solutions of the nitrates of lithium, sodium, potassium, calcium, strontium, barium and lanthanum were measured over a wide range of concentrations.

The mole fraction activity coefficients of silver acetate in the presence of sodium and strontium nitrate and of silver monochloroacetate in the presence of sodium and lithium nitrate were found to attain minima.

The experimental results were compared with the values calculated on the basis of the theories of Debye-Hückel, Hückel, and Gronwall-La Mer-Sandved.

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(12) J. N. Brönsted, THIS JOURNAL, 44, 877 (1922).

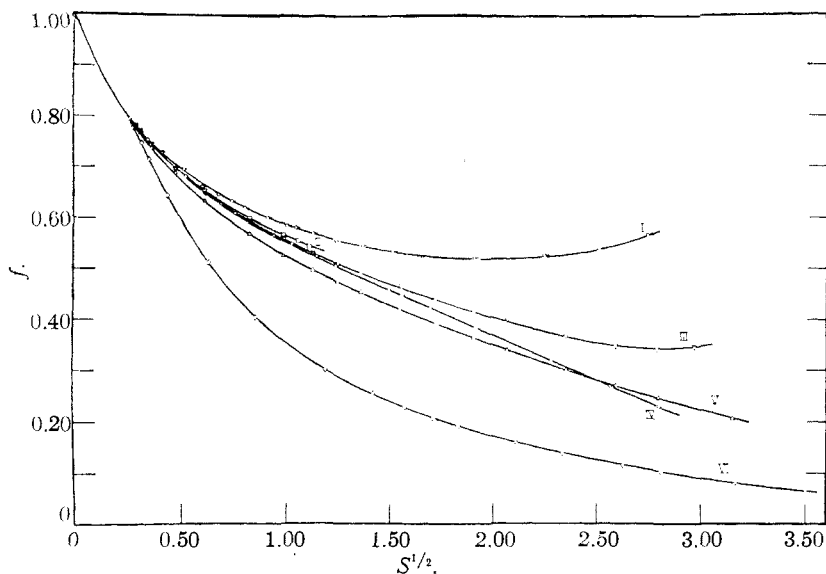


Fig. 1.—Activity coefficient of silver acetate in presence of nitrates at 25°: I,  $\text{NaNO}_3$ ; II,  $\text{Ba}(\text{NO}_3)_2$ ; III,  $\text{Sr}(\text{NO}_3)_2$ ; IV,  $\text{LiNO}_3$ ; V,  $\text{Ca}(\text{NO}_3)_2$ ; VI,  $\text{La}(\text{NO}_3)_3$ .

$a_1$  that becomes negligible at higher ionic strengths because of the asymptotic behavior of the second and third terms in the right member of equation (3). It is apparent that the values of  $a_3$  are no more constant than those of  $a_1$ , and it is doubtful whether even an *exact* mathematical development of the Poisson-Boltzmann equation could remove this variation.

Figure 1 shows that  $f$  reaches a minimum for silver acetate in the presence of the nitrates of sodium and strontium at approximate ionic strengths of 4 and 8, respectively. For silver monochloroacetate in the presence of the nitrates of sodium and lithium the minimum is reached at approximately 6 and 5.5, respectively. The curve for the chloroacetate in the presence of potassium nitrate tends toward a minimum. It was found