THE SOLUBILITY OF SILVER ACETATE IN MIXED SOLVENTS AND THE INCOMPLETE DISSOCIATION OF TERNARY ELECTROLYTES[1]

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INTRODUCTION

The experimental work described in the present paper is a continuation of studies (7, 8, 9, 10) designed to test the applicability of the theory of Debye and Hückel to solutions of electrolytes in water and in mixed solvents. For this purpose, we determined the solubility of silver acetate in mixtures of water and acetone containing 10, 20, and 30 per cent of acetone. In addition the solubility was determined when these solvents contained various amounts of the nitrates of sodium, potassium, calcium, or strontium.

In previous investigations as well as in the present one, somewhat abnormal results were obtained when the solvent contained calcium or strontium nitrate. We hoped to find out if this abnormal behavior could be accounted for by assuming that the second-stage ionization of calcium acetate or strontium acetate is incomplete.

By studying the variation of certain equilibrium constants with the dielectric constant of the medium, we planned to test Born's (2) electrostatic theory.

For a summary of previous determinations of the solubility of silver acetate in water at 25°C., reference may be made to the paper by MacDougall and Bartsch (8).

EXPERIMENTAL PART

Materials used

The silver acetate, obtained from Mallinckrodt, was 64.61 per cent silver (theoretical value, 64.64 per cent), and was used without further purification. The potassium and sodium nitrates were of Mallinckrodt's "analytical reagent" grade. They were dried at 150°C. for twenty hours and used without any further treatment. The calcium and strontium nitrates were

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[1] This paper gives the essential portions of the dissertation presented by William D. Larson to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, March, 1936.

recrystallized twice from conductivity water and dried at 175°C. until no further loss in weight was shown. A sample of the calcium nitrate, analyzed by the method of Willard and Furman (11), gave 24.40, 24.31, and 24.26 per cent calcium, as compared with the theoretical value of 24.42 per cent.

The acetone used was a commercial acetone of unknown source. It was purified by the method of Conant and Kirner (3). To check the purity of the acetone, a sample was dried over calcium oxide and fractionated with a 30-in. column packed with 5-mm. lengths of glass tubing having an outside diameter of 6 mm. The fraction that came over between 56.0°C. and 56.1°C. at 746 mm. was used. The density of this acetone at 25°C., determined by means of a Weld precision-type pycnometer, was 0.7844 ± 0.0002. The value given in the International Critical Tables (4) is 0.7844. The acetone was also analyzed by the iodometric method of Messinger (6). Two analyses gave 99.99 and 99.85 per cent acetone.

The water used was conductivity water, prepared by distillation from alkaline permanganate with a block tin condenser.

Experimental procedure

Acetone solutions, prepared by thorough mixing of appropriate amounts of acetone and water, were stored in glass-stoppered bottles, sealed with paraffin. The density of a given mixture at 25°C. was determined with the Weld pycnometer. The composition was calculated by means of the equation (5)

$$d = d_w + Ap + Bp^2 + Cp^3$$

where d is the density of the mixture, p is the per cent by weight of acetone, and $d_w = 0.99707$, $A = -1.171 \times 10^{-3}$, $B = -9.04 \times 10^{-6}$, and $C = -5.6 \times 10^{-9}$.

The nitrate solutions were prepared by weighing out the acetone–water mixture into brown glass-stoppered bottles and adding a previously weighed amount of the nitrate. Buoyancy corrections were applied to all weighings. An excess of silver acetate was then added, and the glass stoppers were heavily coated with paraffin. The bottles were rotated for at least twenty-four hours in a constant-temperature bath at 25.00° ± 0.05°C. Preliminary experiments showed that agitation for fifteen hours was sufficient to insure saturation.

The solutions saturated with silver acetate were sampled and analyzed as follows: With the bottle clamped upright in the bath, the glass stopper was removed and a two-hole rubber stopper carrying a delivery tube was put in its place. The end of the tube was loosely plugged with absorbent cotton. Somewhat more than 100 cc. of the solution (which had a total volume of nearly 200 cc.) was forced by compressed air into a graduated

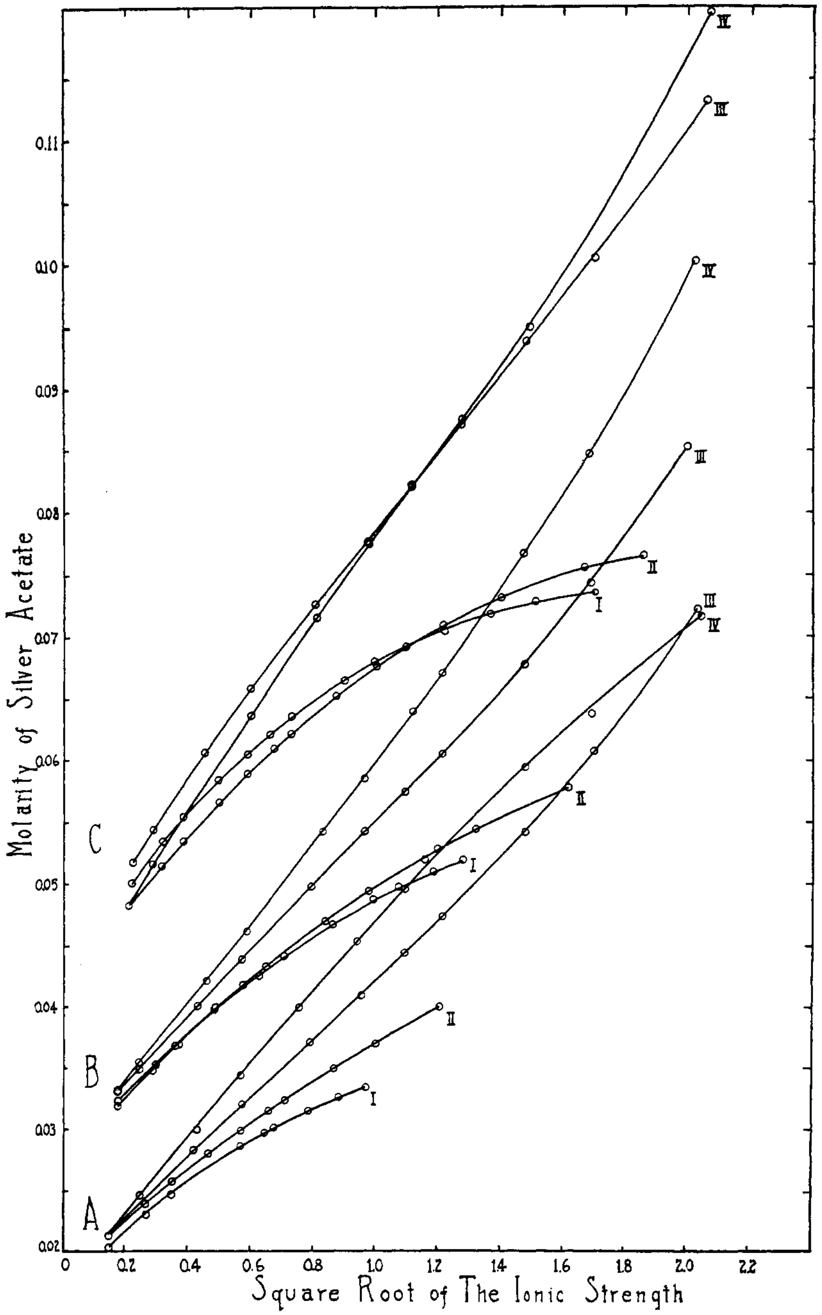

Fig. 1. Solubility of silver acetate in mixed solvents

		Per cent acetone		
		A	*B*	*C*
I.	KNO_3	30.95	18.83	9.81
II.	$NaNO_3$	28.25	20.50	10.35
III.	$Sr(NO_3)_2$	29.23	19.48	9.27
IV.	$Ca(NO_3)_2$	30.02	20.03	10.35

TABLE 1

Solubility at 25°C. of silver acetate in mixtures of acetone and water

PER CENT ACETONE	DENSITY OF SATURATED SOLUTION	C SILVER ACETATE	PER CENT ACETONE	DENSITY OF SATURATED SOLUTION	C SILVER ACETATE
9.27	0.9920	0.05160	20.03	0.9740	0.03217
9.81	0.9910	0.04990	20.50	0.9724	0.03189
10.35	0.9900	0.04815	28.25	0.9592	0.02140
18.83	0.9758	0.03237	29.23	0.9584	0.02134
19.48	0.9748	0.03228	30.02	0.9564	0.02131

TABLE 2

Solubility at 25°C. of silver acetate in mixtures of acetone and water containing sodium nitrate

10.35 PER CENT ACETONE $D = 72.8$; $d = 0.9840$			20.50 PER CENT ACETONE $D = 66.7$; $d = 0.9692$			28.25 PER CENT ACETONE $D = 62.1$; $d = 0.9566$		
m $NaNO_3$	d Satd. soln.	10^3X Ag^+	m $NaNO_3$	d Satd. soln.	10^3X Ag^+	m $NaNO_3$	d Satd. soln.	10^3X Ag^+
0.0	0.9900	0.9494	0.0	0.9724	0.6908	0.0	0.9592	0.5006
0.05228	0.9943	1.014	0.04951	0.9756	0.7569	0.0494	0.9620	0.5625
0.09728	0.9976	1.053	0.1006	0.9792	0.8003	0.1002	0.9648	0.6011
0.2010	1.0028	1.114	0.2097	0.9856	0.8665	0.1999	0.9704	0.6524
0.3052	1.0088	1.159	0.3067	0.9908	0.8993	0.3191	0.9760	0.6970
0.3997	1.0132	1.198	0.4020	0.9956	0.9400	0.4288	0.9820	0.7312
0.5005	1.0184	1.220	0.4371	0.9980	0.9416	0.5229	0.9872	0.7519
0.7434	1.0316	1.277	0.7170	1.0116	1.003	0.7908	1.0004	0.8077
1.0010	1.0448	1.321	0.9818	1.0252	1.050	1.054	1.0132	0.8526
1.521	1.0704	1.381	1.429	1.0460	1.103	1.569	1.0372	0.9215
2.082	1.0940	1.423	1.905	1.0688	1.154	2.089	1.0603	0.9698
3.072	1.1380	1.466	2.936	1.1116	1.216			
3.908	1.1711	1.480						

TABLE 3

Solubility of silver acetate at 25°C. in mixtures of acetone and water containing potassium nitrate

9.81 PER CENT ACETONE $D = 73.1$; $d = 0.9848$			18.83 PER CENT ACETONE $D = 67.7$; $d = 0.9718$			30.95 PER CENT ACETONE $D = 60.4$; $d = 0.9520$		
m KNO_3	d Satd. soln.	10^3X Ag^+	m KNO_3	d Satd. soln.	10^3X Ag^+	m KNO_3	d Satd. soln.	10^3X Ag^+
0.0	0.9910	0.9790	0.0	0.9758	0.6906	0.5125	0.9582	0.5532
0.05986	0.9952	1.048	0.05193	0.9768	0.7587	0.1048	0.9616	0.5892
0.09878	0.9979	1.089	0.1023	0.9800	0.8022	0.2088	0.9672	0.6681
0.2007	1.0051	1.147	0.2055	0.9872	0.8544	0.3159	0.9744	0.6720
0.3001	1.0108	1.186	0.2898	0.9926	0.8871	0.4110	0.9804	0.7109
0.4002	1.0162	1.218	0.3773	0.9980	0.9135	0.4599	0.9824	0.7245
0.5001	1.0223	1.249	0.4948	1.0044	0.9433	0.6395	0.9928	0.7495
0.7913	1.0398	1.308	0.7453	1.0190	0.9934	0.8133	1.002	0.7806
1.000	1.0512	1.332	1.028	1.0340	1.038	0.9671	1.010	0.8058
1.250	1.0641	1.360	1.230	1.0432	1.063			
1.500	1.0767	1.382	1.522	1.0592	1.097			
2.000	1.1021	1.419	1.772	1.0722	1.107			
2.500	1.1267	1.435						

cylinder supported in the bath. Four 25-cc. samples were withdrawn with an accurately calibrated pipet and transferred to weighing bottles. After they had been weighed, the samples were washed into Erlenmeyer flasks and analyzed for silver by means of a potassium thiocyanate solution with ferric nitrate as indicator. The thiocyanate solution was standardized against pure silver acetate.

TABLE 4

Solubility of silver acetate at 25°C. in mixtures of acetone and water containing calcium nitrate

10.35 PER CENT ACETONE $D = 72.8$; $d = 0.9840$			20.03 PER CENT ACETONE $D = 67.0$; $d = 0.9700$			30.02 PER CENT ACETONE $D = 61.0$; $d = 0.9536$		
m $Ca(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Ca(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Ca(NO_3)_2$	d Satd. soln.	10^3X Ag^+
0.0	0.9900	0.9494	0.0	0.9740	0.6934	0.0	0.9564	0.5076
0.01227	0.9928	1.0159	0.009057	0.9752	0.7633	0.01262	0.9584	0.5854
0.06436	0.9972	1.1349	0.06103	0.9808	0.9057	0.05617	0.9636	0.7126
0.1049	1.0044	1.2516	0.1068	0.9860	0.9927	0.1073	0.9696	0.8138
0.2052	1.0172	1.4026	0.2283	1.0004	1.1656	0.2009	0.9804	0.9529
0.3090	1.0288	1.523	0.3120	1.0100	1.259	0.3048	0.9923	1.064
0.4133	1.0400	1.613	0.4303	1.0232	1.373	0.4224	1.0052	1.173
0.5102	1.0508	1.698	0.5051	1.0312	1.439	0.5033	1.0136	1.247
0.7552	1.0776	1.862	0.7566	1.0580	1.643	0.7862	1.0432	1.348
1.014	1.1036	2.069	0.9865	1.1074	1.761	1.046	1.0680	1.471
1.542	1.1556	2.307	1.494	1.1292	2.168	1.578	1.1192	1.630
2.057	1.2015	2.687	1.874	1.1655	2.453	2.093	1.1632	1.974

TABLE 5

Solubility of silver acetate at 25°C. in mixtures of acetone and water containing strontium nitrate

9.27 PER CENT ACETONE $D = 73.4$; $d = 0.9854$			19.48 PER CENT ACETONE $D = 67.3$; $d = 0.9708$			29.23 PER CENT ACETONE $D = 61.5$; $d = 0.9550$		
m $Sr(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Sr(NO_3)_2$	d Satd. soln.	10^3X Ag^+	m $Sr(NO_3)_2$	d Satd. soln.	10^3X Ag^+
0.0	0.9920	1.0076	0.0	0.9748	0.6920	0.0	0.9584	0.5038
0.01100	0.9936	1.0638	0.01078	0.9768	0.7484	0.00987	0.9604	0.5579
0.05130	1.0012	1.1845	0.05149	0.9840	0.8591	0.05223	0.9672	0.6705
0.1019	1.0096	1.315	0.09963	0.9915	0.9396	0.1044	0.9760	0.7596
0.2051	1.0272	1.421	0.2051	1.0092	1.064	0.2099	0.9924	0.9749
0.3055	1.0432	1.517	0.3084	1.0252	1.163	0.3134	1.0084	0.9619
0.4060	1.0592	1.592	0.4122	1.0420	1.222	0.4183	1.0282	1.059
0.5061	1.0732	1.661	0.5096	1.0564	1.268	0.5222	1.0391	1.108
0.7608	1.1131	1.819	0.7727	1.0967	1.438	0.7852	1.0763	1.263
1.019	1.1491	1.965	1.031	1.1323	1.573	1.052	1.1131	1.412
1.520	1.2170	2.200	1.545	1.1982	1.804	1.566	1.1795	1.672
2.045	1.2830	2.395						

The experimental data are given in tables 1 to 5 and are also represented graphically in figure 1. In this paper, m is the molality (moles per 1000 grams of solvent), C is the molarity (moles per liter of solution), and X is the mole fraction. The mole fraction of any constituent is calculated on the assumption that all salts present are completely ionized.

It is readily seen from figure 1 that for a solution of a given ionic strength the effect of a nitrate in increasing the solubility of silver acetate is given in general by the order $KNO_3 < NaNO_3 < Sr(NO_3)_2 < Ca(NO_3)_2$.

THEORETICAL PART

Theory of Debye and Hückel

According to the theory of Debye and Hückel, the mole-fraction activity coefficient f of a univalent ion (or of a uni-univalent salt) at 25°C. is given by the equations

$$\log_{10} f = \log_{10} x_0 - \log_{10} x = -\frac{BS^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} \tag{1}$$

$$B = \frac{352.61}{D^{\frac{3}{2}}} \tag{2}$$

$$A = \frac{2.914 \times 10^8}{D^{\frac{1}{2}}}\, a \tag{3}$$

where D is the dielectric constant of the solvent, a is a suitable mean ionic diameter, and S is the ionic strength of the saturated solution. In equation 1, as applied to our data, X is the mole fraction of silver ion in a given saturated solution and X_0 is the extrapolated value of X for an ionic strength equal to zero; in other words, we may call X_0 the activity of silver ion (or rather the mean activity of silver ion and acetate ion) in any solution saturated with silver acetate. The dielectric constant D of an acetone–water mixture was calculated by linear interpolation from the values given by Åkerlöf (1).

Values of A and X_0 were obtained for each series of solutions by substituting in equation 1 the observed values of X and $S^{\frac{1}{2}}$ for two solutions, one of which was always the solution that contained no added nitrate (in one series, the solution that contained the smallest amount of potassium nitrate). From the two simultaneous equations so obtained, a value of A and a value of X_0 were calculated. We give in table 6 the results of our calculations for 9.81 per cent acetone solutions containing various amounts of potassium nitrate.

Results similar to those given in table 6 were obtained for the other solutions containing potassium nitrate and for the solutions containing sodium nitrate. For solvents containing strontium nitrate or calcium nitrate, the calculated values of A showed much greater variations. A summary of the calculations is given in table 7. The solvents are described as 10, 20, and 30 per cent acetone; the exact composition is given in following tables.

TABLE 6

Silver acetate in 9.81 per cent acetone containing potassium nitrate

m KNO_3	$S^{\frac{1}{2}}$	A	m KNO_3	$S^{\frac{1}{2}}$	A
0.0	0.2234		0.7913	0.9102	1.455
0.04986	0.3200	1.321	1.000	1.006	1.478
0.09878	0.3901	1.404	1.250	1.112	1.476
0.2007	0.5043	1.461	1.500	1.207	1.480
0.3001	0.5933	1.486	2.000	1.373	1.476
0.4002	0.6700	1.484	2.500	1.516	1.507
0.5001	0.7384	1.454			

Average $A = 1.472$; $X_0 = 0.7869 \times 10^{-3}$

TABLE 7

Summary of values of A and of the ionic diameter, a

PER CENT ACETONE	A KNO_3	A $NaNO_3$	A $Sr(NO_3)_2$	A $Ca(NO_3)_2$	a IN A.U. KNO_3	a IN A.U. $NaNO_3$
0	1.43	1.21			4.35	3.69
10	1.46	1.45	1.3 to 1.8	1.2 to 1.6	4.28	4.26
20	1.39	1.35	1.1 to 1.7	1.2 to 1.8	3.93	3.77
30	1.41	1.33	1.0 to 1.7	1.0 to 1.7	3.76	3.59

TABLE 8

Saturated solutions of silver acetate in various solvents

SOLVENT	D	10^3X	10^3X_0	f	C_0	10^7K_x	10^3K_c
Water	78.5	1.200	0.960	0.800	0.0531	9.22	2.823
10 per cent acetone	73.0	0.969	0.779	0.804	0.0397	6.07	1.577
20 per cent acetone	67.0	0.693	0.558	0.805	0.0259	3.11	0.671
30 per cent acetone	61.0	0.504	0.402	0.798	0.0169	1.62	0.285

The data for aqueous solutions containing no acetone are taken from the papers by MacDougall (7) and MacDougall and Rehner (10).

Table 8 gives data referring to saturated solutions of silver acetate in water and several mixed solvents. C_0 is the mean activity of silver and acetate ions when the activity of a constituent is set equal to its molar concentration in a solution of zero ionic strength. The activity products for silver acetate, K_x and K_c, are defined by the equations

$$K_x = X_0^2 \tag{4}$$

$$K_c = C_0^2 \tag{5}$$

From the data presented we can conclude that:

(1) The solubility of silver acetate in a given acetone–water mixture increases with the ionic strength.

(2) The equation of Debye and Hückel is valid up to relatively high ionic strengths when sodium nitrate or potassium nitrate is the added salt.

(3) The solubility of silver acetate in the presence of calcium nitrate or of strontium nitrate is considerably greater than in solutions of the same nominal ionic strength which contain sodium nitrate or potassium nitrate.

Ionization of ternary electrolytes

To account for the observed data the authors suggest the hypothesis of incomplete ionization of whatever ternary salts may be present or may be formed in the solutions investigated. In the present case, such ternary electrolytes would be not only calcium nitrate or strontium nitrate but also calcium acetate or strontium acetate. To simplify the treatment it is assumed that the first stage of ionization, as represented by the equation

$$\mathrm{Ca(OAc)_2 \rightleftharpoons CaOAc^+ + OAc^-}$$

is virtually complete and that the second stage

$$\mathrm{CaOAc^+ \rightleftharpoons Ca^{++} + OAc^-}$$

is, in general, incomplete.

The assumption that only the added ternary salt, calcium nitrate or strontium nitrate, is incompletely ionized will not account for the observed fact that in solutions of the same nominal ionic strength the solubility of silver acetate is greater in the presence of calcium nitrate or of strontium nitrate than in the presence of sodium nitrate or of potassium nitrate. In fact, the reverse effect should be observed, since the actual ionic strength of a calcium nitrate solution would be less than the nominal value (calculated on the basis of complete ionization). On the other hand, since the solutions considered contain calcium (or strontium) ions and acetate ions, we must consider the possibility of the formation of $\mathrm{CaOAc^+}$ (or $\mathrm{SrOAc^+}$) as well as of $\mathrm{Ca(OAc)_2}$ (or $\mathrm{Sr(OAc)_2}$). The formation of an appreciable amount of the intermediate ion, $\mathrm{CaOAc^+}$ or $\mathrm{SrOAc^+}$, would obviously result in an increased solubility of silver acetate.

We shall simplify our calculations by supposing that for our present purpose we may assume calcium nitrate and strontium nitrate to be completely ionized.

For any solution saturated with silver acetate and containing calcium nitrate, we may write

$$K_c = a_{\mathrm{Ag^+}} \times a_{\mathrm{OAc^-}} \tag{6}$$

$$K_1 = \frac{a_{\mathrm{Ca^{++}}} \times a_{\mathrm{OAc^-}}}{a_{\mathrm{CaOAc^+}}} \tag{7}$$

Values of K_c are given in table 8. K_1 is the ionization constant of $\mathrm{CaOAc^+}$.

The method followed in calculating K_1 for solutions containing either calcium nitrate or strontium nitrate as added salt may now be briefly outlined. In solutions in which the added salt is sodium nitrate, we suppose that the silver acetate is completely ionized and that $C_{\mathrm{Ag^+}} = C_{\mathrm{OAc^-}}$. Knowing the value of K_c (equation 6), we readily calculate the mean activity coefficients of $\mathrm{Ag^+}$ and $\mathrm{OAc^-}$ in solutions of sodium nitrate. We assume further that in a given solution all univalent ions have practically equal activity coefficients, and that the activity coefficient of a divalent ion is equal to the fourth power of the activity coefficient of a univalent ion. We also assume that in a solution containing calcium nitrate the activity coefficient of an ion is practically the same as in a solution of the same ionic strength in which the added salt is sodium nitrate.

The value of $C_{\mathrm{Ag^+}}$ in a given calcium nitrate solution is known by experiment. Comparing this solution with a sodium nitrate solution of the same nominal ionic strength, we find the activity coefficient of univalent ions in the calcium nitrate solution and hence from equation 6, the value of $C_{\mathrm{OAc^-}}$. Now according to our hypothesis

$$C_{\mathrm{CaOAc^+}} = C_{\mathrm{Ag^+}} - C_{\mathrm{OAc^-}}$$

The value of $C_{\mathrm{CaOAc^+}}$ so obtained is used to make a more accurate estimate of the actual concentration of $\mathrm{Ca^{++}}$ and therefore of the actual ionic strength. From this corrected value of the ionic strength, a new comparison is made with a sodium nitrate solution of equal ionic strength and a new set of values of $C_{\mathrm{OAc^-}}$, $C_{\mathrm{CaOAc^+}}$, and $C_{\mathrm{Ca^{++}}}$ is obtained. Proceeding in this way, we are finally able to calculate the value of K_1 of equation 7. It should be pointed out that the activity coefficients used in these calculations are molarity activity coefficients, γ_c, obtained readily from the values of the mole-fraction activity coefficients, f. To illustrate our results, we give in table 9 the values of K_1 obtained for $\mathrm{CaOAc^+}$ in 10.35 per cent acetone. The first column gives the square root of the ionic strength of the equivalent sodium nitrate solution; the second column gives the corresponding molarity activity coefficient, γ_1, of univalent ions. It will be seen that the values of K_1 given in the last column of table 9 agree remarkably well when one considers the simplifying assumptions made to facilitate their calculation.

In table 10, we summarize the values of K_1 for $CaOAc^+$ and $SrOAc^+$ obtained by the application of our method to the solubility data for water and various acetone–water mixtures. We include also the activity product, K_x, for silver acetate in water and in various acetone–water and alcohol–water mixtures.

TABLE 9

Ionization constant, K_1, of $CaOAc^+$ from solubility of silver acetate in 10.35 per cent acetone in the presence of calcium nitrate

$S^{\frac{1}{2}}$ $NaNO_3$	γ_1	c_{CaOAc^+}	$c_{Ca^{++}}$	c_{OAc^-}	K_1
0.3	0.770	0.00223	0.01079	0.04946	0.0841
0.6	0.662	0.01003	0.0914	0.05405	0.0934
0.7	0.635	0.01072	0.1339	0.05622	0.1142
0.8	0.618	0.01458	0.1763	0.05624	0.0992
0.9	0.600	0.01723	0.2304	0.05718	0.0991
1.0	0.582	0.02031	0.2876	0.05761	0.0936
1.2	0.544	0.02236	0.4304	0.06264	0.1056
1.5	0.533	0.03818	0.6804	0.05707	0.0821
1.7	0.522	0.05055	0.8707	0.05445	0.0703

TABLE 10

Ionization constants of $CaOAc^-$ and $SrOAc^+$ and activity product, $K_x = a_{Ag^+} \times a_{OAc^-}$, in various solvents

SOLVENT	$SrOAc^+$		$CaOAc^+$		$a_{Ag^+} \times a_{OAc^-}$ 10^7K_x	SOLVENT	$a_{Ag^+} \times a_{OAc^-}$ 10^7K_x
	K_c	10^3K_x	K_c	10^3K_x			
Water.......	0.34	6.1	0.15	2.7	9.22	Water.......	9.22
10% acetone.	0.12	2.3	0.094	1.8	6.07	10% alcohol.	5.78
20% acetone.	0.087	1.9	0.058	1.2	3.11	20% alcohol..	3.55
30% acetone.	0.037	0.88	0.019	0.44	1.62	30% alcohol..	2.17

Dielectric constant of solvent and equilibrium constant

For a process in a solution of sufficiently low ionic strength, we have the relation

$$\Delta F = - RT \log_e K_x + RT\Sigma\nu_i \log_e x_i \tag{8}$$

If, for a given solvent, the ionic strength is not low, the mole fraction, X_i, in equation 8 must be replaced by f_iX_i, where f_i is an activity coefficient;

the value of K_x remains, however, essentially unchanged. In passing from one solvent to another, there will be a change in K_x. The magnitude of this change in K_x can be determined if we can calculate the difference between the free energies of an ion in two solvents when the ionic strength is low and when the mole fraction of the ion is the same in both solvents. If we adopt the simple hypothesis that a given ion of charge $z_i\epsilon$, where ϵ is the unit charge and z_i is the valence, remains essentially identical in the various solvents considered and hence is characterized by the same effective radius r_i, this difference in free energy in two media of dielectric constants D_1 and D_2 will be given by the Born equation

$$F_2 - F_1 \text{ (for a given ion)} = \frac{1}{2}\frac{\epsilon^2 z_i^2}{r_i}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) \tag{9}$$

For a given process involving ions in the two media, we find from equations 9 and 8

$$\Delta F_2 - \Delta F_1 = -RT\log_e (K_x)_2 + RT\log_e (K_x)_1$$
$$= \tfrac{1}{2}N\epsilon^2\left(\frac{1}{D_2} - \frac{1}{D_1}\right)\sum\frac{\nu_i z_i^2}{r_i} \tag{10}$$

For our purpose we may write equation 10 in the form

$$\log_e K_x = \text{constant} - \frac{N\epsilon^2}{2DRT}\sum\frac{\nu_i z_i^2}{r_i} \tag{11}$$

In equations 10 and 11, N is Avogadro's number and ν_i is the coefficient of the ion in the chemical equation. Changing to ordinary logarithms and introducing the numerical values of N, ϵ, and R, we find for 25°C.

$$\log_{10} K_x = \text{constant} - \frac{121.0}{D}\sum\frac{\nu_i z_i^2}{r_i} \tag{12}$$

The radius, r_i, is to be expressed in Ångström units.

We therefore see that the simple theory of Born leads to the result that the equilibrium constant in various solvents of a reaction involving ions should be given by an equation of the form

$$\log_{10} K_x = A - \frac{B}{D} \tag{13}$$

The data presented in table 10 offer an opportunity of testing the relation given in equation 12 or 13. Applying the method of least squares, we find that the dependence of the various equilibrium constants on the dielectric constant of the solvent is reproduced satisfactorily by the following equations.

(1) For $SrOAc^+$ in water and acetone–water mixtures:

$$\log_{10} K_x = 0.379 - \frac{210}{D}$$

(2) For $CaOAc^+$ in water and acetone–water mixtures:

$$\log_{10} K_x = 0.165 - \frac{212}{D}$$

(3) For the activity product, $K_x = a_{Ag^+} \times a_{OAc^-}$, in water and acetone–water mixtures:

$$\log_{10} K_x = \bar{4}.6615 - \frac{211}{D}$$

(4) For the activity product, $a_{Ag^+} \times a_{OAc^-}$, in water and ethyl alcohol–water mixtures:

$$\log_{10} K_x = \bar{4}.1511 - \frac{173}{D}$$

From the equations for the ionization constants of $SrOAc^+$ and of $CaOAc^+$, we find on comparing equations 12 and 13

$$B = 210 = 121.0\left[\frac{4}{r_{Sr^{++}}} + \frac{1}{r_{OAc^-}} - \frac{1}{r_{SrOAc^+}}\right]$$

$$B = 212 = 121.0\left[\frac{4}{r_{Ca^{++}}} + \frac{1}{r_{OAc^-}} - \frac{1}{r_{CaOAc^+}}\right]$$

Assuming that the intermediate ions, $SrOAc^+$ and $CaOAc^+$, are approximately equal in size to the acetate ion, we find

$$r_{Sr^{++}} = r_{Ca^{++}} \cong 2.3 \text{ A.U.}$$

Similarly we obtain

$$B = 121.0\left(\frac{1}{r_{Ag^+}} + \frac{1}{r_{OAc^-}}\right) = 211 \text{ in aqueous acetone}$$

$$B = 121.0\left(\frac{1}{r_{Ag^+}} + \frac{1}{r_{OAc^-}}\right) = 173 \text{ in aqueous alcohol}$$

These equations give for an average value of the radii of Ag^+ and OAc^- 1.2 in aqueous acetone and 1.4 in aqueous alcohol. No claim of course is made for the accuracy of these calculated values of ionic radii. The point of importance is that they turn out to be of the right order of magnitude. In our opinion, the results obtained in these calculations confirm our values for the ionization constants of the intermediate ions, $SrOAc^+$ and $CaOAc^+$.

SUMMARY

We have determined the solubility at 25°C. of silver acetate in various acetone–water mixtures and in the presence of various amounts of potassium nitrate, sodium nitrate, strontium nitrate, and calcium nitrate.

The equation of Debye and Hückel can be applied satisfactorily to the solutions containing either sodium nitrate or potassium nitrate as added salt.

The greater solubility of silver acetate in the presence of strontium nitrate or calcium nitrate is assumed to be due chiefly to the incomplete ionization of the acetates of strontium and of calcium.

From the solubility data, we have calculated the ionization constants of the intermediate ions, $SrOAc^+$ and $CaOAc^+$, in water and in aqueous acetone.

The Born theory, which gives a relation between the equilibrium constant and the dielectric constant of the medium, is applied with some success to the data presented in this paper.

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