[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Binary and Ternary Solutions of Nitrates in Anhydrous Acetic Acid

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In a previous paper,[1] the authors reported solubility data for the nitrates of sodium, ammonium, barium and silver in anhydrous acetic acid; in none of these cases was a solid solvate obtained, and the saturated solution of the most soluble salt, ammonium nitrate, was found to be only 0.074 molal at 30°. The present paper includes data for the nitrates of lithium and calcium, which were found to be far more soluble than the ammonium salt. In addition, solubility data are presented for the ternary systems silver nitrate–ammonium nitrate–acetic acid and silver nitrate–lithium nitrate–acetic acid.

Method

Preparation of Materials.—Pure anhydrous acetic acid, and the nitrates of silver and ammonium, were prepared as described in previous papers of this series. Lithium nitrate was recrystallized from a solution which had been acidified with nitric acid, and was dried at 160° to constant weight. A filtered solution of calcium nitrate was evaporated to dryness, and the residue was dehydrated almost completely over a Bunsen flame; it was then heated for twenty-four hours in an oven maintained at 160°. Analysis of the product gave Ca, 24.50% (calcd. for $Ca(NO_3)_2$, 24.42%).

Determination of Solubility.—In the binary systems the synthetic method, as described in previous papers, was used; duplicate determinations were made of equilibrium temperatures, with the usual precautions. The synthetic method was employed also for the system $AgNO_3$–NH_4NO_3–$HC_2H_3O_2$. A number of solutions, each containing acetic acid and one of the other components in a fixed ratio by weight, were used as solvents, and the change in freezing point with varying concentration of the third component was determined. From the data so obtained, solubility isotherms readily could be derived, as in previous work.[2]

The system $AgNO_3$–$LiNO_3$–$HC_2H_3O_2$, however, was studied by the analytical method. An excess of the saturating salt, silver nitrate, was added to solutions containing various fixed ratios of acetic acid and lithium nitrate. These solutions, in tightly stoppered bottles sealed with paraffin, were maintained at 30° in a thermostat, with frequent agitation, for from ten days to two weeks. Filtered samples were then withdrawn, weighed, and analyzed for silver by the Volhard method.

Analysis of Solid Phases.—In the binary systems, the crystalline phases obtained were analyzed for acetic acid of solvation by direct titration with 0.1 normal sodium hydroxide solution. In the ternary systems, the solids were analyzed for silver by the usual gravimetric method. When ammonium nitrate was present, ammonia was determined by distillation with concentrated aqueous sodium hydroxide solution into standard hydrochloric acid.

Results

I. Binary Systems.—In Tables I and II, S denotes the mole percentage of solute, and T is the corresponding equilibrium temperature. These data are presented graphically in Fig. 1.

TABLE I

LITHIUM NITRATE–ACETIC ACID

(a) Solid phase $HC_2H_3O_2$		(b) Solid phase $LiNO_3$	
S	T	S	T
0	16.60	9.38	39.0
0.156	16.30	10.31	46.3
.983	16.03	11.26	54.2
2.013	15.71	12.64	66.7
4.115	15.00	14.66	82.6
5.305	14.46	15.66	91.6
7.693	12.80	17.08	101.0
9.384	11.80	19.84	118.3
10.310	10.92	22.34	132.2

Analysis of the solid phase (b) by titration showed no appreciable amount of acidity; hence it was concluded that the solute separating from these solutions was unsolvated.

TABLE II

CALCIUM NITRATE–ACETIC ACID

(a) Solid phase $HC_2H_3O_2$		(b) Solid phase $Ca(NO_3)_2 \cdot 3HC_2H_3O_2$	
S	T	S	T
2.70	15.86	7.87	30.3
3.65	15.72	8.27	32.0
4.59	15.60	8.71	33.5
6.57	15.18	8.90	33.9
7.87	14.83		
8.90	14.37		

Solutions containing more than 9 mole per cent. of calcium nitrate could not be obtained, even by means of prolonged contact of solution with solid salt at 120°. On the other hand, separation of a solid phase from the rather viscous concentrated solutions occurred only after the solution had been cooled well below the eutectic temperature. The mean of eight analyses of the solid phase (b) gave $HC_2H_3O_2$, 53.9% (calcd. for $Ca(NO_3)_2 \cdot 3HC_2H_3O_2$, 52.32%). This solvate, which has not been reported previously, is both extremely hygroscopic and rather unstable.

II. Ternary System $AgNO_3$–NH_4NO_3–$HC_2H_3O_2$.—In Table III, the mole percentage of ammonium nitrate in the binary solvent is rep-

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[1] Davidson and Geer, THIS JOURNAL, **55**, 642 (1933).

[2] Davidson and Griswold, *ibid.*, **57**, 423 (1935).

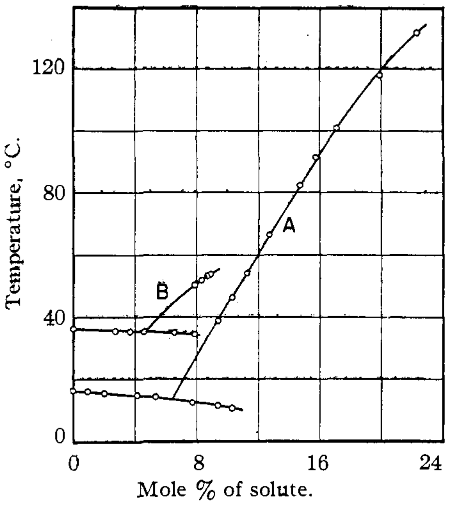

Fig. 1.—A, system $LiNO_3$–$HC_2H_3O_2$; B, system $Ca(NO_3)_2$–$HC_2H_3O_2$, subtract 20° from temperature scale.

resented by R, while S denotes the mole percentage of silver nitrate in the ternary solution in equilibrium with solid phase at the temperature T. New data for the solubility of silver nitrate in pure acetic acid are given in the columns headed "R = 0." The composition of the solid phase is given at the head of each series of data, the abbreviation D. being used to denote the double salt $AgNO_3 \cdot NH_4NO_3$.

TABLE III

SOLUBILITY OF SILVER NITRATE IN AMMONIUM NITRATE SOLUTIONS

S	T	S	T	S	T
R = 0		R = 0.253%		R = 0.383%	
$AgNO_3$		D.		D.	
0.0338	32.0	0.0279	25.3	0.0323	34.3
.0599	50.2	.0358	32.6	.0470	40.8
.0957	64.5	$AgNO_3$		.0774	49.5
.1400	80.0	0.0613	41.1	$AgNO_3$	
.1900	91.6	.0887	54.0	0.0975	54.1
		.1083	63.3	.1188	62.0
		.1463	73.5	.1605	74.0
		.2030	86.8	.2050	83.9
		.2560	96.5	.2380	90.1
R = 0.506%		R = 0.768%		R = 0.866%	
D.		D.		D.	
0.0359	37.7	0.0562	45.8	0.0711	49.8
.0665	49.4	.0574	48.0	.1041	57.6
.0822	52.2	.0984	56.5	.1640	67.5
.1102	58.0	.1430	65.0	.2030	71.3
		.2040	71.5		
$AgNO_3$		$AgNO_3$		$AgNO_3$	
0.148	66.6	0.265	81.9	0.262	80.4
.208	82.2	.305	89.6	.288	84.7
.251	89.4	.358	97.4	.328	89.6
.287	94.7			.388	96.9
R = 1.016%		R = 1.852%		R = 2.940%	
D.		D.		D.	
0.081	53.8	0.184	67.0	0.231	67.2
.122	62.0	.239	72.4	.350	75.7
.161	66.3	.320	78.2	.480	82.8
.193	70.2	.421	82.8	.596	87.2
.239	73.7	.482	85.1	.734	91.1
$AgNO_3$		$AgNO_3$		$AgNO_3$	
0.281	80.4	0.571	95.6	0.874	96.6
.319	85.4	.598	97.9	.889	99.1
.357	90.0	.641	100.2		
R = 5.13%		R = 8.67%		R = 15.30%	
D.		D.		NH_4NO_3	
0.446	74.0	1.071	83.8	1.923	86.3
.616	81.4	1.192	86.5	D.	
.806	87.1	1.428	90.5	2.14	85.0
1.094	92.1	1.563	92.6	2.35	88.6
1.357	95.3	1.704	94.5	2.61	90.5
$AgNO_3$		2.002	97.0	2.83	92.6
1.507	102.5			3.09	94.5

Quantitative data were not obtained for higher concentrations of ammonium nitrate, but qualitative experiments in this range showed that, due to the low melting point of the double salt, a second liquid phase appeared at temperatures in the neighborhood of 100°.

In Table IV, the mole percentage of silver nitrate in the binary solvent is designated by R', while S' denotes the mole percentage of ammonium nitrate in the ternary solution in equilibrium with the solid phase indicated, at the temperature T.

TABLE IV

SOLUBILITY OF AMMONIUM NITRATE IN SILVER NITRATE SOLUTIONS

S'	T	S'	T	S'	T
R' = 0.028%		R' = 0.052%		R' = 0.074%	
D.		D.		D.	
0.401	30.6	0.472	44.9	0.617	51.0
NH_4NO_3		.662	45.2	.923	50.8
0.529	31.8	NH_4NO_3		1.098	50.3
.784	41.1	1.03	46.9	NH_4NO_3	
1.120	48.4	1.42	55.0	1.31	51.7
		2.09	62.6	2.30	63.0
		3.28	69.8	3.53	70.7
R' = 0.118%		R' = 0.131%			
D.		D.			
1.08	60.1	1.26	62.1		
1.42	58.9	1.80	59.5		
1.63	57.7				
NH_4NO_3		NH_4NO_3			
1.87	58.0	2.06	60.3		
2.70	64.5	2.64	64.4		
3.25	69.7				

The data of Tables III and IV were plotted in a series of curves, not reproduced here, from which were derived the isotherms shown in Fig. 2.

Analysis of the solid phase which separated under conditions corresponding to the middle portion of the isotherms gave: Ag, 42.57; NH_3, 6.68 (calcd. for $AgNO_3 \cdot NH_4NO_3$: Ag, 43.16; NH_3, 6.81). A sample of this same solid, on heating, did not melt sharply but had become completely liquid at 108.5°. It is evident that this compound is the well-known double salt first reported by Ditte,[3] the m. p. of which is given by Zawidzki[4] as 109.6°.

III. Ternary System $AgNO_3$–$LiNO_3$–$HC_2H_3O_2$.—The data given in the first two columns of Table V are based on analyses of solutions saturated at 30°. The solid phase was $AgNO_3$ throughout. The third and fourth columns of the table give, respectively, the total ionic strength, μ, of the solutions, and the mean molality, $m_{\pm}$, of the ions of silver nitrate (the square root of the solubility product).

TABLE V

SOLUBILITY OF SILVER NITRATE IN LITHIUM NITRATE SOLUTIONS AT 30°

$LiNO_3$, mole %	$AgNO_3$, mole %	μ	$m_{\pm}$
0	0.0388	0.00646	0.00646
0.072	.0333	.0176	.00987
.252	.0341	.0478	.0165
.332	.0348	.0613	.0189
.348	.0357	.0641	.0196
.733	.0457	.131	.0317
1.54	.0721	.273	.0578
2.52	.100	.448	.0877
3.66	.136	.657	.124
4.83	.171	.877	.162
5.97	.200	1.10	.197
6.88	.216	1.27	.222

The solubility isotherm is plotted in Fig. 3.

Discussion

Binary Systems.—The solubilities at 30° of the three nitrates here studied, in moles per 1000 g. of acetic acid, are as follows:[5] $AgNO_3$, 0.0065; $LiNO_3$, 1.49; $Ca(NO_3)_2$ (trisolvate), 1.41. The solubility of the lithium salt thus proved to be twenty times as great as that previously determined[1] for ammonium nitrate at this temperature; at 100°, however, the solubilities of these two salts are very nearly the same (about 3.3 moles per 1000 g. of solvent).

Since freezing point depression data for lithium and calcium nitrates in acetic acid over a wide concentration range were also made available by this work, it appeared to be of interest to calculate the values of the freezing point divergence function, j,[6] for these solutions. This was done with the aid of a large-scale plot, not reproduced here. The molal freezing point constant was taken as 3.60.[7]

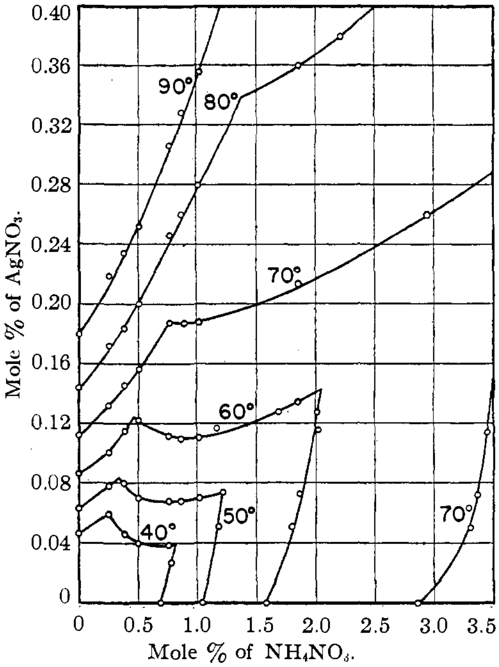

Fig. 2.—Isotherms for the system $AgNO_3$–NH_4NO_3–$HC_2H_3O_2$.

In the case of lithium nitrate, the value of j was found to remain practically constant, for molalities between 0.2 and 1, at 0.67; at higher concentrations its value decreased. This figure is in good agreement with that of 0.663 previously obtained for a 0.225 molal solution by Webb,[8] who pointed out that j values often remain constant over an appreciable concentration range in this solvent. Eichelberger[7] (p. 802) also called attention to the constant value of j (about 0.62) for dilute solutions of ammonium nitrate in acetic acid.

For the solutions of calcium nitrate, considered as a ternary electrolyte, j was found to remain constant at 0.88 for molalities from 0.15 to 1.5. With the exception of the acetates of lead[9] and

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[3] Ditte, *Compt. rend.*, **101**, 878 (1885).

[4] Zawidzki, *Z. physik. Chem.*, **47**, 721 (1904).

[5] The present value for silver nitrate, somewhat higher than that obtained from our previous data, is believed to be more nearly correct.

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 342.

[7] Eichelberger, THIS JOURNAL, **56**, 799 (1934).

[8] Webb, *ibid.*, **48**, 2263 (1926). See, however, ref. 7, p. 799.

[9] Davidson and McAllister, THIS JOURNAL, **52**, 507 (1930).

nickel,[10] for which maxima of about 0.90 are reached, calcium nitrate shows the highest value of j so far encountered in acetic acid solutions; this undoubtedly corresponds to an exceedingly high degree of ionic association or clustering.

Ternary Systems.—The isotherms of Fig. 2 exhibit the double salt $AgNO_3 \cdot NH_4NO_3$ as stable solid phase throughout a considerable portion of the region studied. In this respect the acetic acid system resembles the corresponding system with water as solvent,[11] although in that case, due to the far greater solubility of the salts, the concentration range investigated was much wider. Moreover, whereas the double salt dissolves in water without decomposition, it is not stable in contact with acetic acid solutions unless they contain a large excess of ammonium nitrate. From the present work it is evident, also, that in the regions in which the single nitrates occur as solid phases, the solubility of each increases markedly with increasing concentration of the other.

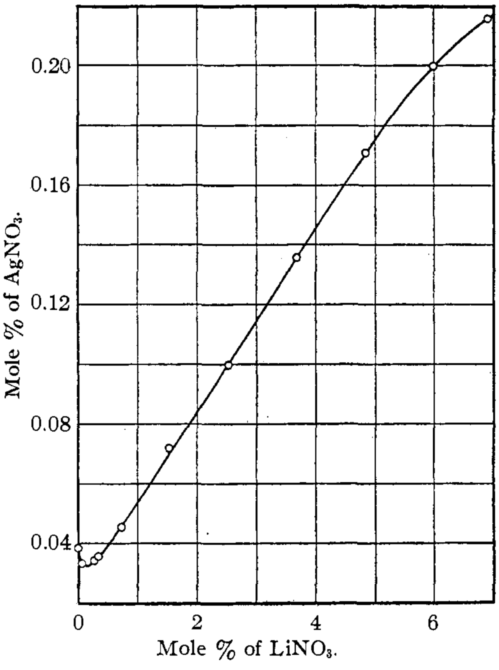

Fig. 3.—Solubility of silver nitrate in acetic acid solutions of lithium nitrate at 30°.

According to Fig. 3, the solubility of silver nitrate at 30° decreases from 0.0388 mole % in pure acetic acid to a minimum of 0.0325 mole % in a solution containing approximately 0.15 mole % of lithium nitrate, after which it increases steadily with increasing concentration of lithium salt. Solubility minima of this type, in the case of salts with a common ion, are of familiar occurrence in aqueous solution; only one instance in acetic acid, however, has been reported previously, namely, that of potassium perchlorate as solute in the presence of ammonium perchlorate.[12]

Despite the initial decrease in actual solubility, we should expect the *solubility product* of the silver nitrate to increase continuously with increasing total salt concentration, as in the case of other salts in this solvent.[2,12,13] The last two columns of Table V show that the mean molality of the ions of silver nitrate does indeed increase markedly with increasing ionic strength, throughout the entire concentration range. From a plot of log $m_{\pm}$ against log μ (not reproduced here), it was found that in moderately dilute solutions ($\mu = 0.02$ to 0.1) $m_{\pm}$ is very nearly proportional to $\mu^{0.6}$. Hence it is evident that, in this concentration range, the activity coefficient of silver nitrate in the ternary solution is inversely proportional to the 0.6 power of the ionic strength.

Summary

1. Solubility data have been obtained for lithium nitrate in acetic acid over a wide range of temperature, and for calcium nitrate in the neighborhood of 30°.

2. The new solvate $Ca(NO_3)_2 \cdot 3HC_2H_3O_2$ has been isolated and analyzed.

3. The system $AgNO_3$–NH_4NO_3–$HC_2H_3O_2$ has been studied at temperatures from 40 to 90°. The double salt $AgNO_3 \cdot NH_4NO_3$ occurs as stable solid phase over a small concentration range in this system.

4. The system $AgNO_3$–$LiNO_3$–$HC_2H_3O_2$ has been studied at 30°. Although the solubility of silver nitrate goes through a minimum in 0.025 molal lithium nitrate solution, the solubility product of the former salt increases throughout with increasing total ionic strength.

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(10) Davidson and Chappell, THIS JOURNAL, **55**, 3531 (1933).

(11) Schreinemakers and de Baat, *Chem. Weekblad*, **7**, 259 (1910).

(12) Seward and Hamblet, THIS JOURNAL, **54**, 554 (1932).

(13) Scholl, Hutchison and Chandlee, *ibid.*, **55**, 3081 (1933).