[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

The Effect of Some Salts on the Solubility of Silver Acetate and of Silver Nitrate in Acetic Acid at 30°[1]

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The solubility of silver acetate in acetic acid at 30° is found to be 0.00470 molal, while that of silver nitrate is 0.00617 *m*. The solubility of each is decreased somewhat in the presence of small concentrations of the other. In the presence of sodium acetate in concentrations of about 0.001 to 0.07 *m*, the solubility of silver acetate increases progressively without showing any evidence of the common ion effect. On the other hand the solubility of silver nitrate in the presence of lithium nitrate goes through a minimum and then increases, as has been previously reported by other investigators. The solubility of silver acetate in solutions of the heteroionic salt, lithium nitrate, shows a marked increase which can be accounted for quantitatively by assuming that equilibrium is reached in a reaction of the following type (presumably between ion-pairs) in solution: $AgX + MA \rightleftarrows AgA + MX$. Similarly, silver nitrate shows a marked increase in solubility in the presence of low concentrations of sodium acetate. At higher concentrations of added salt, however, first silver acetate and then sodium nitrate are precipitated out.

Most of the studies of salt effects on the solubilities of electrolytes in acetic acid which have been reported[2] show the absence of any significant common-ion effect such as is so well known in aqueous systems. In view of the evidence[3] that many electrolytes in acetic acid show only very slight ionic dissociation, this is, perhaps, not very surprising. However, two examples of apparent common-ion effect in this solvent have been noted, one involving the solubility of potassium perchlorate in the presence of ammonium perchlorate,[2a] the other the solubility of silver nitrate in the presence of lithium nitrate.[4] As part of a series of studies on the behavior of electrolytes in acetic acid, it was decided to investigate solubility effects in some systems involving silver salts in acetic acid. This paper presents the results of this work, which included a study of the solubility of silver acetate in the presence of various concentrations of silver nitrate and of sodium acetate; the solubility of silver nitrate in the presence of silver acetate and of lithium nitrate; and two heteroionic systems, silver acetate in the presence of lithium nitrate, and silver nitrate in the presence of sodium acetate.

Experimental

Materials.—Anhydrous acetic acid was prepared by refluxing about two liters of C.P. glacial acid with a slight excess of acetic anhydride and 300 ml. of dry, thiophene-free benzene for 24 hours, then distilling through a 1.5-meter fractionating column. The excess benzene and the azeotrope containing any free water came off at about 78°, and a portion of acid distilling 116–117° (uncor.) was collected. The melting point of the product was 16.67° (cor.). Reagent grade sodium acetate and lithium nitrate were each recrystallized three times and suitably dried. Qualitative spectrographic tests gave no evidence of metallic impurity. Silver nitrate was purified by the method of Richards and Wells,[5] and a gravimetric determination of silver corresponded to 99.96% $AgNO_3$. Silver acetate was shaken with acetic acid for three days, the process repeated with fresh acid, and the solid was then dried in a vacuum oven at 40° for 48 hours. Analysis corresponded to 99.86% $AgC_2H_3O_2$.

Method.—Stock solutions of a given solvent in acetic acid were prepared, and a series of more dilute solutions were then made from these in 20-cm. test-tubes which had been previously drawn out and which contained an excess of the saturating salt. The tubes were sealed off and then tumbled in a bath maintained at 30.00 ± 0.01°. It was found that after one week of agitation the results were consistent with those obtained after a month. Most of the samples were actually tumbled for about two weeks. In some cases approach to equilibrium was made from above the bath temperature with results again consistent with those obtained when the approach was made from undersaturation. At the end of the equilibration period the solutions were filtered under pressure through a fritted glass filter, two portions being collected for analysis. If the solid was to be analyzed it was dried in a vacuum oven at 40°. The loss in weight was never sufficiently large to indicate decomposition of a solvate. All transfers were carried out in a dry-box.

Analysis.—Silver was determined by titration with approximately 0.005 *M* potassium iodide solution which had been standardized against silver nitrate under conditions very similar to those involved in the analyses. A Fisher titrimeter equipped with a silver indicating electrode and a saturated calomel reference electrode with a salt bridge of sodium nitrate solution, was used to follow the titration. Duplicate analyses, agreeing to within two parts per thousand, were run in every case. Sodium was determined by the zinc uranyl acetate method, after the silver had first been removed as chloride.

Results and Discussion

System Silver Acetate–Silver Nitrate–Acetic Acid.—Although the solubilities of silver acetate and silver nitrate in acetic acid are not very high, they are sufficient to permit each salt to be used over a limited concentration range as solvent salt for the other. Thus a series of dilute solutions of silver acetate in acetic acid were prepared, saturated with silver nitrate, and the saturated solution analyzed for total silver. The difference between this and the silver initially present as silver acetate gives the solubility of silver nitrate. The solid phase in equilibrium with the highest concentration of silver acetate was analyzed for silver and for carbon and hydrogen.[6] The silver analysis corresponded to 99.97% $AgNO_3$, and only trace amounts of carbon and hydrogen were found, indicating that the solid phase was simply $AgNO_3$. A similar procedure was followed using silver nitrate as solvent salt and silver acetate as saturating salt. Analysis of the solid phase indicated it to be $AgC_2H_3O_2$ throughout. Results of this study are given in Table I. All concentrations throughout this paper are expressed in moles per thousand grams of acetic acid.

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[1] From part of a thesis presented to the Graduate School of the University of Kansas by Ralph K. Birdwhistell in partial fulfillment of the requirements for the Ph.D. degree, 1953.

[2] See, for example (a) R. P. Seward and C. H. Hamblet, THIS JOURNAL, **54**, 554 (1932); (b) E. Griswold, M. M. Jones and R. K. Birdwhistell, *ibid.*, **75**, 5701 (1953).

[3] M. M. Jones and E. Griswold, *ibid.*, **76**, 3247 (1954).

[4] A. W. Davidson and H. A. Geer, *ibid.*, **60**, 1211 (1938).

[5] T. W. Richards and R. C. Wells, *ibid.*, **27**, 459 (1905)

[6] Microanalytical determinations of carbon and hydrogen were made by G. Weiler, Microanalytical Laboratory, 164 Banbury Road, Oxford, England.

Table I

Solubility Relations of Silver Nitrate and Silver Acetate in Acetic Acid at 30°

(a) Solid phase $AgNO_3$ C, concn. $AgC_2H_3O_2$	S, concn. $AgNO_3$	(b) Solid phase $AgC_2H_3O_2$ C, concn. $AgNO_3$	S, concn. $AgC_2H_3O_2$
0	0.00617	0	0.00470
0.0005529	.00595	0.0007541	.00461
.001073	.00583	.001957	.00426
.001110	.00582	.003421	.00383
.002661	.00535	.005208	.00337
.002757	.00536	.005939	.00317
.003871	.00497	.006790	.00297

It is seen from the data in Table I that each silver salt exerts a common-ion effect upon the other. This may indicate that these silver salts are somewhat more highly dissociated than most other uni-univalent salts which have been examined, but in the absence of additional information no definite conclusion on this point can be drawn.

A plot of the two solubility curves shows them to intersect at a point corresponding to about 0.0034 *m* silver acetate and 0.0051 *m* silver nitrate, which would represent the composition of a solution in equilibrium with both solids. Both curves were carried beyond this point into regions representing supersaturation with respect to one or the other solid phase. Neither solid appears to have much tendency to induce crystallization of the other under these conditions.

Systems Silver Nitrate–Lithium Nitrate–Acetic Acid and Silver Acetate–Sodium Acetate–Acetic Acid.—The solubility of silver nitrate in solutions of lithium nitrate ranging in concentration up to about 0.09 *m* is given in Table II. These values are found to run parallel to, although slightly lower than, those reported by Davidson and Geer.[4] The existence of a minimum in the solubility curve is clearly evident. In aqueous systems such phenomena can be interpreted in terms of a common-ion effect plus complex ion formation in solution, and methods of determining the nature and stability of such complex ions from solubility data have been proposed.[7,8] In the present case the solubility behavior of silver nitrate may indicate, first, a significant degree of ionic dissociation of both silver nitrate and lithium nitrate in acetic acid, and, second, interaction between the two salts to form a complex or association product of some kind. However, any quantitative calculations of the kind employed in aqueous solutions are greatly complicated here by the fact that the added salt, lithium nitrate, is almost certainly incompletely dissociated in this solvent, and information concerning its degree of dissociation at various concentrations is lacking.

Table II

Solubility of Silver Nitrate in Lithium Nitrate Solutions and of Silver Acetate in Sodium Acetate Solutions in Acetic Acid at 30°

$AgNO_3$–$LiNO_3$–$HC_2H_3O_2$ C, concn. $LiNO_3$	S, concn. $AgNO_3$	$AgC_2H_3O_2$–$NaC_2H_3O_2$–$HC_2H_3O_2$ C, concn. $NaC_2H_3O_2$	S, concn. $AgC_2H_3O_2$
0	0.00617	0	0.00470
0.00595	.00552	0.000929	.00472
.01031	.00545	.002309	.00478
.01602	.00525	.002791	.00479
.01699	.00522	.01606	.00506
.02290	.00510	.02062	.00512
.03288	.00518	.02572	.00519
.03417	.00514	.02638	.00518
.04902	.00533	.03038	.00524
.05914	.00559	.03669	.00530
.08945	.00698	.03789	.00531
Solid phase: $AgNO_3$ throughout		.04440	.00540
		.05845	.00556
		.07165	.00571
		Solid phase: $AgC_2H_3O_2$ throughout	

In the third and fourth columns of Table II are presented data showing the effect of sodium acetate at various concentrations on the solubility of silver acetate. In this case there is no manifestation of a common-ion effect. Instead there is a progressive increase in solubility with increasing concentration of added salt. Beyond about 0.016 *m* sodium acetate the solubility curve appears to be linear, which would be consistent with the formation of an association product or complex between the two salts in solution requiring one mole of sodium acetate per mole of product formed were it not for the more rapid initial increase in solubility with very low sodium acetate concentration, which seems to indicate a more complicated type of interaction. In reference to the absence of the common-ion effect it should be pointed out that sodium acetate shows only a very slight degree of ionic dissociation in acetic acid, the dissociation constant having been found[3] to be 2.1×10^{-7}.

System Silver Acetate–Lithium Nitrate–Acetic Acid.—The effect of lithium nitrate upon the solubility of silver acetate is shown by the data in Table III.

Table III

Solubility of Silver Acetate in Lithium Nitrate Solutions in Acetic Acid at 30°

C, concn. $LiNO_3$	S, concn. $AgC_2H_3O_2$	K (eq. 1)
0	0.00470	
0.000400	.00499	0.00076
.001002	.00526	.00071
.008727	.00692	.00076
.01110	.00720	.00073
.01715	.00789	.00073
.01757	.00793	.00073
.01844	.00804	.00074
.02021	.00823	.00075
.02178	.00837	.00074
.02518	.00868	.00075
.03384	.00936	.00074
.03471	.00943	.00076
.04141	.01003	.00079
.05933	.01109	.00077
.06030	.01118	.00078
.08631	.01253	.00078
.1285	.01441	.00079
Solid phase: $AgC_2H_3O_2$ throughout	Mean	0.00075
	Av. dev.	.00002

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[7] A. B. Garrett, M. V. Noble and S. Miller, *J. Chem. Educ.*, **19**, 485 (1942).

[8] C. A. Reynolds and W. J. Argersinger, Jr., *J. Phys. Chem.*, **56**, 417 (1952).

There is evident in this case a pronounced increase in solubility amounting to approximately 200% at about 0.13 *m* added salt. This behavior is very similar to that of potassium bromide in the presence of various heteroionic salts, previously described.[2b] In connection with this earlier work it was pointed out that the results could be satisfactorily interpreted by postulating a metathetical reaction between the undissociated ion-pairs in solution, reaching equilibrium with some of all four species of ion-pairs present. In the present case the reaction would be formulated

$$AgC_2H_3O_2 + LiNO_3 \rightleftharpoons AgNO_3 + LiC_2H_3O_2 \quad (a)$$

It was previously shown that, if one assumes the concentration of free ions to be negligible in comparison with that of the ion-pairs, and also that the activity coefficients of the ion-pairs are equal and constant, then the equilibrium equation for reaction *a* may be written as

$$\frac{[AgNO_3][LiC_2H_3O_2]}{[LiNO_3]} = \frac{(\Delta S)^2}{C - \Delta S} = K \qquad (1)$$

where ΔS represents the increase in solubility of silver acetate in a solution of initial concentration C in lithium nitrate, over its solubility in acetic acid alone. In the third column of Table III values of K from equation 1 are given and are seen to remain essentially constant over the entire range in concentration of added salt, a result which is quite consistent with the hypothesis previously proposed.

It must be pointed out that in the more concentrated solutions of lithium nitrate the concentration of the silver nitrate constituent in solution exceeds the solubility of silver nitrate in acetic acid alone. It seems probable that these solutions may actually be supersaturated with respect to silver nitrate, although, unfortunately, seeding was not tried. In a somewhat similar system, described in the next section, precipitation of a product does, in fact, occur.

System Silver Nitrate–Sodium Acetate–Acetic Acid.—In Table IV are presented the results of a study of the solubility of silver nitrate in sodium acetate solutions. Again there is a marked increase in solubility, amounting to about 50% in approximately 0.004 *m* sodium acetate. As has been done with other heteroionic systems, this may be ascribed largely to a metathetical reaction between undissociated ion-pairs in solution, although an application of equation 1 is unsatisfactory in this case, and is usually not very significant in solutions as dilute as this.

TABLE IV

SOLUBILITY OF SILVER NITRATE IN SODIUM ACETATE SOLUTIONS IN ACETIC ACID AT 30°

C, concn. $NaC_2H_3O_2$	S, concn. $AgNO_3$	C, concn. $NaC_2H_3O_2$	S, concn. $AgNO_3$
0	0.00617	0.001041	0.00688
0.000259	.00636	.003067	.00835
.000735	.00668	.004250	.00943

Solid phase: $AgNO_3$ throughout

Additional experiments, using more concentrated solutions of sodium acetate, demonstrated that somewhere between about 0.004 and 0.006 *m* initial sodium acetate concentration the slope of the solubility curve undergoes an abrupt change, becoming much less steep. In this region, which extends to some place between 0.02 and 0.03 *m* sodium acetate, the solid presents the appearance of a mixture of silver nitrate and silver acetate crystals. Analysis gave a silver content corresponding to such mixtures, and showed the absence of significant amounts of sodium in the solid. When solutions containing initial concentrations of sodium acetate higher than about 0.028 *m* were equilibrated with excess silver nitrate, they were found to contain constant percentages of sodium and silver. From phase rule considerations, the presence of three solid phases was indicated. Crystals of silver nitrate and of silver acetate were identified in the solid, and analysis showed the presence of a sodium compound also. Since the solubility of sodium nitrate in acetic acid alone at 25° has been reported[9] to be 0.0202 *m*, while that of sodium acetate is much higher, the third solid phase is presumed to be sodium nitrate. These phenomena can all be accounted for, qualitatively at least, by supposing that a metathetical reaction occurs between ion-pairs forming silver acetate and sodium nitrate in solution, causing at first a sharp increase in solubility of silver nitrate. As the concentration of sodium acetate is increased the saturation value of silver acetate is reached, and it appears as solid phase together with silver nitrate. Additional sodium acetate results chiefly in converting solid silver nitrate into silver acetate, replacing an equivalent amount of sodium acetate by sodium nitrate in solution. In this region the concentration of silver in solution shows only a very slight increase with increase in alkali metal concentration. At sufficiently high sodium concentration sodium nitrate precipitates as a third solid phase, and the system becomes isothermally invariant. In order to be able to express the molal composition of this solution accurately, the percentage of a third component would have to be determined. Since our interest was primarily in the two-phase systems this was not done. However, inasmuch as the equivalent weights of nitrate and acetate differ by only about 5%, it is possible to calculate the approximate molalities of sodium and silver from their percentages in the invariant solution. These correspond to about 0.022 *m* and 0.0095 *m*, respectively.

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(9) A. W. Davidson and H. A. Geer, THIS JOURNAL, **55**, 642 (1933).