estimated, nevertheless, from the concentration of sodium iodate along the two curves, that the isothermally invariant point representing equilibrium between the two forms of the iodate must have the approximate composition 2.2% $NaIO_3$ and 45% $NaClO_3$. At higher concentrations of sodium chlorate the anhydrous sodium iodate has the lower solubility and is therefore the stable phase. These relationships are indicated in the table of results for this isotherm, but cannot be shown with any clearness in the figure.

Summary

Solubility measurements are given for the two ternary systems KIO_3–$KClO_3$–H_2O and $NaIO_3$–$NaClO_3$–H_2O at 25 and 50°. Neither compound formation nor solid solution is observed for either system at these temperatures. In the 50° isotherm of the system $NaIO_3$–$NaClO_3$–H_2O, anhydrous sodium iodate is found to exist as a stable phase over a limited range of the solubility curve at high concentrations of sodium chlorate.

NEW YORK, N. Y. RECEIVED JUNE 17, 1938

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

The Solubility of Halides in Anhydrous Acetic Acid

BY ARTHUR W. DAVIDSON AND WILBERT CHAPPELL

It was reported by Benrath,[1] as early as 1905, that a large number of chlorides are appreciably soluble in glacial acetic acid and may be crystallized unchanged from such solutions. Quantitative data on the solubility of halides in this solvent are limited, however, to the still earlier work of Étard[2] on mercuric chloride, the studies of Menschutkin on systems of acetic acid with calcium chloride, magnesium bromide and iodide,[3] and antimony chloride and bromide,[4] and the recent determination by Scholl, Hutchison and Chandlee[5] of the solubility of barium chloride in pure acetic acid and in the presence of various concentrations of sodium bromide.

The present paper includes solubility data, over a wide range of temperature, for sodium, potassium, ammonium, barium, strontium, cupric and mercuric chlorides, as well as for mercuric bromide and iodide. Of these salts, strontium chloride proved to be by far the most soluble at room temperature, and mercuric chloride to have the greatest solubility at the boiling point of the solvent. Experiments with cadmium chloride showed the solubility of this salt to be too small to be measured.

Method

Preparation of Materials.—Pure anhydrous acetic acid was prepared as described in previous papers of this series. All the salts used, except mercuric bromide and iodide, were purified by recrystallization and dried to constant weight under suitable conditions. Mercuric bromide and iodide were prepared by precipitation, and were dried for several days at 110 to 115°.

Determination of Solubility.—In every case except for the chlorides of barium and strontium, the synthetic method, as described in previous papers, was used. Duplicate determinations, with the usual precautions, were made of the equilibrium temperatures. The values given are believed to be correct to within 1° in the case of ammonium chloride and the mercuric halides, and to within 3° elsewhere, even in the case of cupric chloride, which gives a very steep temperature–concentration curve.

For barium and strontium chlorides the analytical method was used for determining solubilities. About 100 cc. of the solvent was placed in contact with an excess of the solid solute in a tightly stoppered bottle, which was then maintained at the desired temperature in a suitably adjusted thermostat. After equilibrium had been reached, filtered samples were withdrawn by means of a pipet with a bit of cotton fitted over its tip, and the chlorine content of each sample was determined by the usual gravimetric method.

Analysis of Solid Phases.—The solids to be analyzed were separated from their saturated solutions by filtration with gentle suction, rapidly pressed between dried pieces of porous tile, and allowed to remain over pellets of sodium hydroxide in a desiccator, for a few minutes only. Samples were then weighed as quickly as possible, and their chlorine content was determined in the usual way.

Results

Cupric, Sodium, Potassium and Ammonium Chlorides.—In the tables given below, S denotes the mole percentage of solute, and T the corresponding equilibrium temperature. These data are presented graphically in Fig. 1.

---

[1] Benrath, *J. prakt. Chem.*, [2] **72**, 228 (1905); see also Davidson, THIS JOURNAL, **50**, 1890 (1928).

[2] Étard, *Ann. chim. phys.*, [7] **2**, 555 (1894).

[3] Menschutkin, *Z. anorg. Chem.*, **54**, 89 (1907).

[4] Menschutkin, *J. Russ. Phys.-Chem. Soc.*, **43**, 1785 (1911).

[5] Scholl, Hutchison and Chandlee, THIS JOURNAL, **55**, 3081 (1933).

I. Cupric chloride

S	T
Solid phase $CuCl_2$	
0.0081	35
.0150	50
.0163	62
.0218	75

II. Sodium chloride

S	T
Solid phase NaCl	
0.076	30
.081	41
.085	45
.097	54
.105	60
.115	68
.130	76
.145	84
.166	92

III. Ammonium chloride

(a) Solid phase $HC_2H_3O_2$	
0	16.60
0.053	16.53
(b) Solid phase NH_4Cl	
0.053	21
.065	25
.084	32
.095	38
.110	43
.134	53
.150	58
.178	65
.209	72
.224	77
.259	84
.282	87
.312	92
.348	98

IV. Potassium chloride

(a) Solid phase $HC_2H_3O_2$	
0.168	16.45
(b) Solid phase KCl	
0.157	24
.170	30
.188	39
.207	47
.229	55
.239	59
.257	63
.272	70
.295	76
.336	87
.367	93

In the case of the alkali chlorides, the solid phases that separated from the saturated solution were shown, by analysis, to be the unsolvated salts. In the case of the copper salt it was impossible to obtain sufficient solid for an accurate analysis, but the brownish-yellow color of the crystals indicated that they probably consisted of unsolvated cupric chloride.

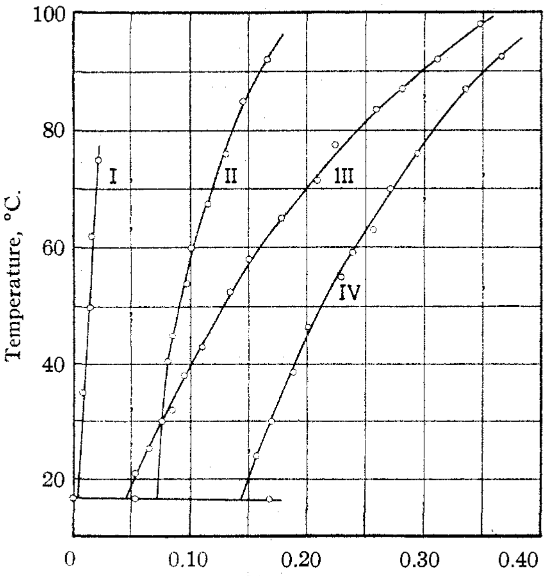

Fig. 1.—Solubility curves for $CuCl_2$ (I), NaCl (II), NH_4Cl (III) and KCl (IV) in anhydrous acetic acid.

Because of the extremely slow rate at which the alkali chlorides dissolve in acetic acid at low temperatures, there was room for some doubt as to whether or not the temperatures at which disappearance of crystals was observed, corresponded to true equilibrium. In order to check this point, analyses were made on solutions which had been maintained at 30°, with continuous agitation, for ten days, after having been heated to 100° for an hour in contact with excess solute. The solubility values so obtained, in mole %, are compared below with those obtained by interpolation from the preceding tables. It will be

	NaCl	NH_4Cl	KCl
Solubility, synth.	0.076	0.076	0.170
Solubility, anal.	.073	.080	.175

noted that the agreement, even at this low temperature, is fairly good. Incidentally, the value given by Eichelberger[6] for the solubility of ammonium chloride (temperature not specified) corresponds to 0.078 mole %.

Barium and Strontium Chlorides.—The solubility of barium chloride is too low to be determined accurately by the synthetic method. Analysis of solutions saturated by contact with excess solid for a week at 30 and at 45° gave, respectively, 0.0077 and 0.0100 mole % of solute. The figure given by Scholl, Hutchison and Chandlee[5] (p. 3084) for the solubility at 25° is equivalent to 0.0059 mole %.

Preliminary experiments with strontium chloride immediately revealed that its solubility in acetic acid rapidly diminishes with increasing temperature. An attempt was made to determine the solubility by noting the temperature at which the last of the solid phase just disappeared, on *cooling* the solution; the crystals dissolved too slowly, however, for concordant results to be obtained by this method. Accordingly, a saturated solution was prepared at about 15°, and transferred to a thermostat at the desired temperature. An abundant crop of crystals was formed, and equilibrium was attained after agitation of the mixture for twelve hours. That portion of the freezing point curve in which acetic acid was the solid phase, however, was obtained by the determination of equilibrium temperature in the usual manner.

---

(6) Eichelberger, THIS JOURNAL, **56**, 799 (1934).

The data are tabulated below, and plotted in Fig. 2.

STRONTIUM CHLORIDE–ACETIC ACID

S	*T*	*S*	*T*
(a) Solid phase $HC_2H_3O_2$		(b) Solid phase $SrCl_2$	
0	16.60	1.67	98.9
0.55	16.32	2.22	83.0
1.09	16.05	3.28	60.0
1.81	15.68	4.04	45.0
3.07	15.05	5.12	30.0
3.93	14.50	6.11	19.0
5.11	13.65		

Analysis of solid phase (b) showed it to be unsolvated. It will be noted that the solubility of the salt at 20° is almost four times as great as at 100°; up to the present, this is the only case of retrograde solubility to have been observed in an acetic acid system.[7]

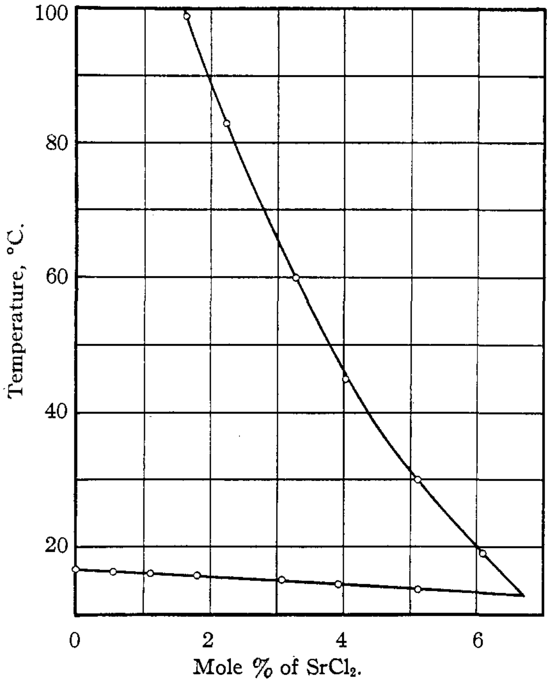

Fig. 2.—System $SrCl_2$–$HC_2H_3O_2$.

Mercuric Halides.—Unlike the alkali chlorides, the mercuric halides were found to dissolve rather rapidly in acetic acid, so that saturation equilibria were readily attained in these systems. It is noteworthy that when a solution of mercuric iodide, saturated at 100°, was suddenly chilled to about 60°, the crystals deposited consisted of the metastable yellow variety of the salt; when the mixture was stirred, this gradually changed to the stable scarlet form. The intense color of the latter greatly facilitated the accurate determination of equilibrium temperatures.

The data are tabulated below, *S* and *T* having

I. Mercuric iodide

S	*T*
Solid phase HgI_2	
0.011	31
.021	47
.030	56
.045	67
.065	76
.097	90
.134	100
.192	110

II. Mercuric bromide

(a) Solid phase $HC_2H_3O_2$	
0.194	16.50
(b) Solid phase $HgBr_2$	
0.261	25
.287	32
.350	41
.413	51
.477	58
.650	71
.707	75
.860	86
.998	92
1.13	97
1.29	103
1.50	110

III. Mercuric chloride

S	*T*
(a) Solid phase $HC_2H_3O_2$	
0	16.60
0.270	16.45
.477	16.35
(b) Solid phase $HgCl_2 \cdot 2HC_2H_3O_2$	
0.477	17
.680	24
.936	30
1.06	33
1.19	36
(c) Solid phase $HgCl_2$	
1.15	40
1.30	46
1.46	53
1.61	60
1.81	66
2.01	72
2.22	78
2.42	84
2.74	92
3.05	97
3.55	106
4.21	117

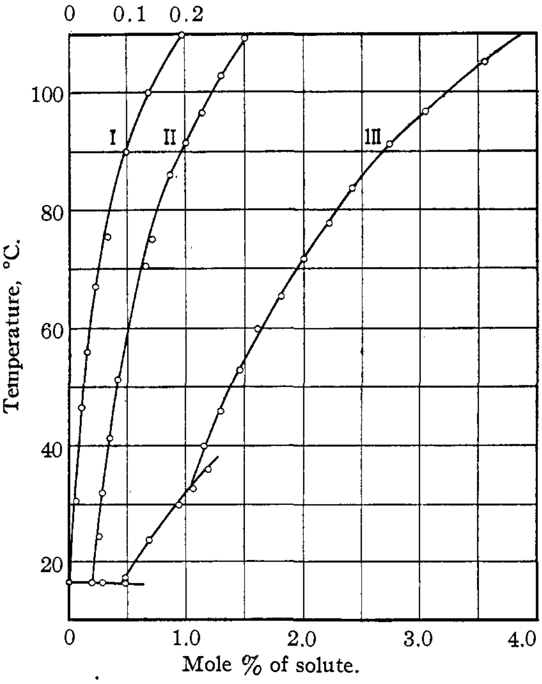

Fig. 3.—Solubility curves for HgI_2 (use upper concentration scale), $HgBr_2$ (II) and $HgCl_2$ (III) in anhydrous acetic acid.

---

[7] The solubility of strontium chloride in water shows no such trend. In aqueous solution, however, the solid phases in equilibrium with the saturated solution, at least up to 200°, are hydrates, not the unsolvated salt. See Menzies, THIS JOURNAL, 58, 934 (1936).

the same significance as before, and are presented graphically in Fig. 3.

In series I, the solid phase was shown to be unsolvated by the fact that a 1-g. sample did not impart any appreciable acidity to the water in which it was suspended. In II, analysis for bromine gave a result in accord with the composition of the unsolvated salt.

Benrath[1] (p. 237) reported that mercuric chloride may be recrystallized unchanged from glacial acetic acid. The course of the solubility curve here obtained, however, clearly indicated the existence of two distinct solid phases of the solute, with a transition point at 33°. The mean of two analyses[8] of the solid phase III (b) gave Cl, 17.68% (calcd. for $HgCl_2 \cdot 2HC_2H_3O_2$, 18.11%); while the mean of three analyses of solid phase III (c) gave Cl, 25.61% (calcd. for $HgCl_2$, 26.12%). Phase (b), then, is evidently a disolvate, which has not been reported previously. The solubility values presented in series III (b) and III (c) are, for the most part, considerably lower than those of Étard,[2] who represented the solubility curve throughout this region as a straight line, and overlooked the presence of a solvate.

Discussion

For purposes of comparison, the solubilities at 30° of the nine halides here studied have been brought together in Table I.

TABLE I

SOLUBILITY OF HALIDES IN ANHYDROUS ACETIC ACID AT 30°

Salt	Mole %	Moles per 1000 g. solvent	Salt	Mole %	Moles per 1000 g. solvent
$CuCl_2$	0.0070	0.0012	$SrCl_2$	5.12	0.899
NaCl	.075	.0125	$HgCl_2$	0.936	.157
NH_4Cl	.080	.0133	(disolvate)		
KCl	.175	.0292	$HgBr_2$	.284	.047
$BaCl_2$	.0077	.0013	HgI_2	.011	.0018

As might have been expected from their high melting points and small tendency toward solvation in this relatively slightly polar solvent, the first five of these salts are but slightly soluble in acetic acid. No explanation can be offered at present for the highly anomalous behavior of strontium chloride, whose differential heat of solution, at saturation, must be negative. The greater solubility of mercuric chloride, as compared to the alkali chlorides, is probably due to the lower melting point of the former and its greater tendency toward solvation. This salt is almost as soluble in acetic acid as in water, while mercuric bromide and iodide, especially the latter, are distinctly *more* soluble in acetic acid than in water.

Freezing point depression data, which were available over a wide concentration range in the case of strontium chloride, were used to calculate values of the freezing point divergence function, j, for these solutions. The value of j was found to remain practically constant, for molalities between 0.1 and 0.7, at 0.72. Such constancy in the value of j is in accord with previous observations for this solvent,[9] and its magnitude for this salt is almost identical with that found for the same concentration range in the case of strontium acetate.[10]

Summary

1. Solubility data over a wide range of temperature have been obtained for cupric, sodium, potassium, ammonium, strontium and mercuric chlorides, and mercuric bromide and iodide, and at 30 and 45° for barium chloride, in anhydrous acetic acid.

2. Strontium chloride has been found to exhibit retrograde solubility in this solvent.

3. The new solvate $HgCl_2 \cdot 2HC_2H_3O_2$ has been isolated and analyzed.

LAWRENCE, KANSAS RECEIVED JUNE 27, 1938

---

(8) In these and other analyses of mercuric halides, mercuric ion was removed by precipitation as mercuric oxide, before the precipitation of the halide ion.

(9) Davidson and Geer, THIS JOURNAL, **60**, 1211 (1938).

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