

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

Further Studies on Acetic Acid-Acetate Solutions

BY ARTHUR W. DAVIDSON AND WILBERT CHAPPELL

Introduction

The purpose of this investigation was to supplement the existing data on the solubility of acetates in anhydrous acetic acid¹ by the study of two additional acetates, namely, those of strontium and nickel, each of which presented certain points of interest.

It was to be expected,^{1b} in the case of strontium acetate, that the solid phase in equilibrium with the solutions at ordinary temperatures would be a solvate, and that the solubility of this compound would be intermediate between that of barium and that of calcium acetate. In the case of nickel acetate, previous statements as to solubility have been extremely conflicting. Spaeth² stated that this salt was easily soluble in acetic acid, but Adler³ reported its solubility as only 0.44 mole per cent. even at 140°, and Schall and Markgraf⁴ gave a figure of 0.1971 normal (0.60 mole per cent.) for the concentration of a solution which they apparently considered saturated at 65°.

A study was made also of the effect of ammonium acetate upon the solubility of nickel acetate, in the expectation that this ternary system would be analogous to the ammonium acetate-cupric acetate-acetic acid solutions previously described.^{1c}

Method

Preparation of Materials.—Acetic acid (m. p. 16.55–16.62°) and ammonium acetate were prepared as described in previous papers. Strontium acetate prepared from strontium carbonate was recrystallized from dilute acetic acid and the product kept at 165° for four days. Nickel acetate was prepared similarly. The recrystallized tetrahydrate was dehydrated at 90°, the product moistened with pure acetic acid and again heated at the same temperature to constant weight. The pale green anhydrous salt was analyzed for nickel by means of dimethylglyoxime, giving 33.11% as compared with the calculated 33.21%.

Strontium Acetate-Acetic Acid System.—Freezing points were determined by the synthetic method described in previous articles. The freezing points of the acetic acid are believed to be correct to $\pm 0.2^\circ$, other equilibrium temperatures to $\pm 0.5^\circ$.

Nickel Acetate-Acetic Acid System.—It soon became apparent why the recorded data for the solubility of nickel acetate had been so discordant. The salt dissolved fairly readily on gentle heating, the solutions showing a faint turbidity which did not disappear at higher temperatures. When the concentration of solute was less than 12 mole per cent., only acetic acid was obtained as solid phase on cooling. Solutions containing 12 to 13 mole per cent. of solute, however, deposited abundant quantities of a finely

(1) (a) Kendall and Adler, *THIS JOURNAL*, **43**, 1470 (1921); (b) Davidson and McAllister, *ibid.*, **52**, 507, 519 (1930); (c) Davidson and Griswold, *ibid.*, **53**, 1341 (1931).

(2) Spaeth, *Monatsh.*, **33**, 235 (1912).

(3) Adler, Thesis, Columbia University, 1920.

(4) Schall and Markgraf, *Trans. Am. Electrochem. Soc.*, **45**, 161 (1924).

divided greenish-white solid, which did not redissolve even on heating to the boiling point. The extreme slowness with which equilibrium was attained in these solutions (if, indeed, it was a true equilibrium) eliminated all possibility of employing the synthetic method for determining solubility. There remained as an alternative the analysis of solutions apparently saturated at a fixed temperature. Accordingly, a 13 to 14% solution was prepared at 100°; on slow cooling, a solid phase appeared. The mixture was then kept at 30° in a thermostat, with frequent stirring, for twelve hours, after which some of the solution was drawn off through a Gooch crucible provided with a thick mat of asbestos. The filtering device remained immersed in the thermostat throughout the filtration, precautions being taken to exclude moisture. The concentration of the filtrate was determined by analysis for nickel by the dimethylglyoxime method.

Ammonium Acetate-Nickel Acetate-Acetic Acid System.—The same difficulty was encountered here as in the case of the binary solutions just referred to, namely, that the solid phase, although it separated readily enough from supersaturated solutions, redissolved only extremely slowly. The same procedure was therefore employed as in the binary system. Solutions containing both ammonium and nickel acetates were prepared at elevated temperatures and allowed to come to equilibrium at 30°. After filtration, the nickel content of the solution was determined as before, while another portion of the filtrate was analyzed for ammonium by making it alkaline with sodium hydroxide solution and distilling the ammonia into standard hydrochloric acid. The concentration of acetic acid could then be found by difference.

Analysis of Solid Phases.—The desired solid having been obtained by the cooling of a solution of suitable concentration, the mother liquor was filtered off by suction, and the crystals rapidly dried between porous tiles. In the case of strontium acetate, the product was analyzed for acetic acid by titration with sodium hydroxide solution. In the product containing nickel acetate, nickel was determined by means of dimethylglyoxime, and in the ternary system the solid was analyzed for both nickel and ammonium, as in the case of the corresponding solutions.

Results

I. System $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2\text{-HC}_2\text{H}_3\text{O}_2$.—Concentrations in mole per cent. of solute, and the corresponding equilibrium temperatures, T , are tabulated.

		(a) SOLID PHASE $\text{HC}_2\text{H}_3\text{O}_2$							
$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$, %		0.0	0.42	1.08	1.60	2.08	2.91		
T		16.60	16.35	16.05	15.80	15.50	15.20		
$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$, %		4.31	4.82	5.73	6.06	6.52	7.15		
T		14.50	14.25	13.69	13.57	13.42	13.02		
		(b) SOLID PHASE $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2\text{HC}_2\text{H}_3\text{O}_2$							
$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$, %		4.76	4.85	4.98	5.20	5.39	5.53	5.89	6.28
T		17.0	29.7	41.5	50.5	55.5	57.3	66.5	73.8
$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$, %		6.52	7.12	7.42	7.89	8.57	8.93	9.52	9.95
T		77.5	86.0	89.3	94.6	101.1	104.3	108.8	111.5
		(c) SOLID PHASE $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$ (?)							
$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$, %		10.45	10.76						
T		118.5	121.8						

The freezing point curve for this system is shown in Fig. 1. Three analyses of the solid phase (b) gave a mean value of 50.08 mole per cent.

$\text{HC}_2\text{H}_3\text{O}_2$, corresponding to the compound $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$, which has not previously been reported. In the neighborhood of 113° this compound undergoes transition to another substance (c) which could not be obtained in sufficient quantity for analysis, but which appears to be unsolvated $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$.

II. System $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 - \text{HC}_2\text{H}_3\text{O}_2$.—These solutions were green at ordinary temperatures, changing to olive-green at 115 to 120° ; the most concentrated solutions were very viscous. Freezing point depression data are tabulated below.

Four solubility determinations at 30° gave values of 11.87, 13.15, 12.06 and 12.39 mole per cent., mean 12.37 mole per cent. The wide divergence among these values seems to indicate that we had here no true equilibrium between solution and crystalline solid, but that colloidal phenomena were involved. This conclusion is

supported by the high viscosity of these solutions, by the marked Tyndall effect exhibited by them, and by the nature of the solid phase. This was

$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$, %	0.0	0.32	0.61	1.00	1.73	2.47	3.22	
T	16.55	16.45	16.40	16.30	16.15	16.00	15.85	
$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$, %	4.47	5.68	7.32	8.90	10.57	12.19	13.67	14.89
T	15.60	15.35	15.10	14.90	14.55	14.15	13.80	13.55

a very finely divided greenish-white substance, which had very little tendency to redissolve in acetic acid. It showed no detectable crystalline structure upon microscopic examination, and analyses of three samples gave results varying from 54 to 66 mole per cent. of $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$. This range is far in excess of any possible experimental error, and indicates that the solid is not a definite crystalline compound, but a solvated product of variable composition.

III. System $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 - \text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 - \text{HC}_2\text{H}_3\text{O}_2$.—These solutions were green with a slight olive tinge at ordinary temperatures; at the boiling point the color was distinctly yellow-green.

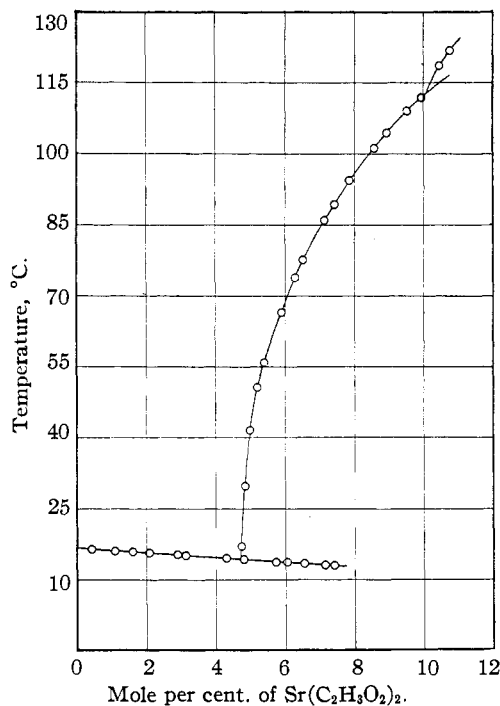


Fig. 1.—System $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 - \text{HC}_2\text{H}_3\text{O}_2$.

At low concentrations of ammonium acetate the saturated solutions were viscous and of high nickel acetate content; in general, the solubility of the nickel compound decreased with increasing concentration of ammonium salt, but no consistent quantitative data were obtainable, nor was the solid phase even approximately constant in composition, although it always contained all three components. However, when the concentration of ammonium acetate exceeded 15 mole per cent., true equilibrium was apparently attained, concordant solubility values were found, and the solid phase appeared to be a definite compound.

The compositions of saturated solutions at 30°, in mole per cent., are

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, %	15.13	17.44	19.67	22.79	24.79
$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$, %	0.214	0.111	0.071	0.039	0.028

The solid phase was a finely divided greenish-white substance which showed under the microscope a distinctly crystalline structure; accurate analysis was difficult because of its instability on exposure to the atmosphere. Nine analyses gave the following mean values in mole per cent.: $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, 25.49; $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$, 25.62; $\text{HC}_2\text{H}_3\text{O}_2$, 48.89. This composition was confirmed by the analysis of several wet residues; it corresponds to the compound $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$.

Discussion

Solubility Data.—The solubility of the monosolvate of strontium acetate in pure acetic acid at 25° was found to be 0.842 mole per 1000 g. of solvent, or 4.81 mole per cent. Comparison of this figure with the previously determined value^{1b} of 0.068% for the corresponding calcium compound, and 6.40% (by extrapolation) for disolvated barium acetate,⁵ shows that the solubility of these bases increases in the order of increasing atomic weight of the metal, just as in the case of the corresponding hydroxides in aqueous solution.

In the case of nickel acetate we can scarcely avoid the conclusion that the binary solutions are, at least in part, colloidal in nature. The concentration of an apparently saturated solution might then be expected to vary with particle size, conditions of stirring, temperature at which solution occurs, and other factors. Although this difficulty has not arisen in any of the previous work on acetic acid solutions in this Laboratory, phenomena of the same nature were apparently encountered by Seward and Hamblet⁶ in attempting to determine the solubility of sodium iodate in this solvent, while McBain and Kistler⁷ concluded that "colloidal constituents are of very common occurrence in non-aqueous solutions of electro-

(5) The solubility of a monosolvate of barium acetate at this temperature would undoubtedly be even greater than that of the disolvate. See Kendall, Davidson and Adler, *THIS JOURNAL*, **43**, 1489 (1921).

(6) (a) Seward and Hamblet, *ibid.*, **54**, 554 (1932). See also (b) Hill and Ricci, *ibid.*, **53**, 4305 (1931).

(7) McBain and Kistler, *J. Phys. Chem.*, **35**, 130 (1931).

lytes that are usually regarded as quite simple." This case should perhaps be regarded as parallel to the behavior of nickelous hydroxide in water. The latter compound, although known to have a crystalline structure, may, of course, be precipitated in an apparently amorphous form of variable composition (hydrous nickel oxide), and colloidal solutions of this substance are readily obtained.

Ternary solutions containing moderate concentrations of ammonium acetate show anomalies similar to those of the binary system. While the tendency toward colloidal behavior is apparently somewhat reduced by the presence of the third component,^{6b} it nevertheless persists to so high a concentration of the latter as to prevent the observation of any similarity between this case and the corresponding copper system, except that at very high concentrations of ammonium acetate a solvated double salt is formed whose solubility decreases with further increase in ammonium acetate concentration. The color of the ternary nickel solutions, on heating, undergoes a pronounced reversible change toward the yellow; but since the same change occurs in similar solutions containing potassium acetate instead of ammonium, it cannot be attributed, as in the case of cupric acetate,^{1c} to the formation of a complex cation containing ammonia.

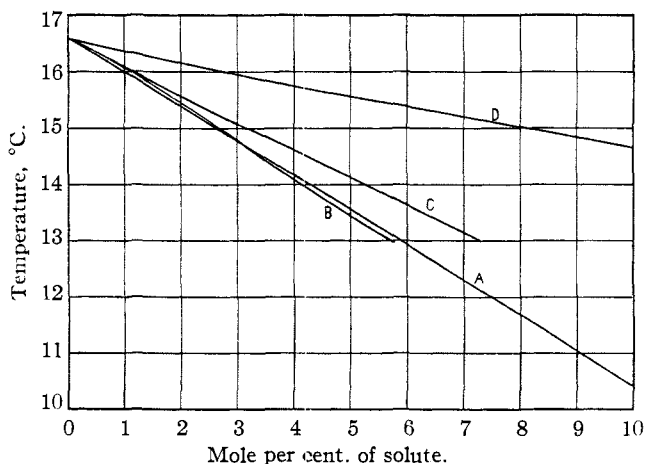


Fig. 2.—Freezing point depression curves, acetic acid as solvent: A, ideal solute; B, sodium acetate; C, strontium acetate; D, nickel acetate.

Freezing Point Depression Data.—The freezing point depression curves for the two acetates which have been studied in this work are shown in Fig. 2; for purposes of comparison we have included also the curve for sodium acetate^{1a,3} and the ideal curve for a perfect *undissociated* solute. It will be noted that, in spite of the fact that all these acetates

(8) Webb, *THIS JOURNAL*, **48**, 2263 (1926).

are known to be ionized, and might therefore be expected to show freezing point depressions greater than the ideal values, the sodium acetate curve approaches the ideal rather closely, while the other two lie far *above* it. Now, although it is obviously impossible to determine quantitatively the molecular state of an electrolyte from freezing point data, yet valid qualitative conclusions as to the molecular complexity or type of ionization of solutes have been reached, in certain cases, by means of a simple interpretation of such data, not only for aqueous solutions, but also for such solvents as formic⁹ and sulfuric¹⁰ acids. In the case of the acetic acid solutions here considered, however, it is evident that such an interpretation might well be entirely misleading. The reason for the difficulty lies, of course, in the very low dielectric constant of acetic acid, in consequence of which interionic forces are far greater than in the other solvents mentioned, and may even become the predominant factor causing deviation from the behavior of an ideal ionized solute throughout the entire concentration range in which experimental data are obtainable. Sharply conflicting opinions as to the molecular state of simple electrolytes in acetic acid have resulted from varying interpretations of the facts just mentioned. Sodium acetate, for instance, has been regarded at one extreme as being associated to some extent into polymeric molecules,¹¹ at the other, as being practically completely dissociated into ions.^{8,12}

Thermodynamic treatment of freezing point data, which does not demand any particular theory as to the molecular state of the solute, yields values of the mean activity coefficient of sodium acetate varying from 0.37 at $m = 0.001$ to 0.010 at $m = 1$. In the case of strontium acetate the activity coefficients cannot be determined satisfactorily, both because of the lack of data at high dilutions and because of uncertainty as to the type of dissociation of this electrolyte, but it is evident from Fig. 2 that the values must be even smaller than those for sodium acetate.

Our knowledge of acetic acid solutions is as yet scarcely adequate to permit a decision as to whether the low values of the freezing point depressions, observed even in dilute solutions of these typical electrolytes, are due to polymerization or to incomplete dissociation, or merely to the very large interionic forces prevailing in this solvent.¹³ In the case of nickel acetate, however, the extremely small slope of the freezing point

(9) Kendall, Adler and Davidson, *THIS JOURNAL*, **43**, 1846 (1921).

(10) Hammitt and Deyrup, *ibid.*, **54**, 2724 (1932).

(11) Walden, "Molekulargrößen von Elektrolyten in nichtwässrigen Lösungsmitteln," Theodor Steinkopff, Dresden, Germany, 1923, pp. 132-135.

(12) For an intermediate viewpoint, see Hall and Werner, *THIS JOURNAL*, **50**, 2367 (1928).

(13) It is true that several authors [Refs. 6a, 8; also Conant and Werner, *THIS JOURNAL*, **52**, 4436 (1930); Hutchison and Chandler, *ibid.*, **53**, 2887 (1931); and La Mer and Eichelberger, *ibid.*, **54**, 2763 (1932); have been fairly successful in calculating various properties of electrolytes in acetic acid on the basis of the Debye-Hückel theory and its modifications. Various arbitrary values of the parameter " a " are employed, however, in these calculations, as well as other hypotheses on which the several writers are not always in accord, so that experimental results may scarcely be said to have been accounted for on an entirely theoretical basis.

depression curve, as compared to that of the corresponding strontium compound, is in accord with the hypothesis advanced above that the solute is at least partially in the form of aggregates of considerably larger than molecular dimensions.

Summary

1. The solubility of strontium acetate in pure acetic acid has been determined over a wide range of temperatures, and is found to be intermediate between those of the corresponding barium and calcium salts.

2. The solubility of nickel acetate in acetic acid at 30°, as well as the composition of the solid phase in equilibrium with the solution, is found to be variable. This anomalous behavior is attributed to the presence of colloidal constituents.

3. In the presence of high concentrations of ammonium acetate, the solubility of nickel acetate is found to decrease with increasing concentration of ammonium salt.

4. Two new compounds, $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$ and $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$, have been isolated and analyzed.

5. The freezing point depression curves of several acetates in acetic acid have been compared with the curve for an ideal solute, and their deviations therefrom have been discussed.

LAWRENCE, KANSAS

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Properties of Electrolytic Solutions. VI. Conductance of Sodium Triphenylstannide, Sodium Triphenylgermanide and Sodium Triphenylmethide in Liquid Ammonia¹

BY CHARLES A. KRAUS AND W. HARLOW KAHLER²

I. Introduction

In the preceding paper of this series, values were given for the conductance of various salts in which nitrogen functioned as central element of the negative ion. The constitution of such ions may be modified by means of two substituent groups attached to the nitrogen atom. It seemed of interest to study corresponding ions of the elements of the fourth group, which form anions of the type R_3A^- , where R is an organic group or hydrogen. The salts of these ions are readily soluble in liquid ammonia and are appreciably soluble in ether and other similar solvents. Excepting the derivatives of tin and lead, the salts are stable in the pure state. Since

(1) This and the preceding paper of this series formed the subject matter of the Edgar F. Smith Birthday Lecture delivered by the senior author at the University of Pennsylvania, May 23, 1930.

(2) Metcalf Fellow in Chemistry in Brown University.