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Cobalt and Nickel Acetates in Anhydrous Acetic Acid

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Both cobalt and nickel acetates form hemisolvates with acetic acid. Both of these compounds exhibit retrograde solubility in anhydrous acetic acid between 16 and 65°, solubility equilibrium being attained very slowly. From ternary mixtures of cobalt acetate, ammonium acetate, and acetic acid at 30°, the solvated double salt $NH_4C_2H_3O_2 \cdot 2Co(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ has been isolated. The course of freezing point depression curves, as well as the composition of the solvates, suggests that these acetates exist mainly as dimeric species in their acetic acid solutions.

Introduction

Fantastically conflicting statements concerning the solubilities of the acetates of cobalt and nickel in anhydrous acetic acid are to be found in the literature. Thus, whereas Späth[2] reported both of these compounds to be readily soluble in acetic acid, other German workers[3] gave figures of 0.0381 *N* (0.11 mole %) and 0.107 *N* (0.30 mole %) for the concentrations at 25° of saturated solutions of the cobalt and the nickel salt, respectively. In later studies in this Laboratory, apparently saturated solutions containing at 30° as much as 2.3 mole % of cobalt acetate[4] or 13 mole % of nickel acetate[5] were obtained. It is significant that in most of these cases, as well as in a very recent study of cobaltous acetate in acetic acid,[6] the authors reported their inability to obtain completely clear solutions, mentioning a slight insoluble residue, apparently quite unresponsive to changes in temperature, which was variously characterized as a "silky turbidity" or a "powdery sludge." The present study was undertaken in the hope that, with the identification of these residues, an explanation might be found for the apparently anomalous solubility behavior.

In view of the previously observed formation of a ternary addition compound in the systems ammonium acetate–cupric or zinc acetate–acetic acid,[7] it seemed of interest also to determine the effect of ammonium acetate on the solubility of cobalt acetate.

Experimental Methods

Preparation of Materials.—Anhydrous acetic acid (m.p. 16.55–16.60°) was prepared by adding the calculated amount of acetic anhydride to reagent grade (99.8%) glacial acetic acid, refluxing for 20 hr., and distilling. Anhydrous cobalt(II) acetate was prepared by heating reagent grade tetrahydrate for 2 hr. at 156°. Anhydrous nickel acetate was prepared by heating reagent grade tetrahydrate for 8 hr. at 165°. A saturated ammonium acetate solution was prepared by passing pure dry ammonia gas over anhydrous acetic acid in a desiccator until crystallization occurred.

Equilibrium Data.—All solubility data were determined by the analytical method. Ground-glass stoppered tubes containing solution and excess solid were agitated from 1 to 4 days at a fixed temperature, the mixture was filtered through a sintered glass filter, and the filtrate was analyzed as described below. The solid phase was dried between porous tiles in a desiccator over a solution of the same composition as that from which it had separated, and analyzed by the same method.

Cobalt was determined by precipitation as the 1-nitroso-2-naphthol complex, followed by filtration, ashing, and conversion to the anhydrous sulfate. Nickel was determined by precipitation with dimethylglyoxime. For the determination of ammonium, the solution was made alkaline with sodium hydroxide solution, the liberated ammonia was distilled into a measured volume of standard hydrochloric acid, and the excess acid was titrated with sodium hydroxide solution.

Freezing point depression data for cobalt acetate solution were obtained by means of a Beckmann differential thermometer.

Results

Cobalt Acetate–Acetic Acid.—Dilute solutions (<2 mole % of cobalt acetate), which could readily be obtained at room temperature, deposited only acetic acid on being cooled below 16°. Freezing points of these solutions were as given in Table I.

TABLE I

Mole % $Co(C_2H_3O_2)_2$	0	0.308	0.462	0.87	1.51	2.46
Freezing pt., °C.	16.60	16.45	16.38	16.29	16.13	16.00

When a mixture containing 10–12 mole % of cobalt acetate was heated to 60°, the dark blue salt dissolved fairly readily, giving a viscous deep blue solution which showed only a slight trace of silky turbidity and gave no immediate deposit on being cooled even to 0°. However, when such a solution was allowed to stand for 3–4 days at room temperature, or for a few hours at 60°, a voluminous deposit of a pink solid was formed. Samples of this substance separated by filtration from five different solutions and dried as described yielded on analysis 27.4, 26.3, 29.7, 29.0, and 31.0% (mean 28.50%) Co; calculated for $2Co(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, 28.47%. In view of the considerable spread of the individual values, this close agreement is clearly fortuitous; nevertheless, it seems fairly certain that the pink compound is indeed a hemisolvate.

Accurate determination of the solubility of this compound was difficult because of the extreme slowness with which saturation equilibrium was attained. By equilibration of mixtures of high initial concentration

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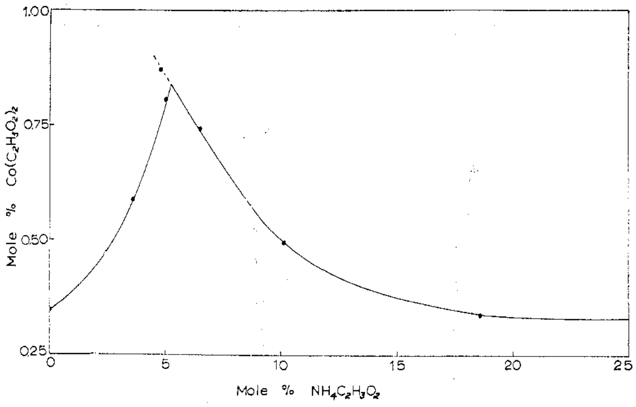

Fig. 1.—Effect of $NH_4C_2H_3O_2$ on the solubility of $Co(C_2H_3O_2)$ in $HC_2H_3O_2$ at 30°.

for periods of 3 to 4 days at four different temperatures, the solubility data shown in Table II were obtained.

TABLE II

Temperature, °C.	30	60	80	98
Mole % $Co(C_2H_3O_2)_2$	0.348	0.218	0.248	0.281

Each piece of the data represents a mean value of at least three determinations, none of which deviated from the mean by more than 4%.

Nickel Acetate–Acetic Acid.—When a mixture containing 15 to 20 mole % of nickel acetate was heated to 98°, the pale green salt dissolved slowly, giving a viscous dark green solution which contained a trace of a greenish white substance which appeared to be quite unresponsive to changes in temperature. When such a solution was maintained at 98° for 6–8 hr., however, an abundant greenish white deposit settled out. Samples of this solid separated by filtration from five different solutions and dried as in the case of the cobalt salt yielded on analysis 28.4, 28.0, 28.6, 28.6, and 28.3% (mean 28.38%) Ni; calculated for $2Ni(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, 28.39%. These results leave no room for doubt that the stable solid phase is a hemisolvate.

Since it was evident from the work on the cobalt system that saturation equilibrium was attained more rapidly when approached from the higher temperature side, the following solubility data were obtained by formation of the hemisolvate at 98° and subsequent equilibration for 24 hr. or more at each of three temperatures, as shown in Table III.

TABLE III

Temperature, °C.	23	60	98
Mole % $Ni(C_2H_3O_2)_2$	0.557	0.403	0.332

Each piece of the data represents the mean of two or more values, and may well be in error by as much as 10% due to the slowness with which the system came to equilibrium, although equilibration for longer periods of time seemed to have no significant effect on the results. It is again evident that the solubility slowly decreases with increasing temperature.

Ammonium Acetate–Cobalt Acetate–Acetic Acid.—When solid cobalt acetate, in excess, was allowed to equilibrate at 30° with solutions containing various concentrations of ammonium acetate, the data plotted in Fig. 1 were obtained. The solubility of cobalt acetate at 30° was found to increase with increasing concentration of ammonium acetate to a maximum of 0.84 mole % in a solution containing 5.2 mole % of ammonium acetate, the stable solid phase in this region being the pink hemisolvate. Beyond this point a distinctly different solid phase, maroon in color, separated from the purple solution, and the concentration of cobalt acetate in the saturated solution diminished with increasing ammonium acetate concentration, falling to a value of 0.33 mole % (about the same as in acetic acid alone) in a solution containing 18.7 mole % of ammonium acetate.

Four samples of the maroon solid, dried between tiles over the equilibrated solution, gave on analysis 22.9, 23.8, 24.0, and 23.6% (mean 23.58%) Co, and 4.06, 3.61, 3.45, and 3.71% (mean 3.71%) NH_3; calculated for $NH_4C_2H_3O_2 \cdot 2Co(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, 24.00% Co, 3.47% NH_3. Thus there can be little doubt that the maroon solid is a solvated ammonium cobalt acetate, the formula of which might alternatively be written $NH_4Co_2(C_2H_3O_2)_5 \cdot HC_2H_3O_2$.

Discussion

The results of this work clearly indiate that the high solubility values previously reported[4,5] for cobalt and nickel acetates in acetic acid are to be accounted for by (1) the readiness with which the unsolvated salts form viscous concentrated solutions, possibly in part colloidal, certainly highly supersaturated with respect to the hemisolvates and (2) the extraordinarily slow rate at which equilibrium is attained between the hemisolvates and their saturated solutions. It is of interest that similar behavior has been observed for the hemisolvate of plumbous acetate,[8,9] whose true solubility in acetic acid, however, is very much greater than that of the corresponding cobalt or nickel compound.

The behavior of cobalt acetate in ammonium acetate solutions is entirely analogous to that which was previously observed in the case of cupric and zinc acetates, and which, because of its similarity to the behavior of the corresponding hydroxides in aqueous alkali solutions, was characterized in an early paper from this Laboratory[7b] as amphoteric. In this connection it seems appropriate to point out that cobalt hydroxide, although not ordinarily regarded as amphoteric, is nevertheless appreciably soluble in concentrated solutions of sodium hydroxide.[10,11]

In the earlier study of nickel acetate referred to previously,[5] the freezing point depression curve for nickel acetate was found to lie far above that calculated for an ideal undissociated solute; for a 1 mole % solu-

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tion (0.168 molal) the actual depression was found to be only 0.25°, slightly less than half the calculated value of 0.60°. In the present work, the curve for cobalt acetate was found to follow a course only slightly lower than that previously observed for the nickel salt; at 1 mole % the depression, by interpolation, is 0.35°. Although it would be unwarranted to draw any quantitative conclusion as to the molecular state of the solute from such freezing point data, they suggest the presence of dimeric species of the salts, even in these dilute solutions, thus confirming the postulate of dimerism of cobalt acetate recently proposed by Benson and co-workers[12] to account for the kinetics of the Co(II)–Pb(IV) oxidation–reduction reaction in acetic acid. In this connection it appears significant also that the empirical formula of each of the solid compounds isolated in this work includes two molecules of nickel or cobalt acetate.

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Alkoxychlorosilanes and Alkoxysilanes Containing Silane Hydrogen[1]

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Syntheses and new compounds are reported for silanes $SiHCl_{3-x}(OR)_x$ and $SiH_{4-x}(OR)_x$ with $x = 1$–3, $R = CH_3, C_2H_5$. New silanes $CH_3SiHClOR$ and CH_3SiH_2OR are reported. Ligand exchanges of such silanes are described. Properties of some alkoxides of carbon and silicon are compared on the basis of new data.

Trialkoxysilanes $SiH(OR)_3$ were originally prepared from trichlorosilane and alcohols.[2-4] Recently rather low yields have been found.[5] Alkoxychlorosilanes $SiHCl_{3-x}(OR)_x$, obviously the intermediates in any direct formation of trialkoxysilanes from trichlorosilane, were obtained only indirectly.[6] Dialkoxysilanes $SiH_2(OR)_2$ and alkoxysilanes SiH_3OR were unknown at the beginning of this study. New syntheses and reactions of the simplest members of these little known classes of silanes are now reported.

Dialkyl sulfites $SO(OR)_2$[7] react with trichlorosilane in two steps, each followed by an elimination of SO_2 at higher temperature.

$$SiHCl_3 + 2SO(OR)_2 \longrightarrow 2RCl + SiHCl[O(SO)OR]_2 \longrightarrow SiHCl(OR)_2 + 2SO_2 \quad (1)$$

Alkyl nitrites RONO, known to alkoxylate $SiCl_4$,[8] react quantitatively with trichlorosilane

$$SiHCl_3 + xRONO \longrightarrow SiHCl_{3-x}(OR)_x + xNOCl \qquad x = 1\text{–}3 \quad (2)$$

Lithium borohydride reacts with alkoxychlorosilanes to give alkoxysilanes

$$SiHCl_{3-x}(OR)_x + (3 - x)LiBH_4 \longrightarrow (3 - x)LiCl + (3 - x)/2B_2H_6 + SiH_{4-x}(OR)_x \qquad x = 1, 2 \quad (3)$$

The syntheses (2 and 3) make possible the preparation of pure samples of several new silanes. Previous difficulties are explained in terms of the properties and reactions of silanes.

Results

Properties of Silanes and Methanes.—Tables I and II contain physical data obtained in this study. For the compounds I,[9] II, III, IX, X,[10] XI, XIII, XIV,[10] XV,[11] XVI, XVIII,[12] and XIX, improved and more complete data are presented. Compounds VI,[6] VIII,[13] and XII[14] are now characterized; IV, V, VII, and XVII are new. Limited data were obtained for other new compounds which disproportionate slowly at ambient temperature: $CH_3SiHClOCH_3$ (XX) with P_0 88 mm., $SiH_3OC_2H_5$ (XXI) with b.p. near 0°, $CH_3SiH_2OC_2H_5$ (XXII) with P_0 near 186 mm. The vapor pressure equations are valid up to 500 mm.

Reactions of Silanes.—Silane hydrogen is surprisingly stable toward nitrosyl chloride at room temperature. On the other hand, trichlorosilane (XXIII) reacts with methyl nitrite (MN) or ethyl nitrite (EN) even at −127°. Temperatures within the liquid range of $NOCl$[15] are, therefore, practical for the method repre-

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