[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Solubilities of Salts in Trifluoroacetic Acid

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Approximate solubilities of many salts in trifluoroacetic acid have been measured and the solubilities of the trifluoroacetates of several metals have been determined with care. As a class salts are very soluble, but the anions of many react with the solvent. The solvent is acidic and most of the trifluoroacetates behave as soluble bases. Zinc trifluoroacetate is amphoteric.

Trifluoroacetic acid is a remarkably good solvent. At 20° it is completely miscible with ether, acetone, ethanol, benzene, carbon tetrachloride, *n*-heptane, water[2] and with perfluoro-*n*-hexane. It dissolves bromine and iodine, apparently without solvolysis or complexing.[3] The rather low conductivities of its solutions[4] indicate that it is not a very good ionizing solvent, a fact in agreement with the dielectric constant of only 8.22 at 30°.[5] Since little information is available about its behavior as a solvent for salts, the study now to be described was made.

Experimental

Approximate Solubilities of Various Salts.—In this general survey trifluoroacetic acid as supplied by the manufacturer (Minnesota Mining and Manufacturing Co.) was used without further purification. Salts of reagent or C.P. quality were employed, and, with the exception of those which decomposed upon heating, they were dried at 110°. Approximately one or two grams of salt was placed in a small test-tube; then about 5 ml. of trifluoroacetic acid was added. A few drops of trifluoroacetic acid anhydride was added to remove any trace of water which might have been present. After hermetically sealing the end, the tube was shaken for a week at room temperature. The solid was then allowed to settle, the tube was opened, and the supernatant liquid was decanted into another small test-tube. If turbidity was observed in the supernatant liquid, the solution was centrifuged before decantation. The clear solution was then evaporated to dryness, and the residue was dried under vacuum at 100°. From the weight of the solution and of the resulting solid, the "solubility" of the salt was calculated. Table I presents the results of these studies.

The solubilities obtained in this manner were only approximate, and in many cases because of solvolysis they were not the solubilities of the solutes indicated in the table. No effort was made to establish equilibrium at a definite temperature and the solid residue was in many cases largely the trifluoroacetate of the metal. The colors of the solutions were in general very much like those of aqueous solutions of the same solutes.

Perchloric acid (70%) was found to be very soluble in trifluoroacetic acid containing enough trifluoroacetic anhydride to combine with water in the acid. The resulting solution was used to precipitate the perchlorates of metals from trifluoroacetic acid solutions. A concentrated solution of orthophosphoric acid was practically immiscible with trifluoroacetic acid. When 95% sulfuric acid was mixed with trifluoroacetic acid two liquid phases were present at first. After a few hours only one liquid phase remained. This solution was used to precipitate sulfates of barium, calcium and other metals from trifluoroacetic acid solutions.

Action of the Solvent, Trifluoroacetic Acid upon Salts.—As the "solubilities" of the above salts were being studied, it became obvious that the solvent reacted with many of the solutes. The nature of some of these reactions was determined by one or more of the following techniques: (1) visual observation of the evolution of a gas or the formation of a colored substance, (2) chemical analysis of the solid formed by crystallization as the solvent evaporated from the solution, (3) change in mass of the solute resulting from repeated mixing with trifluoroacetic acid followed by evaporation of the solvent and subsequent drying of the residue at 100°. While some salts were converted more readily than others to the trifluoroacetates, it was in general the case that more than one treatment of the salt by the solvent, followed by evaporation to dryness, was required. For example, a 0.063-g. sample of sodium chloride was mixed with about 3 g. of the acid; then the solvent was evaporated. The weight of solid remaining was 0.1270 g. Repetition of the operation left 0.1430 g. and finally 0.1480 g. For complete conversion to the sodium trifluoroacetate, the weight should have been 0.1464 g. No chloride remained in the residue and the chemical analysis for sodium by zinc uranylacetate method corresponded to CF_3COONa.

The length of time of standing of a solution before evaporation was also a factor involved in the conversion of a salt to the trifluoroacetate. For example, a solution of sodium nitrate was allowed to stand in a sealed tube for a week with the result that a brown gas (NO_2) was formed. When the solution was evaporated to dryness the remaining solid failed to give a "ring test" for nitrate ion. When a freshly prepared solution of sodium nitrate was evaporated, the solid contained nitrate ion. An aged solution of sodium bromide was brown (due to bromine, probably formed by oxidation by air) and the residue gave no precipitate with

TABLE I

APPROXIMATE SOLUBILITIES OF SALTS IN TRIFLUOROACETIC ACID AT ABOUT 25°

Amount dissolved greater than 10 g. anhydrous salt per 100 g. CF_3COOH

Acetates: Na, K, NH_4, Sr, Ba, Cd, Hg(II), Cu(II), Co(II), Ni, Pb(II)

Other salts: CsCl, NH_4NO_3, K_2SO_4, K_3PO_4

Amount dissolved from 1 to 10 g. anhydrous salt per 100 g. CF_3COOH

Fluorides: Na, K, Ba, Cu(II), Ag(I), Cd

Chlorides: Na, K, Mg, Ca, Fe(III)

Bromides and iodides: Na, K, Ca. Sulfates: Na, NH_4

Nitrates, nitrites, oxalates, chlorates, bromates, iodates, acid sulfates and dichromates of Na and K

Thiocyanates: Na, K, NH_4. Phosphates: Na, Ca, Co, Zn, HPO_4^{--} and $H_2PO_4^-$ salts of Na, K, Ca

Chromates: Na, K, Ca, Ba, Pb, Co, Zn

Others: $KMnO_4$, $K_4Fe(CN)_6$, CrO_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6](NO_3)_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_5H_2O](NO_3)_3$, *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$, *trans*-$[Co(NH_3)_4NO_2Cl]Cl$, $[Co(NH_3)_3(NO_3)_3]$

Amount dissolved from 0.1 to 1 g. per 100 g. CF_3COOH

Halogenides: $BeCl_2$, $SrCl_2$, $BaCl_2$, $CdCl_2$, $CoCl_2$, $CrCl_3$, $CdBr_2$, CdI_2, MgF_2, NiF_2

Others: $Ca(NO_3)_2$, $Ba(NO_3)_2$, $Cr_2(SO_4)_3$

Amount dissolved less than 0.1 g. per 100 g. CF_3COOH

Halogenides: CaF_2, PbF_2, MnF_2, FeF_3, AgCl, $ZnCl_2$, $AlCl_3$, $PbCl_2$, $HgCl_2$

Perchlorates: Na, K, Zn. Periodates: Na, K

Sulfates: Be, Mg, Ca, Ba, Zn, Ni, Co, Fe(II), Cu(II)

Other: $Ce_2(C_2O_4)_3\cdot 9H_2O$, $BaS_2O_6\cdot 2H_2O$

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(2) Booklet, "Trifluoroacetic Acid," Minnesota Mining and Manufacturing Co., 1949.

(3) R. E. Buckles and J. F. Mills, THIS JOURNAL, **75**, 552 (1953).

(4) J. H. Simons and K. E. Lorentzen, *ibid.*, **74**, 4746 (1952).

(5) W. Dannhauser and R. H. Cole, *ibid.*, **74**, 6105 (1952).

silver nitrate solutions. A fresh solution was colorless and the residue contained bromide ions.

By treatment with trifluoroacetic acid the following salts have been converted to trifluoroacetates: NaF, AgF, NaCl, KCl, CsCl, NaBr, KBr, $CaBr_2$, KI, CaI_2, $NaNO_3$, $RbNO_3$, $Na_2C_2O_4$, $NaClO_3$, $KClO_3$, $NaBrO_3$, $KBrO_3$, $NaNO_2$, Na_2SO_3, CH_3COONa, $(CH_3COO)_2Ni$. Other salts containing the same anions appeared to behave similarly, but quantitative studies were not made. Recognized volatile products were: HF from fluorides, HCl from chlorides, HBr and Br_2 (probably formed by air oxidation) from bromides, HI and I_2 from iodides, NO_2 from nitrates, NO_2 and N_2O_3 from sodium nitrite (N_2O_3 was recognized by the blue green color of the solution of sodium nitrite in trifluoroacetic acid), SO_2 from sodium sulfite, Br_2 from bromates, a greenish-yellow gas (probably ClO_2 and/or Cl_2) from chlorates, and acetic acid from acetates.

Some salts which reacted with the solvent were not completely converted to trifluoroacetates. Chromates, for example potassium chromate, gave orange-brown solutions apparently due to the formation either of a polychromate anion or a polychromic acid. (Upon long storage some of these solutions yielded small amounts of green chromium(III) compounds.) Potassium sulfate yielded a mixture of equal numbers of moles of potassium trifluoroacetate and potassium acid sulfate.

$$K_2SO_4 + CF_3COOH = KHSO_4 + CF_3COOK$$

Sodium sulfate reacted similarly. The salts $KHSO_4$ and $NaHSO_4$, $NaIO_3$ and KIO_3 were recovered unchanged after treatment with trifluoroacetic acid. In the cases of potassium permanganate, ammonium molybdate, potassium ferrocyanide, potassium thiocyanate and various phosphates the anions reacted with the solvent but products were not identified.

When in solution the complex cobalt(III) compounds listed in Table I were relatively stable; however, some of them changed slowly into cobalt(II) compounds. Those which changed were *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$, *trans*-$[Co(NH_3)_4NO_2Cl]Cl$ and $[Co(NH_3)_3(NO_2)_3]$. The solvent converted nitrates and chlorides of the other cobalt(III) complexes to the corresponding trifluoroacetates without decomposition of the complex radical.

Preparation of Trifluoroacetates of Metals.—Swarts[6] has described the preparation of several trifluoroacetates. In the present study, the metal trifluoroacetates were made by several methods. Sodium, potassium, calcium, strontium, barium, cadmium, silver, cobalt, nickel and copper trifluoroacetates were made by dissolving the corresponding carbonates in aqueous trifluoroacetic acid. After filtration, the solutions were evaporated to dryness care being taken to avoid decomposition of the salts by overheating. Finally, the solids were dried under vacuum at 100°. Magnesium and zinc trifluoroacetates were made by two methods: by dissolving the corresponding carbonates in aqueous trifluoroacetic acid (50%), and by dissolving the metal in the aqueous acid. In both cases, glassy substances which failed to crystallize were obtained. These glassy substances were treated with trifluoroacetic anhydride followed by evaporation. Magnesium and zinc trifluoroacetates were obtained as crystalline solids. Trifluoroacetates of lanthanum, cerium(III), praseodymium, neodymium and mercury(II) were made by dissolving the corresponding oxides or hydroxides in aqueous trifluoroacetic acid. By evaporation, crystalline trifluoroacetates were obtained. Thorium trifluoroacetate was made from the corresponding carbonate which had been freshly precipitated from thorium nitrate solution. By evaporation, a glassy material was obtained but after the addition of trifluoroacetic anhydride followed by evaporation, thorium trifluoroacetate was obtained as a crystalline powder. Uranyl trifluoroacetate was prepared in two ways. One was by treating uranium oxide, U_3O_8 with aqueous trifluoroacetic acid. After filtration, a yellow solution was obtained. By evaporating away the acid and water, uranyl trifluoroacetate was obtained in a glassy form. Addition of trifluoroacetic acid anhydride followed by evaporation of the liquid left a yellow powder. The other method was the direct conversion of uranyl acetate to the trifluoroacetate. Uranyl acetate was treated with anhydrous trifluoroacetic acid several times. Uranyl acetate dissolved in trifluoroacetic acid easily. By evaporation of the acid, a glassy substance was obtained. By treating with trifluoroacetic anhydride, this glassy substance was changed into a yellow powder. Uranyl trifluoroacetate was found to be very hygroscopic. Aluminum trifluoroacetate was prepared by dissolving freshly amalgamated aluminum in aqueous trifluoroacetic acid. The clear solution was then decanted and was evaporated to dryness, care being taken to avoid decomposition of the salt by overheating. Addition of trifluoroacetic acid anhydride was necessary to change a glassy substance into a crystalline powder.

Determination of the Solubilities of Trifluoroacetates.—Anhydrous trifluoroacetic acid was prepared by distilling a mixture of about 250 ml. of trifluoroacetic acid and 50 ml. of trifluoroacetic anhydride (high quality products obtained from the Minnesota Mining and Manufacturing Company) in an atmosphere of dry nitrogen. The anhydride distilled first and was collected as a separate fraction. The acid, boiling from 71 to 72°, was collected for use and was stored in a glass receiver under dry nitrogen. It was handled only in dry vessels and was transferred with precautions to exclude atmospheric water.

Saturated solutions were prepared in tubes shaped something like the letter h. An excess of the anhydrous salt was placed in the bottom of the long leg of the tube and was boiled in a 2- to 5-ml. quantity of trifluoroacetic anhydride until the latter had distilled away leaving a dry solid. Approximately 6 ml. of anhydrous trifluoroacetic acid was then added. The tube was sealed. A number of these tubes were fastened side by side and shaken mechanically for about a week, the temperature being at 29.8°. The tubes were allowed to stand at this temperature until the solutions were clear, and some of the saturated solution in each tube was then decanted into the short leg. The leg was promptly sealed causing it to become a closed tube of about 7-ml. capacity containing a few grams of saturated solution. To obtain the concentration, the tube was scratched with a file near its tip; it was then weighed; the tip was broken off and the solvent was evaporated leaving a solid residue. This was then dried at 100° and the tube was weighed again. From the various weights the solubility was calculated.

Determination of Solid Phase Composition.—After the solubility measurement had been made, the solubility tube was cut near the bottom of the longer leg and some of the solid phase was at once removed on a spatula. This slurry was placed on an 80-mesh stainless gauze filter and the liquid was quickly removed by centrifugation. The solid was weighed promptly in a small test-tube and then dried under vacuum at 100°. From the loss in weight, the composition of solid phase was calculated. In many cases, it may have been somewhat in error because of liquid adhering to the crystals.

TABLE II

SOLUBILITIES OF TRIFLUOROACETATES AT 29.8°

Solute, trifluoroacetate of	Solubility g. anhydrous salt/100 g. CF_3COOH	Solid phase apparent no. moles CF_3COOH/mole of salt
Na	13.10 ± 0.05	2.1
K	50.13 ± .31	1.0
Mg	0.570 ± .009	1.9
Ca	6.260 ± .07	3.8
Sr	23.19 ± .32	2.2
Ba	41.66 ± .66	3.5
Zn	0.87 ± .01	0.2
Cd	7.61 ± .12	0.1
Hg(II)	49.72 ± .20	0.4
Ag(I)	15.15 ± .08	0.1
Cu(II)	19.73 ± .08	0.1
Al	0.01	0.0
La	.142 ± .006	3.1
Ce(III)	.101 ± .004	..
Pr(III)	.084 ± .005	3.0
Nd	.059 ± .002	2.6
Th(IV)	.016 ± .002	0.4
UO_2^{++}	.035 ± .003	..
Co(II)	16.65 ± .17	1.7
Ni(II)	16.48 ± .24	1.7

(6) F. Swarts, *Bull. soc. chim. Belg.*, **48**, 176 (1939).

Tests were made with a few solutes which showed that a week of shaking allowed the solution to become saturated. Solubility measurements were least precise for nearly insoluble substances. This was due to the small size of the sample of solid remaining from the evaporation of the solution. A one-mg. sample in one ml. of solvent corresponded to a solubility of 0.07 g. per 100 g. of acid. Since weighings were made estimating to the nearest 0.1 mg., large errors were made in low solubilities.

In Table II both the apparent composition of the solid and its solubility are given. The quantity following the ± sign is the probable error calculated from the experimental data.

Effect of Sodium Trifluoroacetate upon the Solubilities of Other Trifluoroacetates.—A few tests were made to learn whether the presence of sodium trifluoroacetate had a marked effect upon the solubility of other metal trifluoroacetates. In each case, trifluoroacetic acid was saturated both with sodium trifluoroacetate and with the other trifluoroacetate. The amounts of the two metals in solution were determined by analysis of the residue remaining after evaporation of the solvent. Results are presented in Table III.

TABLE III

SIMULTANEOUS SOLUBILITIES OF TWO SOLUTES AT 29.8°

Solution saturated with CF_3COONa and	Concn. of CF_3COONa g./100 g. trifluoroacetic acid	Concn. of other salt, g./100 g. solvent
$(CF_3COO)_2Zn$	23.0	13.0
$(CF_3COO)_2Mg$	13.2	0.59
$(CF_3COO)_3Al$	13.0	Trace
$(CF_3COO)_3Nd$	13.1	Trace

Discussion

Trifluoroacetic acid acts as a highly acidic solvent. It reacts with the anions of many solutes to form volatile acids and the trifluoroacetates of many metals behave as bases in the sense that they are soluble in the solvent. It is of interest to compare their solubilities in the acid with the solubilities of the hydroxides of the same metals in water. In the larger families of groups 1, 2 and 3 of the periodic system one finds a close parallelism. The solubility of the base increases within a family with increasing atomic weight of the metal. The bases of group 1 elements are more soluble than those of their neighbors in group 2 and the latter are in turn more soluble than those of group 3. Trifluoroacetates of cobalt and nickel and of the sub-group elements of groups 1 and 2 are much more soluble in trifluoroacetic acid than are the hydroxides of the same elements in water. The greater solubility of the trifluoroacetates is in keeping with the fact that trifluoroacetic acid is a more highly acidic solvent than water.

Zinc trifluoroacetate is amphoteric. Its solubility in trifluoroacetic acid is increased by the addition of the soluble base, sodium trifluoroacetate. By contrast, the solubility of magnesium trifluoroacetate is changed very little by the addition of sodium trifluoroacetate. It is not amphoteric and its solubility is apparently not decreased due to the common ion effect. This may be due in part to the low degree of ionization of the solutes.[3]

Both perchloric and sulfuric acids behave as acids when in trifluoroacetic acid. When a solution of perchloric acid is added to a solution of a trifluoroacetate, neutralization occurs and a precipitate of the perchlorate of the metal appears. In many cases a solution of sulfuric acid forms a precipitate of a sulfate. Equations representing such reactions are

$$Zn(CF_3COO)_2 + 2HClO_4 = Zn(ClO_4)_2 + 2CF_3COOH$$
$$Co(CF_3COO)_2 + H_2SO_4 = CoSO_4 + 2CF_3COOH$$

Most of the trifluoroacetates used in this study were white solids and their solutions were colorless. Colors of the trifluoroacetates of certain metals and of their solutions in trifluoroacetic acid follow: Cu(II), blue green; Ni(II), green; Co(II), dark pink; Pr(III), pale green; Nd(III), pale pink. Cobalt(III) complex compounds had colors when dissolved in trifluoroacetic acid like those of aqueous solutions of the same substances.

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Partial Molal Volumes and Molar Refractions of the System Bromine Trifluoride–Bromine Pentafluoride

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The refractive indices and densities of the system bromine trifluoride–bromine pentafluoride have been measured at 25°. Equations have been derived which express refractive index and density as functions of composition. The partial molal volumes are smaller than the molar volumes of the pure compounds, but the volume contraction upon mixing is always less than one per cent. The Lorentz–Lorenz molar refraction of the trifluoride is 13.22 cc. and that of the pentafluoride is 15.41 cc. The maximum deviation of the molar refraction from that of an ideal solution is −0.06 cc.

Introduction.—The partial molal volumes and molar refractions of the system bromine trifluoride–bromine pentafluoride have been determined, and the variations in these properties have been used to indicate the extent of molecular interactions. On the basis of their chemical similarity and apparent freedom from solvation effects, bromine trifluoride and bromine pentafluoride would be expected to form relatively ideal binary solutions. This investigation reveals some aspects of their behavior and points out the small magnitude of any effects attributable to the ionic species which are present.

The symbols to be used are defined as

M = molecular weight
N = mole fraction
d = density
n = index of refraction
$\bar{V}$ = partial molal volume
R = molar refraction
ϕ = prism angle
δ = angle of deviation of light beam
1 = BrF_3
2 = BrF_5