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Cryoscopy in Acidic and Basic Aqueous Solvents. II. Eutectic Trifluoroacetic Acid[1]

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Freezing points of eutectic aqueous trifluoroacetic acid (CF_3COOH, 10.6 mol %) and of solutions of ten ionic solutes in this solvent were determined from cooling curves. It was found that the molal freezing point depression was constant (within the experimental error) in all solutions (except nitric acid), with no noticeable dependence on the type of the ionic solute or its concentration. The average K_f was 6.53 ± 0.01°. Solutions of nitric acid had a formal freezing point depression of 3.34 ± 0.05°. This result confirmed conclusions of an earlier study on the dimerization of this acid in aqueous perchloric acid solutions.

Introduction

The precision of cryoscopic determinations of molecular weights of ionic species is greatly improved through the replacement of water by an aqueous electrolyte solution at its eutectic composition or at any other composition having a definite transition point. The lowering of the freezing point of such a solution is given by[2]

$$\lim_{m \to 0} \frac{\Delta T}{m} = \nu \frac{RT^{02}}{\lambda} = \nu K_f^0 \qquad (1)$$

where ΔT is the lowering of the freezing temperature T^0 of the pure solvent, K_f^0 is the cryoscopic constant, m is the molality of the solute, λ is the specific (latent) heat of fusion of the pure solvent, and ν is the number of "foreign" particles produced per molecule (formula) of solute, e.g., $\nu = 1/2$ for dimerization and $\nu = 2$ for dissociation into two "foreign" species. "Foreign" species are those solute species which are not components of the pure solvent system. With one exception,[1] all solvent systems used were aqueous solutions of *salts*,[3-5] hence the term "Salzkryoskopie". The classical and most widely used solvent of Salzkryoskopie is the saturated solution of Na_2SO_4 in water at the transition temperature of the decahydrate to the anhydrous salt (32.382°C). The transition temperature is depressed by "foreign" cations or anions but is not affected by ions common to the solvent and solute (i.e., Na^+ or SO_4^{2-}) in accordance with (1). This characteristic relation improves the precision of Salzkryoskopie as compared to ordinary water cryoscopy, since the relative change in ΔT caused by polymerization of an ion is much greater in the former.[1]

The main drawback of Salzkryoskopie was its being restricted to solute species existing in neutral solutions (pH ~7). Many acidic solutes such as most transition metal aquoions are precipitated in neutral solutions and form stable solutions only in acidic media. Corrections for the acid added to stabilize such species were applied to cryoscopic data of Salzkryoskopie in order to overcome this difficulty,[6] but the error introduced by the additional "foreign" ions (H^+ and HSO_4^-) increased rapidly with acid concentration and eventually wiped out the relative advantage of Salzkryoskopie over ordinary water cryoscopy. Some unwarranted conclusions were drawn from cryoscopic measurements in such systems.[6,7]

In order to meet the specific requirements of acidic species, Ardon, Linenberg, and Halicz[1,8] introduced the use of a strongly acidic solvent, eutectic aqueous perchloric acid (40.75% $HClO_4$), and demonstrated its suitability for cryoscopic measurements with many mononuclear species as well as with binuclear ionic species[1,7,8] such as $Cr_2(OH)_2^{4+}$ and $Mo_2O_4^{2+}$. Cryoscopic measurements of dilute solutions of *nitric acid* ($m \sim 0.02$) in this solvent revealed that this species exists as dimers in the perchloric acid solvent.[1,9] In view of this surprising yet conclusive evidence it seemed desirable to check whether dimerization of dilute HNO_3 solution is confined to this solvent and temperature (−60°) or is a more general phenomenon, taking place in other acidic aqueous solvents and at higher temperatures. The purpose of the present work was to extend the scope of cryoscopy in acidic solutions by introducing a new acidic aqueous solvent and investigating its freezing-point depression by "normal" cationic and anionic species and by nitric acid. The solvent chosen was aqueous trifluoroacetic acid. This system had been reported[10] as having a eutectic point at −21.55°C at a composition of 10.59 mol % CF_3COOH. The solid phases in equilibrium with the liquid are $CF_3COOH{\cdot}4H_2O$ + ice.

Experimental Section

The eutectic solvent was prepared by dilution of an appropriate weight of pure trifluoroacetic acid with water. The solutions of Zn(II), Mg(II), and Fe(II) in HTFAc were prepared by dissolving weighed samples of each metal in the eutectic acid. Solutions of H_2SO_4, HNO_3, and $HClO_4$ were prepared by dissolving the appropriate weights of their concentrated solutions in eutectic HTFAc. The solution of Fe(III) was prepared by dissolving freshly precipitated $Fe(OH)_3$ in the solvent. Solutions of Cr(III) and Th(IV) were prepared by absorption of solutions of their nitrates in HCl 0.1 *N* on cation exchange columns (Dowex 50WX2) and elution with eutectic HTFAc. The HCl solution was prepared by passing dry HCl gas through the eutectic solvent. Standard analytical methods were used to determine the concentration of each solute. The concentrations were adjusted to those given in Table I by dilution with eutectic HTFAc. Small quantities of water were added to some solutions in the process of their preparation (e.g., by neutralization of ferric hydroxide). No correction was made for this change in solvent composition since the eutectic temperature is not affected at all by this change and the increase of solute concentration *at the freezing point* is always less than 1%.

Freezing-point determinations were carried out in a double-walled Pyrex cell placed in a thermostated cooling bath which was maintained at −27.00 ± 0.02°C. The solution in the cell was stirred with a Pyrex stirrer at a constant rate of 100 rpm. The constancy of the cooling bath temperature and of the rate of stirring resulted in a constant rate of cooling of all solutions which, in turn, produced cooling curves of constant and equal slope in all measurements. This experimental

Table I. Freezing Temperatures and K_f Values of Solutions in Eutectic HTFAc

Solute	Molality	Temp, °C	K_f
$Zn(CF_3COO)_2$	0.05	−22.797 ± 0.06	6.6 ± 0.2
	0.03	−22.658 ± 0.05	6.4 ± 0.3
	0.02	−22.596 ± 0.06	6.6 ± 0.5
$Mg(CF_3COO)_2$	0.05	−22.783 ± 0.06	6.4 ± 0.2
	0.03	−22.656 ± 0.05	6.4 ± 0.3
	0.02	−22.598 ± 0.06	6.6 ± 0.5
$Fe(CF_3COO)_2$	0.05	−22.792 ± 0.04	6.5 ± 0.2
	0.03	−22.657 ± 0.04	6.4 ± 0.3
	0.02	−22.595 ± 0.06	6.6 ± 0.5
$Fe(CF_3COO)_3$	0.05	−22.790 ± 0.06	6.5 ± 0.2
	0.03	−22.661 ± 0.05	6.5 ± 0.3
	0.02	−22.599 ± 0.06	6.7 ± 0.5
$Cr(CF_3COO)_3$	0.05	−22.799 ± 0.05	6.7 ± 0.2
	0.03	−22.663 ± 0.05	6.6 ± 0.3
	0.02	−22.595 ± 0.05	6.5 ± 0.5
$Th(CF_3COO)_4$	0.05	−22.800 ± 0.04	6.7 ± 0.2
	0.03	−22.667 ± 0.06	6.7 ± 0.3
	0.02	−22.598 ± 0.05	6.6 ± 0.5
HCl	0.05	−22.795 ± 0.05	6.6 ± 0.2
	0.03	−22.656 ± 0.06	6.4 ± 0.3
	0.02	−22.597 ± 0.04	6.6 ± 0.5
H_2SO_4	0.05	−22.788 ± 0.04	6.5 ± 0.2
	0.03	−22.654 ± 0.05	6.3 ± 0.3
	0.02	−22.592 ± 0.06	6.4 ± 0.5
$HClO_4$	0.05	−22.791 ± 0.05	6.5 ± 0.2
	0.03	−22.659 ± 0.05	6.5 ± 0.3
	0.02	−22.597 ± 0.06	6.6 ± 0.5
HNO_3	0.10	−22.802 ± 0.07	3.4 ± 0.1
	0.06	−22.664 ± 0.04	3.3 ± 0.2
	0.05	−22.632 ± 0.06	3.3 ± 0.2
	0.04	−22.595 ± 0.05	3.2 ± 0.2

arrangement improved the reproducibility of the results.

The temperature of the solution in the cell was determined by a thermistor (Standard Telephones and Cables, Type F23) dipping into the solution. Thermistor resistance was measured by a Wheatstone bridge (100,000 ohm, O. Wolf, Berlin) and a galvanometer (Leeds and Northrup 2430 D). Resistance measurements were taken during the cooling, supercooling, and freezing of each solution and were continued as long as the freezing temperature remained constant (about 10 min after freezing). The thermistor was calibrated with a Hewlett Packard 2801A quartz thermometer in the range −16 to −25°C. The linear equation $\log R = 616.9245 \times 1/T + 1.6311$ was calculated from these measurements by least squares.

Results

The freezing temperature of the pure solvent (trifluoroacetic acid, 10.6 mol %) was found to be −22.465 ± 0.005°C. The freezing temperatures of 31 solutions containing ten solutes at different concentrations are presented in Table I. The freezing temperatures were determined from cooling curves. Temperature measurements (thermistor resistance readings) were taken at 1-min intervals. The linear equations representing the two sections of the cooling curve near the freezing point (before and after freezing) were computed by the least-squares method. The computer program used for this purpose also included the calculation of the point of intersection of the two straight lines (i.e., the extrapolated freezing point) and the conversion of the freezing temperature from resistance units (ohms) to temperature units (centigrade; see Experimental Section). A computer plot of typical cooling curves is given in Figure 1. The first reading after the end of supercooling (point A in Figure 1) was discarded in all computations. Each freezing point in Table I is the average of four determinations. The confidence limit was calculated by the Gosset equation[11] using a confidence probability level ($1 - \alpha$) of 95%. The molal freezing-point depression K_f of each solution ($K_f = \Delta T/m$) is given in Table I. All solutes, with the exception of nitric acid, have K_f values of ~6.5. The combined data of the first nine solutes (which represent 27 solutions and 108 cooling curves) were used to derive an average value of $\bar{K}_f = 6.53 \pm 0.01°$. The average molal freezing-point depression derived from four different concentrations of nitric acid was 3.34 ± 0.05°.

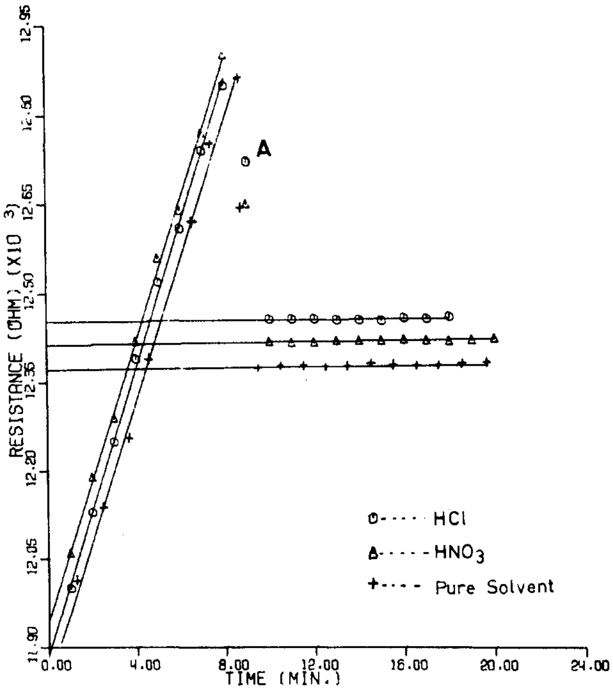

Figure 1. Computer plots of cooling curves of the pure eutectic solvent and of solutions of HCl, 0.05 *m*, and HNO_3, 0.05 *m*.

Discussion

The results presented in Table I demonstrate the close agreement between the molal freezing-point depression of eutectic trifluoroacetic acid by a variety of ionic solutes: dipositive cations (Zn^{2+}, Mg^{2+}, and Fe^{2+}), tripositive cations (Fe^{3+} and Cr^{3+}), tetrapositive cations (Th^{4+}), and negative ions (Cl^-, HSO_4^-, and ClO_4^-). This agreement, while not suprising, in view of the relatively low concentration of all solutes (0.02–0.05 *m*), cannot be assumed a priori. The dependence of K_f on solute concentration in eutectic electrolyte–water solvents is small and linear as has been demonstrated experimentally for a number of solvents[1,4,12] and justified on theoretical grounds.[12,13] Therefore, K_f values of different solutes at low concentration are expected to approach each other and the limiting value (for infinite dilution) K_f^0. There is however no theoretical basis for the presumption that the difference $K_f - K_f^0$ is small enough to be neglected in an arbitrarily chosen concentration range, such as 0.02 to 0.05 *m*. Since the experimental error in ΔT measurements limits solute concentrations to $m > 0.01$ *m*, it had to be verified experimentally that the assumption $K_f \sim K_f^0$ was indeed justified, in the case of the eutectic HTFAc solvent, for a variety of solutes at the concentration range 0.02 to 0.05 *m*.

It is noteworthy that there is no systematic dependence of K_f on solute concentration for any of the solutes, i.e., any dependence must be smaller than the experimental error. Furthermore, K_f values for all solutes, some as different from each other as Th^{4+} and ClO_4^-, are the same within the experimental error. Hence, the justification for the use of the combined data for calculation of the mean value $K_f = 6.53 \pm 0.01°$. This interagreement proves the reliability of cryoscopy in this solvent.

The ratio between the K_f value for HNO_3 and the "normal" mean K_f value is almost one-half, 0.051 ± 0.01, as expected for a binuclear nitric species. The fact that K_f of nitric acid solutions does not increase with decreasing concentration of nitric acid rules out the possibility that we are dealing with a monomer–polymer equilibrium here, but with a true dimer.

These results are in agreement with results obtained in eutectic perchloric acid.[1] The K_f ratio obtained in that solvent was 0.53. The temperature difference between the melting point of the two solvents, 38°C, indicates that dimerization of HNO_3 is not confined to temperatures as low as −60°C. Proof of dimerization at −22°C as well as at −60°C indicates that dimerization of HNO_3 in these solvents may well take place even at room temperature.

The two solvents are comparable in two important aspects: (a) the formal (H^+) concentration is 5.2 *M* in eutectic perchloric acid and 5.1 *M* in eutectic trifluoroacetic acid; (b) water constitutes 89.0 mol % in eutectic perchloric acid and 89.4 mol % in HTFAc. The similarity between the solvents leaves unanswered the question as to whether dimerization takes place in other H^+ concentrations. Dimerization in aqueous solutions of pure nitric acid itself, in concentration of ~5 *N*, is a distinct possibility in the light of results of the other two solvents. A detailed Raman study is being undertaken in order to test this hypothesis. Raman studies may also furnish an answer to the major problem which cannot be solved by cryoscopic data, namely that of the structure and bonding of the nitric dimer.[1]

Cryoscopic investigation of ionic species in acidic or basic aqueous solvents may provide a new source of information on the constitution of some important solute species in aqueous solutions. A wide range of eutectic aqueous solutions, ranging from strong acids to strong bases, may be used at different pH ranges, including solutes such as amphoteric metal anions in basic solutions. Forthcoming papers in this series will deal with solute species in new solvents of this type.

Registry No. HTFAc, 76-05-1; $Zn(CF_3COO)_2$, 21907-47-1; $Mg(CF_3COO)_2$, 38482-84-7; $Fe(CF_3COO)_2$, 5781-22-6; $Fe(CF_3COO)_3$, 21907-43-7; $Cr(CF_3COO)_3$, 16712-29-1; $Th(CF_3COO)_4$, 16424-71-8; HCl, 7647-01-0; H_2SO_4, 7664-93-9; $HClO_4$, 7601-90-3; HNO_3, 7697-37-2.

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Some Sulfur(VI)–Nitrogen Compounds Which Contain $CF_3SF_4^-$

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Photolysis reactions of CF_3SF_4Cl with H_2, CF_3CN, and ClCN give $CF_3SF_4SF_4CF_3$, $CF_3SF_4N{=}C(Cl)CF_3$, and $CF_3SF_4N{=}CCl_2$, respectively. Cesium fluoride fluorinates the $CF_3SF_4N{=}C(Cl)CF_3$ to $CF_3SF_4N{=}CFCF_3$ and fluorinates and isomerizes $CF_3SF_4N{=}CCl_2$ to $CF_3SF_3{=}NCF_3$. The >C=N– and >S=N– systems undergo nucleophilic attack by ClF and HF to prepare the new chloramines, $CF_3SF_4N(Cl)CF_2CF_3$ and $CF_3SF_4N(Cl)CF_3$, and amines, $CF_3SF_4N(H)CF_2CF_3$ and $CF_3SF_4N(H)CF_3$. These compounds are stable and boil 20–40° higher than their SF_5 analogs.

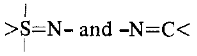
Introduction

Several straightforward synthetic routes to CF_3SF_4Cl enhance its attractiveness as a precursor for a variety of CF_3SF_4-containing compounds which are comparable in stability to their SF_5 analogs[1] but which have the advantage of being somewhat less volatile. Chlorine reacts with CF_3SF_3 in the presence of CsF to give *trans*-CF_3SF_4Cl.[2] Although we find that ClF with CF_3SF_3 results in a quantitative preparation of the latter compound, the preferred route is the reaction of CF_3SSCF_3 with ClF[3] in a molar ratio of 1:>8

$$CF_3SSCF_3 + ClF \xrightarrow{25°} CF_3SF_4Cl\ (70\%)$$

The radical reactions of CF_3SF_4Cl with olefins and fluoroolefins[4] are essentially the same as those of the extensively studied SF_5Cl.[5-11] The photochemical reduction of SF_5Cl by hydrogen provides a facile route to S_2F_{10}.[5]

We now wish to report the preparation of a new series of $CF_3SF_4N<$ compounds which arise from the photolysis of CF_3SF_4Cl with nitriles and the subsequent substitution of fluorine for chlorine by using CsF as a fluorinating reagent. The relative reactivities of



$$>\overset{|}{\underset{|}{S}}{=}N–\ \text{and}\ –N{=}C<$$

are markedly demonstrated by comparing the ease of saturation of the double bond in $CF_3SF_3{=}N–CF_3$ and in $CF_3SF_4N{=}CFCF_3$ with ClF and HF.

Results and Discussion

The charge distribution within the $CF_3SF_4^{\delta-}Cl^{\delta+}$ molecule suggests that reactions with compounds which contain negative chlorine should be useful in synthesizing new CF_3SF_4X compounds. This is supported by the reaction with hydrogen chloride to form chlorine where the likely intermediate, CF_3SF_4H, if formed, is not isolable, viz.

$$CF_3SF_4Cl + HCl \rightarrow Cl_2 + [CF_3SF_4H] \rightarrow CF_3SF_3 + HF(SiF_4)$$

Similarly, thermolysis of CF_3SF_4Cl and NOCl results in decomposition products and chlorine which suggests that CF_3SF_4NO could have been an unstable intermediate

$$CF_3SF_4Cl + NOCl \xrightarrow{180°} Cl_2 + [CF_3SF_4NO] \rightarrow CF_3NO + SF_4$$

Identical products are formed when these reactants were subjected to photolysis through quartz at 25°.

As is the case with SF_5Cl, photolysis of CF_3SF_4Cl with H_2 enhances the formation of the very stable disulfur decafluoride analog, $CF_3SF_4SF_4CF_3$. Unfortunately, in all photolysis reactions described below, a large fraction of the CF_3SF_4Cl