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Cryoscopy in Eutectic Perchloric Acid. Nitric Acid Dimerization

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The molal freezing point depression of eutectic aqueous perchloric acid (40.75%) by foreign cations and anions is 5.2 ± 0.4° for solutes at the concentration range of 0.015–0.03 *m*. The molal depression for nitric acid is only 2.7°. Since no solid solution of nitric acid is formed, it is concluded that it exists in dimeric form in eutectic perchloric acid. Raman and uv spectra indicate existence of nitric acid species in eutectic perchloric acid solutions that do not exist in aqueous solution or in concentrated salt solutions.

In a preliminary investigation it was observed that the freezing point depression, by nitric acid, of a eutectic perchloric acid-water system (40.75% $HClO_4$) was only one-half of the depression caused by other acids of equal molalities (HCl, $HClO_3$, H_2SO_4). This observation was interpreted by assuming that nitric acid exists in this solvent in a dimeric form. An alternative, though less plausible interpretation by assuming the existence of a solid solution was not ruled out.[1]

Although there is some evidence for the existence of nitric acid dimers in the pure compound,[2,3] the cryoscopic evidence for their existence in dilute solution[1] (~0.02 *m*) was quite unexpected. It was therefore undertaken to reinvestigate the subject cryscopy in eutectic perchloric acid in order to examine critically the preliminary results for nitric acid. We also investigated the possibility that the abnormal depression of the freezing point was caused by a solid solution of the solute in the solvent.[4]

The system $HClO_4$-H_2O was investigated by Van Wyk,[5] Brickwedde,[6] and Mascherpa.[7] At 40.75% perchloric acid the system has a eutectic point. The solid phases in equilibrium with the solution are ice and a perchloric acid hydrate of unknown composition.[6] The perchloric acid phase probably consists of a solid solution of $HClO_4 \cdot 5.5H_2O$ in water.[7] The freezing point of the solution is −60.2° according to Mascherpa,[7] −59.7° according to Brickwedde,[6] and −57.5° according to Van Wyk.[5]

In an earlier work it was established that the depression of the freezing temperature of this eutectic solvent by foreign cations can be used for molecular weight determinations of such cations.[8] This cryoscopic system belongs to the field of "Salzkryoskopie."[9-11] Solvent water is replaced in Salzkryoskopie by electrolyte solutions having a eutectic composition or another definite transition point. The classical solvent of Salzkryoskopie[9,10] was the saturated solution of Na_2SO_4 in water at the transition temperature of the decahydrate to the anhydrous salt (32.382°). The transition temperature is depressed by foreign cations or anions but is not affected by ions common to the solvent and solute (*e.g.*, Na^+ or SO_4^{2-} in the Glauber salt system). This characteristic behavior 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; if the degree of polymerization n of a certain cation M_n^{nm+} is investigated in a eutectic solvent containing the ions A^+ and B^-, one may use the salt $M_n^{nm+}B_{nm}^-$ as solute, thus eliminating any contribution to ΔT of the counter ion B^-. The ratio of ΔT's for a monomer M^{m+} and a dimer M_2^{2m+} will be 2:1 in this solvent, compared to $(2m + 2)/(2m + 1)$ in water. An additional advantage of Salzkryoskopie is the very small and linear dependence of the molal freezing point depression K_f on solute concentration which is due to the slight change of ionic activity coefficients in such solvents.[10]

The eutectic solvent $HClO_4$-H_2O is especially suitable for cryoscopy of cations that are stable only in acid solutions[8] and for acids.[1] In the case of acids, the depression of the freezing point is not affected by the degree of acid dissociation, since the undissociated molecule HB and the dissociated anion B^- will contribute equally to ΔT whereas the dissociated cation H^+ which is common to solvent and solute will not affect ΔT at all. Thus, ΔT for sulfuric acid will not be changed by the equilibrium $H_2SO_4 \rightleftarrows H^+ + HSO_4^- \rightleftarrows 2H^+ + SO_4^{2-}$. On the other hand, polymerization of the acid molecule (or its dissociated anion) will decrease ΔT by a factor equal to the degree of polymerization.

Experimental Section

Freezing point determinations were carried out in a double-walled Pyrex cell containing a magnetic stirrer, a thermistor, and 3 ml of solution. The cell was placed in a thermos containing a cooling bath of acetone and Dry Ice. The rate of cooling was 0.3–0.4° per minute. The thermistor was of type F23 (Standard Telephones & Cables); its resistance was measured by a Wheatstone bridge (100,000 ohm, O. Wolf, Berlin) and a galvanometer (Leeds & Northrup 2430D). The thermistor was calibrated with an ethanol-filled thermometer in the range −51 to −62°. The calibration curve of log R *vs.* $1/T$ was linear in this range. The resistance at the freezing point of the pure solvent was 72,740 ± 10 ohms. The change of R was 427 ohms per 0.1° at the freezing temperature. The change of ΔT with R is nearly linear for $\Delta T < 0.2°$ and the relation $\Delta T = R/4270$ was used for calculating the experimental ΔT values.

Preparation of Solutions. Perchloric acid solution (41.7%) was prepared by mixing appropriate weights of water and 71.6% perchloric acid. $Zn(ClO_4)_2$, $Mg(ClO_4)_2$, and $Fe(ClO_4)_2$ solutions were prepared by dissolving the required weight of the metal in 41.7% perchloric acid. In the case of the iron salt the dissolution was carried out under nitrogen. No reduction of perchloric acid occurred. $Mn(ClO_4)_2$ and $Cu(ClO_4)_2$ solutions were prepared by dissolving the carbonates in 41.7% perchloric acid and $Hg_2(ClO_4)_2$ was prepared by dissolving HgO in 41.7% perchloric acid and reducing with metallic mercury. The nitric, hydrochloric, and sulfuric acid solutions were prepared by dissolving the appropriate weights of the concentrated acids in perchloric acid.

Separation and Analysis of the Solid Phases. The solution was placed in a sintered glass tube together with a magnetic stirrer. The

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sintered glass tube was placed in a thermos containing ethanol cooled to a temperature slightly below the freezing point of the perchloric acid solution. The rate of cooling was approximately 0.2° per minute. When the solution began to freeze it was removed from the bath and the liquid phase was quickly removed by vacuum suction. The wet solid could not be rinsed but was partly melted by air and the melted liquid containing some of the adhering mother liquor was removed by suction. The remaining solid was melted and the solute content was determined; Cl^- was analyzed by Mohr's method, SO_4^{2-} was analyzed nephelometrically as $BaSO_4$, and NO_3^- was analyzed spectrometrically as the ammonium salt of nitrophenoldisulfonic acid.

Raman spectra were taken on a Spex 1400 monochromator and samples were illuminated by a Spectra Physics 125 helium-neon laser. Uv spectra were taken with a Cary 14 spectrophotometer.

Results

Freezing Point Depression by Foreign Cations and Anions. The freezing point depression of the eutectic perchloric acid solvent by ten different solutes was measured. The results are presented in Table I. Freezing temperatures were read from cooling curves of thermistor resistance *vs.* time. When eutectic perchloric acid (40.75% $HClO_4$) was used, no supercooling was observed and the temperature failed to stabilize at the freezing point. When a solution of 41.7% $HClO_4$ was used, an average supercooling of 0.2-0.3° was obtained and a stable freezing temperature was determined; therefore 41.7% $HClO_4$ was used as solvent for all solutes. As a result of the difference between solvent composition and eutectic composition, the actual concentration of solutes in solution was slightly higher at the freezing temperature than in the warm solution, since some of the perchloric acid phase was precipitated before the freezing temperature was attained. The exact magnitude of this concentration increase could not be calculated since the composition of the perchloric acid hydrate is unknown, but it must be smaller than 2.5% and higher than 2.0% because the hydrate contains more than 40.7% perchloric acid but less than 50.4% of the acid (the composition of $HClO_4 \cdot 5.5H_2O$[7]). This correction was not applied to data presented in Table I.

Solid Solutions. All solutes investigated except HNO_3 and $Hg_2(ClO_4)_2$ yielded K_f values of 5.2 ± 0.4. In order to determine whether the large deviations of K_f of nitric acid ($K_f = 2.7$) and $Hg_2(ClO_4)_2$ ($K_f = 3.0$) are due to polymerization or to formation of a solid solution, the composition of the wet solid phases separated from these solutions was determined.

The content of two other solutes (HCl and H_2SO_4) in the solid phases separating from their solution was determined for comparison in order to estimate the extent of contamination of the solid phases by adhering liquid solution. The results are presented in Table II.

Raman and Uv Spectra. The Raman spectrum of 0.5 *N* HNO_3 in eutectic perchloric acid was measured and compared to the spectra of 0.5 *N* HNO_3 in water and in an aqueous solution containing 41.7% $NaClO_4$. A sharp peak at 1309 cm^{-1} was observed in the eutectic perchloric acid solution but was absent from the aqueous solution and from the sodium perchlorate solution. This band is known from spectra of anhydrous HNO_3 and of concentrated aqueous solutions of nitric acid.[2] The NO_3^- band at 1040 cm^{-1} was much smaller in the eutectic perchloric acid solution than in the aqueous solution and in the sodium perchlorate solution. The uv spectrum of 0.04 *N* HNO_3 in eutectic perchloric acid was measured and compared to the spectra of 0.04 *N* HNO_3 in water and in 41.7% $NaClO_4$, respectively. The peak at 302 mμ found in both aqueous and sodium perchlorate solutions is shifted to 288 mμ in the eutectic perchloric acid solution.

Table I

Solute	Molality of solute	ΔT	K_f
$Mg(ClO_4)_2$	0.015	0.079	5.27
$Mg(ClO_4)_2$	0.020	0.103	5.15
$Mg(ClO_4)_2$	0.030	0.150	5.00
$Cu(ClO_4)_2$	0.015	0.075	5.00
$Cu(ClO_4)_2$	0.020	0.110	5.50
$Cu(ClO_4)_2$	0.030	0.152	5.07
$Zn(ClO_4)_2$	0.015	0.082	5.47
$Zn(ClO_4)_2$	0.020	0.103	5.15
$Zn(ClO_4)_2$	0.030	0.154	5.13
$Ni(ClO_4)_2$	0.015	0.077	5.13
$Ni(ClO_4)_2$	0.020	0.112	5.60
$Ni(ClO_4)_2$	0.030	0.148	4.93
$Mn(ClO_4)_2$	0.015	0.077	5.13
$Mn(ClO_4)_2$	0.020	0.108	5.40
$Mn(ClO_4)_2$	0.030	0.152	5.07
$Fe(ClO_4)_2$	0.015	0.082	5.47
$Fe(ClO_4)_2$	0.020	0.103	5.15
$Fe(ClO_4)_2$	0.030	0.154	5.13
HCl	0.020	0.108	5.40
HCl	0.030	0.156	5.20
H_2SO_4	0.020	0.103	5.15
H_2SO_4	0.030	0.156	5.20
HNO_3	0.020	0.056	2.80
HNO_3	0.030	0.082	2.73
$Hg_2(ClO_4)_2$	0.010	0.030	3.00

Table II. Distribution of Solutes in 41.7% Perchloric Acid between Solid and Liquid Phases

Solute	Molality in liquid phase	Molality in solid phase	Distribution coefficient
HNO_3	0.020	<0.002	<0.1
H_2SO_4	0.020	<0.002	<0.1
HCl	0.020	<0.003	<0.15
$Hg_2(ClO_4)_2$	0.010	0.005	0.5

Discussion

The results presented in Table I prove that the molal depression of the freezing point of eutectic perchloric acid by +2 cations and by strong acids (−1 anions or undissociated molecules) is independent of the nature of the solute at the low concentration range of 0.015-0.03 *m*. All cryoscopic constants are within the range of 5.2 ± 0.4 except for nitric acid and mercurous perchlorate.

Earlier preliminary work yielded an average value of $K_f = 4.2$ for +2 cations[8] and of $K_f = 4.0$ for acids.[1] A reexamination of the former results and calculations revealed an error in calculations of K_f; these values were calculated by dividing ΔT by the *molarity* rather than by the *molality* of the solutions. The correct values can be obtained by multiplying the results by the *density* of eutectic perchloric acid at room temperature[6] ($d = 1.3$). When this correction is applied, average values of $K_f = 5.5$ for cations and of $K_f = 5.2$ for acids are obtained, in good agreement with the present work.

The results of analysis of the solid phases presented in Table II show that formation of a solid solution occurs in the case of $Hg_2(ClO_4)_2$. This solid solution is responsible for the abnormal K_f found with this solute. The experimental value of 3.0 instead of the expected value of 5.2 is caused by the existence of a solid solution of $Hg_2(ClO_4)_2$ in the solid phases with a distribution coefficient of 0.5 between solid and liquid. In an ideal system,[4] this distribution coefficient would lead to a K_f value of 2.6.

The results of Table II for HNO_3, HCl, and H_2SO_4 rule out the existence of a solid solution of nitric acid. The incomplete separation of the solid from the solution (see Experimental Section) causes some contamination of the solid by adhering liquid solution. That this contamination is not due to a solid solution is shown by the fact that equal or larger amounts of HCl and H_2SO_4 are found with the solid phases although these solutes yield normal K_f values (Table I).

The inescapable conclusion of the results of this work is that nitric acid does indeed exist in dimeric form in eutectic perchloric acid[1] at least in the experimental range investigated (temperature around −60° and molalities of 0.02–0.03). Two questions remain unanswered. (a) What is the structure of the nitric acid dimer? (b) Does it exist in solution at higher temperatures? Results of Raman and uv spectra indicate that new species of nitric acid appear in eutectic perchloric acid solutions which are not found in aqueous or perchlorate-salt solutions. However, these spectra were taken at room temperature and the spectral changes observed may be due to monomeric species formed in the eutectic solution at room temperature such as undissociated HNO_3 and do not necessarily belong to a nitric acid dimer. The dimer exists at −60° but not necessarily at room temperature. A detailed investigation of Raman spectra may reveal the structure of the species and the temperature range in which they exist. No detailed structure of the dinuclear nitric acid species can be offered at present since cryoscopic behavior cannot be used to distinguish between different structural formulas of the dimer $H_2N_2O_6$. Furthermore, it cannot distinguish between the dimer $H_2N_2O_6$ and dinuclear species such as $HN_2O_6^-$, $N_2O_6^{2-}$, etc. Even the nitric acid anhydride N_2O_5 is not ruled out by the cryoscopic data, although its existence as a solution containing 59% water by weight is highly improbable.

Registry No. $HClO_4$, 7601-90-3; $Mg(ClO_4)_2$, 10034-81-8; $Cu(ClO_4)_2$, 13770-18-8; $Zn(ClO_4)_2$, 13637-61-1; $Ni(ClO_4)_2$, 13637-71-3; $Mn(ClO_4)_2$, 13770-16-6; $Fe(ClO_4)_2$, 13933-23-8; HCl, 7647-01-0; H_2SO_4, 7664-93-9; HNO_3, 7697-37-2; $Hg_2(ClO_4)_2$, 13932-02-0.

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Reduction of Bromate Ion by Chlorous Acid in Acid Perchlorate Solution

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The stoichiometry of the reduction of bromate ion by chlorous acid in acid perchlorate solution is $[(2-n)/4]BrO_3^- + HClO_2 = nClO_2 + (1-n)ClO_3^-$ provided allyl alcohol is present to scavenge a hypobromous acid intermediate. The value of n is 0.667 with large excesses of chlorous acid; otherwise it is smaller. The reaction scheme shown below is

$$BrO_3^- + HClO_2 + H^+ \overset{k_a}{=} BrO_2 + ClO_2 + H_2O$$

$$BrO_2 + HClO_2 \overset{k_b}{=} HBrO_2 + ClO_2$$

$$BrO_2 + ClO_2 + H_2O \overset{k_c}{=} HBrO_2 + ClO_3^- + H^+$$

$$HBrO_2 + HClO_2 \overset{k_d}{=} HOBr + ClO_3^- + H^+$$

proposed to accommodate the stoichiometric and kinetic data. The hydrogen ion and temperature dependence of the rate parameter k_a is presented. It was also possible to determine k_c/k_b. The results are comparable to earlier predictions for the reduction of bromate ion by bromous acid.

Introduction

Studies of the reduction of bromate ion by several weak, one-electron reducing agents have led to the conclusion that the reaction proceeds not *via* a direct interaction of the reactants but instead by the sequence

$$BrO_3^- + HBrO_2 + H^+ = 2BrO_2 + H_2O \qquad (1)$$

$$BrO_2 + R + H^+ = HBrO_2 + O_x \qquad (2)$$

$$2HBrO_2 = BrO_3^- + HOBr + H^+ \qquad (3)$$

where R is the reducing agent and O_x its oxidized form.[1-3] An induction period is observed in these systems during which, presumably, a steady-state concentration of the bromous acid intermediate is established. A paradoxical feature is that reaction 1 accomplishes a direct, one-electron reduction of bromate ion by the weak reductant bromous acid and is postulated to not exhibit an induction period. Buxton and Dainton have published results of a radiolysis study of bromate ion in which they conclude that the reverse of reaction 1 occurs in basic solution through the intermediate formation of Br_2O_4.[4] Thus, one resolution of the paradox is that bromous acid is an unusual weak, one-electron reducing agent in that it can react directly with bromate ion in acidic solution to form Br_2O_4 which rapidly dissociates into bromine dioxide as summarized in (1). A direct study of (1) would be of interest in this context but is infeasible experimentally owing to the rapid disproportionation of bromous acid in acidic solution.[3,5] However, a related system is amenable to study if one is willing to

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