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Osmotic and Activity Coefficients of Aqueous $HTcO_4$ and $HReO_4$ Solutions at 25 °C

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Isopiestic vapor pressure comparison experiments were conducted with aqueous perchloric, pertechnetic, and perrhenic acid solutions to concentrations of approximately 7 *m*. Osmotic coefficients for these solutions and mean molal ionic activity coefficients for $HTcO_4$ and $HReO_4$ were derived from the isopiestic molalities. The magnitudes of the activity coefficients and their concentration dependence relative to $HClO_4$ solutions were consistent with Raman band intensity measurements which have indicated all three acids are completely ionized to concentrations at least as great as 6 M. There is evidence that condensation and hydration equilibria become increasingly important in more concentrated $HTcO_4$ and $HReO_4$ solutions.

Introduction

A knowledge of the relative basicities of the singly charged oxyanions MnO_4^-, TcO_4^-, and ReO_4^- is of interest in the light of the predictions of Pauling[1] and Ricci[2] that their respective acids in water will be very strong and their strengths will differ negligibly from one another and from those of $HClO_4$ and $HBrO_4$. It was possibly unexpected, therefore, that spectrophotometric studies[3] on the protonation of several transition-metal oxyanions in concentrated sulfuric and perchloric acids have given approximate pK values for $HMnO_4$ and $HReO_4$ which surprisingly differ from one another and are significantly larger (i.e., less negative) than that for $HClO_4$. In a subsequent investigation[4] of $HReO_4$ by Raman and ^1H NMR techniques, however, it has been concluded that perrhenic acid is completely ionized to concentrations as great as 7 M. The disagreement of this result with the spectrophotometric method was attributed to the neglect in the latter of activity coefficients, of medium effects on the spectra, and of the fact that the extrapolation procedure used covered a wide concentration range.

In a recent investigation we have conducted Raman scattering measurements[5] with concentrated aqueous $HTcO_4$ solutions which indicate that this acid also is completely ionized. The intensity of the strong, composite Raman band of the TcO_4^- ion at 912 cm^{-1} increased linearly with acid concentration up to ca. 6 M. The determination of thermodynamic activity coefficients for pertechnetic and perrhenic acid in their binary aqueous solutions was carried out concurrently so as to be able to evaluate pK_a values, but unfortunately the latter could not be estimated because of the indicated complete dissociation of the acids at all concentrations measured. The gravimetric isopiestic vapor pressure comparison method was used wherein $HTcO_4$ and $HReO_4$ solutions of accurately predetermined composition are brought to isotonic equilibrium with standard solutions (NaCl in this work) of precisely known water vapor pressure and composition. The activity coefficients reported below also will be useful for computations of chemical reactions in solution because of recent advances in the treatment of electrolyte mixtures[7,8] which make possible the estimation of mean molal activity coefficients $\gamma_\pm$ of solutes in mixtures from the parameters which describe their concentration dependence in binary solutions.

Experimental Section

Source and Preparation of Acids. Measurements with aqueous permanganic acid solutions failed because of the instability of this compound and therefore solutions or perchloric acid were employed instead. The 71% $HClO_4$ was ultrapure "electronic grade" reagent (Alfa Inorganics) and was used as received. An aqueous "stock solution" of pertechnetic acid was prepared starting with ca. 23.5 mmol of pure $NH_4{}^{99}TcO_4$ received from the Isotopes Division of the Oak Ridge National Laboratory, Oak Ridge, Tenn. The small amount of TcO_2 produced by self-radiolysis of this compound on standing was removed by repeated treatment of an ammoniacal solution of the NH_4TcO_4 with 30% hydrogen peroxide and evaporation to dryness. Potassium pertechnetate was formed by dissolving the treated NH_4TcO_4 in pure water and evaporating after adding a slight excess of 2.0 N KOH solution. The solid $KTcO_4$ was recrystallized from water three times, dissolved in pure water to a volume of ca. 250 mL, and passed through a 60-cm^3 bed of strong-acid cation exchanger (Dowex 50-X8 H-form) to give a dilute solution of $HTcO_4$ which was evaporated to ca. 25 mL and stored in a closed vessel.[9] Concentrated $HReO_4$ "stock solution" was prepared starting with ca. 20 g of Re_2O_7 (Alfa Inorganics) which was dissolved in 200 mL of pure water and filtered to remove small amounts of ReO_2 initially present. This solution was neutralized with a slight excess of 2.3 N KOH solution, and $KReO_4$ was precipitated by cooling the mixture to 0 °C. After two recrystallizations, the $KReO_4$ was dissolved in pure water and converted to a $HReO_4$ solution by passage through a deep bed of a strong-acid cation exchanger in the hydrogen form.

The $HTcO_4$ and $HReO_4$ solutions were tested for purity by measurement of their UV and visible absorption spectra with a Cary 14P recording spectrophotometer. Peak frequencies, absorbancy ratios, and molar absorbancies determined with dilute solutions of accurately known concentration were in good agreement with literature values.[10,11]

Analysis of Stock and Reference Solutions. The approximately 1 M stock solutions of $HClO_4$, $HTcO_4$, and $HReO_4$ were analyzed gravimetrically by precipitation with recrystallized reagent grade (G. F. Smith Chemical Co.) tetraphenylarsonium chloride following published procedures.[12,13] Final concentrations precise to better than 0.1% were based on triplicate analyses. The sodium chloride reference solution with which the acid solutions were compared was prepared from "Baker Analyzed" reagent previously dried in air at 110 °C. The concentration of these solutions was determined by triplicate analyses to a precision of better than 0.1% by precipitation of AgCl and weighing after drying at 120 °C. The water employed in the preparation of the reference solution and in all the dilutions of the acid solutions was laboratory distilled water which had been redistilled from quartz.

Isopiestic Apparatus and Procedure. The gravimetric isopiestic vapor pressure comparison apparatus and the procedure employed have been described.[14] The temperature of the large water bath in which the units were rocked to obtain vapor pressure equilibrium was maintained at 25.00 ± 0.01 °C for long periods of time. In each of the six series of equilibrations at least two and usually three platinum dishes holding solutions with approximately the same mass of solute but initially different masses of water were placed in the apparatus so that equilibrium would be approached from higher and lower initial concentrations. The criterion for isopiestic equilibrium was the agreement in the molalities of the replicate solutions to ±0.1%.

A basic assumption in the isopiestic method is that the solute is nonvolatile. However, the heptoxides of both technetium and rhenium are known to be volatile at elevated temperatures. Using the published[15] vapor pressure data for Tc_2O_7, a pressure at room temperature of ca. 10^{-6} Torr may be estimated for the solid and 10^{-3} Torr for the liquid. Corresponding pressures for Re_2O_7(s) and Re_2O_7(l) estimated for literature data[14] are 10^{-9} and 10^{-4} Torr, respectively. Loss of solute by volatilization from the $HTcO_4$ and $HReO_4$ solutions during the time for the attainment of vapor pressure equilibrium with the most concentrated solutions was considered to be negligible.

Results and Treatment of Data

A summary of the isopiestic molalities of the reference sodium chloride solution, m_{ref}, with those of $HClO_4$, $HTcO_4$,

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Table I. Isopiestic Molalities for Binary Solutions of $HClO_4$, $HTcO_4$, and $HReO_4$ at 25 °C

m_{ref}	m_{HClO_4}	m_{HTcO_4}	m_{HReO_4}
0.105 22	0.104 40	0.105 81	0.105 05
0.105 83	0.105 10	0.106 23	0.105 74
0.107 71	0.106 18	0.107 84	0.107 72
0.208 19	0.204 28	0.208 55	0.208 04
0.210 22	0.207 12	0.210 83	0.210 43
0.218 01	0.212 25	0.217 59	0.218 40
0.364 33	0.349 95	0.362 55	0.364 39
0.546 89	0.515 69	0.542 09	0.546 24
0.754 57	0.698 35	0.743 00	0.750 09
1.057 6	0.954 92		1.040 4
1.095 8	0.987 36		1.079 6
2.560 7	2.115 7		2.386 2
3.137 9		2.817 6	2.867 0
5.142 5	3.885 2	4.255 5	4.454 2
6.122 8	4.503 5	4.890 7	5.189 4
a	5.062 7	5.440 4	5.861 2
b	7.249 2		8.599 3

[a] Saturated $SrCl_2 \cdot 6H_2O$ solution. [b] Saturated $Mg(NO_3)_2 \cdot 6H_2O$ solution.

Table II. Parameters in Eq 2 for the Concentration Dependence of the Osmotic Coefficients of Pure Binary Aqueous NaCl, $HClO_4$, $HTcO_4$, and $HReO_4$ Solutions

	NaCl	$HClO_4$	$HTcO_4$	$HReO_4$
α	1.5^a	1.5^a	1.5^a	1.5^a
$a^{(1)}$	0.0377	0.1234	−0.0030	0.0105
$a^{(2)}$	0.0208	0.0142	0.0866	0.0347
$a^{(3)}$	−0.0013	−0.000211	−0.0271	−0.0035
$a^{(4)}$	0.0^a	0.0^a	0.0030	0.00012
$\sigma(\phi)$	0.0007	0.0021	0.0025	0.0015
m_l/mol kg^{-1}	0.0	0.0	0.0	0.0
m_u/mol kg^{-1}	6.0	4.5	5.4	8.6

[a] Fixed at value shown; not varied.

and $HReO_4$ is given in Table I. All equilibrium solutions were colorless except that for $HTcO_4$ at $m = 5.44$ which was pink and that for $HReO_4$ at $m = 8.6$ which was pale yellow.

Osmotic coefficients ϕ_x for the acid solutions were estimated from the condition for isopiestic equilibrium (i.e., equal vapor pressure):

$$\nu_r m_r \phi_r = \nu_x m_x \phi_x \tag{1}$$

where ν_r and ν_x are the number of ions formed per molecule of sodium chloride and acid, respectively, m_r and m_x are the isopiestic molalities, and ϕ_r is the osmotic coefficient (known) of the reference electrolyte solution at concentration m_r. The required values for ϕ_r at 25 °C were interpolated to 0.0001 from a semiempirical equation[17] consisting of a Debye–Hückel term plus a polynomial in the molality m (eq 2) which was

$$\phi = 1 - \frac{S}{\alpha^3 m}\sigma(\alpha m) + a^{(1)}m + a^{(2)}m^2 + a^{(3)}m^3 \tag{2}$$

fitted to tabulated data for NaCl[18] using a nonlinear least-squares procedure. The osmotic coefficients for the acid solutions derived using eq 1 also were fitted to eq 2. A summary of the values for the parameters of eq 2 obtained with the data for the four electrolytes employed in this research is given in Table II together with the standard deviation of the fit $\sigma(\phi)$ and the concentration interval. The standard deviation is defined as $\sigma(\phi) = \{\sum d^2/(n-k)\}^{1/2}$ where d is the deviation, n, the number of observations, k, the number of disposable parameters, and the summation is over all observations.

Mean molal activity coefficients $\gamma_\pm$ may be computed from the equation

$$\ln \gamma_\pm = -S(m)^{1/2}/(1 + \alpha(m^{1/2})) + 2a^{(1)}m + {}^3/_2 a^{(2)}m^2 + {}^4/_3 a^{(3)}m^3 \tag{3}$$

Table III. Osmotic and Activity Coefficients for Aqueous $HTcO_4$ and $HReO_4$ Solutions at 25 °C

	$HTcO_4$		$HReO_4$	
Molality	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$
0.1	0.9321	0.778	0.9329	0.779
0.2	0.9321	0.732	0.9329	0.735
0.3	0.9212	0.709	0.9212	0.709
0.4	0.9228	0.694	0.9214	0.694
0.5	0.9268	0.685	0.9234	0.683
0.6	0.9325	0.680	0.9267	0.676
0.7	0.9396	0.678	0.9310	0.672
0.8	0.9477	0.679	0.9361	0.669
0.9	0.9566	0.681	0.9421	0.669
1.0	0.9663	0.685	0.9487	0.669
1.2	0.9874	0.696	0.9636	0.674
1.4	1.010	0.712	0.9808	0.682
1.6	1.033	0.731	0.9998	0.695
1.8	1.057	0.752	1.020	0.710
2.0	1.081	0.776	1.043	0.728
2.5	1.138	0.842	1.104	0.787
3.0	1.195	0.918	1.172	0.863
3.5	1.254	1.009	1.245	0.958
4.0	1.326	1.126	1.321	1.074
4.5	1.423	1.296	1.400	1.212
5.0	1.564	1.570	1.479	1.375
5.5	1.771	2.057	1.559	1.565
6.0	···	···	1.639	1.784
7.0	···	···	1.794	2.327
8.0	···	···	1.943	3.034

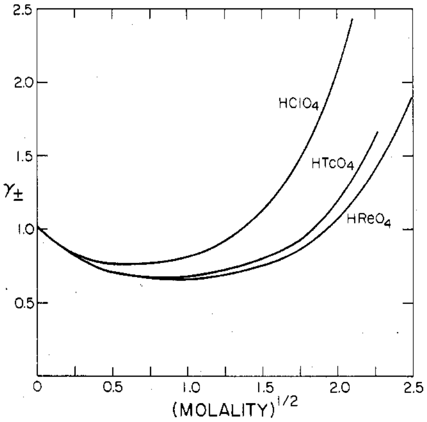

Figure 1. Concentration dependence of the mean molal ionic activity coefficients for aqueous binary solutions of $HClO_4$, $HTcO_4$, and $HReO_4$ at 25 °C.

which results on applying the Gibbs–Duhem equation to eq 2. Values of ϕ and $\gamma_\pm$ for $HTcO_4$ and $HReO_4$ interpolated with eq 2 and 3 for selected concentrations are presented in Table III.

An indication of the reliability of the osmotic coefficients measured in this investigation was obtained by comparing the values for $HClO_4$ solutions interpolated with eq 2 and the parameters of Table II with those given by Robinson and Stokes[19] over the same concentration range. Agreement with an average deviation of 0.002 without regard to sign and a maximum deviation of 0.005 was observed.

It should be noted that eq 2 and 3 are suitable for use in the prediction of osmotic and activity coefficients for $HTcO_4$ and $HReO_4$ in electrolyte mixtures at 25 °C using either the "neutral-electrolyte" or the "ion-component" treatment of Scatchard.[7]

Discussion

A plot (Figure 1) of the concentration dependence of the mean ionic activity coefficient values for $HClO_4$, $HTcO_4$, and $HReO_4$ shows that the curves for the latter two acids fall distinctly below that for $HClO_4$ for all concentrations above

0.1 *m*, while that for $HReO_4$ drops below $HTcO_4$ at a somewhat larger concentration. The general similarity of the curves in Figure 1 is consistent with Raman line intensity measurements which indicate all three acids to be completely ionized to concentrations as high as 7 M. At higher concentrations, however, there appears to be evidence that condensation and hydration equilibria become increasingly important. The coloration of concentrated $HTcO_4$ and $HReO_4$ solutions suggest such changes or the formation of undissociated acid. With concentrated perrhenic acid the latter possibility appears to be excluded by qualitative Raman studies conducted by Ulbricht et al.[20] In addition to the known band frequencies at 972, 919, 367, and 330 cm^{-1} in $HReO_4$ solutions of 16 and 24 *m*, a new band at 850–854 cm^{-1} appears which may be assigned to a stretching mode of Re–O–Re. Condensation in acid pertechnetate and perrhenate solutions is known to occur, as dark red $Tc_2O_7 \cdot H_2O$ and yellow $Re_2O_7 \cdot 2H_2O$, respectively, are formed from them by evaporation.[21,22]

Registry No. $HClO_4$, 7601-90-3; $HTcO_4$, 14332-45-7; $HReO_4$, 13768-11-1.

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Correlations of Solvent-Exchange Activation Enthalpies

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The kinetics of solvent exchange on an $L_5Ni(solvent)^{2+}$ system, where L_5 is a five-coordinate Schiff base ligand, have been measured in *N,N*-dimethylformamide and acetonitrile, by proton NMR methods. These systems are compared to the corresponding $Ni(solvent)_6{}^{2+}$ complexes in order to assess the kinetic effect of the coordinated solvent molecules. Contrary to previous proposals it appears that the basicity of the solvent, as measured by Gutmann's donor numbers, does not have a significant influence on the solvent-exchange rates. A correlation of the activation enthalpy for exchange and crystal field and solvation effects is proposed.

Introduction

A correlation of the activation enthalpy for solvent exchange ($\Delta H^{\ddagger}_{\mathrm{ex}}$) and solvent basicity has been proposed recently.[1] This correlation was based on the idea[2,3] that, if the mechanism is dissociative, i.e.

$$S_5MS^{2+} \rightarrow \{S_5M\} + S \xrightarrow{*S} S_5M{*}S \tag{1}$$

then, $\Delta H^{\ddagger}_{\mathrm{ex}} \propto$ (acidity of S_5M) × (basicity of S) and (acidity of S_5M) $\propto$ (acidity of M^{2+}) − (basicity of S). If the solvent basicity is proportional to the Gutmann donor number (D_N), then

$$\Delta H^{\ddagger}_{\mathrm{ex}} = aD_N - bD_N{}^2 \tag{2}$$

where *a* and *b* are empirical fitting constants depending on M^{2+}. This equation was found to satisfactorily correlate 20 out of 23 available experimental values for nickel(II), cobalt(II), iron(II), and manganese(II).

The validity of the assumptions leading to eq 2 has not been tested, however. The present study presents such a test by studying solvent exchange on an (L_5NiS^{2+}) type complex, where L_5 is a nonexchanging Schiff base ligand.[4] The relationships leading to eq 2 imply that the Lewis acidity of (L_5Ni^{2+}) should be independent of solvent since the acid contains no solvent molecules. Then it is predicted that

$$\Delta H^{\ddagger}_{\mathrm{ex}} \propto D_N \tag{3}$$

Two solvents, acetonitrile and *N,N*-dimethylformamide (DMF), have been studied because they have quite different and well-established D_N values (14.1 and 26.6, respectively). Therefore $\Delta H^{\ddagger}_{\mathrm{ex}}$ in DMF is predicted to be almost twice as large as in acetonitrile.

Experimental Section

Materials. The $[Ni(pyDPT)OH_2](BF_4)_2$ and $[Ni(pyDPT)OH_2](PF_6)_2$ salts, where pyDPT represents the pentadendate ligand derived from 2-pyridinecarboxaldehyde and bis(3,3′-aminopropyl)amine, were prepared by minor modifications of the method described by Spencer and Taylor.[4] Each compound was recrystallized twice from warm water. Anal. Calcd for $[Ni(pyDPT)OH_2](BF_4)_2$: C, 38.62; H, 4.50; N, 12.51. Found: C, 38.71; H, 4.55; N, 12.76. Calcd for $[Ni(pyDPT)OH_2](PF_6)_2$: C, 31.98; H, 3.73; N, 10.36. Found: C, 31.82; H, 3.75; N, 10.28. The compounds were characterized also

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