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Conductivity of D_2O and Micromolar DNO_3 in D_2O from 0 to 100 °C

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Electrical conductivity values for D_2O and for dilute nitric acid in D_2O from 0 to 100 °C were calculated using literature values of ionic and molar conductances, dissociation constants, densities, and viscosities. The concentration of DNO_3 covered the pD *(15)* range of 4.5–7.4 at 25 °C. Computations were validated by the agreement between calculated conductivities of the DNO_3 system at pD 7.4 (near-neutral) and those for D_2O. Walden's rule was only marginally followed, as would be expected for solvated anions and cations.

Introduction

Heavy water (D_2O) is commonly used as a moderator for neutrons in nuclear systems. The chemical quality of this heavy water is determined by measuring its electrical conductivity.

In the production reactors at the Savannah River Site, heavy water serves as both coolant and moderator in the primary system. Because of aluminum components in the system, the water is maintained slightly acidic with nitric acid to minimize aluminum corrosion *(1)*. The water is normally maintained at pD *(15)* 5.0–5.2 at 25 °C, with an allowable range of 4.5–7.4. Other ionic impurities are minimal, so that conductivity and pD serve as good indicators of the chemical quality of the water. Online conductivity measurements serve as a primary control of the water chemistry.

Conductivity values up to 100 °C for D_2O and for the nitric acid system were needed for moderator studies and for interpretation of process parameters. Data in the literature for electrical conductivities in D_2O are meager, and most of the reported values are near room temperature.

This work reports conductivities of D_2O and of DNO_3 in D_2O from 0 to 100 °C for solutions in the pD range 4.5–7.4 at 25 °C. Quadratic fits of literature values for ionic and molar conductances, dissociation constants, and densities in H_2O and D_2O were used in physicochemical calculations.

Discussion

Description of Calculations. This section describes the rationale and derivations for the calculations. Definitions of parameters and the equations fitted to the literature data for use in the calculations are given in the Glossary and in the Appendix.

Conductivity. Conductivity κ was calculated from the equation

$$\kappa = \sum \lambda_i c_i \tag{1}$$

where λ_i is the molar ionic conductance of species i and c_i is the concentration of species i. The volume-based concentration unit c_i was not suited for temperature studies and was replaced by the weight-based unit m_i. For dilute solutions m_i is related to concentration c_i by

$$c_i = m_i \rho \tag{2}$$

where ρ is the density of the solvent. The solvent was D_2O.

The conductivity defined in eq 1 was converted to molality concentration units and applied to the D_2O–DNO_3 system, as shown in the Appendix to produce eq A1. Evaluation of the temperature-dependent terms ρ, λ_{D^+}, λ_{OD^-}, $\lambda_{NO_3^-}$, and m_{D^+} is described below.

Density. The density–temperature relationship was calculated from a combination of two sets of density data for D_2O. One set *(2)* covered the temperature range 5–70 °C and the other *(3)* the range 20–100 °C. Values at the same temperature in both sets were averaged. The equation for the quadratic fit of the combined data is given in eq A3.

Ionic and Molar Conductances. Conductances of D_2O, D^+, and OD^-. Incomplete data for the D_2O system were supplemented by assuming that the D_2O system and H_2O system show similar overall behavior. Quadratic fits were made for the conductances Λ_{H_2O}, λ_{H^+}, and λ_{OH^-} from 0 to 100 °C *(4)*. The equations are eqs A4, A5, and A6.

Because ionic conductances are additive, the data of Gierer *(5)* were used to calculate (Λ_{D_2O}) from 5 to 95 °C by summing the molar conductances as follows:

$$\Lambda_{DCl} + \Lambda_{NaOD} - \Lambda_{NaCl} = \lambda_{D^+} + \lambda_{OD^-} = \Lambda_{D_2O} \tag{3}$$

The quadratic fit of the calculated conductance values gave eq A7 for Λ_{D_2O} as a function of temperature. The fitted curve and the data points are included in Figure 1.

The ionic conductances of D^+ and OD^- were computed by assuming that their behavior with temperature would be the same as for H^+ and OH^-. The fits of the literature data in H_2O demonstrated that coefficients of the linear and quadratic temperature (t/°C) terms for λ_{H^+} and λ_{OH^-} are additive, giving the corresponding coefficients in the Λ_{H_2O} (i.e., $\lambda_{H^+} + \lambda_{OH^-}$) equation. Coefficients for the D^+ and OD^- equations were derived by assuming that they too are additive and proportioned like the H_2O system. Defining these coefficients determined the shape of the curve, but did not determine the constants A_{D^+} and A_{OD^-} of eqs A8a and A9a.

Values of the constants were assigned from literature values of λ_{D^+} and λ_{OD^-} at 25 °C. For λ_{D^+} this work uses a recently reported value *(6)* of 249.9 $S \cdot cm^2 \cdot mol^{-1}$ at 25 °C. Equation A8b describes λ_{D^+} as a function of temperature. For λ_{OD^-} in D_2O at 25 °C, the best value of 116.8 $S \cdot cm^2 \cdot mol^{-1}$, obtained by averaging the values of Gierer *(5)* and Hetland *(7)*, was used. Equation A9b describes λ_{OD^-} in D_2O as a function of temperature. Figure 1 shows the curves for λ_{D^+} and λ_{OD^-} calculated by eqs A8b and A9b.

The validity of separating the coefficients of the Λ_{D_2O} equation to obtain λ_{D^+} and λ_{OD^-} curves was confirmed through another approach that independently produced a set of λ_{D^+} and λ_{OD^-} values from 0 to 95 °C. Since ionic conductances

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Table I. Conductivity κ of D_2O and DNO_3 in D_2O from 0 to 100 °C at Various pD Values

	$\kappa/(10^{-6}$ S cm$^{-1})$							
	4.5[a]	5.0	5.5	6.0	6.5	7.0	7.4	$[D^+] = [OH^-]$
t/°C	2.86×10^{-5} [b]	9.05×10^{-6}	2.86×10^{-6}	9.04×10^{-7}	2.83×10^{-7}	7.87×10^{-8}	6.38×10^{-9}	0
0	5.79	1.83	0.579	0.183	0.0572	0.0162	0.00315	0.00250
5	6.60	2.09	0.660	0.208	0.0653	0.0188	0.00437	0.00365
10	7.40	2.34	0.740	0.234	0.0733	0.0214	0.00598	0.00520
15	8.19	2.59	0.819	0.259	0.0814	0.0244	0.00807	0.00724
18	8.67	2.74	0.867	0.274	0.0863	0.0263	0.0096	0.00874
20	8.98	2.84	0.898	0.284	0.0896	0.0277	0.0108	0.0099
25	9.76	3.09	0.976	0.309	0.0978	0.0316	0.0142	0.0132
30	10.5	3.33	1.05	0.333	0.106	0.0362	0.0185	0.0175
35	11.3	3.57	1.13	0.357	0.115	0.0418	0.0237	0.0227
40	12.0	3.80	1.20	0.382	0.124	0.0484	0.0302	0.0290
45	12.8	4.04	1.28	0.406	0.134	0.0564	0.0379	0.0367
50	13.5	4.27	1.35	0.430	0.145	0.0658	0.0471	0.0458
55	14.2	4.49	1.42	0.454	0.157	0.0769	0.0578	0.0565
60	14.9	4.71	1.49	0.479	0.171	0.0896	0.0703	0.0689
65	15.6	4.93	1.56	0.504	0.186	0.104	0.0845	0.0831
70	16.3	5.14	1.63	0.529	0.203	0.121	0.101	0.0991
75	16.9	5.35	1.70	0.555	0.221	0.139	0.119	0.117
80	17.6	5.56	1.77	0.582	0.241	0.159	0.138	0.137
85	18.2	5.76	1.83	0.610	0.263	0.181	0.160	0.158
90	18.8	5.96	1.90	0.638	0.287	0.204	0.182	0.181
95	19.4	6.15	1.96	0.667	0.312	0.229	0.206	0.205
100	20.0	6.34	2.02	0.697	0.338	0.254	0.231	0.230

[a] This row gives the values of pD(25 °C). pD = $-[\log$ (moles of D^+/liter)]. [b] This row gives the values of $m_{NO_3^-}$. $m_{NO_3^-}$ = moles of NO_3^-/1000 g of D_2O.

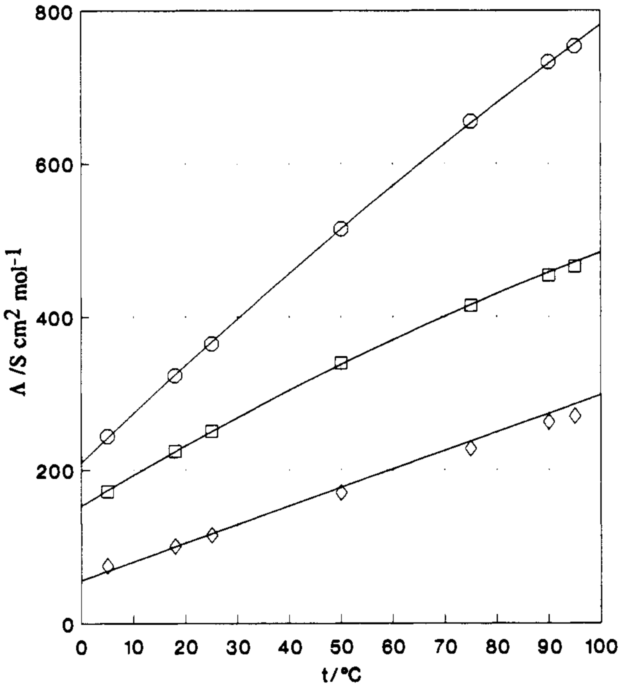

Figure 1. Ionic and molar conductances in D_2O: variation with temperature. Lines are quadratic fits. Symbols are ○, D_2O, calculated values used for the fit; ◇, OD^-, and □, D^+, individual values calculated independent of fit (see text).

are additive, the following relationships from the Gierer (*5*) data were derived:

$$\Lambda_{DCl} - \Lambda_{NaCl} = \lambda_{D^+} - \lambda_{Na^+} \tag{4}$$

$$\Lambda_{NaOD} - \Lambda_{NaCl} = \lambda_{OD^-} - \lambda_{Cl^-} \tag{5}$$

λ_{D^+} and λ_{OD^-} were then calculated by adding the respective values of λ_{Na^+} and λ_{Cl^-} in D_2O, which were determined as follows. First, values at different temperatures in H_2O (*8, 9*) were fitted to determine the shapes of the curves; it was assumed the curves in D_2O would be similar to those in H_2O. Then intercepts were defined by literature data for λ_{Cl^-} and λ_{Na^+} in D_2O at 25 °C (*10*). From the resulting equations λ_{Cl^-} and λ_{Na^+} were determined at the appropriate temperatures and used in eqs 4 and 5 to calculate λ_{D^+} and λ_{OD^-}.

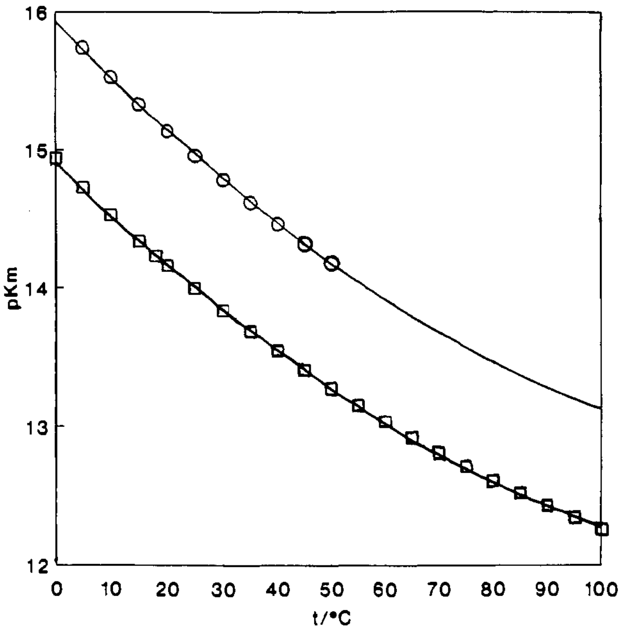

Figure 2. Literature and fitted pK_m for H_2O and D_2O: variation with temperature. Lines are quadratic fits. Symbols are experimental values: □, H_2O (*4*); ○, D_2O (*11*).

The individual values calculated for λ_{D^+} and λ_{OD^-} are included in Figure 1. The agreement for D^+ with the calculated curve is excellent; that for OD^- is less good, but the difference is still only about 5% at higher temperatures where the major disagreement occurs.

Conductance of NO_3^-. To determine the value of $\lambda_{NO_3^-}$ in D_2O at 25 °C, it was assumed the behavior would be the same in D_2O as in H_2O. Therefore, the H_2O data (*8, 9*) were fitted by a quadratic equation. The value of the intercept was calculated as follows. Swain and Evans (*10*) report that λ_{Cl^-} in D_2O at 25 °C is 62.83 S·cm^2·mol^{-1} and that the ratio of λ_i values in D_2O and H_2O is the same for a number of ions.

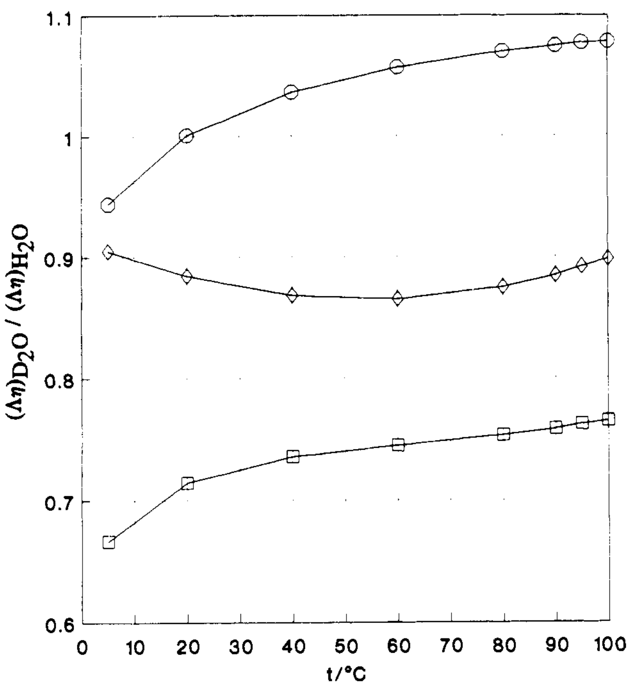

Figure 3. Application of Walden's rule. Ratios of ionic conductivity-viscosity products in D_2O and H_2O for ○, NO_3^-/NO_3^-; ◇, D^+/H^+; and □, OD^-/OH^-.

Assuming this constancy holds for NO_3^- and that NO_3^- and Cl^- behave similarly

$$[\lambda_{NO_3^-}/\lambda_{Cl^-}](D_2O) = [\lambda_{NO_3^-}/\lambda_{Cl^-}](H_2O) \qquad (6)$$

so that $\lambda_{NO_3^-}(D_2O)(25°C) = 62.83(71.46/76.35) = 58.8$ $S\cdot cm^2\cdot mol^{-1}$. Equation A10 describes $\lambda_{NO_3^-}$ in D_2O as a function of temperature.

Dissociation Constant. The molal concentrations of D^+ and OD^- must satisfy the dissociation constant for D_2O, K_m, at all temperatures. The only values found for $K_m(D_2O)$ were from 0 to 50 °C (*11*), but values for H_2O from 0 to 100 °C were available (*4*). The $pK_m(H_2O)$ from 0 to 100 °C and the ratios of $[pK_m(D_2O)]/[pK_m(H_2O)]$ from 0 to 50 °C were fitted to quadratic equations. The D_2O data were then extended to 100 °C by assuming that the relationship for the ratio would apply up to 100 °C. This ratio equation was multiplied by the quadratic fit of the $pK_m(H_2O)$ values, to give $pK_m(D_2O)$ from 0 to 100 °C, eq A12. Literature values and the fitted values of pK_m for H_2O and D_2O are shown in Figure 2.

Calculation of Ionic Concentrations. The concentration of NO_3^- was determined from the pD at 25 °C. The volume-based unit defined by pD was converted to the weight-based unit m_{D^+} by dividing by the solvent density at 25 °C, eq A13. With the reference m_{D^+} at 25 °C defined, the value of $m_{NO_3^-}$ was calculated from the requirement of electrical neutrality for the system. Equation A14 includes K_m, which defines the relationship between m_{D^+} and m_{OD^-} at 25 °C. $m_{NO_3^-}$ will be the same at all temperatures, whereas m_{D^+} and m_{OD^-} will be governed by K_m, which changes with temperature. With $m_{NO_3^-}$ defined, the value of m_{D^+} at each temperature was determined by solving the resulting quadratic equation for m_{D^+}, eq A15.

Results

The conductivity as a function of temperature was calculated by eq A1 for solutions defined by pD at 25 °C. Conductivity values from 0 to 100 °C are summarized in Table I for nitric acid solutions from pD 4.5 to pD 7.4 (at 25 °C) and for D_2O. The calculated conductivities for the DNO_3 system approach those of D_2O as the pD approaches the near-neutral point of 7.4.

The classical Walden rule (*12*) was applied as a conventional test, even though it is generally considered applicable for ions where solvation is limited. Conductances were those calculated for D^+, OD^-, and NO_3^-; viscosities for D_2O were taken from the literature (*13*). The results plotted in Figure 3 show that D^+/H^+ values are fairly constant over the temperature range; the OH^-/OD^- and the NO_3^-/NO_3^- ratios are less constant. It is not surprising that Walden's rule applies only marginally well for these small solvated ions.

The values for the limiting molar conductances in $S\cdot cm^2\cdot mol^{-1}$ at 25 °C for D^+ (249.9) and NO_3^- (58.8) were chosen individually for this work as "best values". The validity of the choices is substantiated by the sum, 308.7, which is very close to the experimental limiting molar conductance of 308 $S\cdot cm^2\cdot mol^{-1}$ for DNO_3 at 25 °C measured earlier (*14*).

Glossary

SEE	standard error of estimate $[=[\sum(y - y_{fit})^2/n]^{1/2}$, where y is the dependent variable, known and calculated, for n values]
κ	conductivity
ρ	density
λ_i,Λ_i	ionic or molar conductance of species i
t	temperature
A_j	constants in eqs A9 and A10 for species j
K_m	dissociation constant, $K_m(D_2O) = m_D m_{OD}$
pK_m	$-[\log K_m]$
c	concentration, M
m	molality

Appendix

Definitions and Derivations

A. Conductivity, κ

1. $\kappa(D_2O)/(10^{-6}\ S\ cm^{-1}) =$

$$1000\rho[\lambda_{D^+}m_{D^+} + \lambda_{OD^-}m_{OD^-} + \lambda_{NO_3^-}m_{NO_3^-}]$$

$$= 1000\rho[(\lambda_{D^+} + \lambda_{OD^-})(m_{D^+}) + (\lambda_{NO_3^-} - \lambda_{OD^-})(m_{NO_3^-})] \quad (A1)$$

$$\text{since } m_{D^+} = m_{OD^-} + m_{NO_3^-} \quad (A2)$$

B. Density, ρ

1. $\rho(D_2O)/(g\ cm^{-3}) = 1.10622 + 0.00001624(t/°C) - 0.000004509(t/°C)^2$ (A3)

SEE = 0.0005

C. Ionic and Molar Conductances, λ, Λ

1. $\Lambda_{H_2O}/(S\ cm^2\ mol^{-1}) = \lambda_{H^+} + \lambda_{OH^-}$

$$= 336.261 + 9.0571(t/°C) - 0.01663(t/°C)^2 \quad (A4)$$

SEE = 2.6

2. $\lambda_{H^+}/(S\ cm^2\ mol^{-1}) = 220.582 + 5.6572(t/°C) - 0.01608(t/°C)^2$ (A5)

SEE = 1.6

3. $$\lambda_{OH^-}/(\mathrm{S\ cm^2\ mol^{-1}}) = 115.645 + 3.4013(t/°\mathrm{C}) - 0.0005625(t/°\mathrm{C})^2 \quad \text{(A6)}$$

$$\mathrm{SEE} = 1.0$$

4. $$\Lambda_{D_2O}/(\mathrm{S\ cm^2\ mol^{-1}}) = \lambda_{D^+} + \lambda_{OD^-}$$
$$= \Lambda_{NaOD} + \Lambda_{DCl} - \Lambda_{NaCl}$$
$$= 209.3599 + 6.4861(t/°\mathrm{C}) - 0.007666(t/°\mathrm{C})^2 \quad \text{(A7)}$$

$$\mathrm{SEE} = 2.0$$

5. $$\lambda_{D^+}/(\mathrm{S\ cm^2\ mol^{-1}}) = A_{D^+} + 4.506(t/°\mathrm{C}) - 0.007407(t/°\mathrm{C})^2 \quad \text{(A8a)}$$

$$= 249.9 + 3.6802(t/°\mathrm{C} - 25) - 0.007407(t/°\mathrm{C} - 25)^2 \quad \text{(A8b)}$$

6. $$\lambda_{OD^-}/(\mathrm{S\ cm^2\ mol^{-1}}) = A_{OD^-} + 2.4355(t/°\mathrm{C}) - 0.0002591(t/°\mathrm{C})^2 \quad \text{(A9a)}$$

$$= 116.8 + 2.4226(t/°\mathrm{C} - 25) - 0.0002591(t/°\mathrm{C} - 25)^2 \quad \text{(A9b)}$$

7. $$\lambda_{NO_3^-}(D_2O)/(\mathrm{S\ cm^2\ mol^{-1}}) = 58.8 + 1.2632(t/°\mathrm{C} - 25) + 0.003554(t/°\mathrm{C} - 25)^2 \quad \text{(A10)}$$

D. Dissociation Constant

1. $$\mathrm{p}K_m(H_2O) = 14.90854 - 0.039193(t/°\mathrm{C}) + 0.00012963(t/°\mathrm{C})^2 \quad \text{(A11)}$$

$$\mathrm{SEE} = 0.012$$

2. $$\mathrm{p}K_m(D_2O) = [\mathrm{p}K_m(H_2O)](1.068848 - 0.000009060(t/°\mathrm{C}) - 0.00000000298(t/°\mathrm{C})^2 \quad \text{(A12)}$$

$$\mathrm{SEE} = 0.011$$

E. Calculation of Ionic Concentrations

1. $$\mathrm{pD}(25\ °\mathrm{C}) = -[\log (m_{D^+}/\rho_{25})]$$
$$= -[\log m_{D^+}] - [\log 1.1044]$$

$$\text{so that } m_{D^+}(25\ °\mathrm{C}) = 10^{-\mathrm{pD}}/1.1044 \quad \text{(A13)}$$

2. $$m_{NO_{38^-}} = m_{D^+} - m_{OD^-}$$

$$= m_{D^+} - [K_m(D_2O)]/m_{D^+} \quad \text{(A14)}$$

$$= \text{constant value for given pD at 25 °C}$$

3. $$m_{D^+} = {}^1/_2\{m_{NO_3^-} + (m_{NO_3^-}{}^2 + 4[K_m(D_2O)]^{1/2}\} \quad \text{(A15)}$$

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(15) pD is defined as the negative logarithm of the deuterium ion activity; for the micromolar concentrations of nitric acid in this paper, the molarity is assumed to be the same as the activity.

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