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Interdiffusion Coefficients, Densities, and Viscosities of $KNO_2 + H_2O$ and $KClO_3 + H_2O$ at 25 °C

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Interdiffusion coefficients of the systems $KNO_2 + H_2O$ and $KClO_3 + H_2O$ at 25 °C were measured by free-diffusion optical-interferometric methods from low concentrations to near saturation. Density and viscosity data were also obtained for these systems. Low concentration conductance data were obtained for the $KNO_2 + H_2O$ system at 25 °C for calculation of the limiting molar conductance of the NO_2^- ion. The diffusion coefficients of $KClO_3 + H_2O$ dropped over the whole concentration range as concentration increased. This was similar to the concentration dependence in the same concentration range for $KNO_3 + H_2O$ and $KHCO_3 + H_2O$ at 25 °C. The diffusion coefficients of the system $KNO_2 + H_2O$ initially dropped, plateaued, and dropped again as concentration increased. The diffusion results were compared to data of other potassium salts.

Introduction

This paper represents a continuation of the study of the diffusion properties of potassium salts with various anions (*1–3*). Presented in this paper are values of the diffusion coefficients of binary solutions of KNO_2 and $KClO_3$ in water at 25 °C. Also included are values of viscosity and densities of the binary salt solutions. It had been found that the salts $KHCO_3$ and KNO_3 have diffusion coefficients that decrease sharply as concentration increases, whereas the diffusion coefficients for the potassium halides and KSCN go through a minimum and then increase as concentration increases. For KSCN at very high concentrations the diffusion coefficients go through a maximum and then decrease. As was anticipated, the concentration dependence of the diffusion coefficients of KNO_2 was found to be between that of KNO_3 and the potassium halides. The concentration dependence of the diffusion coefficients of $KClO_3$ over its relatively short range of solubility was similar to that of KNO_3 and $KHCO_3$.

Experimental Section

Materials. Fluka KNO_2 (assay > 98.0%) was used without further purification for all experiments. The molar mass was assumed to be 85.11 g mol^{-1}. Two stock solutions of $KNO_2 + H_2O$ were prepared, filtered, and used for all experiments. Concentrations of the stock solutions were determined by drying three preweighed samples of the solutions at 120 °C in a vacuum oven. For each stock, one of the dried samples was heated to 600 °C to convert it to potassium oxide. It was further converted to the chloride by addition of concentrated HCl solution. It was then dried and weighed. Agreement between the concentrations determined according to the two methods was within ±0.1%. The molarities of the stock solutions were 5.887 and 10.857 M. The first was used to prepare solutions in the concentration range 0–5.887 M, and the latter stock was used for solutions in the range above 5.887 M.

Mallinckrodt analytical reagent grade $KClO_3$ (assay 99.6%) was used without further purification for all experiments. The molar mass was assumed to be 122.55 g mol^{-1}. A stock solution was prepared for all experiments and measurements. The concentration of the stock solution was determined by drying three weighed samples of solution at 120 °C in a vacuum oven. Agreement among the samples was ±0.1%. One of the dried samples was heated to 600 °C to convert it to potassium chloride and then weighed. This analysis agreed with the first analysis within ±0.1%. The concentration of the stock solution was 0.598 M.

Measurements. Diffusion measurements were made with a Beckman-Spinco Model H electrophoresis diffusion instrument operating in the Rayleigh optical-interferometric mode. This instrument had a magnification factor of 1.0017. Its light source was the 546.07 nm "green line" from a mercury vapor lamp with filters. The experimental procedures have been previously described by Albright et al. (*1*). The inside dimension of the diffusion cell along the optic axis was 2.490 cm. Fringe patterns were recorded on 4 × 5 in. photographic glass plates. These were either Kodak Technical Pan or Tmax-100 plates. An $x-y$ scanner that was interfaced to a computer was used to measure fringe positions in the Rayleigh fringe patterns. Diffusion coefficients were calculated from fringe positions by using equations for the free diffusion of a binary system with a constant diffusion coefficient. At low concentrations these calculated coefficients were corrected for the concentration dependence of the diffusion coefficients and refractive index by using equations given by Miller and Albright (*4*). At 0.0494 and 0.1694 M KNO_2 the diffusion coefficients of 0.18305×10^{-9} and 1.7847×10^{-9} m^2 s^{-1} were corrected to 1.8194×10^{-9} and 1.7840×10^{-9} m^2 s^{-1}, respectively. At 0.0508 and 0.1504 M $KClO_3$ the diffusion coefficients of 1.6875×10^{-9} and 1.6324×10^{-9} m^2 s^{-1} were corrected to 1.6839×10^{-9} and 1.6254×10^{-9} m^2 s^{-1}, respectively.

Density measurements were made with a Mettler/Parr DMA 40 density meter that is interfaced to a computer for time averaging. A precision of $\pm 2.0 \times 10^{-5}$ g cm^{-3} was obtained. The temperature of the density meter was regulated at (25.00 ± 0.01) °C by circulating water from a large well-regulated water bath. The meter was calibrated with air and water where the density of air-saturated water was assumed to be 0.997045 g cm^{-3}.

Viscosity measurements were made with an Ostwald type viscometer. It was mounted in a large water bath that was regulated at (25.00 ± 0.01) °C. The viscosity was equated to flow time, t, and density, d, by the equation,

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Table 1. Densities of $KNO_2 + H_2O$ Solutions at 25 °C

c/ (mol dm^{-3})	d/ (g cm^{-3})	c/ (mol dm^{-3})	d/ (g cm^{-3})	c/ (mol dm^{-3})	d/ (g cm^{-3})
0.0988	1.0020	2.1371	1.1007	6.7282	1.3093
0.2400	1.0091	2.9537	1.1389	6.9960	1.3210
0.3009	1.0121	3.0868	1.1450	7.8010	1.3561
0.4120	1.0176	3.9375	1.1842	8.2451	1.3753
0.6005	1.0296	4.1097	1.1922	9.3592	1.4233
0.7212	1.0328	4.9187	1.2287	9.5088	1.4297
0.9399	1.0435	5.1113	1.2373	10.6761	1.4791
1.0273	1.0477	5.7422	1.2653	10.8577	1.4791
1.9669	1.0928	5.8874	1.2712		

Table 2. Densities of $KClO_3 + H_2O$ Solutions at 25 °C

c/(mol dm^{-3})	d/(g cm^{-3})	c/(mol dm^{-3})	d(g cm^{-3})
0.1016	1.0049	0.3987	1.0275
0.1992	1.0123	0.4985	1.0350
0.2991	1.0199	0.5980	1.0424

$\eta/d = At + B/t$, where the constants A and B were obtained by calibration with water (0.8904 mPa s) and toluene (0.5559 mPa s).

Conductance measurements of dilute $KNO_2 + H_2O$ solutions were made to obtain the limiting molar conductance of the KNO_2. From this value and the literature value (*5*) for the limiting molar conductance of K^+ the limiting molar conductance of NO_2^- was calculated. Conductances were measured by using a YSI Model 34 conductance–resistance meter. The analog output from the meter was connected a precision millivolt meter to gain an extra significant figure in the readings. A dip type of conductance cell with $K \approx 0.1$ was used. Solutions were in large test tubes that were immersed in a well-regulated water bath at (25.00 ± 0.01) °C. The conductance cell was moved up and down in the solution container. This procedure caused the readings to settle to reproducible values. The meter was calibrated with $KCl + H_2O$ solutions through the concentration range in which measurements were made. Values of the molar conductances of KCl were calculated by using parameters from Table 6-3-3 in eq (6-3-5) in Harned and Owen (*6*).

Results and Discussion

Densities. The values of the measured densities of the systems $KNO_2 + H_2O$ and $KClO_3 + H_2O$ are listed in Tables 1 and 2, respectively. For the system $KNO_2 + H_2O$ at 25 °C, the following equation in molarity was fit to the density data by the method of least squares:

$$d = 0.997045 + 0.051197c - 0.0018497c^{3/2} \quad (1)$$

d is the density (g cm^{-3}) and c is the concentration (mol/dm^{-3}). The standard deviation of the fit was $\pm 8 \times 10^{-5}$ g cm^{-3}. However, because of uncertainties in the purity of the KNO_2 the accuracy of the density values will be considerably less than the precision of measurement at high concentrations and should be considered to be no better than $\pm 1 \times 10^{-3}$ g cm^{-3}.

By using the method of least-squares analysis, the density for the system $KClO_3 + H_2O$ was represented by the equation

$$d = 0.997045 + 0.076439c - 0.0017534c^{3/2} - 0.0032706c^2 \quad (2)$$

The standard deviation of the fit was $\pm 3 \times 10^{-5}$ g cm^{-3}. Because of uncertainties in the purity of the $KClO_3$, the accuracy of measurement will be somewhat less than the precision and should be considered to be no better than $\pm 1 \times 10^{-4}$ g cm^{-3} at the higher concentrations.

Table 3. Viscosities of $KNO_2 + H_2O$ Solutions at 25 °C

c/ (mol dm^{-3})	η/ (mPa s)	c/ (mol dm^{-3})	η/ (mPa s)	c/ (mol dm^{-3})	η/ (mPa s)
0.0000	0.890	0.9399	0.881	6.7282	1.189
0.1596	0.895	2.1371	0.889	7.8010	1.331
0.3009	0.892	3.0868	0.918	9.5088	1.647
0.4120	0.892	4.1097	0.967	10.8577	2.031
0.6005	0.889	4.9187	1.023		
0.7212	0.889	5.8873	1.110		

Table 4. Viscosities of $KClO_3 + H_2O$ Solutions at 25 °C

c/(mol dm^{-3})	η/(mPa s)	c/(mol dm^{-3})	η(mPa s)
0.0000	0.890	0.3987	0.894
0.1016	0.894	0.4985	0.892
0.1991	0.895	0.5980	0.892
0.2991	0.895		

Table 5. Conductances of $KNO_2 + H_2O$ Solutions at 25 °C

c/ (mol dm^{-3})	κ/ (cm^2 ohm^{-1} mol^{-1})	c/ (mol dm^{-3})	κ/ (cm^2 ohm^{-1} mol^{-1})
0.000925	146.42	0.008495	139.47
0.002400	143.62	0.01914	135.85
0.004262	142.04		

Viscosities. Viscosity data for the systems $KNO_2 + H_2O$ and $KClO_3 + H_2O$ at 25 °C are listed in Tables 3 and 4, respectively. For the system $KNO_2 + H_2O$ the viscosity remains fairly constant up to about 2 M concentration and then starts to increase; the rate of increase becomes sharp at the higher concentrations. The viscosity for the system $KClO_3 + H_2O$ remains nearly constant up to saturation.

Conductances. Conductances at low concentrations for the system $KNO_2 + H_2O$ are listed in Table 5. The molar conductances were fit by eq 6-3-8 in Harned and Owen (*6*), where two adjustable parameters were used. The limiting molar conductance was found to be 148 cm^2 ohm^{-1} mol^{-1}. Using the value of 73.5 cm^2 ohm^{-1} mol^{-1} given by Robinson and Stokes (*5*) for the limiting ionic molar conductance of K^+, the value for NO_2^- is calculated to be (74.5 ± 1) cm^2 ohm^{-1} mol^{-1}. These molar conductance values for K^+ and NO_2^- were used to calculate the limiting diffusion coefficient of KNO_2 at (25.00 ± 0.1) °C.

A literature value (*5*) for the limiting ionic molar conductance of ClO_3^- is 64.6 cm^2 ohm^{-1} mol^{-1}. This was used in the calculation of the limiting diffusion coefficient of $KClO_3$ at 25.00 °C. Measurements similar to those performed for the NO_2^- ion were also made for ClO_3^-, for which a value of (63.9 ± 1) cm^2 ohm^{-1} mol^{-1} was found.

Interdiffusion Coefficients. Interdiffusion coefficients, D_v, for $KNO_2 + H_2O$ and $KClO_3 + H_2O$ at (25.00 ± 0.01) °C are presented in Tables 6 and 7, respectively. Because of the impurities in the KNO_2, uncertainties of D_v should be considered to be ±1% at high concentrations. Uncertainty in the values of D_v for $KClO_3$ should be considered to be ±0.5% or less. Also given in Tables 6 and 7 are the mean molarities, $\bar{c}$ (mol dm^{-3}), the difference in the molarities of the top and bottom solutions of the experiments, Δc, the square root of the mean molarities $(\bar{c})^{1/2}$, the molalities, m (mol kg^{-1}), at the mean molar concentration, the number of fringes, J, in the Rayleigh fringe patterns taken during the experiments, and the thermodynamic diffusion coefficient, M.

The interdiffusion coefficients listed in the tables at infinite dilution were calculated from the Nernst–Hartley equation (*5*) by using limiting ionic molar conductances of K^+, NO_2^-, and ClO_3^- listed above.

Thermodynamic Diffusion Coefficients. The thermodynamic diffusion coefficients were calculated from the equation

Table 6. Interdiffusion Coefficients of $KNO_2 + H_2O$ at 25 °C

$\bar{c}$/(mol dm^{-3})	$\Delta\bar{c}$/mol dm^{-3})	$(\bar{c})^{1/2}$/(mol$^{1/2}$ dm$^{-3/2}$)	m/(mol kg^{-1})	J	$D_V \times 10^9$/(m^2 s^{-1})	$M \times 10^9$/(m^2 s^{-1})
0.0000		0.0000	0.0000		1.970	1.970
0.0494	0.0988	0.2223	0.0497	72.72	1.819	2.007
0.1694	0.1412	0.4116	0.1711	101.31	1.784	2.066
0.3564	0.1111	0.2970	0.3921	77.97	1.773	2.113
0.5063	0.1885	0.7115	0.5174	130.23	1.771	2.136
0.6609	0.1207	0.8129	0.6789	82.22	1.770	2.152
0.9836	0.0874	0.9918	1.023	57.93	1.769	2.173
2.052	0.1702	1.4325	2.226	105.23	1.768	2.206
3.020	0.1332	1.7379	3.413	77.94	1.751	2.212
4.024	0.1722	2.0059	4.758	95.23	1.715	2.204
5.015	0.1925	2.2394	6.221	102.21	1.663	2.190
5.815	0.1452	2.4114	7.519	76.43	1.606	2.171
6.862	0.2678	2.6196	9.387	131.52	1.509	2.133
8.023	0.4442	2.8325	11.76	208.53	1.381	2.087
9.434	0.1495	3.0715	15.13	66.52	1.207	2.043
10.767	0.1816	3.2813	18.98	72.03	1.037	2.035

Table 7. Interdiffusion Coefficients of $KClO_3 + H_2O$ at 25 °C

$\bar{c}$/mol dm^{-3})	$\Delta\bar{c}$/mol dm^{-3})	$(\bar{c})^{1/2}$(mol$^{1/2}$ dm$^{-3/2}$)	m/(mol kg^{-1})	J	$D_V \times 10^9$/(m^2 s^{-1})	$M \times 10^9$/(m^2 s^{-1})
0.0000		0.0000	0.0000		1.830	1.830
0.0508	0.1016	0.2254	0.00512	94.65	1.677	1.849
0.1504	0.0976	0.3878	0.1520	89.10	1.625	1.891
0.2491	0.0999	0.4463	0.2529	89.99	1.593	1.981
0.3489	0.0996	0.5907	0.3558	88.77	1.571	1.977
0.4486	0.0998	0.6698	0.4596	87.94	1.540	2.011
0.5482	0.0995	0.7404	0.5645	86.89	1.518	2.058

$$M = D_V/[1 + m(\mathrm{d}\ln\gamma_\pm/\mathrm{d}m)] \qquad (3)$$

The activity data of Chekhunova and Protsenko (*7*) at 25 °C were used to calculate the thermodynamic diffusion coefficients of the $KNO_2 + H_2O$ system. Coefficients a_1–A_3 in the following equation were obtained from their data by the method of least-squares:

$$\log_{10}(\gamma) = -A^*\sqrt{m}/(1 + A_0\sqrt{m}) + A_1m + A_2m^2 + A_3m^3 \qquad (4)$$

The coefficient A^* from the Debye–Hückel limiting law was taken to be (*8*) 0.5108. The coefficients A_0, A_1, A_2, and A_3 were, respectively, 0.8232, −0.003216, −0.0002441, and 0.000003746.

The activity data at 25 °C of Jones and Froning cited by Hamer and Wu (*8*) were used to calculate the thermodynamic diffusion coefficients of $KClO_3 + H_2O$.

It is seen for both $KNO_2 + H_2O$ and $KClO_3 + H_2O$ that the thermodynamic diffusion coefficients increase at low concentrations as concentration increases. This is typical for other electrolyte systems. At the high concentrations of the $KNO_2 + H_2O$ system the thermodynamic diffusion coefficient starts to decrease slightly.

Comparison of Diffusion Coefficients of Potassium Salts. Shown in Figure 1 are normalized diffusion coefficients of several potassium salts which were obtained by dividing the measured diffusion coefficient by the infinite dilution diffusion coefficient. These normalized diffusion coefficients are plotted against the square-root of the molar concentration. It is seen that the normalized diffusion coefficients of KI (*9*), KCl (*10*), and KSCN (*3*) in water initially decrease and then increase at higher concentrations. At very high concentrations the coefficients for KSCN decrease again. The normalized diffusion coefficients for $KHCO_3$ (*1*), $KClO_3$, and KNO_3 (*2*) in water all decrease over the full concentration range of their data. Furthermore, their data curves nearly overlap. Values of the normalized *D* for KH_2PO_4 (*11*) fall more rapidly than the salts for which the anions only have three oxygen atoms. The curve for the diffusion of KNO_2 first decreases, plateaus, and then decreases at higher concentrations. This is an intermediate behavior between the first category, where hydrogen bonding should not be a factor, and the second category, where the anions have three oxygen atoms that can hydrogen bond. The results show that the nature of the anion plays a key role in the concentration dependence of the diffusion coefficients. An increase in the number of oxygen atoms on the anion appears to cause a greater decrease in the diffusion coefficients as concentration increases.

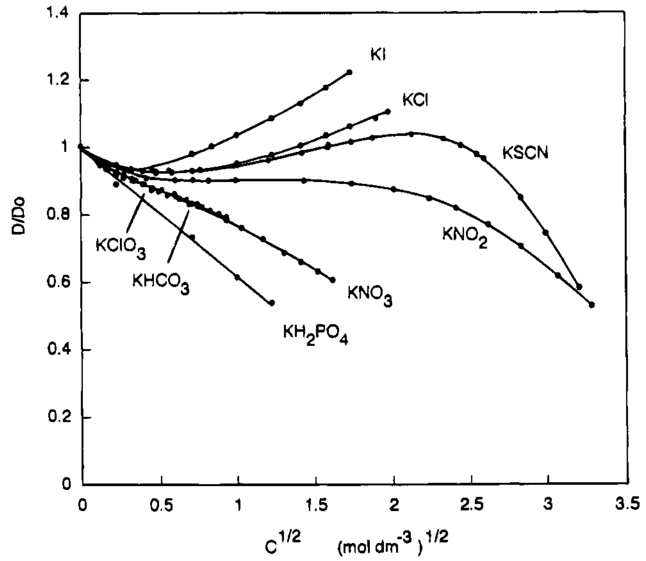

Figure 1. Ratio of the interdiffusion coefficients of KI, KCl, KSCN, KNO_2, KNO_3, $KHCO_3$, $KClO_3$, and KH_2PO_4 in water at 25 °C to their respective diffusion coefficients at zero concentration.

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