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Diaphragm Cell Measurement of Mutual Diffusion Coefficients for Potassium Hydroxide in Water from 1 °C to 25 °C

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Integral diffusion coefficients were measured for potassium hydroxide over a concentration range of 0.1 M to 11 M at 1, 10, and 25 °C using the simplified diaphragm cell procedure of Mills, Woolf, and Watts. Differential diffusion coefficients were calculated using the iterative regression method of Stokes over the same concentration and temperature range. An empirical correlation relating the differential diffusion coefficients as a function of temperature and concentration was made with a standard error of 8×10^{-7} $cm^2 \cdot s^{-1}$ and an average deviation of 5×10^{-7} $cm^2 \cdot s^{-1}$.

Introduction

Despite its industrial importance, diffusion coefficients for concentrated potassium hydroxide solutions in water are sparsely reported in the literature. Zaytsev and Aseyev (1992) tabulated diffusion coefficients for potassium hydroxide over a temperature range of 13−70 °C, but since the sources of the tabulated data were not cited, it is unclear whether the diffusion coefficients are integral or differential and what experimental techniques were used to obtain them. Bhatia et al. (1968) conducted the most comprehensive diffusion experiments to date, reporting integral and differential diffusion coefficients for solutions of potassium hydroxide over a concentration range of 0.103 M to 12.616 M at 25 °C, 45 °C, and 65 °C. Their integral diffusion coefficients were experimentally measured using a diaphragm cell, and the differential diffusion coefficients were subsequently calculated using the method of Stokes (1950). The work presented here extends the range of known potassium hydroxide diffusion coefficients to lower temperatures. These temperatures are of interest for low-temperature battery applications such as nickel−hydrogen batteries in satellites.

Experimental Section

Materials. A calibration solution of 0.1 M potassium chloride was prepared by weighing potassium chloride (Aldrich, A.C.S. reagent grade) on a Sartorius E5500 S scale (precision ±0.005 g). The measured potassium chloride was dissolved in and diluted to 1 L with distilled, deionized water (Aldrich, A.C.S. reagent grade) at 25 °C.

The potassium hydroxide solutions were prepared by diluting a stock solution of "carbonate-free" 45 mass % potassium hydroxide with distilled, deionized water (Aldrich, A.C.S. reagent grade). Care was taken to avoid carbonate contamination of the solutions. The reagent grade water was boiled for 30 min to remove any dissolved gases and subsequently cooled under argon with a soda-lime trap attached. Solutions at mass ratios of 0.56, 2.75, 5.37, 10.30, 19.11, 33.85, and 43.20 were mixed and stored in high-density polyethylene containers in an argon atmosphere until needed for testing.

Apparatus. Pyrex diaphragm cells were constructed by Southeastern Laboratory Apparatus (North Augusta, SC) with fine (4−5.5 μm) pore diaphragms following the modified design proposed by Asfour (1983). Teflon-coated stir bars were placed on either side of the diaphragm and were rotated at 60 rpm by means of magnets rotating outside the cells. The two-cell, stainless steel support and stirring apparatus was constructed by HydroTech (Anderson, SC). A complete description of the apparatus is given by Asfour and Dullien (1983). The cells were secured in the apparatus and immersed in a large-volume, temperature-controlled circulating bath (0.01 °C).

Diffusion Experiments. The cells were first calibrated with 0.1 M potassium chloride following the simplified procedure of Mills et al. (1968). In summary, the cells were filled with the 0.1 M potassium chloride solution and were placed in the circulating bath at the testing temperature. After thermal equilibration, a period of 1 to 2 h, the solution in the top compartment was carefully aspirated out and the top compartment was twice rinsed and subsequently filled with the solvent (distilled, deionized water) at the desired temperature. The top plug was quickly replaced, and the rotation of the stirring bars was begun. The test run was considered to start at this time.

All diffusion experiments were conducted for 24 h and 15 min (±15 min). After completion of the test, the compartment solutions were transferred to 100 mL high-density polyethylene storage bottles and stored under argon until the sample temperature reached 25 °C. The concentration of potassium chloride in each compartment after completion of the calibration tests was determined using a conductivity meter (YSI model 35 with a YSI 3401 dip cell, $K = 1$/cm, accuracy ±1%) and a calibration curve prepared using the original 0.1 M solution in known dilutions also at 25 °C. The calibration tests were repeated four times for both cells initially and subsequently checked at the end of each temperature measurement. The cell constants were calculated using the procedure introduced by Stokes (1951) and replicate determinations agreed within ±0.8%. The cell constants did not vary systematically with either increasing temperature or time. Therefore, it may be assumed that potential alkali corrosion and frictional wear on the Pyrex cell diaphragms did not occur to a measurable degree.

The diffusion experiments with potassium hydroxide were conducted using the same procedure stated above, but with solutions at an initial concentration of C_1 being used

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Table 1. Integral Diffusion Coefficients of Aqueous KOH Solutions

$100w_1$	C_1/mol·L^{-1}	10^5D_i/cm^2·s^{-1}
	1 °C	
0.56	0.1011	1.520
2.75	0.5060	1.497
5.37	1.0108	1.535
10.30	2.0222	1.617
19.11	4.040	1.704
33.85	8.0724	1.750
43.20	11.0929	1.761
	10 °C	
0.56	0.1007	1.978
2.75	0.5039	2.004
5.37	1.0065	2.095
10.30	2.0140	2.249
19.11	4.0253	2.414
33.85	8.0455	2.600
43.20	11.0586	2.636
	25 °C	
0.56	0.0999	2.688
2.75	0.5002	2.715
5.37	0.9994	2.722
10.30	2.0004	2.860
19.11	4.0000	3.186
33.85	8.0007	3.516
43.20	11.0014	3.626

Table 2. Differential Diffusion Coefficients of Aqueous KOH Solutions

$100w_1$	c/mol·L^{-1}	10^5D/cm^2·s^{-1}
	1 °C	
0.56	0.1011	1.492
2.75	0.5060	1.553
5.37	1.0108	1.615
10.30	2.0222	1.706
19.11	4.040	1.795
33.85	8.0724	1.755
43.20	11.0929	1.611
	10 °C	
0.56	0.1007	1.972
2.75	0.5039	2.101
5.37	1.0065	2.243
10.30	2.0140	2.447
19.11	4.0253	2.649
33.85	8.0455	2.669
43.20	11.0586	2.597
	25 °C	
0.56	0.0999	2.679
2.75	0.5002	2.725
5.37	0.9994	2.882
10.30	2.0004	3.186
19.11	4.0000	3.590
33.85	8.0007	3.715
43.20	11.0014	3.410

instead of potassium chloride. The concentrations, C_1, corresponding to the mass % and temperature of the solutions, were calculated from a regressed equation using density data from Akerloff and Bender (1941). Each diffusion test was repeated two to three times. The final concentrations of potassium hydroxide in each compartment were determined using a high-precision densiometer (Anton Paar DMA 48, accuracy ±0.0005 g/L).

Results and Discussion

Table 1 lists the experimental integral diffusion coefficients and the initial concentrations of potassium hydroxide at the start of the experiments. The values reported are the mean of the measured diffusion coefficients. The largest differences between the measured diffusion coefficients occurred at lower concentrations. The maximum variation in the measured diffusivity was 4.6% at 0.1 M and 1 °C. The average variation between the repeated diffusivity measurements was 1.1%. Using the method first proposed by Gordon (1945) and further developed by Stokes (1950), the differential diffusion coefficients were calculated. These calculated values are shown in Table 2.

A nonlinear regression package was used to fit the data in Table 2, resulting in the following empirical correlation

$$D/\text{cm}^2\cdot\text{s}^{-1} = K_1 + K_2T + K_3T^2 + K_4c^{1/2} + K_5c + K_6c^{3/2} + K_7\frac{c^{1/2}}{T^2} \quad (1)$$

in which D is the differential diffusion coefficient, T is the solution temperature in K, c is the concentration of the solution in mol/L, and K_1−K_7 are constants as presented in Table 3. Figure 1 shows the results of the correlation, comparing three predicted isotherms to the corresponding differential diffusion coefficients. The Nernst limiting diffusion coefficients at zero concentration were calculated using limiting equivalent ion conductivities from Prentice (1991). The standard error of the estimate was 8×10^{-7} with an average deviation of 5×10^{-7}. The maximum deviation for any observation was 2×10^{-6}. This deviation occurred at 11 M and 10 °C. The square of the correlation coefficient (R^2) is 0.9901. As this is an empirical correlation with no theoretical basis, it should not be applied outside of the specified temperature and concentration range.

Table 3. Correlation Constants for the Empirical Equation Relating Differential Diffusion Coefficients of Aqueous KOH Solutions to Concentration and Temperature[a]

correlation constant	value	units
K_1	-7.56×10^{-4}	cm^2/s
K_2	4.94×10^{-6}	cm^2/(s K)
K_3	-7.77×10^{-9}	cm^2/(s K^2)
K_4	1.10×10^{-5}	cm^2 L/(s mol)
K_5	4.93×10^{-6}	cm^2 L^2/(s mol^2)
K_6	-1.18×10^{-6}	cm^2 L^3/(s mol^3)
K_7	-1.07	cm^2 L K^2/(s mol)

[a] This empirical correlation should only be used within the concentration range of 0 to 11 M and the temperature range of 1 °C to 25 °C.

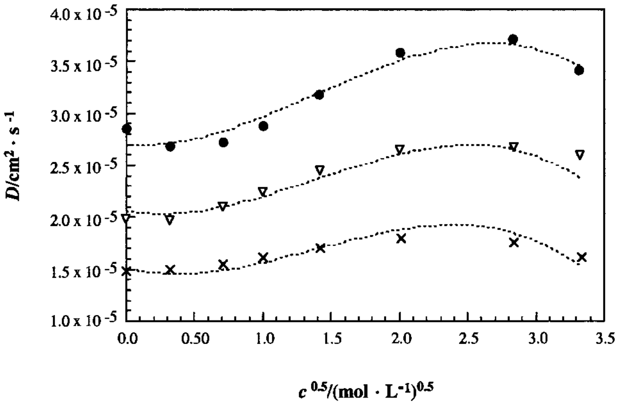

Figure 1. Comparison of differential diffusion coefficients to predicted values: ●, data from Table 1 at 25 °C; ▽, data from Table 1 at 10 °C; ×, data from Table 1 at 1 °C.

A comparison to previously reported integral diffusion data was made and is shown in Figure 2. The data of Bhatia et al. must be considered to be the most reliable, as they clearly differentiated between the integral and differential diffusion coefficients that they reported. The

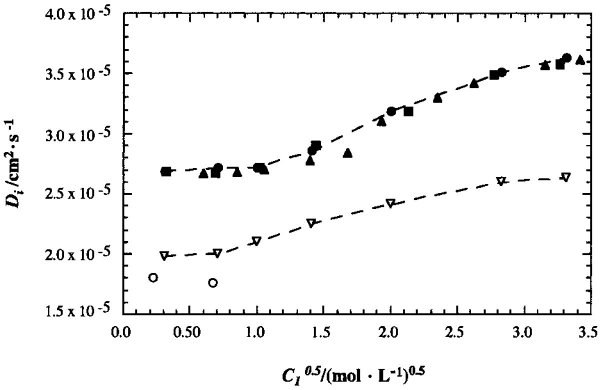

Figure 2. Comparison of experimental integral diffusion coefficients to literature values: ●, data from Table 1 at 25 °C; ▽, data from Table 1 at 10 °C; ■, data from Bhatia et al. at 25 °C; ▲, data from Zaytsev and Aseyev at 25 °C; and ○, data from the International Critical Tables at 10 °C.

data presented in Zaytsev and Aseyev (1992) does not specify whether the diffusion coefficients are integral or differential. Agreement is fairly good, with the largest variation occurring around 4 M. Two integral diffusion coefficients (at 0.005 and 0.45 M) were reported in the literature at 10 °C in the International Critical Tables (1929). These two diffusion coefficients are approximately 10% lower than the values found in this study.

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