Temperature and Concentration Dependence of the Specific Conductivity of Concentrated Solutions of Potassium Hydroxide

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The specific conductivity of concentrated solutions of potassium hydroxide was measured over a temperature range of −15 to 100 °C for concentrations of 15 to 45 mass %. An empirical correlation relating temperature, mass % KOH, and specific conductivity was made with a correlation coefficient of 0.9995. Using experimental density data from Akerlof and Bender, the correlation was extended to relate temperature, molarity, and conductivity.

Introduction

Large sets of conductivity data for concentrated solutions of potassium hydroxide are not available over a large temperature range. There is a need for accurate conductivity data in the electrolytic industry for applications such as fuel cells and batteries in which potassium hydroxide is the primary constituent of the electrolyte. It was toward this end that conductance measurements were made for aqueous potassium hydroxide solutions at concentrations of 15, 20, 25, 30, 35, 40, and 45 mass % over a temperature range of −15 to 100 °C.

Experimental Section

Materials. The solutions were prepared using a stock solution of "carbonate-free" 45 mass % potassium hydroxide and 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. The 45 mass % stock solution was stored under argon after opening.

For each run, approximately 1 L of solution was made. The solutions were prepared by diluting the 45 mass % stock solution with the degassed water. The solution components were weighed on a Sartorius E 5500 S scale (precision ±0.005 g) with an accuracy of 0.02% prior to each run. After thorough mixing, the solution was quickly placed in the testing system under a positive argon atmosphere.

Apparatus. The apparatus consisted of a testing vessel, a conductance meter, a gas washing bottle, and a circulating temperature-controlled bath. The apparatus was constructed of a 500 mL Nalgene wide-mouth bottle with a poly(propylene) cap. The cap had three ports, which held an ASTM precision thermometer (VWR), a conductivity cell, and Nalgene gas supply tubing. A diagram of the testing vessel is shown in Figure 1. Conductivity measurements were made using a YSI Model 35 Conductance Meter (resolution 0.001 S/cm) with a YSI 3440 dip cell (K = 10/cm, accuracy ±1%) designed for use with highly conductive electrolytes. The ultrahigh-purity argon (National Specialty Gases, Durham, NC) was presaturated with water by bubbling the gas through 500 mL of the electrolyte solution in a gas washing bottle. A positive pressure of saturated argon was maintained over the solution in the vessel for the duration of the run. The vessel and the gas washing bottle were partially immersed in a large-volume, temperature-controlled circulating bath (±0.01 °C).

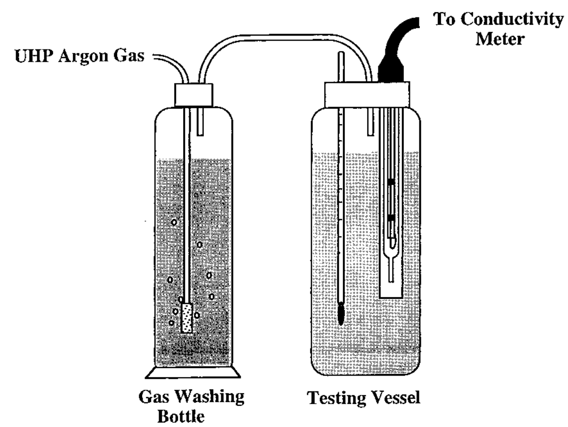

Figure 1. Testing apparatus.

Conductance Experiments. After the vessel and gas washing bottle were filled with the freshly mixed electrolyte, both devices were placed under a positive argon pressure and secured in the water bath at 100 °C. The vessel and its contents were gently agitated at 10 min intervals until consistent temperature and conductance readings were obtained. Equilibration of the system required approximately 45 min per reading. The bath temperature was subsequently lowered, and additional conductance readings were obtained until the entire temperature range from 100 to −15 °C had been covered. A total of 21 runs were made at concentrations of 15, 20, 25, 30, 35, 40, and 45 mass % potassium hydroxide. Three runs were made at each concentration. Two of the runs were started at 100 °C; the remaining run was started at −15 °C. Fresh solution was made up prior to each run. The runs were highly reproducible; the maximum percent difference between readings in the repeated runs was 1.9%. The conductance values were converted to specific conductivity by multiplying the meter readings by the cell constant of 10.0/cm.

Results and Discussion

The experimental data are presented in Table 1. The values shown are an average of the three readings. Figure 2 shows the experimental results graphically for three concentrations. Conductivity increases in an approximately linear manner with temperature. Figure 3 shows the variation of specific conductivity with concentration for seven isotherms. It may be observed that conductivity varies in a parabolic fashion with concentration, and the maximum conductivity occurs over a range of 30 to 35 mass

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Table 1. Specific Conductivity of Aqueous Solutions of Potassium Hydroxide

T/°C	κ/S·cm^{-1}	T/°C	κ/S·cm^{-1}	T/°C	κ/S·cm^{-1}
		15 mass % KOH			
−15	0.203	25	0.498	65	0.854
−10	0.235	30	0.536	70	0.903
−5	0.268	35	0.578	75	0.954
0	0.304	40	0.622	80	1.005
5	0.341	45	0.666	85	1.058
10	0.379	50	0.711	90	1.112
15	0.418	55	0.758	95	1.166
20	0.450	60	0.805	100	1.222
		20 mass % KOH			
−15	0.225	25	0.562	65	0.985
−10	0.270	30	0.605	70	1.046
−5	0.310	35	0.654	75	1.109
0	0.343	40	0.705	80	1.173
5	0.383	45	0.758	85	1.239
10	0.433	50	0.800	90	1.307
15	0.467	55	0.868	95	1.376
20	0.511	60	0.926	100	1.45
		25 mass % KOH			
−15	0.236	25	0.625	65	1.119
−10	0.280	30	0.679	70	1.189
−5	0.328	35	0.736	75	1.261
0	0.372	40	0.795	80	1.335
5	0.415	45	0.857	85	1.410
10	0.464	50	0.920	90	1.487
15	0.514	55	0.984	95	1.566
20	0.565	60	1.051	100	1.627
		30 mass % KOH			
−14	0.227	30	0.712	75	1.277
−10	0.261	35	0.774	80	1.329
−5	0.307	40	0.844	85	1.407
0	0.362	45	0.913	90	1.472
4.5	0.411	50	0.938	95	1.580
10	0.460	55	1.002	96	1.600
15	0.531	60	1.070	99	1.660
20	0.587	65	1.141	100	1.670
25	0.641	70	1.206		
		35 mass % KOH			
−15	0.195	25	0.610	65	1.138
−10	0.234	30	0.677	70	1.214
−5.0	0.279	35	0.733	75	1.284
0.0	0.328	40	0.786	80	1.361
5.0	0.376	45	0.848	85	1.434
10	0.430	50	0.928	90	1.509
15	0.490	55	0.995	94	1.569
20	0.552	60	1.073	100	1.660
		40 mass % KOH			
−15	0.154	25	0.562	65	1.088
−10	0.192	30	0.625	70	1.164
−5.0	0.230	35	0.676	75	1.254
0.0	0.280	40	0.736	80	1.326
5.0	0.332	45	0.795	85	1.396
10	0.385	50	0.874	90	1.465
15	0.442	55	0.941	93	1.517
20	0.500	60	1.021	100	1.618
		45 mass % KOH			
−15	0.100	25	0.470	65	0.979
−10	0.122	30	0.533	70	1.050
−5.0	0.150	35	0.592	75	1.121
0.0	0.215	40	0.653	80	1.195
5.0	0.264	45	0.715	85	1.270
10	0.300	50	0.800	90	1.347
15	0.364	55	0.844	95	1.425
20	0.421	60	0.911	100	1.500

% at 100 °C. The location of the maximum varies slightly with temperature, moving to lower concentrations with diminishing temperature.

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

$$\kappa = K_1(100\cdot w) + K_2(T) + K_3(T^2) + K_4(T\cdot 100\cdot w) + K_5(T^2(100\cdot w)^{K_6}) + K_7(T/(100\cdot w)) + K_8(100\cdot w/T) \quad (1)$$

in which κ is the specific conductivity in S/cm, $100\cdot w$ is the mass % of potassium hydroxide, T is the temperature in K, and K_1-K_8 are constants as presented in Table 2.

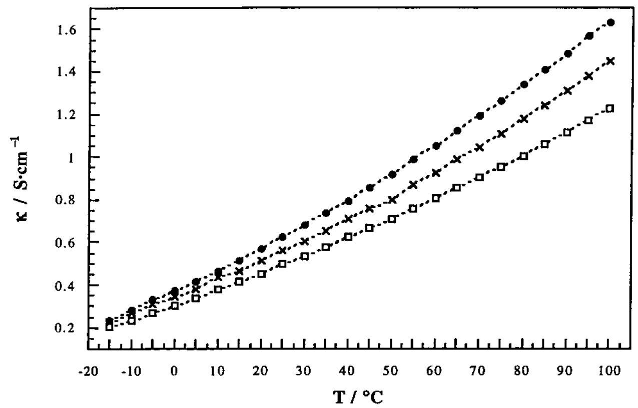

Figure 2. Variation of specific conductivity, κ, with temperature, T: ●, 15 mass %; ×, 20 mass %; ■, 25 mass % KOH.

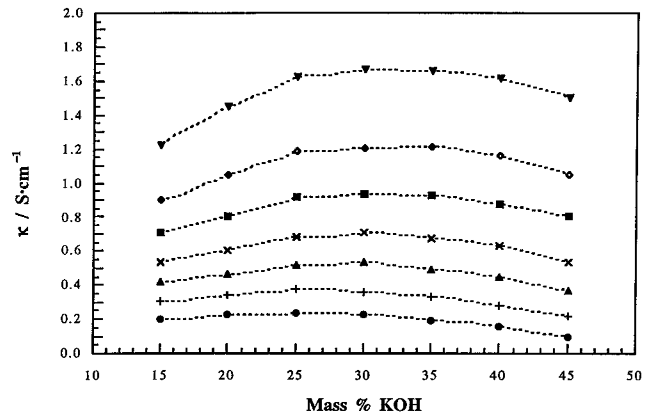

Figure 3. Experimental specific conductivity, κ, isotherms: ●, 15 °C; +, 0 °C; ▲, 15 °C; ×, 30 °C; ■, 50 °C; ◇, 70 °C; ▼, 100 °C.

Table 2. Correlation Constants for Equations Relating Conductivity to Concentration and Temperature

correlation constant	value	units
K_1	0.279 844 803	S/cm
K_2	−0.009 241 294 82	S/(cm K)
K_3	−0.000 149 660 371	S/(cm K^2)
K_4	−0.000 905 209 551	S/(cm K)
K_5	0.000 114 933 252	S/(cm K^2)
K_6	0.176 5	
K_7	0.069 664 851 8	S/(cm K)
K_8	−28.981 565 8	S K/cm
K_9	−0.003 420 006 14	S/(cm K)
K_{10}	1.196 997 71 × 10^{-5}	S/(cm K^2)
K_{11}	−1.172 980 91	S L/(cm mol)
K_{12}	−0.005 167 940 41	S L/(cm mol)^2
K_{13}	0.003 282 926 38	S L/(cm K mol)
K_{14}	119.604 837	S L K/(cm mol)
K_{15}	0.000 624 311 676	S L^3/(cm mol^3)
K_{16}	−1.883 200 99 × 10^{-7}	S L^2/(cm mol^2 K^2)

Figure 4 shows the results of the correlation, comparing seven predicted isotherms to the corresponding experimental values. The standard error of the estimate was 0.013 with an average deviation of 0.0097. The maximum deviation for any observation was 0.045. This deviation occurred at 45 mass % and −15 °C. The square of the correlation coefficient (R^2) is 0.999.

The correlation may also be expressed in terms of molarity, using the following equation

$$M = \frac{1000\cdot\rho\cdot w}{M_W} \quad (2)$$

in which M is the molarity in mol/L, w is the mass fraction of potassium hydroxide, ρ is the density in g/cm^3, and M_W is the molecular weight of potassium hydroxide in g/mol.

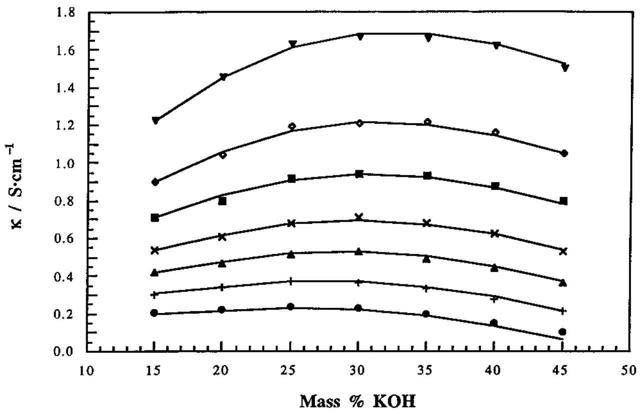

Figure 4. Comparison of experimental specific conductivity, κ, data to predicted values: ●, 15 °C; +, 0 °C; ▲, 15 °C; ×, 30 °C; ■, 50 °C; ◇, 70 °C; ▼, 100 °C.

Using the experimental density data of Akerlof and Bender (1941), the following equation was obtained

$$\kappa = K_9(T) + K_{10}(T^2) + K_{11}(M) + K_{12}(M^2) + K_{13}(T\cdot M) + K_{14}(M/T) + K_{15}(M^3) + K_{16}(T^2M^2) \quad (3)$$

in which κ is the specific conductivity in S/cm, T is the temperature in K, M is the molarity of the solution in mol/L, and K_9-K_{16} are correlation coefficients presented in Table 2. The square of the correlation coefficient (R^2) is 0.999.

Specific conductivity values predicted by eq 1 were compared to literature values reported by Klochko and Godneva (1959), Lang (1956) [presented by Falk and Salkind (1969)], Guanti and Moran (1986), and *Landolt-Börnstein Taballen* (1960) [presented by Lown and Thirsk (1971)]. Figure 5 shows the results of this comparison.

The largest amount of data available for comparison is at 25 °C. As can be seen in Figure 5, the data of Lang, Klochko and Godneva, and Guanti and Moran agree reasonably well with the predicted values. However, the data of *Landolt-Börnstein Taballen* has poor qualitative and quantitative agreement with both the predicted values and the data of other researchers, with a maximum percent difference of 41.3 at 32.2 mass %.

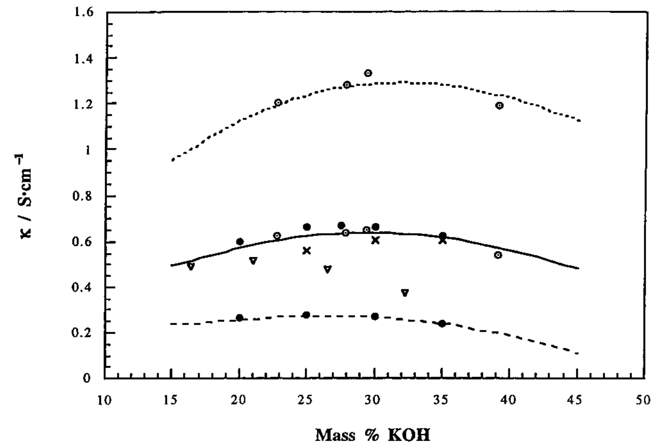

Figure 5. Comparison of predicted specific conductivity values from eq 1 to literature values: ⊙, data from Klochko and Godneva; ●, data from Falk and Salkind; ×, data from Guanti and Moran; ▽, data from Lown and Thirsk; - - -, predicted 75 °C isotherm; —, predicted 25 °C isotherm; · · ·, predicted −10 °C isotherm.

At 75 °C, the experimental data of Klochko and Godneva have good agreement with the predicted values, with the largest deviation occurring at 29.38 mass % (3.48% difference). Similarly, the data of Lang agrees well with the predicted values at −10 °C. The maximum deviation occurs at 20 mass % with 3.87% difference between the predicted and experimental values.

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