Available online at www.sciencedirect.com
ScienceDirect
International Journal of Hydrogen Energy 32 (2007) 359–364
International Journal of HYDROGEN ENERGY
www.elsevier.com/locate/ijhydene

A review of specific conductivities of potassium hydroxide solutions for various concentrations and temperatures

R.J. Gilliam[a,*], J.W. Graydon[b], D.W. Kirk[b], S.J. Thorpe[a]

[a]Department of Materials Science and Engineering, University of Toronto, Toronto, Ont., Canada M5S 3E4
[b]Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ont., Canada M5S 3E5

Received 20 October 2006; received in revised form 23 October 2006; accepted 27 October 2006
Available online 11 December 2006

Abstract

This article gives a critical review of the current data on the specific conductivity of aqueous potassium hydroxide (KOH) solutions. Empirical correlations relating concentration to density were developed to compare specific conductivity data given in weight percentage KOH and molarity of KOH. Available data on specific conductivity is related with respect to one another and compared to experimental data. Based on these comparisons, specific sets of reported data were used to develop an equation relating specific conductivity of aqueous KOH to temperature and concentration. This empirical correlation was developed over a molarity range of 0–12 at temperatures of 0–100 °C. The correlation has been compared with that proposed by See and White and shows greater accuracy over the concentration range modeled.

Keywords: Specific conductivity; Potassium hydroxide; Alkaline electrolyte

1. Introduction

In the areas of alkaline fuel cells (AFCs), alkaline water electrolysers (AWEs) and alkaline batteries, an accurate value for the specific conductivity of the electrolyte is required. Limited conductivity of the electrolytic solution is a major cause of energy loss in these applications, specifically when they are operating at higher currents. As a result, it is necessary to determine accurate values of conductivity at high concentrations and temperatures.

For AFCs, AWEs and alkaline batteries, aqueous potassium hydroxide (KOH) is used as a primary electrolyte. To date, little data with respect to the specific conductivity of KOH is available over large concentration and temperature ranges. For the data that is available, significant discrepancies exist in reported values. To clarify this problem, this article compares the current sets of reported data with respect to one another, as well as to experimental data obtained within our laboratory. Based on this comparison, reported sets of data that showed good agreement to one another were used in developing an empirical relationship between specific conductivity, temperature and concentration.

2. Experimental details

To determine which sets of available data provide the most reliable values, reported data were compared to specific conductivity measurements carried out within our laboratory. These specific conductivity measurements were carried out for a 27 wt% KOH solution at temperatures of 0, 15, 25, 35, 45, 55, 65 and 75 °C in a modified Jones conductivity cell.

The modified cell was constructed from a block of polymethylmethacrylate to resist attack by the caustic electrolyte. The cell consisted of a cylindrical cavity 1.1 cm in diameter with two parallel, platinized-platinum electrodes held at either end. The geometric cell constant was measured to be $4.15\,cm^{-1}$.

Conductivity measurements were performed using a Radiometer CDM83 conductivity meter operating at 50 kHz. The cell was calibrated at 18 and 25 °C with an electrolyte of 74.264 g of KCl per litre of solution.

* Corresponding author. Tel.: +1 416 978 8573; fax: +1 416 978 4155.
E-mail address: ryan.gilliam@utoronto.ca (R.J. Gilliam).

0360-3199/$ - see front matter
doi:10.1016/j.ijhydene.2006.10.062

For reported data within the same concentration and temperature range, values of specific conductivity were extrapolated and plotted versus temperature. Through comparison of the reported data to the experimental data, the reliability of each reported data set was determined.

3. Results and discussion

In developing a correlation between specific conductivity, temperature and concentration, six separate sets of reported values were used; Klochko and Godneva [1], Zaytsev and Aseyev [2], See and White [3], Dobos [4], Landolt-Börnstein [5], and DeWane and Hamer [6]. The values reported by Landolt-Börnstein were tabulated from five separate sources which are referenced [7–11].

For each reference, values of specific conductivity were reported at various concentrations and temperatures. An overview of the number of values of specific conductivity reported from each reference is provided in Table 1.

In reporting values of specific conductivity, two commonly reported concentration units were used in the reported data; wt% KOH and molarity. To convert between these units, the following equation was used:

$$M = \frac{\text{wt\%(KOH)}\rho}{100 M_w}, \quad (1)$$

where ρ represents the density of the aqueous KOH solution in kg/m^3, and M_w represents the molar mass of KOH in g/mol. To determine the density of KOH at a given temperature and concentration, empirical correlations relating wt% KOH to density and molarity of KOH to density were developed.

3.1. Development of density equations

In developing empirical correlations of wt% KOH to density and molarity of KOH to density, three separate sets of reported data were used; Klochko and Godneva [1], Zaytsev and Aseyev [2] and Akerlof and Bender [12]. An overview of the number of values of density reported from each reference is outlined in Table 2.

In comparing the values reported from all three sources, deviation in the reported data for density varied by a maximum of ±1%. Based on this close correlation, all three sets of data were used in developing the empirical relationships between concentration and density.

Table 1
Specific conductivity values reported in literature

Reference	Temperature (°C)	Concentration range	Number of data points
1	25	2–49 wt%	9
	75	2–60 wt%	10
2	5, 10, 15, ..., 70	16–48 wt%	17 at each T
3	−15, −10, −5, ..., 100	15–45 wt%	7 at each T
4	18	0.001–10 M	15
	25	0.1–1 M	3
	50, 55, 60, ..., 80	20–40 wt%	11 at each T
5	18	0.001–10 M	18
	25	10^{-7}–7.5 M	50
	30	0.05–1 M	7
	90	0.05–1 M	6
6	25	0.0001–13 M	42
	30	0.01–10 M	28
	60	1–13 M	13
	100	1–13 M	13

Table 2
Density values reported in literature

Reference	Temperature (°C)	Concentration range (wt%)	Number of data points
1	25	3–23	6
	75	3–32	8
2	0, 5, 10, ..., 200	2–50	25 at each T
7	0, 10, 20, ..., 70	0–50	26 at each T

Table 3
Relationship between density of KOH and wt% KOH for various temperatures

Temperature (°C)	A	Temperature (°C)	A
0	1001.9	50	988.45
5	1001.0	55	985.66
10	1000.0	60	983.20
15	999.06	65	980.66
20	998.15	70	977.88
25	997.03	80	971.89
30	995.75	90	965.43
35	994.05	100	958.35
40	992.07	150	916.99
45	990.16	200	867.07

$\rho = A \cdot e^{(0.0086 \cdot \text{wt\%})}$ where ρ represents density in kg/m^3.

Table 4
Relationship between density of KOH and molarity of KOH for various temperatures

Temperature (°C)	A	B	C
0	−0.5031	45.876	1004.4
5	−0.4821	45.648	1003.8
10	−0.5026	45.889	1002.5
15	−0.4820	45.659	1002.0
20	−0.4824	45.649	1001.0
25	−0.4931	45.761	999.63
30	−0.4812	45.568	998.66
35	−0.4918	45.698	996.70
40	−0.4863	45.601	994.89
45	−0.4912	45.620	992.84
50	−0.4756	45.336	991.51
55	−0.4898	45.543	988.40
60	−0.4916	45.530	985.91
65	−0.4906	45.450	983.39
70	−0.4876	45.396	980.71
80	−0.4942	45.409	974.59
90	−0.5021	45.432	967.98
100	−0.5010	45.361	960.99
150	−0.5206	45.217	919.52
200	−0.5538	45.173	869.35

$\rho = A \cdot M^2 + B \cdot M + C$ where ρ represents density in kg/m^3 and M represents molarity in mol/L.

These equations were developed for temperatures of 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 80, 90, 100, 150 and 200 °C. The empirical correlations between density and wt% can be found in Table 3 while the empirical correlations for density and molarity can be found in Table 4. All of the developed correlations have an R^2 value of greater than 0.9999.

3.2. Comparison of reported data

In developing an empirical relationship for specific conductivity with respect to concentration and temperature, an assessment of the validity of each set of reported data was carried out. This was done through the comparison of reported data sets to one another, as well as to experimental results obtained within our laboratory.

From Table 1, it can be seen that the greatest number of reported values for specific conductivity are at 25 °C. Based on this, the reported values of Klochko and Godneva [1], Zaytsev and Aseyev [2], See and White [3], Dobos [4], Landolt-Börnstein [5] and DeWane and Hamer [6] were plotted (see Fig. 1).

From Fig. 1 it can be seen that three separate trends exist within the reported data. Firstly, close correlation exists between the values reported by Klochko and Godneva [1], See and White [3], Dobos [4] and DeWane and Hamer [6]. Secondly, the values reported by Zaytsev and Aseyev [2] have a higher specific conductivity at concentrations above 4 M. These reported values can be up to 10% higher than those in the first group. Thirdly, the values reported by Landolt-Börnstein [5] are significantly lower then the other reported values. These values can be up to 50% lower then those reported in the first group.

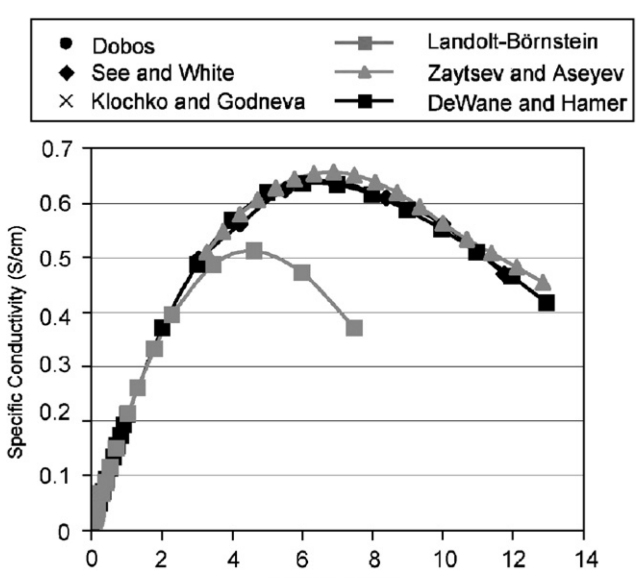

Fig. 1. Specific conductivity vs. molarity at 25 °C showing comparison of reported data [1–6].

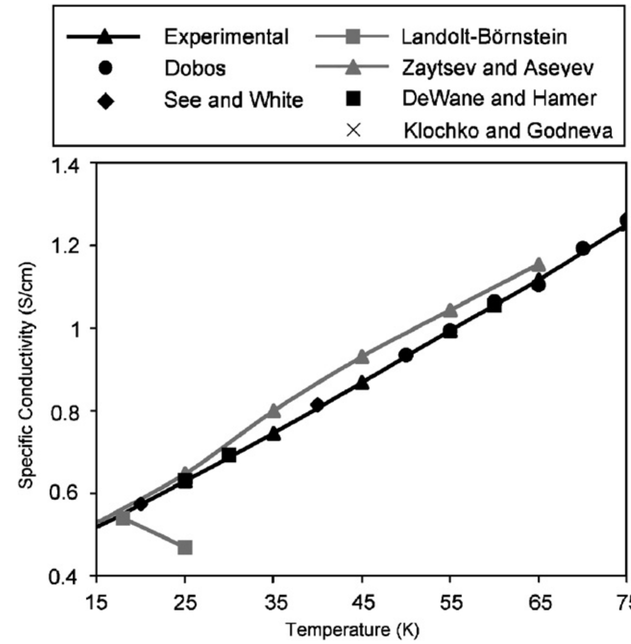

Fig. 2. Specific conductivity vs. temperature for 27 wt% KOH showing comparison of reported data [1–6] to experimental data.

To determine which trend of reported values was the most accurate, a comparison was also done with the experimental values previously obtained within our laboratory (see Fig. 2). From Fig. 2, it can be seen that there is close correlation between the experimental results, and those reported by Klochko and Godneva [1], See and White [3], Dobos [4] and DeWane and Hamer [6].

3.3. Development of specific conductivity equation

Based on comparison of reported data sets to one another, as well as to experimental results, the reported data of Klochko and Godneva [1], See and White [3], Dobos [4], DeWane and Hamer [6], as well as the experimental data obtained within our laboratory was used in developing a correlation for specific conductivity with respect to concentration and temperature. From these sources, all of the reported data, over 300 data values, were used in developing the model.

Using a non-linear regression analysis program (SAS Version 9.1), a six variable relationship between specific conductivity, concentration in molarity, and temperature in Kelvin was developed. The resultant empirical relationship was

$$\kappa = A(M) + B(M^2) + C(M \cdot T) + D(M/T) + E(M^3) + F(M^2 \cdot T^2), \quad (2)$$

where κ represents the specific conductivity in S/cm, M represents the molarity in mol/L, T represents the temperature in Kelvin, and A–F are constants which are presented in Table 5.

Table 5
Constants for equation relating specific conductivity with temperature (K) and concentration (M)

Constant	Value
A	−2.041
B	−0.0028
C	0.005332
D	207.2
E	0.001043
F	−0.0000003

Comparison of this equation to reported values shows good correlation for temperatures from 0 to 100 °C for KOH concentrations from 0 to 12 M. At concentrations or temperatures above these ranges, greater deviation is expected to occur due to a lack of data beyond 12 M and above 100 °C used in the non-linear regression analysis. The standard deviation for the specific conductivity at concentrations between 0 and 12 M and temperatures between 0 and 100 °C was found to be 0.02524.

Through comparison of the equation to reported data, three separate trends exist based on temperature ranges. Below 25 °C, the average deviation in specific conductivity was 3.9% with a maximum error of 9%. Between 25 and 75 °C the average deviation in specific conductivity was 1.9% with a maximum error of 5%. Above 75 °C the average deviation was 3.2% with a maximum error of 8%.

Below 25 °C there was a higher average deviation in the specific conductivity due to a disproportional number of reported values at low concentrations within this temperature range. For concentrations below 0.1 M, the average error in the specific conductivity was 4.7%. At temperatures greater then 75 °C, there was an increase in average error due to discrepancies which exist in the reported values at these temperatures.

The correlation between the reported data and values obtained from the proposed equation can be seen in Fig. 3. Discrepancies arising between the reported values at higher temperatures can also be seen in Fig. 3.

A three-dimensional representation of specific conductivity with respect to concentration and temperature, based on the proposed equation, can be seen in Fig. 4. Values of specific conductivity, calculated using the proposed equation at various concentrations and temperatures, can be found in Tables 6 and 7.

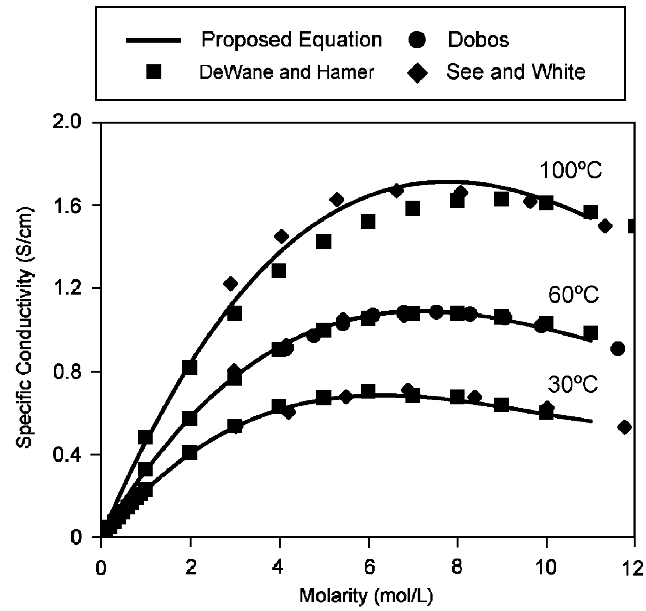

Fig. 3. Specific conductivity vs. molarity at 30, 60 and 100 °C comparing reported data [3,4,6] to proposed equation.

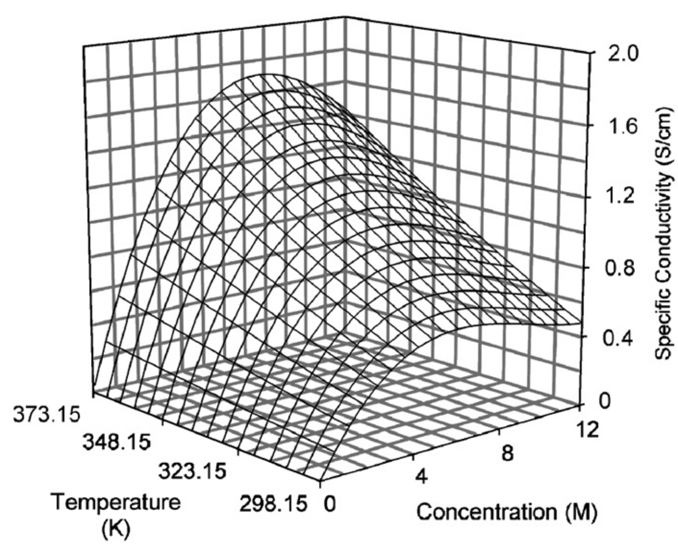

Fig. 4. 3D plot of proposed equation showing specific conductivity with respect to temperature and concentration.

3.4. Comparison of reported equations

See and White [3], developed an empirical relationship relating specific conductivity to temperature and concentration. In developing their relationship, values in the concentration range of 15–45 wt%, from −15 to 100 °C were used. Within these ranges, the empirical relationship developed by See and White works well, yet deviates significantly at concentrations below 15 wt%. The present work serves to increase the range over which an empirical relationship is valid. A graph illustrating the difference between the empirical relationship developed by See and White, and the empirical relationship proposed within this paper to that of the reported data at low concentrations is shown in Fig. 5. As seen in this figure, the empirical relationship developed in this work provides greater accuracy at lower concentrations.

At concentrations between 3 and 11 M over the entire temperature range, the equation developed by See and White [3] and the equation proposed within this article differ by

Table 6
Calculated values of specific conductivity in (S/cm) at various concentrations (M) and temperatures (°C)

Concentration (M)	Temperature (°C)											
	0	10	20	25	30	40	50	60	70	80	90	100
0.01	0.00174	0.00200	0.00229	0.00243	0.00259	0.00290	0.00323	0.00357	0.00392	0.00428	0.00465	0.00503
0.02	0.00347	0.00400	0.00457	0.00486	0.00517	0.00579	0.00645	0.00713	0.00783	0.00856	0.00930	0.0101
0.03	0.00520	0.00599	0.00684	0.00728	0.00774	0.00868	0.00967	0.0107	0.0117	0.0128	0.0139	0.0151
0.05	0.00864	0.0100	0.0114	0.0121	0.0129	0.0144	0.0161	0.0178	0.0195	0.0213	0.0232	0.0251
0.1	0.0171	0.0198	0.0226	0.0241	0.0256	0.0287	0.0320	0.0354	0.0389	0.0425	0.0462	0.0499
0.2	0.0338	0.0390	0.0446	0.0476	0.0506	0.0568	0.0633	0.0700	0.0770	0.0841	0.0915	0.0990
0.3	0.0500	0.0578	0.0661	0.0705	0.0750	0.0842	0.0939	0.1040	0.1143	0.1250	0.1360	0.1472
0.5	0.0808	0.0937	0.1074	0.1146	0.1220	0.1373	0.1532	0.1698	0.1868	0.2044	0.2225	0.2409
1	0.1499	0.1747	0.2013	0.2153	0.2296	0.2592	0.2901	0.3222	0.3554	0.3895	0.4246	0.4604
2	0.2556	0.3020	0.3518	0.3778	0.4046	0.4602	0.5183	0.5786	0.6408	0.7049	0.7706	0.8379
3	0.3235	0.3881	0.4576	0.4940	0.5315	0.6093	0.6907	0.7752	0.8625	0.9524	1.0445	1.1387
4	0.3598	0.4392	0.5250	0.5700	0.6164	0.7128	0.8136	0.9184	1.0267	1.1382	1.2525	1.3692
5	0.3708	0.4617	0.5603	0.6121	0.6656	0.7768	0.8933	1.0144	1.1397	1.2686	1.4007	1.5356
6	0.3627	0.4618	0.5697	0.6266	0.6853	0.8077	0.9360	1.0696	1.2077	1.3499	1.4955	1.6441
7	0.3417	0.4457	0.5594	0.6196	0.6818	0.8117	0.9481	1.0901	1.2370	1.3882	1.5431	1.7011
8	0.3142	0.4197	0.5359	0.5976	0.6614	0.7950	0.9356	1.0822	1.2339	1.3900	1.5498	1.7127
9	0.2864	0.3900	0.5052	0.5666	0.6304	0.7640	0.9050	1.0522	1.2046	1.3614	1.5218	1.6852
10	0.2646	0.3630	0.4737	0.5331	0.5949	0.7249	0.8625	1.0063	1.1554	1.3087	1.4655	1.6249
11	0.2550	0.3449	0.4476	0.5032	0.5612	0.6839	0.8142	0.9508	1.0925	1.2381	1.3869	1.5380
12	0.2638	0.3419	0.4332	0.4832	0.5357	0.6473	0.7666	0.8920	1.0221	1.1560	1.2925	1.4308

Table 7
Calculated values of specific conductivity in (S/cm) at various concentrations (wt% KOH) and temperatures (°C)

Concentration (wt%)	Temperature (°C)											
	0	10	20	25	30	40	50	60	70	80	90	100
0.1	0.00310	0.00357	0.00407	0.00432	0.00459	0.00513	0.00569	0.00626	0.00683	0.00742	0.00801	0.00860
0.5	0.01540	0.01773	0.02022	0.02151	0.02283	0.02553	0.02833	0.03116	0.03406	0.03699	0.03994	0.04289
1	0.03053	0.03518	0.04015	0.04274	0.04537	0.05077	0.05636	0.06203	0.06782	0.07368	0.07958	0.08549
2	0.05994	0.06923	0.07915	0.08430	0.08957	0.1003	0.1115	0.1228	0.1344	0.1461	0.1580	0.1698
4	0.1153	0.1338	0.1535	0.1637	0.1742	0.1957	0.2180	0.2406	0.2637	0.2871	0.3107	0.3344
6	0.1657	0.1932	0.2226	0.2379	0.2536	0.2856	0.3189	0.3527	0.3873	0.4224	0.4577	0.4932
8	0.2110	0.2473	0.2862	0.3064	0.3271	0.3696	0.4138	0.4587	0.5046	0.5512	0.5982	0.6454
10	0.2509	0.2958	0.3439	0.3690	0.3946	0.4474	0.5021	0.5579	0.6151	0.6730	0.7315	0.7903
12	0.2852	0.3384	0.3954	0.4252	0.4557	0.5184	0.5835	0.6500	0.7181	0.7872	0.8570	0.9272
14	0.3138	0.3749	0.4405	0.4748	0.5099	0.5823	0.6575	0.7344	0.8132	0.8931	0.9740	1.0553
16	0.3365	0.4052	0.4790	0.5176	0.5572	0.6388	0.7237	0.8106	0.8997	0.9902	1.0819	1.1741
18	0.3534	0.4291	0.5107	0.5534	0.5972	0.6876	0.7818	0.8783	0.9773	1.0780	1.1799	1.2826
20	0.3645	0.4468	0.5355	0.5820	0.6298	0.7285	0.8314	0.9370	1.0454	1.1558	1.2676	1.3804
22	0.3700	0.4582	0.5535	0.6035	0.6549	0.7614	0.8723	0.9865	1.1038	1.2232	1.3444	1.4667
24	0.3702	0.4636	0.5648	0.6179	0.6726	0.7861	0.9045	1.0265	1.1519	1.2798	1.4097	1.5409
26	0.3654	0.4633	0.5695	0.6254	0.6830	0.8027	0.9277	1.0569	1.1897	1.3253	1.4631	1.6024
28	0.3562	0.4577	0.5681	0.6263	0.6864	0.8114	0.9421	1.0775	1.2168	1.3593	1.5042	1.6509
30	0.3434	0.4474	0.5610	0.6211	0.6831	0.8125	0.9479	1.0885	1.2334	1.3816	1.5327	1.6857
32	0.3277	0.4332	0.5490	0.6104	0.6738	0.8064	0.9454	1.0901	1.2393	1.3923	1.5484	1.7067
34	0.3104	0.4162	0.5329	0.5950	0.6592	0.7937	0.9351	1.0826	1.2349	1.3914	1.5512	1.7137
36	0.2928	0.3976	0.5139	0.5759	0.6402	0.7753	0.9176	1.0665	1.2206	1.3792	1.5413	1.7065
38	0.2765	0.3788	0.4932	0.5544	0.6181	0.7523	0.8940	1.0427	1.1969	1.3560	1.5189	1.6852
40	0.2634	0.3617	0.4726	0.5322	0.5944	0.7259	0.8652	1.0121	1.1647	1.3224	1.4845	1.6501
42	0.2558	0.3484	0.4540	0.5111	0.5709	0.6978	0.8329	0.9759	1.1250	1.2795	1.4386	1.6018
44	0.2565	0.3413	0.4397	0.4933	0.5497	0.6700	0.7988	0.9358	1.0791	1.2282	1.3823	1.5407
46	0.2684	0.3434	0.4324	0.4815	0.5333	0.6448	0.7650	0.8936	1.0288	1.1701	1.3167	1.4681
48	0.2951	0.3580	0.4354	0.4788	0.5249	0.6249	0.7340	0.8516	0.9761	1.1070	1.2434	1.3851

a maximum of ± 6%, with an average deviation of 1.5%. It should be noted that this discrepancy in the modeled values is less than the discrepancy between the reported data.

At concentrations less the 3 M, the equation proposed by See and White can be orders of magnitude different from both the reported values and those obtained with the equation proposed in this article.

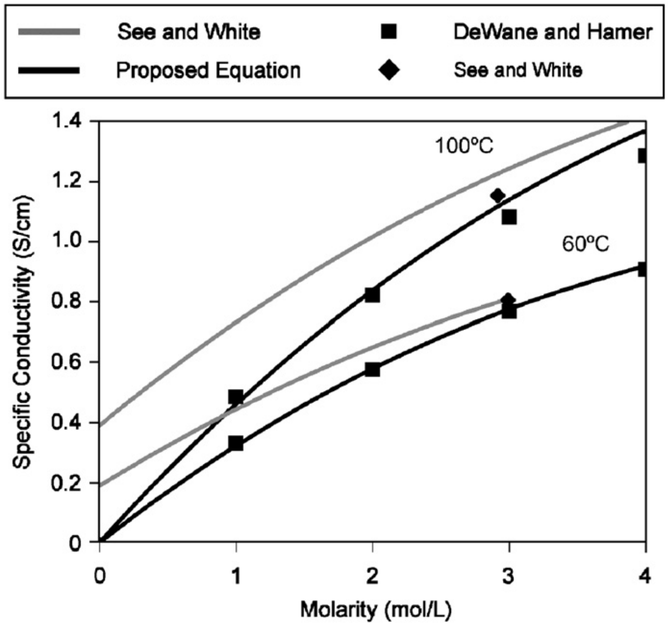

Fig. 5. Specific conductivity vs. molarity at 60 and 100 °C showing deviation in the empirical equation proposed by See and White from the proposed equation and reported data [3,6].

4. Conclusion

In this review article, a critical review was taken with respect to the current reported data available for specific conductivities of aqueous potassium hydroxide (KOH) solutions. It was shown that significant deviation occurs in the reported values between sources. Based on the comparison of reported data to experimental measurements, it was concluded that the experimental values put forth by Klochko and Godneva [1], See and White [3], Dobos [4] and DeWane and Hamer [6] were the most reliable.

These values were used to develop an empirical relationship for specific conductivity with respect to temperature and concentration. The correlation coefficient for the empirical relationship was 0.998 over a concentration range of 0–12 M and a temperature range of 0–100 °C. The empirical correlation developed provides greater accuracy over a broader concentration range then that proposed by See and White [3].

Acknowledgment

This work was supported through the Ontario Graduate Scholarship for Science and Technology (OGSST) as well as the University of Toronto Materials Engineering Open Fellowship.

References

[1] Klochko MA, Godneva MM. Electrical conductivity and viscosity of aqueous solutions of NaOH and KOH. J Inorg Chem (USSR) 1959;4:964–8.
[2] Zaytsev ID, Aseyev GG, editors. Properties of aqueous solutions of electrolytes. Boca Raton, FL: CRC Press; 1992.
[3] See DM, White RE. Temperature and concentration dependence of the specific conductivity of concentrated solutions in potassium hydroxide. J Chem Eng Data 1997;42:1266–8.
[4] Dobos D. Electrochemical data: a handbook for electrochemists in industry and universities. Amsterdam: Elsevier Scientific; 1975. p. 55, 84–85, 93.
[5] Landolt H, Börnstein R. Zahlenwerte und funktionen. Berlin: Springer; 1960. p. 36, 54, 87.
[6] DeWane HJ, Hamer WJ. Electrochemical data part X: electrolytic conductivity of aqueous solutions of the alkali metal hydroxides, National Bureau of Standards Report 9876, U.S. Department of Commerce.
[7] Darken LS, Meier HF. Conductances of aqueous solutions of the hydroxides of lithium, sodium and potassium at 25°. J Amer Chem Soc 1942;64:621–3.
[8] Hlasko M, Salitówna A. Direct determination of the limiting conductivity of strong electrolytes, and the conductivity of very dilute weak electrolytes. Roczniki Chem 1934;14:1038–51.
[9] International critical tables of numerical data, physics, chemistry and technology VI. New York: McGraw-Hill; 1929.
[10] Kohlrausch F. Saturated aqueous solutions of sparingly soluble salts (II): their solubilities and their change with temperature. Z Physik Chem 1908;64:129–69.
[11] Sivertz V, Reitmeier RE, Tartar HV. The ionization constant of monoethanolammonium hydroxide at 25° from electrical conductance measurements. J Amer Chem Soc 1940;62:1379–82.
[12] Akerlof G, Bender P. The density of aqueous solutions in potassium hydroxide. J Amer Chem Soc 1941;63:1085–8.