JOURNAL OF APPLIED ELECTROCHEMISTRY 19 (1989) 95–99

On the conductivity of phosphoric acid electrolyte

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Received 14 June 1988

The specific electric conductivity and viscosity of 7.5–100 wt% aqueous phosphoric acid electrolyte have been measured in the temperature range 25–200° C. The product of conductivity and viscosity was found to decrease exponentially with increasing temperature. This suggests that the electric conduction in phosphoric acid follows the Grotthus proton switching mechanism. The measured conductivity data were correlated by the following empirical equation:

$$k\mu = A \exp [BT]$$

$$A = 702.7X^{1.5} - 1734.2X^2 + 1446.5X^{2.5} - 350.7X^3$$

$$B = -0.010163 + 0.011634X - 0.08313X^2$$

where k is conductivity in mho cm^{-1}; μ is viscosity in centipoise; T is the absolute temperature in K; and X is mole fraction of phosphoric acid in the electrolyte. The standard deviation for the percentage difference between the calculated and experimental values of 188 data points was less than 7.5%.

1. Introduction

Although the phosphoric acid fuel cell is in an advanced state of development, there has been no complete data base in the open literature on the electric conductivity of aqueous phosphoric electrolyte. Early data presented in Monsanto Technical Bulletin IC/DP-239 were summarized in a report by Sarangapani *et al.* [1]. Maksimova and Yushkevich [2] reported the conductivity of 0–6 wt% phosphoric acid over the temperature range of 0–300° C. Most published works dealt with highly concentrated phosphoric acid. These included the conductivity data of Greenwood and Thompson [3] for 100 wt% phosphoric acid at 25–60° C; Kakulin and Fedorchenko [4] and Fedorchenko *et al.* [5] for 93–108 wt% phosphoric acid at 20–90° C; Wydeven [6] for 89–122 wt% phosphoric acid at 25–60° C; Atanasyants and Georgiev [7] for 60–100 wt% phosphoric acid at 20–60° C; Fedorchenko *et al.* [8] for 93–108 wt% phosphoric acid at 100–200° C; and MacDonald and Boyack [9] for 85–100 wt% phosphoric acid at 130–170° C. No conductivity data are available in the concentration range of 6–60 wt% at temperatures greater than 25° C and for 60–85 wt% phosphoric acid at temperatures greater than 60° C. Some of the published data did not agree with those reported by the other workers. The data of Wydeven [6] and Atanasyants and Georgiev [7] were 10–15% higher than those of Greenwood and Thompson [3] and Kakulin and Fedorchenko [4]. The conductivity data obtained by Fedorchenko *et al.* [8] were 30% smaller than those measured by MacDonald and Boyack [9]. The discrepancies seem to arise from the composition differences caused by the contamination of pyro- and poly-phosphates during the experiments.

This paper presents the conductivities of 7.5–100 wt% phosphoric acid electrolyte over the temperature range 25–200° C. The mechanism of electric conduction is examined with the behavior of conductivity-viscosity (or Walden's) product. A single empirical equation is developed to correlate the measured conductivity data over the entire range of phosphoric acid concentrations and temperatures investigated.

2. Experimental details

2.1. *Phosphoric acid electrolytes*

The electrolytes were prepared from ACS certified 85 wt% phosphoric acid. For concentrations of 7.5–85 wt%, the solutions were prepared by diluting the 85 wt% phosphoric acid with distilled water. For concentrations greater than 85 wt%, the solutions were made by concentrating purified phosphoric acid in a vacuum oven. The purification procedure consisted of treating the 85% phosphoric acid with hydrogen peroxide, heating the resulting solution in a Teflon flask at 50–70° C for 1 h, and raising the temperature to 100° C for another hour to decompose unreacted hydrogen peroxide. The purified phosphoric acid was concentrated to the desired concentration by evaporating excess water under a vacuum of 29 in. Hg at 90° C to avoid the polymerization of phosphoric acid to pyro or poly phosphates.

2.2. *Specific conductivity*

The specific conductivity of phosphoric acid was measured over a concentration range of 7.5–100 wt% and a temperature range of 25–200° C. The measurement was made with an a.c. conductivity bridge and a conductivity probe cell (Beckman RS-16), whose cell

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constant had been calibrated with standard 0.01 N KCl solution. The phosphoric acid solution was contained in a three-armed flask, and was immersed in a constant-temperature oil bath (Fisher, Model 160). A reflux column connected to the middle arm of the flask was used to condense water and acid vapors caused by heating at high temperatures. One of the side arms was used for insertion of the conductivity probe cell into the phosphoric acid solution. A thermometer inserted through the second side arm was used to monitor the temperature of the solution. For a given solution concentration, the specific conductivity data were taken at 10° C temperature increments until the normal boiling point of the solution was reached. The temperature control of the oil bath was within $\pm 0.5°$ C.

2.3. *Viscosity measurement*

To interpret the electric conductivity data, a set of runs was made to determine the viscosity of 7.5–100 wt% phosphoric acid in the temperature range 25–180° C. The viscosity was measured using Canon–Fenske viscometers whose time constants had been calibrated with distilled water and glycerol solutions. The measurement was carried out in a constant temperature oven with an estimated error of $\pm 5\%$ in the entire concentration and temperature range investigated.

3. Results and discussion

The results of the specific conductivity and viscosity measurements are tabulated in Table 1. The present data agreed with those of Refs [1–5, 9] to within $\pm 5\%$. The specific conductivity values at selected temperatures are plotted in Fig. 1 against the weight per cent of phosphoric acid. For a given temperature the specific conductivity exhibited a maximum at a certain phosphoric acid concentration, and this maximum shifted toward higher concentrations with increasing temperature as shown in Fig. 1.

It has been suggested [1] that in dilute phosphoric acid solution, the major contribution to electric conductivity is from the Stokesian ion transport mechanism; whereas in more concentrated phosphoric acid solutions, the major contribution to conductivity comes from the Grotthus proton switching conduction mechanism. The proton switching mechanism was initially proposed to explain the high mobility values of hydrogen and hydroxyl ions. In this mechanism, the electric conduction occurs by the hopping of protons from one solvated acid or water molecule to the other without actual transport of hydrogen ions in the solution [10]. A criterion for identifying the proton switching conduction mechanism is the Walden product [11] defined as

$$\Lambda\mu = (eF/6)(z_+/r_+ - z_-/r_-) = \text{constant} \quad (1)$$

where Λ is the equivalent conductivity of the electrolyte; μ is the solution viscosity; e is the charge of an electron; F is the Faraday constant; z_+ and z_- are the valences of the cation and anion; and r_+ and r_- are the radii of solvated cations and anions, respectively. Equation 1 was derived from the well-known Stokes law for an ion moving through a viscous fluid under the influence of an electric field. The radii of solvated ions generally depend only on the electrolyte concentration. If the electric conduction is caused by the Stokesian ion transport mechanism, the Walden product, $\Lambda\mu$, for a given electrolyte concentration should be a constant independent of temperature. On the other hand, the proton switching conduction mechanism would lead to a decrease of the Walden product with increasing temperature. Peled *et al.* [12] proposed that a significant decrease in the Walden product with increasing temperature be taken as an indication of the proton switching mechanism of electrolyte conduction.

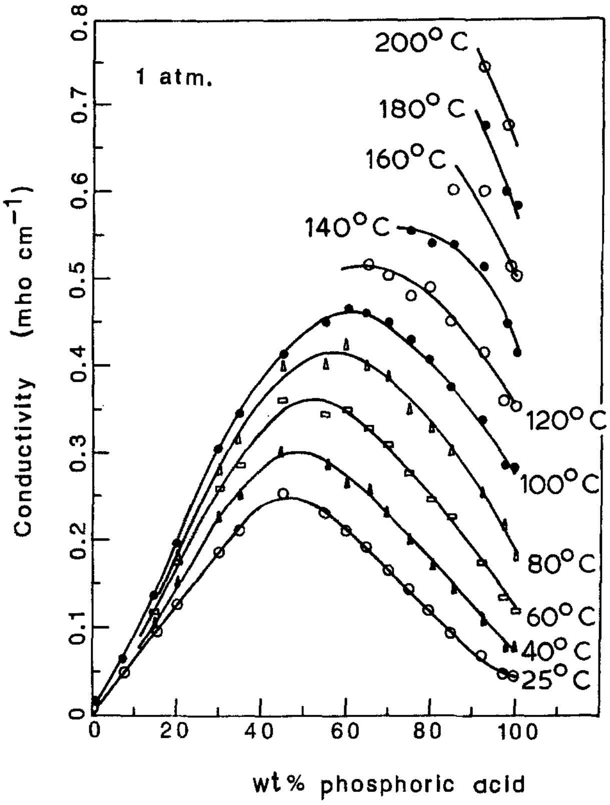

Fig. 1. Specific conductivity vs wt% of phosphoric acid in the temperature range 25–200° C.

Since the equivalent conductivity of an electrolyte is related to its specific conductivity, k, and concentration in normality, C_e, by:

$$\Lambda = k/C_e \quad (2)$$

we calculated the Walden product of the phosphoric acid electrolyte in the form of a conductivity–viscosity product, $k\mu$, using the measured conductivity and viscosity data. The calculated conductivity–viscosity products (represented by open and filled circles) are plotted against the absolute temperature in Fig. 2 on a semi-logarithmic scale for 7.5–100 wt% phosphoric acid. For comparison, the literature data reported in Refs [1, 3] are also plotted in the figure as open triangles; the agreement is within $\pm 10\%$. It is seen that the conductivity–viscosity product substantially

Table 1. Specific conductivity (k) *and viscosity* (μ) *of 7.5–100 wt% phosphoric acid electrolyte*

T (°C)	7.5 wt%		15 wt%		20 wt%		30 wt%		35 wt%		45 wt%		55 wt%		60 wt%	
	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)
23											0.251		0.225			
25	0.048	0.93	0.092	1.20	0.124	1.55	0.183	2.12	0.211	2.67	0.254	3.95	0.230	5.75	0.212	7.71
30	0.049	0.86	0.095	1.09	0.141	1.44	0.200	1.90	0.223	2.43	0.270	3.30	0.246	5.17	0.227	7.04
40	0.053	0.74	0.101	0.90	0.152	1.22	0.226	1.70	0.251	1.94	0.300	2.65	0.284	4.15	0.263	5.96
50	0.055	0.62	0.108	0.76	0.164	1.02	0.240	1.34	0.268	1.58	0.338	2.22	0.318	3.36	0.304	4.89
60	0.056	0.54	0.113	0.66	0.177	0.87	0.257	1.22	0.286	1.34	0.360	1.89	0.343	2.75	0.348	4.07
70	0.058	0.47	0.116	0.57	0.186	0.77	0.268	0.98	0.300	1.21	0.386	1.60	0.372	2.32	0.384	3.24
80	0.062	0.41	0.123	0.50	0.190	0.67	0.281	0.91	0.316	1.09	0.400	1.39	0.400	2.07	0.424	2.70
90	0.064	0.36	0.126	0.45	0.192	0.60	0.292	0.81	0.330	0.96	0.408	1.24	0.432	1.81	0.450	2.38
100	0.066	0.33	0.133	0.39	0.193	0.53	0.304	0.62	0.345	0.86	0.415	1.09	0.450	1.56	0.470	2.11
110													0.470	1.39	0.500	1.87

T (°C)	65 wt%		70 wt%		75 wt%		80 wt%		85 wt%		92.5 wt%		97.5 wt%		100 wt%	
	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)	k (mho cm^{-1})	μ (cp*)
23											0.064		0.048		0.043	
25	0.193	9.70	0.164	13.6	0.144	18.2	0.119	24.9	0.091	39.3	0.069	90.7	0.049	147	0.045	210
30	0.212	8.93	0.196	12.1	0.164	16.2	0.135	21.8	0.108	31.2	0.079	73.8	0.057	120	0.053	174
40	0.257	7.36	0.230	9.97	0.200	13.3	0.169	16.9	0.140	24.3	0.107	54.2	0.077	80.7	0.077	110
50	0.296	5.97	0.270	7.70	0.237	10.4	0.208	13.2	0.180	17.7	0.139	36.9	0.108	54.3	0.086	76.0
60	0.327	4.87	0.309	6.20	0.277	7.42	0.245	10.4	0.225	13.8	0.174	24.3	0.135	38.6	0.120	51.7
70	0.366	3.78	0.348	5.29	0.313	6.52	0.281	8.44	0.257	10.7	0.212	19.2	0.196	30.7	0.154	39.5
80	0.393	3.28	0.386	4.22	0.348	5.20	0.327	6.43	0.300	8.63	0.254	14.3	0.216	22.2	0.180	29.2
90	0.432	2.87	0.415	3.63	0.400	4.57	0.366	5.36	0.338	7.07	0.284	12.1	0.270	16.7		21.8
95															0.270	
100	0.460	2.48	0.450	2.93	0.432	3.79	0.408	4.55	0.372	5.86	0.338	10.2	0.284	14.8	0.284	19.0
110	0.491	2.17	0.480	2.71	0.460	3.32	0.438	3.92	0.400	4.86	0.386	8.45	0.338	12.6	0.318	15.3
120	0.514	1.94	0.502	2.42	0.480	2.99	0.491	3.42	0.450	4.36	0.415	7.02	0.360	10.6	0.354	12.6
130					0.514	2.54	0.514	2.98	0.491	3.69	0.470	6.12	0.432	8.74	0.400	10.5
140					0.554	2.18	0.540	2.60	0.540	3.33	0.514	5.23	0.450	7.17	0.415	8.85
150									0.568	2.93	0.554	4.86	0.491	6.58	0.470	7.93
160									0.600	2.63	0.600	4.17	0.514	5.51	0.502	7.15
170									0.635		0.635	3.65	0.568	4.97	0.540	6.26
180											0.675	3.30	0.600	4.60	0.584	5.42
190											0.720		0.635			
200											0.745		0.675			

* cp = centipoise.

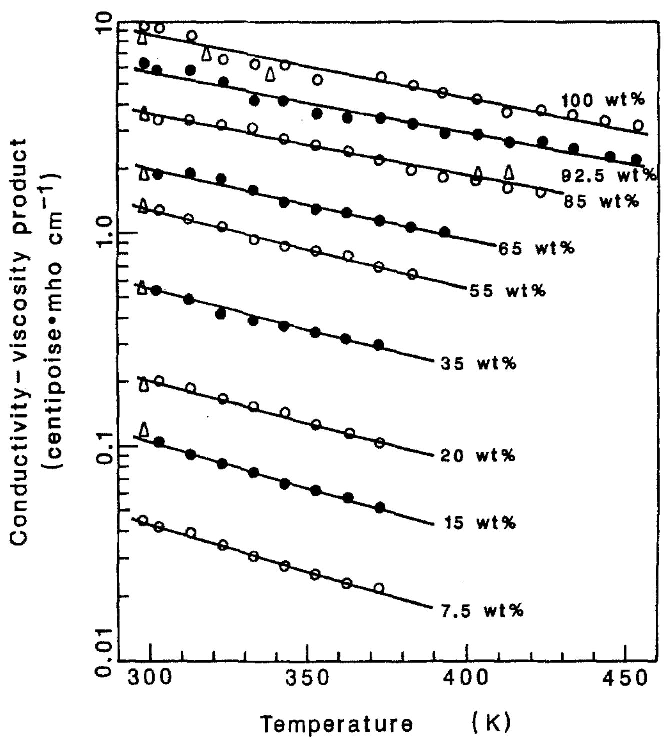

Fig. 2. Semi-logarithmic plot of conductivity–viscosity product vs absolute temperature for 7.5–100 wt% phosphoric acid. The present data are represented by the open and filled circles. For comparison, the values reported in Refs [1] and [3] are also plotted in the figure as triangles.

decreases with increasing temperature, suggesting that proton switching is the dominant mechanism of electric conduction in 7.5–100 wt% phosphoric acid.

Figure 2 indicates that a plot of the logarithm of the conductivity–viscosity product vs absolute temperature is linear for all phosphoric acid solutions investigated. This suggests that the present conductivity and viscosity data can be correlated with an empirical equation of the type:

$$k\mu = A \exp[BT] \tag{3}$$

where A and B are the y intercept and slope of the straight lines in Fig. 2. The values of A and B are functions of phosphoric acid concentrations. It has been found that if the mole fraction of phosphoric acid, X, is used as the solution concentration, A and B could be correlated with a polynomial curve fit in the concentration range of 7.5–100 wt% ($0.0147 \leqslant X \leqslant 1.0$):

$$A\,(\text{centipoise mho cm}^{-1}) = 702.7X^{1.5} - 1734.2X^{2} + 1446.5X^{2.5} - 350.7X^{3} \tag{3a}$$

$$B\,(\text{K}^{-1}) = -0.010163 + 0.011634X - 0.08313X^{2} \tag{3b}$$

To determine the accuracy of the empirical correlation, values of conductivity–viscosity products were

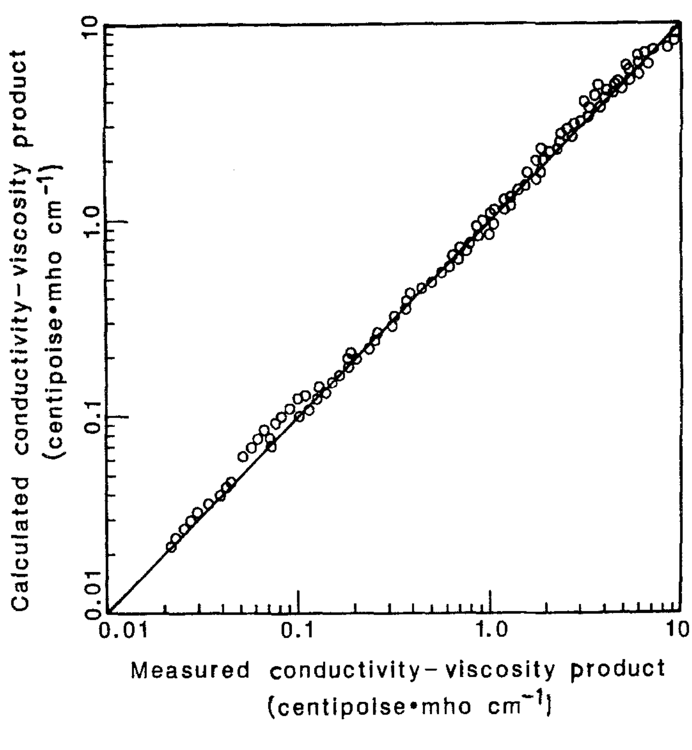

Fig. 3. Calculated conductivity–viscosity product vs experimental conductivity–viscosity product.

calculated from Equations 3a and 3b and compared to the experimental results in Fig. 3 over the concentration range 7.5–100 wt% and temperatures 25–180°C. The standard deviation for the per cent difference between the calculated and experimental values of 188 data points shown in Table 1 was 7.4%. It should be noted that Equations 3, 3a and 3b are purely empirical in nature; further theoretical investigation is needed to examine the exponential temperature dependence of the conductivity–viscosity product. Equations 3, 3a and 3b can be used to calculate the conductivity of 7.5–100 wt% phosphoric acid electrolyte with known viscosity over the temperature range 25–180° C with an error of less than $\pm 7.5\%$.

4. Conclusions

The specific conductivity and viscosity of 7.5–100 wt% aqueous phosphoric acid electrolyte have been measured in the temperature range 25–200° C. The conductivity–viscosity product was found to decrease exponentially with the increasing temperature, and the measured data over the entire concentration and temperature range were correlated with a single empirical relation in the form of Equations 3, 3a and 3b with less than $\pm 7.5\%$ standard deviation. The results indicate that the electric conduction in the phosphoric acid follows the Grotthus proton switching mechanism.

Acknowledgement

This work was supported by the US Department of Energy through a grant NAG3-238 from the National Aeronautics and Space Administration.

References

[1] S. Sarangapani, P. Bindra and E. Yeager, 'Physical and Chemical Properties of Phosphoric Acid', Case Western Reserve University, Cleveland, Ohio, Report to be published on a Brookhaven National Laboratory Subcontract.
[2] I. M. Maksimova and V. P. Yushkevich, *Soviet Electrochem.* **2** (1966) 532.
[3] N. N. Greenwood and A. Thompson, *J. Chem. Soc.* 3485 (1959).
[4] G. P. Kakulin and I. G. Fedorchenko, *Russ. J. Inorg. Chem.* **7** (1962) 1282.
[5] I. G. Fedorchenko, Z. V. Kondratenko and I. A. Kovalev, *Zh. Prikla. Khim.* **8** (1968) 1730.
[6] T. Wydeven, *J. Chem. Eng. Data* **11** (1966) 174.
[7] A. G. Atanasyants and Tsv. Georgiev, *Russ. J. Phys. Chem.* **44** (1970) 1522.
[8] I. G. Fedorchenko, G. P. Kakulin and Z. V. Kondratenko, *Russian J. Inorg. Chem.* **10** (1965) 1061.
[9] D. I. MacDonald and J. R. Boyack, *J. Chem. Eng. Data* **14** (1969) 380.
[10] J. O'M. Bockris and A. K. N. Reddy, 'Modern Electrochemistry', Plenum Press, New York (1970) Vol. I, pp. 474–488.
[11] H. Sadek, *J. Electroanal. Chem.* **144** (1983) 11.
[12] E. Peled, M. Brand and E. Gileadi, *J. Electrochem. Soc.* **128** (1981) 1697.