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Diffusion Coefficients for Aqueous Boric Acid

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Diffusion coefficients of aqueous boric acid up to 2.0 mol·dm^{-3} have been measured at 25 °C without pH control and at a pH of 7.0. The Stokes diaphragm method was used, and the results were analyzed by a regression analysis. The experimental and data analysis methods were checked with HCl.

Introduction

The concentration of borate ions varies with pH, the solution temperature, and the concentration of boric acid. Equilibria of borate ions in aqueous boric acid solution have been extensively studied by Ingri (1963a−c), Maya (1976), and Hirao et al. (1979). Ingri (1963a−c) utilized emf (pH) measurements with a hydrogen electrode to indirectly determine the borate ion concentration up to 3.0 mol·dm^{-3} as boric acid at 25 °C. Maya (1976) and Hirao et al. (1979) identified the species with Raman spectroscopy. They concluded that the main species were $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$, and there were also strong indications for the formation of $B_3O_3(OH)_5^{2-}$ and $B_5O_6(OH)_4^-$.

Mesmer et al. (1972a,b) studied the equilibria of boric acid in 0.13−0.1 mol·dm^{-3} KCl over the temperature range of 50−290 °C and at concentrations up to 0.6 mol·dm^{-3} boric acid. They employed a high-temperature potentiometric technique. They suggested the formation of a polynuclear species like $B_2(OH)_7^-$ and $B_3(OH)_{10}^-$, and minor amounts of either $B_4(OH)_{14}^{2-}$ or $B_5(OH)_{18}^{3-}$. They reported the possibility of a new dimeric species at 200 °C, and with an increase in temperature they reported a decrease in the average number of OH^- ions and the amount of polyborates at a given boron concentration.

Boric acid diffusion in a liquid can be described as the combined diffusion of nonelectrolytes and electrolytes because of the existence of both undissociated boric acid and several borate ions in a boric acid solution.

Most diffusion studies on aqueous nonelectrolytes have been performed to estimate diffusivities (or diffusion coefficients) in dilute solutions. Several empirical correlations have been developed (Skelland, 1974). Diffusivities in concentrated solutions are characterized by a concentration dependence which can be expressed in terms of the activity coefficient of the solute. If the system is composed of many components, the situation is complex because of interactions between the flows of the various species, and these complications increase with increasing departure of the system from ideality.

For a solution containing two different cations and a common anion, diffusion can be described well by the exact ternary theory (Cussler, 1976). However, for diffusion involving more than four ions, it is almost impossible to estimate diffusivities with analytic relationships because the relevant physical and chemical data for each ion are often not available.

The diffusion coefficient of boric acid in aqueous solution cannot be predicted through theoretical equations because the chemical and physical data of all the borate ions are not available and the diffusion relations are not known. Diffusion experiments were made at different concentrations of boric acid solution with no pH control or a pH control of 7.0. The results were analyzed by a regression method.

Experimental Section

Theory. The Stokes diaphragm cell method is a pseudo-steady-state method. The advantages of this method are that it is simple to operate and inexpensive to build. The disadvantage is that it is difficult to locate the cause when occasionally inconsistent results are obtained. Good results are hard to obtain at <0.05 mol·dm^{-3} because solutes adsorb on the glass diaphragm. An accuracy of 0.2% at high concentrations can be obtained if the experiment is carried out carefully (Robinson and Stokes, 1959; Stokes, 1950).

The basic apparatus consists of two well-stirred compartments separated by a porous diaphragm. It is assumed that the diaphragm is in a steady state during the experiment and there is no solute accumulation in or loss from the diaphragm; the flux of solute across any plane in the diaphragm parallel to its surface is everywhere the same at any given time. However, this flux will decrease slowly with time as the process of diffusion reduces the concentration difference in the two compartments. Stokes defines the integral diffusion coefficient as $\bar{D} = (1/t)\int_0^t \bar{D}(t)\,\mathrm{d}t$, and then he obtains

$$\bar{D} = \frac{1}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \quad \text{and} \quad \beta = \frac{A}{l}\left(\frac{1}{V_1} + \frac{1}{V_u}\right) \qquad (1)$$

where A is the total effective cross section of the diaphragm pores; c_1 and c_2 are the initial concentrations of the lower and upper compartments, respectively, c_3 and c_4 are the final concentrations of the lower and upper compartments, respectively, l is the effective average length along the diffusion path, t is the diffusion duration, V_1 and V_u are the liquid volumes of the lower and upper compartments, and the cell constant β is determined by calibration with a solute with a known $\bar{D}$.

Now defining a new integral diffusion coefficient, $\bar{D}°$, which is the average D over the concentration range of 0 to c, we derive easily that (Robinson and Stokes, 1959; Stokes, 1950)

$$\bar{D}°(c_l^m) = \bar{D} - (c_u^m/c_l^m)[\bar{D} - \bar{D}°(c_u^m)] \qquad (2)$$

where $c_l^m = (c_1 + c_3)/2$ and $c_u^m = (c_2 + c_4)/2$.

This relationship enables us to calculate the integral diffusion coefficients at an average concentration in the lower compartment. In order to handle the results, Stokes utilized a graphical method. In this study, however, results

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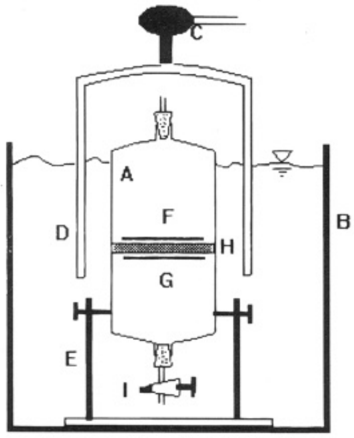

Figure 1. Schematic of the diaphragm cell: (A) glass cell; (B) thermostat; (C) electric motor; (D) magnet; (E) frame supporting cell; (F, G) glass stirrers enclosing iron wire; (H) porous glass frit; (I) stopcock with Teflon plug.

were treated as follows: (1) For the selection of a model having the best statistics, the data of $\bar{D}$ (which is obtained by experimental data and eq 1) against c_1 (initial concentration in the lower compartment) are analyzed on several regression models with SAS (Statistical Analysis System)/REG. (2) With the selected model, $\bar{D}°(c_u^m)$ values for c_u^m of each run are estimated, and $\bar{D}°(c_l^m)$ values are calculated by the substitution of these values into eq 2. (3) The calculated $\bar{D}°(c_l^m)$ values for each c_l^m are used in the estimation of new parameters of the model, and $\bar{D}°(c_u^m)$ values are again calculated by the model with new parameters. (4) The new $\bar{D}°(c_u^m)$ values are again substituted into eq 2, and $\bar{D}°(c_l^m)$ values are recalculated. (5) This procedure is repeated until $\bar{D}°(c_l^m)$ does not change. (6) With the finally calculated $\bar{D}°(c_l^m)$ over c_l^m, regression analysis is carried out and the final parameters of the model are determined. (7) From the model with final parameters, the differential diffusion coefficients are estimated by the equation

$$D = \bar{D}° + c(\mathrm{d}\bar{D}°/\mathrm{d}c) \qquad (3)$$

Materials and Procedures. Diaphragm cells were made by fusing sintered glass disks into 40 mm i.d. glass tubing. The disks were of medium porosity, about 3 mm thick, and were manufactured by the Lab Glass Co. The upper compartment of the cell was somewhat larger than the lower one. This structure made it easy to control the liquid volume of each compartment which should be the same to get good results (Baird and Friden, 1987; Clunie et al., 1990). Figure 1 shows the schematic of the experimental setup. The cell was operated according to the procedure suggested by Stokes (1950).

Double-distilled water was used to make up all solutions and had a conductivity $\sim 10^{-6}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$. All reagents such as boric acid, sodium hydroxide, hydrochloric acid, potassium chloride, etc. were of extrapure grade and were used without further purification. In order to determine the cell constant, 0.5 $\mathrm{mol \cdot dm^{-3}}$ KCl solution, whose integral diffusion coefficient is $1.847 \times 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$ at 25 °C, was used. The chloride ion was determined by the Mohr method (Williams, 1984; Snell, 1968), and was titrated with an autotitrator manufactured by Solea Tacussel (France).

In order to validate the experimental and the data analysis methods, experiments on the diffusion of HCl were performed at 25 °C at concentrations up to 5.0 $\mathrm{mol \cdot dm^{-3}}$. The concentration of HCl was determined by automatic potentiometric titration in which the end point was at a pH of 8.5. In the case of boric acid, the diffusion coefficient was determined from measurements at a pH of 7.0 or in a no pH control solution at 25 °C. NaOH solution was used to control the pH.

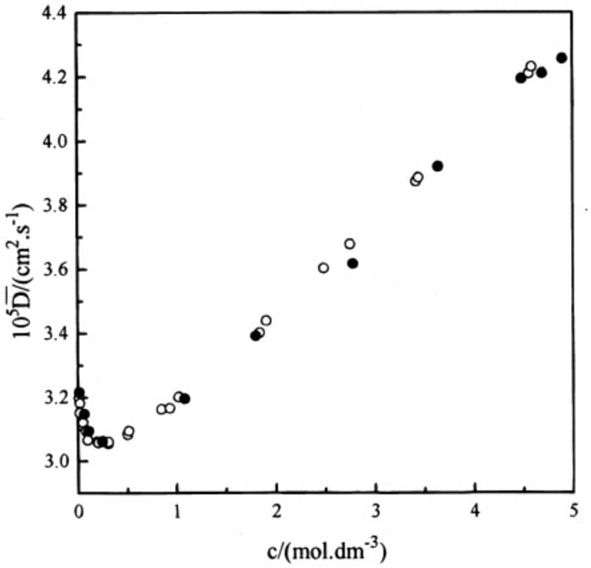

Figure 2. Comparison of integral diffusion coefficient $\bar{D}$ for aqueous HCl at concentration c: ○, Stokes; ●, this work.

Table 1. Integral Diffusion Coefficients for HCl at 25 °C

$c_1/(\mathrm{mol \cdot dm^{-3}})$	$10^5\bar{D}/(\mathrm{cm^2 \cdot s^{-1}})$	$c_l^m/(\mathrm{mol \cdot dm^{-3}})$	$10^5\bar{D}°(c_l^m)/(\mathrm{cm^2 \cdot s^{-1}})$
4.896 8	4.2563	4.432 8	4.135 82
4.691 9	4.2101	4.119 65	4.058 22
4.483 2	4.1925	3.881 05	4.026 22
3.648 8	3.9198	3.361 95	3.850 13
2.786 5	3.6173	2.464 6	3.549 92
1.800 1	3.3924	1.587 0	3.354 84
1.081 9	3.1961	0.965 65	3.189 79
0.242 4	3.0618	0.216 45	3.081 56
0.106 0	3.0939	0.095 165	3.113 07
0.063 74	3.1478	0.056 6	3.163 91
0.011 28	3.2159	0.010 13	3.226 85

The prediffusion duration was about 2 h, and the diffusion duration of HCl and boric acid was about 1 and 2 days, respectively. Prediffusion was performed after the upper compartment was filled with double-distilled water. The boric acid was determined by the same method as the HCl case, but some mannitol ($\mathrm{HOCH_2(CHOH)_4CH_2OH}$) was added so that boric acid can be dissociated fully (Midgley, 1988; Lawrence, 1964). Either 0.1 or 0.01 $\mathrm{mol \cdot dm^{-3}}$ NaOH solution was used as the titrant for boric acid. In the case of the experiment at a pH of 7.0, boric acid was determined after NaOH (added for pH control) was neutralized by 0.01 $\mathrm{mol \cdot dm^{-3}}$ HCl solution. That is, the added NaOH was titrated by HCl solution to a strong acid end point (pH = 5.0), and then boric acid was determined with the NaOH solution and mannitol (Williams, 1984).

Results and Discussion

Validation of Experimental and Data Analysis Method. To verify a correct experimental and analysis method, a diffusion experiment of HCl was made. Figure 2 compares these results with those of Stokes. Several regression models were investigated, and the best model equation was

$$10^5\bar{D}/(\mathrm{cm^2 \cdot s^{-1}}) = \beta_0 + \beta_1 c/(\mathrm{mol \cdot dm^{-3}}) + \beta_2\{c/(\mathrm{mol \cdot dm^{-3}})\}^2 + \beta_3\{c/(\mathrm{mol \cdot dm^{-3}})\}^{0.5} + \epsilon \qquad (4)$$

The first regression analysis on $\bar{D}$ and initial concentration c_1 was performed with this model. Its R-square (1 −

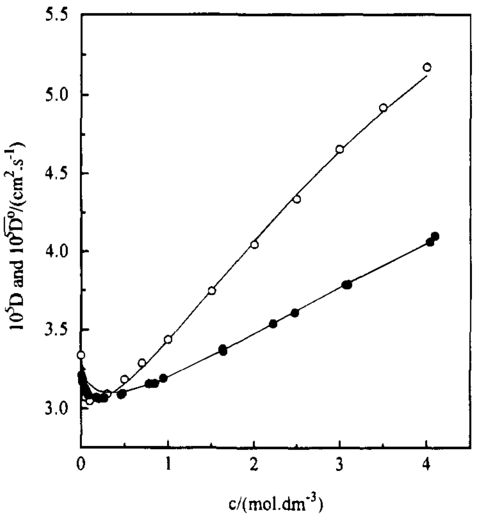

Figure 3. Comparison between Stokes' results for aqueous HCl concentration *c*: Stokes' value for integral diffusion coefficient, ●; differential diffusion coefficient, ○; calculated values, this work, —.

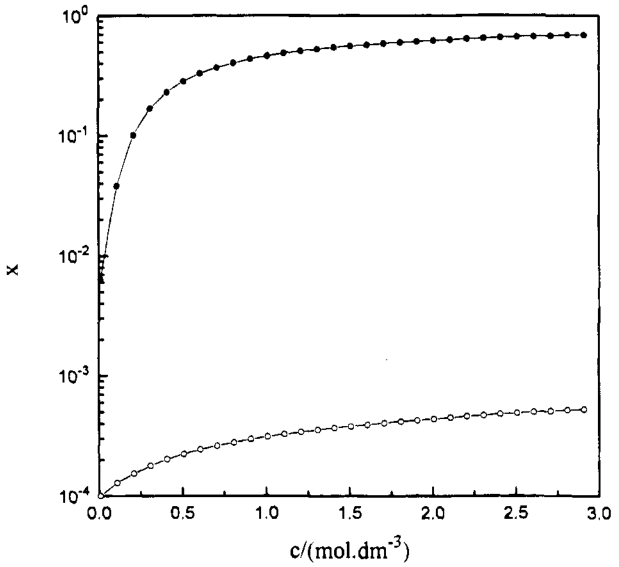

Figure 4. Ion mole fraction *x* at 25 °C for (●) pH 7.0 and (○) no pH control.

Table 2. Statistics and Values of the Parameters for Models 6 and 7

	model 6	model 7
β_0	1.640 516	1.412 311
β_1	−0.452 398	−0.536 202
β_2	N/A	0.248 385
R-square	0.9866	0.9465
adj *R*-square	0.9840	0.9286
significance level	<0.0001	<0.0003

error sum of squares/total sum of squares) and adjusted *R*-square were 0.9973 and 0.9963, respectively, and the parameters β_0, β_1, β_2, and β_3 proved satisfactory over a significance level of 0.014 and less. The residual analysis for the model showed the aptness of eq 4 (Draper, 1981; Devore, 1991).

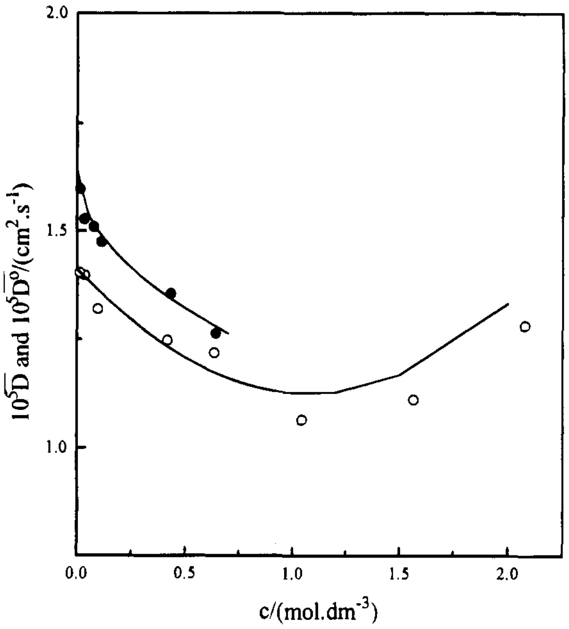

Figure 5. Experimental data and integral diffusion coefficients calculated with the models: ●, no pH control; ○, pH 7.0.

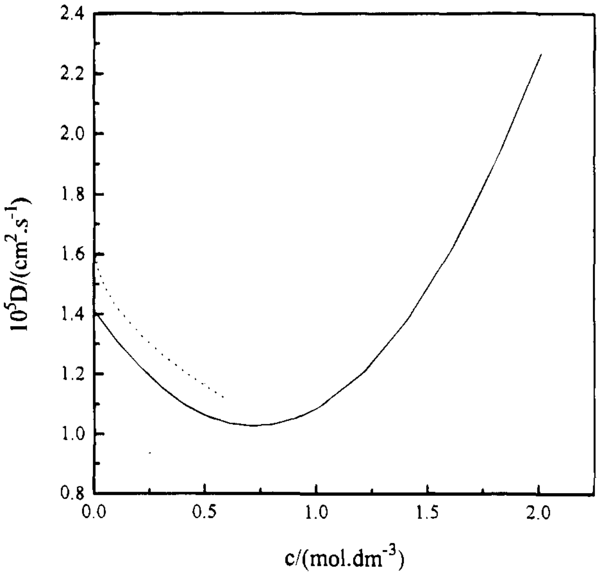

Figure 6. Differential diffusion coefficients for boric acid concentration *c* with respect to pH at 25 °C: - - -, no pH control; —, pH 7.0.

Table 3. Integral Diffusion Coefficients for Boric Acid with Respect to pH at 25 °C

c_1/ (mol·dm^{-3})	$10^5\bar{D}$/ (cm^2·s^{-1})	c_1^m/ (mol·dm^{-3})	$10^5\bar{D}°(c_1^m)$/ (cm^2·s^{-1})	c_{Na}/ (mol·dm^{-3})	notes
0.642 6	1.262 8	0.594 85	1.284 95		no pH control
0.431 22	1.355 5	0.396 61	1.372 79		
0.113 09	1.475 5	0.103 52	1.486 48	N/A	
0.077 25	0.510 1	0.070 55	1.518 80		
0.33 763	1.527 5	0.031 75	1.535 74		
0.014 586	1.597 8	0.014 59	1.600 05		
2.077 3	1.280 6	1.849 35	1.283 36	0.4520	pH 7.0
1.563 2	1.109 6	1.411 35	1.134 03	0.3072	
1.043 9	1.063 1	0.946 75	1.093 83	0.1705	
0.635 52	1.217 88	0.566 41	1.237 23	0.7576 × 10^{-1}	
0.416 89	1.246 60	0.372 345	1.263 63	0.3454 × 10^{-1}	
0.094 44	1.320 29	0.873 9	1.327 41	0.1348 × 10^{-2}	
0.033 94	1.399 3	0.029 953	1.400 75	0.2460 × 10^{-3}	
0.011 931	1.405 2	0.010 508	1.406 06	0.7366 × 10^{-4}	

The data analysis procedure was repeated until $\bar{D}°(c_1^m)$ did not change. The final parameters could be obtained through three repetitions, and their values were β_0 = 3.3390, β_1 = 0.698 681, β_2 = −0.028 765, and β_3 = −0.809 963, and all parameters had a significance level of 0.01 and less. The c_1^m and $\bar{D}°(c_1^m)$ which are calculated by eq 4 with the final parameters are listed in the last two columns of Table 1 and plotted in Figure 3 with a comparison with Stokes' values. *D* (HCl, 25 °C) values were estimated from the following equation which was derived from the model with final parameters and eq 3:

$$10^5D/(\mathrm{cm^2{\cdot}s^{-1}}) = 3.3390 + 1.397362c/(\mathrm{mol{\cdot}dm^{-3}}) - 0.086295\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^2 - 1.2149445\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^{0.5} \quad (5)$$

$$0 \le c \le 4.5\ \mathrm{mol{\cdot}dm^{-3}}$$

The calculated D was compared with Stokes' results in Figure 3. It was known that the maximum and average difference were 2.08 and 0.13%, respectively, in the case of D and 2.49 and 0.91% in the case of $\bar{D}$.

Diffusion Coefficients of Boric Acid with pH Conditions. The solutions of boric acid were prepared from 0.01 to 0.65 mol·dm^{-3} when the experiment was carried out for solutions without pH control. Measurements were made at concentrations of 0.01–2.0 mol·dm^{-3} for solutions of pH 7.0.

The results show that the diffusion coefficients of boric acid in solution without pH control are somewhat larger than those in solution with pH control. These phenomena can be explained with Figure 4 which was plotted with data calculated by the computer program developed with Mesmer's equilibria (Mesmer et al., 1972a,b). We can see that the ion mole fraction x (mole concentration ratio of borate ions to total boron) in a solution of pH 7.0 changes considerably compared with that in a solution with no pH control. However, the diffusion coefficients decrease insignificantly because of composite effects like ion–ion interaction, the electrophoretic effect (Robinson and Stokes, 1959), the amount of NaOH added, etc. The concentration of sodium ion c_{Na} for the initial concentration of boric acid c_1 was calculated by the above computer program and is given in Table 3. A boric acid solution of pH 7.0 is a three-component solution, yet experimental results were treated like pseudobinary diffusion because the concentration of sodium ion was lower than that of boric acid. Therefore, D values in boric acid a solution of pH 7.0 are really effective or pseudobinary diffusion coefficients (Cussler, 1976).

The following equations proved satisfactory:

no pH control

$$10^5\bar{D}/(\mathrm{cm^2{\cdot}s^{-1}}) = \beta_0 + \beta_1\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^{0.5} + \epsilon \quad (6)$$

$$0 \le c \le 0.65\ \mathrm{mol{\cdot}dm^{-3}}$$

pH 7

$$10^5\bar{D}/(\mathrm{cm^2{\cdot}s^{-1}}) = \beta_0 + \beta_1 c/(\mathrm{mol{\cdot}dm^{-3}}) + \beta_2\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^2 + \epsilon \quad (7)$$

$$0 \le c \le 2.0\ \mathrm{mol{\cdot}dm^{-3}}$$

The residual analysis was carried out for each model. The statistics and the values of the parameters are given in Table 2. The initial $\bar{D}$ and the final $\bar{D}^\circ(c_1^{\mathrm{m}})$ values for each case are listed in Table 3, and Figure 5 shows the initial experimental $\bar{D}$ and final $\bar{D}^\circ(c_1^{\mathrm{m}})$ calculated by each model with parameter values. Figure 6 shows differential diffusion coefficients calculated by the following equations derived from eq 3 and models 6 and 7:

$$10^5D/(\mathrm{cm^2{\cdot}s^{-1}}) = 1.640516 - 0.678597\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^{0.5} \quad (8)$$

$$0 \le c \le 0.65\ \mathrm{mol{\cdot}dm^{-3}}$$

$$10^5D/(\mathrm{cm^2{\cdot}s^{-1}}) = 1.412311 - 1.072404c/(\mathrm{mol{\cdot}dm^{-3}}) + 0.745155\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^2 \quad (9)$$

$$0 \le c \le 2.0\ \mathrm{mol{\cdot}dm^{-3}}$$

Conclusion

The method using a regression analysis was developed to analyze experimental results obtained by the Stokes diaphragm cell method. The regression model gives the following equation for the differential diffusion coefficient of aqueous HCl over the concentration range 0.0–4.5 mol·dm^{-3} at 25 °C: $10^5D/(\mathrm{cm^2{\cdot}s^{-1}}) = 3.3390 + 1.397362c/(\mathrm{mol{\cdot}dm^{-3}}) - 0.086295\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^2 - 1.2149445\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^{0.5}$. It was verified that the differential diffusion coefficients of boric acid in solution without pH control and its pseudobinary diffusion coefficient for pH 7.0 could be calculated from the following relations, respectively, over each concentration range at 25 °C: $10^5D/(\mathrm{cm^2{\cdot}s^{-1}}) = 1.640516 - 0.678597\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^{0.5}$ ($0 \le c \le 0.65$ mol·dm^{-3}) and $10^5D/(\mathrm{cm^2{\cdot}s^{-1}}) = 1.412311 - 1.072404c/(\mathrm{mol{\cdot}dm^{-3}}) + 0.74155\{c/(\mathrm{mol{\cdot}dm^{-3}})\}^2$ ($0 \le c \le 2.0$ mol·dm^{-3}). These models may be available for simulation of diffusion-based devices such as the membrane extractor for acid separation, etc.

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