J. Chem. Eng. Data 1982, 27, 255-256

Diffusion Coefficients for One Composition of the System H_2O–NaCl–KCl

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Four diffusion coefficients for one composition of the system H_2O–NaCl–KCl in which the molar concentrations of NaCl and KCl are 1.9 and 0.1, respectively, are obtained at 25 °C by using a Gouy optical diffusiometer. These were compared with values predicted by using the ionic transport coefficients of corresponding binary systems according to the methods developed by Miller.

Introduction

Miller (*1*, *2*) has developed procedures of estimating the diffusion coefficients of ternary electrolyte systems from the ionic transport coefficients, l_{ij}, of corresponding binary systems. In one method (LN), the l_{ij} values are determined at a binary concentration equal to the total solute concentration of the ternary system. In another method (LNI), the main ionic transport coefficients of cations are taken at the binary concentrations equal to the component concentrations in the ternary system while other l_{ij} values are taken as in the LN method. Miller found that the LNI method gives better results than the LN method for the available ternary electrolyte systems despite the fact that the LN method is more "natural".

In an earlier communication (*3*) we reported the diffusion studies of H_2O–KCl–HCl and H_2O–NaCl–HCl systems. It was found that Miller's LNI method gives better predictions of the diffusion coefficients for the compositions where the molar concentrations of two electrolytes are about equal. On the other hand, the LN method gave much better results when the concentration difference of two electrolytes was large.

It may be noted that for the electrolyte systems tested by Miller (H_2O–NaCl–KCl, H_2O–LiCl–KCl, and H_2O–LiCl–NaCl), the concentration differences between the two electrolytes were relatively small. In order to see whether the LN method gives better results for certain compositions of H_2O–KCl–HCl and H_2O–NaCl–HCl systems because of the presence of acid or whether it is due to a more general property of ternary electrolyte systems, we have chosen the system of H_2O–NaCl–KCl.

Experimental Section

Materials. The recrystallized NaCl and KCl used were part of the samples prepared for a previous study from this laboratory (*3*). The purities of these salts were already tested. The areas under the fringe deviation graphs for the above salts were less than 1×10^4. The molecular weights used are 18.016 for H_2O, 74.555 for KCl, and 58.443 for NaCl. Solutions were prepared with Barnstead purified and air-saturated distilled water. The density values used to calculate the air-buoyancy corrections in preparing the solutions were 1.984 for KCl, 2.165 for NaCl, and 8.4 g/mL for the metal weights of the balance.

Diffusion Experiments. The optical diffusiometer and the procedures for diffusion experiments, measurements of photographic plates, and calculation of diffusion coefficients are already described (*3*–*5*). A Tiselius-type fused quartz cell with a cell thickness of 2.5075 cm and an optical lever arm of 308.868 cm was used for the experiments.

Table I. Primary Data for the System H_2O–NaCl–KCl[a]

expt no.	T 16	T 19	T 18	T 15
C_{1A}, mol/L	1.900 22	1.885 09	1.820 19	1.809 57
C_{2A}, mol/L	0.032 93	0.039 64	0.079 83	0.099 73
d_A, g/mL	1.072 989	1.072 710	1.072 030	1.072 468
C_{1B}, mol/L	1.900 20	1.914 89	1.979 85	1.980 26
C_{2B}, mol/L	0.167 08	0.160 36	0.120 17	0.099 73
d_B, g/mL	1.078 782	1.079 043	1.079 748	1.078 888
$\bar{C}_1$, mol/L	1.900 21	1.899 99	1.900 02	1.894 92
$\bar{C}_2$, mol/L	0.100 01	0.100 00	0.100 00	0.099 73
J_{exptl}	54.17	60.98	81.86	70.11
J_{calcd}	54.16	60.99	81.86	70.10
α_1	−0.0002	0.2007	0.8010	1.0000
$10^5(\mathcal{D}_A)_{exptl}$, cm^2/s	1.7615	1.7106	1.5674	1.5246
$10^5(\mathcal{D}_A)_{calcd}$, cm^2/s	1.7619	1.7100	1.5677	1.5245
$10^4 Q_{exptl}$	−5.5	−1.2	4.3	6.0
$10^4 Q_{calcd}$	−5.8	−1.2	5.3	5.2

[a] Component 1 = NaCl; component 2 = KCl.

Table II. Diffusion Coefficients, Density Data, Partial Molal Volumes, and Refractive Index Derivatives for the System H_2O–NaCl–KCl

$\tilde{C}_1$[a]	1.9	$10^3 R_1$[e]	8.944
$\tilde{C}_2$[a]	0.1	$10^3 R_2$[e]	8.795
$\tilde{C}_0$[a]	53.141	$10^5 (D_{11})_V$[f]	1.4461 ∓ 0.0151
$d(\tilde{C}_1,\tilde{C}_2)$[b]	1.075881	$10^5 (D_{12})_V$[f]	0.0882 ∓ 0.0153
H_1[c]	0.03753	$10^5 (D_{21})_V$[f]	0.0890 ± 0.0172
H_2[c]	0.04317	$10^5 (D_{22})_V$[f]	1.6619 ± 0.0174
$\overline{V}_1$[d]	20.91	$10^5 (D_{11})_0$[f]	1.5117
$\overline{V}_2$[d]	31.37	$10^5 (D_{12})_0$[f]	0.1954
$\overline{V}_0$[d]	18.011	$10^5 (D_{21})_0$[f]	0.0925
		$10^5 (D_{22})_0$[f]	1.6654

[a] Units: mol/L. [b] Units: g/mL. [c] Units: g L/(mol mL). [d] Units: mL/mol. [e] Units: L/mol. [f] Units: cm^2/s.

The density measurements were made as before.

Results

The primary data from the diffusion experiments for H_2O–NaCl–KCl are given in Table I, where all of the concentrations, C_i, are expressed in mol/L. Here $\bar{C}_i = (C_{iA} + C_{iB})/2$ where A and B designate the upper and lower solutions, respectively. The quantity d is the density of the solution in g/mL. The quantities J_{exptl}, $(\mathcal{D}_A)_{exptl}$, and Q_{exptl} are the experimental values of total fringe numbers, reduced height/area ratios, and the areas under the fringe deviation graphs, respectively; J_{calcd}, $(\mathcal{D}_A)_{calcd}$, and Q_{calcd} are those of calculated values, and α is the solute refractive index fraction. The methods for calculating J_{calcd}, $(\mathcal{D}_A)_{calcd}$, and Q_{calcd} have been described in earlier publications from this laboratory (*6*, *7*). The agreement between J_{exptl} and J_{calcd} is within 1/100 of a fringe. The agreement between $(\mathcal{D}_A)_{exptl}$ and $(\mathcal{D}_A)_{calcd}$ is within 0.03%, and that between Q_{exptl} and Q_{calcd} is within 1×10^{-4}.

Table II gives the volume-fixed diffusion coefficients, $(D_{ij})_V$, and the solvent-fixed diffusion coefficients, $(D_{ij})_0$, obtained from

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0021-9568/82/1727-0255$01.25/0

Table III. Comparison of Experimental and Calculated Values of $(D_{ij})_V$[a]

	exptl	LN	LNI
$10^5(D_{11})_V$	1.45	1.48	1.47
$10^5(D_{12})_V$	0.09	0.19	0.15
$10^5(D_{21})_V$	0.09	0.04	0.40
$10^5(D_{22})_V$	1.66	1.71	1.85

[a] Units: cm^2/s.

the primary data in Table I. The density at the prefixed mean concentration, $d(\tilde{C}_1,\tilde{C}_2)$ and the density derivatives, H_i, are calculated by fitting the density data in Table I to an expansion about $d(\tilde{C}_1,\tilde{C}_2)$ by the method of least squares using the expression

$$d_{calcd} = d(\tilde{C}_1,\tilde{C}_2) + H_1(C_1 - 1.9) + H_2(C_2 - 0.1)$$

The average deviation between d_{calcd} and the experimental values was found to be ±0.000 005. The Fortran program for this calculation was prepared by Dr. M. A. Loewenstein, formerly of this laboratory. Table II also contains the partial molal volumes, $\bar{V}_i$, and the refractive index derivatives, R_i. In this table, C_0 and $\bar{V}_0$ denote the concentration and the partial molal volume of water, respectively.

The results of the experiments were examined to determine whether the system had been gravitationally stable throughout the duration of diffusion. Values for gravitational criteria I and II (*6*, *8*) were calculated for each experiment, and all experiments were found to satisfy these criteria.

Table III gives the comparison of experimental and calculated diffusion coefficients. For these calculations the activity coefficients were obtained (*9*) by assuming that the Harned relationship holds for this system. Both LN and LNI approximations give less satisfactory estimates for the cross-term diffusion coefficients compared to the case where the concentrations of two electrolytes are not too different. However, as in the cases of the H_2O-KCl-HCl and H_2O-NaCl-HCl systems, the LN approximation gives overall better values for the $(D_{ij})_V$'s. Thus, it appears that, for strong electrolyte systems, the LN approximation generally gives better estimates of diffusion coefficients than the LNI method.

Acknowledgment

I thank Dr. Donald G. Miller for reading the manuscript.

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Received for review September 28, 1981. Accepted April 1, 1982.

Ethanol Densities between −50 and 20 °C

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The density of ethanol was measured between −50 and 20 °C to ±0.01%. The measurements were made by using a procedure similar to ASTM D1217-54, "Standard Method of Test of Density and Specific Gravity of Liquids by Bingham Pycnometer". The results were correlated by the equation $\ln D = -0.215231 - (1.05037 \times 10^{-3})T - (7.837 \times 10^{-7})T^2 - (7.47 \times 10^{-9})T^3$ (D in g/cm^3, T in °C).

Introduction

In order to measure densities with a vibrating tube densimeter, one must first calibrate the densimeter with a fluid for which densities are known to the desired accuracy. Above 0 °C, water is a suitable calibration fluid. Below 0 °C, water is not suitable and densities of the desired accuracy could not be found for any other common fluid. Thus, ethanol densities between −50 and 20 °C were measured to ±0.01% with a pycnometer technique. These new data will be useful for calibrating devices such as the vibrating tube densimeter.

Experimental Section

The experimental procedure was similar to ASTM D1217-54 (*1*). In this procedure a pycnometer (see Figure 1) is filled to the mark with water at a known temperature. The weight of the pycnometer thus filled minus the weight of the empty pycnometer allows calculation of the pycnometer volume. Ethanol densities can then be obtained by determining the weight of ethanol required to fill the pycnometer to the mark at the desired temperature. In this work, the water used in the calibration was distilled in stainless steel, boiled, and then allowed to cool to room temperature before injection into the pycnometer. Ethanol was obtained as absolute ethanol and further purified by distillation over sodium metal and ethyl phthalate in water-free air (*2*). This purification method gave ethanol with a water content of 0.003 wt % as determined by a Karl Fischer analysis. For the water calibrations and ethanol measurements, temperature was measured with a Rosemount Model 162 platinum resistance thermometer with a calibration traceable to the NBS. The thermometer and the Mueller resistance bridge used were tested by measuring the triple point of water to ±0.02 °C. Between −20 and 30 °C, a Neslab-RTE-8 circulating bath with a Bayley proportional band controller, Model 123, was used. At −30, −40, and −50 °C, a Neslab Endocal LT 50 bath was used. All measurements were made at least once in each of two different pycnometers.

Several modifications were required to extend the ASTM D1217-54 procedure to low temperatures. First, the volume of the bulb above the mark on the pycnometer was increased from <1 to 3.8 cm^3. This allowed for expansion of the ethanol from −50 °C to room temperature. One problem that arose at the low temperatures was condensation of water on the inside of the pycnometer. This problem was eliminated by using a rubber serum stopper on the pycnometer during part of the procedure. In this procedure, a syringe was used to fill the pycnometer bulb with ethanol at room temperature. A serum stopper was placed in the pycnometer neck, a syringe needle

0021-9568/82/1727-0256$01.25/0