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Mutual Diffusion Coefficients of Aqueous KCl at High Pressures Measured by the Taylor Dispersion Method

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ABSTRACT: Diffusion coefficients of potassium chloride in potassium chloride solutions of molality (0, 1, 2.5, and 4.5) mol·kg^{-1} were measured at temperatures of (298.15, 323.15, 348.15, 373.15, and 423.15) K and at pressures from (0.1 to 69) MPa using the Taylor dispersion technique. The results have an overall estimated expanded relative uncertainty of 1.6 % with a coverage factor $k = 2$. When compared with standard reference data for the diffusion coefficient of KCl in KCl solutions at $T = 298.15$ K and $p = 0.1$ MPa, a relative deviation of 0.5 % is observed. The effect of pressure was found to be very small. A satisfactory multiparameter correlation of all of the data in terms of pressure, temperature, and molality was obtained; this exhibits an absolute average relative deviation of 1.2 % in comparison with our data. The model also provides a good account of the majority of the data available in the literature.

INTRODUCTION

The thermophysical properties of systems comprising water, salts, hydrocarbons, and/or carbon dioxide are important factors in the design, optimization, and control of water and gas injection processes in both petroleum reservoirs and saline aquifers. Carbonate reservoirs are especially interesting as strong chemical interactions between reservoir fluids and minerals are possible. The present research contributes to a program of measurements and modeling of the physical and chemical properties of systems comprising carbon dioxide, hydrocarbons, brines, and minerals at reservoir conditions that is being undertaken as part of a multidisciplinary research center.[1] The research is directed toward an improved understanding of the detailed physical and chemical processes occurring at the pore- and fracture-scale in carbonate reservoirs during water and gas injection processes, including both geological storage of CO_2 and CO_2-enhanced hydrocarbon production.

Diffusion is one of the properties that are of interest, especially at the pore-scale. To measure this property for systems containing carbon dioxide and/or hydrocarbons and/or brines at reservoir conditions, a new apparatus has been built. The method used is the chromatographic peak broadening technique which is based on the fundamental work of Taylor,[2,3] as extended by Aris,[4] which involves the dispersion of a solute injected into the steady-state laminar flow of a mobile solvent phase passing through a long tube of uniform diameter. Due to the combined effects of convective flow and molecular diffusion, an initially sharp pulse develops a Gaussian distribution. The temporal variance of this Gaussian distribution is dependent on both the average flow velocity and the molecular diffusivity. At the end of the diffusion tube, the concentration is measured as a function of time. In the present work, this was accomplished by means of a chromatographic refractive index detector. As built, the apparatus is capable of operating with the diffusion column at temperatures of up to 473 K and pressures up to 70 MPa. In this work, we begin by studying a simple electrolyte solution, aqueous potassium chloride, with two objectives. The first was to validate the new experimental apparatus by means of measurements at ambient pressure and $T = 298.15$ K where the diffusion coefficient of KCl in pure water is well-known. The second was to gather data for diffusion of KCl in KCl solutions over extended ranges of temperature, pressure, and molality.

The Taylor dispersion technique for measuring diffusion coefficients in liquids was introduced by Pratt and Wakeham[5] and Grushka and Kikta.[6] The method has a number of advantages including relatively rapid measurements, ease of automation, use of standard high-performance liquid chromatography (HPLC) components, and especially, a fully developed working equation that permits absolute measurements to be made. Since these early works, the method has been widely used for the measurement of diffusion coefficients in a wide range of fluids and conditions,[7−11] especially organic mixtures,[12,13] and in supercritical fluids.[14−20] Tominaga et al.,[21] Leaist,[22] and Castillo and Garza[23] showed that this method can be applied successfully for measuring the diffusion coefficient of electrolytes at atmospheric pressure.

An extensive literature review revealed that numerous papers[23−72] report diffusion coefficients for aqueous potassium chloride solutions, but most of them are measured at ambient conditions and for dilute solutions. The majority of the studies relating to diffusion in aqueous solutions of electrolytes are concerned with the development of reliable techniques for the measurement of the concentration dependence.[23] In addition, according to Lobo et al.,[73] there are few cases in which the results from different researchers can be compared directly. However, the diffusion coefficients of aqueous potassium chloride solutions

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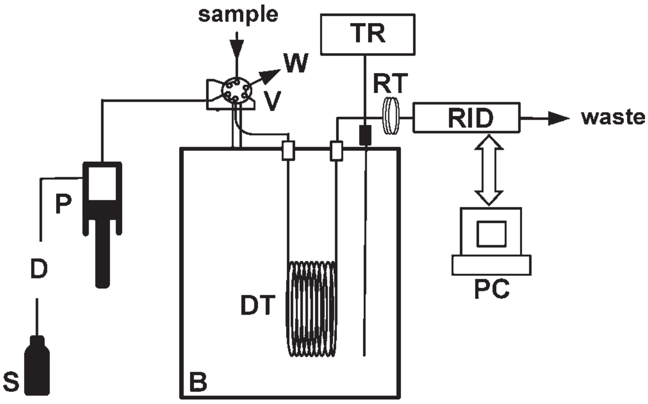

Figure 1. Schematic diagram of the Taylor dispersion experimental apparatus: S, solvent bottle; D, degasser; P, pump; V, six ports valve; W, waste; B, oil bath; DT, diffusion tubing; RT, restrictor tubing; TR, thermometer readout; RID, refractive index detector; PC, computer.

at T = 298.15 K and at concentrations of up to 1 $\text{mol}\cdot\text{L}^{-1}$ are recommended[50,74,75] as a reference standard for the liquid phase.

In this work, we measured the diffusion coefficients for KCl in aqueous KCl solutions at molalities of (0, 1, 2.5, and 4.5) $\text{mol}\cdot\text{kg}^{-1}$, pressures up to 69 MPa, and temperatures ranging from (298.15 to 423.15) K. As far as we are aware, this is the first study of the KCl(aq) system to address high pressures. The ability to work at an elevated pressure also facilitated measurements at temperatures above the normal boiling point of the solution, where no previous data have been reported.

EXPERIMENTAL SECTION

Materials. Potassium chloride was supplied by Sigma-Aldrich with a claimed mass fraction purity >0.990; the KCl was dried in an oven at T = 423 K but otherwise used without further purification. Ultrapure deionized water with an electrical resistivity of > 18 $\text{M}\Omega\cdot\text{cm}$ was obtained from a Millipore system (Direct-Q, Millipore UK, Ltd.).

Apparatus and Procedure. Figure 1 is a schematic diagram of the Taylor dispersion apparatus used in this work comprising three modules: a solvent delivery system with solute injection valve, a thermostatic oil bath housing the diffusion capillary, and a differential refractive-index detector. The solvent was drawn through a filter from the supply bottle via an inline degasser (Knauer, Model A5328, Germany) to charge the 100 mL capacity syringe pump (Teledyne ISCO 100DM Hastelloy, USA), which was kept at a constant temperature of 293 K by circulating water supplied by a chiller unit (Huber, model Minichiller-NR, Germany) through a cooling jacket fitted to the syringe. The solvent was delivered at a constant flow rate of between (0.05 and 0.425) $\text{mL}\cdot\text{min}^{-1}$, through a six-port injection valve (VICI Cheminert, model C72H-1696D, Switzerland) fitted with a 5 μL sample loop, into the diffusion capillary. The latter was maintained at the desired temperature by immersion in a thermostatic oil bath (Fluke Hart Scientific, model 6022, USA) controlled to within 0.01 K. The outflow from the column passed through a short restrictor tube and into the refractive index detector (Agilent 1200 Series, model G1362A, USA), from which it passed to waste.

Preliminary tests showed that even a passivated stainless steel diffusion tube was not suitable for KCl solutions, due to pitting corrosion. Therefore, a Hastelloy C-276 tube of nominal external radius 0.8 mm (Vindum Engineering Inc., USA) was used. The length of the tube, L = (4.52 ± 0.01) m, was measured with an ordinary tape measure. The internal radius of the tube, R = (0.541 ± 0.001) mm, was determined by weighing the tube, both empty and after filling with pure water, on an analytical balance having a resolution of 0.1 mg. For the installation in the oil bath, the tube was coiled on a drum of radius of 0.109 m.

The temperature of the oil bath was measured with a secondary-standard platinum resistance thermometer (Fluke Hart Scientific model 5615) and readout unit (Fluke Hart Scientific, model 1502A). The thermometer was calibrated on ITS-90 at the temperature of the triple point of water and by comparison in a constant temperature bath with a standard platinum resistance thermometer at nominal temperatures of (323, 373, 423, and 473) K. The expanded uncertainty of the temperature measurements was 0.02 K. The solvent delivery pressure was measured at the outflow of the pump by means of the pressure transducer integrated into the pump. According to the manufacturer, the relative uncertainty of the pressure was 0.5 % of reading.

The refractive index detector used in this work was limited to a maximum operating pressure of 0.5 MPa, and as the outlet was open to the atmosphere, it was in practice operated close to ambient pressure. To permit elevated pressures upstream, a selection of restrictor tubes were inserted between the column and the detector with a length and diameter chosen to provide the desired back pressure. The restrictor tubes were either a Siltek (deactivated stainless steel) capillary of length 0.58 m and internal radius 0.127 mm, for low-pressure operation (p < 1 MPa) or PEEK clad fused silica tubes with lengths between (0.05 and 0.5) m and an internal radius of 12.5 μm for higher pressures. With a given restrictor tube fitted, the column pressure could be varied by changing the solvent flow rate within the range stated above.

The flow rate accuracy of the pump was checked by weighing the outflow under steady-flow conditions for a precisely timed period of about 1 h. This was repeated for three different flow rates spanning the normal experimental range, and the results were all within ± 0.35 % of the set flow rate.

The experiment was operated under computer control using a program written in Agilent VEE that logged the experimental temperature, actuated the injection valve, and collected readings every 5 s from the refractive index detector. The pump was operated under manual control at the chosen flow rate and the pressure under steady-state flow was recorded before, during, and after the passage of a solute injection through the column.

Once steady-state flow and thermal equilibrium were established, the measurements were started. The solute solution was loaded into the sample loop and injected into the solvent stream at time t = 0. At least three solute injections were made per run, and they were spaced at (15 to 30) min intervals to avoid any overlap of peaks. Solutions were carefully prepared by dissolving weighed amounts of dried KCl in a known amount of the mobile phase, typically to produce a solution with a molality exceeding that of the solvent by 0.1 $\text{mol}\cdot\text{kg}^{-1}$. As discussed in the literature,[76] the solute concentration (mass per unit volume of solution) averaged over the cross section at the end of the diffusion tube is given by:

$$c(t) = \frac{m}{\pi R^2 (4\pi K t)^{1/2}} \exp\left[-\frac{(L - vt)^2}{4Kt}\right] \tag{1}$$

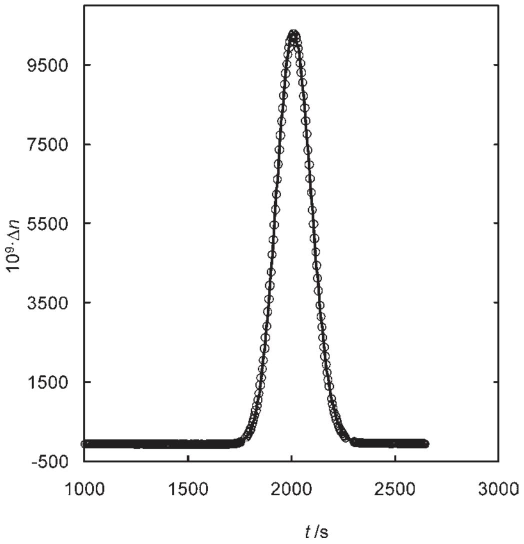

Figure 2. Differential refractive index signal $s(t) = \Delta n$ for the measurement of the diffusion coefficient of KCl in water at $T = 298.15$ K and $p = 0.1$ MPa: ○, experimental data; solid line, fit with eq 3.

In eq 1, m is the mass of solute injected, R is the internal radius of the column, L is the length of the column, v is the axial velocity of the solvent averaged over the cross section of the tube, t is the time, and K is the dispersion coefficient which is related to the binary diffusion coefficient, D, by[4]

$$K = D + \frac{R^2v^2}{48D} \tag{2}$$

Wakeham and co-workers[77−79] discussed the constraints that must be placed on the experimental conditions to satisfy the assumptions made in the derivation of eq 1, as well as the corrections required. The dimensions of the diffusion tubing, the coil radius, and the flow rates were therefore chosen to meet the criteria discussed in those studies. Thus, in our experiments, the flow was always laminar as the Reynolds number, Re, was in the range $1.3 < \mathrm{Re} < 24$. To ensure that secondary flow effects are negligible, the criterion $\mathrm{De}^2\mathrm{Sc} < 20$ must be met, where $\mathrm{De} = \mathrm{Re}(R/R_{\mathrm{coil}})^{1/2}$ is the Dean number, $\mathrm{Sc} = \eta/(\rho D)$ is the Schmidt number, R_{coil} is the coil radius, η is the solvent viscosity, and ρ is the solvent density. In the present work, this criterion was easily exceeded as the experiment was operated such that $0.01 < \mathrm{De}^2\mathrm{Sc} < 0.5$. Finally, the criterion for the concentration profile resulting from dispersion of the initial solute pulse to become spatially Gaussian (also known as the Levenspiel−Smith[80] criterion) is $K/(vL) < 0.01$; in our experiments this was always fulfilled as $3.8 \cdot 10^{-4} < K/(vL) < 7.6 \cdot 10^{-3}$.

The diffusion coefficient can be calculated from the measured concentration−time curves in different ways:[81] the height−area method, moments calculations, or by fitting the parameters of the following equation to the experimental data:

$$s(t) = a + bt + \alpha c(t) \tag{3}$$

Here, $s(t)$ is the signal at the detector, parameters a and b compensate for baseline drift, assumed to be linear in time, α is the detector sensitivity, and $c(t)$ is given by eq 2. The latter method is generally the more accurate and therefore preferred in this work. Figure 2 illustrates an example set of data together with the fitting curve. The average absolute deviations between the experimental data and the fitting curve are approximately 0.5 % of the maximum signal (Figure 3). The detector used measures not concentration directly but the difference Δn between the refractive index of the eluent at time t and that of the solvent. There is therefore an assumption that, for small changes in concentration c, Δn is proportional to Δc. In the present case, Δc was of order 0.1 $\mathrm{g \cdot dm^{-3}}$ which may be considered sufficiently small so as to ensure linearity.

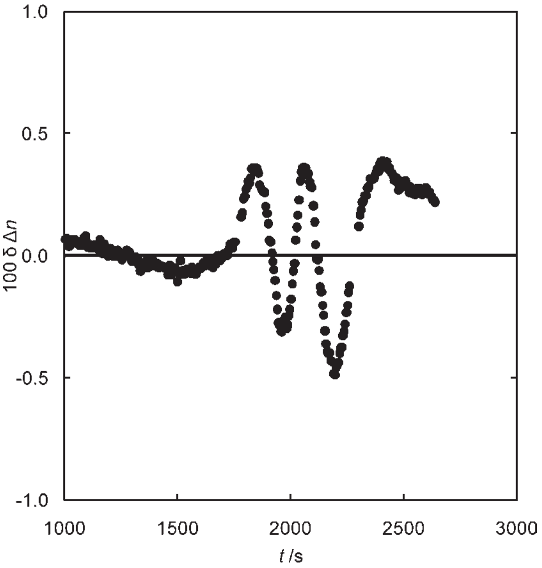

Figure 3. Relative deviations $\delta\Delta n/n$ between the experimental differential refractive index signal $s(t) = \Delta n$ and the fit with eq 3 as a function of time t for KCl in water at $T = 298.15$ K and $p = 0.1$ MPa.

One of the difficulties encountered with diffusion coefficient measurements by the Taylor method is the influence of injection, detection, and connecting tube volumes.[77] An analysis of the effects of these hold-up volumes to either side of the diffusion tubing on the interpretation of the final signal was carried out. This showed that the effect of tubing sections of radius R_i and length L_i inserted before or after the column combine to introduce excess dispersion that is equivalent to an additional length δL of the main column, where

$$\delta L = \sum_i \{D(T)/D(T_i)\}(R_i/R)^4 L_i \tag{4}$$

Here T_i is the temperature for tubing section i. Accordingly, the effective column length used in the analysis was increased by δL. In the configuration used for the present work, there were three significant sections of additional tubing: between the injection valve and the column ($R_1 = 0.39$ mm, $L_1 = 0.3$ m), between the column and the inlet of the detector ($R_2 = 0.13$ mm, $L_2 = 0.6$ m), and finally the internal flow path in the detector itself ($R_3 = 0.22$ mm, $L_3 = 0.4$ m). For example, with $D(T_i) = 2 \cdot 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$ in each section this led to $\delta L = 0.096$ m or about 2 % of L. These corrections could be made smaller by reducing the internal radius of these tubing sections, especially the first, or by increasing the length of the main column. The restrictor tubes added to obtain high column pressures had negligible additional effect on the dispersion due to their very small internal radii.

In analyzing the results, we obtained v from the programmed flow rate. Inevitably, the actual flow rate differed slightly from the programmed value and, to account for this in the analysis, the time origin for each peak was an adjustable parameter. However,

Table 1. Experimental Values of Diffusion Coefficients D at Temperature T, Pressure p, and Molality m for KCl in KCl(aq)[a]

T	p	$D \cdot 10^9$	T	p	$D \cdot 10^9$
K	MPa	$m^2 \cdot s^{-1}$	K	MPa	$m^2 \cdot s^{-1}$
m/mol·kg^{-1} = 0.0 (infinite dilution)					
298.15	0.16	1.945	348.15	29.27	4.441
298.15	14.99	1.942	348.15	46.78	4.495
298.15	30.92	1.947	348.15	66.70	4.522
298.15	48.17	1.954	373.15	0.82	6.107
298.15	62.94	1.968	373.15	24.18	6.145
323.15	0.64	3.022	373.15	43.13	6.112
323.15	15.46	3.016	373.15	64.28	6.182
323.15	33.58	3.085	423.15	3.08	10.263
323.15	68.56	3.093	423.15	18.51	10.271
348.15	0.65	4.481	423.15	33.58	10.329
348.15	15.72	4.488	423.15	63.30	10.310
m/mol·kg^{-1} = 1.0 ± 0.0001					
298.15	0.24	1.892	348.15	39.76	4.232
298.15	10.17	1.907	348.15	41.21	4.245
298.15	28.21	1.918	348.15	41.98	4.249
298.15	38.63	1.925	348.15	45.33	4.263
298.15	45.59	1.947	348.15	62.42	4.243
298.15	59.03	1.958	348.15	64.02	4.247
298.15	67.07	1.978	348.15	67.09	4.250
323.15	0.61	3.034	373.15	0.82	5.942
323.15	15.30	3.062	373.15	23.41	5.932
323.15	43.40	3.084	373.15	42.09	5.936
323.15	52.06	3.095	373.15	64.21	5.973
323.15	68.97	3.097	423.15	3.41	9.432
348.15	0.66	4.229	423.15	15.13	9.446
348.15	25.82	4.246	423.15	34.72	9.455
348.15	31.12	4.257	423.15	61.62	9.479
348.15	35.87	4.241	423.15	65.64	9.486
m/mol·kg^{-1} = 2.5 ± 0.0001					
298.15	0.29	2.018	298.15	37.39	2.038
298.15	2.29	2.023	298.15	47.43	2.043
298.15	4.50	2.039	298.15	64.97	2.069
298.15	24.92	2.037	298.15	66.17	2.079
298.15	32.60	2.047	298.15	67.63	2.080
323.15	0.58	3.152	373.15	24.36	5.940
323.15	40.89	3.122	373.15	31.32	5.886
323.15	45.21	3.177	373.15	47.55	5.984
323.15	47.48	3.173	373.15	57.26	5.857
323.15	60.49	3.118	373.15	59.59	5.955
323.15	64.86	3.152	373.15	63.05	5.961
348.15	0.70	4.522	423.15	4.44	9.685
348.15	18.05	4.548	423.15	15.18	9.673
348.15	29.96	4.573	423.15	15.26	9.675
348.15	45.15	4.580	423.15	34.63	9.698
348.15	68.90	4.594	423.15	34.63	9.698
373.15	0.94	5.920	423.15	56.03	9.702
373.15	17.14	5.915	423.15	65.05	9.716
m/mol·kg^{-1} = 4.5 ± 0.0001					
298.15	0.48	2.172	348.15	65.91	4.628
298.15	27.06	2.144	373.15	0.74	6.251
298.15	43.80	2.171	373.15	17.78	6.222
298.15	66.02	2.184	373.15	41.28	6.239
323.15	0.50	3.335	373.15	47.90	6.209
323.15	3.95	3.324	373.15	54.29	6.244
323.15	31.37	3.347	373.15	54.41	6.240
323.15	49.57	3.285	373.15	65.70	6.274
323.15	62.69	3.352	423.15	13.02	9.265
348.15	0.73	4.645	423.15	40.54	9.294
348.15	12.83	4.587	423.15	68.93	9.301
348.15	32.97	4.619			

[a] Standard uncertainties u are $u(T) = 0.02$ K, $u(p) = 0.005 \cdot p$, $u(m) = 0.0001$ mol·kg^{-1}, and the combined expanded uncertainty $U_c(D) = 0.0035 \cdot D$ (level of confidence = 0.95).

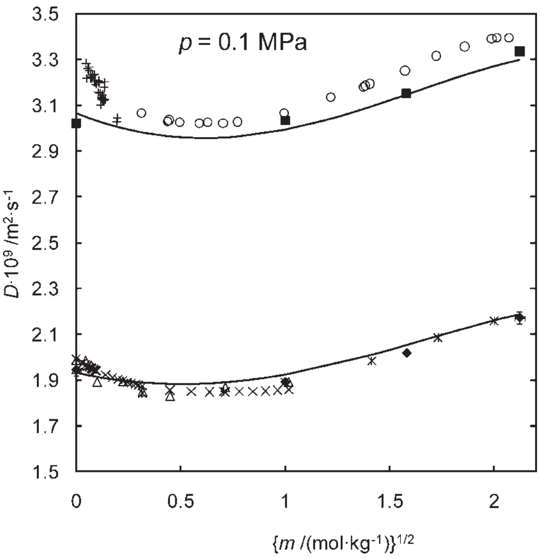

Figure 4. Diffusion coefficients of KCl in KCl(aq) as a function of molality m at $T = 298.15$ K (◆, this work; ×, Woolf and Tilley;[50] ∗, Pinto and Graham;[62] △, Lobo et al.[71]) and at $T = 323.15$ K (■, this work; ○, Lobo;[64] +, Fell and Hutchison.[54]).

fitted value was normally within 5 s of the actual time of the solute injection, which may be compared to a typical elution time of 2000 s. A further detail, to be considered when the experimental temperature differs from that in the syringe pump, is the effect of thermal expansion on the volumetric flow rate in the column. Corrections for this small effect were included.

RESULTS AND DISCUSSION

The measured diffusion coefficients of potassium chloride in pure water (infinitesimal concentration) and in potassium chloride solutions, together with the temperatures, pressures, and molalities at which the experiments were carried out, are given in Table 1. The values of the diffusion coefficients are averages of at

Table 2. Parameters of Equations 7 to 9

a_0	a_1	a_2	a_3	a_4	b_0	b_1	c_0	c_1
−15.5	−0.315	0.085	$-0.684 \cdot 10^{-2}$	$0.132 \cdot 10^{-3}$	−910.2	62.6	−134343	2007.2

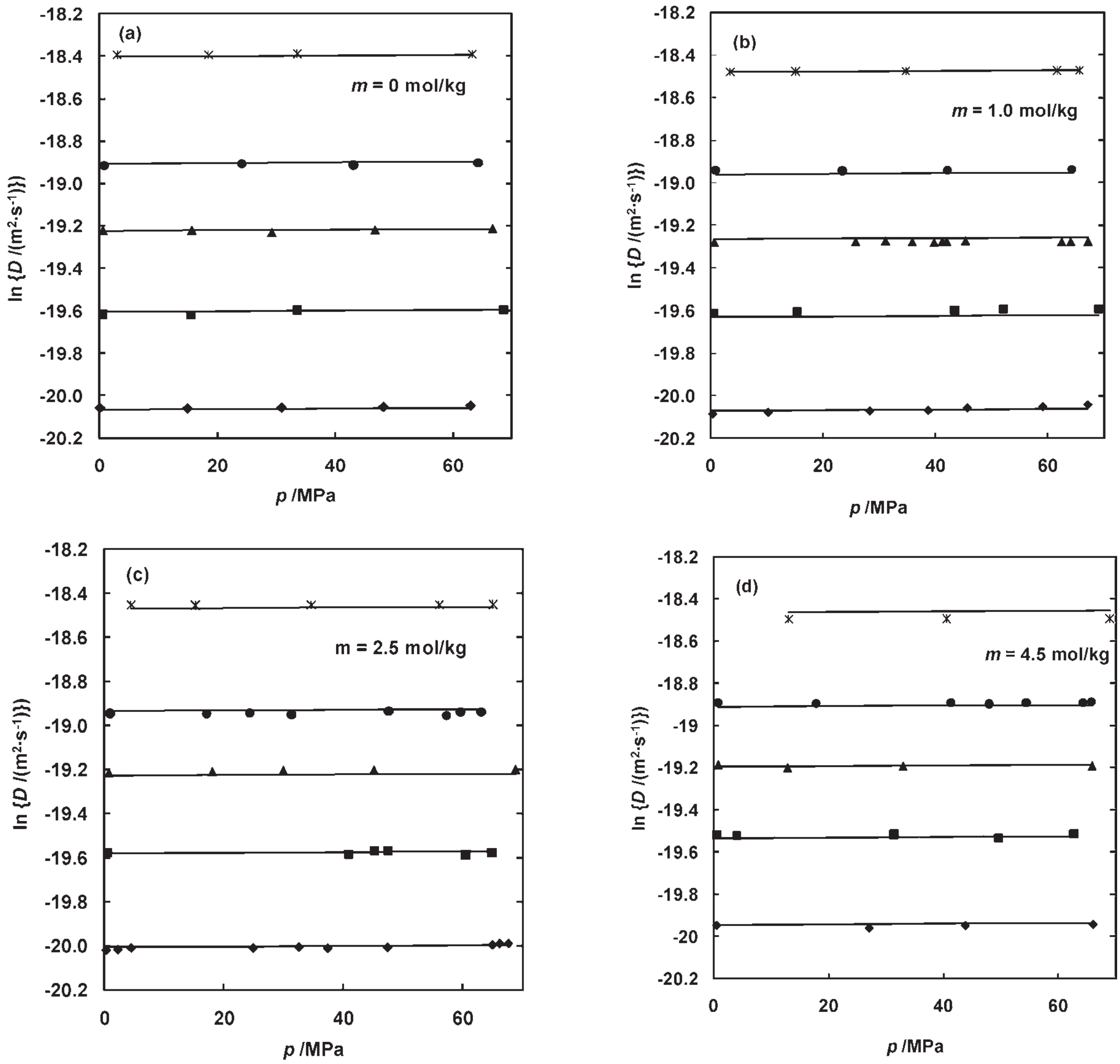

Figure 5. Diffusion coefficients of KCl in KCl(aq) as a function of pressure at (a) infinite dilution, (b) $m = 1.0\ \text{mol} \cdot \text{kg}^{-1}$, (c) $m = 2.5\ \text{mol} \cdot \text{kg}^{-1}$, and (d) $m = 4.5\ \text{mol} \cdot \text{kg}^{-1}$: ◆, $T = 298.15$ K; ■, $T = 323.15$ K; ▲, $T = 348.15$ K; ●, $T = 373.15$ K; ∗, $T = 423.15$ K; solid line, eqs 6 to 9.

least three measurements, but typically five. The reproducibility of the results is generally good as the relative standard deviation $u_r(K)$ of the dispersion coefficient was 0.35 % on average, and it never exceeded 1.3 %.

The estimated standard relative uncertainty of D may be obtained from consideration of eq 2, in which the first term was always negligible. Thus

$$u_r^2(D) = 4u_r^2(R) + 4u_r^2(v) + u_r^2(K) \tag{5}$$

where $u_r(R)$, $u_r(v)$, and $u_r(K)$ are the standard relative uncertainties of the column radius, flow velocity, and the dispersion coefficient. In the present case, $u_r(R) = 2.2 \cdot 10^{-3}$, $u_r(v) = 3 \cdot 10^{-3}$, and $u_r(K) = 3.5 \cdot 10^{-3}$, the latter estimated from the standard deviation of K in repeated injections. The value of $u_r(v)$ was the flow-rate uncertainty specified by the pump manufacturer, rather than the smaller value implied by our three check measurements. Additional errors propagated from the uncertainties in temperature, pressure, and molality were negligible, and thus the final estimated relative expanded uncertainty of D was 1.6 % with a coverage factor $k = 2$.

Figure 4 shows a detailed comparison of our results at $T = (298.15 \text{ and } 323.15)$ K for $p < 1$ MPa with existing atmospheric-pressure literature data. It can be seen that D remains constant at low molalities or even decreases slightly, possibly due to increased electrostatic interactions as molality increases and mean ionic separation decreases. Above $m \approx 0.7\ \text{mol} \cdot \text{kg}^{-1}$, the diffusion coefficient increases gently with molality due to increased screening of the electrostatic interactions. These changing electrostatics

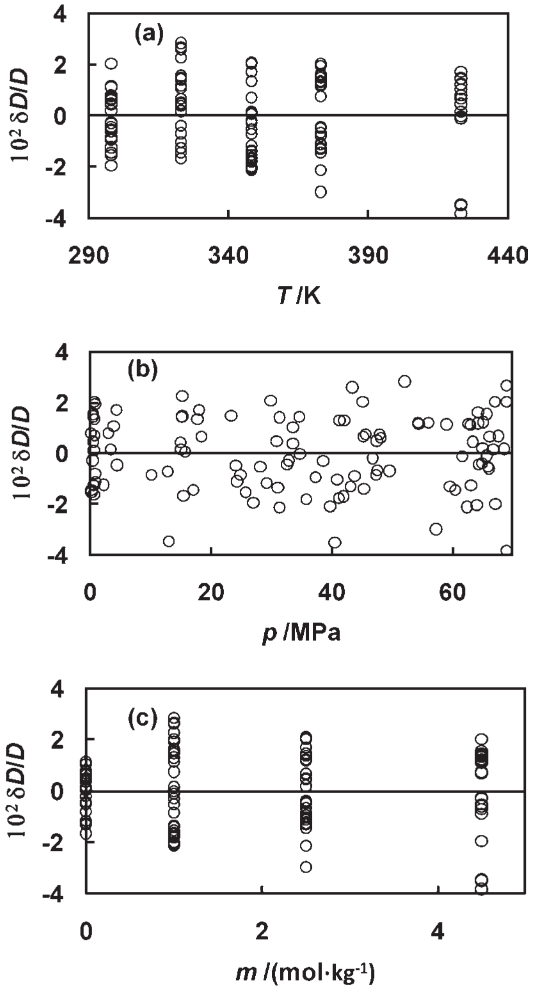

Figure 6. Difference of δD diffusion coefficients D of KCl in KCl(aq) from the eqs 6 to 9 as a function of (a) temperature T, (b) pressure p, and (c) molality m.

will affect both the direct ion—ion interactions and their interaction with the water solvent molecules, as reflected in the effective hydrated ionic radius. Our data at (infinitesimal concentration, 1.0, 2.5, and 4.5) mol·kg^{-1} are in good agreement with all sources, except Fell and Hutchison[54] who measured D at very low concentrations. The relative difference between the diffusion coefficient measured in this work ($1.8580 \cdot 10^{-9}$ m^2·s^{-1}) and that recommended as a standard reference value[50] ($1.8585 \cdot 10^{-9}$ m^2·s^{-1}) at T = 298.15 K, p = 0.1 MPa, and concentration 1 mol·L^{-1} is less than 0.5 %, which confirms the reliability of our apparatus and procedure.

All experimental data obtained in this work were fitted with a multiple parameter model of the form

$$\ln(D/\mathrm{m^2 \cdot s^{-1}}) = A + B(\mathrm{K}/T) + C(\mathrm{K}/T)^2 \tag{6}$$

$$A = a_0 + a_1(m/\mathrm{mol \cdot kg^{-1}})^{1/2} + a_2(m/\mathrm{mol \cdot kg^{-1}}) + a_3(m/\mathrm{mol \cdot kg^{-1}})^2 + a_4(p/\mathrm{MPa}) \tag{7}$$

$$B = b_0 + b_1(m/\mathrm{mol \cdot kg^{-1}})^{1/2} \tag{8}$$

$$C = c_0 + c_1(m/\mathrm{mol \cdot kg^{-1}}) \tag{9}$$

Table 3. Average Absolute Relative Deviation Δ_{AAD} and Maximum Absolute Relative Deviation Δ_{MAD} from Equations 6 to 9 Calculated for All Available Literature Data at Temperature T, Molality m, and Atmospheric Pressure

T	m range				
K	mol·kg^{-1}	N_{exp}^{a}	$10^2 \cdot \Delta_{\mathrm{AAD}}$	$10^2 \cdot \Delta\mathrm{MAD}$	ref
273.15	0.0984−3.0233	11	15.5	17.0	64
277.15	0.0167−0.5691	5	13.9	15.1	36
288.15	1.0000−4.0000	4	3.8	5.6	45
291.15	0.0502−4.5630	13	6.0	10.2	29
291.15	0.0641−3.7355	16	4.0	5.1	64
291.65	0.0502−4.5890	48	6.2	10.6	24
291.65	0.0000−2.0000	8	5.1	8.1	27
293.15	0.0013−0.0112	5	0.9	2.0	34
293.15	0.0673−5.1563	8	6.1	8.2	64
298.15	0.0201−0.5090	3	2.0	3.7	25
298.15	0.0000−2.1346	13	2.5	12.8	26
298.15	0.0025−0.0050	4	0.8	1.8	31
298.15	0.1006−0.0025	7	1.4	3.1	32
298.15	0.0013−0.0098	6	1.1	2.0	33
298.15	0.0013−0.5376	15	1.4	2.5	35
298.15	0.0100−0.5090	7	1.6	3.5	38
298.15	0.0000−3.9251	13	1.7	3.3	39
298.15	0.0010−4.4337	35	3.1	8.7	40
298.15	0.1950−0.2018	2	2.5	2.5	42
298.15	0.5090−4.4337	2	2.0	3.0	44
298.15	0.1258−0.5091	8	2.3	2.5	46
298.15	1.0000−4.0000	4	0.9	1.6	45
298.15	0.8966−0.9181	2	3.8	3.8	52
298.15	0.2096−0.2627	2	2.2	2.3	53
298.15	0.2018−3.3084	4	1.6	2.8	61
298.15	0.0019−0.5376	8	3.5	6.2	65
298.15	0.0100−0.5090	5	5.8	13.9	67
298.15	0.0136−4.6227	18	1.2	2.4	59
298.15	0.4145−0.5249	2	2.5	2.8	53
298.15	0.5090−3.3084	5	1.2	2.0	51
298.15	0.0001−3.3084	15	1.5	2.8	49
298.15	0.0502−0.5090	5	1.3	2.6	64
298.15	0.1006−4.4347	11	1.3	2.3	37
298.15	0.0012−0.5376	15	1.4	2.5	34
298.15	0.0000−1.0340	4	1.4	3.2	30
298.15	0.1006−2.1346	6	3.4	12.7	29
298.15	0.0005−0.0100	6	1.3	2.3	31
298.15	0.0000−4.0000	7	1.5	3.2	62
298.15	0.0010−1.0327	11	1.9	3.2	71
298.15	0.0010−1.0339	28	1.7	3.9	50
298.15	0.0100−2.0000	9	2.6	5.1	27
298.15	0.0049	1	1.4	1.4	23
303.15	0.0049	1	3.8	3.8	23
303.15	0.0032−0.0123	4	1.8	2.4	34
308.15	0.0049	1	6.1	6.1	23
308.15	1.0000−4.0000	4	7.9	10.5	45
308.15	0.0597−3.9767	16	1.0	4.4	64
308.15	0.1006−3.3084	6	1.9	3.4	47
313.15	0.0049	1	6.1	6.1	23

Table 3. Continued

T	m range				
K	$\mathrm{mol\cdot kg^{-1}}$	N_{exp}[a]	$10^2\cdot\Delta_{\mathrm{AAD}}$	$10^2\cdot\Delta\mathrm{MAD}$	ref
313.15	0.0017−0.0224	16	2.7	7.2	54
318.15	0.0049	1	3.5	3.5	23
318.15	1.0000−4.0000	4	2.8	3.1	45
318.15	0.1006−3.3084	6	2.4	2.8	47
323.15	0.0023−0.0393	31	4.8	7.3	54
323.15	0.0989−4.2832	19	3.1	4.0	64
333.15	0.0026−0.0378	32	4.9	7.3	54
343.15	0.0030−0.0369	9	5.0	6.3	54
353.15	0.0046−0.0101	4	7.3	7.5	54

[a] Number of experimental points.

where a_i, b_i, and c_i are parameters, the values of which are given in Table 2.

The goodness of fit was measured by the average absolute relative deviation (Δ_{AAD}),

$$\Delta_{\mathrm{AAD}} = N^{-1}\sum_{i=1}^{N}|(D_{i,\mathrm{exp}} - D_{i,\mathrm{calc}})/D_{i,\mathrm{exp}}| \tag{10}$$

and by the maximum absolute relative deviation,

$$\Delta_{\mathrm{MAD}} = \mathrm{Max}_i|(D_{i,\mathrm{exp}} - D_{i,\mathrm{calc}})/D_{i,\mathrm{exp}}| \tag{11}$$

where N is the number of experimental points ($N = 113$) and subscripts "exp" and "calc" refer to experimental and calculated values of D at the ith state point. For the present data, $\Delta_{\mathrm{AAD}} = 1.2$ % and $\Delta_{\mathrm{MAD}} = 3.8$ %.

The experimental diffusion coefficients obtained in this study are plotted as a function of pressure at constant temperature and molality in Figure 5 together with isotherms computed from eqs 6 to 9. It is clear that the dependence upon pressure is very weak, presumably as a consequence of the low compressibility of these aqueous solutions. However, the parameter a_4, which accounts for the effect of pressure in our correlation, was found to make a significant improvement in the fit and so was retained. The relative deviation of the data from the correlation is shown in Figure 6 as functions of temperature, pressure, and molality; it can be seen that most are < 2.0 % and that there are no obvious systematic trends.

The predictions of the empirical fit were tested by a comparison with all available literature data (some 556 experimental points, all at ambient pressure), and the deviations for each literature source are summarized statistically in Table 3. Considering all literature sources, $\Delta_{\mathrm{AAD}} = 3.5$ %. Where necessary, concentration units were converted from molarity C to molality m, using the equation

$$m = C/(\rho - CM_2) \tag{12}$$

where ρ is the solution density and M_2 is the molar mass of the solute. Density and viscosity values necessary for the calculation of the m, Re, and Sc criteria were taken from the NIST[82] and DETHERM 2007[83] databases.

CONCLUSIONS

Diffusion coefficients of potassium chloride in water and potassium chloride aqueous solutions were measured as function of molality, temperature, and pressure by means of the Taylor dispersion method. The new dispersion apparatus was validated by comparing the results with very accurate literature data for aqueous KCl at ambient pressure, $T = 298.15$ K, and a concentration of 1 $\mathrm{mol\cdot L^{-1}}$. The new data significantly extend the range of temperature over which diffusion coefficients of KCl in KCl(aq) are known. The effect of pressure on D was found to be very small.

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