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Measurements of Interdiffusion Coefficients and Densities for the System HCl + H_2O at 25 °C

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Interdiffusion (mutual diffusion) coefficients have been measured by Gouy interferometry for the system HCl + H_2O at 25 °C from 0.100 M to 11.991 M concentration. They vary from 3.336×10^{-9} m^2 s^{-1} at infinite dilution, to a minimum of about of 3.03×10^{-9} m^2 s^{-1} near 0.1 M, to a maximum of about 6.0×10^{-9} m^2 s^{-1} near 7.25 M, and back down to 4.306×10^{-9} m^2 s^{-1} at 11.99 M. Thermodynamic diffusion coefficients have been calculated and appear to decrease monotonically and smoothly from 3.3368×10^{-9} m^2 s^{-1} at infinite dilution to a value of 0.947×10^{-9} m^2 s^{-1} at 11.99 M. Densities of HCl solutions have been measured from 0.125 M to 12.186 M at 25 °C. These increase approximately linearly with molarity M from the density of pure water of 0.997 045 g cm^{-3} to a density of 1.1827 g cm^{-3} at 12.186 M.

Introduction

Because aqueous hydrochloric acid is a very important industrial chemical, many of its physical-chemical properties have been measured and published. These include diffusion coefficients (Haase and Richter, 1967; Harpst et al., 1965; James et al., 1939; Lobo and Teixeira, 1979; Stokes, 1950) and density values at 25 °C, including some densities at higher concentrations (Åkerlöf and Teare, 1938; Geffcken, 1931; Török and Berecz, 1989).

Careful examination of the diffusion data by us suggested that there were significant discrepancies among the published data sets for this system at 25 °C. Specifically, the authors were concerned about a possible discontinuity (which will be apparent from Figure 1 below) between the data of Stokes (1950) which ranged from about 0.01 M to about 4 M and that of Haase and Richter (1967) which ranged from about 4.5 M to about 12 M, where M denotes molarity. Consequently, we decided to remeasure the diffusion coefficients of HCl + H_2O from 0.1 M to 12 M with the precise Gosting (Gosting et al., 1973) diffusiometer using Gouy interferometry. We have also measured the densities of our solutions over this same range of concentrations.

Experimental Section

Solutions. As is well-known, HCl forms a constant-boiling mixture with H_2O at about 6.09 M. The constant-boiling mixture is a particularly suitable choice for a stock solution when preparing solutions of 6 M and less. There are two reasons for this. (1) There is minimal change in concentration due to evaporation when transferring the stock solution during preparation of these solutions. (2) Constant-boiling HCl solutions have been carefully analyzed by Foulk and Hollingsworth (1923), who measured the concentration of the constant-boiling HCl + H_2O mixture as a function of barometric pressure. (Small corrections to their values of mass % versus barometric pressure were made for our study because of changes in the accepted molar masses ("atomic weights") since their publication.)

In our experimental work, all solution concentrations from the highest to the lowest are by some procedure referenced against concentrations of constant-boiling HCl + H_2O mixtures. Thus, all our concentrations are based on the constant-boiling data of Foulk and Hollingsworth, although some direct acid−base titrations were made to confirm that this approach is satisfactory.

Four stock solutions were used to prepare solutions for the diffusion experiments and density measurements and are identified in Tables 1 and 2. In all calculations the molar masses of HCl and H_2O were assumed to be 36.461 and 18.015 g mol^{-1}, respectively.

Water for all solutions had been distilled from deionized water and then passed through a MilliPore Milli-Q Water Purification System.

The first stock solution was used to prepare solutions by mass for experiments in the concentration range 0.1 M to 6 M. To prepare this stock solution, Mallinckrodt AR 37.6 mass % HCl was diluted as nearly as possible to the constant-boiling composition at about 20.25 mass % and distilled in four batches of approximately 1500 cm^3 each. The first two-thirds or more of the distillate of each batch was discarded, and all but about the final 100 cm^3 of the remainder was collected. It was assumed that the constant-boiling composition had been reached, and the composition for each batch was calculated from the data of Foulk and Hollingsworth (1923) using the barometric pressure measured at the time of distillation.

The collected distillates were mixed and then stored in two 1 L bottles with glass stoppers greased with Corning silicone grease to prevent evaporation. The composition of stock no. 1 was calculated to be 20.249 mass %, based on averaging the composition of the batches weighted by the amounts in each of the four batches. This composition was verified by preparing a 0.1 M acid solution by mass dilution and then performing a mass titration against standard Na_2CO_3 (99.99%), using a pH meter to determine the end point. The concentration determined by this method was 20.250 mass %, which is in excellent agreement with the concentration of the stock solution based on the constant-boiling method. The authors believe the constant-boiling value of concentration to be more accurate than the value obtained by direct titration and used it when

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calculating concentrations of solutions prepared from this stock.

The density of the constant-boiling stock was measured both pycnometrically and with a density meter. The density value obtained with a Mettler Paar density meter was (1.096 231 ± 0.000 005) g cm^{-3} (the average of two measurements). A value of 1.096 264 g cm^{-3} was obtained by using a 30 cm^3 pycnometer.

As a check, 2 L of constant-boiling HCl solution, obtained by the procedures outlined above, were redistilled. The last one-third of the distillate was retained except for the final approximately 100 cm^3. This double-distilled solution was also analyzed. A sample, whose mass was carefully measured, was diluted to about 0.1 M acid and used to titrate by mass a weighed sample of the 99.99% Na_2CO_3. This analysis yielded a concentration of 20.257 mass % (an average of three values 0.202 666 mass %, 0.202 403 mass %, 0.202 632 mass %). This again was in reasonable agreement with the value 20.245 mass % calculated for 99.85 kPa pressure at the time of distillation, using the data of Foulk and Hollingsworth. The density of this solution was determined with the density meter and found to be (1.096 290 ± 0.000 003) g cm^{-3} (the average of two measurements). The density was also measured with a pycnometer and found to be 1.096 265 g cm^{-3}. This is in reasonable agreement with the values obtained from the first constant-boiling stock. This check solution was used only to verify preparation methods, not for diffusion experiments.

The second stock solution was used for a set of experiments in the concentration range 6 M to 9.5 M. This stock was also obtained by distillation, but collected at changing concentrations and at a higher average concentration than the constant-boiling mixture. It was stored in two 1 L bottles, again with greased ground-glass stoppers. Densities of the solutions stored in each of the two bottles were measured initially and after the last samples were removed for the diffusion experiments. The concentration of the second stock solution was determined in two ways. First a sample of the solution was diluted by mass to near the constant-boiling composition and the density measured. This density value was used to calculate concentration by using eq 6 below. This equation was obtained by least squares from the densities of the solutions (0−6.1 M) prepared from the first constant-boiling stock solution. The concentration determined by this method was 31.403 mass % [9.9309 M]. As a second method of analysis, duplicate samples of the stock were titrated into the 99.99% standard Na_2CO_3 by mass titration, as before using a pH meter to determine the end point. The concentration determined by this method was 31.366 mass %. The value 31.403 mass % obtained by the density measurement was used to calculate concentrations. This choice more closely ties the concentration of stock no. 2 to the constant-boiling data of Foulk and Hollingsworth on which the concentration of stock no. 1 was based. This makes the concentrations of both stock solutions internally consistent.

The solution in the second bottle of the second stock had to be filtered through a glass-fritted funnel before use because a small amount of grease entered and became suspended in the solution. Apparently, HCl vapor dissolves slightly in the grease. This caused a small amount of grease to expand and squeeze out of the ground joint of the cap. This latter grease had lost its consistency and crumbled, allowing small pieces to fall into the stock solution. [Similar behavior is observed with concentrated H_2SO_4 (J. A. Rard, private communication).] The density of this solution was measured after filtering. A small decrease in density was noted and used to make a small correction in the concentration of the second bottle.

The third set of experiments were in the 10 M to 11 M concentration range. A 2.5 L bottle of Mallinckrodt AR 37.6 mass % HCl was used directly as the third stock solution. The bottle was opened, and the densimeter density was found to be 1.182 631 g cm^{-3}. Then a portion was diluted by mass to near the constant-boiling composition and its density measured. The concentration in the bottle was determined from the mass of added water and this latter density, using the same density versus concentration equation that had been used to obtain the concentration of the second stock. It was found to be 37.566 mass % [12.185 M]. The bottle was kept capped with its original cap tightly screwed on. The density of the acid in the bottle was measured several times to determine if there was significant concentration loss due to loss of HCl vapor while samples were taken for the diffusion experiments. Small changes did occur, and minor corrections to the experimental concentrations were made for them. Less than half of the contents of the bottle were consumed in this set of experiments.

A fourth stock solution was used for the last set of experiments, which were in the range 11.5 M to 12 M. This was a second bottle of Mallinckrodt AR 37.6 mass %. It had the same lot number as the first bottle, and the initial density of its contents, 1.182 653 g cm^{-3}, was nearly the same as for the first bottle as noted above. On the basis of the small density difference between the concentration of the fourth and the third stock solutions, the concentration of the fourth stock solution was determined to be 37.570 mass % [12.186 M]. Again, the density of the acid in the bottle was measured several times during the last set of experiments. Small changes were again noted, and again minor concentration corrections were made.

For preparation of higher concentration solutions with stock solutions above 6 M, the acid solution was added to a screw cap conical flask and weighed. It was then cooled in an ice bath before the water was added so that the mixed solution would not be as warm and as susceptible to evaporation. The final solution was brought to room temperature and weighed. Care was taken to minimize evaporation at every step.

Finally, because of uncertainty about the accuracy of solution concentrations, it was decided to make a third set of density measurements on constant-boiling HCl solutions. This was done after the rest of the experimental work had been completed. A solution was prepared that had a densimeter density of 1.096 26 g cm^{-3}. This solution was distilled with the middle portion taken for analysis. On the basis of the barometric pressure, the concentration of this distillate according to the data of Foulk and Hollingsworth was 20.264 mass %. Six pycnometric measurements (volume of the pycnometer = 27.5444 cm^3 calibrated with water six times and averaged) gave (1.096 221 ± 0.000 03) g cm^{-3}, and nine density meter measurements gave (1.096 261 ± 0.000 02) g cm^{-3}. After the concentration differences are taken into account, these values are lower than expected from the values noted earlier, particularly for the second set of constant-boiling measurements. On the basis of this, the authors estimate the error of the measured concentrations to be as much as ±0.1%. It is clear that the accuracy with which concentrations are known is the limiting factor in the determination of solution density as a function of concentration.

Diffusion Experiments. The Gosting diffusiometer was used in the Gouy mode for all experiments (Kegeles and Gosting, 1947; Coulson et al., 1948). A 543.5 nm (in vacuum) laser was used as a light source, and the interference patterns were recorded on Kodak TMax-100 photographic plates. Well-established procedures were followed while the experiments were performed (Gosting and Morris, 1949; Miller and Albright, 1991). The reference fringes were shifted to a position above the Gouy fringe patterns by using a tilted, flat glass plate positioned in the reference optical path (Wu et al., 1994). Usually, 15 or 16 Gouy patterns were photographed during the course of each experiment.

For experiments up to 9.5 M, the diffusion boundary was formed by siphoning with a platinum needle. At higher concentrations, the acid attacked the solder joint between segments of this siphon needle. Therefore, a gold needle, which did not have this problem because its segments were glued together, was used above 9.5 M.

Gouy fringe positions on the photographic plates were read with a Gaertner's Toolmakers Microscope (comparator). The comparator is fitted with a rotating scanner that is connected to an oscilloscope (Albright, 1962; Wendt, 1960). This facilitates accurate determination of the fringe minima positions. The measurement precision of these fringe minima was $\pm 2-4$ μm. The digital output of the comparator $x-y$ positions was recorded by an Apple IIgs computer. On completion of plate reading, the data were transferred to a VAX mainframe computer for analysis.

The value of the total number of fringes J for each experiment was obtained from the PQ program (Miller et al., 1992). This program determines the number of fringes by an extrapolation procedure of the inner fringe positions to the undeviated fringe position and is particularly suitable for binary systems with low values of Q_0. (Q_0 is defined in Fujita and Gosting (1960) and denoted there by Q.) The J value was also determined by using the F3J program (Albright and Miller, 1989), which uses all the fringe positions and has J as an adjustable parameter. Though the latter program was designed for ternary systems, one of the eigenvalues is an input quantity. If that eigenvalue is set to be very large, the program is forced to treat the data as if it were for a binary system. The value of J obtained by this method almost always agreed within ± 0.02 with PQ values. Values of $J/\Delta C$ were calculated for all diffusion experiments and plotted versus C to provide diagnostic information relating to the accuracy of $J/\Delta C$. Four experiments were discarded, based partly on discrepant values of $J/\Delta C$.

For all but five runs, diffusion coefficients were calculated by the procedures developed by Kegeles and Gosting (Kegeles and Gosting, 1947), where the Z_j values used in calculating the values of $f(\zeta_j)$ were those given by Gosting and Morris (Gosting and Morris, 1949). The diffusion coefficients were obtained by averaging the C_t values for the outer nine fringes (fringes 0−8) and calculating an apparent diffusion coefficient for each pattern. These apparent diffusion coefficients were extrapolated versus the reciprocal of elapsed time, t', to $1/t' = 0$ to obtain the measured diffusion coefficient for the experiment. These 19 runs all had Q_0 values less than 2×10^{-4}.

Of the remaining five runs, the two lowest concentration ones require corrections to D because of a $C^{1/2}$ concentration dependence (Albright and Miller, 1980). These corrections will be described in the next section. The other three runs had Q_0 values larger than 2×10^{-4} and less than 8.6×10^{-4}. For these runs, an apparent D was obtained from the F2P program (Albright and Miller, 1989) using an input value of σ_+ about twice as large as $1/D_A$. The resulting apparent D values were also extrapolated to $1/t' = 0$ for each of these three runs.

Two diffusion cells were used in these experiments. Both are of the Tiselius design. One cell has windows that extends to the side. These windows form part of the optical path for reference fringes as well as being part of the diffusion channel optical path. This cell (C-1235) had an optical path length of 2.4887 cm, and was used for all experiments up to 9.5 M.

The authors were very concerned that concentrated acid might destroy the seals of the first good cell and thus the cell itself. An experiment on a broken cell demonstrated that prolonged exposure to HCl vapor could indeed destroy seals. Therefore the second cell, of lesser quality and without the window extensions, was used for experiments from 10 M to 12 M. It was used because the authors were willing to risk sacrificing it. As it turned out, this second cell survived. It had an optical path length of 2.4936 cm.

The top reservoir unit used for experiments up to 8 M was of the standard type used with Tiselius cell assemblies. Two cylinders, one for the top solution and one for the bottom solution, extend out of the diffusion bath and have ground joint top fittings to partially seal off the reservoir from the outside to limit evaporation.

For experiments in the 8 M to 12 M concentration range, much more confined types of reservoirs were used to suppress evaporation. These reservoirs are short glass cylinders with nearly flat glass tops and bottoms. They have small-bore glass tubes (7 mm o.d.) extending both up and down from the tops and bottoms of the cylinders. The tubes are collinear and allow a straight siphon tube (or filling tube) to pass completely and freely through the reservoir and into the diffusion cell itself. The glass tubes that extend down from the reservoir cylinders fit into a Teflon plate with nonslotted collet type seals. The Teflon plate in turn is sealed to the Tiselius diffusion cell with grease. When the cell holder and its cell are placed in the constant-temperature water bath, the reservoirs are completely submerged in the bath except that the top tubes extend above the water level. Reservoirs with 100 cm^3 volume were used in experiments for the concentration range 8 M to 9.5 M, and reservoirs with only 50 cm^3 volume were used for experiments at the higher concentrations.

In the concentration range 0.1 M to 6 M, Vaseline was used to grease the joints of the bottom and top fittings to the Tiselius cell. At higher concentrations, Fluorolube Grease GR-290 from Fisher Scientific was used. This latter grease was chosen because it is resistant to attack by corrosive liquids and vapors and because it had a good consistency at 25 °C.

The water thermostat of the Gosting diffusiometer was kept at (25.00 ± 0.01) °C using a Bayley Instrument Precision Temperature Controller (a proportional temperature controller). The temperature was measured with a 1 deg range calorimeter thermometer. This thermometer had a 0 °C calibration point, and the thermometer was calibrated in an ice bath prior to the start of this work.

The physical distances of all optical elements of the two diffusion cells were carefully measured relative to the back flanges of the cells. These flanges reference the position of the cells to the cell holder. The measurements showed that the optical center of the two cells sitting in the same cell holder are the same within 0.1 mm. The b distance from the center of the cells to the photographic plates for both diffusion cells was 308.89 cm, based on the measured value for cell C-1235.

Density Measurements. Except for cases noted above where the pycnometric methods were used, all density measurements were made with a Mettler Parr DMA-40 density meter which had been interfaced to an Apple IIe

Table 1. Interdiffusion Coefficients of HCl + H_2O at 25 °C

$\bar{C}$/mol dm^{-3}	ΔC/mol cm^{-3}	m/mol kg^{-1}	J	$10^4 Q_o$	$10^9 D_v$/m^2 s^{-1}	$10^9 \boldsymbol{M}$/m^2 s^{-1}
0		0			3.337	3.337
0.1000[a]	0.2	0.1005	78.97	8.40av[g]	3.055	3.251
0.2501[a]	0.2501	0.2520	97.44	1.30av	3.083	3.185
0.5003[a]	0.2503	0.5065	95.98	1.16av	3.196	3.092
1.0007[a]	0.2514	1.0231	95.28	6.65[f]	3.448	2.913
2.0036[a]	0.2505	2.0905	91.99	8.57[f]	4.037	2.644
3.0054[a]	0.2509	3.2030	89.56	1.74av	4.663	2.442
4.0057[a]	0.2502	4.3644	87.22	−0.65av	5.212	2.254
4.5051[a]	0.2496	4.9645	86.19	−0.28av	5.447	2.167
5.0036[a]	0.2505	5.5777	85.19	−0.88av	5.639	2.080
5.5025[a]	0.2492	6.2064	84.23	−0.88av	5.788	1.995
6.0003[a]	0.1758	6.8494	58.87	−0.05av	5.898	1.915
6.0217[b]	0.2506	6.8771	83.90	−0.37av	5.900	1.911
6.5221[b]	0.2500	7.5402	82.55	0.64av	5.959	1.831
7.0219[b]	0.2493	8.2196	81.27	0.50av	5.959	1.751
7.5215[b]	0.2496	8.9166	80.45	0.72av	5.902	1.670
8.0196[b]	0.2496	9.6300	78.92	1.13av	5.829	1.598
8.5070[c]	0.2597	10.3467	81.35	−0.81av	5.709	1.527
9.0077[c]	0.2460	11.1033	73.45	−1.91av	5.561	1.457
9.5016[c]	0.2459	11.8706	73.53	0.02av	5.403	1.392
10.0252[d]	0.2262	12.7074	65.93	−0.92av	5.205	1.319
10.5373[d]	0.2599	13.5508	73.41	−0.23av	5.005	1.244
11.0098[d]	0.2929	14.3509	78.27	−1.63av	4.795	1.162
11.5545[e]	0.2154	15.3050	56.99	−1.31av	4.531	1.051
11.9908[e]	0.3908	16.0882	98.87	3.29[f]	4.306	0.947

[a] Solutions were prepared from stock solution 1. [b] Solutions were prepared from the first bottle of stock solution 2. [c] Solutions were prepared from the second bottle of stock solution 2. [d] Solutions were prepared from stock solution 3, i.e., directly from reagent bottle 1. [e] Solutions were prepared from stock solution 4, i.e., directly from reagent bottle 2. [f] Q_0 values from the F2P "extrapolated" procedure (Albright and Miller, 1989). [g] Average Q_0 values when C_t was obtained from averaging the C_{tj} of the nine outer fringes (0−8).

computer to allow time averaging. (This meter repeatedly displays a five-digit number which is proportional to the time elapsed for a fixed number of vibrations. The measure of elapsed time immediately starts over for each new display without missing a count. By taking sums of 50 displays, dividing by 50, and then displaying the results on a computer, we get seven digit numbers whose last digit is an even number.) The temperature of the vibrating tube compartment was regulated by circulating water from a large, well-regulated water bath. High concentrations of hydrochloric acid could be used with the meter because the vibrating tube itself is glass and connectors to the vibrating tube are Teflon. The meter in the above configuration appeared to have a precision of ±0.000 02 g cm^{-3} or better. It was calibrated with air and pure water. In all cases the density of the air in the density meter at 25 °C was calculated from the barometric pressure and from the humidity corrected to 25 °C. As noted above, pycnometric measurements made on the constant-boiling stock solution agreed reasonably well with the density meter measurements. The densities of all solutions prepared for diffusion experiments were measured and used to calculate concentrations. Densities were also used as a method to check for changes in stock solution concentrations and make small corrections to the concentration values.

Experimental Results

Diffusion Coefficients. Results of the diffusion experiments are given in Table 1. Included are the mean molar concentration $\bar{C}$, the concentration difference across the initial boundaries ΔC, the square root of the mean concentration $\bar{C}^{1/2}$, the molality m at the mean molar concentration, the total number of fringes J, the area under the fringe deviation graph Q_0, the interdiffusion coefficient on the volume-fixed frame of reference D_v, and the thermodynamic diffusion coefficient $\boldsymbol{M}$ defined below.

The quantity Q_0 is an important diagnostic. Its value will equal zero in a hypothetical perfect binary diffusion experiment as defined by perfect optics, a diffusion coefficient independent of concentration, and the refractive index n dependent only on the first power of concentration. With the exception of the 0.1 M and 0.25 M experiments, the concentration dependence of the diffusion coefficients and the nonlinear contribution to the concentration dependence of the refractive index are sufficiently small in relation to the experimental ΔC that the values of Q_0 should be zero within $\pm 2 \times 10^{-4}$. Larger values of Q_0 indicate experiments of lesser quality, where the uncertainty of the diffusion coefficients is considered to be ±0.3%.

Corrections to D at Low Concentrations. For the experiment performed at a mean concentration of 0.1 M, 0.2 M HCl diffused into pure water (i.e., $\Delta C = 0.2$ M). In this concentration range, the diffusion coefficient depends strongly on $C^{0.5}$ and C, and the value of refractive index depends not only on C but also significantly on $C^{1.5}$ and C^2 as well. Consequently, the diffusion coefficient calculated by the usual protocol for a binary system is slightly incorrect, and the value of Q_0 deviates significantly from zero partly because of this concentration dependence. A similar but lesser correction is required for the 0.25 mean concentration (0.375 M HCl diffused into 0.125 M HCl).

Expressions have been published (Albright and Miller, 1980) for correcting a diffusion coefficient measured by the Gouy method when an electrolyte diffuses into water. To make this correction, it is necessary to have values of the first, second, and third derivatives of D_v versus C and the first, second, and third derivatives of refractive index n versus C at the mean concentration.

With these derivatives, the correction can be made in two ways. One way is to correct the value of D_{av}. This quantity is the intercept of the plot of the apparent D_{av} for each fringe pattern vs its $1/t'$. The apparent D_{av} for each pattern is calculated from the average value of C_{tj} from fringes 0−8. The other way is to correct the value of D_A. This quantity is obtained from the intercept of the apparent D_A for each fringe pattern vs its $1/t'$. The apparent D_A for each fringe pattern is obtained from C_t, obtained in turn by extrapolating C_{tj} versus $f(\zeta)^{2/3}$ to $f(\zeta) = 0$ (see Albright and Miller (1980) and Gosting and Fujita (1957) for the definition of $f(\zeta)$ and the theory of this extrapolation method). The calculation of an apparent D from C_t is given in Gosting and Morris (1949). Both corrected values should be the same, and their comparison is a diagnostic of the correction procedure.

To get the derivatives for D_v vs C at 0.1 M and 0.25 M, an expression for D_v as a fifth degree polynomial in $R(C)$ was obtained by the method of least squares. Data used in the regression included literature values of D_v measured at low concentrations by the Harned method (Harpst et al., 1965) as well as our values from 0.1 M to 4 M included in Table 1.

We note that the constant term of the polynomial, i.e. D_v at $C = 0.0$, was fixed at 3.3368×10^{-9} m^2 s^{-1} in the regression analysis. This value was calculated from the Nernst−Hartley equation (eq 11.4 of Robinson and Stokes (1970)) using the limiting equivalent conductances λ^o given in Appendix 6.2 of Robinson and Stokes (1970). These conductances were based on the Jones and Bradshaw calibration standard $1.408\,77 \times 10^{-3}$ Ω^{-1} cm^{-1} for 0.01 Demal KCl solutions found in Table I of Marsh (1980), which in turn was based on the international Ω and 1948 temperature scale (already being used in the 1930s). They have been adjusted to the latest corresponding calibration standard as redetermined by Wu and Koch (1991). Their recommended value 1.4086×10^{-3} Ω^{-1} cm^{-1} (in their Table V) is based on the absolute Ω and the 1990 temperature scale. However, our thermometers were calibrated on the 1968 temperature scale. Consequently, we have used their value 1.4084×10^{-3} Ω^{-1} cm^{-1} (in their Table III), which is based on the absolute Ω and the 1968 temperature scale. It was assumed that the molar gas constant R is 8.314 510 J mol^{-1} K^{-1} and the Faraday constant F is 96 485.309 C mol^{-1} (Wu and Koch, 1991).

The derivatives of the refractive index n as a function of concentration are obtained as follows. The total number of fringes J of an experiment is given by the equation

$$J_i = [n(\bar{C}_i + \Delta C_i/2) - n(\bar{C}_i - \Delta C_i/2)]a/\lambda \qquad (1)$$

where a is the inside width of the diffusion cell along the optical path and λ is the wavelength of the light source. Assuming $n = n_0 + b_1C + b_2C^{1.5} + b_3C^2$, values of these b_i coefficients were obtained by the method of least squares from values of J_i, $\bar{C}_i$, and ΔC_i for the six experiments from $\bar{C} = 0.1$ M to 3.0 M (n_0, the value for pure water, cancels). We note that back-calculation of J from these coefficients for experiments at higher concentrations showed reasonable agreement even up to 7.0219 M, thus verifying the order of the polynomial and the validity of the b_i coefficients. This polynomial was used to calculate the required refractive index derivatives.

Parameters k_1, k_2, k_3, a_1, and a$_2$ needed for skewing corrections based on eq 74 and coefficients from the columns labeled $[D_{av} - D(\bar{C})]/D(\bar{C})$ and $[D_A - D(\bar{C})]/D(\bar{C})$ of Table III of Albright and Miller (1980) were calculated from the derivatives discussed above. At the mean concentration of 0.1 M, (k_1, k_2, k_3, a_1, a_2) are respectively −0.050 78, 1.4990, 1.1137, 0.040 72, and 0.0600. The measured D_{av} (using C_t from fringes 0−8 average) before correction was 3.0538×10^{-9} m^2 s^{-1}, and after correction $D(\bar{C})$ is 3.0552×10^{-9} m^2 s^{-1}. The measured D_A was 3.0490×10^{-9} m^2 s^{-1}, and after correction $D(\bar{C})$ is 3.0556×10^{-9} m^2 s^{-1}. The agreement of the two methods is good, and a value of 3.055×10^{-9} m^2 s^{-1} is tabulated in Table 1. The calculated value of Q_0 based on coefficients of the column headed Ω (area) of Table III in Albright and Miller (1980) is 10.48×10^{-4}, which is in satisfactory agreement with the measured value of 8.40×10^{-4}.

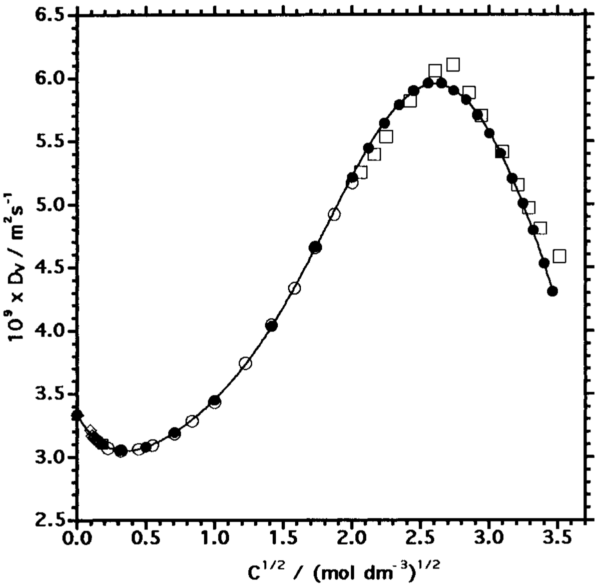

Figure 1. Plot of measured diffusion coefficients versus the square root of molar concentration for HCl + H_2O at 25 °C: (◇) (■ Gouy point) Harpst, Holt, and Lyons; (○) Stokes; (□) Haase and Richter; (●) this study.

At the mean concentration of 0.25 M and $\Delta C = 0.25$ M, there is still sufficient concentration dependence to require correction. Here parameters k_1, k_2, k_3, a_1, and a_2 are needed at 0.25 M and were determined by methods described above. They are respectively 0.139 23, 0.281 55, 0.451 931, −0.027 756, and 0.015 34. In order to use eq 74 of Albright and Miller (1980), the quantity ΔC must be replaced by $\Delta C/2$ everywhere it appears in eq 74. The values of the A_i in Albright and Miller (1980) were derived for the infinite dilution case, but it was shown that they work moderately well for cases near infinite dilution (Albright and Miller, 1980). The measured D_{av} (using C_t from fringes 0−8 average) without correction was 3.0826×10^{-9} m^2 s^{-1}, and with correction $D(\bar{C})$ is 3.0831×10^{-9} m^2 s^{-1}. The measured D_A was 3.0763×10^{-9} m^2 s^{-1}, and with correction $D(\bar{C})$ is 3.0784×10^{-9} m^2 s^{-1}. The agreement is not as good as at 0.1 M. Since there was significantly less statistical uncertainty in the calculation of D_{av}, its corrected value, 3.083×10^{-9} m^2 s^{-1}, is tabulated in Table 1. The value of Q_0 calculated from column 6 of Table III of Albright and Miller (1980) was found to be 3.08×10^{-4}, which is in satisfactory agreement with the value of 1.30×10^{-4} obtained by using fringes 0−8.

The least squares procedures were cycled twice to use corrected values of D_v in the final regression to make the low-concentration corrections. However, further corrections to D_v due to the second cycle were found to be negligible.

Comparison of Diffusion Data. A plot of the diffusion coefficients versus $\bar{C}$ is shown in Figure 1. Included in the figure are the results from the better previous studies on this system. Our data appears self-consistent over the whole concentration range and does not show the discontinuity that occurred around 4 M in the 0 to 4 M range of diffusion coefficients measured by Stokes (1950) and the 4 M to 12 M range of diffusion coefficients measured by Haase and Richter (1967).

Our results are in excellent agreement with the diaphragm cell data of Stokes (1950), which range from 0 to 4 M. The agreement appears to be always within 0.4% and usually better. Integrations of our data by Prof. Stokes

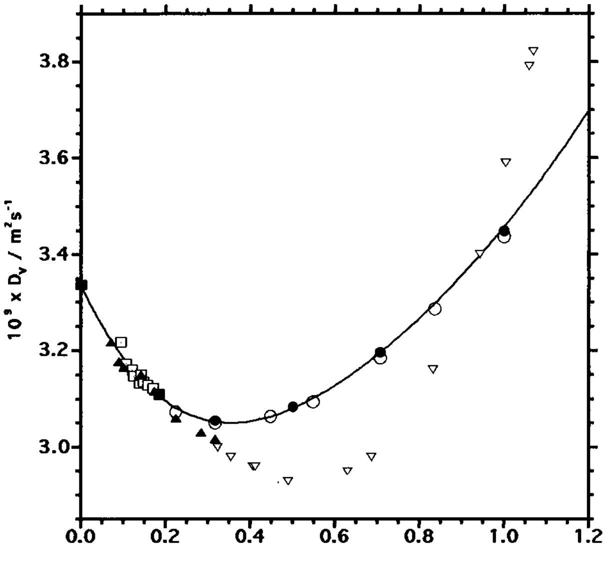

Figure 2. Plot of measured diffusion coefficients versus the square root of molar concentration for HCl + H_2O at 25 °C from 0 to 1.44 M: (□) (■ Gouy point) Harpst et al.; (○) Stokes; (▲) Lobo and Teixeira; (▽) James et al.; (●) this study.

gave integral D values that were on the average only 0.1% higher (with a STD of 0.24% from the mean deviation) than his experimentally determined integral D values (private communication, January 1997).

Our data also merges well with the low-concentration conductimetric method (and one Gouy point) data of Harpst et al. (1965). Our agreement with the Jamin interferometric data of Haase and Richter (1967) at higher concentrations (4 M to 12 M) is less good. The maximum diffusion coefficients occur at about 7.25 M, and our maximum D_v value appears to be 3% lower than values of Haase and Richter. In the 9 M to 12 M region, we do not show the inflection point that appears in their data. Our measured diffusion coefficients decrease more rapidly with increasing concentration at the higher concentrations, and as a consequence Haase and Richter's values are up to 7% higher than ours at 12 M. These differences are not surprising, since the Jamin interferometer used by Richter (1967) was a small commercial model not capable of high accuracy (Richter, private communication, 1995).

A plot of our diffusion data, the data of Harpst et al. (1965), the data of Stokes (1950), the data of Lobo and Teixeira (1979), and most of the data of James et al. (1939) over the concentration range from 0 to 1.4 M are presented in Figure 2. Also included is the low-concentration segment of the line that was passed through our data and conductimetric (and one Gouy point) data of Harpst et al. included in Figure 1. It is seen that the data of Lobo and Teixeira, which were obtained by the dual open end capillary method, are in good agreement with the data of Harpst et al. in the region of concentration overlap, but above this concentration and into the concentration range of our data their data drops significantly below our data and those of Stokes. The data of James et al. are seriously discordant with our data and those of Stokes. They fall below and then rise sharply above ours and Stokes'. Beyond the range of Figure 2, their remaining data follow the same rising discordant trend. Their data had been obtained by an early diaphragm cell method, in which the solutions were not mechanically stirred and the technique depended on density gradients to keep the solutions uniform. Consequently, it suffered from bulk flow as well as diffusion through the diaphragm.

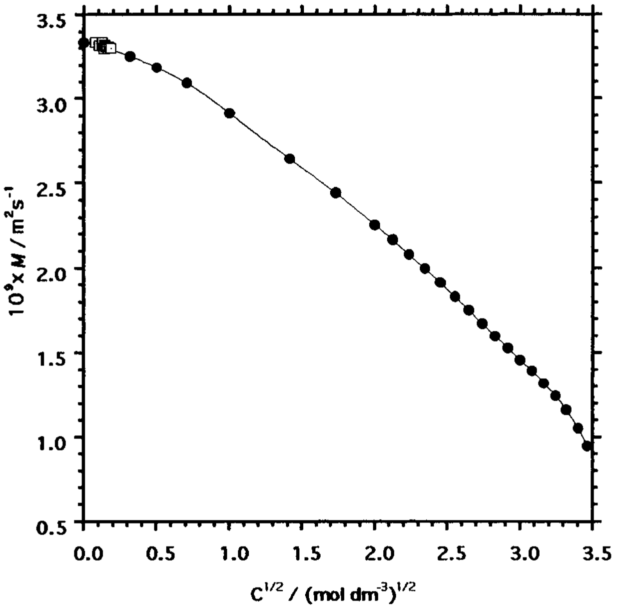

Figure 3. Plot of the calculated thermodynamic coefficients versus molar concentration: (□) calculated from the data of Harpst et al.; (●) this study.

We estimate the accuracy of our diffusion coefficient measurements to be ±0.1% (except where Q_0 is large) up to 9.5 M and ±0.3% or better at the high concentrations, i.e., 3 to 9 in the third place in Table 1. This takes into account some experimental difficulties encountered in the high-concentration region and the use of a diffusion cell of lower quality for the higher concentration measurements.

An expression for D_v was obtained by the method of linear least squares from our corrected D_v for the whole concentration range (four decimals were kept to avoid round-off errors, rather than the three presented in Table 1) and the data of Harpst et al. (1965) omitting their anomalous D_v point at 0.006 M. However, the constant term was fixed at 3.3368 × 10^{-9} m^2 s^{-1}. This expression is

$$10^9 D_v = \frac{3.3368 + a_1\sqrt{C}}{1 + a_2\sqrt{C}} + a_3C + a_4C^3 + a_5C^4 + a_6C^5 + a_7C^7 \quad (2)$$

The units of $10^9 D_v$ are m^2 s^{-1}. When C is in mol dm^{-3}, the coefficients a_i in order from $i = 1$ to 7 are 9.724 744 9, 3.584 113 0, 0.590 819 82, 0.012 469 576, −0.003 971 658 1, 0.000 273 804 87, and −3.593 927 × 10^{-7}. The standard deviation was ±0.0063 m^2 s^{-1}. (The statistical analysis was performed using the JMP statistical program from SAS Institute Inc.)

Thermodynamic Diffusion Coefficients. Thermodynamic diffusion coefficients $\boldsymbol{M}$ are defined by the equation:

$$\boldsymbol{M} = \frac{D_v}{1 + m\dfrac{\mathrm{d}\ln\gamma}{\mathrm{d}m}} \quad (3)$$

where m is the molality (mol kg^{-1}). An expression for the activity coefficient γ versus m for HCl was taken directly from Hamer and Wu (1972). Figure 3 shows a graph of the thermodynamic diffusion coefficient $\boldsymbol{M}$ versus the square root of molarity M. Included in the figure are thermodynamic diffusion coefficients calculated from the low-concentration data of Harpst et al. (1965). It is seen that our data and the data of Harpst et al. again connect

Table 2. Density Values for the System HCl + H_2O at 25 °C

C/mol dm^{-3}	d/g cm^{-3}	C/mol dm^{-3}	d/g cm^{-3}	C/mol dm^{-3}	d/g cm^{-3}
0.000 00	0.997 045	4.629 97[a]	1.073 659	8.636 88[c]	1.134 392
0.124 99[a]	0.999 306	4.878 40[a]	1.077 318	8.884 68[c]	1.137 991
0.200 01[a]	1.000 638	4.880 08[a]	1.077 644	9.130 72[c]	1.141 424
0.375 03[a]	1.003 724	5.128 89[a]	1.081 447	9.378 68[c]	1.145 064
0.375 13[a]	1.003 749	5.129 25[a]	1.081 527	9.624 56[c]	1.148 504
0.375 13[a]	1.003 758	5.377 89[a]	1.085 280	9.912 08[d]	1.152 691
0.624 40[a]	1.008 107	5.627 04[a]	1.089 130	10.138 28[d]	1.155 820
0.625 39[a]	1.008 119	5.896 35[b]	1.093 248	10.140 71[d]	1.155 844
0.875 01[a]	1.012 442	5.912 40[a]	1.093 526	10.407 35[d]	1.159 482
1.126 45[a]	1.016 734	6.088 21[a]	1.096 228	10.667 22[d]	1.162 981
1.878 33[a]	1.029 448	6.146 97[b]	1.097 092	10.863 32[d]	1.165 703
2.128 80[a]	1.033 616	6.397 09[b]	1.100 906	10.906 79[d]	1.166 151
2.879 95[a]	1.045 884	6.647 04[b]	1.104 700	10.908 51[d]	1.166 158
3.130 89[a]	1.049 958	6.897 22[b]	1.108 502	11.139 17[d]	1.169 082
3.880 59[a]	1.061 835	7.146 49[b]	1.112 241	11.150 11[d]	1.169 307
3.880 85[a]	1.061 835	7.396 71[b]	1.116 022	11.156 24[d]	1.169 438
4.130 45[a]	1.065 842	7.646 32[b]	1.119 752	11.446 83[e]	1.173 111
4.380 32[a]	1.069 747	7.894 84[b]	1.123 454	11.662 19[e]	1.175 912
4.380 55[a]	1.069 781	8.144 40[b]	1.127 142	11.795 40[e]	1.177 462
4.629 86[a]	1.073 628	8.377 14[c]	1.130 568	12.186 20[e]	1.182 653

[a] Solutions were prepared from stock solution 1. [b] Solutions were prepared from the first bottle of stock solution 2. [c] Solutions were prepared from the second bottle of stock solution 2. [d] Solutions were prepared from stock solution 3, i.e., directly from reagent bottle 1. [e] Solutions were prepared from stock solution 4, i.e., directly from reagent bottle 2.

smoothly. Note that ***M*** drops smoothly over the whole concentration range. This is in contrast with most salts, which have a maximum in ***M*** at low concentrations. This smooth drop also indicates that the more complicated concentration dependence of the interdiffusion coefficient D_v is strongly influenced by the concentration dependence of the activity coefficient of HCl.

Density Values. The values of molarities C and densities d (g cm^{-3}) for HCl at 25 °C are given in Table 2. The stock solutions from which the solutions were prepared are also noted in Table 2. The number of significant figures for density values reflect the precision of the density meter, but not the accuracy of measurement. Moreover, the number of significant figures shown for the concentrations and densities are more than the data warrant. However, the numbers presented in Table 2 were used to avoid round-off errors in the least squares technique used to relate density to concentration.

When fitting the data, points at 12.1862 M and 4.8784 M were removed from the data base as being outliers. Both points appeared to deviate from fitted curves by more than four standard deviations. (However, comparison of our data to the data of Török and Berecz (1989), see Figure 4, suggests that the density at 12.186 M may in fact be valid.) When all data in Table 2 except the two discarded points are kept, the equation

$$d = 0.997045 + 0.01792259C - 0.000402994C^2 + 0.00002448101C^3 - 6.6010 \times 10^{-8}C^5 \quad (4)$$

fits the data with a standard deviation of 4.34 × 10^{-5} g cm^{-3} and maximum deviations of ±0.000 12. Four adjustable parameters were determined in the fit. The same density data set was fit with the following polynomial in molality

$$d = 0.997045 + 0.0177876m - 0.000674479m^2 + 0.0000257851m^3 - 4.7322 \times 10^{-8}m^5 + 5.2122 \times 10^{-11}m^7 \quad (5)$$

where the standard deviation was 5.41 × 10^{-5} g cm^{-3} and the maximum deviation was ±0.000 15. Correct molalities for the data set can be calculated from molarity and density values in Table 2.

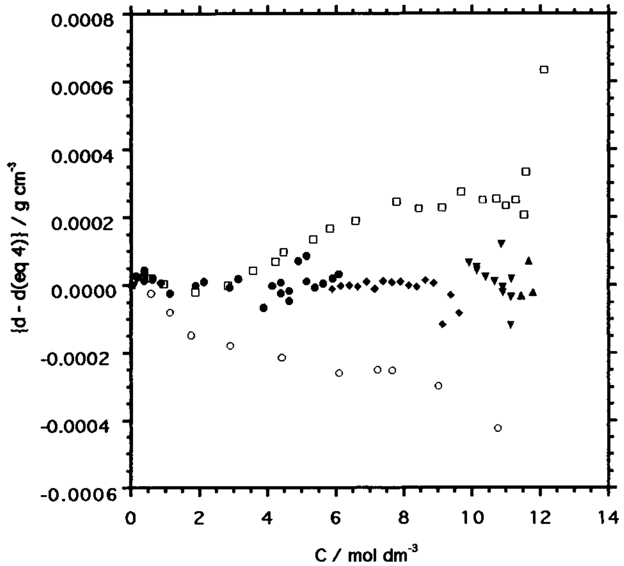

Figure 4. Plot of deviations of density from eq 4: (□) Török and Berecz; (○) Geffcken; (●) 0–6 M; (◆) 6–9 M; (▼), 9–11 M; (▲) 11–12 M (this study).

When data from solutions prepared only from stock solutions 1–3 (0–9.624 96 M) are used, the following equation is obtained

$$d = 0.997045 + 0.01798402C - 0.0004587010C^2 + 0.00004023619C^3 - 0.000001747403C^4 \quad (6)$$

that fits the density with a standard deviation of 3.09 × 10^{-5} g cm^{-3}. Again, four adjustable parameters were determined in the fit. Finally, when measured densities of solutions from only the first stock solutions are used (0–6.088 21 M), the following expression is obtained:

$$d = 0.997045 + 0.0184018C - 0.000858213C^{3/2} \quad (7)$$

with a standard deviation of 3.75 × 10^{-5} g cm^{-3}. In this case just two adjustable parameters were determined. All three fits agree within 3 × 10^{-5} g cm^{-3} in the lower concentration range (0–6.088 21 M). The two higher concentration fits agree within 6 × 10^{-5} g cm^{-3} in the higher range where they overlap (6.088 21 M to 9.624 96 M).

The two-parameter fit of density was used to calculate densities for the measurements made on constant-boiling solutions. Comparisons were made only with density meter measurements. At 20.250 mass % the measured density was 1.096 231 g cm^{-3}, and that calculated from the equation was 1.096 188 g cm^{-3}, in reasonably good agreement. At 20.245 mass %, the double-distilled case, the measured value was 1.096 290 g cm^{-3}, but the calculated value from the two-parameter fit was 1.096 171 g cm^{-3}. This is a significant discrepancy but was based on only two measurements. Use of the concentration based on analysis would have improved the agreement. When a third analysis was performed, the concentration was 20.264 M based on Foulk and Hollingsworth's data. The average of nine density measurements was 1.096 261 g cm^{-3}, and the value calculated from the two-parameter fit was 1.096 255, which is very good agreement.

A residual plot of measured density minus densities calculated from eq 4 is given in Figure 4. Included in the figure are values of Török and Berecz (1989) and the values of Geffcken (1931). Our results are in fair agreement with and lie between the results of Török and Berecz and those of Geffcken, but closer to the former. Those two data sets and ours tend to parallel each other in such a way that suggests that the difference in the data sets lies in differences in the determination of concentrations of stock solutions. We have chosen to anchor our concentrations to the concentrations of the constant-boiling solutions whose concentrations have been calculated from the data of Foulk and Hollingsworth (1923), which in turn are based on barometric pressure. Old density data at higher concentrations (Åkerlöf and Teare, 1938; ICT, 1928), are in lesser agreement and are not included in Figure 4.

We note that there have been a large number of density measurements made on the HCl + H_2O system at 25 °C by other researchers. Most of the measurements were made at lower concentrations and are not included in Figure 4 for this comparison.

When everything is considered, we believe that our measured density values are accurate to ±0.0001 g cm^{-3}.

Conclusions

The importance of the system and discrepancies between this work and the work of previous investigators indicates that an accurate remeasurement of the diffusion coefficients was justified. The diffusion coefficients now appear to be a smooth function of concentration. These results will allow an improved calculation of ionic transport coefficients l_{ij} when these data are coupled with conductance data and transference number data. This calculation is in progress, and literature density values at lower concentrations will be reviewed there along with ours.

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