Densities in the Liquid Hydrogen Chloride Solvent System

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Densities were measured in the hydrogen chloride solvent system over the normal liquid range of the solvent. In addition to pure hydrogen chloride, solutions of tetramethylammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide, and trimethylsulfonium iodide in hydrogen chloride were measured at compositions up to about 2 M. Attempts to measure densities of tetraethylammonium halide solutions failed, as the salts were found to be insoluble in liquid hydrogen chloride. Solutions were prepared by condensing hydrogen chloride over solute in a graduated borosilicate glass cell. The densities were measured by a direct Archimedean technique using a fused quartz helix to indicate the weight of a submerged sinker. The accuracy of the method is 0.0006 g/cm^3 with a precision of 0.0005 g/cm^3. The measured densities of pure hydrogen chloride are consistent with values reported in other recent studies. The molar volume and the thermal expansion coefficient of the pure liquid are calculated. The molar volume indicates a void space of roughly 50% in the pure liquid; this finding is consistent with the view that liquid hydrogen chloride does not self-associate to any appreciable extent. The thermal expansion coefficient is on the same order of those of other room-temperature molecular liquids but is 1 order of magnitude larger than that of water. The measured densities of the electrolyte solutions are found to obey Root's equation.

In 1985 Rose and Sadoway were awarded a U.S. patent for electrodeposition of several reactive metals and silicon from liquefied halogenous gases at subambient temperatures in a process they termed cryoelectrodeposition.[1] One of these solvents was anhydrous hydrogen chloride. Theirs was the first reported instance of liquid HCl's serving as a medium for electrodeposition. The cryoelectrodeposition work was motivated by a need for alternatives to high-temperature or high-energy processes for the formation of thin coatings and the preparation of smooth clean surfaces and sharp interfaces.[2]

It was necessary to accomplish these syntheses on an exploratory basis and by an almost entirely empirical approach because, as for most liquids that are gaseous at room temperature, few chemical and electrochemical data are available for liquid HCl. The history of chemical systems comprising liquid hydrogen chloride begins with the first report of liquefaction of hydrogen chloride in the early 1800s by Faraday.[3,4] However, although the chronicle of the use of hydrogen chloride as a solvent covers a long period of time, little is known about its solutions. Waddington attributed the deficiency of knowledge about hydrogen chloride chemistry to two factors: experimental difficulties that hamper data collection and physical properties that would discourage investigators seeking effective ionizing solvents.[5] The liquid range of hydrogen chloride (−114.2 to −85.04 °C) is narrow and exists at an inconvenient temperature, so that study under normal pressures requires more cooling power than simple dry ice slush baths but much less than standard liquid nitrogen techniques. These difficulties are easily avoided with more conventional solvents that also have a more auspicious dielectric constant than that of HCl (~10).

The purpose of this work has been to begin to gather fundamental quantitative data about solutions in liquid hydrogen chloride in the normal liquid range and to develop the experimental apparatus required for well-controlled, systematic study of this solvent system as a function of composition and temperature. As a first step toward broadening the understanding of solutions in liquid anhydrous hydrogen chloride, a study of the composition and temperature dependence of the density of electrolyte solutions was conducted. The experimental technique and data are reported in this document.

The salts were chosen on the basis of likely suitability as a supporting electrolyte for electrochemical studies and sufficient solubility to produce detectable changes in density. An overview of the history of the observation of dissolution of substances in liquid anhydrous hydrogen chloride and reasons for choosing those measured in the present study are given elsewhere.[6] The initial list of solutes to be measured comprised the following: tetramethylammonium chloride, bromide, and iodide; tetraethylammonium chloride, bromide, and iodide; and trimethylsulfonium iodide. Pursuant to experimental difficulties discussed below, it was not possible to measure solutions of the tetraethylammonium halides.

1. Experimental Equipment

1.1. Reagents. The hydrogen chloride used in this study was Matheson (Gloucester, MA) ULSI purity >99.999%, which contains less than 2 ppm H$_2$O. The commercial HCl was further dried by passage through magnesium perchlorate. Dew point measurements in this laboratory have shown that this treatment reduces the water content to about 6 ppb.[7] A good review of the efficacy of various drying agents for hydrogen chloride has been published.[8]

All of the tetraalkylammonium halides used in this study are water sensitive and required purification of the commercially available forms and subsequent care to maintain their purity. For removal of solvents after recrystallization, salts (except Me$_4$NCl) were placed in borosilicate glass recovery flasks which were attached to a vacuum line and immersed in a water bath carefully thermostated at 60 °C. The assembly was wrapped to exclude light. Vacuum-line techniques were used to prevent exposure of the dried salts to the room atmosphere. After treatment all salts were transferred to an argon-filled glovebox, where they were stored in amber glass bottles.

Tetramethylammonium chloride, Me_4NCl (Lancaster, Windham Hill, NH, 98+%), is extremely hygroscopic. The commercially available salt was recrystallized from methanol by the addition of acetone according to the method of Pickard *et al.*[9] in a nitrogen-filled glovebag and then dried by azeotropic distillation of benzene. Excess solvent was removed by flash evaporation at 20 μmHg (3 Pa) for at least 24 h. When the recrystallization was not followed by the benzene treatment, the irreproducibility of the density measurements was on the order of 20 times the calculated statistical error. Low-temperature solutions in hydrogen chloride were water-clear.

Tetramethylammonium bromide, Me_4NBr (Fluka, Ronkonkoma, NY, purum >99%), was recrystallized from a mixture of methanol and ethanol (roughly 1:1 by volume),[10] and the crystals were dried for at least 3 days *in vacuo* at 60 °C. Tetramethylammonium iodide, Me_4NI (Lancaster 99%), was recrystallized from methanol and then dried for at least 3 days *in vacuo* at 60 °C. At first Me_4NBr and Me_4NI were recrystallized from distilled, deionized water as reported in accounts of precise work in the literature. However, hydrogen chloride solutions of salts treated in this manner were turbid, with fine sandlike white particles settling to the bottom of the cell during the course of a measurement. The precipitate was probably one of several insoluble compounds formed by hydrogen chloride and residual water. Hydrogen chloride solutions of salts recrystallized from alcohol were colorless and perfectly clear. More concentrated solutions of the iodide were straw-colored.

Trimethylsulfonium iodide, Me_3SI (Lancaster 99%), received from the manufacturer is a light yellow grainy powder. Recrystallization from distilled, deionized water yielded large white crystals. After washing, the crystals were dried for at least 3 days *in vacuo* at 60 °C. Solutions of this salt in hydrogen chloride were straw-colored to yellow. There was no evidence of water entrainment by the salt.

Tetraethylammonium chloride, Et_4NCl (Fluka purum >98%), as received from the manufacturer is a light beige powder with the consistency of fine flour. Two different methods were tested for their ability to remove water from the salt: recrystallization and distillation. The product of recrystallization from acetone[11] was white acicular crystals. Azeotropic distillation of benzene followed by flash evaporation at room temperature changed neither the appearance of the salt nor its solubility in liquid HCl. Contrary to the report by Waddington *et al.*[5] of a conductivity measurement of a 0.13 M solution at −95 °C, in the present investigation Et_4NCl treated in either of these manners was not found to be soluble. Attempts to make solutions at concentrations around 0.01 M in hydrogen chloride at −90 °C were unsuccessful, even after 8 h of continuous stirring. Tetraethylammonium bromide, Et_4NBr (Fluka puriss. >99%), and tetraethylammonium iodide, Et_4NI (Lancaster 98+%), were recrystallized from methanol. The crystals of both compounds were dried for at least 3 days *in vacuo* at 60 °C. Neither compound was found to be soluble in hydrogen chloride.

1.2. Density-Measurement Apparatus and Technique. Methods for measurement of density have been reviewed by Bauer and Lewin.[12] The direct Archimedean technique was chosen for this investigation because the nonambient-temperature liquid range and the necessity of a closed system make other methods commonly used at room temperature unwieldy.

Glass and fluorocarbon plastics are used for most parts of the system. Tubing (Fluoroware, Chaska, MN) is PFA (perfluoroalkoxy fluorocarbon), chosen for its inertness and low permeability. Stopcocks have PFA bodies with polytetrafluoroethylene (PTFE) plugs. The plastic-to-plastic connections (Galtek integral ferrule fittings, Fluoroware) are made by PFA
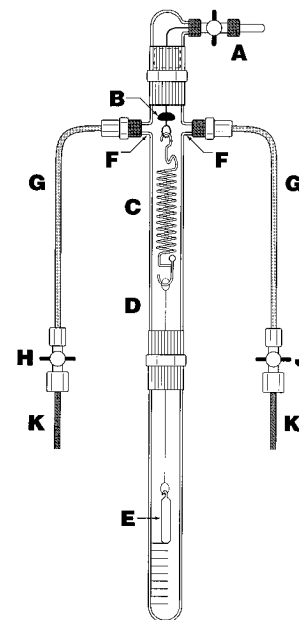

Figure 1. Measurement apparatus for Archimedean technique.

fittings. PFA fittings (Quikgrip fittings, Fluoroware) designed for use with plastic tubing were tested and found satisfactory for the 1/4 and 1/2 in. plastic-to-glass connections at pressures up to 30 psi. Check valves are PFA with fluorocarbon elastomer seals. The solutions are prepared and measured in a closed system to protect the surroundings from corrosion and the specimen from contamination.

The apparatus used for density measurements is shown in Figure 1. The specimen solution is contained in the graduated borosilicate glass test tube at the bottom, which is immersed in the cryostat bath (not shown). An elastic fused quartz helix (Ruska Instruments, Houston, TX) C is housed in the middle portion of the vertical glass column. The pieces forming the column terminate at one or both ends in lengths of glass tubing ground to 1.1 in. o.d. so that they can be joined by 1.1 in. fittings (Teqcomm, Santa Ana, CA). These have bodies and front ferrules of PTFE with nuts and back ferrules of polyvinylidene fluoride. Just above the lower joint L a magnet (not shown in the figure) was affixed to the exterior of the column for holding the interior borosilicate-encased magnetic stirrer bar in place until it was dropped into the specimen. The fused quartz sinker E suspends into the test tube from the spring by a 0.005 cm diameter tantalum wire D. Gas-tight reel A, fashioned using a notched PTFE plug machined to fit the body of a PFA stopcock, closed opposite its connection to the column cap by a small sealed piece of glass tubing, moves the spring vertically. Two lengths of 30-filament PTFE fiber (FP305722, Goodfellow, Malvern, PA) that have been twisted together are wound on the reel. To promote smooth operation of the reel, a tantalum weight B of about 1 g is affixed above the thread loop from which the spring hangs. The thread passes through a hole in the center of a Teflon bushing held in the column cap by friction. The bushing serves to center the spring in the column. The 1/4 in. horizontal tubulations F near the top of the column are the gas inlet and vent. They are joined to lengths of 1/8 in. tubing G terminated by stopcocks H and J. The more flexible smaller diameter tubing facilitates the positioning of the cell in the cryostat once it is connected to the rest of the gas train by the 1/4 in. tubing K. The column is mounted at lower joint L in a clamp (not shown) that is vertically movable along a rack and pinion for axial adjustment of the cell position. The clamp isolates the apparatus very well from the vibrations caused by vigorous stirring of the cryostat bath.
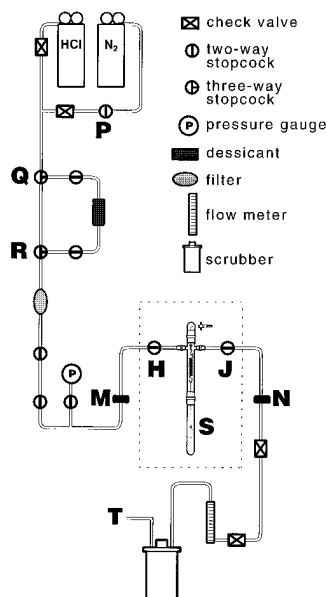
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Figure 2. Gas train.

The tantalum wires suspending the sinker did not gain weight over time and were used repeatedly, as long as they remained unkinked. Springs were cleaned with deionized water after each use and air-dried. The springs are very fragile and so have a limited lifetime; several were used in this study. Only one sinker was used for all the reported measurements of solutions, and its weight was verified often.

An Eberbach (Ann Arbor, MI) cathetometer measured the spring extension in increments of 0.005 cm. It was positioned vertically with the aid of a bubble level in its base and secured in place about 40 cm from the spring column by lead blocks.

1.3. Gas Train. The gas train is depicted in Figure 2. Fittings at M and N join the density measurement apparatus to the rest of the gas train. From the tank hydrogen chloride gas is conducted in 1/4 in. × 1/8 in. tubing first to a glass vessel containing 500 g of magnesium perchlorate and then through a fritted glass filter before entering the cell S. Exclusive of the desiccant, which is always kept under HCl pressure, the system upstream of point M is kept under 8 psi of nitrogen when not in use.

Gas leaving the cell passes through the vent stopcock J, which is joined by 1/4 in. tubing to two PFA check valves in series. The gas passes through a flow meter before entering the scrubber, which neutralizes the corrosive gas before venting at T to a fume hood. The scrubber has been described in detail elsewhere.[6]

2. Experimental Procedure

2.1. Typical Experiment. A typical measurement was conducted in the following manner. Before each use the test tube, sinker, stirrer bar, and wire were washed with boiling dilute sodium carbonate solution followed by repeated rinsing with distilled water. In a glovebox, under dry argon atmosphere, the solute was weighed into the bottom of the test tube shown in Figure 1. The tube with the solute was then attached to the column housing the spring, and the stopcocks H and J were closed. The apparatus was removed from the glovebox, mounted in the clamp, and connected to the gas train under nitrogen pressure. The cell was leak tested under 8 psi of nitrogen. The cell and gas train back to point P in Figure 2 were evacuated to about 150 μm using a vacuum pump temporarily connected at fitting N. A temperature probe was attached to the outside of the test tube. The test tube was

positioned in an unsilvered Dewar flask containing methylcyclohexane, and cooling was begun. The cryostat provided a large cold zone uniform to ±0.03 °C. Over the hydrogen chloride liquid range the cold zone temperature was held to within better than ±0.05 °C of the set point, for which the measurement accuracy was about 0.17 °C. Construction and operation of the cryostat have been described in detail elsewhere.[6]

During cooling the stopcocks Q and R were adjusted to direct the gas flow through the desiccant container, and hydrogen chloride filled the gas train. The stopcock at H was opened periodically to fill the cell with hydrogen chloride. After the temperature reached −85 °C, stopcock H remained open until the desired amount of liquid had accumulated. During condensation an external magnetic stirrer was turned on and the magnet attached to the exterior of the column removed to allow the stirrer bar to drop into the specimen. Stirring continued throughout the rest of the condensation and afterward until the solution appeared to be completely uniform. The total stirring time for about 13 cm^3 of solution ranged from 15 to 30 min for the most concentrated solutions. The sinker was lowered into the solution and positioned by means of the reel. When the temperature had stabilized at the chosen set point, the solution volume was read and density measurement begun. Four readings each were taken of the top and bottom pointers of the helix to determine its length. Then the next temperature set point was chosen. When the new temperature was established, the reel was adjusted to reposition the sinker at the appropriate distance from the meniscus. In measurements of the pure liquid, the readings were taken at 5 °C intervals descending from −90 to −110 °C and then ascending from −107.5 to −87.5 °C. There is no discernible difference between data taken early in the run and those taken later or between those taken while the temperature was decreasing stepwise and those taken while it was increasing. For solutions, the usual order for the temperatures was from −110 to −90 °C at intervals of 5 °C. As was the case with the measurements of the pure solvent, the observed density of a given solution did not depend on the direction from which the temperature was approached and, once the set point was established, was constant over time.

In some cases, after this sequence, additional hydrogen chloride was condensed to make a more dilute solution for measurement. In these cases the stirring was accomplished by movement of the sinker in the region near the boundary between the newly condensed pure hydrogen chloride and the denser solution. The stirrer bar alone was not effective in making the larger solution volumes up to 25 cm^3 uniform but did provide enough energy to move the sinker. When the solution was uniform and at the desired temperature, the measurement sequence was repeated again.

When the measurements were completed, the cryogen flow was stopped. The vent J was opened to the scrubber. The stirrer was turned on to aid the nucleation of bubbles, and the hydrogen chloride was evaporated to the scrubber. When evaporation appeared to be complete, usually at about −60 °C, the cell was removed from the cold bath. The stopcocks Q and R were adjusted to remove the desiccant container from the gas flow path, the gas train and cell were flushed with nitrogen gas before the apparatus was disconnected from the gas train under nitrogen pressure, and the gas train was sealed at M.

2.2. Calculation of Densities. According to Archimedes' principle, the liquid density ρ_l can be calculated from $\rho_l = (w_f - w_l)/V_s$, in which w_f is the combined weight of the sinker and wire in vacuum, w_l is the combined weight of the wire and sinker immersed in the liquid, and V_s is the volume displaced by the

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TABLE 1: Representative Values of Parameters Used in Density Calculations

V_s	0.39 cm³
k	22 cm/g
x	7 cm
c	4 cm
w_f	0.6 g
z	9 cm
ρ_l	1.25 g/cm³
ρ_w	1 g/cm³
a	0.0016 g/cm³
m	0.6 g
θ_l	10°
θ_w	43°
γ_l	25 dyn/cm
γ_w	72 dyn/cm
r	0.0025 cm

sinker. Each of these quantities was calculated as described below. Representative values of the parameters used in these calculations are given in Table 1.

The electronic balance (Mettler AT261, Mettler Instruments Corp., Hightstown, NJ) was calibrated with steel weights of density 8.000 g/cm³, so w_f was calculated from the balance display m according to $w_f = aV_s + m(1 - a/8.000)$, in which a is the density of the argon atmosphere of the glovebox during the weighing. This correction was applied to the fused quartz sinker. A vacuum correction for the wire would have been on the order of the resolution of the balance.

The measured spring extension and calibration constants were used to calculate the submerged weight w_l from $w_l = (x - c)/k$, in which x is the measured spring extension, and c and k are the intercept and slope of the spring equation, respectively. The nominal sensitivity of a spring was 22 cm/g. Each spring was calibrated individually by measuring its extension under a series of 12 calibration weights of stainless steel. Owing to the match between the density of the spring calibration weights and the density of the calibration weights in the electronic balance, the calibration weight reported by the balance did not require correction for buoyancy. Also, no correction was made for the buoyancy of air on the weights during the actual spring calibration because the magnitude of the effect was much smaller than the sensitivities of the spring and cathetometer. A least-squares line was fit to the calibration data. The springs showed good linearity over the load range used. Details of the calibrations have been presented elsewhere.[6]

The downward force indicated by the spring extension includes the action of the surface tension of the liquid on the wire. If the liquid wets the wire, its surface tension will exert a downward force on the wire. As a result, the submerged sinker will appear to be heavier than it actually is, and the calculated densities will be systematically too low. Thus, the weight of the wire and the submerged sinker is $w_l = (x - c)/k - Q_l$, in which x is the measured spring extension, c and k are the intercept and slope of the spring equation, respectively, and Q_l is the force on the wire due to surface tension of the solution. A vertical force balance shows that $Q_l = (2\pi r \gamma_l \cos\theta_l)/g$, in which r is the radius of the suspending wire, γ_l is the surface tension of the liquid, θ_l is the contact angle of the liquid with tantalum, and g is the acceleration of gravity.[13] The surface tension data of Steele *et al.*[14] for pure liquid hydrogen chloride in its normal liquid range were used in all calculations. No contact angle for liquid hydrogen chloride on any material is available from the literature. Stepanov *et al.*[15] have reported contact angles on tantalum ranging from 0° to 19° for organic liquids with surface tensions comparable to that of HCl. The value $\theta_l = 10°$ was adopted for this correction.

The fused quartz spring becomes more elastic as its temperature decreases.[16] If the spring were at a lower temperature during the density measurements than during calibration, the calculated densities would be lower than the actual densities, and the addition of another correction term to w_l would be necessary. However, no lengthening of the spring could be detected upon cooling the apparatus from room temperature to -105 °C and holding at this temperature for 6 h.

The sinker volume V_s was determined using the direct Archimedean technique from $V_s = [w_f - ((z - c)/k - Q_w)]/\rho_w$, in which z is the spring extension measured during immersion of the sinker in water, Q_w is the force due to the surface tension of water, and ρ_w is the density of water at the temperature of the measurement. Water wets tantalum, so ignoring the surface tension effect will cause the calculated sinker volume to be too small and, consequently, the calculated solution densities too large. The sinker volume was corrected using surface tension data.[17] The contact angle value $\theta = 43°$ for water on tantalum was taken from Stepanov *et al.*[15,18] For calculation of density for the low-temperature solutions, V_s was corrected for the contraction of the sinker upon cooling using an average of literature values, $\Delta L/L = -0.000\,031$, for the linear thermal expansion of fused silicon dioxide from room temperature to the liquid range of hydrogen chloride.[19] The volume of fused quartz varies little from -85 to -110 °C, so the same correction was used for the entire temperature range.

To include all of these considerations, the reported liquid densities were calculated from the formula

$$\rho_l = \frac{w_f - ((x - c)/k - Q_l)}{V_s} \tag{1}$$

The method was used to measure the density of reagent-grade benzene at an ambient temperature of 19.10 °C. Estimating the contact angle of benzene on tantalum to be 10° and using a benzene surface tension value calculated by extrapolating literature data[20] to the temperature of interest, this investigation found the density of benzene to be 0.8798 g/cm³. This result is well within experimental error of 0.8801 g/cm³, the value extrapolated to 19.10 °C from room-temperature densities of commercially available solvent as received.[20]

2.3. Error Analysis. Uncertainty in each of the terms in eq 1 contributes to error in the calculated value of ρ_l. The statistical errors are due to the calculation of w_l; most of the systematic errors enter through the sinker properties. Errors in temperature and concentration also contribute to uncertainty in the functional description of the density data. If all errors are assumed to be mutually independent and are summed in a root-mean-square fashion, the total statistical error due to the factors considered above is 0.0005 g/cm³. The total systematic error is 0.0006 g/cm³. In the case of the pure liquid the statistical error is slightly lower because the concentration is known absolutely. The error analysis and limitations of this density-measurement technique have been documented elsewhere.[6]

The fitted form of the density $\rho_o = A + Bt$ was used in the calculation of molar volume and thermal expansion coefficient of the pure liquid as a function of temperature. Error in these quantities was estimated in terms of the standard errors of the fit parameters. Contributions of the parameters were summed in root-mean-squares fashion.

3. Results

The density of pure liquid hydrogen chloride determined in this work as a function as temperature is shown in Figure 3.
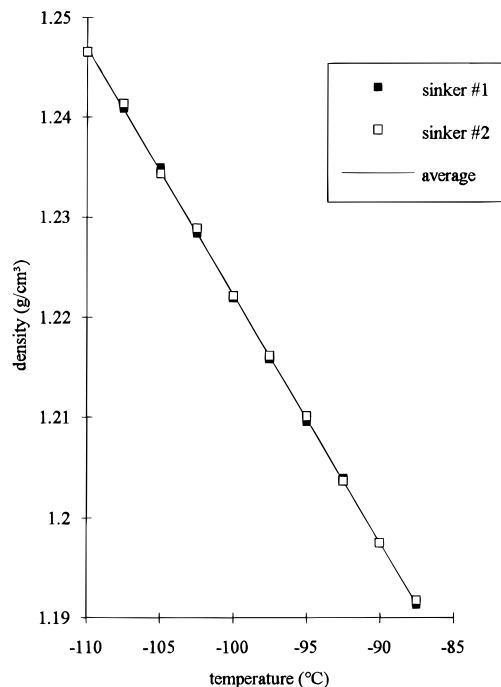
Figure 3. Density of liquid hydrogen chloride.

TABLE 2: Density, Molar Volume, and Thermal Expansion Coefficient of Pure HCl Derived from Density Measurements Made in the Present Investigation

t (°C)	ρ_o (g/cm^3)	V_1° (cm^3/mol)	α_1 (1/K)
−87.5	1.1915	30.60	0.002 069
−90.0	1.1975	30.45	0.002 059
−92.5	1.2038	30.29	0.002 048
−95.0	1.2098	30.14	0.002 038
−97.5	1.2160	29.98	0.002 028
−100.0	1.2220	29.83	0.002 017
−102.5	1.2286	29.68	0.002 007
−105.0	1.2347	29.53	0.001 997
−107.5	1.2412	29.39	0.001 987
−110.0	1.2465	29.24	0.001 977

The two symbols on the graph indicate the use of two different sinkers. The two sets of measurements agree within the calculated experimental error; the values used in all other calculations are the averages of values from these two measurements, listed in Table 2. The densities are described by

$$\rho_o = -0.002465t + 0.9757 \text{ g/cm}^3 \qquad (2)$$

in which t is temperature in °C and $R^2 = 0.9999$ with no indication of curvature.

Figures 4 −7 show solution density isotherms of the four salts at the five temperatures studied. In every case the density versus concentration isotherm shows $\partial\rho/\partial c > 0$ and $\partial^2\rho/\partial c^2 < 0$, both of which tend to increase in magnitude with increasing temperature for a given compound. The curves drawn through the points were calculated using a least-squares fit of the densities to the equation

$$\rho = A + Bc + Ec^{3/2} \qquad (3)$$

Table 3 shows the parameters of the curve fits. In each case, the goodness of the curve's fit to the data is consistent with the calculated statistical error in density discussed in the previous section. The individual data points have been tabulated elsewhere.[6]

If an equation comprising a constant plus a term linear in concentration represents the density data, then the addition of
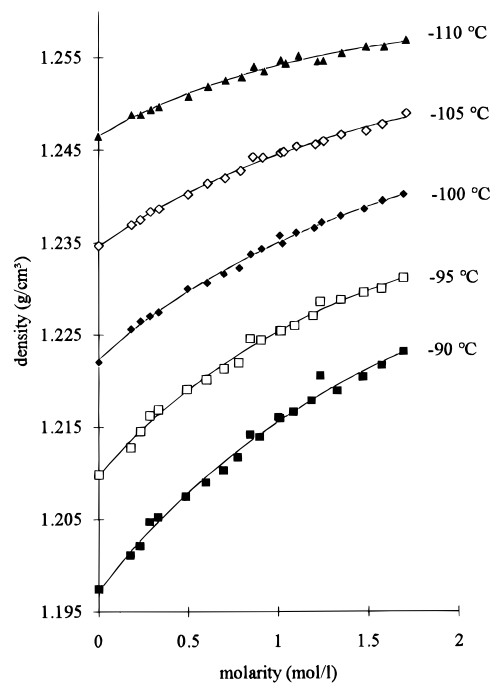

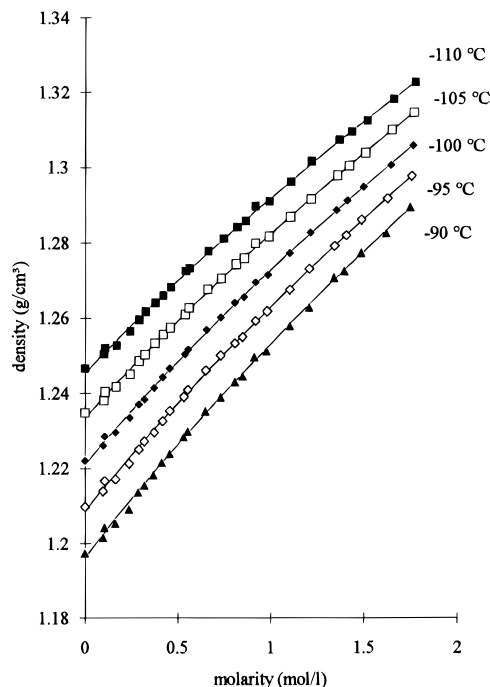**Figure 4.** Density of solutions of Me$_4$NCl in HCl.

Figure 5. Density of solutions of Me$_4$NBr in HCl.

a term proportional to $c^{3/2}$ gives the most appropriate description of each data set. This behavior conforms to Root's equation.[21]

For the sake of comparison, Figure 8 displays isotherms at −90 °C for all four compounds. At −90 °C the coefficient of the linear term becomes more positive in the order Me$_4$NCl, Me$_4$NBr, Me$_4$NI, Me$_3$SI.

4. Discussion

Analysis and interpretation of the binary solution data in terms of solute partial molar volume are reported elsewhere.[22] Also included is a critical examination of reports of molar volumes of a few nonelectrolytes that have been measured in hydrogen chloride near the normal liquid range. The present section addresses the behavior of the one-component system.
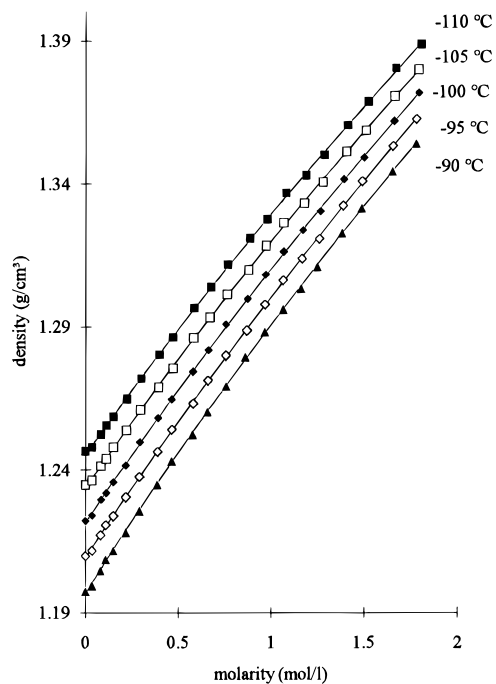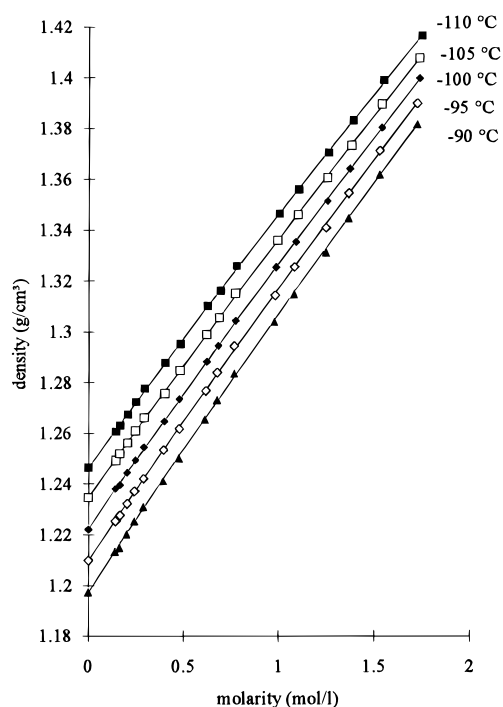
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Figure 6. Density of solutions of Me$_4$NI in HCl.

TABLE 3: Parameters for Fit of Density Data to $\rho = A + Bc + Ec^{3/2}$ ^{a}

	A (g/cm^3)	B (g L/cm^3 mol))	E (g L$^{3/2}$ (cm^3 mol$^{3/2}$))	R^2
Me$_4$NCl, t_1	1.2465	0.012 979	0.005 392 5	0.9870
Me$_4$NCl, t_2	1.2346	0.015 598	0.005 720 0	0.9953
Me$_4$NCl, t_3	1.2223	0.019 682	0.007 050 0	0.9964
Me$_4$NCl, t_4	1.2097	0.025 422	0.009 841 4	0.9934
Me$_4$NCl, t_5	1.1972	0.028 553	0.010 210 0	0.9911
Me$_4$NBr, t_1	1.2452	0.055 772	0.009 180 0	0.9991
Me$_4$NBr, t_2	1.2334	0.058 369	0.009 450 0	0.9994
Me$_4$NBr, t_3	1.2208	0.063 225	0.011 380	0.9994
Me$_4$NBr, t_4	1.2085	0.065 086	0.010 791	0.9992
Me$_4$NBr, t_5	1.1962	0.068 19	0.011 320	0.9992
Me$_4$NI, t_1	1.2450	0.097 355	0.013 169	0.9998
Me$_4$NI, t_2	1.2334	0.100 13	0.013 830	0.9998
Me$_4$NI, t_3	1.2211	0.103 63	0.014 700	0.9999
Me$_4$NI, t_4	1.2090	0.105 52	0.014 360	0.9999
Me$_4$NI, t_5	1.1964	0.110 26	0.016 190	0.9999
Me$_3$SI, t_1	1.2461	0.108 23	0.008 221 9	0.9999
Me$_3$SI, t_2	1.2345	0.109 50	0.007 550 0	0.9999
Me$_3$SI, t_3	1.2222	0.112 42	0.007 980 0	0.9999
Me$_3$SI, t_4	1.2095	0.117 00	0.009 509 8	0.9999
Me$_3$SI, t_5	1.1972	0.011 951	0.009 770 0	0.9998

^{a} $t_1 = -100$ °C; $t_2 = -105$ °C; $t_3 = -100$ °C; $t_4 = -95$ °C; $t_5 = -90$ °C.

Figure 7. Density of solutions of Me$_3$SI in HCl.
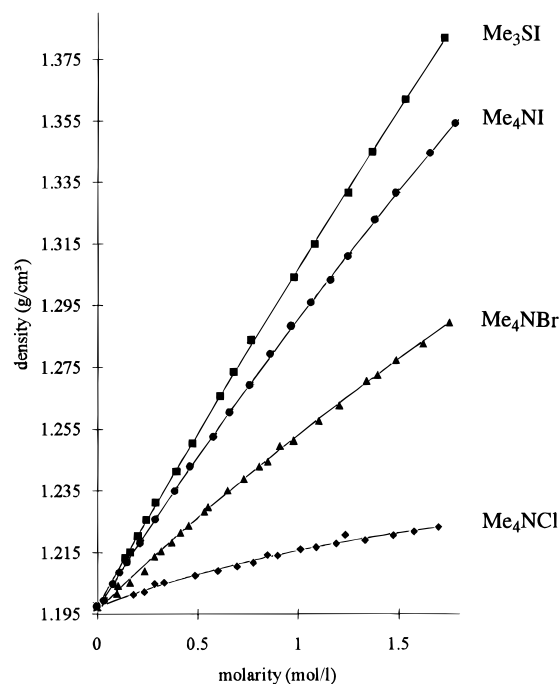
Figure 8. Concentration dependence of density isotherms at -90 °C for all solutes.

Densities for hydrogen chloride in the normal liquid range were first reported by McIntosh *et al.* in 1906.[23] A capillary dilatometer was used to measure density at seven temperatures below the boiling point, which was determined to be -82.9 °C (190.3 K). The mass of liquid HCl was determined either by absorption by aqueous potassium hydrate or by direct weighing of the dilatometer, the two methods agreeing to the third decimal place. In 1914 Baume and Perrot reported a line fit to measurements taken "at diverse temperatures" between the "approximately" determined melting and boiling points, 161.6 K (-111.6 °C) and 189.9 K (-83.3 °C).[24] The mass of liquid in the dilatometer was determined by the change in pressure of hydrogen chloride in a volumetric flask thermostated at 0 °C. The maximum error in the technique is reported to be 0.0014

g/cm^3. In 1937 Kanda measured densities in support of a study of dielectric constants of liquefied gases.[25] The observed liquid range was 159 K (-114 °C) to 188 K (-85 °C). The densities are reported at intervals of roughly 3 deg from 160 K (-113 °C) to 183 K (-90 °C). The values are tabulated to three decimal places. The author did not include an estimate of accuracy or procedural details that would allow its assessment. In 1977 Calado *et al.* presented four molar density values in the normal liquid range designated only as unpublished data by Prichard and Staveley.[26] As part of a study of liquid hydrogen chloride and its binary liquid mixtures with other condensed gases over the normal liquid range and at elevated temperatures, Nunes da Ponte *et al.* reported the molar volume of liquid hydrogen chloride in 1981.[27] The pycnometer was
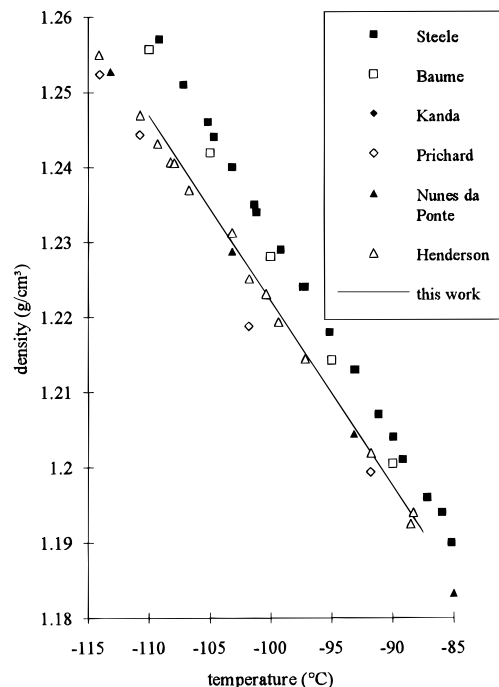
Figure 9. Reported densities of pure liquid hydrogen chloride.

calibrated with liquid HCl at the triple-point temperature of N_2O and the technique checked by determination of the volume of ethene. The reported imprecision of the volume measurements is 0.1%, which would render an uncertainty of about 0.0012 g/cm^3 in the density. In 1986 Henderson *et al.* reported molar volumes of liquid HCl determined pycnometrically from 159 to 236 K. No estimate of error is included.

   Figure 9 shows data reported in the literature along with those measured in the present investigation. There is an obvious discrepancy between the data taken in the first half of this century and those taken more recently. The two groups also differ in the liquid temperature range reported with the data. The melting and boiling temperatures observed in more recent studies are close to the current standard values of 158.96 and 188.12 K, respectively.[28] Both McIntosh *et al.* and Baume *et al.* report phase transition temperatures that are several degrees higher than the standard values. This disparity was pointed out by Giauque *et al.*[29] and may indicate an impure specimen or a systematic error in temperature measurement. Shifting the abscissa values for these data a few degrees negative brings them into much better agreement with the more recent measurements. Kanda's work is exceptional in that his melting and boiling points agree with the standard values, yet his density values lie in the cluster with the data of McIntosh *et al.* and Baume *et al.* The figure shows that the results of the present investigation are within the range of values reported since 1970.

   The molar volume of pure liquid hydrogen chloride can be calculated directly from the molecular weight and the density: $V_1° = M_l/\rho° = M_l/(A + Bt)$. The molar volumes thus calculated from the densities measured in this work with $M_l = 36.46$ [30] are reported in Table 2. The line $V_1° = 35.89 + 0.0605t$ cm^3/mol fits the data in Table 2 with $R^2 = 0.9998$. The data show very slight systematic upward curvature with respect to temperature, consistent with neglect of the quadratic term in the Taylor series expansion of $a/(1 + bt)$. The largest residuals have magnitude around 0.009 cm^3/mol. The error in $V_1°$ is the root-mean-square sum of $M_l/\rho_o^2\delta A$ and $M_l/\rho_o^2\delta B$, with δA and δB equal to the standard errors of A and B, respectively. The net error is about $\delta V_1° = 0.037$ cm^3/mol. Error associated with the temperature control is negligible compared to this.

The volume of the hydrogen chloride molecule V_{HCl} can be calculated using the geometry of intersecting spheres, as shown by Bondi,[31] his van der Waals radii of chlorine (1.75 Å) and hydrogen (1.20 Å), and the H−Cl bond length reported by Jones and Gordy (1.2746 Å).[32] The result is 15.013 cm^3/mol. On the basis of this V_{HCl} and the molar volume measured in this work, the void space in liquid hydrogen chloride is about 50%. This is within a few percent of the void space calculated for a simple cubic lattice of hydrogen chloride molecules separated by the effective spherical radius and is much smaller than the value of 63% found for the open structure of water by the same method. This result is consistent with observations of the Trouton constant,[29] dielectric constant,[33] and spectra,[34] all of which indicate that liquid hydrogen chloride does not appreciably associate.[30]

   The isobaric coefficient of thermal expansion is defined to be

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_P = -\frac{1}{\rho_o}\frac{\partial \rho_o}{\partial T}\bigg|_P \tag{4}$$

If eq 2 for $\rho°$ is substituted into eq 4, the coefficient for pure liquid hydrogen chloride is

$$\alpha_1 = \frac{1}{395.7 - t}\,K^{-1} \tag{5}$$

The values in Table 2 calculated from this equation are about 1 order of magnitude larger than the values for water at room temperature. The line $\alpha_1 = 0.002427 + 4.09 \times 10^{-6}t$ K^{-1} fits the values in Table 2 with $R^2 = 0.9998$. The residual curvature is upward. For the measurements in this work, the root-mean-square sum of the errors B/$\rho_o^2\delta A$ and A/$\rho_o^2\delta B$ is $\delta\alpha_1 = 7 \times 10^{-6}$ K^{-1}. The temperature uncertainty causes a negligible error in α_1.

   Strictly speaking, the quantity thus calculated is not exactly equal to α_1 because the measurements were taken under the saturation vapor pressure, which is not constant over temperature. However, the increment in vapor pressure attendant upon a change in temperature of 1 K is on the order of only 20 mmHg. This change does not result in a significant error in α_1.

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