Table IV. Comparison of Pure Component Vapor Pressures with Literature Values

	vapor pressure, kPa			
	ethanol		aniline	
T, K	this work	lit.	this work	lit.
313.15	17.935	17.895	0.248	0.246
350.81	98.923	98.764	2.16	2.11
386.67	350.3	351.4	10.5	10.4

for B_{11} (*1*).

Effect of Equation of State. Data reduction was performed with three different equations of state (ideal gas, unmodified Redlich–Kwong (*5*), and the truncated virial equation) to demonstrate the effect of the equation of state on the calculated properties. Three different correlations (Pitzer–Curl (*3*), O'Connell–Prausnitz (*4*), and Tsonopoulos) were used to predict the B_{ii} and B_{ij} values. (Toluene was used as the homomorph for aniline in the O'Connell–Prausnitz correlation.) Table III plus Table II show how the calculated γ_1, γ_2, and G^E values varied with the equation of state used.

Despite being at relatively low pressures, and despite the fact that the fugacity coefficients appear as a ratio in the equation for γ_i, the departures from the ideal gas model are sufficient to have a nonnegligible effect on the γ_i and G^E values calculated. Presumably, the virial equation is more accurate than the unmodified Redlich–Kwong for these data, and the O'Connell–Prausnitz and Tsonopoulos correlations should give better B_{ii} and B_{ij} values than the Pitzer–Curl equation. However, there is no easy way of identifying that set of results which is most accurate. All sets are consistent with the Gibbs–Duhem equation and it is not likely that the Gibbs–Helmholtz test (consistency between G^E and H^E values) would be sensitive enough to discriminate between the various sets.

Vapor Pressure Checks. The two most important points measured on any VLE device are the pure component vapor pressures. If good values of those vapor pressures have been established by previous workers, comparisons to those values provide information on the purities and the stabilities of the chemicals used and on the accuracies of the temperature and pressure measurements.

The comparisons for the two components are shown in Table IV. The literature values given there were obtained from fits of selected values. The selection process involved plotting all known literature values in residual (deviation from a simple fitting equation) form to emphasize the scatter and identify obviously incorrect points, and then making repeated fits with a reliable equation to obtain smaller and smaller root-mean-squared deviation values as large deviation points were eliminated. The final ethanol fits utilized original experimental data points from 29 literature documents (the data from all the others were rejected) and two different four-term equations were used to fit the following two ranges: 233–411 K and 343–516 K.

Only nine literature documents reporting aniline vapor pressure data were available, and of these, five were used to provide the literature values in Table IV. The fit of the literature data was made with a four-term equation over the range 267.3–393.2 K.

Chemical Stabilities. Ethanol is very stable over the temperature range covered and was still perfectly clear at the end of the experiment. Aniline, as normally produced, has impurities that will cause it to turn reddish brown when exposed to air or light. However, the aniline removed from the cells after the last isotherm was clear, indicating that no significant reactions had occurred.

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Densities of $AlCl_3$-Rich, Molten $AlCl_3$–LiCl Mixtures

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Densities of seven aluminum chloride–lithium chloride mixtures containing 50–75 mol % aluminum chloride were measured by a dilatometric procedure from 148 to 270 °C. An empirical equation was obtained which expresses density as a function of composition and temperature with an overall root-mean-square error of 0.06%.

As part of an investigation aimed at employing $AlCl_3$-based electrolytes in high-energy density batteries, accurate densities of $AlCl_3$-rich binary $AlCl_3$–LiCl mixtures were required in order to compute equivalent conductivities, kinematic viscosities, and molar volumes. We required densities at more composition values and over more extended temperature ranges than were available from the chemical literature (*7*, *9*).

Experimental Section

All operations associated with sample preparation were performed in a nitrogen-filled glovebox (Vacuum/Atmospheres Co., Model HE-43-8 Dri Lab) having a moisture content of less than 2 ppm. The samples were made by mixing accurately weighed amounts of purified, solid lithium tetrachloroaluminate with purified, solid aluminum chloride. The $AlCl_3$ was purified by the method of Giner and Holleck (*5*), which involves digesting a mixture of $AlCl_3$–NaCl–KCl (molar ratio 9.8:1.0:1.5) with Mg turnings at ca. 130 °C and then evaporating the $AlCl_3$ at ca. 215 °C. The lithium tetrachloroaluminate was prepared by fusing at approximately 170 °C an excess of Mallinckrodt Analytical Reagent Grade LiCl, which had been vacuum-dried at 120 °C, with Fluka *puriss* $AlCl_3$ (Fe content < 0.008%). The tetra-

Table I. Sample Parameters

tube	mass of mixture in tube, g[a]	compn mole fraction $AlCl_3$[b]	total enclosed vol, cm^3 (25 °C)[c]
I	19.351	0.4925	12.43
II	16.115	0.5472	11.02
III	24.411	0.5999	16.09
IV	17.592	0.6529	11.82
V	19.414	0.6979	12.98
VI	18.905	0.7323	12.58
VII	15.984	0.7504	11.00

[a] Individual weighings are known to ±0.002 g; however, overall uncertainties in mass are estimated to be ±0.02 due to sample transfer losses and volatilization during dilatometer preparation (*2*). [b] Estimated uncertainty in mole fraction = ±0.001. [c] Estimated uncertainty in total enclosed volume = ±0.01 cm^3.

chloroaluminate melt was subsequently purified by the constant current electrolysis procedure which is used routinely in preparing sodium tetrachloroaluminate melts (*4*). Electrolysis was continued until a water-clear melt was produced which was free of any impurities which could be detected by cyclic voltammetry. The composition of this $AlCl_3$ melt which was saturated with LiCl was determined to be 49.25 mol % $AlCl_3$ by the coulometric procedure of Boxall et al. (*1*). The melt was then filtered, allowed to solidify, and ground into a powder.

The experimental apparatus and procedures were identical with those developed earlier in this laboratory for $AlCl_3$-NaCl density measurements (*2*), except as noted below. The dilatometers utilized precision bore capillaries (radius = 0.14 cm) having a single index mark on them. Better temperature control (±0.03 °C) was obtained by employing a Bayley Model 124 proportional temperature controller. In brief, the densities were measured in sealed Pyrex dilatometers whose volumes were calibrated with distilled H_2O in the conventional manner. A small arrow on the capillary stem was used as a reference mark with respect to which the liquid menisus levels were measured using a precision M-911 Gaertner cathetometer.

Sample masses and compositions and the total dilatometer volumes are given in Table I. The experimental temperatures and densities are given in Table II. The data have been corrected for air bouyancy, for thermal expansion of the glassware, and for meniscus effects as indicated in ref 6. The data in Table II were not all taken in the order listed; measurements were made with both ascending and descending temperatures.

Results

Measurements were made at values of mole fraction and temperature that lay within a polygon on the X, t plane described by the coordinates (X, t) = (0.49, 189), (0.75, 189), (0.75, 248), (0.65, 270), (0.60, 270), (0.49, 248). In addition, the density of the X = 0.49 sample was measured to 148 °C.

We assumed the densities of $AlCl_3$-LiCl mixtures could be represented by the equation (*2*)

$$\sum_{i=0}^{2}(X_k - 0.5)^i \sum_{j=0}^{1} a_{ij}(t_k - 200)^j = D_k \qquad (1)$$

We chose to least-squares fit the data in such a way that uncertainties in mole fraction, temperature, and density all could be taken into account. This was done by minimizing the perpendicular distance (z_k) from the experimental point to the function surface in X, t, and D given by eq 1. The minimum distance fitting technique, where the usual sharp distinction between independent and dependent variables is not necessary, is described in detail elsewhere (*3*). The perpendicular, z, does not quite reach the surface itself but contacts a plane drawn through the projections parallel to the X, t, and D axes of the experimental point onto the surface. Obviously z can be either longer or shorter than the true perpendicular distance, depending upon which side of the surface the datum lies. The root mean square value of the quantity ($|z$ − true perpendicular$|$)/(true perpendicular) was 0.001.

Table II. Experimental Data

t, °C	D, g/cm^3	t, °C	D, g/cm^3	t, °C	D, g/cm^3
Sample I					
147.78	1.6397	183.14	1.6126	230.27	1.5770
147.83	1.6400	198.16	1.6012	239.65	1.5700
162.52	1.6284	206.11	1.5953	249.63	1.5628
168.76	1.6236	212.22	1.5905	257.16	1.5571
174.88	1.6189	221.77	1.5834		
Sample II					
195.90	1.5967	221.09	1.5763	240.49	1.5609
205.01	1.5889	231.01	1.5685	247.96	1.5550
213.59	1.5824				
Sample III					
188.79	1.5903	213.59	1.5688	233.90	1.5518
191.90	1.5873	214.71	1.5664	240.02	1.5466
195.90	1.5840	218.78	1.5645	240.49	1.5462
197.97	1.5824	221.09	1.5624	245.26	1.5423
198.29	1.5821	222.38	1.5614	247.96	1.5399
205.01	1.5762	223.19	1.5607	250.70	1.5378
206.14	1.5753	229.01	1.5559	260.27	1.5301
208.22	1.5733	231.01	1.5540	270.40	1.5226
Sample IV					
188.79	1.5690	214.71	1.5454	240.02	1.5225
191.90	1.5662	218.78	1.5416	245.26	1.5179
197.72	1.5609	222.38	1.5386	250.70	1.5131
198.29	1.5601	223.19	1.5377	260.27	1.5048
206.14	1.5533	229.01	1.5324	270.40	1.4962
208.22	1.5512	233.90	1.5280		
Sample V					
188.79	1.5521	208.22	1.5326	229.01	1.5120
191.90	1.5490	214.71	1.5260	233.90	1.5072
197.72	1.5431	218.78	1.5222	240.02	1.5011
198.29	1.5425	222.38	1.5186	245.26	1.4960
206.14	1.5347	223.19	1.5176		
Sample VI					
188.79	1.5405	206.14	1.5220	218.79	1.5084
191.90	1.5371	208.22	1.5195	222.38	1.5047
197.72	1.5307	214.71	1.5127	223.19	1.5037
198.29	1.5303				
Sample VII					
195.90	1.5202	221.09	1.4922	240.49	1.4709
205.01	1.5101	231.01	1.4813	247.96	1.4626
213.59	1.5005				

We solved for values of a_{ij} which minimized the sum $\sum_{k=1}^{N} z_k^2$ where

$$z_k = \left[\left(\frac{\delta X}{\Delta X_k}\right)^2 + \left(\frac{\delta t}{\Delta t_k}\right)^2 + \left(\frac{\delta D}{\Delta D_k}\right)^2\right]^{-1/2} \qquad (2)$$

Equation 2 was derived elsewhere (*3*). In eq 2, the quantities ΔX_k, Δt_k, and ΔD_k are the differences between the experimentally measured value of each variable and the value of the variable calculated from eq 1 and the experimental values of the remaining variables. Equation 1 was solved directly from X_k, t_k, and D_k.

The uncertainties δX, δt, and δD were estimated to be 0.001, 0.05 °C, and 0.001 g/cm^3, respectively. The uncertainty in mole fraction of each sample, δX, was calculated by propagating the weighing errors given in Table I and the uncertainty in composition of LiCl-saturated melt into X. The most sensitive parameter in this calculation was the latter uncertainty, which in turn was found to be ±0.001 by a least-squares fit of the coulometric titration data. The uncertainty in temperature, δt, was determined by actual measurements of temperature constancy with time and location in the region of the bath

Table III. Empirical Polynomial for Densities of $AlCl_3$-LiCl Melts

$$D = a_{00} + a_{01}(t - 200) + a_{10}(X - 0.5) + a_{11}(X - 0.5)(t - 200) + a_{20}(X - 0.5)^2 + a_{21}(X - 0.5)^2(t - 200)$$

where $a_{00} = 1.599\,737$, $a_{01} = -7.4951 \times 10^{-4}$, $a_{10} = -0.131\,58$, $a_{11} = -1.584 \times 10^{-4}$, $a_{20} = -0.795\,77$, and $a_{21} = -5.933 \times 10^{-3}$ and root-mean-square error in $D = 0.06\%$, root-mean-square error in $t = 0.004\%$, and root-mean-square error in $X = 0.2\%$

occupied by the dilatometers. The remaining uncertainty, δD, also was calculated by propagating into D the weighing errors, meniscus location uncertainty, and dilatometer calibration errors. Here, the weighing errors were the most significant.

It was not necessary to make corrections for volatilization of the samples into the vapor space within the dilatometers, for sample masses were chosen such that the capillaries were very nearly filled at the highest temperatures. The vapor pressures of $AlCl_3$–LiCl mixtures have not been reported but reasonably cannot exceed the saturated vapor pressure of $AlCl_3$ itself. The largest volatilization correction, assuming this extreme condition (*8*), would have been only $0.1\delta X$.

The least-squares fit was iterative. Iterations were continued until

$$\frac{2|\sigma - \sigma_{\text{previous iteration}}|}{\sigma + \sigma_{\text{previous iteration}}} < 10^{-7} \tag{3}$$

where σ, the standard deviation, was calculated from

$$\sigma = \left(\frac{1}{N}\sum_{k=1}^{N} z_k^{\,2}\right)^{1/2}$$

The values of a_{ij} when the criterion of eq 3 was first satisfied are given in Table III.

Safety

Appropriate precautions should be taken for the containment of liquids above their normal boiling points in glass vessels.

Glossary

a_{ij}	empirical coefficients
D	liquid density, g/cm^3
i	exponent on mole fraction
j	exponent on temperature
k	index for individual experimental points
N	total number of experimental points
t	temperature, °C
X	mole fraction of $AlCl_3$
z	perpendicular distance to plane along X, t, D surface; function to be treated by least-squares fitting
δD	estimated uncertainty in density, 0.001 g/cm^3
δt	estimated uncertainty in temperature, 0.05 °C
δX	estimated uncertainty in mole fraction, 0.001
$\Delta\xi$	the difference between the experimentally measured value of the quantity ξ and the value of ξ calculated from eq 1 and the remaining variables ($\xi = D$, t, or X)
σ	standard deviation

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Viscosity of Nonpolar Gases (Quaternary Mixtures)

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Viscosities of quaternary mixtures of N_2–O_2–CO_2–N_2O have been measured in the temperature range 40–140 °C by the capillary flow method. The experimental values of viscosity are compared with theoretical values obtained from the kinetic theory in conjunction with the extended law of corresponding states proposed by Kestin, Ro, and Wakeham. The comparison shows the existence of very good agreement.

A very precise extended principle of corresponding states has been formulated by Kestin, Ro, and Wakeham (*3*, *5–7*). It has made possible the correlation of low-density equilibrium and transport properties of the monatomic gases and their multicomponent mixture over the entire experimental temperature range available, with an accuracy comparable to the best measurements.

The Chapman–Enskog theory and its extension to multicomponent mixtures (*4*) predicts that the viscosity of an n-component mixture, using standard symbols, may be written in the form

$$\mu = -\frac{\begin{vmatrix} H_{11} \ldots\ldots H_{1n} & X_1 \\ H_{n1} \ldots\ldots H_{nn} & X_n \\ X_1 \ldots\ldots X_n & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} \ldots\ldots H_{1n} \\ H_{n1} \ldots\ldots H_{nn} \end{vmatrix}} \tag{1}$$

Here

$$H_{ii} = \frac{x_i^{\,2}}{\mu_i} + \sum_{\substack{k=1 \\ k \neq i}}^{n} \frac{2x_i x_k}{\mu_{ik}} \frac{M_i M_k}{(M_i + M_k)} \left(\frac{5}{3A_{ik}{}^*} + \frac{M_k}{M_i}\right)$$

and

$$H_{ij} = -\frac{2x_i x_j}{\mu_{ij}} \frac{M_i M_j}{(M_i + M_j)^2} \left(\frac{5}{3A_{ij}{}^*} - 1\right) \quad i \neq j$$

In this expression X_i and M_i represent the mole fraction and molecular weight of ith component, respectively. The interaction viscosity μ_{ij} is given by

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