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Technical Report No. 1

Viscosity, Density and Conductivity of $ImCl(HCl)_{1.3}$

by

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February 22, 1990

INTRODUCTION

1-ethyl-3-methylimidazolium hydrogen dichloride, ($ImHCl_2$), was originally synthesized in our laboratory (1). This material, an ambient temperature molten salt, is currently under investigation by Hughes Aircraft, El Segundo, California, under a related ONR Contract, as a fluid for a thermally regenerative electrochemical fuel cell device. Although we had discovered this material, and utilized it in a number of our studies as a source for the quantitative addition of proton to ambient temperature molten salts consisting of 1-ethyl-3-methylimidazolium chloride (ImCl) and aluminum chloride, we had not carried out any investigations of the physical properties of the material. Here we report on a determination of the density, viscosity and specific conductivity of 1-ethyl-3-methylimidazolium hydrogen dichloride, ($ImHCl_2$) over a limited temperature range.

EXPERIMENTAL

Sample Preparation

The synthesis of 1-ethyl-3-methylimidazolium hydrogen dichloride ($ImHCl_2$) was carried out as previously reported (1), and consisted of the reaction of 1-ethyl-3-methylimidazolium chloride (ImCl) with gaseous hydrogen chloride. The HCl gas used was semiconductor purity 99.995% min. (Matheson Gas Products). Before the HCl gas was introduced into a Shlenkware flask including ImCl, the gas was passed through glass wool to minimize metallic contamination from the pressure regulator and/or fittings. After the synthesis, the product, a clear liquid, was transferred into an argon-atmosphere dry box (Vacuum Atmospheres Co., model HE-553 box combined with model MO-40 DRI TRAIN), in which the oxygen and moisture concentration were estimated to be less than 5 ppm.

The chemical stoichiometry of the product was analyzed by acid-base titration of the proton content in $ImCl(HCl)_x$; distilled water was injected by syringe through a septum into a volumetric flask containing a weighed amount of the $ImCl(HCl)_x$ product to minimize loss of HCl. Titrations were carried out using standard solutions on a Model 636 Titroprocessor (Metrohm Ltd.). Results of the titration indicated x to be 1.33, and we estimate this to be valid to ±0.01. Thus, these experiments were all carried out on material containing HCl in excess of that expected for $ImHCl_2$. We have found that preparation of exactly stoichiometric (1.0:1.0 ImCl to HCl) material is quite difficult.

Density Measurements

Densities of $ImCl(HCl)_x$, x=1.33, at several temperatures were measured inside the dry box using pycnometers with (< 38 °C) and without (> 38 °C) a thermometer; pycnometer volumes were calibrated with degassed distilled water at several temperatures in the conventional manner.

Pycnometers were placed for more than one hour at each temperature in an aluminum block whose temperature was kept constant by a heater and temperature controller (Thermo Electric Model 400).

Sample temperatures below 38 °C were measured with a thermometer enclosed in the pycnometer to ±0.1 °C. At temperatures above 38 °C, the uncertainty of the sample temperature was estimated to be less than ±0.5 °C; the temperature was monitored by a thermometer in the aluminum block.

Viscosity measurements

Viscosities of $ImCl(HCl)_x$, x=1.33, were measured in the temperature range of 16 to 45 °C using a falling ball type viscometer (Gilmont Instruments). A glass ball (density = 2.53 $g{\cdot}cm^{-3}$) was used. The viscometer was calibrated with 60 wt% glycerol water mixture at 20 °C (2).

The $ImCl(HCl)_x$ sample was filled in the viscometer tube inside the drybox. The loaded viscometer was capped, sealed, and then transferred outside the drybox. The viscometer was placed vertically in a water bath which was kept at constant temperature (less than ±0.1 °C fluctuation). The temperature was measured by a standard thermometer with an accuracy of ±0.1 °C immersed in the bath.

The time of ball descent between two sets of fiducial lines was measured with a stopwatch. At least four runs were carried out at each temperature. The mean descent time, which had less than 1% standard deviation at each temperature, was used in the viscosity calculations.

Conductivity Measurements

A Yellow Springs Instrument Model 3403 conductivity cell was used and was held in a glass cell fitted with a threaded adapter (Ace Glass, Inc.). Conductivity measurements were made with a Yellow Springs Instruments Model 31 conductivity bridge which is accurate to 1%.

The conductivity cell was calibrated at 25 °C by using 0.1 N and 0.05 N aqueous KCl solutions (3).

The $ImCl(HCl)_x$, x=1.32, sample was loaded into the glass cell inside the drybox. The loaded cell was sealed with the Ace-Thred adapter and

Teflon tape; the cell was placed in the same water bath as for the viscosity measurements. Conductivity measurements were carried out in the temperature range 0 to 45 °C.

RESULTS

Density of $ImHCl_2$

Densities of $ImCl(HCl)_x$, x=1.33, at several temperatures are shown in Fig. 1. The experimental data was fitted by the least square method to a linear equation;

$$\rho = a + bT \quad (15\ °C < T < 45\ °C) \tag{1}$$

where a=1.1680 $g \cdot cm^{-3}$, b= -6.8944×10^{-4} $g\ cm^{-3}\ °C^{-1}$, and T is the temperature in °C. The equation with the fitted parameters reproduced the observed densities within a deviation of 0.0006 $g \cdot cm^{-3}$ (maximum difference 0.052%). The calculated value from eq. (1) is shown in Fig. 1 as solid line.

Viscosity of $ImHCl_2$

The temperature dependence of $ImCl(HCl)_{1.33}$ viscosity is shown in Fig. 2. The observed viscosities could be fitted by the least square method to a parabolic equation;

$$\eta = a + bT + cT^2 \quad (15\ °C < T < 45\ °C) \tag{2}$$

where a=13.477 cP, b=-0.28463 cP•°C^{-1}, c=2.2246 x 10^{-3} cP•°C^{-2}, where η is viscosity in cP. The equation with the fitted parameters reproduced the experimental data within a deviation of 0.063 cP (1.0% of maximum deviation). The solid curve in Fig. 2 indicates the calculated temperature dependence of the viscosity from eq. (2).

Specific conductivity of $ImHCl_2$

The specific conductivities of $ImCl(HCl)_{1.32}$ at several temperatures are shown in Fig. 3. These values could be fitted to a parabolic equation;

$$\kappa = a + bT + cT^2 \quad (0°C < T < 45 °C) \qquad (3)$$

where a=3.2473 x 10^{-2} mho cm^{-1}, b=8.5468 x 10^{-4} mho•cm^{-1}•°C^{-1}, c=3.3296 x 10^{-6} mho•cm^{-1}•°C^{-2}, and κ is the specific conductivity in mho•cm^{-1}. The calculated values from eq. (3) reproduced the observed data with a deviation of 0.0004 mho•cm^{-1} (0.75 % of the maximum difference). The solid curve in Fig. 3 shows the temperature dependence of the conductivity calculated from eq. (3).

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1) T.A. Zawodzinski, Jr. and R.A. Osteryoung, Inorg. Chem., 27, 4383 (1988).

2) "Handbook of Chemistry and Physics", 66th ed., CRC Press (1985).

3) R.A. Robinson and R.H. Stokes, "Electrolyte Solutions", 2nd ed., p. 466, Butterworths, London (1959).

Figure Captions

1. Plot of viscosity of $ImCl:HCl_{1.3}$ vs temperature.
2. Plot of density of $ImCl:HCl_{1.3}$ vs temperature.
3. Plot of specific conductivity of $ImCl:HCl_{1.3}$ vs temperature.

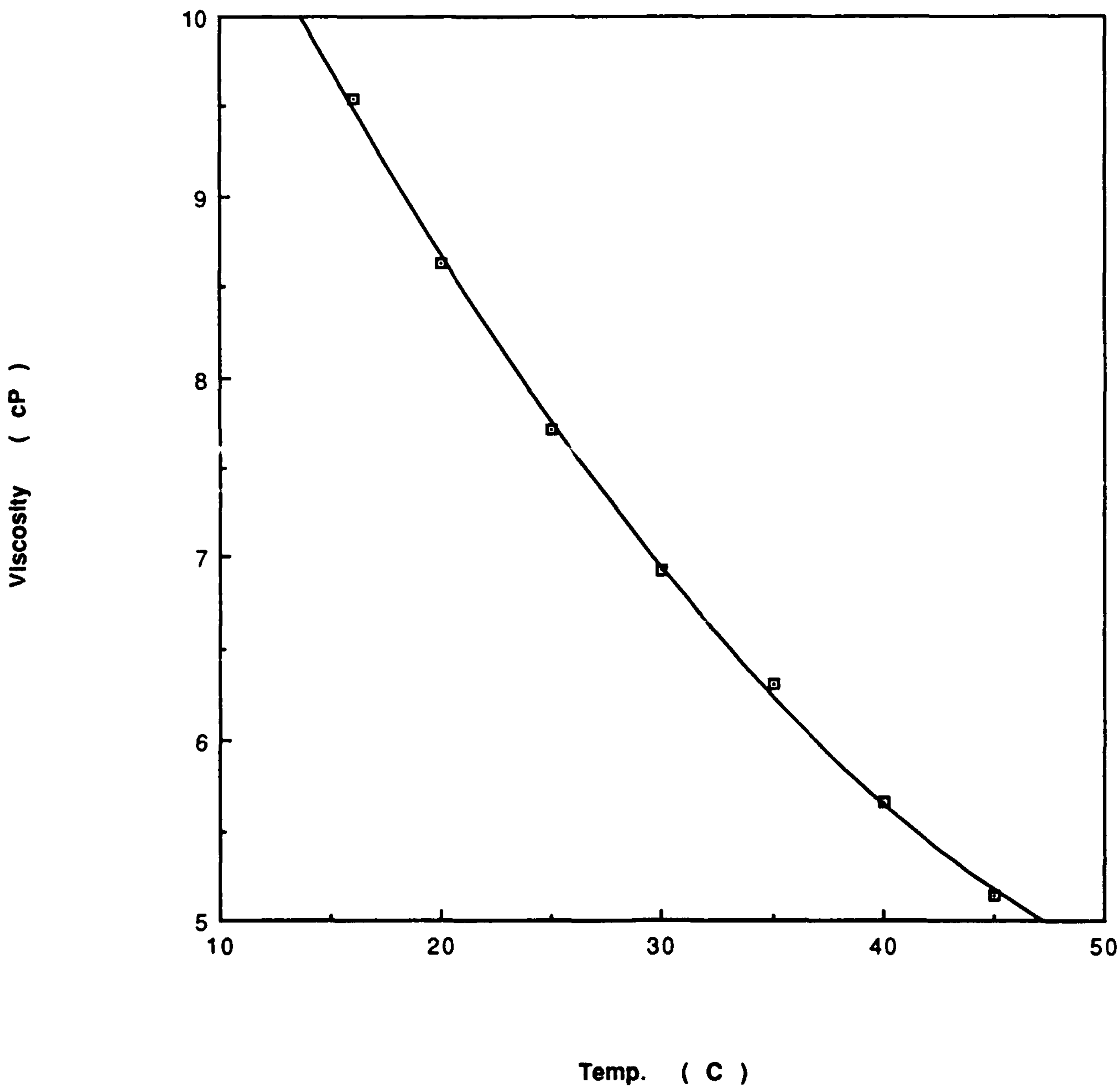


Figure 1

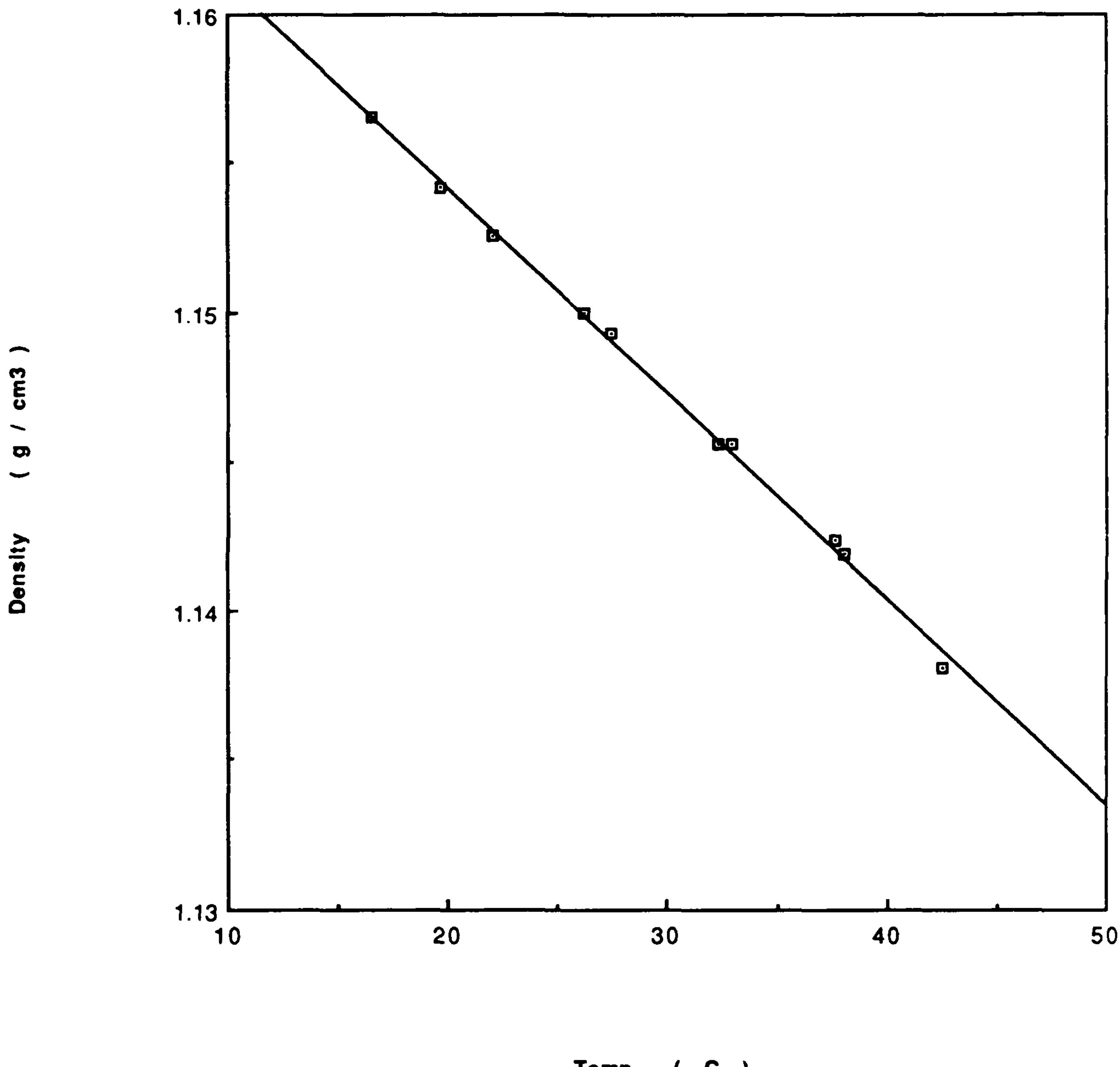
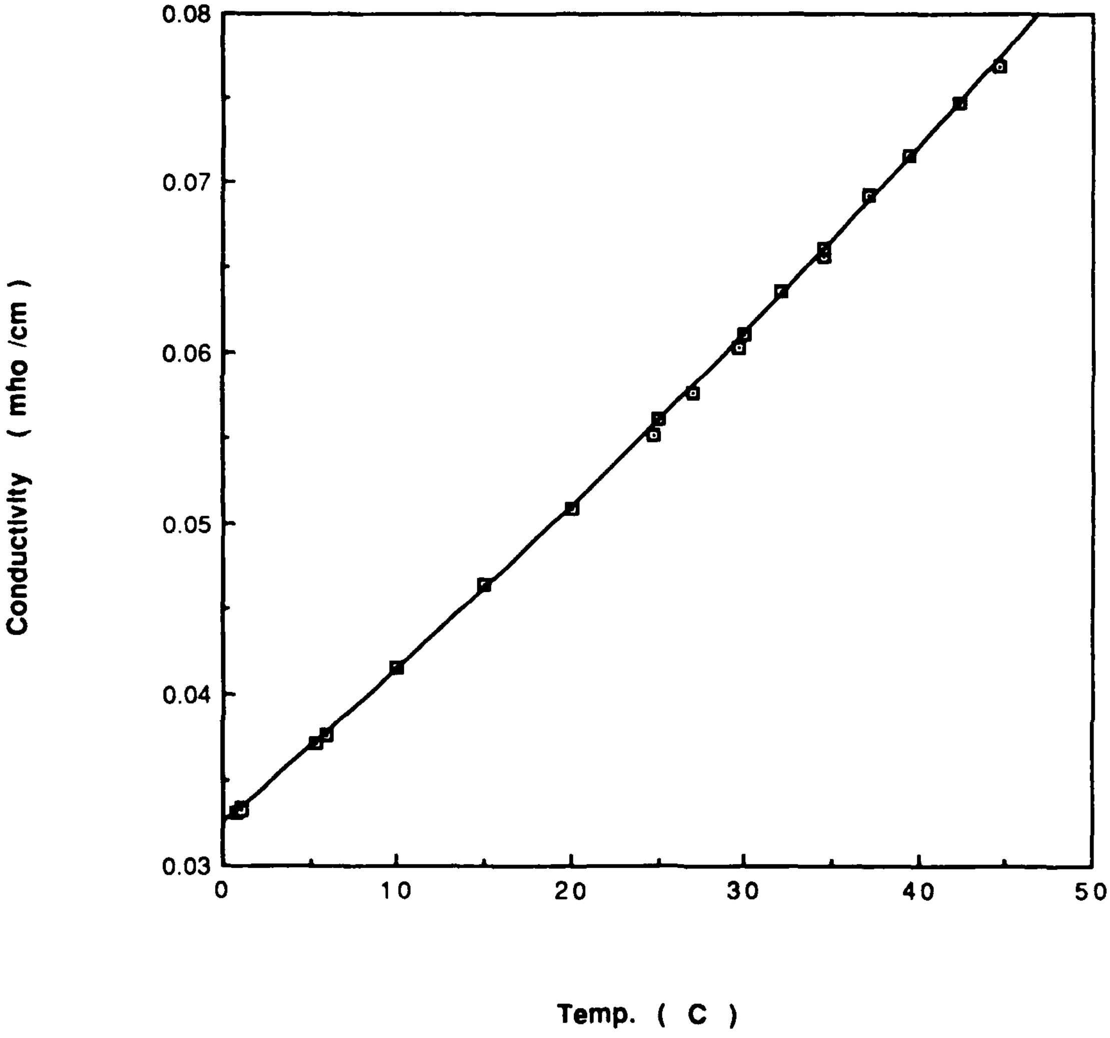


Figure 2



0.08
0.07
0.06
0.05
0.04
0.03
0
10
20
30
40
50
Conductivity (mho /cm)
Temp. (C)

Figure 3

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