ALUMINIUM BROMIDE-1-METHYL-3-ETHYLIMIDAZOLIUM BROMIDE IONIC LIQUIDS.
DENSITIES, VISCOSITIES, ELECTRICAL CONDUCTIVITIES, AND
PHASE TRANSITIONS

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ABSTRACT

The solid-liquid phase diagram, experimental glass transition points, densities, viscosities, and electrical conductivities are reported for the aluminium bromide-1-methyl-3-ethylimidazolium bromide ionic liquid. Certain compositions of this two component molten salt are liquid at room temperature. Density, viscosity, and conductivity data were collected over the range of aluminium bromide mole fractions from ca. 0.35 to 0.75 and over the range of temperatures from ca. 25 to 100 °C. Equations are presented which describe both the composition and temperature dependence of the densities and transport properties. Both the viscosities and the conductivities displayed the non-Arrhenius temperature dependence typically associated with glass forming ionic liquids. Temperature dependent activation energies were derived for these transport processes by using the Vogel-Tammann-Fulcher equation.

INTRODUCTION

Certain mixtures of aluminium bromide (AlBr₃) and 1-methyl-3-ethylimidazolium bromide (MeEtimBr) are liquid at room temperature and display physical and chemical characteristics similar to binary aluminium chloride-organic chloride molten salt systems like aluminium chloride-1-butylpyridinium chloride (AlCl₃-BupyCl) and aluminium chloride-1-methyl-3-ethylimidazolium chloride (AlCl₃-MeEtimCl). In fact, the AlBr₃-MeEtimBr system is the bromide analog of the latter melt. All of these molten salts fall into the same general class of solvents that are known as room temperature haloaluminate ionic liquids. Several reviews which discuss these systems have been published (1-3).

AlBr₃-MeEtimBr molten salts may be useful solvents for electrochemical and spectroscopic investigations that are concerned with the chemistry of bromo complexes and related species since they are expected to display adjustable Lewis acid-base characteristics similar to those exhibited by the related chloroaluminate systems. However,
the utilization of these melts as solvents presupposes knowledge of their physical properties and liquid range. The study reported herein was undertaken in an effort to obtain information about the densities, transport properties, and phase transitions of this new ionic solvent system. It is the first reported comprehensive investigation of the preparation and physical properties of a room temperature bromo-aluminate melt.

EXPERIMENTAL

Melt preparation.—The preparation of melt samples and the loading of these samples into the apparatus described below were conducted in the nitrogen-filled drybox system described previously (4). Anhydrous aluminium bromide (Fluka, 98%) was sublimed under vacuum in this drybox a minimum of three times before use. 1-Methyl-3-ethylimidazolium bromide was prepared by combining stoichiometric quantities of ethyl bromide (Baker, reagent grade) and freshly distilled 1-methylimidazole (Aldrich, 99%). The ethyl bromide was added drop wise to the chilled 1-methylimidazole in a flask fitted with a reflux condenser. (Caution: a rapid exothermic reaction takes place between these components.) The flask was cooled and the resulting white solid was recrystallized twice from anhydrous acetonitrile in Kontes Airless-ware. Great care was taken to avoid exposure of the salt to atmospheric moisture. The melting point of the purified product was 77 °C. The aluminium bromide-1-methyl-3-ethylimidazolium bromide melts were prepared by combining precisely weighed quantities of the purified components inside the drybox. These melts appeared somewhat photosensitive and developed a yellow coloration due to the formation of free bromine after exposure to ordinary room lighting for several days. Appropriate precautions were taken to avoid unnecessary exposure of the AlBr₃-MeEtImBr melt to light, and no measurements were performed with highly discolored samples.

Phase transition measurements.—Melting and glass transition points were determined in sealed quartz EPR tubes with the temperature controlled apparatus described in a recent publication (5). The experimental methodology used during these experiments was similar to that described previously. In addition, some melting points were measured in melting point capillaries with a MEL-TEMP apparatus (Laboratory Devices, Cambridge, Mass.).

Density measurements.—Densities were determined in a Pyrex dilatometer that was constructed from the bulb of a 10 mL pipet and a length of graduated capillary tubing. The diameter of the capillary tube bore was 1.74 mm, and etched graduations were provided every 1.00 mm on the capillary tube. One end of the capillary tube was attached to the pipet bulb while a ROTAFLOR TF6/13 Teflon vacuum stopcock was affixed to the other end. A similar stopcock was also attached to the remaining end of the pipet bulb. The dilatometer was weighed, filled and sealed in the drybox, and then weighed again before being placed in an external water bath. The temperature of the water bath was

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controlled to + 0.1°C by means of either a Precision Scientific
No. 66330 constant temperature bath controller or a B. Braun Model
1420 Thermomix immersion controller. The temperature of the bath was
monitored with calibrated Brooklyn thermometers. The upper stopcock
protruded above the surface of the water bath and was vented to the
atmosphere through a drying tube and then sealed each time the water
bath temperature was changed. The dilatometer was calibrated over its
entire working volume with distilled water. No corrections for thermal
expansion of the apparatus were found necessary over the range of
temperatures that was investigated. It was estimated that the density
measurements could be reproduced with a precision of + 0.11 %.

Viscosity measurements.-Viscosity measurements were made with a
modified Cannon-Fenske No. 200 viscometer (Fisher Scientific). The
viscometer was made airtight by cutting-off both upright tubes
horizontally just above the upper reference mark and then attaching
the open ends of a U-shaped piece of large bore Pyrex tubing to the
ends of the severed tubes of the viscometer. A ROTOFLO TF6/18 vacuum
stopcock was also attached to the viscometer. With these modifi-
cations the viscometer could be filled and sealed in the drybox and
then removed and evacuated prior to immersion in the water bath
described above. The viscometer was mounted in the water bath on a
vertical plate which could be manually rotated in order to recharge
the viscometer. The bearings which supported this plate were fitted
with a mechanism which stopped the rotation of the plate in a repro-
ducible manner when the viscometer was exactly horizontal. The
viscometer was calibrated with freshly distilled ethylene glycol over
the appropriate range of temperatures. The viscometer was typically
charged with 10.0 mL of sample. The efflux time of the sample in the
viscometer was measured with a stopwatch to + 0.1 s. The estimated
reproducibility of a given measurement was + 2 %.

Conductivity measurements.-Conductivity measurements were made
with a Yellow Springs Instrument Co. No. 3403 dip type conductivity
electrode equipped with platinized platinum-iridium electrodes. When
in use, the electrode was sealed airtight with a Teflon bushing and
Teflon encased o-ring into a cell constructed by closing the end of a
#15 Ace-Thred adapter tube. This cell could be filled and sealed in
the drybox before immersion in the water bath (vide supra). Resis-
tance measurements were made at 1 kHz with a General Radio Type 1650-A
impedance bridge. Resistance measurements taken at 5 kHz with this
bridge and an auxiliary oscillator were identical to those made at 1
kHz. The conductivity cell was calibrated at 25 °C with 0.001, 0.01,
0.1, and 1.0 M solutions of KCl in freshly boiled, distilled, deion-
ized water. The data given by Janz and Tompkins (6) were used to
calculate the cell constant which was ca. 1.0. No corrections for
changes in the cell constant with temperature were found necessary
over the range of temperatures examined in this study. It was
determined that the resistance of a given solution at a fixed tempera-
ture could be reproduced to within + 0.31 %.
RESULTS AND DISCUSSION

Phase transitions.—A phase diagram for the AlBr$_3$-MeEtimBr melt system is shown in Fig. 1. Both melting points and glass transition points were obtained for some of the AlBr$_3$-MeEtimBr mixtures. In a few cases it was not possible to induce the crystallization of certain melts even at the temperature of liquid nitrogen, and therefore, only experimental glass transition points are reported for these liquids.

The phase diagram for the AlBr$_3$-MeEtimBr system is similar in general appearance to that for its chloroaluminate analog (5). However, there are some important temperature differences between the phase diagrams for the bromoaluminate and chloroaluminate systems that should be noted. The solid-liquid phase transitions for the latter system are considerably lower than those for the former melts for mixtures in the range 0 < X < 0.60 while the melting points for AlBr$_3$-MeEtimBr mixtures with X > ca. 0.75 are lower than those for the corresponding AlCl$_3$-MeEtimCl mixtures. The lower melting points found in very acidic AlBr$_3$-MeEtimBr melts versus those for the AlCl$_3$-MeEtimCl system probably reflect the lower melting point of AlBr (Al$_2$Br$_3$) relative to that of AlCl$_3$(Al$_2$Cl$_6$).

Densities.—Experimental density data for all of the melt compositions examined in this study are shown in Fig. 2. Experimental densities, $\rho$, were found to vary linearly with temperature. Data for each composition were fitted to equations of the form

$$\rho = a + bT$$

The solid lines that appear in Fig. 2 were calculated for each composition from the values of $a$ and $b$ obtained from these fits. It was found that the variation of the parameters $a$ and $b$ with $X$ could be represented by polynomials of the type

$$a = a_0 + a_1X + a_2X^2 + a_3X^3 + \ldots$$

$$b = b_0 + b_1X + b_2X^2 + b_3X^3 + \ldots$$

A third order polynomial was needed in order to adequately represent the variation of $a$ and $b$ with $X$ in melts with compositions in the range 0.50 < $X$ < 0.75 (acidic melts) while a second order polynomial was found to be sufficient for melts in the range 0.30 < $X$ < 0.50 (neutral and basic melts). The parameters obtained from non-linear least squares fits of $a$ and $b$ as a function of $X$ are collected in Table I. The parameters collected in this table reproduced the experimental density data in acidic melts with a standard deviation, $\sigma$, of 1.69 x 10$^{-3}$ and in neutral and basic melts with $\sigma$ = 1.81 x 10$^{-3}$. The standard deviations reported here and elsewhere (vide infra) were corrected for the total number of model parameters used to reproduce the experimental data. Figure 3 shows a three dimensional plot, produced from the constants in Table I with Eq. [1] to [3], which gives an overall perspective of the

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variation of density with composition and temperature and, in addition, delineates the range in which densities were determined.

Viscosity.—The experimental kinematic viscosities for AlBr⁻₃-MeEtimBr mixtures were converted to absolute viscosities with the density data presented above. Arrhenius plots for the absolute viscosities, $\eta$, are shown in Fig. 4, and it can be seen that $\ln \eta$ does not vary linearly with $1/T$. Similar behavior was noted for the viscosities of the AlCl₃-MeEtimCl and related 1,3-dialkylimidazolium chloride-based chloroaluminate molten salts (5). This non-Arrhenius behavior is a characteristic of glass forming melts (7). Therefore, the logarithmic form of the three parameter Vogel-Tammann-Fulcher (VTF) equation (7) was used to represent the variation of the absolute viscosities as a function of the absolute temperature:

$$\ln \eta = k_\eta / (T-T_0) + 1/2 \ln T + \ln A_\eta$$  \[4\]

$k_\eta$, $T_0$, and $\ln A_\eta$ are empirical parameters in this equation. However, $k_\eta R$, where $R$ is the universal gas constant, is frequently identified with the Arrhenius activation energy, and $T_0$, often designated as the "ideal" glass transition temperature, has been given quasi-thermodynamic significance through the free volume theory of Cohen and Turnbull (8) and the configurational entropy approach of Adams and Gibbs (9). However, a detailed study of these parameters was not the goal of this study.

It was determined that each of the three parameters in Eq. \[4\] could be fitted as a function of $X$ to cubic polynomial equations of the form

$$f(X) = c_0 + c_1 X + c_2 X^2 + c_3 X^3$$  \[5\]

in neutral and basic melts and to to quadratic equations of the form

$$f(X) = c_0 + c_1 /X + c_2 /X^2$$  \[6\]

in acidic melts. Values obtained for the constants in these equations are collected in Tables II and III. Eq. \[4\] and \[5\], with the appropriate parameters from Table II, reproduced the experimental viscosity data in neutral and basic melts with $s = 2.71 \times 10^{-2}$ while a value of $s = 4.63 \times 10^{-2}$ was obtained in acidic melts by using Eq. \[4\] and \[6\] and the parameters in Table III.

A three dimensional plot of viscosity as a function of temperature and composition, constructed by using Eq. \[4\] - \[6\] and the parameters collected in Tables II and III, is depicted in Fig. 5. Qualitatively, the viscosities of the melt rise from a poorly defined minimum at $X = 0.50$ as $X$ is increased or decreased from this value. The irregular increase in the viscosity in acidic melt as $X$ is increased was experimentally reproducible and did not appear to be the result of an artifact in the experimental method or the procedure used to fit the data. These results are somewhat different than those obtained for the chloro-
aluminate analog (5) where the viscosity was found to decrease continuously with $X$.

Conductivity.—Experimental specific conductivity values, $\kappa$, were converted to equivalent conductivities by using the equation

$$\Lambda = \kappa M_e / \rho$$  \[7\]

where $M_e$ is the equivalent weight of the molten mixture and is given by the equation

$$M_e = 191.07 + x/(1-x)266.71$$  \[8\]

This method for representing the molecular weight of a haloaluminate melt is advantageous because it takes into consideration the number of ions in the mixture (5,10).

Arrhenius plots for the equivalent conductance of the AlBr$_3$-MeEtimBr melt are shown in Fig. 6. Like viscosity (vide supra), the equivalent conductance exhibits non-Arrhenius behavior. Therefore, the equivalent conductivities were fitted to the logarithmic form of the VTF equation for equivalent conductance (7):

$$\ln\Lambda = -kA/(T-T_\theta) - (1/2)lnT + \ln\Lambda_\theta$$  \[9\]

As for viscosity, the parameters $kA$, $T_\theta$, and $\ln\Lambda_\theta$ were fitted to Eq. [5] in basic and neutral melt and to Eq. [6] in acidic melt. The values of the constants that resulted are collected in Tables II and III. These equations and the associated model parameters reproduced the experimental data in acidic melts with $\gamma = 4.58 \times 10^{-2}$ and in basic melt and neutral melts with $\gamma = 5.13 \times 10^{-2}$.

A three dimensional plot which delineates the range of composition and temperature over which conductance was studied is shown in Fig. 7. The maximum conductivity of the AlBr$_3$-MeEtimBr system occurs at exactly $X = 0.50$, and the conductivity decreases noticeably as $X$ is increased or decreased from this composition. The organic cation has been determined to transport over 70% of the charge in the AlBr$_3$-MeEtimBr (11) and the AlCl$_3$-MeEtimCl systems (4,12,13). In addition, the formation of ion pairs and larger aggregates between the organic cation and the anions in basic melt, especially bromide ion, have been shown to be important (14). Therefore, the decrease in equivalent conductance shown in Fig. 7 as $X$ is decreased from 0.50 probably results from a decrease in the mobility of the organic cation as the relatively weak aggregates that involve MeEtim$^+\ldots$AlBr$^-\ldots$ ion pairs are substituted for those containing the stronger MeEtim$^+\ldots$Br$^-$ ion-pair interactions. The replacement of relatively weak aggregates by those with stronger anion-cation interactions may also account for the concomitant increase in viscosity that is found when $X$ is decreased in basic melt. The decrease in the equivalent conductance and the increase in viscosity with increasing $X$ noted in acidic melts can not be explained in this fashion since ion-ion interactions are believed to become less important as $X$ is increased in this composition region (14).
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REFERENCES

1. H. L. Chum and R. A. Osteryoung in "Ionic Liquids", D. Inman and D. G. Lovering, Eds., Plenum Press, New York, N.Y., 1981, pp. 407-423.
2. C. L. Hussey, Adv. Molten Salt Chem., 5, 185 (1983).
3. R. J. Gale and R. A. Osteryoung in "Molten Salt Techniques", Vol. I, D. G. Lovering and R. J. Gale, Eds., Plenum Press, New York, N.Y., 1983, pp. 55-78.
4. C. L. Hussey and H. A. Øye, This Journal, 131, 1621 (1984).
5. A. A. Fannin, Jr., D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, and J. L. Williams, J. Phys. Chem., 88, 2614 (1984).
6. G. J. Janz and R. F. T. Tompkins, This Journal, 124, 55c (1977).
7. C. A. Angell and C. T. Moynihan in "Molten Salts Characterization and Analysis", G. Mamantov, Ed., Marcel-Dekker, New York, N.Y., 1969, pp. 315-375.
8. M. H. Cohen and D. Turnbull, J. Chem. Phys., 31, 1164 (1959).
9. G. Adam and J. H. Gibbs, ibid., 43, 139 (1965).
10. R. A. Carpio, L. A. King, R. E. Lindstrom, J. C. Nardi, C. L. Hussey, This Journal, 126, 1644 (1979).
11. J. R. Sanders and C. L. Hussey, unpublished data.
12. C. L. Hussey, J. R. Sanders, and H. A. Øye, This Journal, in press.
13. C. J. Dymek, Jr. and L. A. King, This Journal, 132, 1375 (1985).
14. J. S. Wilkes, C. L. Hussey, and J. R. Sanders, Polyhedron, in press.
Table I. Parameters for density, Eq. [1]-[3].

| Range | $a_0$   | $a_1$   | $a_2$    | $a_3$   |
|-------|---------|---------|----------|---------|
| 0.30 ≤ X ≤ 0.50 | 1.0588  | 3.8594  | -2.8945  | 0.00    |
| 0.50 < X ≤ 0.75  | -5.8410 | 3.7009 × 10^1 | -5.6829 × 10^1 | 3.0474 × 10^1 |

| Range | $b_0$    | $b_1$    | $b_2$ | $b_3$ |
|-------|----------|----------|-------|-------|
| 0.35 ≤ X ≤ 0.50 | 1.2907 × 10^{-3} | -1.0448 × 10^{-2} | 1.1519 × 10^{-2} | 0.0 |
| 0.50 < X ≤ 0.75  | 1.7946 × 10^{-2} | -9.0089 × 10^{-2} | 1.4121 × 10^{-1} | -7.4099 × 10^{-2} |

Table II. Parameters for conductivity and viscosity in basic melt, 0.35 ≤ X ≤ 0.50, Eq. [4], [5] and [9].

|            | $c_0$    | $c_1$    | $c_2$    | $c_3$    |
|------------|----------|----------|----------|----------|
| conductivity | $T_0$ | -4.0191 × 10^1 | 1.9867 × 10^3 | -4.5874 × 10^3 | 2.4562 × 10^3 |
| $k_A$      | 3.3582 × 10^3 | -2.0888 × 10^4 | 4.8630 × 10^4 | -3.3051 × 10^4 |
| $\ln A_A$ | -2.8631 × 10^{-1} | 1.8526 × 10^2 | -4.4919 × 10^2 | 3.4788 × 10^2 |
| viscosity  | $T_0$ | 2.1405 × 10^3 | -1.5128 × 10^4 | 3.9396 × 10^4 | -3.4596 × 10^4 |
| $k_N$      | -1.4147 × 10^4 | 1.1709 × 10^5 | -3.0743 × 10^5 | 2.6769 × 10^5 |
| $\ln A_N$ | -1.3581 × 10^1 | 1.8522 × 10^2 | -5.1772 × 10^2 | 4.7652 × 10^2 |

Table III. Parameters for conductivity and viscosity in acidic melt, 0.50 < X ≤ 0.75, Eq. [4], [6], and [9].

|            | $c_0$    | $c_1$    | $c_2$    |
|------------|----------|----------|----------|
| conductivity | $T_0$ | -8.8020 × 10^2 | 1.3485 × 10^3 | -4.2335 × 10^2 |
| $k_A$      | 9.3588 × 10^3 | -1.1072 × 10^4 | 3.4117 × 10^3 |
| $\ln A_A$ | -3.2068 × 10^2 | 3.5633 × 10^1 | -1.0983 × 10^1 |
| viscosity  | $T_0$ | -3.8691 × 10^2 | 7.6383 × 10^2 | -2.6176 × 10^2 |
| $k_N$      | 6.6201 × 10^3 | -7.8145 × 10^3 | -2.5214 × 10^3 |
| $\ln A_N$ | 2.5515 × 10^1 | -2.2656 × 10^1 | 7.3019 |
Figure 1. Phase diagram for the AlBr\textsubscript{3}-MeEtImBr molten salt system; (○) melting points; (●) experimental glass transition points.

Figure 2. Density data as a function of temperature for melts with the following mole fractions of AlBr\textsubscript{3}: (○) 0.3496; (□) 0.3750; (▼) 0.4000; (●) 0.4444; (■) 0.4752; (◇) 0.4996; (◇•) 0.5251; (□•) 0.5490; (▼•) 0.5750; (○•) 0.6003; (■•) 0.6671; (◇) 0.7500.

Figure 3. Dependence of the fitted densities on composition and temperature; (---) limit defined by phase transitions; (.....) projected data.

Figure 4. Absolute viscosity data as a function of temperature for melts with the following mole fractions of AlBr\textsubscript{3}:(a.); (▼) 0.3496, (■) 0.3750, (●) 0.4000, (◇) 0.4450, (■) 0.4752, (○) 0.4998, (b.); (○) 0.4998, (□) 0.5251, (▼) 0.5490, (●) 0.5750, (■) 0.6003, (▼) 0.6671, (○) 0.7498.
Figure 5. Dependence of the fitted values of the absolute viscosities on composition and temperature; (---) limit defined by phase transitions; (-----) projected data.

Figure 6. Equivalent conductivity data as a function of temperature for melts with the following mole fractions of AlBr₃:
(a); (●) 0.3493, (■) 0.3750, (▼) 0.4000, (○) 0.4444, (▲) 0.4450, (□) 0.4752, (□) 0.4999,
(b); (▼) 0.4999, (■) 0.5490, (○) 0.5750, (▲) 0.6003, (□) 0.6671, (○) 0.7500.

Figure 7. Dependence of the fitted values of the equivalent conductivity on composition and temperature; (---) limit defined by phase transitions; (-----) projected data.