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Room Temperature Fused Salts Based on Copper(I) Chloride–1-Methyl-3-ethylimidazolium Chloride Mixtures. 1. Physical Properties

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Mixtures of CuCl and 1-methyl-3-ethylimidazolium chloride form room temperature ionic liquids over the composition range $0.33 <$ mole fraction CuCl $\chi < 0.67$, with glass transition temperatures of about –50 °C. Densities, viscosities, and specific conductivites are reported in the range 25–50 °C. Density increases monotonically with χ. Viscosity η goes through a pronounced minimum and specific conductivity κ a pronounced maximum at $\chi = 0.5$; these properties have more desirable values than for the previously studied CuCl–triethylammonium chloride fused salt. Activation energies for viscous flow and for specific and equivalent conductivity are calculated. The Frenkel function $\kappa^{E_\eta^\dagger/E_\kappa^\dagger}(\eta) = $ constant is obeyed.

Introduction

Room temperature fused salts containing chlorocuprate(I) anions have been described with various trialkylammonium and with triethylphosphonium and triethylchlorophosphonium cations. The density, conductivity, and viscosity of the prototype of these copper-based liquids, triethylammonium dichlorocuprate(I), have been reported over a range of temperatures (1). That compound was used in electrochemical studies of the copper(II,I) and copper(I,0) couples (1). Practical application, e.g., in batteries, is limited by its excessively high viscosity and by the excessively low exchange current densities of the above couples.

An important recent advance in the study of low-melting chloroaluminate electrolytes was the development by Wilkes and co-workers of the 1,3-dialkylimidazolium chloride–aluminum chloride melts. The 1-methyl-3-ethylimidazolium system was found to have favorable conductivity and viscosity behavior and a wide liquid range (2). This has prompted us to investigate the copper(I) chloride–1-methyl-3-ethylimidazolium chloride (MeEtImCl) system to see if low-melting ionic liquids with more desirable physical and electrochemical properties could be obtained for chlorocuprates. If so, the combination of chloro-aluminate and chlorocuprate systems in batteries might prove useful.

Experimental Section

Materials. Copper(I) chloride was prepared by the method of Keller and Wycoff (3). 1-Methyl-3-ethylimidazolium chloride was prepared and purified as described by Wilkes and co-workers (4); its density as a solid at 21.5 °C was determined by flotation in carbon tetrachloride/hexane to be 1.186 g/mL. The dried chlorides were stored and their mixtures were prepared and transferred in a dry nitrogen-filled glovebox which has been described previously (1).

Melting Points. Samples were in sealed glass capillaries under nitrogen. Measurements below room temperature were made by a visual method which has been shown (2) to be in agreement with the differential scanning calorimetric technique. The sample capillary and an iron–constantan thermocuple were immersed in ethanol in a small tube which was suspended from the bottom of a rubber stopper in a 400-mL vessel. This vessel was swept with dry nitrogen which first passed through a copper coil immersed in liquid nitrogen; temperature control was achieved by varying the rate of flow of gas. The vessel was mounted in an insulated jacket with a port permitting illumination and observation with a magnifier. Glass transitions were characterized by a discontinuous increase in viscosity on cooling, with fracturing of the melt. The transition temperatures were actually measured as melting points on slow warming after initial quenching to –100 °C. Measurements above room temperature were made using a conventional melting point apparatus.

Other Physical Measurements. Densities of CuCl/MeEtImCl melts were measured by a dilatometric method as previously described (1). Viscosities were measured by using a modified Cannon-Fenske viscosimeter whose calibration has been described (1). For conductivity measurements, an Industrial Instruments RC16 B2 bridge and a cell of constant 11.65 ± 0.07 cm⁻¹ were used. Measurements at 60 and 1000 Hz agreed
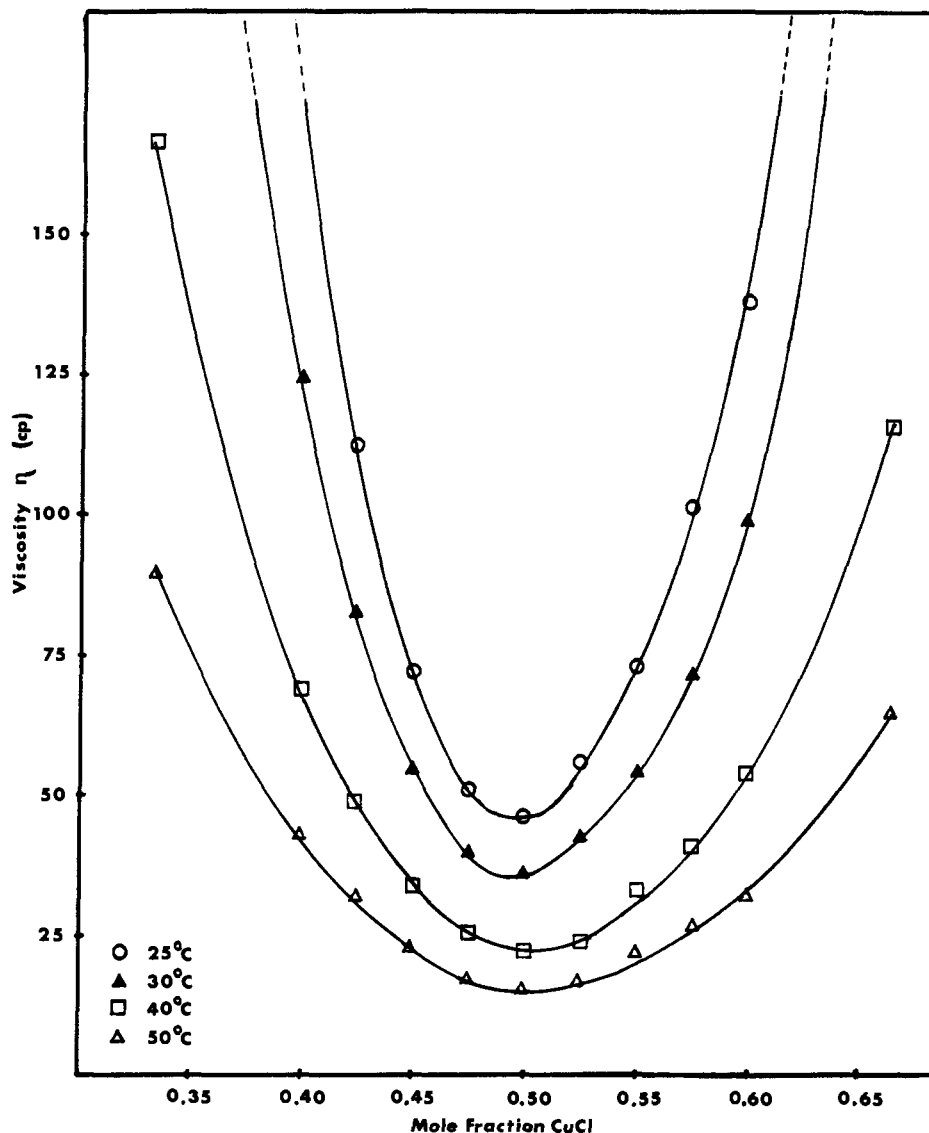
Figure 1. Viscosity isotherms for CuCl/MeEtImCl melts.

well and their average was taken. Temperature control was to ±0.1 °C.

Results

Melting Points. The χCuCl/(1 - χ)MeEtImCl mixtures are room temperature liquids over the composition range 0.33 < mole fraction χ < 0.67. On cooling, sudden glass transitions were observed. The melting points of these glasses fell between -40 and -64 °C over the composition range 0.33 < χ < 0.67. At compositions just above and below this range, the mixtures separated into two phases, liquids which formed glasses at a low temperature plus normal solids. In the composition range 0 < χ < 0.20 the melting points dropped from 82 to 52 °C, while for the range 0.85 < χ < 1.00 the melting points rose from 296 to 430 °C.

Densities and Molar Volumes. In the temperature range 25-50 °C, the data are well represented by linear functions. The results are given in Table I. At a given temperature, density increases monotonically with mole fraction of copper(I) chloride, and densities of melts of compositions other than those in Table I were obtained by curvilinear interpolation. Also shown in Table I are values of the coefficients of thermal expansion, evaluated at 40 °C by using

$$\alpha = (1/V)(\mathrm{d}V/\mathrm{d}T) = (d_{40^\circ})(1/d_{50^\circ} - 1/d_{30^\circ})/20.0 \quad (1)$$

The volumes of the χCuCl/(1 - χ)MeEtImCl melts exceed the

Table I. Densities in the Range 25-50 °C and Coefficients of Expansion $(\alpha_{40^\circ})^a$

CuCl mole fraction	a	b	linear correln coeff	coeff of expansion, $\deg^{-1}$
0.332	1.3835	7.59×10^{-4}	0.9968	5.92×10^{-4}
0.400	1.4058	8.44×10^{-4}	0.9961	6.57×10^{-4}
0.498	1.5423	1.08×10^{-3}	0.9999	7.34×10^{-4}
0.604	1.7162	1.07×10^{-3}	0.9988	6.61×10^{-4}
0.666	1.9041	1.24×10^{-3}	0.9998	5.65×10^{-4}

$^a \rho \ (\mathrm{g/mL}) = a - b(t \ ^\circ\mathrm{C}).$

sum of the molar volumes of their components, e.g., by 9.0% for χ = 0.5. This behavior closely resembles that of the CuCl/Et$_3$NHCl system and is attributed to the existence of holes in the liquid structure (5).

Viscosities and Conductivities. Isotherms showing the variation in viscosity η and specific conductivity κ with composition are given in Figures 1 and 2. Pronounced extrema are seen at mole fraction 0.5 corresponding to the nominal MeEtImCuCl$_2$ composition. Quantitatively, the decrease in viscosity at the composition midpoint is relatively greater than the increase in conductivity, so that the Walden product $\eta\kappa$ passes through a minimum at mole fraction 0.5 at each temperature studied. Although at 25 °C the viscosity of the equimolar CuCl/MeEtImCl melt, 45.9 cP, is significantly less than that of
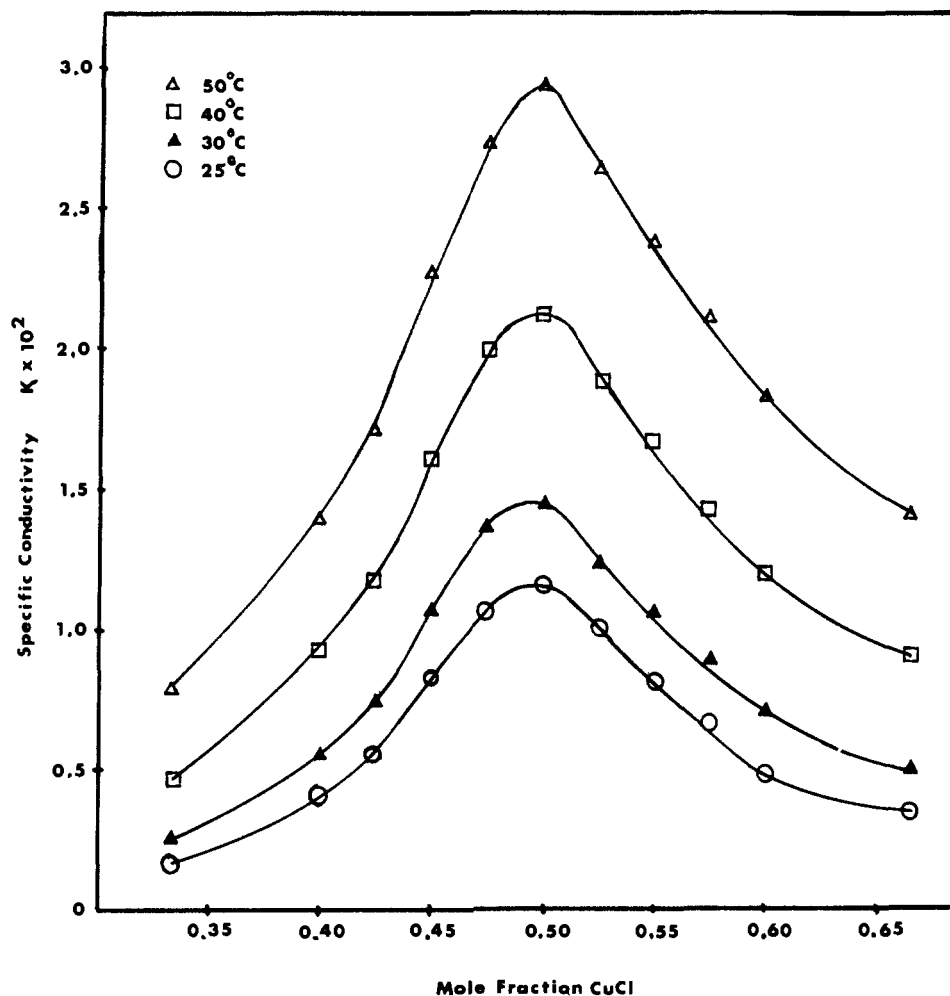
Figure 2. Specific conductivity isotherms for CuCl/MeEtImCl melts.

Table II. Activation Energies (kcal/mol), Viscosities (η), Specific Conductivities (κ), and Values of the Frenkel Function FF = $(\eta)(\kappa)^{E_\eta^\dagger/E_\kappa^\dagger}$

CuCl mole fraction	$E_\eta^\dagger$, kcal/mol	$E_\kappa^\dagger$, kcal/mol	25.0 °C			30.0 °C			40.0 °C			50.0 °C			mean FF and std dev
			η, cP	$10^3\kappa$, ohm^{-1} cm^{-1}	FF	η, cP	$10^3\kappa$, ohm^{-1} cm^{-1}	FF	η, cP	$10^3\kappa$, ohm^{-1} cm^{-1}	FF	η, cP	$10^3\kappa$, ohm^{-1} cm^{-1}	FF	
0.334	13.8	12.1	539	1.64	0.352	361	2.45	0.374	167	4.64	0.360	89.8	7.98	0.359	0.361 ± 0.009
0.400	10.7	9.42	173	4.10	0.329	124	5.50	0.331	68.7	9.32	0.334	42.7	13.9	0.328	0.331 ± 0.002
0.425	9.68	8.54	112	5.58	0.314	82.3	7.38	0.316	48.4	11.7	0.313	31.7	17.1	0.315	0.315 ± 0.001
0.450	8.79	7.67	72.0	8.28	0.296	54.6	10.7	0.301	33.8	16.1	0.297	22.8	22.7	0.298	0.298 ± 0.002
0.475	8.40	7.10	51.6	10.8	0.242	39.7	13.6	0.246	25.1	19.9	0.244	17.2	27.3	0.248	0.245 ± 0.003
0.500	8.29	7.15	45.9	11.6	0.262	35.3	14.5	0.260	22.5	21.3	0.260	15.5	29.5	0.262	0.261 ± 0.001
0.525	8.81	7.51	55.9	9.95	0.250	42.5	12.6	0.250	26.3	18.8	0.249	17.7	26.6	0.251	0.250 ± 0.001
0.550	9.02	8.09	72.5	8.19	0.342	53.4	10.7	0.340	33.3	16.7	0.346	22.1	23.8	0.342	0.343 ± 0.003
0.575	10.4	8.62	101	6.85	0.253	71.8	8.91	0.248	41.0	14.3	0.250	26.0	21.1	0.252	0.251 ± 0.002
0.600	11.1	10.1	138	4.82	0.377	93.5	7.04	0.387	53.3	11.9	0.394	32.5	18.2	0.385	0.386 ± 0.007
0.666	13.2	10.8	357	3.45	0.360	235	4.86	0.360	115	8.98	0.370	64.1	14.0	0.357	0.362 ± 0.006

the CuCl/Et$_3$NHCl melt, 123 cP, and the specific conductivity higher, 1.16 × 10^{-2} vs. 4.30 × 10^{-3} ohm^{-1} cm^{-1}, the values of their Walden products are the same within experimental error, 0.532 vs. 0.529 cP ohm^{-1} cm^{-1}.

Equivalent conductivites, ohm^{-1} cm^2 equiv^{-1}, were calculated by using

$$\Lambda = \kappa \bar{W}/\rho \qquad (2)$$

where the equivalent weight is given by

$$\bar{W} = \chi(98.99) + (1 - \chi)(146.63) \qquad (3)$$

and ρ is the density at the temperature at which κ was measured. Over the range 25–50 °C, linear plots vs. 1/T were obtained of ln κ (correlation coefficients −0.9963 to −0.9994),

In Λ (correlation coefficients −0.9963 to −0.9995), and ln η (correlation coefficients 0.9987 to 0.9994), permitting calculation of energies of activation for specific conductivity $E_\kappa^\dagger$ and equivalent conductivity $E_\Lambda^\dagger$, and for viscous flow $E_\eta^\dagger$. Although Walden products are not constant for a given molten salt composition as viscosity and conductivity vary over a temperature range, the empirical Frenkel function (6, 7)

$$FF = (\kappa^{E_\eta^\dagger/E_\kappa^\dagger})(\eta) = \text{constant} \qquad (4)$$

has been found to describe the behavior of CuCl/Et$_3$NHCl melts (1) as well as molten alkali halides (8) and cadmium halides (9). The data in Table II show that this function is remarkably constant for each composition studied in the CuCl/MeEtImCl system.

Table III. Comparison of Activation Energies $E_A{}^\dagger$ (kcal/mol) Calculated from (I) $E_A{}^\dagger = E_\kappa{}^\dagger + \alpha RT^2$ and (II) from the Arrhenius Equation

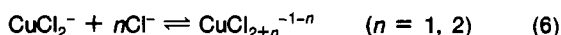| CuCl mole fraction	$E_A{}^\dagger$(I)	$E_A{}^\dagger$(II)
0.334	12.2	12.2
0.400	9.55	9.53
0.500	7.19	7.29
0.600	10.2	10.2
0.666	10.9	10.9

The two conductivity activation energies are theoretically related by (10)

$$E_A{}^\dagger = E_\kappa{}^\dagger + \alpha RT^2 \qquad (5)$$

and values of $E_A{}^\dagger$ calculated by this equation using the 40 °C coefficient of expansion α values from Table I are compared in Table III with values of $E_A{}^\dagger$ obtained from Arrhenius plots.

Discussion

Just as 1-methyl-3-ethylimidazolium chloride was found by Wilkes and co-workers to be a desirable component in aluminum chloride room temperature melts from the standpoint of the wide liquid range available, low viscosity, and high conductivity, so it is now found superior to triethylammonium chloride as a component of low melting copper(I) chloride-based fused salts. Two reasons have been proposed for the liquid nature of these copper(I) electrolytes: first, low lattice energies related to the bulk and low symmetry of the cations and consequent poor packing of these with the chlorocuprate(I) anions, and, second, the existence of a mixture of species depressing each other's melting points, arising from such chloride ion transfer equilibria as

$$CuCl_2{}^- + nCl^- \rightleftharpoons CuCl_{2+n}{}^{-1-n} \qquad (n = 1, 2) \qquad (6)$$

$$CuCl_2{}^- + yCuCl \rightleftharpoons Cu_{1+y}Cl_{2+y}{}^- \qquad (y = 1, \text{etc.}) \qquad (7)$$

$$2CuCl_2{}^- \rightleftharpoons Cu_2Cl_3{}^- + Cl^- \qquad (8)$$
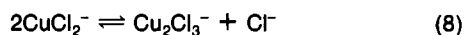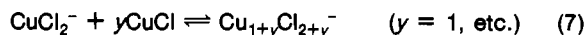
Spectroscopic evidence has been presented (11) for species such as $CuCl_3{}^{2-}$ in the chloride-rich (basic) and $Cu_2Cl_3{}^-$ in the chloride-poor (acidic) CuCl room temperature fused salts. The $CuCl_3{}^{2-}$ and $CuCl_4{}^{3-}$ species were found in CuCl solutions in the basic AlCl$_3$/MeEtImCl melts (12), and various polynuclear complexes $Cu_mCl_n{}^{-(n-m)}$ have been reported (13) in aqueous CuCl + Cl$^-$ systems. Clearly, a much wider variety of anions is present than in the aluminum chloride ionic liquids where the anionic species present are completely described (14) by the equation

$$2AlCl_4{}^- \rightleftharpoons Al_2Cl_7{}^- + Cl^- \qquad (9)$$

A solid compound MeEtIm$^+$CuCl$_2{}^-$ has not been observed, but in the liquid in the temperature range 25–50 °C and at the mole fraction 0.5CuCl/0.5MeEtImCl composition, the predominant anionic species is certainly CuCl$_2{}^-$. The isotherms of Figures 1 and 2 show a pronounced minimum in viscosity and maximum in conductivity at this composition, corresponding to the predominance of this simplest of the chlorocuprate(I) anions. In both the MeEtImCl-enriched basic melts and the CuCl-enriched acidic melts, the lower mobilities of the CuCl$_3{}^{2-}$ and CuCl$_4{}^{3-}$ anions or the polynuclear Cu$_m$Cl$_n{}^{-(n-m)}$ anions are clearly reflected in the increased viscosity and decreased specific conductivity. The coefficients of thermal expansion also pass through at maximum at the equimolar composition.

All past experience with molten salts shows that the energy of activation for viscous flow is greater than that for electric conductivity, since flow is limited by the ion with lower mobility while conductivity is influenced more by the ion with higher mobility. The $E_\eta{}^\dagger/E_\kappa{}^\dagger$ ratio ranges from 3 to 7 for molten alkali halides, and is about 2 for bivalent metal halides (9). The present data on CuCl/MeEtImCl melts provide a contrast with $E_\eta{}^\dagger/E_\kappa{}^\dagger$ ratios 1.1 to 1.2. These values suggest that the substituted imidazolium cation and the chlorocuprate(I) anions have similar mobilities.

Acknowledgment

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