Densities, Molar Volumes, and Thermal Expansivities of 1-Methyl-3-ethylimidazolium Chloride + $AlCl_3$ + Alkali-Metal Halide Molten Salts

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Density measurements are reported for 1-methyl-3-ethylimidazolium chloride + $AlCl_3$ binary melts and for 1-methyl-3-ethylimidazolium chloride + $AlCl_3$ + MX ternary melts, where M = Li, Na, K, Rb, or Cs and X = Cl, Br, or I in the temperature range 15–105 °C. From these measurements molar volumes and thermal expansion coefficients were calculated. The behavior of these properties is explained by the formation of complex tetrachloro- and heptachloroaluminates in these ionic liquids and by the radii of the alkali-metal cations and halide anions. The binary and ternary melts mix ideally with respect to volume. The effective ionic radius of the 1-methyl-3-ethylimidazolium cation increases with the molar fraction of $AlCl_3$ in the binary melt.

Introduction

Mixtures of 1-methyl-3-ethylimidazolium chloride (MEIC) and aluminum chloride are produced by mixing anhydrous $AlCl_3$ with MEIC (mp 85 °C) (*1*). These systems, potential electrolytes for batteries, have melting points that range from +7 °C for $x(AlCl_3) = 0.500$ to −33 °C for $x(AlCl_3) = 0.610$ and are frequently called room temperature molten salts. $x(AlCl_3)$ is the apparent mole fraction of $AlCl_3$ in the mixture, although little or no $AlCl_3$ actually exists in the mixtures.

The 1-methyl-3-ethylmidazolium chloride acts as a chloride donor to $AlCl_3$, a Lewis acid, and the result is the formation of the chloraluminate anions. Previous studies showed that melts with $x(AlCl_3) > 0.5$ are acidic, and the predominant anions are $AlCl_4^-$ and $Al_2Cl_7^-$, while those with $x(AlCl_3) < 0.5$ are basic because they contain chloride ion from MEIC not covalently bonded to aluminum (*2*).

Understanding of the physics and chemistry of chloroaluminate melts is required for their development as electrolytes for electrochemical cells and for their use as nonaqueous solvents. Two of the principal variables having a significant effect on the molar volume of a system are temperature and composition (*3–5*). Thermal expansion, i.e., the change in the volume of a system when subjected to a change in temperature (*6–10*), is also affected by composition.

The present study was performed in the acidic range of binary systems with $x(AlCl_3) = 0.500, 0.550, 0.600$, and 0.667. The effect of alkali-metal halides (MX) upon those properties was determined.

Experimental Procedure

The 1-methyl-3-ethylimidazolium chloride + aluminum chloride + alkali-metal halide molten salt mixtures were prepared as previously described (*1*). Sample preparation and handling were conducted under an anhydrous helium gas atmosphere in a helium-filled glovebox. Densities were measured using a Mettler-Paar DMA 40 densimeter calibrated with air and conductivity water. The internal capillary of the instrument was maintained under a stream of helium gas before filling with the samples. These were transported in a closed syringe from the glovebox to the instrument. The internal capillary of the instrument was maintained under helium gas. The temperature was controlled to ±0.05 °C by a modified Haake E3 thermoregulator. For each sample at each temperature 10 readings were taken. No correction was necessary for the loss of Al_2Cl_6 vapor. The experimental uncertainty was $\pm 1 \times 10^{-4}$ g·cm^{-3}.

The low solubility of cesium and rubidium chlorides in the binary melts limits the range of measurements.

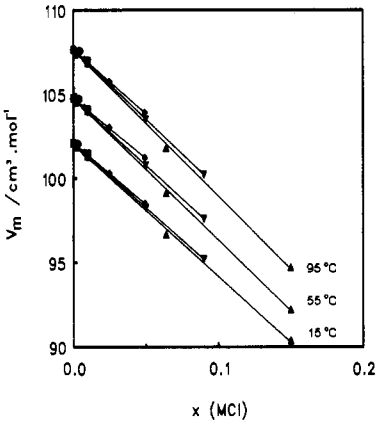

Figure 1. Molar volumes as a function of the mole fraction of MCl for 15, 55, and 95 °C, where M = Li (▲), Na (▼), K (◆), Rb (■), and Cs (●). The initial composition of the binary system MEIC + $AlCl_3$ was $x(AlCl_3) = 0.600$.

Results and Discussion

The results for the binary and ternary systems are given in Table 1. The density results were fitted to the equation

$$\rho/(\text{g·cm}^{-3}) = a + b(t/°\text{C}) \quad (1)$$

where a and b are constants. The values of the constants are also given in Table 2. The temperature range of the measurements was 15–105 °C. From the density data, the molar volumes of the binary and ternary mixtures were calculated. The molar volume of a mixture, V_m, is defined by

$$V_m = (\sum x_i M_i)/\rho \quad (2)$$

where M_i and x_i are the molar mass and fraction, respectively, of component i.

Figure 1 shows the variation of molar volumes with

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Table 1. Experimental Densities for Aluminum Chloride + MEIC and Aluminum Chloride + MEIC + MX Systems

			ρ/(g·cm^{-3})									
x = ($AlCl_3$)	x = (MEIC)	x = (MX)	t/°C = 15.0	t/°C = 25.0	t/°C = 35.0	t/°C = 45.0	t/°C = 55.0	t/°C = 65.0	t/°C = 75.0	t/°C = 85.0	t/°C = 95.0	t/°C = 105.0
						MX = NaCl						
0.5000	0.5000	0.0000	1.304 69	1.296 71	1.288 73	1.280 74	1.272 76	1.264 77	1.256 79	1.248 81	1.240 82	1.232 84
0.5500	0.4500	0.0000	1.329 10	1.320 29	1.312 90	1.303 90	1.296 25	1.287 30	1.278 70	1.270 73	1.262 40	1.254 02
0.5230	0.4270	0.5000	1.341 46	1.332 66	1.325 44	1.316 51	1.309 04	1.300 19	1.290 93	1.283 54	1.275 53	1.266 99
0.6000	0.4000	0.0000	1.357 96	1.348 80	1.340 68	1.331 62	1.323 76	1.314 50	1.305 14	1.296 94	1.287 93	1.279 38
0.5940	0.3960	0.0100	1.360 93	1.351 94	1.343 69	1.334 17	1.326 26	1.316 94	1.307 55	1.299 04	1.290 36	1.281 59
0.5700	0.3800	0.0500	1.370 42	1.361 18	1.353 57	1.344 04	1.336 12	1.326 72	1.317 54	1.309 31	1.300 79	1.291 90
0.5460	0.3640	0.0900	1.390 55	1.371 92	1.363 79	1.354 63	1.346 77	1.337 48	1.328 39	1.320 05	1.311 47	1.302 88
0.6667	0.3333	0.0000	1.401 02	1.390 64	1.381 89	1.372 16	1.362 71	1.353 56	1.343 51	1.333 65	1.324 28	1.314 91
0.6616	0.3284	0.0100	1.404 75	1.395 30	1.385 85	1.376 40	1.366 95	1.357 49	1.348 04	1.338 59	1.329 14	1.319 69
0.5896	0.2997	0.1007	1.420 58	1.410 79	1.402 88	1.393 05	1.384 72	1.374 97	1.365 17	1.356 69	1.347 65	1.338 42
0.5000	0.2500	0.2500	1.469 58	1.460 16	1.452 47	1.443 20	1.435 06	1.425 69	1.416 16	1.407 45	1.399 45	1.390 27
						MX = KCl						
0.5953	0.3969	0.0078	1.360 71	1.351 53	1.343 40	1.334 40	1.325 71	1.317 00	1.308 01	1.298 99	1.290 36	1.281 63
0.5850	0.3900	0.0250	1.366 47	1.357 16	1.347 86	1.339 96	1.330 25	1.322 45	1.313 65	1.304 84	1.296 04	1.287 24
0.5700	0.3806	0.0494	1.374 15	1.345 00	1.355 03	1.347 66	1.338 57	1.330 51	1.321 38	1.312 34	1.303 96	1.295 40
						MX = LiCl						
0.5942	0.3961	0.0097	1.360 88	1.352 03	1.343 19	1.334 34	1.325 50	1.316 66	1.307 81	1.298 97	1.290 13	1.281 28
0.5602	0.3734	0.0664	1.368 43	1.359 17	1.351 61	1.342 36	1.334 33	1.325 17	1.315 86	1.307 48	1.299 24	1.290 36
0.5100	0.3400	0.1500	1.380 60	1.371 36	1.363 91	1.354 70	1.346 76	1.338 31	1.328 71	1.320 21	1.311 58	1.302 95
0.5091	0.3394	0.1515	1.382 20	1.375 59	1.365 02	1.356 40	1.348 51	1.339 20	1.330 60	1.322 01	1.313 20	1.304 80
						MX = RbCl						
0.5991	0.3994	0.0015	1.360 84	1.351 47	1.343 91	1.334 40	1.326 43	1.317 27	1.307 86	1.299 15	1.291 03	1.282 01
0.5991	0.3960	0.0100	1.364 64	1.355 21	1.347 65	1.338 07	1.330 05	1.320 55	1.311 86	1.302 81	1.294 25	1.285 46
						MX = CsCl						
0.5989	0.3993	0.0018	1.361 19	1.351 81	1.344 14	1.334 84	1.326 87	1.317 60	1.308 14	1.299 71	1.291 25	1.282 40
0.5969	0.3979	0.0052	1.364 55	1.355 21	1.347 54	1.308 07	1.320 21	1.320 88	1.311 48	1.303 15	1.294 47	1.285 74
						MX = NaBr						
0.5579	0.3719	0.0702	1.405 18	1.396 49	1.386 68	1.378 78	1.370 12	1.361 79	1.351 16	1.344 21	1.334 51	1.325 68
0.5190	0.3460	0.1350	1.450 31	1.441 09	1.432 77	1.423 13	1.415 23	1.405 73	1.396 21	1.387 96	1.378 90	1.369 96
						MX = NaI						
0.5766	0.3862	0.0350	1.389 35	1.379 93	1.372 19	1.362 58	1.354 93	1.345 18	1.335 75	1.327 69	1.318 65	1.309 88
0.5056	0.3374	0.1570	1.513 11	1.503 51	1.495 58	1.485 27	1.477 52	1.467 81	1.457 99	1.449 32	1.440 50	1.431 27

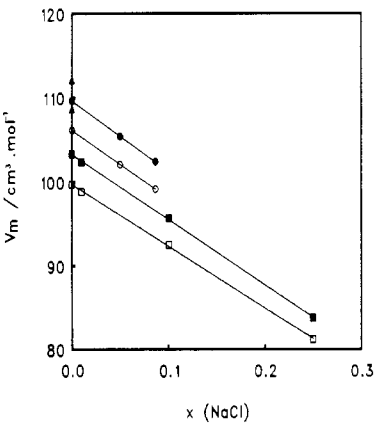

Figure 2. Molar volume as a function of the mole fraction of NaCl for initial compositions of the binary system MEIC + $AlCl_3$ of $x(AlCl_3)$ = 0.500 (▲), 0.550 (●), 0.667 (■) for 85 °C and 0.500 (△), 0.550 (○), 0.667 (□) for 35 °C.

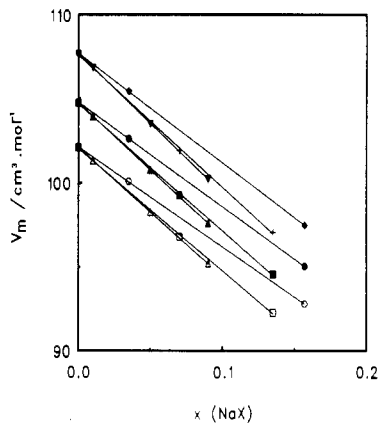

Figure 3. Molar volume as a function of the mole fraction of NaX for an initial composition of the binary system MEIC + $AlCl_3$ of $x(AlCl_3)$ = 0.600, where X = Cl (▼), Br (+), and I (◆) for 95 °C, X = Cl (▲), Br (■), and I (●) for 55 °C, and X = Cl (△), Br (□), and I (○) for 15 °C.

composition for mixtures containing CsCl, RbCl, KCl, NaCl, and LiCl in a melt with an initial composition of $x(AlCl_3)$ = 0.600.

Figure 2 contains plots of the variation of the molar volume with x(NaCl) for two melts of different $AlCl_3$ content. For binary mixtures with $x(AlCl_3)$ = 0.550 or 0.667, addition of NaCl produces a decrease in V_m. In the cases where $x(AlCl_3)$ = 0.500, 0.550, and 0.667, the addition of any alkali-metal chloride (not shown) also produces the same behavior in V_m with respect to the binary solvent, and the order of this change is $Li^+ > Na^+ > Rb^+ > Cs^+$. For all systems, the molar volume increases with temperature. In the presence of Li^+, Na^+, and K^+, which create strong polarizing fields, V_m exhibits an additive dependence. For the range of compositions and temperatures under study the system shows ideal behavior.

The molar volumes decrease with sodium halide content in the $x(AlCl_3)$ = 0.600 binary melt, following ideal behavior, as shown in Figure 3. This decreasing effect is more pronounced for chloride relative to iodide, i.e., $Cl^- > Br^- \gg I^-$. The addition of the other anions (since the cation is the same in all cases) gives rise to a contraction of the systems, as was described before for alkali-metal cations. The temperature has the opposite effect as noted before. In the

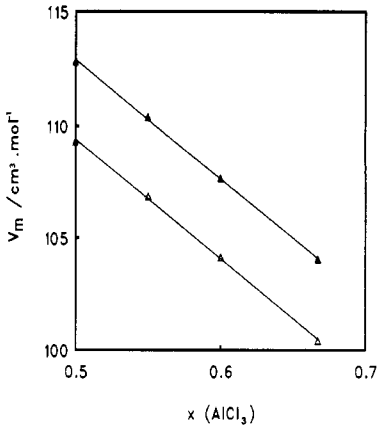

Figure 4. Molar volume as a function of the mole fraction of $AlCl_3$ for the binary MEIC + $AlCl_3$ system at 45 °C (△) and at 95 °C (▲).

Table 2. Density Parameters for Aluminum Chloride + MEIC and Aluminum Chloride + MEIC + MX

			regression parameter for eq 1	
$x(AlCl_3)$	x(MEIC)	x(MX)	a	-10^4b
		MX = NaCl		
0.5000	0.5000	0.0000	1.316 67	7.984 07
0.5500	0.4500	0.0000	1.341 60	8.341 90
0.5230	0.4270	0.5000	1.353 87	8.273 90
0.5023	0.4110	0.8670	1.363 20	9.365 51
0.6000	0.4000	0.0000	1.371 06	8.731 90
0.5940	0.3960	0.0100	1.373 92	8.793 50
0.5700	0.3800	0.0500	1.383 51	8.724 61
0.5460	0.3640	0.0900	1.393 49	8.629 80
0.6667	0.3333	0.0000	1.415 47	9.568 20
0.6616	0.3284	0.0100	1.418 93	9.451 64
0.5896	0.2997	0.1007	1.434 27	9.128 91
0.5000	0.2500	0.2500	1.482 79	8.811 91
		MX = KCl		
0.5953	0.3969	0.0078	1.373 90	8.787 01
0.5850	0.3900	0.0250	1.379 13	8.752 76
0.5700	0.3806	0.0494	1.386 25	8.650 31
		MX = LiCl		
0.5942	0.3961	0.0097	1.374 14	8.843 48
0.5602	0.3734	0.0664	1.381 47	8.676 93
0.5100	0.3400	0.1500	1.393 53	8.618 72
0.5091	0.3394	0.1515	1.395 23	8.612 64
		MX = RbCl		
0.5991	0.3994	0.0015	1.373 98	8.759 09
0.5991	0.3960	0.0100	1.337 79	8.798 41
		MX = CsCl		
0.5989	0.3993	0.0018	1.374 32	8.754 66
0.5969	0.3979	0.0052	1.377 68	8.760 44
		MX = NaBr		
0.5579	0.3719	0.0702	1.418 35	8.804 93
0.5190	0.3460	0.1350	1.463 68	8.925 29
		MX = NaI		
0.5788	0.3862	0.0350	1.402 59	8.829 80
0.5056	0.3374	0.1570	1.526 75	9.093 21

composition range $x(AlCl_3) = 0.500$–0.667 the addition of $AlCl_3$ to the MEIC produces a linear decrease in the molar volume of the melt, as shown in Figure 4.

Molar volumes are well described by a linear equation

$$V_m/(cm^3 \cdot mol^{-1}) = V_m°/(cm^3 \cdot mol^{-1}) - mx \qquad (3)$$

where $V_m°$ is the molar volume of the solvent, x is the mole fraction, and m is a constant dependent on the temperature and solute. An example is given in Table 3 for three different temperatures.

For the MEIC + $AlCl_3$ binary systems, at 45 °C, for all

Table 3. Equation 3 m Parameter[a]

solute MX	t/°C 15.0	t/°C 55.0	t/°C 95.0
LiCl	79.513	83.818	86.673
NaCl	76.498	79.355	82.744
KCl	70.816	71.294	75.968
RbCl	57.163	57.565	58.739
CsCl	45.363	49.092	52.438
NaBr	72.854	75.444	78.564
NaI	59.349	61.942	64.968
$AlCl_3$[b]	53.822	53.411	52.785

[a] These parameter values are for ternary systems, with an initial $x(AlCl_3) = 0.600$ solvent composition. [b] For binary MEIC + $AlCl_3$ systems with $x(AlCl_3) = 0.500$, 0.550, 0.600, and 0.667.

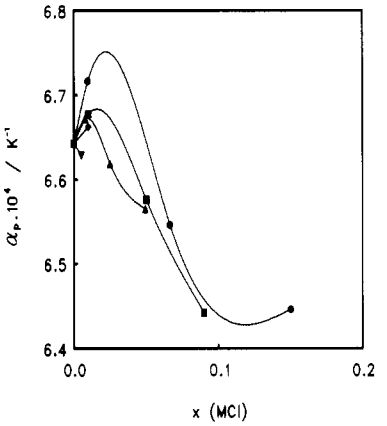

Figure 5. Thermal expansion coefficients as a function of the mole fraction of MCl for 65 °C, where M = Li (●), Na (■), K (▲), Rb (◆), and Cs (▼). The initial composition of the binary system MEIC + $AlCl_3$ was $x(AlCl_3) = 0.600$.

compositions in the range $0.50 < x(AlCl_3) < 0.667$, the molar volume contracts 8.10%. At 55 °C, for x(MCl) = 0.050 in ternary melts, the contraction shown in Figure 1 decreases from lithium chloride to potassium chloride by 4.06% for LiCl, 3.87% for NaCl, and 3.47% for KCl. Cesium and rubidium chlorides are not sufficiently soluble to compare at the x(MCl) = 0.050 composition. At 15 °C, for the x(MCl) = 0.090 sodium halides, the contraction of V_m shown in Figure 4 decreases from Cl^- to I^- by 6.80% for NaCl, 6.60% for NaBr, and 5.41% for NaI. The m parameter for eq 3 is also correlated with this change of contraction. Taken together, all of the molar volume evidence for binary melts and ternary melts suggests that an extensive structural rearrangement accompanies the addition of $AlCl_3$ and alkali-metal halide salts. This rearrangement produces considerable decreases in molar volume that are related to the cation and anion volumes and/or cation–anion interactions that lead to the formation of complex species.

The coefficients for thermal expansion (expansivity) at constant pressure, α_p, may be calculated from the temperature dependence of the densities using the expression

$$(\partial \ln V/\partial T)_p \equiv \alpha_p = 1/\rho(\partial\rho/\partial T)_p \qquad (4)$$

The concentration dependence of thermal expansion coefficients calculated from eq 4 is shown in Figure 5. As it is apparent, α_p decreases with the content of alkali-metal chlorides. This decrease is in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Also, considering only the addition of NaCl to the binary mixtures (Figure 6), in the composition range $0.550 < x(AlCl_3) < 0.667$, the expansivity of the melt is larger for the $x(AlCl_3) = 0.667$ initial binary and exhibits a minimum for the ternary melt that originates from an $x(AlCl_3) = 0.550$ binary melt.

Figure 7 shows that the expansivity of the binary melt as a function of $x(AlCl_3)$ passes through a minimum value in the

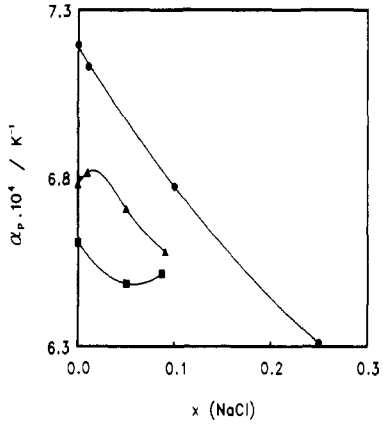

Figure 6. Thermal expansion coefficients as a function of the mole fraction of NaCl, at 95 °C, for initial compositions of the binary system MEIC + $AlCl_3$ of $x(AlCl_3)$ = 0.550 (■), 0.600 (▲), and 0.667 (●).

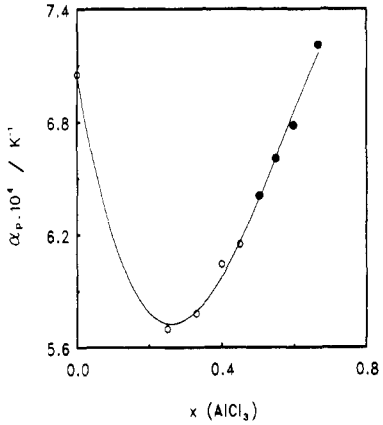

Figure 7. Thermal expansion coefficients as a function of the solvent composition for the binary system MEIC + $AlCl_3$, at 95 °C: (○) ref 2, (●) this work.

basic range and rises to its highest value in the most acidic composition. The mixture with $x(AlCl_3)$ = 0.33 in the basic binary melts is a special case, since the Lewis base Cl^- has an anion fraction equal to $AlCl_4^-$ (*11*). The addition of $AlCl_3$ to the Lewis neutral $AlCl_4^-$ follows the well-established reaction (at 40 °C)

$$AlCl_4^- + AlCl_3 \rightarrow Al_2Cl_7^- \quad K_{40} = 1.6 \times 10^3 \qquad (5)$$

to produce the acidic heptachloroaluminate. The addition of MCl to this melt consumes the $Al_2Cl_7^-$ (*12*) by

$$Al_2Cl_7^- + Cl^- \rightarrow 2AlCl_4^- \quad K_{40} = 10^{16} \qquad (6)$$

The thermal expansion coefficient behavior seems well-correlated with the above reactions, since the α_p values increase from 6.4×10^{-4} K^{-1} for $x(AlCl_3)$ = 0.290 to 7.22×10^{-4} K^{-1} for $x(AlCl_3)$ = 0.667 in the binary melt. The addition of NaCl to the $x(AlCl_3)$ = 0.667 binary melt causes a decrease in the α_p values from 7.22×10^{-4} to 6.30×10^{-4} K^{-1} due to the reaction depicted above in eq 6 where $AlCl_4^-$ is formed from $Al_2Cl_7^-$. We anticipate that for the $x(AlCl_3)$ = 0.667 melt, the addition of NaCl also produces associated Na^+ and $AlCl_4^-$ ions (*13*).

Figure 8 shows plots of the isotherms, at t = 25, 55, and 87 °C, of the thermal expansion coefficients vs composition of the ternary melts, for initial $x(AlCl_3)$ = 0.60, with NaX added (X = Cl^-, Br^-, I^-). The increase in the molar fraction of halide ions in each mixture generally causes a decrease in α_p in the order $I^- > Br^- > Cl^-$. An increase in the temperature

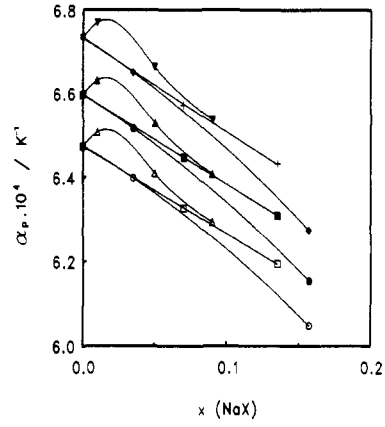

Figure 8. Thermal expansion coefficients as a function of the mole fraction of NaX for an initial composition of $x(AlCl_3)$ = 0.600 in the binary system MEIC + $AlCl_3$, where X = Cl (▼), Br (+), and I (◆) for 85 °C, X = Cl (▼), Br (■), and I (●) for 55 °C, and X = Cl (△), Br (□) an d I (○) for 25 °C.

produces the expected increase in the thermal expansion of these ionic liquids.

Conclusions

Density measurements of the low-melting chloroaluminates over a 100 °C temperature range were used to calculate molar volumes and thermal expansion coefficients. Ternary melts prepared with varying alkali-metal cations or halide anions displayed changes in molar volumes that are dependent on the size of the cation or anion, with the smallest being most effective. The formation of complex tetrachloro- and heptachloroaluminates in these ionic liquids affects both molar volumes and thermal expansions. Within the range of temperature and composition of the data, both binary and ternary mixtures mix ideally.

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