

## Acidity of Neutral Buffered 1-Ethyl-3-methylimidazolium Chloride–AlCl<sub>3</sub> Ambient-Temperature Molten Salts

Peter Koronaios, Dawn King,<sup>†</sup> and Robert A. Osteryoung\*

Department of Chemistry, North Carolina State, Raleigh, North Carolina 27695-8204

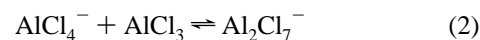
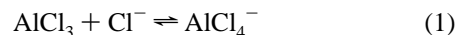
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A series of studies on the acidity of AlCl<sub>3</sub>–1-ethyl-3-methylimidazolium chloride (EMIC) melts buffered with alkali metal chlorides were carried out. The solubility of HCl, a strong Brønsted acid in these melts, was measured in melts buffered with LiCl, NaCl, and KCl. The solubility of HCl in all three melts is 450–475 mM under 1 atm of HCl, approximately the same as that in the acidic (AlCl<sub>3</sub>-rich) melts. The relative solubility products of LiCl, NaCl, and KCl were measured, and it was found that  $K_{sp}(\text{NaCl})/K_{sp}(\text{LiCl}) = 72 \pm 6$  and  $K_{sp}(\text{KCl})/K_{sp}(\text{NaCl}) = 1000 \pm 400$ . It is likely that the differences in the acidity of HCl in the various melts are due to the differences in the solubility product of the relevant alkali metal chlorides. These ratios are consistent with the results of previous studies on the acidity of HCl in the melts. The concentrations of the strongly Lewis acidic Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> ion in melts buffered with LiCl were measured using an aluminum electrode. The results of the potentiometric work indicate that a melt containing 1 M Li<sup>+</sup> (approximately  $n_{\text{AlCl}_3}/n_{\text{EMIC}} = R = 1.25:1$  prior to buffering) would contain about 200 μM Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup>. This corresponds to a solubility product of about  $(1.5 \pm 0.5) \times 10^{-12} \text{ M}^2$ . The liquid junction potentials between unbuffered and buffered melts were found to be about 49 mV × ([Li<sup>+</sup>]/M). These results are related to previous work on the acidity of HCl in these melts, and it is shown that it is possible to explain many of the acidity and latent acidity results on the basis of the solubility products of the alkali metal chlorides.

### Introduction

1-Ethyl-3-methylimidazolium chloride (EMIC)–AlCl<sub>3</sub> room-temperature molten salts, produced by mixing AlCl<sub>3</sub> and EMIC, are liquid over a wide range of mole ratios and have a wide electrochemical window.<sup>1</sup> These melts are defined as acidic, basic, or neutral if the AlCl<sub>3</sub>:EMIC mole ratio (referred to as *R*) is greater than, less than, or equal to 1, respectively. The strongly Lewis acidic Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> ion acts as the main acidic species in the acidic melts, while the weakly Lewis basic Cl<sup>−</sup> ion acts as the main basic species in the basic melts. It has been found<sup>2</sup> that it is possible to buffer acidic melts to neutrality by stirring with solid alkali metal chlorides. The alkali metal chloride reacts with excess Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> in the melt, forming the AlCl<sub>4</sub><sup>−</sup> ion (eq 4). When all the Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> has reacted, the solubility of the metal chloride in the melt is minimal, so the resulting melt has very low concentrations of both Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup> and Cl<sup>−</sup>. The concentrations of both these ions are too low to detect voltammetrically,<sup>2</sup> so the resulting “neutral buffered” melts have an electrochemical window of about 4.4 V at a Pt electrode, considerably wider than those of either the basic (2.6 V—limited by oxidation of chloride) or the acidic (2.2 V—limited by the deposition of aluminum from Al<sub>2</sub>Cl<sub>7</sub><sup>−</sup>) melts.

The acid–base and buffering chemistry of the melt can be defined by the following equations:



Equation 3 may be regarded as the “solvolysis” reaction. The acidity of the melts can be defined by the concentration of the chloride ion, or by the pCl value, where  $\text{pCl} = -\log([\text{Cl}^-]/\text{M})$ . The pCl value may be regarded as the equivalent of the pOH value in water, as chloride is a Lewis base.

King et al.<sup>3</sup> have measured the acidity of HCl in various neutral buffered melts, using arenes as weak indicator bases. Mantz et al.<sup>4</sup> have measured the Gutmann acceptor numbers of the neutral buffered melts themselves. Both the Brønsted and Lewis acidities decrease in the following order according to the buffering agent:



The reasons for this have not previously been investigated and are the focus of this paper.

Quarmby and Osteryoung<sup>5</sup> reported that acetylferrocene (AcFc), which forms an AlCl<sub>3</sub> adduct in acidic but not in basic melts, also forms an adduct in the neutral buffered melts. The

<sup>†</sup> Present address: Cycolor, Inc., 3385 Newmark Dr., Miamisburg, OH 45342.

(1) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263–4.

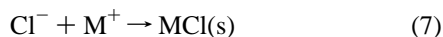
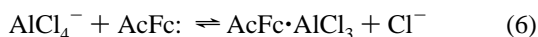
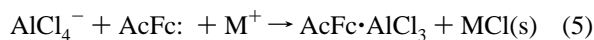
(2) Melton, T. J.; Joyce, J.; Maloy, T. J.; Boon, J. A.; Wilkes, J. S. *J. Electrochem. Soc.* **1990**, *137*, 3865–9.

(3) King, D.; Mantz, R. A.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11933–8.

(4) Mantz, R. A.; Trulove, P. C.; Carlin, R. T.; Theim, T. L.; Osteryoung, R. A. *Inorg. Chem.* **1997**, *36*, 1227–32.

(5) Quarmby, I. C.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 2649–50.

source of  $\text{AlCl}_3$  was proposed to be the  $\text{AlCl}_4^-$  ion, which is normally too weak a Lewis acid to form the adduct. This property has been termed "latent acidity". The formation of  $\text{AlCl}_3$  adducts is probably driven by the precipitation of chloride (formed when a base removes  $\text{AlCl}_3$  from the  $\text{AlCl}_4^-$  ion) by the alkali metal cation. The "latent acidity" reactions can therefore be written as



Equation 5 is eq 6 plus eq 7. If the latent acidity is driven by the precipitation of the alkali metal chloride, then the equilibrium constant for eq 5,  $\text{AlCl}_3$  adduct formation, will depend on the equilibrium constant for eq 7, which is the reciprocal of the solubility product of  $\text{MCl}$ . Reaction 6 does not proceed, while reaction 5 does.

It is possible that the difference in the acidity of melts buffered with different alkali metal chlorides may be due to differences in the residual concentrations of chloride and  $\text{Al}_2\text{Cl}_7^-$  in the melts and, therefore, may be the result of differences in the solubility product of the different alkali metal chlorides. In a neutral buffered melt, if as much alkali metal chloride as possible has dissolved and reacted (i.e., if the melt is fully buffered), it is possible to define a solubility product for the alkali metal chloride as

$$K_{\text{sp}} = [\text{M}^+][\text{Cl}^-] \quad (8)$$

The solubility product and the concentration of the alkali metal ion will define the concentration of chloride (eq 9) and of  $\text{Al}_2\text{Cl}_7^-$  (eq 10, derived from eqs 9 and 3):

$$[\text{Cl}^-] = K_{\text{sp}}/[\text{M}^+] \quad (9)$$

$$[\text{Al}_2\text{Cl}_7^-] = K_3[\text{M}^+][\text{AlCl}_4^-]^2/K_{\text{sp}} \quad (10)$$

where  $K_3$  is the equilibrium constant for reaction 3. Therefore, as  $K_3$  is constant and  $[\text{AlCl}_4^-]$  is approximately constant for neutral buffered melts, the acidity (defined as the concentration of  $\text{Al}_2\text{Cl}_7^-$ ) is determined by  $K_{\text{sp}}$  and the concentration of  $\text{M}^+$ . Due to the complexity of the systems, it is possible that the value of  $K_{\text{sp}}$  may not be constant as  $[\text{M}^+]$  changes. However, for now it will be assumed that  $K_{\text{sp}}$  is constant.

The solubility products may be defined as follows for the different alkali metal chlorides:

$$K_{\text{sp}}(\text{Li}) = [\text{Li}^+][\text{Cl}^-] \quad (11)$$

$$K_{\text{sp}}(\text{Na}) = [\text{Na}^+][\text{Cl}^-] \quad (12)$$

$$K_{\text{sp}}(\text{K}) = [\text{K}^+][\text{Cl}^-] \quad (13)$$

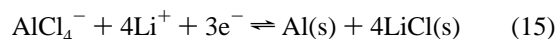
If a melt is buffered with both  $\text{LiCl}$  and  $\text{NaCl}$ , then both eqs 11 and 12 must hold. If eq 12 is divided by eq 11, then the  $[\text{Cl}^-]$  term is eliminated, giving

$$K_{\text{sp}}(\text{Na})/K_{\text{sp}}(\text{Li}) = [\text{Na}^+]/[\text{Li}^+] \quad (14)$$

Therefore, by buffering an acidic melt with two alkali metal chlorides and then filtering and analyzing for the two alkali

metal ions, it would be possible to measure the relative values of the solubility product. This method would not give an absolute value for either solubility product but would only show that the measured amounts of the two alkali metal ions in the melt would give the same residual chloride concentration. This would give the ratio of the two solubility products.

No reports have been published on the solubility products of the alkali metal chlorides in the melts or on the concentrations of chloride or  $\text{Al}_2\text{Cl}_7^-$  in the neutral buffered melts. Melton et al.<sup>2</sup> have reported the solubility of  $\text{NaCl}$  in the basic melts, but the solubilities reported are quite high, and it is possible that anionic complexes such as  $\text{NaCl}_2^-$  may be formed. Reichel and Wilkes<sup>6</sup> have reported an estimate of the concentration of  $\text{Al}_2\text{Cl}_7^-$  (about 2.8 mM) in a  $\text{NaCl}$ -buffered melt (originally  $R = 1.22:1$ ) from the position of a small peak, assumed to be aluminum deposition from the  $\text{Al}_2\text{Cl}_7^-$  ion. Carlin et al.<sup>7</sup> have observed the same peak but attribute it to the deposition of aluminum from the  $\text{AlCl}_4^-$  ion, facilitated by the presence of the  $\text{Li}^+$  or  $\text{Na}^+$  cation:



We also attempted to determine the solubility product for  $\text{LiCl}$  using an aluminum electrode in the neutral buffered melt. The electrode reaction is



The Al electrode has been found to be unstable in the basic melts,<sup>8</sup> and the potential of the Al electrode is

$$E = \frac{4RT}{3F} \ln \frac{[\text{Al}_2\text{Cl}_7^-]_{\text{melt}}}{[\text{Al}_2\text{Cl}_7^-]_{\text{ref}}} + \frac{7RT}{3F} \ln \frac{[\text{AlCl}_4^-]_{\text{ref}}}{[\text{AlCl}_4^-]_{\text{melt}}} + \Delta\Phi \quad (18)$$

assuming the activity coefficients are equal in both melts.  $\Delta\Phi$  is the liquid junction potential. It was therefore necessary to first determine the liquid junction potentials. Although these potentials will be referred to as liquid junction potentials, they may also include potential changes due to changes in activity coefficients or other nonideal terms.

## Experimental Section

The preparation of EMIC, by reaction of ethyl chloride with 1-methylimidazole, followed by recrystallization from acetonitrile/ethyl acetate, has been described previously.<sup>1,9</sup> Aluminum chloride (Fluka, puriss. >99%) was distilled in a sealed, high-pressure glass tube. Basic (EMIC-rich) melts were prepared by mixing the appropriate amounts of EMIC and  $\text{AlCl}_3$ , and then protons and oxide were removed by the application of a high vacuum and by treatment with phosgene, respectively.<sup>10,11</sup> More  $\text{AlCl}_3$  was then added to bring the melt to the required mole ratio. All work was carried out in a glovebox filled with dry nitrogen.

- (6) Reichel, T. L.; Wilkes, J. S. *J. Electrochem. Soc.* **1993**, *140*, 3104–7.
- (7) Carlin, R. T.; Fuller, J.; Kuhn, W. K.; Lysaght, M. J.; Trulove, P. C. *J. Appl. Electrochem.* **1996**, *26*, 1147–60.
- (8) Hussey, C. L.; Scheffler, T. B.; Wilkes, J. S.; Fannin, A. A. *J. Electrochem. Soc.* **1986**, *133*, 1389–91.
- (9) Trulove, P. C.; Osteryoung, R. A. *Inorg. Chem.* **1992**, *31*, 3980–5.
- (10) Zawodinski, T. A., Jr.; Carlin, R. T.; Osteryoung, R. A. *Anal. Chem.* **1987**, *59*, 2639–40.
- (11) Sun, I. W.; Ward, E. H.; Hussey, C. L. *Inorg. Chem.* **1987**, *26*, 4309–11.

**Safety note: Phosgene is extremely toxic, and care must be exercised in its use. The distillation of  $\text{AlCl}_3$  is also hazardous, and care should be exercised.**

The solubility of HCl in the melts was measured using the vacuum system shown in the Supporting Information. The solubility was determined by filling the ballast flask (of known volume, determined by weighing empty and filled with distilled water) with a measured pressure of HCl, while the rest of the system (including the melt flask) was evacuated. The HCl was then allowed to flow into the melt flask and the rest of the system, allowing HCl to dissolve into the melt. The volume of the system, including the melt flask, was determined by carrying out the experiment without any melt in the flask; from the change in pressure, it was possible to calculate the volume of the complete system. From the difference in the new pressure of the HCl and the pressure expected from ideal gas expansion of the gas, it was possible to determine the amount of HCl which had dissolved in the melt. The effects of deviations from ideal gas behavior were calculated and were found to be under 2%. The solubility of HCl is calculated by assuming ideal gas behavior for HCl.

The relative solubility product experiments were carried out by first preparing melts of known acidity and then stirring the melts with solid LiCl and NaCl or with solid NaCl and KCl. After this, the melts were filtered through 1 and 0.2  $\mu\text{m}$  filters (Whatman, glass microfiber syringe filters), to remove solid metal chlorides. The melts were then removed from the glovebox and hydrolyzed, and the solutions were analyzed for the two metals by atomic emission spectroscopy. All glassware was soaked overnight in concentrated nitric acid to remove alkali metal and heavy metal ions.

It was found that the melts buffered with LiCl/NaCl came to equilibrium (constant Na:Li ratio) within about 3–7 days, while melts buffered with NaCl/KCl needed at least a month. Because the ratio of  $\text{K}^+$  to  $\text{Na}^+$  in these melts was large (about 1000:1—see below) and because the maximum concentration of  $\text{K}^+$  which can be dissolved in the melt is not very high (about 400–600 mM), the maximum equilibrium sodium concentration is low, and considerable scatter in the NaCl/KCl data is observed. It is likely that this is due to residual contamination by  $\text{Na}^+$ .

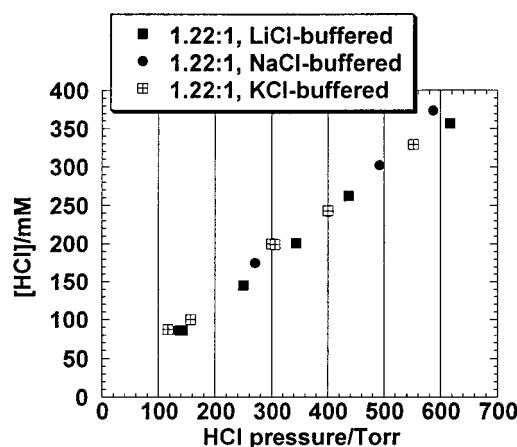
The concentration of  $\text{Al}_2\text{Cl}_7^-$  in the melt was determined using the following potentiometric cell:



It was found that the potential of the Al electrode in the melts required several days to stabilize. Aluminum electrodes gave a relatively stable and reproducible potential in LiCl-buffered melts, but the potential was less stable and reproducible in NaCl- and KCl-buffered melts. It is known<sup>8</sup> that the Al electrode is unstable in basic melts. Once the electrode potentials had stabilized in the LiCl-buffered melts, they remained constant to  $\pm 1$  mV.

The liquid junction potentials were determined by measuring the potential of an Al electrode in an acidic ternary LiCl–EMIC– $\text{AlCl}_3$  melt (an acidic melt partly buffered with LiCl). From the amounts of the three components, the concentrations of  $\text{Li}^+$ ,  $\text{AlCl}_4^-$ , and  $\text{Al}_2\text{Cl}_7^-$  can be calculated. From the concentrations of  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$ , the “expected” potential of the electrode can be calculated by using eq 18, assuming  $\Delta\Phi = 0$ , and then  $\Delta\Phi$  can be calculated as the difference between the “expected” and the measured potentials. The experiments were carried out by preparing an acidic melt, buffering a part of the melt with LiCl, and then mixing the buffered and unbuffered melts in different proportions. From the initial mole ratio and the proportions of buffered and unbuffered melts used, the concentrations of  $\text{Li}^+$ ,  $\text{AlCl}_4^-$ , and  $\text{Al}_2\text{Cl}_7^-$  could be calculated. The potential of an Al electrode in these partly buffered melts was determined and was compared with the “theoretical” potentials.

The complexation of acetylferrocene was determined using cyclic staircase voltammetry (500 mV/s, at a glassy carbon working electrode, 3 mm<sup>2</sup>, with an Al counter electrode). The reference electrode in all cases was an Al wire in an  $\text{R} = 1.5:1$  acidic melt. Uncomplexed acetylferrocene has an oxidation potential of about +0.7 V, while the  $\text{AlCl}_3$  complex has an oxidation potential of about +1.1 V.



**Figure 1.** Plot of the solubility of HCl in neutral buffered melts vs the HCl pressure, at  $23 \pm 2$  °C.

**Table 1.** Solubilities of HCl in Neutral Buffered Melts, at  $23 \pm 2$  °C (Initially  $R = 1.22:1$ )

buffered with LiCl		buffered with NaCl		buffered with KCl	
HCl pressure, Torr	[HCl], mM	HCl pressure, Torr	[HCl], mM	HCl pressure, Torr	[HCl], mM
143	86	133	86	117	87
250	145	270	175	157	100
344	201	401	242	299	200
437	262	492	302	306	199
617	357	587	374	400	243
				552	329

All experiments were carried out at  $23 \pm 2$  °C.

## Results and Discussion

The solubility of HCl in 55 mol %  $\text{AlCl}_3$  melts ( $R = 1.22$ ) buffered with LiCl, NaCl, and KCl was measured. The results are shown in Table 1, as well as in Figure 1.

The data points were fitted to the following equation:

$$[\text{HCl}]/\text{mM} = a(p/\text{Torr}) \quad (19)$$

The values of  $a$  for the three melts with initial  $R = 1.22:1$  are  $a_{\text{MCl-buffered}} = 0.585 \pm 0.005$ ,  $0.625 \pm 0.008$ , and  $0.62 \pm 0.04$  for  $\text{MCl} = \text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$ , respectively.

The differences between the solubility of HCl in the different melts were small and were certainly not enough to account for the large difference in the acidity of HCl. The value of the solubility measured here is only slightly lower than the solubility measured for a 1.22:1 acidic melt by Campbell and Johnson.<sup>12</sup> This indicates that the difference in the acidity of HCl in the different melts is not due to different solubility of HCl.

The results for the relative solubility of LiCl and NaCl in the melts are shown in Table 2 and graphically in Figure 2. It can be seen that the value of  $K_{\text{sp}}(\text{Na})/K_{\text{sp}}(\text{Li})$  does not vary with the initial mole ratio, and the average value of the ratio is  $72 \pm 6$ , with NaCl being more soluble. In the case of the relative solubility of NaCl and KCl, the scatter is larger, and the average value is about  $1000 \pm 400$ , with KCl being more soluble than NaCl. The results are shown in Table 2.

There is considerable scatter in the results for the solubility ratios in both cases. The most likely cause of this scatter is contamination by stray solid particles of the less soluble alkali metal chloride. In the case of the Na/K concentration results, the  $\text{K}^+$  concentration would be in the range 180–450 mM,

(12) Campbell, J. L. E.; Johnson, K. E. *J. Am. Chem. Soc.* **1995**, *117*, 7791–7800.

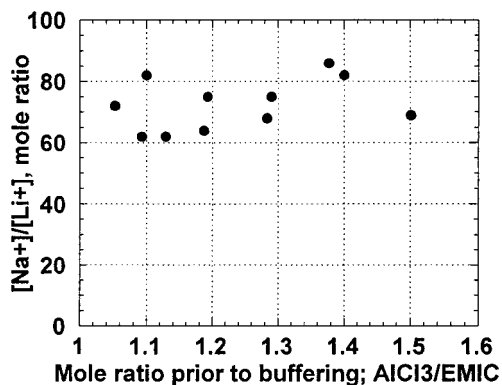


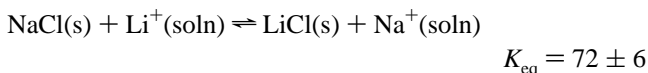
Figure 2. Relative solubility products of NaCl and LiCl, at  $23 \pm 2$  °C.

Table 2. Ratios of Alkali Metals in Mixed Buffered Melts, at  $23 \pm 2$  °C

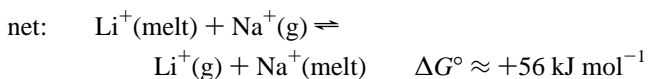
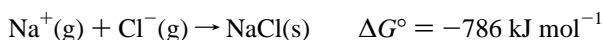
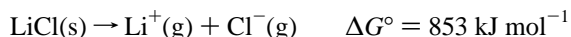
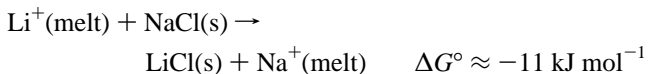
Na/Li		K/Na	
initial <i>R</i>	Na:Li mole ratio	initial <i>R</i>	K:Na mole ratio
1.05	72	1.04	840
1.09	62	1.05	890
1.10	82	1.09	1300
1.13	62	1.10	840
1.19	64		
1.19	75		
1.28	68		
1.29	75		
1.38	86		
1.40	82		
1.50	69		

giving a  $\text{Na}^+$  concentration of 200–500  $\mu\text{M}$ , or about 10–15  $\mu\text{g}$  of  $\text{Na}^+$  in the 1 g melt samples filtered. In the case of the Li/Na results, LiCl breaks up very easily into an extremely fine powder, and therefore it is more likely that stray particles will pass through the filter. It is therefore likely that the scatter is due to stray solid particles.

From the results for LiCl and NaCl



Using the thermochemical cycle lattice energies<sup>13</sup> for LiCl and NaCl gives



This gives the result that  $\text{Li}^+$  is more strongly solvated than  $\text{Na}^+$  and indicates that the higher solubility of NaCl is due to the difference in lattice energy, not to  $\text{Na}^+$  being more strongly solvated. This is in agreement with  $\text{Li}^+$  normally being the most strongly solvated of the alkali metal cations. Similar calculations show that  $\text{Na}^+$  is more strongly solvated than  $\text{K}^+$ , by about 54  $\text{kJ mol}^{-1}$ .

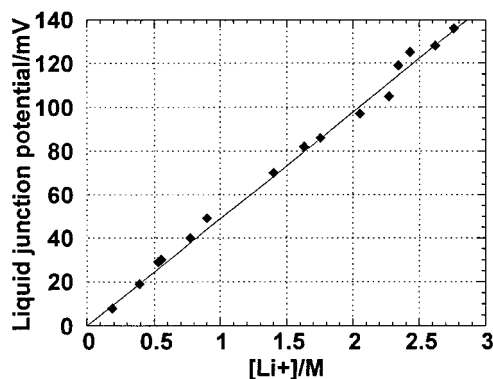


Figure 3. Liquid junction potentials between a 1.5:1 melt and a LiCl-buffered melt vs concentration of  $\text{Li}^+$ , at  $23 \pm 2$  °C.

Since the concentration of  $\text{Na}^+$  required to give a certain concentration of chloride is about 72 times the concentration of  $\text{Li}^+$  required to give the same concentration of chloride, it may be said that the solubility product for NaCl is 72 times as large as that for LiCl.

From the work of King et al.,<sup>3</sup> the protonation ratio (i.e., ratio of protonated to unprotonated arene) of hexamethylbenzene in the LiCl-buffered melt is about  $40 \pm 6$  times larger than that in NaCl-buffered melts. This ratio is of the same order as the ratio obtained here for solubility products, as would be expected if the acid strength were dependent on the solubility product.

The results for the liquid junction potentials are shown in tabular form in the Supporting Information and graphically in Figure 3. The calculated values of  $\Delta\Phi$  were fitted to a linear function of the concentration of the  $\text{Li}^+$  ion and the acidity of the melt, giving

$$\Delta\Phi/\text{mV} = (49 \pm 2)([\text{Li}^+]/\text{M}) \quad (20)$$

with the LiCl-buffered melts more positive than the unbuffered melts.

To calculate the “theoretical” potentials from eq 18, it was necessary to know the concentration of  $\text{AlCl}_4^-$ . For this, it was necessary to know the density of the melts, and the data of Elias and Wilkes<sup>14</sup> were used for this.

To calculate the value of  $K_{\text{sp}}$  for each data point, the potential and the calculated value of  $\Delta\Phi$  were put into eq 18 to obtain the concentration of  $\text{Al}_2\text{Cl}_7^-$ . From this and equilibrium 3, the concentration of chloride could be calculated, and from this and the (known) concentration of  $\text{Li}^+$ , the solubility product was calculated.

The results of the potentiometric work are shown in tabular form in the Supporting Information. The measured values of the solubility product for LiCl vary from  $0.5 \times 10^{-12}$  to  $3.3 \times 10^{-12} \text{ M}^2$ . The average value for  $\log(K_{\text{sp}}/\text{M}^2)$  is  $-11.8 \pm 0.1$ , corresponding to an average value of  $K_{\text{sp}}$  of approximately  $(1.5 \pm 0.5) \times 10^{-12} \text{ M}^2$ . The values of  $K_{\text{sp}}$  are calculated using the value of the equilibrium constant for eq 3 as  $K_{\text{eq}} = 10^{-17}$ . There is still some uncertainty as to the value of  $K_3$ , and the value of  $K_3$  affects the calculated value of  $K_{\text{sp}}$ , as  $K_3$  is needed to calculate the chloride concentration from the concentration of  $\text{Al}_2\text{Cl}_7^-$ . Therefore, this uncertainty in the value of  $K_3$  may introduce a systematic error in the calculated value of  $K_{\text{sp}}$ . However, the measured concentrations of  $\text{Al}_2\text{Cl}_7^-$ , for which a knowledge of the value of  $K_3$  is not necessary, will not be subject to this error.

Because of this difficulty, the concentrations of  $\text{Al}_2\text{Cl}_7^-$  were also fitted to a proportional function of the concentrations of

(13) *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986.

(14) Elias, A. M.; Wilkes, J. S. *J. Chem. Eng. Data* **1994**, *39*, 79–82.

$\text{Li}^+$ . The data were fitted, using a least-squares fit, to the function

$$[\text{Al}_2\text{Cl}_7^-] = x[\text{Li}^+] \quad (21)$$

The least-squares fit was for  $x = (200 \pm 20) \times 10^{-6}$ . This indicates that a melt containing 1 M  $\text{Li}^+$  (about  $R = 1.25:1$  before buffering) would contain 200  $\mu\text{M}$   $\text{Al}_2\text{Cl}_7^-$ , making it much more acidic than a true neutral melt, which contains about  $10^{-8}$  M  $\text{Al}_2\text{Cl}_7^-$ .

Because of the complexity of these melt systems, it is possible that the solubility products for the alkali metal chlorides might not be constant but might vary with the concentration of alkali metal ion. The logarithm of the calculated solubility product for LiCl was fitted to the function

$$\log(K_{\text{sp}}/M^2) = a + b[\text{Li}^+] \quad (22)$$

this gave the values

$$a = -12.0 \pm 0.2 \quad b = 0.12 \pm 0.07 \text{ M}^{-1}$$

The data indicate only a small variation of  $K_{\text{sp}}$  with the concentration of lithium. From the data for the relative solubility product values, it can be seen that the ratios do not vary significantly with the initial mole ratio. This indicates that, if the solubility products do vary with the acidity, the solubility products for LiCl, NaCl, and KCl vary in the same way. Although this is possible, it seems more likely that the solubility products are approximately constant.

Equation 18, used for the determination of the concentration of  $\text{Al}_2\text{Cl}_7^-$ , and thus of the solubility product for LiCl, assumes that the activity coefficient for  $\text{Al}_2\text{Cl}_7^-$  is the same in the neutral buffered and in the reference melt, and likewise for  $\text{AlCl}_4^-$ . It seems likely<sup>7</sup> that the  $\text{AlCl}_4^-$  ion may interact with  $\text{Li}^+$ , and this may change the activity coefficient for  $\text{AlCl}_4^-$  in a neutral buffered melt. However, as the melts used to calculate  $\Delta\Phi$  also contain  $\text{Li}^+$ , the possible effects of  $\text{Li}^+$  in changing the activity coefficient of the  $\text{AlCl}_4^-$  ion will be included in the value of  $\Delta\Phi$ , so the calculated value of  $[\text{Al}_2\text{Cl}_7^-]$  should be correct.

If the "latent acidity" (enhancement of acidity due to the precipitation of LiCl) affects the activity coefficients, or affects the potential in any other way, then this will cause an error in the calculated concentration of  $\text{Al}_2\text{Cl}_7^-$  and the value of  $K_{\text{sp}}$ . However, this seems unlikely, as no basic indicator is used and no plausible electrode reaction would release any basic species, which would cause the precipitation of LiCl.

It should be noted that, as the aluminum electrode potentiometric measurements would only give the concentration of  $\text{Al}_2\text{Cl}_7^-$ , it will not show the "latent acidity" of the melt. Therefore, if the acidity of the melt were to be determined by measurements of complexation of a basic indicator, then this might show the melt as being more acidic, as the latent acidity of the melt will affect a basic indicator but would not affect the potential of an aluminum electrode.

Reichel and Wilkes<sup>6</sup> have reported that a small Al deposition peak is observed in NaCl-buffered melts and have inferred that the concentration of  $\text{Al}_2\text{Cl}_7^-$  in an  $R = 1.22:1$  melt buffered by NaCl is approximately 2.8 mM. From our results for LiCl-buffered melts and the relative solubility products, we would calculate that the residual  $\text{Al}_2\text{Cl}_7^-$  concentration in such a melt would be about 1–5  $\mu\text{M}$ . This seems more reasonable, as, if the  $\text{Al}_2\text{Cl}_7^-$  concentration in a NaCl-buffered melt is about 3 mM, then (from our results for the relative solubility products)

in a LiCl-buffered melt it should be about 200 mM, which would easily be detectable by voltammetry.

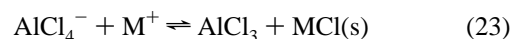
The concentrations of  $\text{Al}_2\text{Cl}_7^-$  and  $\text{Cl}^-$  in a true neutral melt would be between  $10^{-8}$  and  $10^{-9}$  M, so these results show that the neutral buffered melts are considerably more acidic than a true neutral melt. From our results, the concentration of  $\text{Al}_2\text{Cl}_7^-$  in a 1.2:1 melt buffered with LiCl is about 150  $\mu\text{M}$ , in the same melt buffered with NaCl it would be about 2  $\mu\text{M}$ , and in a KCl-buffered melt it would be approximately 2 nM.

Finally, in the case of the work on acetylferrocene, it was found that AcFc is complexed by  $\text{AlCl}_3$  in all buffered melts except those buffered by CsCl. Therefore, the order of base strength is

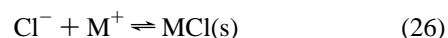
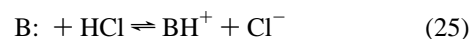


This work suggests strongly that the differences in the "latent acidity" of the different neutral buffered melts are due to differences in the solubility products of the different alkali metal chlorides used to buffer the melts. If the solubility product of LiCl is lower than that of NaCl, then, for a given concentration of  $\text{Li}^+$  or  $\text{Na}^+$ , the chloride concentration will be lower if the alkali metal ion is  $\text{Li}^+$  than if it is  $\text{Na}^+$ . If the concentration of  $\text{Cl}^-$  is lower in the LiCl-buffered melt, then the concentration of  $\text{Al}_2\text{Cl}_7^-$  will be higher. As the acidity of the melt may be defined in terms of the concentrations of  $\text{Al}_2\text{Cl}_7^-$  (a strong Lewis acid) and chloride (a weak Lewis base), this would explain the reason LiCl-buffered melts are more acidic.

It has been argued by Quarmby and Osteryoung<sup>5</sup> that the presence of the alkali metal ion, which can precipitate the chloride ion, enhances the relative acidity of the  $\text{AlCl}_4^-$  ion, and a related argument has been put forward by Carlin et al.<sup>7</sup> In this case, the  $\text{Li}^+$  ion, which precipitates chloride more strongly, would drive reaction 23 further to the right, making the  $\text{AlCl}_4^-$  ion more acidic.



The effect of the buffering agent on the acidity of  $\text{HCl}^3$  can also be explained in terms of the alkali metal chloride solubility product. The reaction of HCl protonating a base in a buffered melt would be represented by reaction 24, which is reaction 25 plus reaction 26.



Therefore the equilibrium constant of reaction 25, which is the reciprocal of the solubility product of MCl, will determine the equilibrium constant for reaction 24, the protonation of a Brønsted base in the buffered melt.

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**Supporting Information Available:** Full listings of the results of the measurements of the liquid junction potentials and of the potentiometric measurements of the LiCl solubility products and a diagram showing the vacuum system used for the HCl solubility measurements (3 pages). Ordering information is given on any current masthead page.