

^1H and ^{13}C Nuclear Magnetic Resonance Spectroscopy Studies of Aluminum Halide-Alkylpyridinium Halide Molten Salts and Their Benzene Solutions

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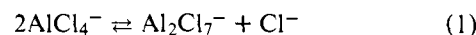
Abstract: The electrical conductivity, density, viscosity, and electrochemical window of four low-temperature molten salt systems (2:1 AlCl_3 -*n*-butylpyridinium chloride, 1:1 AlCl_3 -*n*-butylpyridinium chloride, 2:1 AlCl_3 -ethylpyridinium bromide, and 2:1 AlBr_3 -ethylpyridinium bromide) as well as their mixtures with benzene are reported. The nature of the interactions occurring as the melt is diluted with benzene were investigated using ^1H and ^{13}C nuclear magnetic resonance spectroscopy. The addition of benzene to the melts causes a decrease in the dielectric constant of the medium resulting in ion pair formation between the alkylpyridinium cations and the anions in the melt. No evidence was found for the formation of complexes between benzene and AlCl_3 in the melt.

Introduction

In the past decade there have been a considerable number of reports in the literature of chemical, electrochemical, and spectroscopic studies of both organic and inorganic species in tetrachloroaluminate melts (AlCl_3 -alkali metal chloride mixtures) and the chemical and physical properties of these solvent systems are now fairly well understood.^{1,2} A recent innovation in this area of molten salt research has been the development of AlCl_3 -based fused salts that are molten at or near room temperature. The first such system, a 2:1 AlCl_3 -ethylpyridinium bromide (EtpyBr) mixture, was proposed by Hurley and Weir in 1951^{3,4} and a number of patents by the same authors concerning the use of this melt, and mixtures of the melt with benzene or toluene, as aluminum plating baths were also granted.⁵ No further advances appear to have been made in this area, however, until 1975 with the publication by Chum et al.⁶ of a paper demonstrating the suitability of the 2:1 AlCl_3 -EtpyBr solvent system for the electrochemical investigation of a number of organometallic compounds and hexamethylbenzene. Subsequently there have been several reports by Osteryoung and co-workers of the use of this solvent for both electrochemical^{7,8} and photochemical investigations.⁹ It has also been shown⁷ that this molten salt system is miscible with benzene affording a solvent (50% vol ratio) suitable for both mechanistic and synthetic organic electrochemistry.

As the composition of an alkali metal tetrachloroaluminate melt is varied its Lewis acidity changes also,¹⁰ giving rise to some interesting effects in the electrochemistry of both organic¹¹ and inorganic¹² species. Unfortunately the AlCl_3 -EtpyBr system is only molten at room temperature for the 2:1 mole ratio mixture, and as the mole fraction of AlCl_3 is changed from this value the melting point of the melt rises sharply. We have, however, recently found a system,¹³ AlCl_3 -*n*-butylpyridinium chloride (BupyCl), which is molten at 40 °C over a wide composition range (0.75:1 to 2:1) while the 2:1 mixture, like the EtpyBr-based system, is molten at room temperature. Raman studies of the AlCl_3 -BupyCl melt¹⁴ show that the aluminum in the 1:1 mixture is present entirely as AlCl_4^- ions whereas in the 2:1 system it is present as the Al_2Cl_7^- species. This is in contrast to the behavior of the alkali metal tetrachloroaluminates, where AlCl_4^- and Al_2Cl_7^- ions, as well as molecular Al_2Cl_6 , are present at all melt compositions. A subsequent potentiometric study¹⁵ has shown that the

acid-base properties of the AlCl_3 -BupyCl system can be simply described by one equilibrium:



where Al_2Cl_7^- is the Lewis acid and Cl^- the Lewis base. The equilibrium constant for eq 1 at 30 °C was shown to be 3.83×10^{-13} .

This present paper is concerned with some of the physical properties (density, conductivity, viscosity, and electrochemical window) of three alkylpyridinium halide-aluminum halide molten salt systems and their mixtures with benzene. The principal melt of interest is the AlCl_3 -BupyCl system, which appears to be the most useful, both from the acidity variation point of view as discussed above and also because it has the largest electrochemical window (vide infra). Data will also be presented for the mixed halide 2:1 AlCl_3 -EtpyBr system and the total bromide 2:1 AlBr_3 -EtpyBr melt. The nature of the interactions involved when these melts are diluted with benzene has also been investigated with ^1H and ^{13}C nuclear magnetic resonance spectroscopy. ^1H NMR has been used with success in the study of metal halide-pyridinium halide systems^{16,17} and molten pyridinium salts^{18,19} but ^{13}C NMR does not appear to have been applied previously to the study of any molten salts.

Experimental Section

The alkylpyridinium halide salts were prepared and purified as has been previously described.^{7,13} Those melts based upon EtpyBr were prepared by mixing the salt with either AlCl_3 (Fluka A.G. iron free) or AlBr_3 (Fisher ACS) and were purified by preelectrolysis between two aluminum electrodes. Recent work¹³ has shown that purer melts result if carefully sublimed AlCl_3 is used; the BupyCl based melts were therefore prepared in this way and were used without further purification. All preparations and determinations, except the NMR experiments, were carried out under an argon atmosphere in a drybox (Vacuum Atmospheres Co.) fitted with a purification system (Vacuum Atmospheres Co. Model HE-493 or HE-193-2 Dri Trains). The NMR tubes were filled and capped in the drybox prior to transfer to the spectrometer.

Viscosity measurements were made with an Ostwald viscosimeter calibrated at the temperature of the experiment according to standard procedures. Conductivity measurements were performed using an immersion-type conductivity cell with platinum electrodes (Yellow Springs Instrument Co. Model 3401) in conjunction with a conductivity bridge (Yellow Springs Instrument Co. Model 31) operating at a frequency of 1 kHz. The cell was calibrated using KCl solutions. Those experiments performed above ambient temperature were made in a wire-wound furnace the temperature of which was maintained within ± 1 °C by a controller (Thermo-Electric Model 32422) in conjunction with a chromel-alumel thermocouple.

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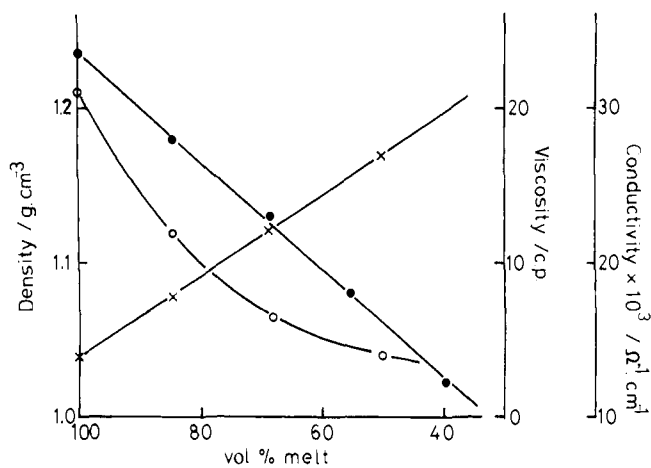


Figure 1. Plots of density (●), viscosity (○), and conductivity (x) of the 1:1 AlCl_3 -BupyCl melt and its mixtures with benzene. Data at 40 °C.

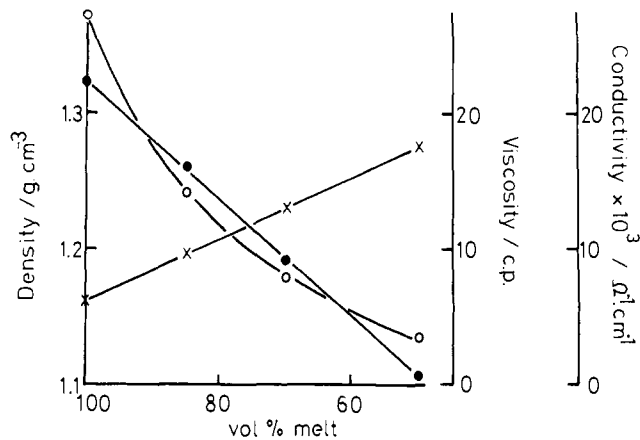


Figure 2. Plots of the density (●), viscosity (○), and conductivity (x) of the 2:1 AlCl_3 -BupyCl melt and its mixtures with benzene. Data at 25 °C.

Table I. Physical Properties of Some Alkylpyridinium Halide-Aluminum Halide Melts

melt	temp/ °C	density/ g cm^{-3}	viscosity/ cP	electro- chemical window/V ^a
2:1 AlCl_3 -BuPyCl	25	1.33	27.0	0.0-2.1
1:1 AlCl_3 -BuPyCl	40	1.24	20.9	-0.4 to 2.0
2:1 AlCl_3 -EtPyBr	25	1.52	25.0	-0.2 to 1.8
2:1 AlBr_3 -EtPyBr	25	2.20	~50	0.2-1.6

^a At a glassy carbon electrode vs. an Al wire reference electrode in the same melt.

The ^1H NMR measurements were made on a JEOLCO MH100 100-MHz spectrometer, a Varian EM 360A 60-MHz spectrometer, or a JEOLCO FX100 Fourier transform spectrometer and the ^{13}C NMR measurements were also made on the latter instrument. The Fourier transform spectrometer was operated with an external deuterium lock and in the ^{13}C mode the protons were noise decoupled. All measurements were made using 5-mm tubes and chemical shifts are reported as parts per million downfield from an internal Me_4Si reference (concentration approximately 2%).

Results and Discussion

Four molten salt systems were investigated (2:1 AlCl_3 -EtpyBr, 2:1 AlBr_3 -EtpyBr, 2:1 AlCl_3 -BupyCl, and 1:1 AlCl_3 -BupyCl) and the values of the density, viscosity, and electrochemical window at a glassy carbon electrode of these systems are given in Table I. These results are reported for 25 °C except for the 1:1 AlCl_3 -BupyCl melt, which has a melting point of 27.0 ± 1.0 °C¹³ and was therefore run at 40 °C. It is immediately seen that the total chloride melts have the largest electrochemical windows due to the higher oxidation potential of chloride ions compared to bromide. The negative value for the cathodic limit of the 1:1 AlCl_3 -BupyCl melt is due to the large nucleation overpotential for Al deposition on glassy carbon electrodes which will be discussed in a future publication.²⁰ A similar effect is probably occurring in the 2:1 AlCl_3 -EtpyBr system also.

It has been shown previously⁷ that mixing the 2:1 AlCl_3 -EtpyBr melt with benzene produces a solvent that is very useful for organic electrosynthesis. The effect this benzene dilution has on the melt density, conductivity, and viscosity of the 1:1 and 2:1 AlCl_3 -BupyCl systems is shown in Figures 1 and 2. It can be seen that the addition of benzene to 50 vol % leads to an approximately 20% decrease in density, a threefold increase in conductivity, and a sixfold decrease in the viscosity. Very similar results were observed for the other molten salt systems. To directly compare the values for the 1:1 and 2:1 total chloride

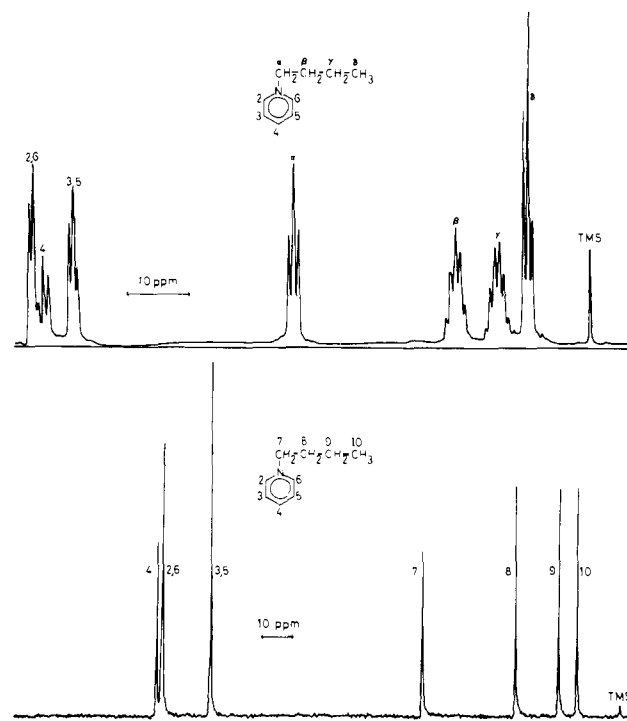


Figure 3. (a) ^1H NMR spectrum of 1:1 AlCl_3 -BupyCl melt at 40 °C. (b) ^{13}C NMR spectrum of 1:1 AlCl_3 -BupyCl melt at 40 °C.

melts the viscosity and conductivity of the 50 vol % benzene mixture with the 1:1 melt were also measured at 25 °C (in contrast to the undiluted melt this system remains molten at this temperature) and were found to be 5.8 cP and $1.76 \times 10^{-2} \omega^{-1} \text{cm}^{-1}$, respectively, which are close to the values for the 50 vol % benzene 2:1 melt system (4.0 cP and $1.75 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$).

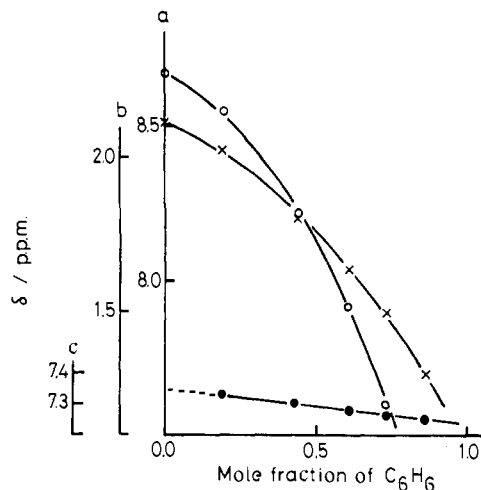
In order to investigate the nature of the interactions involved when the melts are diluted with benzene it was decided to use NMR spectroscopy, both ^1H and ^{13}C , and Figures 3a and 3b show the ^1H and ^{13}C NMR spectra of the undiluted 1:1 AlCl_3 -BupyCl system. The assignments of the various absorptions are as shown on the figures and the values of the ^1H and ^{13}C chemical shifts obtained from such spectra for both the 1:1 and 2:1 total chloride melts are given in Tables II and III. From Figure 3a it can be seen that the ^1H NMR spectra of these melts consists of a doublet due to the 2,6 protons at lowest field, a triplet due to the 4 protons, and a triplet due to the 3,5 protons. In the aliphatic region there are well-defined

Table II. Chemical Shifts in ^1H NMR Spectra of AlCl_3 -BupyCl Melts and Their Mixtures with Benzene

melt	$\chi_{\text{C}_6\text{H}_6}$	2,6-H	4-H	3,5-H	αCH_2	βCH_2	γCH_2	CH_3	C_6H_6
2:1	0	8.67	8.60	8.14	4.62	2.10	1.47	1.00	
	0.192	8.55	8.46	8.00	4.45	2.03	1.35	0.95	7.33
	0.437	8.22	8.15	7.75	4.20	1.80	1.25	0.90	7.30
	0.603	7.92	7.88	7.60	4.00	1.64	1.20	0.85	7.28
	0.730	7.60	7.52	7.32	3.80	1.50	1.00	0.82	7.27
	0.859				3.60	1.30	0.90	0.75	7.26
1:1	0	8.85	8.67	8.20	4.72	2.14	1.48	0.99	
	0.18	8.72	8.56	8.09	4.60	2.04	1.41	0.95	7.33
	0.335	8.54	8.42	7.93	4.45	1.92	1.30	0.90	7.32
	0.563	8.22	8.15	7.65	4.20	1.75	1.25	0.87	7.30
	0.692	8.12	8.09	7.60	4.15	1.68	1.20	0.85	7.29
	0.810	7.80	7.75	7.39	3.95	1.45	1.10	0.80	7.26

Table III. Chemical Shifts in ^{13}C NMR Spectra of AlCl_3 -BupyCl Melts and Their Mixtures with Benzene

melt	$\chi_{\text{C}_6\text{H}_6}$	C-4	C-2,C-6	C-3,C-5	C-7	C-8	C-9	C-10	C_6H_6
2:1	0	145.60	143.19	128.60	62.35	32.78	19.06	13.23	
	0.192	145.40	142.99	128.41	62.26	32.69	18.97	13.13	128.21
	0.437	145.24	142.71	128.21	62.06	32.59	18.97	13.13	128.21
	0.603	145.04	142.51	128.16	62.02	32.59	18.97	13.13	128.16
	0.730	144.89	142.32	128.21	61.97	32.59	19.07	13.18	128.21
	0.859	144.82	142.22	128.21	61.92	32.59	19.09	13.18	128.21
	0.917	144.75		128.21		32.59	19.12	13.18	128.21
1:1	0	145.33	143.58	128.41	62.09	32.73	19.07	13.30	
	0.18	145.24	143.44	128.31	62.02	32.69	19.04	13.28	128.21
	0.563	144.89	142.90	128.16	61.85	32.59	18.99	13.21	128.21
	0.810	144.68	142.56	128.21	61.77	32.59	19.04	13.23	128.21

**Figure 4.** The variations of the ^1H chemical shifts with benzene concentration of three representative protons for the 2:1 AlCl_3 -BupyCl melt-benzene system: (●) benzene; (x) $^2\text{CH}_2$; (○) αH .

multiplets due to each of the methylene groups and finally the methyl group. The proton decoupled ^{13}C spectra show simple singlets for each of carbon nuclei as shown. It is interesting to note that the 2, 6 protons lie downfield of the 4 proton whereas in the ^{13}C spectra the shifts for the corresponding carbon nuclei are reversed, reflecting the fact that in ^{13}C NMR the paramagnetic contribution to the chemical shift is dominant whereas in ^1H NMR the diamagnetic contribution dominates.¹⁶ The same order of chemical shifts for the aromatic protons is seen in the ^1H NMR of molten pyridinium salts¹⁹ while the ^{13}C NMR spectra of *n*-methylpyridinium iodide in several acidic solvents²¹ show the same ordering of chemical shifts as observed in the melts.

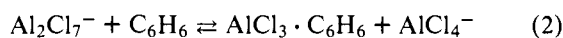
Neither the ^1H nor ^{13}C NMR spectrum of BupyCl, in any solvent, appears to have been published; however, comparisons can be made to the chemical shifts observed for other similar salts. The values of the ^1H chemical shifts for *n*-butylpyridinium iodide in trifluoroacetic acid²² are very similar to the value for the melt while the ^{13}C shifts for the aromatic carbons of methylpyridinium iodide in acidic media²¹ are also similar to those observed for the molten salts. The ^1H NMR spectra of the 2:1 AlCl_3 -EtpyBr and 2:1 AlBr_3 -EtpyBr melts were also recorded and for the aromatic protons the spectra for these melts and for the BupyCl melts were very similar. It was also observed that, within experimental error, the spectra of the total bromide melt and of the mixed chloride-bromide system (6:1 ratio) were identical. It can thus be concluded that no extensive ion pairing is occurring in the melts, i.e., at this composition the pyridinium ions are not able to compete with AlX_3 for the halide ions.

Upon addition of benzene the signals for all the protons of the alkylpyridinium cations undergo a marked upfield shift as is shown in Table II for the AlCl_3 -BupyCl melts. Also reported in Table II are the δ values for the benzene protons, which also show a slight upfield shift with increasing mole fraction of benzene. The effect of benzene addition on the ^{13}C shifts for the total chloride melts is shown in Table III as are the ^{13}C shift values for the benzene carbon atoms. The ^{13}C results are most readily explained so these will be treated first.

As the mole fraction of benzene increases the shifts for C-2, C-6, C-4, and C-7 all show an upfield shift that is linear in the mole fraction of benzene (correlation coefficients greater than 0.99). The upfield shift is greatest for C-2 and C-6 (1 ppm) with the C-4 shift being slightly smaller and the C-7 shift being about half the value for C-2 and C-6. The values for the remaining carbon nuclei show small upfield shifts at low benzene concentrations ($\chi_{\text{C}_6\text{H}_6} < 0.3$) but then show no significant change as the concentration of benzene is increased. This behavior can be rationalized in the following manner. As the

benzene concentration is increased the dielectric constant of the medium is decreased favoring both ion pairing and increased ionic mobility. The best candidates for such ionic interactions with the low polarizing power alkylpyridinium cations are the chloride ions; however, the concentration of these ions in the pure melts is very low;¹⁵ therefore interaction with the tetrachloroaluminate and heptachloroaluminate ions cannot be ruled out. As the ion pairs are formed the positive charge on the nitrogen nucleus will be reduced leading to an increased electron density on C-2, C-6, and C-4 and also the carbon nuclei of the butyl chain. The effect of the aliphatic carbon nuclei will be greatest on the methylene carbon attached to the nitrogen (C-7) and will drop off rapidly as the carbon atoms are more removed from this site. An increased electron density will lead to an upfield shift in the ^{13}C NMR absorption, which is exactly what is observed for C-2, C-6, C-4, and C-7. The observed relative magnitudes of the effects are also as would be predicted, C-2, C-6 > C-4 > C-7.

From vapor pressure measurements²³ and more recently from ^{27}Al NMR studies²⁴ it has been shown that AlBr_3 and AlI_3 react with benzene, a weak base, to form tetrahedral π complexes of the type $\text{AlX}_3\text{C}_6\text{H}_6$. The only reports of complexes between benzene and AlCl_3 are of σ -type complexes that have been observed spectrophotometrically in the 2:1 AlCl_3 -BupyCl melt;¹³ however, the equilibrium constant for the formation of such a complex is very low indeed. From Table III it can be seen that the chemical shift for the benzene carbon atoms is independent of the mole fraction of benzene, indicating that no significant complexation of the type seen between AlBr_3 or AlI_3 and benzene is occurring (the concentration of the σ -type complex would be much too low to be observed by ^{13}C NMR). This conclusion is also supported by the Raman spectrum of the 50 vol % benzene 2:1 AlCl_3 -BupyCl system, which indicates the presence of Al_2Cl_7^- , the butylpyridinium cation, and free benzene only.²⁵ If the complex were formed according to eq 2, AlCl_4^- ions would be detectable in the Raman spectrum, which was not the case.



The chemical shifts in ^1H NMR reflect the electronic environment of the carbon atoms to which the protons are attached. The dilution of the melts with benzene should therefore lead to similar upfield shifts in the ^1H NMR as were observed in the ^{13}C NMR. Reference to Table II shows this to be broadly the case; however, as can be seen in this table and also in Figure 4, the shifts for the protons attached to C-2, C-6, C-4, and C-7 do not vary linearly with the mole fraction of benzene as did the ^{13}C shifts. It can also be seen that large upfield shifts are also observed for the protons attached to C-3 and C-5 as well as those of the butyl group; e.g., δ for the methyl protons changes from 1.0 to 0.75 ppm as the mole fraction of benzene is increased from 0.0 to 0.86 (the ^{13}C δ value for the methyl carbon was essentially constant for a similar composition variation).

While the ion pairing is affecting the ^1H NMR spectra in an analogous manner to that described for the ^{13}C NMR spectra, there is obviously also another effect present. This is most probably due to interactions between the benzene ring currents and the protons of the butylpyridinium cation. Such effects are well characterized;²⁶ e.g., the hydrogen resonance signal of chloroform moves 1.5 ppm to high fields on changing

from pure chloroform to a 5% solution in benzene.²⁷ This upfield shift occurs because the benzene and chloroform form a very weak complex, with the chloroform hydrogen atom pointed toward the benzene ring. The chloroform hydrogen nucleus therefore experiences an applied field which is reduced in magnitude by the induced field arising from diamagnetic ring currents in the benzene molecules. A similar interaction is probably occurring between the protons of the pyridinium cation and benzene. The small (<0.1 ppm) shift that is observed for the benzene protons is probably also due to weak solute-solvent interactions.

From the NMR results discussed above it can be concluded that addition of benzene to alkylpyridinium halide-aluminum chloride melts leads to a decrease in the dielectric constant of the medium resulting in ion pairing between the alkylpyridinium cations and anions in the melt and also increased ionic mobility. This increase in ionic mobility which is coupled to the decrease in melt viscosity explains the increase in electrical conductivity observed as the mole fraction of benzene in the melt is increased. There is no evidence for the formation of any complexes between benzene and the acidic species in the melt.

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