Disproportionation of Polynuclear Chloroethylaluminate Anions in Acidic 1-Butyl-3-methylimidazolium Chloride–$AlEtCl_2$ Molten Salts in the Presence of a Hydrocarbon Phase

Bernard Gilbert,[a] **Yves Chauvin,**[b] **Helene Olivier**[b] **and Françoise Di Marco-Van Tiggelen**[b]
[a] *Université de Liège, Chimie Analytique B6, Sart Tilman, B-4000 Liège, Belgium*
[b] *Institut Français du Pétrole, BP 311, 92506 Rueil-Malmaison, France*

Various 1-butyl-3-methylimidazolium chloride–$AlEtCl_2$ molten salt mixtures have been equilibrated in the presence of cyclopentane, and the resulting products monitored by Raman spectroscopy in the hydrocarbon and molten salt phases. The experiments were conducted either statically by equilibration of a given volume of cyclopentane with an equal volume of molten salt or dynamically by using a continuous-extraction apparatus. The results show for the first time that polynuclear anions disproportionate and/or dissociate. When a full extraction is performed from a melt based on $AlEtCl_2$ with any mole fraction higher than 0.667 the resulting molten phase is comprised of $[AlCl_4]^-$. The nature of the extracted alkylaluminium chloride compound depends on the initial composition. For a melt containing an $AlEtCl_2$ mole fraction of 0.5–0.75 a mixture of $AlEt_2Cl$ and $Al_2Et_3Cl_3$ is extracted by the hydrocarbon phase. When this mole fraction is 0.75 the only product extracted is $Al_2Et_3Cl_3$. The compound $AlEtCl_2$ is extracted from a mixed acidic salt based on $AlCl_3$ and $AlEtCl_2$.

One basic problem of homogeneous catalysed processes is the separation of reaction products from the catalyst. A two-phase solvent system, incorporating a polar phase-soluble catalyst, enables an easy recovery of the catalyst by simple decantation.[1] Several reactions have been tentatively studied using this technique, and at least three of them have been successfully converted into industrial applications: propene hydroformylation catalysed by rhodium complexes dissolved in an aqueous phase (Rhône-Poulenc-Ruhrchemie process[2]), dimerization–hydration of butadiene catalysed by palladium complexes also in an aqueous phase (Kuraray process[3]) and ethylene oligomerization catalysed by nickel complexes dissolved in a butanediol polar phase (Shell-Shop process[4]). However, some organometallic catalysts, highly sensitive to protons or bases, cannot be used in these media. For these systems, only non-aqueous ionic liquids not containing co-ordinating species can be considered. Room-temperature molten salts based on aluminium chloride and dialkylimidazolium chloride proved to be particularly suitable. They are good solvents for inorganic salts and do not dissolve aliphatic hydrocarbons. These systems are liquids at room temperature and below, over a wide range of composition. One of their most interesting properties is that their Lewis acidity can be adjusted by varying their composition. When the mole fraction of aluminium chloride is less than 0.5, the salt contains chloride anions in excess and can be considered as basic; when the mole fraction is higher than 0.5, the salt behaves as an acid.[5]

This type of molten salt has recently been extended to mixtures of dialkylimidazolium chloride and ethylaluminium derivatives such as ethylaluminium dichloride ($AlEtCl_2$),[6] diethylaluminium chloride ($AlEt_2Cl$) and triethylaluminium ($AlEt_3$).[7] All these new mixtures also form ionic liquids at room temperature over a large composition range and, as shown by Raman spectroscopy, they contain single and polymeric anions, responsible for the acidity change with composition.[6,7] Furthermore, recently they have been used successfully as selective solvents for cationic nickel complexes which are well known catalysts for the dimerization of propene into isohexenes.[8] In this process propene dimers formed during the catalytic reaction separate from the ionic melt as an upper phase and can be withdrawn by an aliphatic hydrocarbon. We have observed however that molecular organoaluminium derivatives were also extracted into the hydrocarbon layer.[9] Clearly, the presence of a hydrocarbon layer changes the composition of the ionic liquid itself and dramatically modifies the course of the catalytic reaction.

This paper describes the use of Raman spectroscopy to decide upon the nature of the organochloroaluminium present in the hydrocarbon and ionic phases when one mixes an acidic molten salt made of 1-butyl-3-methylimidazolium chloride (bmic) and $AlEtCl_2$ with cyclopentane. Cyclopentane was selected as the hydrocarbon phase because its Raman spectrum does not exhibit any strong bands in the region of interest.

Experimental

All chemical manipulations were conducted in a glove-box with a water and oxygen content below 1 ppm. The molten salts were prepared as described previously.[10] 1-Butyl-3-methylimidazolium chloride was chosen instead of the more commonly used 1-ethyl-3-methylimidazolium chloride because its synthesis is less hazardous, involving no pressurized vessel. The resulting solid was recrystallized from an acetonitrile–toluene mixture. Aluminium chloride was sublimed twice in the presence of sodium chloride (0.5 g) and some aluminium powder. The compounds $AlEtCl_2$ (98.5% pure), $AlEt_2Cl$ (98% pure) and $AlEt_3$ (93% pure), all from Witco, were distilled before use.

For static equilibrium studies, glass tubing cells (1 cm^2) closed with vacuum-tight fittings were used. The melt (0.7 cm^3) and an equivalent volume of cyclopentane were thoroughly mixed in the cell, then, after equilibration, the spectra of the two phases were recorded. The Raman spectrum was collected from a laser beam focused on the centre of the cell, in order to avoid any interference with the liquid film of the opposite phase possibly present on the cell wall.

For dynamic equilibrium studies a liquid extraction-type apparatus was built (Fig. 1). The molten salt (3.5 g) was carefully placed in a gondola containing a magnetic stirring bar whereas cyclopentane (20 cm^3) was introduced in the bottom.

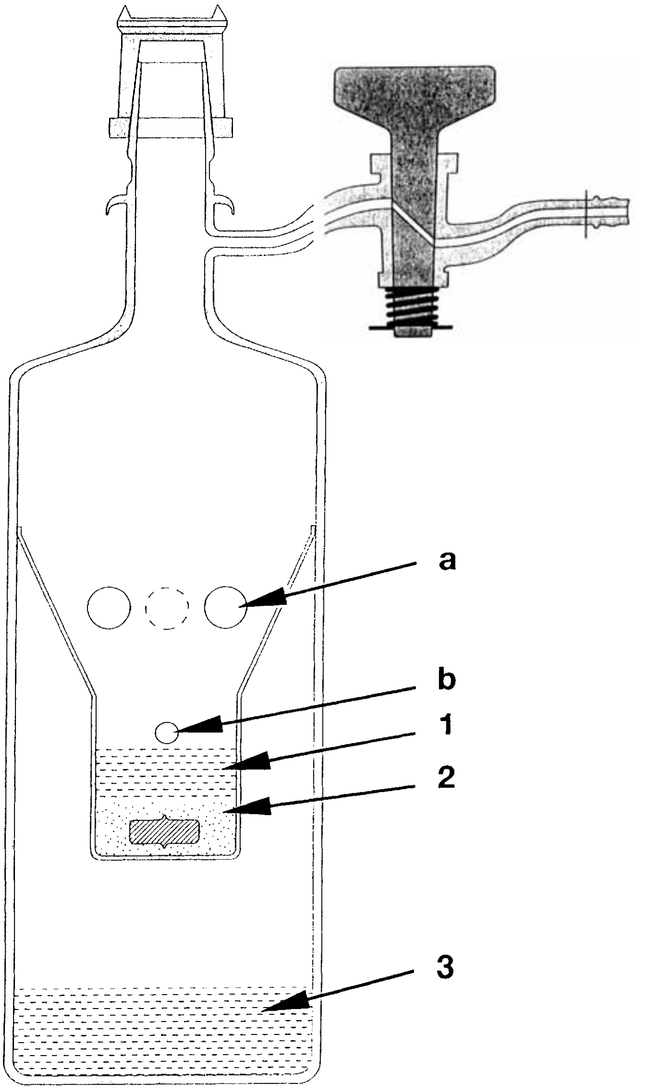

Fig. 1 Liquid–liquid extraction apparatus allowing the recording of the Raman spectrum of each phase during the extraction process. 1, 3, Cyclopentane; 2, molten salt

The apparatus was frozen with liquid nitrogen, degassed under vacuum and sealed. After warming, a gentle reflux of cyclopentane was applied by heating the bottom and cooling the top of the cell. Vapour phase flowed out through holes 'a', and refluxing liquid through hole 'b'. The Raman spectra of phases 1–3 were recorded as a function of time.

The spectra were recorded using a Coherent Radiation model 52-B argon-ion laser (200 mW, 514.5 nm), and a modified Cary 81 spectrometer interfaced with a microcomputer, allowing rapid recording rates and full data treatment. A slit width of 5 cm^{-1}, a time constant of 0.1 s and a scan rate of 250 cm min^{-1} were used for each spectrum.

Results and Discussion

In an earlier paper[6] we described a technique which allows us to identify the various anionic species present in bmic–$AlEtCl_2$ melts. That technique has also been applied to the more general case of the structure of mixtures bmic–$AlEt_xCl_{3-x}$ (x = 0–3).[7] Depending on the mole fraction (m.f.) of the ethylaluminium derivative, the following species were found to be present in the melt: Cl^- and $[(AlEt_xCl_{3-x})Cl]^-$ for m.f. < 0.5; $[(AlEt_xCl_{3-x})Cl]^-$ for m.f. = 0.5; $[(AlEt_xCl_{3-x})Cl]^-$ and $[(AlEt_xCl_{3-x})_2Cl]^-$ for 0.5 < m.f. < 0.667; $[(AlEt_xCl_{3-x})_2Cl]^-$ and $[(AlEt_xCl_{3-x})_3Cl]^-$ for 0.667 < m.f. < 0.75; $[(AlEt_xCl_{3-x})_2Cl]^-$ and $(AlEt_xCl_{3-x})_2$ for m.f. > 0.667 when x = 2 or 3 and for m.f. > 0.75 when x = 1. For salts obtained by mixing $AlCl_3$ and $AlEtCl_2$ the mixed species $[(AlCl_3)(AlEtCl_2)Cl]^-$ was also characterized. The existence of such species is in good agreement with our aluminium electronegativity measurements.[11]

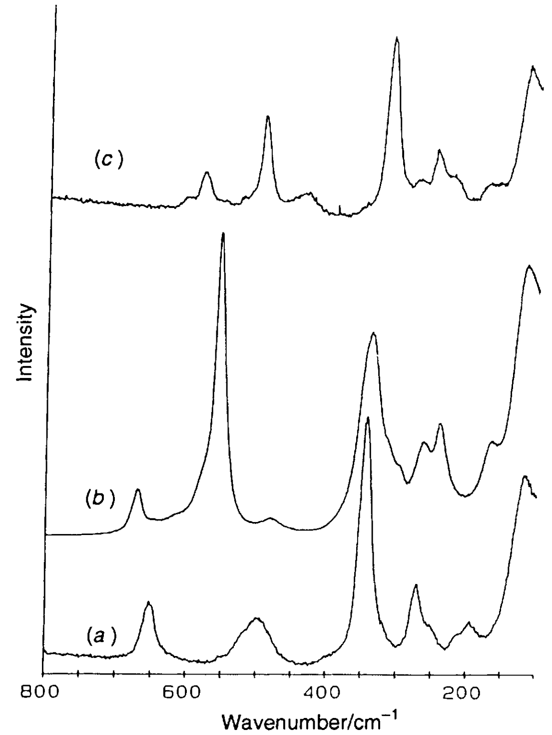

Fig. 2 Raman spectra of liquid $AlEtCl_2$ (*a*), $AlEt_2Cl$ (*b*) and $Al_2Et_3Cl_3$ (the sesquichloride) (*c*) at room temperature

In order to make easier the reading of the following sections, we have summarized in Table 1 the locations of the main vibrational frequencies of each species. It should however be stressed that some of the bands fall at the same location as others and a simple comparison based on only one band per species may lead to erroneous interpretations. In addition, some spectra look very similar. The similarities however are valid only for a few lines and, in any case, the intensity ratios of these lines were clearly different from one species to another. Consequently, our assignments and the subsequent proposed reactions are made by comparing the *full spectrum* of each species and not from only one band. Such a comparison can be made easily by superimposing the spectra of interest on a computer screen, eventually with an appropriate scaling factor.

The present extraction measurements have been made in two different ways. The first involves equilibration of a given volume of cyclopentane with an equal volume of molten salt, directly in the Raman cell. The second involves a continuous extraction with the apparatus shown in Fig. 1.

Since $AlCl_3$ and the ionic species are not soluble in the organic phase, the most probable candidates to be extracted are $AlEtCl_2$, $AlEt_2Cl$ and the sesquichloride $Al_2Et_3Cl_3$. Each of these exhibits a unique, well defined Raman spectrum (Fig. 2). After removing the cyclopentane contribution from the spectrum of the organic phase the extraction products can be easily identified.

Static Equilibrium Measurements.—In a molten salt where the number of moles of bmic exceeds that of $AlEtCl_2$ [m.f.($AlEtCl_2$) = 0.45 for instance] two anions are present: Cl^- and $[AlEtCl_3]^-$. When the salt was left in contact with

Table 1 Species identified from the Raman spectra. The main vibration or pair of main vibration bands (cm^{-1}) are given

Mole fraction of $AlEt_xCl_{3-x}$ (x = 0–3)			
0–0.5	0.50–0.67	0.67–0.75	0.75–1
$[AlCl_4]^-$ 349	$[AlCl_4]^-$ 349	$[Al_2Cl_7]^-$ 312–433	
	$[Al_2Cl_7]^-$ 312–433	$[Al_3Cl_{10}]^-$ 335–395	
$[(AlEtCl_2)Cl]^-$ 367	$[AlEtCl_2)Cl]^-$ 367	$[(AlEtCl_2)_2Cl]^-$ 349–421	$[(AlEtCl_2)_3Cl]^-$ 338–407
	$[(AlEtCl_2)_2Cl]^-$ 349–421	$[(AlEtCl_2)_3Cl]^-$ 338–407	
$[(AlEt_2Cl)Cl]^-$ 366–545	$[(AlEt_2Cl)Cl]^-$ 366–545	$[(AlEt_2Cl)_2Cl]^-$ 411–552	$[(AlEt_2Cl)_2Cl]^-$ 411–552
	$[(AlEt_2Cl)_2Cl]^-$ 411–552	$AlEt_2Cl$ 340–558	$AlEt_2Cl$ 340–558
$[(AlEt_3)Cl]^-$ 492	$[(AlEt_3)Cl]^-$ 492	$[(AlEt_3)_2Cl]^-$ 496	
	$[(AlEt_3)_2Cl]^-$ 496	$AlEt_3$ 437–566	
Mixed species			
$[(AlCl_3)(AlEtCl_2)Cl]^-$ 336–349			
$[(AlEtCl_2)(AlEt_2Cl)Cl]^-$ 272–367–418			
$(AlEtCl_2)(AlEt_2Cl)$ 346–553			

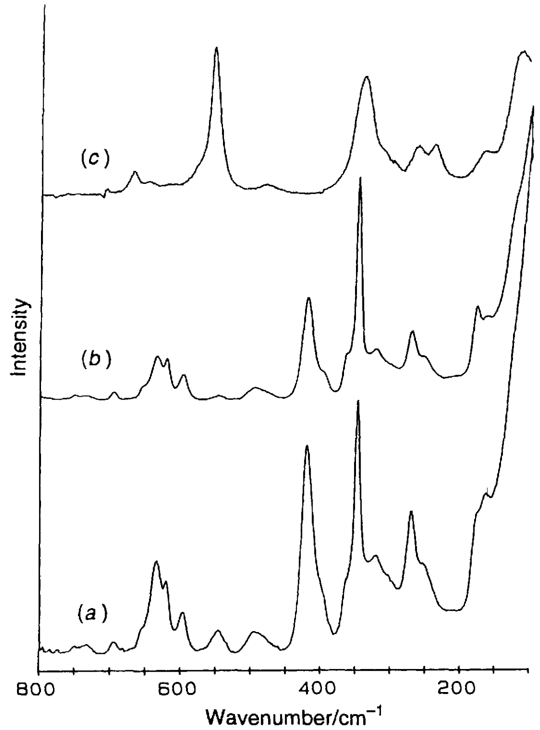

Fig. 3 Extraction results from a 1 : 2 bmic–$AlEtCl_2$ mixture. Raman spectra of the initial molten salt (*a*), molten phase (*b*) and organic phase (*c*) after overnight extraction; in (*c*) the cyclopentane contribution has been subtracted

cyclopentane no variation of the Raman bands assigned to the $[AlEtCl_3]^-$ species (characterized mainly by the ν_1 band at 367 cm^{-1}) was noted and no aluminium compound was detected in the hydrocarbon phase. This means that, as in the case of the neat molten salt itself, the equilibrium '$[AlEtCl_3]^- \rightleftharpoons AlEtCl_2 + Cl^-$' is completely displaced to the left and no extraction occurs.

In a 2:1 $AlEtCl_2$:bmic salt [m.f.($AlEtCl_2$) = 0.667] the major anion is $[(AlEtCl_2)_2Cl]^-$. After equilibration with cyclopentane the spectra of the melt and of the hydrocarbon phase were strongly modified. In the molten phase the Raman bands characteristic of the $[(AlEtCl_2)_2Cl]^-$ species decreased in intensity and new bands appeared. Among these bands, were found (Fig. 3) a band at 349 cm^{-1} characteristic of $[AlCl_4]^-$ [12] and one at 367 cm^{-1} assigned to $[(AlEtCl_2)Cl]^-$.[6]

At the same time, bands characteristic of $AlEt_2Cl$ appear in the cyclopentane phase together with those of $Al_2Et_3Cl_3$. However, the latter are less intense. Equilibria (1)–(3) are suggested to explain the observed spectral variations.

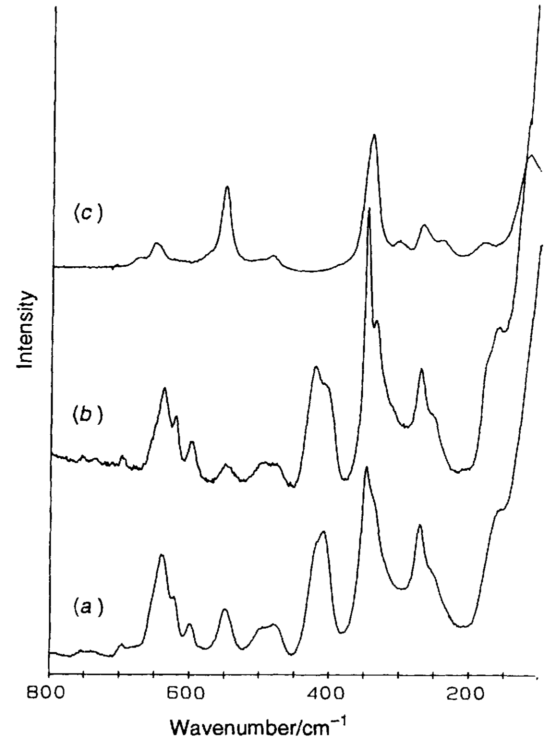

Fig. 4 Extraction results from a 1 : 3 bmic–$AlEtCl_2$ mixture. Details as in Fig. 3

$$[(AlEtCl_2)_2Cl]^- \rightleftharpoons [AlCl_4]^- + AlEt_2Cl \text{ (hydrocarbon phase)} \quad (1)$$

$$[(AlEtCl_2)_2Cl]^- \rightleftharpoons [(AlEtCl_2)Cl]^- + AlEtCl_2 \text{ (hydrocarbon phase)} \quad (2)$$

$$AlEtCl_2 + AlEt_2Cl \rightleftharpoons Al_2Et_3Cl_3 \quad (3)$$

A 3:1 $AlEtCl_2$:bmic salt contains mainly the $[(AlEtCl_2)_3Cl]^-$ anion.[6] When contacted with cyclopentane its spectrum was also strongly modified (Fig. 4). The Raman bands assigned to the main species $[(AlEtCl_2)_3Cl]^-$ decreased in intensity and new bands characteristic of $[AlCl_4]^-$ (349 cm^{-1}) are formed. On the other hand the hydrocarbon phase proved to contain ethylaluminium sesquichloride, *i.e.* $Al_2Et_3Cl_3$. Therefore, equilibrium (4) can be suggested.

$$[(AlEtCl_2)_3Cl]^- \rightleftharpoons [AlCl_4]^- + Al_2Et_3Cl_3 \text{ (hydrocarbon phase)} \quad (4)$$

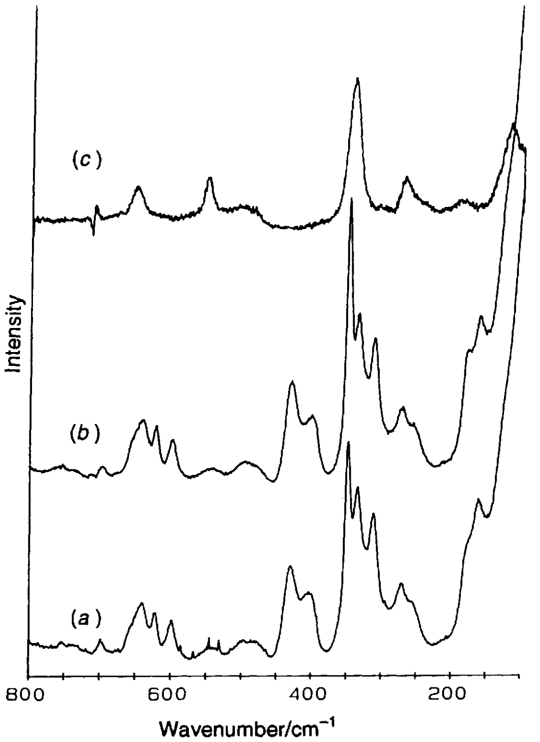

Fig. 5 Extraction results from a 1 : 1 : 1 bmic–$AlEtCl_2$–$AlCl_3$ mixture. Details as in Fig. 3

Finally, a mixed acidic salt was also synthesized using equivalent amounts of $AlCl_3$ and $AlEtCl_2$ ($AlCl_3$: $AlEtCl_2$: bmic = 1 : 1 : 1). As we found previously,[7] such a mixture contains the anions $[Al_2Cl_7]^-$, $[(AlEtCl_2)_2Cl]^-$ and $[(AlCl_3)(AlEtCl_2)Cl]^-$. When equilibrated with cyclopentane, the major band at 349 cm^{-1} characteristic of $[AlCl_4]^-$ appears and that of $[(AlEtCl_2)_2Cl]^-$ increases in intensity, but the intensity ratio of the band at 312 cm^{-1} due to $[Al_2Cl_7]^-$ to that at 333 cm^{-1} due to $[(AlCl_3)(AlEtCl_2)Cl]^-$ was nearly constant (Fig. 5). The only aluminium compound characterized in the hydrocarbon phase was $AlEtCl_2$. For such mixtures, equilibria (5) and (6) can then be proposed.

$$[(AlCl_3)(AlEtCl_2)Cl]^- \rightleftharpoons [AlCl_4]^- + AlEtCl_2 \text{ (hydrocarbon phase)} \quad (5)$$

$$[Al_2Cl_7]^- + [(AlEtCl_2)_2Cl]^- \rightleftharpoons 2[(AlCl_3)(AlEtCl_2)Cl]^- \quad (6)$$

Dynamic Measurements.—In industrial catalytic applications the supernatant hydrocarbon phase in contact with the melt is continuously replaced. To simulate this situation molten salts have been subjected to a continuous extractive distillation with cyclopentane in the extraction apparatus shown in Fig. 1. A 3 : 1 $AlEtCl_2$: bmic melt was treated in this apparatus as described in the Experimental section and the Raman spectra of the three phases were alternately monitored.

From the beginning of the extraction the only ethylaluminium chloride found in the two hydrocarbon phases was $Al_2Et_3Cl_3$. After 5 h of extraction, the volume of the salt was reduced approximately by half and Raman spectroscopy showed that it contained only the $[AlCl_4]^-$ anion [Fig. 6(*b*)]. The supernatant cyclopentane no longer contained any ethylaluminium compound whereas the bottom cyclopentane contained only $Al_2Et_3Cl_3$ [Fig. 6(*c*)]. Thus equilibrium (4) was then completely shifted to the right and the melt became neutral.

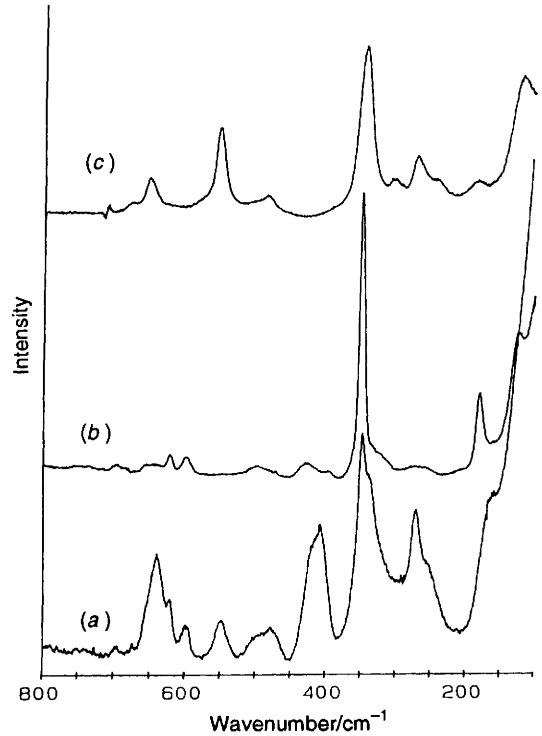

Fig. 6 Extraction results from a 1 : 3 bmic–$AlEtCl_2$ mixture using the apparatus shown in Fig. 1. Raman spectra of the initial molten salt (*a*), molten phase (*b*) and organic phase (*c*) after 5.5 h of continuous extraction; in spectrum (*c*) the cyclopentane contribution has been subtracted

In a similar way, treatment of a 2 : 1 $AlEtCl_2$: bmic melt for 8 h led to a mixture of $AlEtCl_2$ and $Al_2Et_3Cl_3$ in the cyclopentane phase. However, equilibration took more time than for the 3 : 1 melt, and the $Al_2Et_3Cl_3$ content was higher than measured in static experiments, suggesting that equilibrium (2) was favoured over (1). The resulting salt phase contains mainly $[AlCl_4]^-$ with small quantities of $[(AlEtCl_2)Cl]^-$.

For initial melt compositions between 2 : 1 (m.f. = 0.667) and 3 : 1 (m.f. = 0.75) the extraction produces a mixture of $AlEt_2Cl$ and $Al_2Et_3Cl_3$, and when the composition is higher than 3 : 1, $AlEtCl_2$ is preferentially extracted.

As a general consequence, when an extraction is performed from a melt based on $AlEtCl_2$ with any molar fraction higher than 0.5 the resulting molten phase is a neutral melt containing fewer ethyl groups. When the extraction is made from a 3 : 1 $AlEtCl_2$: bmic mixture the resulting molten phase is completely free of ethylaluminium components.

Conclusion

The principle of disproportionation of alkylaluminium chlorides in the presence of bases has already been described for molecular compounds.[13,14] We have shown, from Raman spectroscopy, that it is also observed for polynuclear alkylchloroaluminate anions in room-temperature molten salts. For acidic $AlEtCl_2$-based salts the nature of the extracted alkylaluminium chloride depends on the initial composition. Up to $AlEtCl_2$ mole fractions of 0.667 the extracted product is mainly $AlEt_2Cl$ and a small amount of $Al_2Et_3Cl_3$. The proportion of extracted $Al_2Et_3Cl_3$ increases however with the acidity of the initial melt. For a m.f. = 0.75 salt the only product extracted is $Al_2Et_3Cl_3$, whereas between m.f. = 0.667 and 0.75 a mixture of $AlEt_2Cl$ and $Al_2Et_3Cl_3$ is extracted. The compound $AlEtCl_2$ is the only component extracted from an acidic mixed salt based on $AlCl_3$ and $AlEtCl_2$.

The practical consequence of these findings is as follows: if, for chemical purposes, it is desired that a non-co-ordinating solvent based on alkylaluminium chloride maintains its acidic properties under a continuous flow of a hydrocarbon, it is necessary to choose a molten salt containing not only $AlEtCl_2$ but also an excess of aluminium trichloride.[9]

References

1 J. K. Knifton, in *Aspects of Homogeneous Catalysis*, ed. R. Ugo, Reidel, Dordrecht, 1988, vol. 6, pp. 1–58.

2 E. G. Kuntz, *Chemtech.*, 1987, 570.

3 N. Yoshimura and Y. Tokito, *Petrotech.*, 1993, **16**, 341.

4 E. R. Freitas and C. R. Gum, *Chem. Eng. Prog.*, January 1979, 73.

5 R. A. Osteryoung, in *Molten Salt Chemistry*, eds. G. Mamantov and R. Marassi, Reidel, Dordrecht, 1987, pp. 329–364.

6 B. Gilbert, Y. Chauvin and I. Guibard, *Vibrational Spectrosc.*, 1991, **1**, 299.

7 B. Gilbert, J. P. Pauly, Y. Chauvin and F. Di Marco, *Proceedings of the Ninth International Conference on Molten Salts*, eds. C. L. Hussey, D. S. Newman, G. Mamantov and Y. Ito, The Electrochemical Society, Pennington, NJ, 1994, pp. 218–226.

8 Y. Chauvin, B. Gilbert and I. Guibard, *J. Chem. Soc., Chem. Commun.*, 1990, 1715; H. Olivier, Y. Chauvin and A. Hirschauer, American Chemical Society Meeting, Division of Petroleum Chemistry, San Francisco, 5–10th April 1992, preprint vol. 37, no. 3, pp. 780–785.

9 Y. Chauvin, F. Di Marco, H. Olivier and B. Gilbert, *Proceedings of the Ninth International Conference on Molten Salts*, eds. C. L. Hussey, D. S. Newman, G. Mamantov and Y. Ito, The Electrochemical Society, Pennington, NJ, 1994, pp. 617–621.

10 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263.

11 Y. Chauvin, F. Di Marco-Van Tiggelen and H. Olivier, *J. Chem. Soc., Dalton Trans.*, 1993, 1009.

12 R. J. Gale, B. Gilbert and R. A. Osteryoung, *Inorg. Chem.*, 1978, **17**, 2728.

13 K. Ziegler, *Organoaluminium Compounds in Organometallic Chemistry*, Reinhold, New York, 1960, pp. 194, 269.

14 H. Lehmkuhl, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 107.

Received 18*th April* 1995; *Paper* 5/02463C