Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Aromatic Hydrocarbons Using $M[Al_2Et_6X]$ Complexes

J. J. Harrison[a]; J. C. Montagna[a]
[a] GULF RESEARCH & DEVELOPMENT CO., PITTSBURGH, PENNSYLVANIA

To cite this Article Harrison, J. J. and Montagna, J. C.(1982) 'Separation of Aromatic Hydrocarbons Using $M[Al_2Et_6X]$ Complexes', Separation Science and Technology, 17: 9, 1151 — 1163
To link to this Article: DOI: 10.1080/01496398208060279
URL: http://dx.doi.org/10.1080/01496398208060279

SEPARATION SCIENCE AND TECHNOLOGY, 17(9), pp. 1151–1163, 1982

Separation of Aromatic Hydrocarbons Using $M[Al_2Et_6X]$ Complexes

---

J. J. HARRISON and J. C. MONTAGNA

GULF RESEARCH & DEVELOPMENT CO.
PITTSBURGH, PENNSYLVANIA 15230

Abstract

Complexes of the type $M[Al_2Et_6X]$ (where $M = NMe_4$, C_6H_8N, K, Cs; $X = SCN$, Cl, N_3) selectively interact with aromatic substrates to form liquid clathrates in the presence of nonaromatic hydrocarbons. This phenomenon was used to separate aromatics from nonaromatics. Good separation factors (β) of 2.6 to 11.5 were observed. The separation of *m*-xylene from *p*-xylene was also attempted using $M[Al_2Et_6X]$ complexes [$M = NEt_4$, NPr_4, NBu_4, $N(pentyl)_4$, $N(Me)_3Ph$, C_6H_8N, $NEt_3(allyl)$, $N_2(CH_2)_2(CH_3)_6$; $X = I$, Br, Cl, NO_3]. However, in no case was selective complexation observed.

INTRODUCTION

Aluminum alkyls have been shown to react with metal halides and pseudohalides to form 1:1 and 2:1 complexes (*1, 2*). These complexes are of interest because of their structure (*3*), their thermochemistry (*4a, 4b*), and their utility in separating aluminum alkyls in an α-olefin process (*5a*). In addition, complexes of theoretical interest have been synthesized and characterized recently (*5b, 5c*).

Recently, Atwood (*6, 7*) has reported that compounds $M[Al_2(Me)_6X]$ [$M = K$, Cs, $N(CH_3)_4$; $X = N_3$, SCN, SeCN, Cl, I] interact with aromatics such as benzene, toluene, and *p*-xylene to form nonstoichiometric complexes. The term "liquid clathrate" has been used for these complexes.

The complexing ability of $M[Al_2(Me)_6X]$ with aromatics can potentially be of value in affecting various separations. In particular, one might envision the use of these complexes for the separation of aromatics from nonaromatics or for the separation of selected aromatics from each other. Our results using triethylaluminum complexes $M[Al_2Et_6X]$ to form liquid clathrates and their ability to affect the separation of aromatics from nonaromatics are reported. Our attempts to affect the separation of *m*-xylene from *p*-xylene are also reported.

RESULTS AND DISCUSSION

Triethylaluminum reacts with various salts (MX) to form, in many cases, 1:1 and 2:1 complexes (*1*). The 2:1 complexes examined here, $M[Al_2Et_6X]$ ($M = NMe_4$, C_6H_8N, K, Cs; $X = SCN$, Cl, N_3), in some cases also interacted with aromatics to form two liquid phases. The liquid clathrate terminology used by Atwood (*6, 7*) is used throughout this report. The liquid clathrates that were formed were examined by NMR spectroscopy and were characterized by their aromatic/anion ratio (A/A ratio) (Table 1).

The liquid clathrates were prepared by two equivalent procedures. The first procedure involved reacting 2 mol of triethylaluminum with 1 mol salt MX to first form $M[Al_2Et_6X]$ followed by reaction of $M[Al_2Et_6X]$ with aromatic. The second involved interaction of the salt (MX) suspended in aromatic with triethylaluminum. As the salt MX appeared to dissolve, the liquid clathrate formation could be observed visually by the formation of two layers—a more dense liquid clathrate layer containing $M[Al_2Et_6X]$ and complexed aromatic and a less dense layer containing almost pure aromatic.

TABLE 1

A/A Ratios for $M[Al_2Et_6X]$ Complexes at 25°C

MX	Aromatic	A/A
NMe_4SCN	Benzene	12.0
"	Toluene	10.1
C_6H_8NCl[a]	Benzene	13.0
NMe_4Cl	Benzene	13.8
"	Toluene	12.2
"	*p*-Xylene	9.3
"	*m*-Xylene	10.4
"	*o*-Xylene	12.0
KN_3	Benzene	[b]
"	Toluene	[b]
KSCN	Benzene	[b]
"	Toluene	[b]
CsN_3	Benzene	[b]
"	Toluene	[b]

[a] C_6H_8NCl (methylpyridinium chloride) formed a deep violet complex $C_6H_8N[Al_2Et_6Cl]$.
[b] Liquid clathrate did not form under our conditions.

The salts KN_3, KSCN, and CsN_3 appeared to react with Al_2Et_6 to form a complex $M[Al_2Et_6X]$, but reaction with excess aromatics (benzene, toluene) did not yield two liquid layers. A possible explanation for the absence of liquid layering may be that the liquid clathrate which formed from $M[Al_2Et_6X]$ ($MX = KN_3$, KSCN, CsN_3) and aromatics (benzene, toluene) dissolved in excess aromatic. In support of this assumption, it was observed that the $NMe_4[Al_2Et_6Cl] \cdot 12$ *o*-xylene liquid clathrate which formed two layers in *o*-xylene solution at 30°C, dissolved to a single phase at temperatures of about 38°C and higher. This behavior, which is reversible, is the first reported example of a liquid clathrate that dissolves in excess aromatics at elevated temperatures. Further work is needed to explain this phenomenon.

In contrast to the liquid clathrates formed from $M[Al_2(Me)_6X]$ and aromatics (*6*), $M[Al_2Et_6X]$ liquid clathrates could not be reversed to $M[Al_2Et_6X]$ and free aromatics by cooling. This is probably due to the fact that, in general, $M[Al_2Et_6X]$ complexes are low melting solids or liquids while $M[Al_2Et_6X]$ are usually high melting solids. It has been found, however, that the aromatic can be removed from the $M[Al_2Et_6X]$ liquid clathrate by distillation. This is an important requirement for using liquid clathrate in a selected separation scheme.

Aromatic and Nonaromatic Separations

Atwood has reported that it is possible to substitute a moderate percentage of nonaromatic molecules into a liquid clathrate (*6*). We have investigated this phenomenon to determine whether it is possible to use liquid clathrates to separate aromatics from nonaromatics.

We have examined the liquid clathrate formed from reacting $M[Al_2Et_6X]$ ($MX = KN_3$, C_6H_8NCl, NMe_4Cl) with mixtures of benzene/nonaromatics; this is reported in Table 2. In each case a moderate percentage of nonaromatic is incorporated into the liquid clathrate. The relative amount of nonaromatic in the liquid clathrate is reported as the nonaromatic/anion (NA/A) ratio. The relative amount of aromatic in the liquid clathrate is reported as the aromatic/anion (A/A) ratio.

The results demonstrate that incorporation of nonaromatic in the liquid clathrate varies in the order cyclohexane > hexane > octane = decane. These trends suggest that incorporation of nonaromatic into the liquid clathrate is greater for those compounds similar in size to benzene itself. However, it is actually more complicated than this. In the absence of any nonaromatic, benzene forms a liquid clathrate with $NMe_4[Al_2Et_6Cl]$ which contains 13.8 molecules benzene. In the presence of cyclohexane, however, $NMe_4[Al_2Et_6Cl]$ complexes only 2.6 molecules of benzene and 1.1 mole-

TABLE 2

Analysis of Liquid Clathrate in Benzene and Nonaromatics[a] Using $M[Al_2Et_6X]$

MX Component	Nonaromatic[b]	NA/A	A/A
KN_3	Cyclopentane	3.2	3.5
C_6H_8NCl	Hexane	0.6	2.4
C_6H_8NCl	Cyclopentane	1.6	2.2
NMe_4Cl	Cyclohexane	1.1	2.6
NMe_4Cl	Hexane	0.7	2.7
NMe_4Cl	Octane	0.3	2.4
NMe_4Cl	Decane	0.3	2.6
NMe_4Cl	—	—	13.8

[a] Analysis by NMR.

[b] 5 mL of nonaromatic and 3 mL of benzene were reacted with approximately 1 g of $M[Al_2Et_6X]$ complex.

cules of cyclohexane. Thus 1 cyclohexane has displaced over 10 benzenes in the complex. This is difficult to rationalize on size considerations alone.

The complex $K[Al_2Et_6N_3]$ is of interest. In the absence of nonaromatics, a separate liquid clathrate layer is not formed with benzene and $K[Al_2Et_6N_3]$. However, in the presence of cyclopentane, two layers are formed. This result may be due to the greater insolubility of the $K[Al_2Et_6N_3]$ liquid clathrate in cyclopentane/benzene solution compared to pure benzene solution.

The complexes we examined were selective toward complexing aromatics in the presence of nonaromatics. The selectivity of the operation is reported as the separation factor β:

$$\beta = X'_1X_2/X'_2X_1 \tag{1}$$

where X'_1 and X'_2 equal the mole fractions of nonaromatic and benzene, respectively, in the upper phase, and X_1 and X_2 equal the mole fractions of nonaromatic and benzene, respectively, in the lower phase (*8*).

The results of this study as determined by NMR spectroscopy are reported in Table 3. These data indicate that the selectivity varies from $\beta = 2.6$ to $\beta = 11.5$ for these complexes. Since a goal of $\beta = 1.5$ or higher has been suggested for separating agents (*8*), we see that $M[Al_2Et_6X]$ complexes are good separating agents for aromatics and nonaromatics.

A practical application of these results for an actual separation can also be demonstrated. We attempted to separate aromatics from nonaromatics using an hydrogenated pyrolysis gasoline (HPG) fraction from a refinery stream. The composition of this stream is shown in Table 4. The HPG fraction contained approximately 62% aromatics and 38% hydrocarbons. The

TABLE 3

NMR Determination of Composition of Benzene/Nonaromatic Separation Using $M[Al_2Et_6X]$ Complexes

MX	Nonaromatic	X_1	X_2	X'_1	X'_2	β
KN_3	Cyclopentane	0.41	0.46	0.70	0.30	2.6
C_6H_8NCl	Hexane	0.16	0.60	0.69	0.31	8.3
C_6H_8NCl	Cyclopentane	0.33	0.46	0.25	0.75	4.2
NMe_4Cl	Cyclohexane	0.24	0.55	0.61	0.39	5.7
NMe_4Cl	Hexane	0.15	0.62	0.58	0.42	5.7
NMe_4Cl	Octane	0.07	0.66	0.55	0.45	11.5
NMe_4Cl	Decane	0.07	0.68	ND	ND	ND

aromatics consisted of benzene, 33%; toluene, 17%; ethylbenzene, 7%; and xylenes, 5%. This material was reacted with NMe_4Cl and Al_2Et_6 at room temperature for 3 h under nitrogen atmosphere. A liquid clathrate was formed which was separated from the flask via pipette. The liquid clathrate was then distilled at 100°C, 50 mmHg, to separate the $NMe_4[Al_2Et_6Cl]$ complex from the hydrocarbons.

We observed that the hydrocarbons from distillation of the liquid clathrate contained 84% aromatics and 16% nonaromatics (Table 5). The composition of the aromatics was 50% benzene, 22% toluene, 6% ethylbenzene, and 5% xylenes. This indicates that it is possible to concentrate the aromatics in our sample of HPG using one treatment of a liquid clathrate. Multiple stages of this process would be needed to ultimately obtain more complete separation of aromatics from nonaromatics. This separation which yielded 1 g of product for each gram of $NMe_4[Al_2Et_6Cl]$ used gave a separation factor of $\beta = 4.0$ which is in the range observed in the studies with model compounds reported above.

TABLE 4

Composition of Hydrogenated Pyrolysis Gasoline (HPG)

Compound	Percentage[a]
Benzene	32.93
Toluene	16.73
Ethylbenzene	6.56
Xylenes	5.48
Nonaromatic hydrocarbons	38.30

[a] Analysis by capillary GC.

TABLE 5

Composition of Recovered HPG from Liquid Clathrate[a]

Compound	Percentage
Benzene	50.35
Toluene	22.42
Ethylbenzene	6.42
Xylenes	4.94
Nonaromatic hydrocarbons	15.87

[a] Analysis by capillary GC.

Separation of *m*- and *p*-Xylene

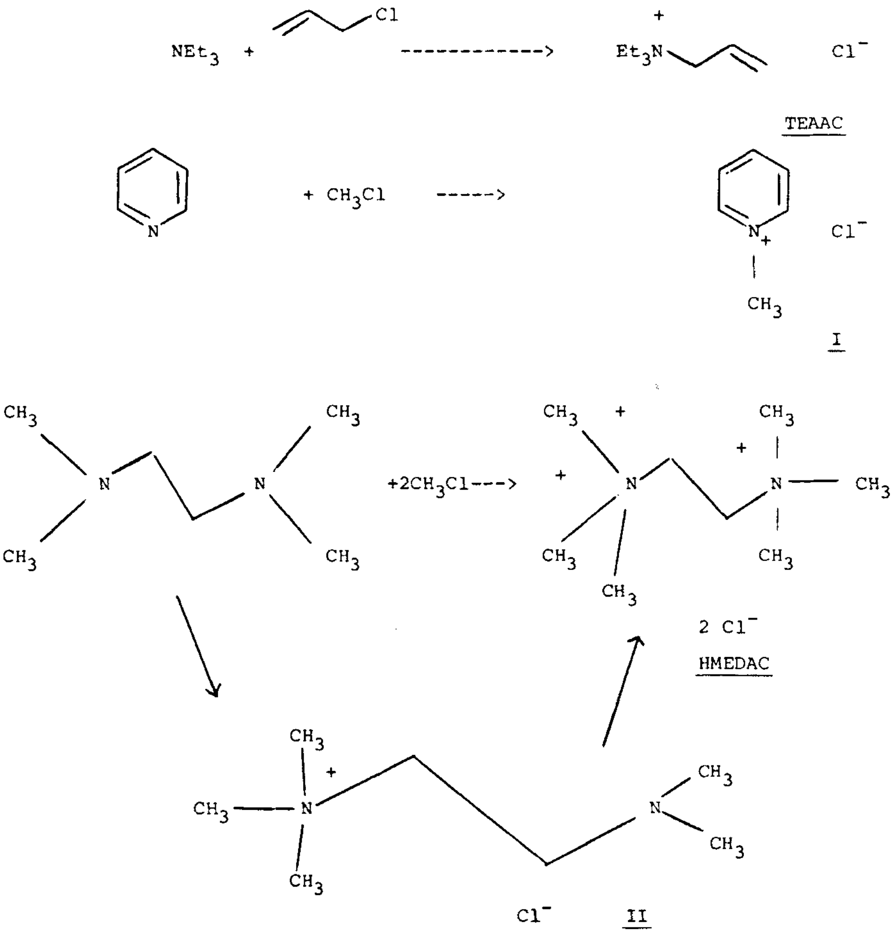
From the data in Table 1 we see that *m*-xylene is complexed in the liquid clathrate to a greater extent than is *p*-xylene. (A/A ratio = 10.4 and 9.3, respectively.) Atwood has examined a variety of ammonium halide complexes of triethylaluminum and *m*- and *p*-xylene and has seen similar effects (7). These data indicate that it may be possible to affect a separation of *m*- and *p*-xylene if one could optimize the effects responsible for the differences in the A/A ratio for *m*- and *p*-xylene.

We have carried out a number of experiments using a series of $NR_4[Al_2Et_6I]$ (R = ethyl, propyl, butyl, and pentyl) and a 50/50 mixture of *m*- and *p*-xylene to determine whether *m*-xylene may be separated from *p*-xylene using liquid clathrates.

Selective complexation of *m*- or *p*-xylene with this series of $NR_4[Al_2Et_6I]$ did not occur (see Table 6). We tried several other $NR_4[Al_2Et_6X]$ complexes which were also not effective as reported in Tables 7 and 8. The effect of temperature on complexation was evaluated for $NMe_4[Al_2Et_6Cl]$, and this is reported in Table 9. These results indicate that neither temperature nor structure of the anion or cation influence the selectivity of $NR_4[Al_2Et_6X]$ for complexing of *m*- and *p*-xylene. Both *m*- and *p*-xylenes are complexed equally as efficiently using the complexes examined. An experiment using a 70:30 ratio of *m*-/*p*-xylene also showed no selectivity (Table 10).

It is instructive to wonder whether other unique structural features of the "R" group on NR_4X might influence the selectivity of the $NR_4[Al_2Et_6X]$ complex for different aromatics. To investigate this possibility, we have synthesized three different types of NR_4X compounds which have structural features different than those examined thus far. These materials are shown in Scheme 1.

These materials prepared by the route in Scheme 1 are triethylallylammonium chloride (TEAAC), methylpyridinium chloride (I), and hexame-



SCHEME. 1.

thylethylene diammonium dichloride (HMEDAC). The HMEDAC was formed in a sequential reaction passing first through the intermediate II. (See experimental section for details of the preparation.)

These three classes of NR_4X compounds possess an isolated double bond as in TEAAC, a hetero-substituted aromatic as in C_6H_8NCl, and a chelate group in HMEDAC capable of bonding through both ammonium groups at the same time.

These materials were then reacted with Al_2Et_6 in the presence of *m*-xylene and *p*-xylene to determine if these structural features provide any

TABLE 6

Separation of *m,p*-Xylene Using $NR_4[Al_2Et_6I]$ at 25°C

	Xylene composition				
	Upper phase		Lower phase		
MX	Para	Meta	Para	Meta	β^a
$N(Et)_4I$	49.50	50.50	49.39	50.61	1.004
$N(Pr)_4I$	50.18	49.72	50.08	49.92	1.006
$N(Bu)_4I$	49.64	50.36	51.39	48.61	1.07
$N(Pent)_4I^b$	49.60	50.40	49.30	50.70	1.01

[a] Defined by Eq. (1).
[b] Run at 0°C.

selectivity toward complexing *m*- or *p*-xylene. the results are shown in Table 11. Essentially, no selectivity was observed for the materials TEAAC, C_6H_8NCl, and HMEDAC. These results demonstrate that even the unique structural of TEAAC, C_6H_8NCl, and HMEDAC-triethylaluminum complexes preclude selective complexation of *m*-xylene or *p*-xylene by the $M[Al_2Et_6X]$ complexes examined.

CONCLUSION

In general, it has been found that liquid clathrates possess the desirable ability to act as agents for hydrocarbon separations. While aromatic, nonaromatic separations can be made with good selectivity ($\beta = 2.6–11.5$), the separation of aromatic isomers such as *m*- and *p*-xylene from each other could not be affected with any of an extensive number of systems examined.

TABLE 7

Separation of *m,p*-Xylene at 0°C

	Xylene Composition				
	Upper phase		Lower phase		
MX	Para	Meta	Para	Meta	β^a
$N(Me)_4NO_3$	49.40	50.60	49.31	50.69	1.004
$N(Et)_4NO_3$	49.57	50.43	49.47	50.53	1.004
$N(Bu)_4NO_3$	49.73	50.27	49.63	50.37	1.004

[a] Defined by Eq. (1).

TABLE 8

Separation of *m,p*-Xylene at 25°C

MX	Xylene composition				β^a
	Upper phase		Lower phase		
	Para	Meta	Para	Meta	
NMe_4Cl	49.33	50.67	49.28	50.72	1.002
NMe_4Br	50.38	49.62	49.66	50.34	1.03
NMe_4I	50.18	49.82	49.88	50.12	1.01
NEt_4I	49.50	50.50	49.39	50.61	1.004
NMe_3PhI	49.18	50.72	49.38	50.62	0.994

[a]Defined by Eq. (1).

In addition, during the course of this work, compounds such as hexamethylethylenediammonium dichloride (HMEDAC), triethylallylammonium chloride (TEAAC), and methylpyridinium chloride (I) were synthesized to evaluate the effect on aromatic isomer selectivities of unique structural features of the "R" group in the $NR_4[Al_2Et_6X]$. In all cases no selectivity toward xylene isomers was found.

EXPERIMENTAL

Experiments were carried out on a schlenk line to avoid contamination of the organoaluminum complexes with oxygen or moisture. Solvents were dried by distillation from sodium and benzophenone under argon. NMR spectra were run on a Varian T60 instrument on samples that had been transferred via syringe into an argon-purged NMR tube fitted with a serum cap. Triethylaluminum was obtained from Texas Alkyls. Tetramethylammonium thiocyanate was prepared according to Markowitz (*9*). The fol-

TABLE 9

Effect of Temperature on *m,p*-Xylene Separation

MX	Temperature (°C)	β^a
NMe_4Cl	0	1.05
	25	1.002
	100	1.006

[a]Defined by Eq. (1).

TABLE 10

Separation of *m,p*-Xylene Using $NMe_4Cl \cdot 2TEA$

Initial phase		Xylene composition			
		Upper phase		Lower phase	
Meta	Para	Para	Meta	Para	Meta
71.76	28.24	71.65	28.35	71.55	28.45

lowing ammonium compounds were purchased from Tridom Chemical and were used as received: NMe_4I, NEt_4I, *N*-propyl$_4$I, *N*-butyl$_4$I, NMe_4NO_3, *N*-pentyl$_4$I, NEt_4NO_3, *n*-butyl$_4$NO$_3$. GC separation of *m*- and *p*-xylene was carried out using a 20-ft 5% bentone/DC 200 column at 100°C.

Preparation of $NMe_4[Al_2Et_6SCN]$ Liquid Clathrates

Into a centrifuge tube equipped with a rubber serum cap was placed 0.90 g NMe_4SCN (6.8 mmol) under argon. To this was added 1.56 g TEA (13.7 mmol). At room temperature the NMe_4SCN readily dissolved. A portion (0.94 g) was then diluted with toluene (5 mL) to form two layers. The lower clathrates layer was examined by NMR. The composition of the toluene clathrates which was measured by integration of toluene vs Al_2Et_6 signal was found to be $NMe_4[Al_2Et_6SCN] \cdot 10.1$ toluene. The same procedure was followed except benzene was substituted for toluene. The composition of the benzene clathrate was $NMe_4[Al_6Et_6SCN] \cdot 12.0$ benzene. Other salts MX were substituted for NMe_4SCN and the corresponding complexes were produced either at room temperature or at elevated temperature. These could

TABLE 11

Separation of *m,p*-Xylene at 25°C

	Xylene composition				
	Upper phase		Lower phase		
MX	Para	Meta	Para	Meta	β^a
$C_6H_8NCl(I)$	49.54	50.46	48.87	51.13	1.03
TEAAC	48.34	51.66	48.34	51.66	1.00
HMEDAC	49.36	50.64	48.75	51.25	1.02

[a] Defined by Eq. (1).

then be reacted with an aromatic to form, in some cases, the liquid clathrates. These are reported in Table 1.

Distillation of Toluene from $NMe_4[Al_2Et_6SCN]$ · 10.1 Toluene

3.1 mL of $NMe_4[Al_2Et_6SCN]$ · 10.1 toluene was distilled at 78–88°C (0.02 mmHg). A total of 2.0 mL toluene was recovered which was pure by NMR. (We estimate that the presence of 5% impurities could have escaped detection.)

Procedure of Determining Aromatic/Nonaromatic Complexation

To a centrifuge tube equipped with a serum cap in argon atmoshphere was added KN_3 2.0 g (25 mmol) and 1/2 Al_2Et_6 6.82 mL (50 mmol). The sample was heated until all the KN_3 dissolved, then cooled to room temperature. A portion of the liquid $K[Al_2ET_6N_3]$ complex was transferred via syringe to a centrifuge tube. To this was added benzene (2 mL) and cyclopentane (5 mL). After brief agitation, two layers formed which were separately analyzed by NMR. These data, and data for other complexes, are found in Table 2. In the sample of the lower phase, integration of the aromatic resonance and comparison with the integration of the resonance due to $M[Al_2Et_6X]$gave the aromatic-to-aluminum anion ratio (A/A ratio). Comparison of the cyclopentane integration and the $M[Al_2Et_6X]$ gave the nonaromatics-to-aluminum anion ratio (NA/A ratio). The aromatic and nonaromatic integration in both upper and lower phase could be converted to β via Eq. (1) (see text for discussion). This procedure was repeated for a variety of MX salts as in Tables 2 and 3.

Preparation of Pyridinium Methyl Chloride

To a three-necked 250-mL flask under nitrogen was added 100 mL pyridine dried by distillation from sodium hydroxide. To this, at reflux, was added methyl chloride gas. Addition was continued for 6 h. Under a nitrogen atmosphere the solid produce was then filtered and washed with hexane. A total of 37.7 g of *N*-methylpyridinium chloride was recovered as a hydroscopic pale salmon solid. NMR $(D_2O)\delta$ 9.00 (brd, 2H, ArH, J = 6Hz), 8.70 (m, 1H, ArH), 8.3 (brt, 2H, J = 6Hz), 4.57 (S, 3H, CH_3).

Preparation of TEAAC

A 76.5-g sample of allyl chloride (1 mol) freshly distilled under nitrogen was added dropwise with stirring to 250 mL of triethylamine (1.8 mol) freshly distilled under nitrogen at reflux temperature. This was kept at reflux overnight under nitrogen. The solid material which formed was filtered under nitrogen and washed with 3 × 30 mL diethyl ether, then dried under a stream of nitrogen. A total of 4.6 g product was recovered. NMR ($DMSOd_6$)δ, 6.2–5.4 (m, 3H, vinyl H), 4.00 (d, 2H, CH_2, J = 6Hz), 3.37 (q, 6H, CH_2, J = 8Hz), 1.20 (t, 9H, CH_3, J = 8Hz).

Preparation of HMEDAC

To a 300-mL flask equipped with a thermometer, condensor, magnetic stirrer, and heating mantle plus gas inlet was added 56.0 g tetramethylethylenediamine (0.48 mol). To this, through a dip tube, was added methyl chloride as the temperature was raised to 45°C. After 3 h a white precipitate had formed which was filtered under nitrogen and washed with ether (50 mL), three times. A total of 14.1 g was obtained which was identified by NMR as monomethyl chloride salt (Compound II). NMR (D_2O)δ 3.62, 3.57 (d × d, H_A, H'_A, 2H), 3.25 (S, (CH_3) N_3+, 9H), 2.95, 2.90 (d × d, 2H, $H_BH'_B$), 2.30 (S, 6H, $(CH_3)_2N$). To 5.0 g of Compound II salt was added 20 mL abolute ethanol and methyl chloride. This was heated at elevated temperatures, and ethalnol was removed by distillation while MeCl was passed through the flask. When the ethanol was totally removed, the dry pot was cooled and the solid was removed. A total of 1.5 g of product was obtained. This was characterized by NMR. NMR (D_2O)δ 4.10 (S, 4H, CH_2), 3.40 (S, 18H, CH_3).

Procedure for Measuring Efficiency of Separating *m*-, *p*-Xylene Using Liquid Clathrates

To an oven-dried centrifuge tube equipped with a rubber stopper was added 1.09 g tetramethylammonium chloride. The tube was then evacuated and flushed with argon three times. To this was added 8.62 g *m*-xylene and 8.56 g *p*-xylene. After thorough mixing, a sample was removed for GC analysis. To this was added, via syringe, 2.15 g triethylaluminum. A liquid clathrate layer gradually formed with stirring. When all TMAC had dissolved, samples of lower liquid clathrate layer and upper xylene layers were taken and analyzed by GC. Aluminum alkyl complexes in some cases pyrolyzed to ethylene in the injection point of GC which was held at 250°C. In some cases a broad low retention time peak was observed which did not interfere with metal*p*-xylene analysis. These data are reported in Table 6–11 for a variety of liquid clathrates. The mixture was then heated to 100°C. In all cases GC analysis of the sample taken at 100°C was identical within experimental error to those taken at 25°C.

Synthesis and Characterization of $NMe_4[Al_2Et_6Cl] \cdot 12$ *o*-Xylene

To 1.1 g tetramethylammonium chloride (10 mmol) was added 20 mL *o*-xylene under argon. To this was then added 2.70 mL triethylaluminum (20 mmol) via syringe. This was then heated under argon to 110° until the tetramethylammonium chloride totally dissolved. Upon cooling to room temperature a liquid clathrate formed. Characterization of the lower phase was carried out by NMR (see Table 1). Heating this sample to elevated temperatures caused disappearance of the two phases to a single phase. This phenomenon was reversible over many cycles. In addition we observed that addition of a slight excess of triethylaluminum to this solution resulted in the disappearance of this phenomenon. Only a single phase could then be observed at all temperatures.

REFERENCES

1. K. Ziegler, R. Koster, H. Lehmkuhl, and K. Reinert, *Justus Liebigs Ann. Chem., 629,* 33 (1960).

2. J. L. Atwood, W. E. Hunter, and K. D. Crissinger, *J. Organometal. Chem., 127,* 403–414 (1977), and references cited therein.

3. J. L. Atwood and W. R. Newberry, III, *Ibid., 66,* 15 (1974).

4a. J. L. Atwood and D. C. Hrncir, *Ibid., 61,* 43–48 (1973).

4b. J. E. Bozik, D. L. Beach, and J. J. Harrison, *Ibid., 179,* 367–376 (1979), and references cited therein.

5a. E. R. Tucci, *Ind. Eng. Chem., Prod. Res. Dev., 5,* 161 (1966).

5b. J. L. Atwood, D. C. Hrncir, R. D. Rogers, and J. A. K. Howard, *J. Am. Chem. Soc., 103,* 6787 (1981).

5c. D. C. Hrncir, R. D. Rogers, and J. L. Atwood, *Ibid., 103,* 4277 (1981).

6. J. L. Atwood and J. D. Atwood, *Inorganic Compounds with Unusual Properties* (Advances in Chemistry Series, 150), 1976, Chapter 11.

7. J. L. Atwood, *Recent Developments in Separation Science,* Vol. III, Part B, CRC Press, 1977, p. 195.

8. A. P. Colburn and E. M. Schoenborn, *Trans. AIChE, 41,* 421 (1945).

9. M. M. Markowitz, *J. Org. Chem., 22,* 983–984 (1957).

Received by editor January 11, 1982