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New Inclusion Methods for Separations Problems

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Abstract

Liquid inclusion complexes called liquid clathrates have been used to effect separations of aromatics from aliphatics, monoenes, and dienes. Conventional separation factors of near 10 are typical for the first two, while 2–4 are found for the latter. The liquid clathrate is based on a parent complex which is a cation–anion pair in combination with an aromatic solvent. New parent complexes are revealed and the direction for diene separations from other dienes and from monoenes is indicated.

INTRODUCTION

The true development of inclusion science began in the late 1940s with the studies of Powell and co-workers (*1, 2*). Although the compounds in question had been in existence for many years, the nature of the interactions could only be revealed by single crystal x-ray diffraction techniques. It was found that quinol crystallizes such that large voids exist in the crystal lattice. Molecules of sulfur dioxide are the correct size to fit, and do so when it is used in a solution of quinol. Powell coined the term "clathrate" to describe the complex. The guest molecule (sulfur dioxide) does not react with the host substance (quinol) in the usual sense of the word. Rather, it is trapped in a solid matrix.

Interest in clathrates peaked in the late 1950s with the realization of the selectivity of the host for certain types of organic molecules, particularly isomers such as *m*- and *p*-xylene. A number of processes were devised and patents were issued. However, commercialization was not realized, primarily because of three factors: (1) the percent by weight of guest was only 10–

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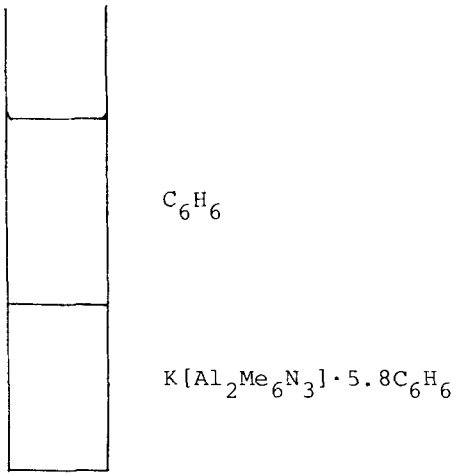

FIG. 1. Schematic view of a liquid clathrate. The composition of the two liquid layers is indicated.

20%, (2) the energy required to remove the guest was prohibitive, and (3) the problem of the handling of solids could not be overcome. Thus, the high selectivity could not be used and enthusiasm waned.

Interest in inclusion was only revived in the 1970s with an expansion in the use of the terms and definitions to encompass new types of behavior. One major extension was the application to the liquid state. Cyclodextrins and crown ethers have had a particularly great impact. We are now poised on the brink of a large expansion as evidenced by the number of recent publications in the area. Davies et al. have reviewed the subject (*3*) and an extensive treatment of inclusion compounds is available (*4*). One of the most promising uses of inclusion technology is in the area of separations science.

Our major contribution has been the application of the clathrate concept to the liquid state. In the following paragraphs the basic idea of the liquid clathrate (*5, 6*) will be put forward and the application to a number of separations will be discussed.

LIQUID CLATHRATE BEHAVIOR

Aluminum alkyls react with MX species to form either 1:1, $M[AlMe_3X]$, or 2:1, $M[Al_2Me_6X]$, complexes (where M = alkali metal or tetraalkylammonium ion and X = halide, pseudohalide, or related ion). For several years interest has been focused on the 2:1 complexes because of the solution

behavior they exhibit. Now, many 1:1 complexes which act in a similar manner have been characterized. The compound with which the effect was initially discovered serves to illustrate the liquid clathrate effect (*7*). $K[Al_2Me_6N_3]$ appears to be a normal organometallic salt. It has a melting point of 106°C and is expected to have minimal solubility in solvents of low polarity. However, when the substance is exposed to an aromatic solvent such as toluene, two liquid layers form (Eq. 1 and Fig. 1).

$$K[Al_2Me_6N_3] \underset{\text{toluene}}{\rightleftharpoons} K[Al_2Me_6N_3] \cdot 3.8 \text{ toluene} \qquad (1)$$

The lower layer contains all the salt and toluene in a ratio of 3.8 toluene molecules/salt formula unit. The upper layer is pure toluene. The lower layer is referred to as a liquid clathrate, and it has several properties of note. First, the composition of the lower layer is fixed in the presence of an excess of toluene; no matter how large the upper layer, only the 3.8:1 ratio is realized. Second, Eq. (1) represents a reversible process. If the temperature of the liquid clathrate is lowered to ~20°C, crystals of the parent complex, $K[Al_2Me_6N_3]$, and free toluene result. If the temperature is raised to ~30°C, the liquid clathrate is again formed. Third, the effect was initially observed only for aromatic hydrocarbons; $K[Al_2Me_6N_3]$ does not dissolve in nor interact with solvents such as cyclohexane.

After the initial discovery of liquid clathrate behavior in the early 1970s, intense activity was directed along two lines: (1) What is the underlying reason for the effect? and (2) Over what range of compounds are liquid clathrates formed? Hundreds of parent complexes of the general form $M[Al_2R_6X]$ were synthesized and thousands of liquid clathrates with such aromatics as benzene, toluene, *o*-, *m*-, and *p*-xylene, and mesitylene were prepared. Each may be characterized by the maximum aromatic/anion ratio (A/A), which was 3.8 for the example in Eq. (1). From a perusal of these data, several generalizations were noted. (1) For a given anion and aromatic, the larger the cation, the larger the A/A number. (2) For a given cation and anion, the larger the anion, the larger the A/A number. (3) For a given cation and anion, the larger the aromatic, the smaller the A/A number. All of these observations are consistent with the properties of clathrates, and since we are dealing with liquids, the term liquid clathrate is used.

In an effort to learn about the origin of liquid clathrate behavior, x-ray crystallographic studies have been carried out on numerous $M[Al_2Me_6X]$ parent compounds. In most cases an angular structure is noted for the anion as in Fig. 2, although this is not a necessity. Attempts have been made to crystallize a compound which will preserve aspects of a liquid clathrate and thereby serve as a model for the phenomenon. A number of solids with high aromatic content have been obtained, but these have only given a hint of the

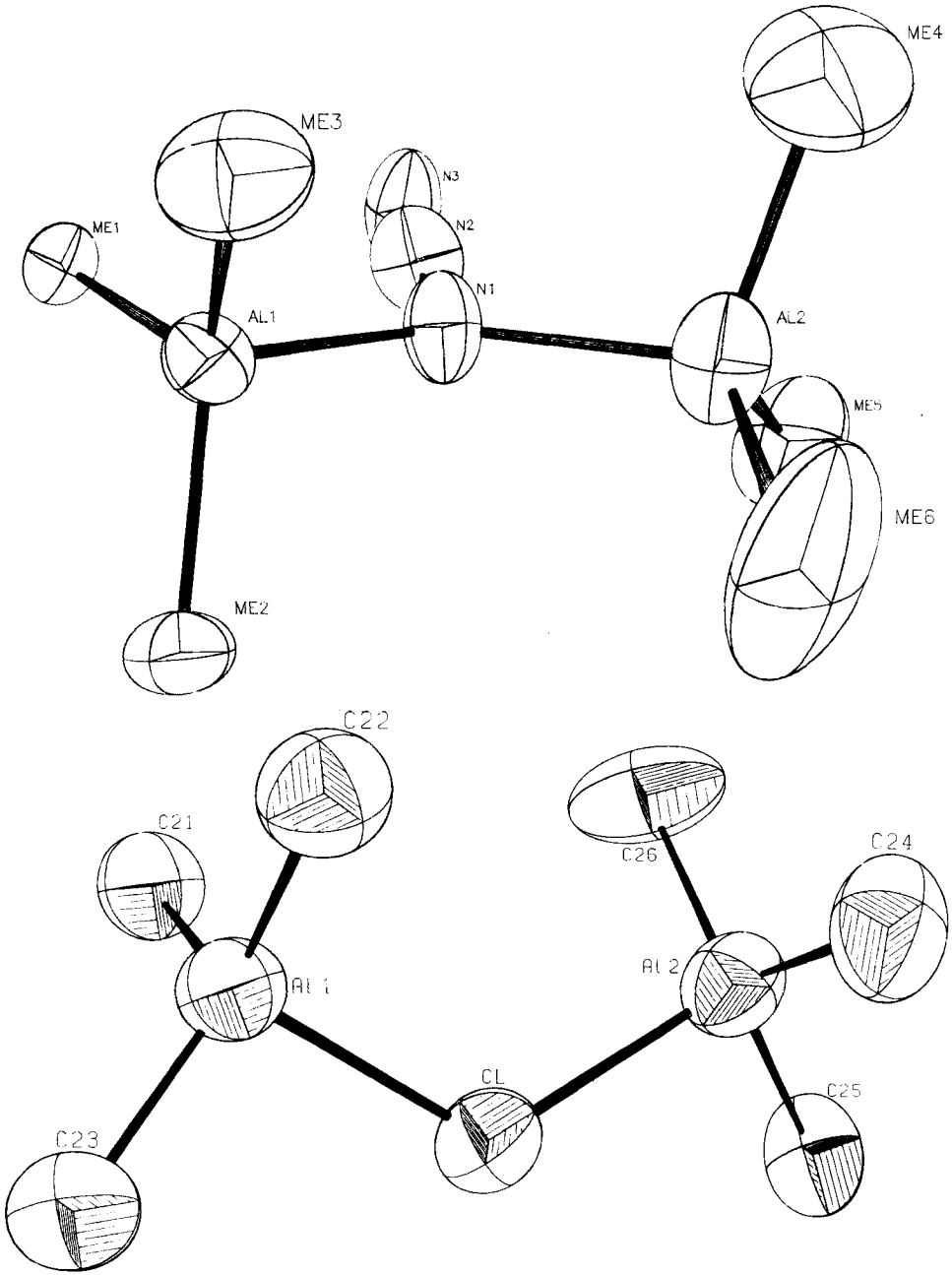

FIG. 2. Angular structure of the anion in (top) $[Al_2Me_6N_3]^-$ and in (bottom) $[Al_2Me_6Cl]^-$.

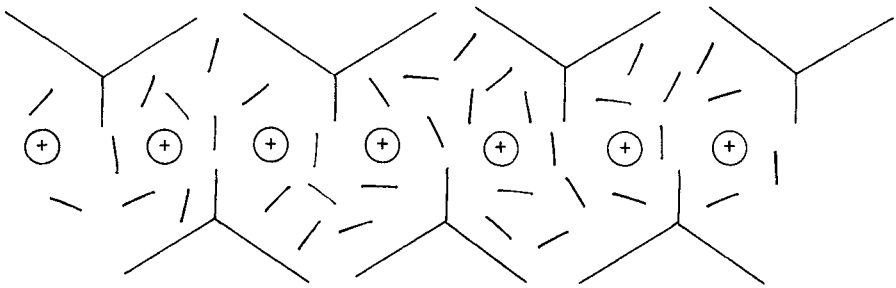

FIG. 3. Model of liquid clathrate behavior in two dimensions. The anions are represented with "Y" and the aromatic molecules with "|".

situation in solution. However, a model which encorporates all the fragments of evidence has arisen and is shown in Fig. 3. Large regions of local order are envisioned.

The model shown in Fig. 3 illustrates that the liquid clathrate effect is based on the presence of cations and anions which interact in a strong fashion with each other. Also implicit in the model is the idea of a cooperative effect. This means that one cation must interact with *several* anions, and vice versa. The association into cation·anion pairs or small units ($[\text{cation}\cdot\text{anion}]_2$ or $[\text{cation}\cdot\text{anion}]_3$) seems to preclude the liquid clathrate formation.

Reasoning based on the ideas presented above has afforded liquid clathrates based on $M[Al_2R_6X]$, $M[AlR_3X]$, $M[N(SiMe_3)_2]$, and [crown ether·$AlCl_2$][$AlCl_4$] (*8*). It is expected that numerous other liquid clathrate parent compounds will be discovered in the near future.

SEPARATIONS RESULTS

Since liquid clathrates were initially thought to form only with aromatic liquids, the best separations would be expected to be those involving aromatics in the presence of aliphatics. Such have been realized. Recent work has opened the scope to now include aromatic/monoene, aromatic/diene, diene/diene, and monoene/diene separations. Before the results are presented, it will be advantageous to compare liquid clathrates to the more familiar solid-state ones. Four factors bear notice. (1) Solid-state clathrates of the Werner type (*9*) can include as much as 20% by weight aromatic guest, but values are commonly in the 10–15% range. Liquid clathrates include 65–90% aromatic by weight. Table 1 illustrates typical values. (2) Guests in Werner-type clathrates may be freed only by destruction of a crystal lattice, an energy-intensive process. Liquid clathrates may be

TABLE 1
Percent by Weight of Aromatic in Selected Liquid Clathrates

Liquid clathrate	% Aromatic
$[N(C_5H_{11})_4][Al_2Me_6I]\cdot 11$ toluene[a]	64
$K[Al_2Me_6N_3]\cdot 5.8$ benzene	67
$[NMe_4][Al_2Me_6Cl]\cdot 5.6$ toluene	69
$[NMe_4][Al_2Et_6I]\cdot 9.2$ *p*-xylene	69
$[NMe_4][Al_2Et_6I]\cdot 18.7$ benzene	77
$[N(C_6H_{13})_4][Al_2Et_6I]\cdot 39$ *o*-xylene	88

[a]It is now recognized that the composition of the iodide-based liquid clathrates is affected by the equilibrium $[NR_4][Al_2R'_6I] \rightleftharpoons [NR_4][AlR'_3I] + AlR'_3$ (*Journal of Inclusion Phenomena*, to be published). In this manuscript the values of A/A are those of Ref. 5.

stripped, in principle at least, by a small change in temperature. (3) Werner-type clathrates involve solids-handling problems in any application. Separations based on liquid clathrates follow the well-established techniques of liquid–liquid extraction. (4) Werner-type clathrates are typically highly selective. The appropriate indices for liquid clathrates are given below, but at the outset we note that the selectivity is in general poorer for liquid clathrates than for solid-state ones.

All of the separations have been carried out in a batch situation. Typically, a parent complex has been exposed to a 50:50 mixture by weight of the two liquids under investigation. The details of the procedure are given in the Experimental Section, but briefly, the liquid clathrate is formed and samples are taken of each of the two liquid layers. The compositions are deduced based on integrations of NMR spectra. The separation factor, α, is calculated as

$$\alpha = \frac{[\text{aromatic/aliphatic}]_{\text{liquid clathrate phase}}}{[\text{aromatic/aliphatic}]_{\text{hydrocarbon phase}}}$$

TABLE 2
Separation Factors for Aromatic/Aliphatic Mixtures[a]

Parent compound	Separation	α
$[Li\cdot 0.5CE][N(SiMe_3)_2]$[b]	Benzene/hexane	3.1
$[NMe_4][Al_2Et_6NO_3]$	Benzene/hexane	5
$[NMe_4][Al_2Me_6NO_3]$	Benzene/hexane	12
$[NMe_4][Al_2Me_6Cl]$	Benzene/hexane	24

[a]Feed mixture was 1:1 by weight.
[b]CE = the crown ether 15-crown-5.

TABLE 3
Separation Factors[a] for Mixtures of Aromatic Compounds with Monenes, Dienes, and Other Aromatics

Parent compound	Separation	α
$[N(C_3H_7)_4][Al_2Me_6I]$	Benzene/1-hexene	8.8
$[N(C_3H_7)_4][Al_2Et_6I]$	Benzene/COD[b]	1.7
$[N(C_3H_7)_4][Al_2Me_6I]$	Benzene/COD	2.2
$[N(C_3H_7)_4][AlMe_3I]$	Benzene/COD	2.2
$[NMe_4][Al_2Me_6Cl]$	Benzene/COD	4.0
$[N(C_3H_7)_4][Al_2Me_6I]$	Benzene/dicp[c]	2.8
$[NMe_4][Al_2Me_6NO_3]$	Benzene/mesitylene	1.8
$[NMe_4][Al_2Et_6NO_3]$	Benzene/mesitylene	1.2

[a]Feed mixture was 1:1 by weight.
[b]COD = 1,5-cyclooctadiene.
[c]dicp = dicyclopentadiene.

Table 2 contains representative values. These are in essential agreement with those found by Harrison and Montagna (*10*) using related compounds.

The data illustrate some apparent generalities. First, the α's are acceptable from a separations standpoint. Second, the smaller, more compact cation–anion systems provide better separations. Third, changes in the anion affect the separations in large but unpredictable ways. By a systematic screening of the known parent compounds, it should be possible to greatly enhance the α's.

As Table 3 shows, the selectivity decreases as one moves toward aromatic/aromatic mixtures. The α of 8.8 for benzene/1-hexene is similar to the values for benzene/hexane. However, benzene/toluene mixtures give near unity α's, and the 1.2 for benzene/mesitylene further illustrates the point.

In the course of extending the range of problems which could be attacked by the liquid clathrate approach, a major difficulty was found. Although liquid clathrates are apparently formed with parent compounds such as $[N(C_3H_7)_4][Al_2Me_6I]$ and dienes such as 1,5-cyclooctadiene, 1,8-octadiene, and dicyclopentadiene, mixtures of dienes (or of monoenes and dienes) often produce sludges instead of well-defined liquid clathrates. Indeed, only the mixture 1,5-cyclooctadiene/dicyclopentadiene with $[N(C_3H_7)_4][Al_2Me_6I]$ could be treated in the normal fashion (an α of 1.3 in favor of 1,5-cyclooctadiene was obtained). A more detailed study of this difficulty has led to observations and realizations which now indicate that even monoene/monoene separations can be effected.

Table 4 shows the composition of liquid clathrates of three dienes compared to one of benzene. It has been previously demonstrated that for

TABLE 4
Composition of Liquid Clathrates Based on Dienes Compared to Aromatic

Parent compound	A/A	Aromatic (or diene)
$[N(C_3H_7)_4][Al_2Me_6I]$	9.4	Benzene
$[N(C_3H_7)_4][Al_2Me_6I]$	6.4	Toluene
$[N(C_3H_7)_4][Al_2Me_6I]$	1.8	1,5-Cyclooctadiene
$[N(C_3H_7)_4][Al_2Me_6I]$	1.8	1,8-Octadiene
$[N(C_3H_7)_4][Al_2Me_6I]$	0.9	Dicyclopentadiene

aromatic molecules a given parent compound produces a cavity of rather equal size regardless of the aromatic (*6*). However, Table 4 shows that this breaks down for dienes. Clearly, 1,5-cyclooctadiene is not five times as bulky as benzene! It seems that the liquid clathrates based on $[N(C_3H_7)_4][Al_2Me_6I]$ exhibit too great an attraction to allow dienes to force the ions into layers. It then occurred to us to use more bulky cations and anions in the hope of forming liquid clathrates of dienes which behave like those of aromatics. Indeed, such has been realized for $[N(C_5H_{11})_4][Al_2Et_6I]$. The complex forms a liquid clathrate with 6.2 molecules of 1,5-cyclooctadiene per cation–anion pair. The value for benzene is 20.2. The pathway toward diene and monoene separations now is apparent. The liquid clathrates with very large A/A values for aromatics must be used for the new task. Note that these are not desirable for aromatics separations because of the poor selectivities. It is hoped that good α's can be obtained for the diene separations, and studies to this end are in progress.

EXPERIMENTAL

All manipulations of aluminum alkyls were performed in an inert atmosphere glove box. Solvents were predried in standard ways and were distilled before use. Trimethylaluminum, triethylaluminum, and all alkali metal and tetraalkylammonium salts were obtained from Alfa Ventron Corporation or Aldrich Chemical Company.

Synthesis of $K[Al_2Me_6N_3]\cdot 5.8C_6H_6$, A Typical Liquid Clathrate. Potassium azide (0.406 g, 5 mmol) was slurried with benzene (10 mL). Trimethylaluminum (1 mL, 10 mmol) was syringed into the mixture. After 5 min of vigorous agitation, the first evidence of a second, more dense liquid layer was observed. Two hours of additional agitation afforded complete reaction (as indicated by the absence of solid and the presence of two liquid layers), but 10 min at 60°C is also sufficient. The composition $K[Al_2Me_6N_3]\cdot 5.8C_6H_6$ was verified by NMR integration.

Separation of Benzene from 1,5-Cyclooctadiene Using $[N(C_3H_7)_4][Al_2Me_6I]$, A Typical Separations Study. A mixture of 20.0 g of benzene and 20.0 g of 1,5-cyclooctadiene (COD) was added to 1.57 g of parent complex. After 10 min of vigorous agitation the flask was allowed to stand for 20 min. At this time an NMR sample was drawn from the bottom layer. The composition of the lower layer was deduced to be $[N(C_3H_7)_4][Al_2Me_6I] \cdot 4.0C_6H_6 \cdot 1.4COD$. Since all the parent complex was in the lower layer, the weights of benzene and COD were calculated as 1.56 and 0.77 g, respectively. By difference, the composition of the top layer was 18.44 g benzene and 19.23 g COD. The value of α was therefore 2.1.

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