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Clathrates in Analytical Separations

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Abstract

Recent advances in clathrate chemistry and their use for analytical and preparative chemistry are discussed. The effect of molecular geometry and substituent groups of guest species on the capabilities of various clathrating compounds is reviewed.

Due in part to improvement in methods available for structural analysis, particularly in x-ray crystallography, the science of clathrate chemistry has made rapid advances in recent years.

The use of clathrates in separation processes has received considerable attention but in relatively restricted application. Further, their potential application in the separation field, particularly in analytical and preparative techniques, has been barely scratched.

This paper will briefly cover the background of clathrate chemistry, the state of the art with respect to separation-analytical techniques, and a projection of the future of clathrates in these fields.

While there are numerous types of guest–host combinations including channels, cages, and layers, emphasis will be placed on layers and cages highly specific in their selective capabilities based on molecular size and shape and capable of being formed and dissociated under fairly mild operating conditions of temperature and pressure or relatively simple chemical change.

A classic example of molecular size selectivity is the inorganic zeolites or "molecular sieves." They function as sieves with the cage or hole size amenable to change on a specific silica–alumina matrix only by exchangeing all or part of the cation associated with the pore structure.

In the clathrate case, some hosts adjust somewhat to the size and shape of the guest component. This may reduce selectivity in some instances but can provide a wide range of compounds and conditions for tailoring a clathrate to achieve a specific separation.

Further, clathrates by virtue of their capabilities of forming and dissociating under relatively modest changes in temperature and pressure offer a broad spectrum of analytical capabilities. At the same time they can provide extremely stable cage-like structures for retention and storage if desired. The hydroquinone complexes of certain rare gases are a case in point and are discussed in detail later.

Molecular compounds such as the gas hydrates, the hydroquinone complexes, and carbohydrate inclusion compounds have been known for decades. However, a basis for extrapolating the behavior and capabilities of a host–guest species has only recently become better understood, and then in a relatively restricted area.

For example, the benzene–nickel cyanide amine complex $[Ni[CN]_2 \cdot NH_3 \cdot C_6H_6]$ has been known since 1897 (*1*). Only in recent years has this chemistry been expanded via the use of other amines in place of ammonia to alter the geometry of the basic lattice structure. This chemistry is also discussed in some detail later.

On the other hand, the chemistry of urea and thiourea adducts was studied in great detail following the discovery of this reaction by Bergen in 1940 (*2*). The chemistry and application of the urea and thiourea adducts for separating alkanes, naphthenes, and their derivatives has been discussed in such detail in numerous publications and patents during the past 25 years that little repetition is needed here.

It should be noted, however, that the investigative activity was probably catalyzed, at least in part, by the interest of the petroleum industry in the potential practical applications of the chemistry to separating valuable hydrocarbon species from crude mixtures.

Urea would probably have been the separating tool of choice for normal paraffin recovery had it not been for the simultaneous development of zeolite molecular sieves for the same purpose. Ingenious engineering concepts in the use of zeolites also aided the tool of choice.

Recent advances in clathrate chemistry indicate that the possibilities with respect to the discovery of new structural types and the application of these compounds and those already known has only been scratched, and we are reviewing their potential in a manner not unlike the iceberg phenomena.

While considerable attention has been directed to the chemistry of these compounds, the methods of exploitation have not been studied as thoroughly.

This is particularly true in the field of liquid phase preparative chromatography as well as vapor phase chromatographic techniques. The possibility of applying a multichemical, multistage technique for class and isomer separation has not received the attention it deserves. We will try to rectify that shortcoming in this brief presentation.

There are available today a spectrum of clathrating agents for separating a wide variety of chemical species as well as geometric isomers. Clathrates may also serve as templates in polymerization or other reaction processes.

A brief description of several clathrating structures and their known or potential application follows.

CLATHRATE TYPES

The molecular geometry of clathrating compounds varies widely as illustrated by the structures indicated in Figs. 1–8.

In the hydroquinone case (Fig. 1), the sulfur dioxide compound was discovered in the preparation of hydroquinone by reduction of an aqueous solution of benzoquinone with sulfur dioxide (*3*).

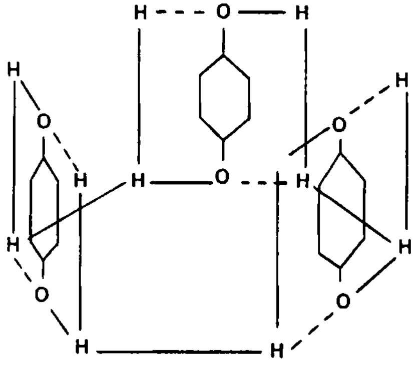

FIG. 1. Hydroquinone.

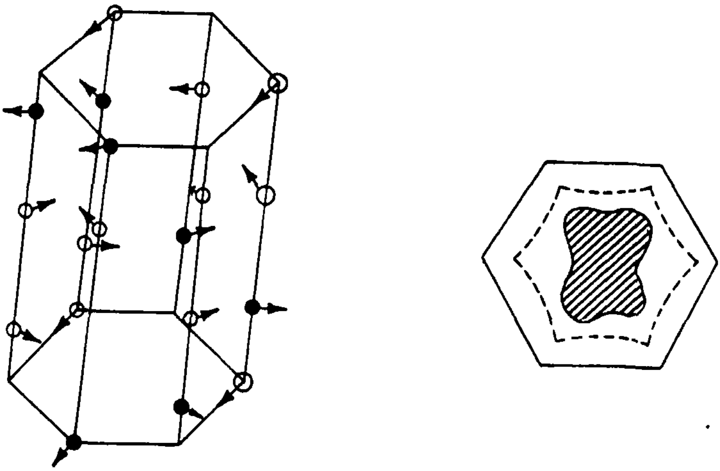

FIG. 2. Basic crystal lattice of urea complexes.

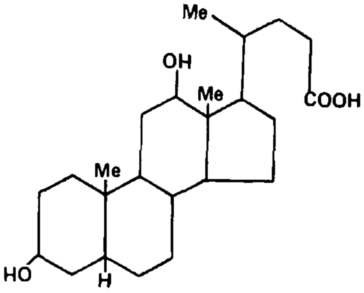

FIG. 3. Deoxycholic acid.

The urea case has already been alluded to in Bergen's discovery, as has the subsequent activity in this field which is continuing (Fig. 2).

Deoxycholic acid's capabilities in clathrating with *n*-alkanes has been known for years (Fig. 3).

An interesting question one could pose would be directed to the difference in this compound and urea, for example, that exhibit similar clathrating capabilities.

A more recent addition to this field is tri-*o*-thymotide, shown in Fig. 4.

In Fig. 5 the unrelated structure of 4,4'-dihydroxy triphenyl methane is illustrated. This is merely an illustration of clathrating compound types.

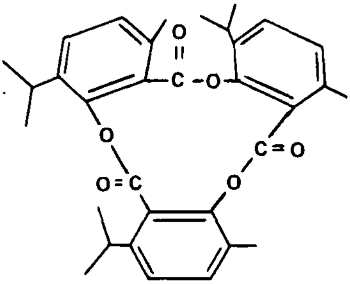

FIG. 4. Tri-*o*-thymotide.

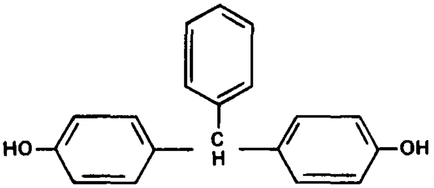

FIG. 5. 4,4'-Dihydroxy triphenyl methane.

One could draw an analogy with the hydroquinone complexes, but the extrapolation of this chemistry needs much more attention.

In Fig. 6 the well-known $Ni[CN]_2 \cdot NH_3$ complex is illustrated, based on the crystallographic studies of Powell and Rayner (*4*).

This chemistry has been expanded by a number of workers, particularly that of Schaeffer and co-workers (*5*), de Radzitsky and Hanotier (*6*), and Williams (*7*). Their work has concentrated essentially on a variety of Werner complexes comprised of the basic components depicted in Table 1. These Werner complexes are also discussed in some detail later.

A more recent entry in the field is the compound shown in Fig. 7. Apparently a layered packing of this chemical forms channels and cages capable of clathrating with a wide variety of structures (*8*).

Cyclodextrins, polysaccharides, amylose, glycogen, amylopectin, and spirochromans (shown in Fig. 8) have clathrating capabilities of varying dimensions in cage and channel structures.

Briefly, this gives us an overview of the type of structures available for clathrate separations.

Many important structures such as hydrates, methyl naphthalenes,

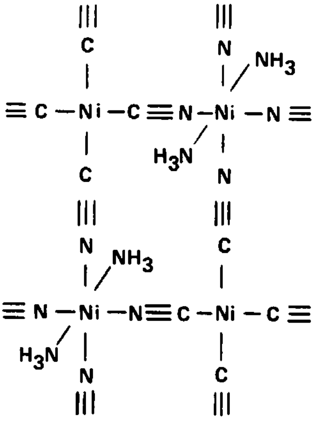

FIG. 6. Sheetlike structure of $Ni(CN)_2NH_3$.

TABLE 1

Werner Complexes

$M(N)_4X_2$

M = metal, Ni, Co, Fe, Mn, etc.
N = pyridene, substituted pyridines, benzylamines, etc.
X = thiocyanate, formate, halide (preferably SCN)

Selection of N compound determines the spacing of the metal complex layers

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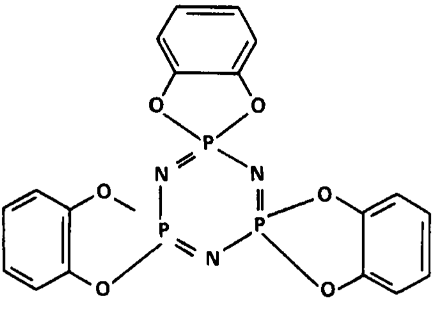

FIG. 7. Tris(*o*-phenylenedioxy)phosphonitrile trimer.

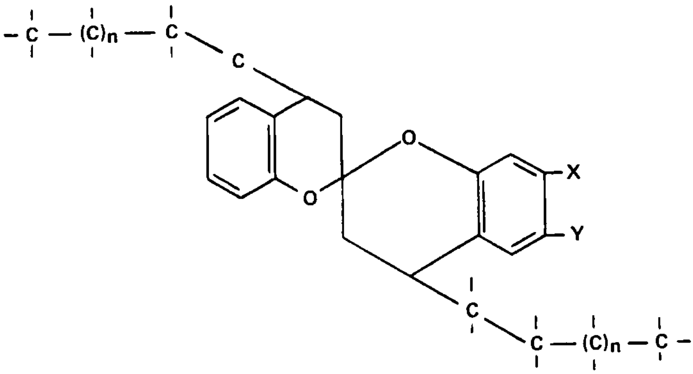

FIG. 8. Spirochromans.

substituted diphenyls, and other carbohydrates are also available for potential exploitation.

CLATHRATE GEOMETRY

Clathrates considered here exist in several geometric types including (a) layer structures, (b) channel or tunnel structures, and (c) cage structures.

As previously noted, the channel or tunnel type has received the greatest attention in recent years via in-depth investigations of the urea and thiourea complexes and their capabilities. This channel-type clathrate of urea involves a helix of molecules with six urea molecules per unit cell with hexagonal spacing. (Carbohydrates and proteins also form clathrates by wrapping around the guest compound.)

Hydrogen bonds tend to make the urea honeycomb cells contract: this force is resisted while the endocytic compound is present, but when the guest compound is liberated from the channel the hexagonal clathrate collapses to the less open and more stable tetragonal urea form.

In the layered structure case the metal nitrile-amine complexes are classics. The variation of the $Ni[CN]_2 \cdot NH_3 \cdot C_6H_6$ case is numerous. The distance between the metallic salt layers can be controlled by the choice of nitrogen containing complexing agent which, in turn, determines the distance between the floor and ceiling of the cage structure. To a degree, the wall dimensions have some latitude via the choice of substituent group on the chosen metal specie.

Cage structures are numerous, including the gas hydrates as well as the hydroquinone complex. In the hydrate case the voids in the structure are partially occupied by the parent clathrate former with additional pockets or cages available for occupancy by the guest compound.

Hydroquinone forms very stable clathrates with a variety of gases such as HCl, H_2S, SO_2, CO_2, Ar, Kr, and Xe, and low molecular weight aliphatics such as methanol and formic acid.

Clathrates of the gases can be stored for long periods of time at ambient temperature and pressure with little or no apparent vapor pressure exerted due to the tight cage structure. Pulverizing the crystals in a mortar and pestle develops the characteristic odor of certain encapsulated species, indicating partial release of the trapped component by mechanical breakdown of the crystal lattice.

These various geometric forms frequently overlap in their molecular sorting and encapsulating capabilities.

Table 2 compares the cage diameters of several clathrating species. The term "cage" is used here to denote the encapsulating geometry. As just pointed out, urea forms channel-type structures, while hydroquinone and the hydrate form cages with tri-*o*-thymotide exhibiting a series of cages connected by channels.

By the same token, the clathrate formers depicted in Table 3 also illustrate more than a single behavioral mode.

Attention is directed to the fact that the geometry of the cage formed is critical with respect to clathrating capabilities. Thus a channel structure such as thiourea can separate very high molecular weight isoalkanes, alkanes, and naphthenes whereas a cage structure such as the hydrates has a much more restricted functional molecular weight range of guest component.

TABLE 2

Cage Diameters of Several Clathrating Species

Host molecule	Cage diameter (Å)	Guest type
Hydroquinone	4.2–5.2	Ar: SO_2
Urea	5.25	*n*-Alkanes and derivatives
Thiourea	6.1	Isoalkanes, naphthenes *n*-alkanes $> C_{16}$
Desoxycholic acid	5–6	*n* + Isoalkanes, naphthenes
Tri-*o*-thymotide	4.8–6.9 (channel-cage)	*n* + Isoalkanes, naphthenes
Hydrates Type I	5.2–5.9	C_1–C_4 Paraffins and olefins
Hydrates Type II	4.8–6.9	

TABLE 3

Cage Diameters of Several Clathrating Species

Host molecule	Cage diameter (Å)	Guest type
4,4′-Dihydroxy triphenyl methane	6.0–6.5	n + Isoalkanes
$Ni(CN)_2 \cdot NH_3$	7.2	Benzene, thiophene, furan, pyrrole, aniline, phenol
$M \cdot (-N)_4X_2$	Est. 7–10	Aromatic isomers
γ-Cyclodextrin[a]	9–10	Aromatics

[a] α and β Cyclodextrins accommodate *n*-alkanes and fatty acids.

Thus urea is highly specific due to its rigidity (inflexibility) and mode of formation. γ-Cyclodextrin does not appear to be as selective as the controlled layered spacing of the $M[N]_4X_2$ complexes which can be tailored to separate geometric isomers.

SEPARATION CAPABILITIES

The urea and thiourea systems have been thoroughly discussed by previous authors and need no repetition here regarding their classic separation behavior.

However, in recent years the urea channel has been used as a polymerization template, a release agent for selected chemicals in a reaction, and the separation of cis-trans isomers. Specificity for unsaturation position has also been noted.

The shorter the chain length required, the greater the ease of urea complex formation. Dialkyl esters of succinic, fumaric, maleic, and acetylenedicarboxylic acid have been studied in this regard (*9*).

The shortest homologs capable of complex formation in the succinate and fumarate series are the diethyl esters which have the “slenderest” cross sections (5.0 and 5.1 Å).

The acetylenedicarboxylate, which has a 5.2 Å cross section, requires the di-*n*-propyl ester as a minimum while the 5.3 Å diameter maleate requires the di-*n*-butyl ester as a minimum for complex formation (*10*).

Further studies in this area indicated the influence of unsaturation position on complex-forming capabilities.

Alkenoic acids, except 3-*n*-hexenoic and 3-*n*-octenoic acids, formed urea inclusion compounds.

All other alkenoic acids differed from these two by the presence of a double bond in the 2-position. The same authors noted a similar trend in studies of alkynes. The triple bond did not prevent complex formation in 1-, 2-, or 3-nonyne and 2- and 3-decyne but did prevent complex formation in 4-nonyne and 5-decyne. Thus, as these authors observed, the isomer with the more centrally located double bond appears less stable and forms less complex or no complex under comparable conditions.

Selenourea exhibits only a small difference in channel diameter from that of urea or thiourea but appears to be more selective with geometric isomers (*11*).

Apparently selenourea is more amenable to adoption to the shape and size of the included molecules. Selenourea seems to be much more selective, however, in its choice of guest components. An example cited noted that *trans*-1-*t*-butyl-4-neopentylcyclohexane formed an adduct but the cis isomer was not included. Thiourea was not selective in this case, which suggests the possible use of selenourea for separating isomeric alkyl naphthenes, alkyl aromatics, and the like.

Clathrates offer an interesting challenge in this period of energy consciousness. By the proper choice of agent and reaction conditions it is possible to recover desired compounds from mixtures with small temperature changes and at a relatively high loading of the clathrate compared to loadings in conventional extraction processes. As pointed out by this author and his associates, hydrates offer some promise in this area (*12*).

Werner complexes are also promising candidates in this regard, but in most cases the reaction rate needs considerable improvement (e.g., by one or two orders of magnitude).

ANALYTICAL AND PREPARATIVE TECHNIQUES

Urea and thiourea have been successfully exploited as separation tools for analytical separations as well as for specialty industrial products.

Although subjected to extensive study in-depth for a quarter of a century, the urea–thiourea field continues to receive attention.

A number of patents have appeared in the United States and abroad during the past year directed toward improving the mechanics of handling the urea adduction process in the petroleum industry.

However, other available clathrating agents have not been as thoroughly studied and applied. For example, the use of hydroquinone complexes for separating and storing gases has had only limited attention. The same chromatographic techniques developed for both gas and liquid separations have received only cursory examination in the clathrate field.

If one considers developed techniques for enhancing the analytical capabilities of gas chromatography via the use of added salts to the substrate, the extrapolation of various clathrating agents such as the Werner complexes, dextrins, hydroquinone, and tri-*o*-thymotide is apparent.

Early work in this area involved successful application of partition and adsorption chromatography for separation of mixtures differing in type and number of functional groups or for separation of members of a homologous series (*13*).

The columns of Kemula and Sybilska consisted of β- and γ-picoline and 2,6-lutidine nickel dithiocyanate complexes. They used concentrated solutions of potassium thiocyanate or the γ-picoline containing some KSCM in aqueous solution as a mobile phase.

More recently (*14*), Werner complexes have been investigated as stationary phases in gas chromatography to determine the influence of various substituents in the aromatic rings of these complexes on the elution order of molecules of varying shapes and structures.

The spirochromans have been used in adsorption chromatography separations (*15*). A number of spirochroman derivatives were investigated with respect to the substituent effect on the resolution of iso- and *n*-alkanes. The spirochromans were added to an appropriate column followed by addition of the hydrocarbon charge with subsequent collection of effluent-containing resolved species.

One can visualize the broad spectrum of potential application of various clathrating agents in analytical and preparative separation considering the choice of structures available and the wide variety of essentially inert subtrates that is available.

Werner complexes dispersed in polyolefin oxide, polyglygols, polyphenyls, and the like could be used for gas chromatography work, or they could be used either in massive form on dispersed or coated on an inert support.

The same techniques could be applied to the other clathrating compounds described, except the hydrates. Most of the hydrates are particularly applicable to lower temperature and/or high pressure operation. A few Freon hydrates are functional at atmospheric pressure and from 0 to about +10°C.

There are exceptions. The hydrates of trialkyl sulfonium salts and tetraalkylammonium salts are similar to the gas hydrates, but the hydrate with the formula $2[i\text{-}C_5H_{11}]_4N^+F^- \cdot 76H_2O$ is a surprising substance consisting of 68% water that remains an ice until heated to 88°F.

A series of chromatographic columns can be employed to separate complex mixtures into normal and iso-structures as well as ortho-, para-, and meta-substituted aromatic species.

Considerable potential latitude is available to the ingenious investigator in both analytical and preparative chemical separations.

SEPARATIONS EXPECTED

In the classic urea or thiourea cases, one can devise multistage extraction or adsorption columns capable of yielding 99+ % purities in two to five equilibria stages depending on the complexity of the feed and the required recovery of the desired specie. In fact, this has been done for specialty hydrocarbons, particularly those of high molecular weight where desorption of zeolite molecular sieves is less practical.

The application of urea adduction for separating polar compounds has been less active. As pointed out by Bergmann (*16*), alkyl halides may be complexed with much shorter chain lengths than hydrocarbons, presumably due to the polarizable functional group.

Werner complexes are particularly useful for separating aromatic hydrocarbons and their derivatives.

To separate ortho isomers, one has quite an effective tool with a nickel dithiocyanate–tetramethyl benzylamine complex as shown in Table 4 (*6*). The separations shown are for a single stage only. It is apparent that relatively few equilibria stages would be required to attain high purity and recovery of most species. The chlorotoluenes are relatively unimpressive but the dichlorobenzenes are readily resolved.

TABLE 4

Separation of Ortho-Isomers: [$Ni(SCN)_2(\alpha$-methylbenzyl amine$)_4$] (*6*)

Compound	Ortho-isomer in Feed	Ortho-isomer in Clathrate	Wt-% guest in clathrate
Ethyl toluenes	33.5	74.3	13.9
Cymenes	41.0	91.7	10.8
Ethyl isopropyl benzenes	29.5	90.3	9.6
Cyclohexyl toluenes	28.6	85.8	15.7
o-Ethyl toluene and mesitylene	50.2	98.2	13.9
Dichlorobenzenes	50.3	85.4	14.2
Chlorotoluenes	35.0	45.5	13.1

TABLE 5

Separation of Para-Isomers: Tetra-(4-methyl pyridino)-nickel dithiocyanate (*5*)

Compound	Para-isomer in Feed	Para-isomer in Clathrate	% Recovery
Chlorotoluenes	50.2	91.4	35
Dichlorobenzenes	52.8	93.0	34.8
Toluidines	49.1	68.4	10.1
Nitrotoluenes	50.0	73.5	7.0
Methyl anisoles	52.2	94.4	25.5

If one is concerned with the separation and/or recovery of para isomers, a change in the base of the complex suffices as shown in Table 5. Here is an excellent example of changing clathrating capabilities by apparent altering of the distance between the plates of the nickel dithiocyanate (*5*).

Para isomer separation was also studied by Williams (*7*) using the metal salt as a variable with surprising results as shown in Table 6. Here is a classic analogy of the nickel ammonium thiocyanate–benzene complex case wherein the 4-methyl pyridine molecule provides a large "box" or cage in the layers compared to the NH_3 case.

A comparison of nickel salt effects on dichlorobenzenes and methyl styrenes indicates excellent agreement on selectivity. The capacity of the complex for methyl styrenes is greatly improved by using the ferrous or cobaltous salts in place of the nickel. Selectivity is somewhat reduced, but this difference would be relatively insignificant in a multistage process such as liquid phase chromatography.

Much more needs to be done to exploit this interesting field. With our present knowledge, almost any desired aromatic isomer may be selectively trapped by the proper Werner complex.

As an example of altering clathrate structures to accommodate a

TABLE 6

Separation of Para-Isomers: 4-Methyl pyridine $(SCN)_2$ Clathrates (*7*)

Metal	Feed	Mole guest per mole metal complex	Composition of guest
Ni^{2+}	Dichlorobenzenes	0.76	90.5%p, 9.5%
Ni^{2+}	Methyl styrenes	0.60	90.0%p, 10.0%
Fe^{2+}	Methyl styrenes	0.94	82.3%p, 17.7%
CO^{2+}	Methyl styrenes	0.86	82.5%p, 17.5%

particular compound, Morita et al. (*17*) described tetracyanopalladate(II) and tetracyanoplatinate(II) aromatic clathrates. Thus $Cd[NH_3]_2Pd[CN]_4$ complex can trap fluorobenzene which apparently has too large a molecular volume to form a clathrate with the lattice $Ni[NH_3]_2Ni[CN]_4$.

The fluorobenzene clathrate $Cd[NH_3]_2Pd[CN]_4 \cdot nC_6H_5$ ($n < 2$) was confirmed by IR spectra, the broad line NMR spectra of ^{19}F, and proton.

Hydrates have been discussed by this author and his co-workers (*12*, *18*) previously in some detail regarding their separation capabilities.

They are particularly useful for separating C_3 to C_5 molecular weight hydrocarbons. Excellent separations of normal and isoalkanes and alkenes have been demonstrated with better separations of paraffins than of the corresponding olefin.

In Table 7 a few of the clathrating agents that have been found to be particularly useful for low molecular weight hydrocarbon separations are tabulated.

The capabilities of the tetrahydrofuran system for separating isobutene

TABLE 7

Properties of Hydrating Agents Studied

			Critical hydrate properties	
Name	Structure	bp (°C)	T (°C)	Pressure (Torrs)
Freon, F-11	CCl_3F	+25	+6.5	410
Freon, F-21	$CHCl_2F$	+8.9	+8.7	760
Freon, F-1426	CH_3CFCl_2	−9.6	+13.1	1743
Methyl bromide	CH_3Br	+3.56	+14.7	1151
Tetrahydrofuran		+64–66		

TABLE 8

C_4 Paraffin, Olefin, Diene System

Component, wt-%	Feed	THF, hydrate
Isobutane	3.1	8.2
n-Butane	3.8	5.1
Butene-1	13.4	5.8
Isobutene	40.3	71.4
cis,trans-Butene-2	12.0	2.8
Butadiene	27.5	6.7

and isobutane from a mixture of the other C_4 hydrocarbons normally found in a cracked gas stream are illustrated in Table 8. These data have been previously reported in the above references but are offered here for review. Again it should be pointed out that these results are for single stage separations.

However, the limitations encountered have been largely attributable to the limitations of the void space in the hydrate structure. Altering the lattice structure of the hydrate via other lattice-forming hydrating agents could be the answer.

THE FUTURE OF CLATHRATE CHEMISTRY

Since the discovery of the diamine nickel(II) tetracyanoniccolate(II) dibenzene ($Ni[NH_3]_3Ni[CN]_4 \cdot 2C_6H_6$) by Hoffmann (*1*) in 1897, the field of clathrate chemistry has broadened to include a wide spectrum of organic and inorganic compounds capable of high selectivity and capacity. The opportunities to tailor a "host" to accommodate a specific guest are apparent. The potential application to analytical and preparative problems are numerous.

In many cases the use of clathrates to achieve a separation may involve relatively small temperature and/or pressure changes. Compared to extractive distillation or liquid–liquid extraction, clathrates can be relatively low in energy requirements to achieve a given separation.

As the cost of energy increases and provides a larger lever in process economics, engineering requirements will be developed to further exploit these useful and interesting compounds beyond the analytical and preparative scope emphasized here.

Acknowledgments

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