Liquid Clathrates

Dianne R. Bond,[a] Graham E. Jackson,[a] Heidi C. João,[a] Michelle N. Hofmeyr,[a] Tomasz A. Modro,[b] and Luigi R. Nassimbeni*[a]

[a] *Chemistry Department, University of Cape Town, Rondebosch 7700, South Africa*
[b] *Chemistry Department, University of Pretoria, Pretoria 0002, South Africa*

Tetra-alkylammonium tetra-alkylborate salts form liquid clathrates with a variety of hydrocarbons and can be used for coal extraction.

J. L. Atwood[1] discovered that host compounds of the type $M^+[Al_2R_6X]^-$, (M^+ = alkali metal or tetra-alkylammonium cation; R = Me, Et, $\mathrm{Pr^n}$, $\mathrm{Bu^n}$, X = halide, N_3^-, SCN^-) interact with a variety of aromatic solvents (guests) to produce liquid inclusion compounds, which he called 'liquid clathrates'. These host–guest compounds ($\mathrm{H}\cdot n\mathrm{G}$) are characterised by a definite host : guest ratio which depends on the natures of the host and guest, and the temperature. Atwood has used these liquid clathrates for coal extraction,[2] and shown that a toluene-based liquid clathrate immediately turned black when put in contact with ground coal. The problem with these host compounds is that they decompose when exposed to moisture and air. Currently there is considerable interest in liquid clathrate systems, and several new air stable liquid clathrates have been found.[3,4,5]

In searching for a new class of such compounds we reasoned that they should be ionic, with alkyl moieties which would yield a liquid or low melting solid, and we synthesised a number of tetra-alkylammonium tetra-alkylborates. These form liquid inclusion compounds with a number of aromatic and aliphatic guest molecules, and can be used directly for coal extraction.

The synthesis may be described by the reactions (1)—(3).

$$3\mathrm{RMgX} + \mathrm{BF_3} \rightarrow \mathrm{R_3B} + 3\mathrm{FMgX} \qquad (1)$$

$$\mathrm{R'Li} + \mathrm{R_3B} \rightarrow \mathrm{Li^+[R_3BR']^-} \qquad (2)$$

$$\mathrm{Li^+[R_3BR']^-} + \mathrm{[NR''_4]^+Br^-} \rightarrow \mathrm{[NR''_4]^+[R_3BR']^-} + \mathrm{LiBr} \qquad (3)$$

This yielded a variety of host compounds with the anion $\mathrm{[(Bu^s)_3B(Bu^n)]^-}$ and the cation $\mathrm{[NR_4]^+} = \mathrm{[NMe_4]^+}$, $\mathrm{[N(Bu^n)_4]^+}$, $\mathrm{[N(n\text{-}C_6H_{13})_4]^+}$, $\mathrm{[N(n\text{-}C_8H_{17})_4]^+}$. The liquid clathrates were prepared by mixing the host compound with excess hydrocarbon. Upon agitation, two immiscible layers separated, the upper layer contained only hydrocarbon and the lower layer contained the host–guest association compound. The latter was analysed by ^{1}H NMR spectroscopy. Representative results of the stoicheiometry of a variety of liquid clathrates formed with the host H1 = $\mathrm{[N(n\text{-}C_6H_{13})_4]^+ [(Bu^s)_3\,B(Bu^n)]^-}$ are shown in Table 1. This shows the greater affinity of the host compound for aromatic over aliphatic hydrocarbons. This led us to carry out a series of competition experiments where the host compound was mixed with excess

Table 1. Composition of liquid clathrate system $\mathrm{H}\cdot n\mathrm{G}$. H1 = $\mathrm{[N(n\text{-}C_6H_{13})_4]^+[(Bu^s)_3\,B(Bu^n)]^-}$; G = hydrocarbon at 25 °C.

Hydrocarbon G	*n*
Benzene	17
Toluene	16
p-Xylene	14
p-Cymene	4
Cyclohexane	3
Cyclohexene	6
n-Hexane	4
1,4-Dioxane	15

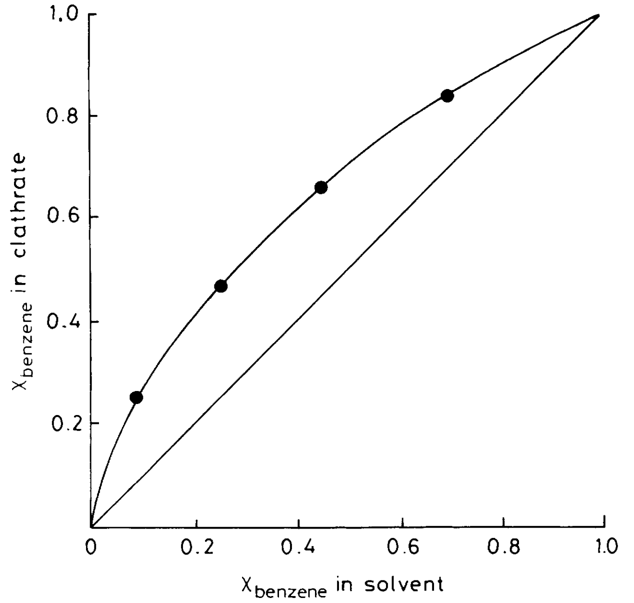

Figure 1. Selectivity of benzene from a benzene/n-hexane mixture by the liquid clathrate.

amounts of mixtures of two guest samples. Figure 1 shows the results of a representative experiment with the host H1 and benzene/n-hexane mixtures. The result clearly indicates that these systems can be used for separating aromatic from aliphatic hydrocarbons, a process which is of potential importance to the petroleum industry.

Attempts to crystallise many of these host–guest compounds failed, so the NOE was used as a probe to the structure in solution. Both inter- and intra-molecular NOEs were detected. Substantial NOE was observed between the guest protons and the host cation protons, but no NOE was observed between the guest protons and the host anion protons. This implies that the guest molecules lie between the arms of the host cation.[6] Distance calculations, based on the approach of Mirau,[7] indicate that the guest molecules lie towards the end of the host alkyl chain, with the bulky guest substituents orientated away from the ammonium nitrogen.

The toluene-based liquid clathrate of H1 was tested for its extraction capability on Grootegeluk, a high grade bituminous South African coal. The method involved mixing dry powdered coal with the liquid clathrate until the mixture reached equilibrium. The extraction procedure was based on the method described by Stobart and West.[8] The coal weight loss was 6% at 25 °C and 10% at 120 °C. This improved considerably by bubbling H_2 gas through the mixture, and the highest weight loss achieved by this method was 18% at 25 °C.

Received, 1st September 1989; Com. 9/03733K

References

1 J. L. Atwood, in 'Inclusion Compounds,' Academic Press, 1984, vol 1, ch. 9.
2 J. L. Atwood, 1977, U.S. Pat. 4,024,170.
3 D. C. Hrncir, L. M. Barden, M. R. Wells, and P. C. Stark, *J. Incl. Phenom.*, 1988, **6**, 233.
4 M. V. Gaudet, D. C. Peterson, and M. J. Zaworotko, *J. Incl. Phenom.*, 1988, **6**, 425.
5 J. L. Atwood, S. G. Bott, A. W. Coleman, K. D. Robinson, S. B. Whetstone, and C. M. Means, *J. Am. Chem. Soc.*, 1987, **109**, 8100.
6 R. Fornasier, V. Lucchini, P. Scrimin, and U. Tonnelato, *J. Incl. Phenom.*, 1986, **4**, 291.
7 P. Mirau, *J. Magn. Reson.*, 1988, **80**, 439.
8 S. R. Stobart and P. R. West, 'Direct Coal Liquefaction under ambient conditions, Phase II,' 1985, (D.S.S. Contract = 12 ST-23440-4-9029), Contract Report = OST84-00012.