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THE THERMAL BEHAVIOUR OF SOME CLATHRATES BASED UPON DIANIN'S COMPOUND

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Clathrates based upon Dianin's Compound (4-p-hydroxyphenyl-2,2,4-trimethylchroman) exhibit shape and size selectivity towards included guest molecules in a manner similar to that shown by some commercially important zeolites. Clathrates derived from Dianin's Compound and a wide range of guest solvents were heated to their melting points and beyond, and their behaviour observed.

Recently, some studies in this laboratory have been directed to the possibility of converting ethanol to a more suitable gasoline-like hydrocarbon fuel by thermal treatment over a zeolite catalyst. Many substances are capable of converting alcohols to hydrocarbons, but the zeolites are particularly attractive because conversions may be achieved at relatively low temperatures (ca. 300°) and because the products contain mixtures of hydrocarbons principally in the range C_5–C_9, with a high proportion of methyl benzenes. The selectivity of these catalysts toward the production of the trimethyl benzenes is most important due to their very high fuel octane rating.

One particular zeolite, which brings about the above conversions with very high efficiency, is the so-called "ZSM–5". The use of this substance has been developed by the Mobil Oil Company and an American patent dealing with the conversion of small, oxygen-containing molecules to useful fuel hydrocarbons has been issued to the Company. ZSM–5 is therefore known as the "Mobil Catalyst" [1].

Earlier reports concerning this catalyst had described the formation of hydrocarbons from methanol and from a wide variety of hetero-organic compounds [2], but it was not until more recently that the successful conversion of ethanol and aqueous ethanol to liquid hydrocarbons was described [3].

Suggested mechanisms for these reactions have involved both the provision of Brönsted acid sites on the internal surfaces of the zeolite cage and the role of cavity geometry [2].

Early difficulties encountered in the conversion of ethanol to hydrocarbons by means of the Mobil Catalyst prompted an investigation into the possibility of using organic "analogues" of the zeolites, i.e. organic compounds having well-defined cage or cavity geometry in their crystalline state. Many such substances, acting as hosts in "clathrate" or "inclusion" compounds, have been described and several excellent reviews on the subject have appeared in recent years (see e.g. [4, 5]).

Clathrates based on Dianin's Compound

Dianin's Compound (4-p-hydroxyphenyl-2,2,4-trimethylchroman) has been shown to form clathrates readily with a wide variety of organic solvents [6] and may be conveniently prepared by the acid-catalysed condensation of phenol and mesityl oxide. X-ray studies carried out on both the unsolvated (empty) host and several of its clathrates have established the dimensions of the cage structure and have shown the internal surface of the cavity to have a shape resembling that of an hour-glass [7].

The possibility of using Dianin's Compound in the manner of the Mobil Catalyst was evaluated by a study of the rules governing the accommodation of guest molecules in the host cavities and the thermal behaviour of Dianin's Compound and its clathrates at temperatures up to melting point.

The present report describes observations made relating to thermal behaviour. Matters pertaining to guest selection and accommodation rules are the subject of further reports [8, 9].

Experimental

Dianin's Compound (DC) was prepared from phenol and mesityl oxide according to the method of Baker et al. [6]. The unsolvated material was derived from the ethanol complex by both precipitation and sublimation following the methods used by the same authors.

Clathrates were formed in all cases by dissolving DC (40 mg) in pure solvent (500 mg) with minimum warming. Where clathrates were prepared from solvent pairs, the host compound was dissolved in solvents mixed in equimolar proportions. Solutions were allowed to crystallise slowly on standing at room temperature. The crystalline products were separated and dried by vacuum filtration on sintered glass. For solvents with high boiling points, crystals were washed on the filter with small amounts of water.

Melting points were determined by means of a Rigaku Thermobalance/Differential Scanning Calorimeter, an Electrothermal glass capillary apparatus and a Reichert Hot-Stage Microscope. All substances were heated at ca. 10°/min. to a few degrees above the melting point, allowed to cool to the freezing point and then re-melted at the same heating rate.

Loss in weight data for the various clathrate compounds were obtained by

(1) direct measurement from the Rigaku Thermobalance;

(2) by change in weight recorded as each sample (40–50 mg) was heated in a glass tube (5 mm X 50 mm) for 5 minutes at 200°.

Quantitative gas chromatographic analyses were performed for guest substances liberated on pyrolysis (200°, 20 seconds) of each DC clathrate. Pyrolyses were carried out in the coil of a CDS Pyroprobe attached directly to the inlet port of a Perkin–Elmer Series 800 Gas Chromatograph equipped with a flame ionisation detector and a column packed with Porapak-Q. The various instrument settings (flow rates, temperatures, etc.), were adjusted to suit the particular guest substance and the detector response for each was calibrated by direct injection of the pure solvent.

Results and discussion

The combined data from both the capillary melting point apparatus and the hot-stage microscope are presented in Table 1. Melting and freezing points are corrected and cooling rates were approximately 15°/min. The appearance of arrows against

Table 1 Melting-freezing behaviour of some DC clathrates

Clathrate	M. pt., °C	F. pt., °C	Re-m. pt., °C
DC Sublimed	159–160	80–85↑	159–160
DC Ppted	159–160	–	159–160
DC Methanol	162–163*	90↑	160–161
DC Methanol/H_2O	162–163*	88↑	160–161
DC Ethanol	167	83↑	159–160
DC 1-Propanol	163	–	160–161
DC 2-Propanol	164–166	–	–
DC 1-Butanol	162–164	–	–
DC t-Butanol	162	135↑	160
DC Aniline	158*	87↑	160–161
DC Pyridine	161	100↓	160–161
DC Piperidine	161	150↓	159–160
DC N,N-Dimethylaniline	157	–	157
DC Diethylamine	165	125↓	161
DC Triethylamine	161–162	145↓	160–161
DC Diethanolamine	166–167	100↓	164–166
DC Acetic acid	162*	90↑	161
DC Acetic acid/H_2O	161–162	110↑	161
DC Acetone	160*	–	161
DC Cyclohexanone	158–159	–	160
DC Benzene	159*	145↓	160
DC Xylene	161	110↑	160

* Denotes vigorous evolution of guest solvent at the melting point.

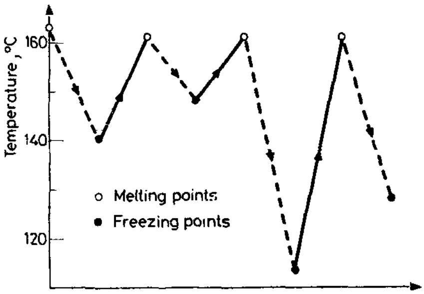

Fig. 1 Melting-freezing cycles for DC-methanol

freezing or solidification point temperatures indicates that the phase change took place on cooling (↓) or during subsequent re-heating (↑). The absence of a value in this column indicates that crystallization from the melt was not spontaneous and occurred only when induced mechanically.

When the melting points and re-melting points in the table are compared, it can be deduced that, in most cases, the DC clathrate loses its included solvent guest on melting and reverts to the unsolvated form with an average melting point of 160°. However, in the cases where the solvent guest has a boiling point greater than the melting point of the clathrate, the guest does not escape on the melting of the host crystal, but rather re-combines with the host on cooling to re-form the original clathrate. The examples illustrated in Table 1 are the clathrates prepared from N,N-dimethylaniline (b. pt. 194°) and diethanolamine (b. pt. 270°).

It is therefore possible that the determination of guest solvent content by the measurement of loss in weight on melting of the clathrate, as carried out for example by Baker et al. [6], could be subject to error, particularly since, as these authors point out, the clathrate should not be heated beyond 200° if decomposition of the DC host is to be avoided. Furthermore, the practice of heating under reduced pressure greatly increases the volatilization of the host.

With the exception of those of the clathrates from N,N-dimethylaniline and diethanolamine, the freezing point temperatures shown in Table 1 represent that of the unsolvated DC and should therefore be the same throughout. That this is not the case is assumed to be due to factors such as difference in rates of cooling, the presence or absence of nucleation centres, accidental vibrations, etc. The point is well illustrated by the behaviour of the DC-methanol clathrate when it is taken through a number of melting-freezing cycles (Fig. 1).

Thermal behaviour and differential scanning calorimetry

An idealised schematic DSC profile for a melting-freezing-melting cycle of the ethanol clathrate of Dianin's Compound is shown in Fig. 2. The first endotherm represents the melting of the ethanol clathrate and shows a weight loss in the thermo-

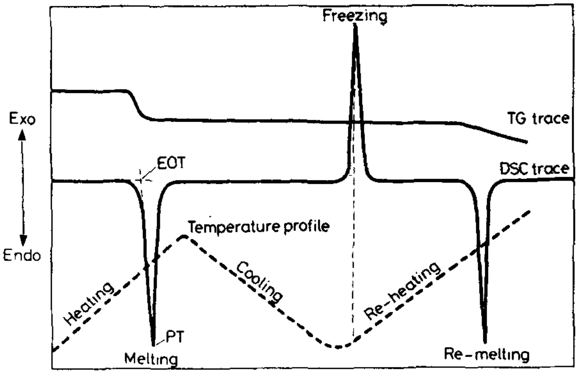

Fig. 2 Schematic differential scanning calorimetry (DSC) and thermogravimetry (TG) traces for ethanol/Dianin's Compound clathrate

gravimetric trace corresponding to the escape of the ethanol guest. The two temperatures to be noted on the endotherm are the extrapolated onset temperature (EOT) and the peak temperature (PT). The exotherm in the centre of the figure represents the liquid-to-solid phase change as the molten substance solidifies. The third peak is the endotherm corresponding to the melting of the unsolvated (guest-free) host compound. Weight loss in this case is due to the sublimation of Dianin's Compound. The temperature profile trace in Figure 2 shows that solidification of the molten host occurred during reheating.

Some uncertainty exists as to whether the extrapolated onset temperature or the peak temperature represents the true phase transition point [10–12]. Values obtained from DSC analysis of a number of DC clathrates are shown in Table 2. Comparison with the data of Table 1 shows that, in general, peak temperatures rather than extrapolated onset temperatures correspond to the values derived from the use of other methods.

Loss in weight

When DC clathrates are heated to their melting points, the crystal lattice structure collapses and substances included in the cages or cavities are free to escape. Thus there should be a loss in weight equivalent to the amount of guest substance included. The data obtained by gravimetric methods by Baker et al. [6] show good agreement with values expected from theoretical considerations. Goldup and Smith [13], however, have shown that the content of guest material may be influenced by the conditions of crystallization of the clathrate and so it is of the utmost importance that losses in weight on heating reflect the *total* evacuation of the guest substance *alone* and do not include contributions from the volatilization or decomposition of the host.

Table 3 presents theoretical loss in weight values (%) which would be expected if 1, 2 and 3 guest molecules per DC host cavity were present.

Table 2 Clathrate thermal behaviour (DSC)

Sample	Melting pt., °C		Freezing pt., °C	Re-melting pt., °C	
	EOT	PT	PT	EOT	PT
DC Sublimed	154	157	–	–	–
DC Ppted	158	162	116↑	154	163
DC Methanol	158	162	124↓	163	168
DC Methanol/H_2O	158	162	–	–	–
DC Ethanol	154	160	113↓	154	160
DC t-Butanol	155	162	119↑	157	162
DC Aniline	156	164	87↑	157	162
DC Pyridine	153	156	119↓	156	159
DC Piperidine	152	156	129↓	154	158
DC Diethylamine	154	161	107↑	154	158
DC Diethanolamine	159	163	–	–	–
DC Acetic acid	155	160	89↑	154	157
DC Acetic acid/H_2O	155	159	–	–	–
DC Benzene	150	161	–	–	–
DC Xylene	152	157	125↓	154	159

Table 3 Theoretical loss in weight, %

DC guest molecule	1 mol/cavity	2 mols/cavity	3 mols/cavity
Methanol	1.95	3.82	5.63
Ethanol	2.78	5.41	7.90
1-Propanol	3.60	6.94	10.07
2-Propanol	3.60	6.94	10.07
1-Butanol	4.40	8.43	12.13
2.Butanol	4.40	8.43	12.13
t-Butanol	4.40	8.43	12.13
Acetic acid	3.60	6.94	10.07
Propionic acid	4.40	8.43	12.13
Diethylamine	4.34	8.32	11.99
Diethanolamine	6.13	11.55	16.38
Pyridine	4.68	8.95	12.85
Benzene	4.62	9.38	12.70
Xylene	6.18	11.65	16.51

Results obtained in the present work are shown in Table 4.

Comments on Table 4

Inspection of TG traces shows that weight loss through volatilization of the host material is significant and becomes noticeable near the melting point of the clathrate, increasing rapidly with rising temperature (Fig. 3). With the present apparatus, loss of host material occurring in this way cannot be avoided; thus, weight losses due to guest solvents alone must be estimated after correcting for background weight loss due to the host. Errors will be introduced if the manner in which the guest solvent escapes (e.g. vigorously) at the melting of the composite causes a loss of host material. It is of interest to note that with the exception of DC-piperidine, no appreciable weight loss could be detected (from the TG trace) at temperatures lower than the melting point of the clathrate. The behaviour of the piperidine compound suggests that leakage of guest solvent from the cage had occurred before the melting point had been reached, as noted by Baker et al. [6]. These authors were not able to report a melting point for the piperidine adduct. In the present work however, a sharp melting point of 161° was recorded.

Gas chromatographic data for guest solvent content was generally in agreement with theoretical values. This method should provide the most accurate data since errors due to sublimation of the host are avoided.

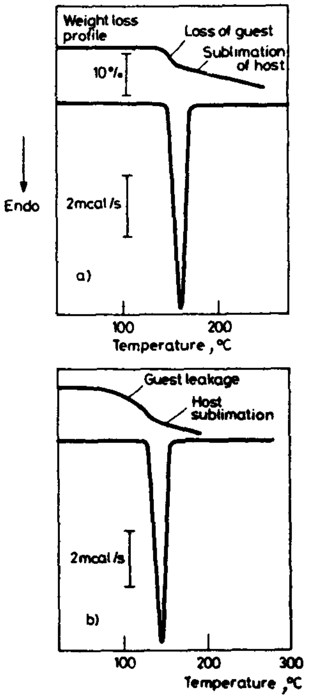

Fig. 3 DSC and TG traces showing weight loss on heating. a) Acetic acid D/C, b) Piperidine D/C; heating rate 10 deg/min

Table 4 Comparison of loss in weight (%) obtained by various methods

DC clathrate	Thermogravimetry (TG)	VPC	Gravimetric
Methanol	4.8	3.8	2.3
Ethanol	4.2	5.1	4.3
1-Propanol	3.3	6.9	4.6
2-Propanol	4.9	6.9	4.6
1-Butanol	5.2	4.1	1.8
2-Butanol	5.0	4.5	1.0
t-Butanol	10.5	4.4	5.3
Acetic acid	7.0	9.8	3.6
Propionic acid	4.9	9.4	2.7
Diethylamine	3.7	6.1	–
Diethanolamine	7.1	–	2.3
Pyridine	4.2	8.2	3.7
Benzene	4.4	2.9	2.6
Xylene	6.8	6.3	3.1

The gravimetric method as used in the present work gave data which were most irregular. Some errors associated with host sublimation and incomplete escape of the guest solvent might explain these irregularities.

Solvent leakage at elevated temperatures

Several DC clathrates were examined to evaluate the extent of guest solvent leakage from the host cavities at temperatures below the melting point. Clathrates were heated at various temperatures and were then pyrolysed (see Experimental). The emerging guest solvents were estimated quantitatively. The results are summarised as follows in Table 5.

Table 5 Solvent leakage at elevated temperatures

Clathrate	Temp., °C	Time, min	Solvent leakage
DC Methanol	105	45	Nil
	130	60	Nil
	150	95	ca. 5% solvent lost in first few minutes only
DC Ethanol	105	60	Nil
	130	60	Nil
	150	60	Nil
DC Acetone	105	105	Nil
DC Methanol/ethanol	105	105	Nil
DC Methanol/2-butanol	105	130	Nil
DC Methanol/1-propanol	105	60	Nil

Conclusions

1. Clathrates based on Dianin's Compound gave up their included guest solvent when heated to the melting point and reverted to the empty "unsolvated" form. Exceptions were found where the guest solvent had a boiling point greater than the melting point of the adduct. In such cases, the original composite was likely to re-form on cooling.
2. Of the clathrates studied under the conditions used in the present work, only that involving piperidine as guest showed evidence of significant solvent escape at temperatures below the melting point.
3. Freezing or solidification point temperatures from the molten state showed little if any reproducibility.
4. Volatilization of host material was shown to occur to a significant extent at the melting point and increased markedly with rise in temperature beyond the melting point.
5. Estimation of guest solvent content by pyrolysis/vapour phase chromatography was shown to be an acceptable technique, since errors arising from host volatilization and decomposition were avoided.

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Zusammenfassung — Auf Dianin's Verbindung (4-p-Hydroxyphenyl-2,2,4-trimethylchroman) basierende Klathrate weisen gegenüber eingeschlossenen Gastmolekülen eine ähnliche Form- und Grössenselektivität auf wie einige wichtige kommerzielle Zeolithe. Von Dianin's Verbindung und einer Reihe von Lösungsmitteln erhaltene Klathrate wurden bis zum Schmelzpunkt und darüber hinaus erhitzt und dabei ihr Verhalten beobachtet.

Резюме — Клатраты на основе соединения Дианин — 4-п-оксифенил-2,2,4-триметилхроман — показали избирательность к форме и размерам, включенных молекул "гостей", подобно некоторым продажным цеолитам. Клатраты, производные соединения Дианин, со многими молекулами "гостями" растворителей были нагреты до температуры плавления и выше, с целью их термического поведения.