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Kevin J. Harrington[a]; Carl P. Garland[a]
[a] CSIRO DIVISION OF CHEMICAL TECHNOLOGY SOUTH MELBOURNE, VICTORIA, AUSTRALIA

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The Sorption of Organic Substances by Dianin's Compound and Its Clathrates

KEVIN J. HARRINGTON and CARL P. GARLAND

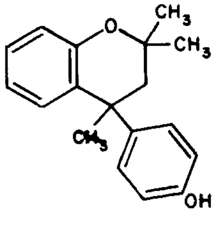
CSIRO DIVISION OF CHEMICAL TECHNOLOGY
SOUTH MELBOURNE, VICTORIA 3205, AUSTRALIA

Abstract

Crystalline Dianin's Compound and several of its clathrates have been shown to sorb organic acids, bases, and alcohols in liquid and vapor states. Some implications of these observations in the field of separation technology are discussed.

INTRODUCTION

Dianin's Compound (DC, 4-*p*-hydroxyphenyl-2,2,4-trimethyl chroman) has been shown to form clathrates by crystallization with many organic solvents (*1*, *2*), and a number of these crystalline adducts have been the subject of intensive x-ray crystal structure analysis (*3*). The host compound, unsolvated Dianin's Compound (US/DC, empty cavities), and most of the adducts examined have been shown to crystallize in the rhombohedral



Dianin's compound

system with hexagonal cell dimensions $a = 2.7$ nm, $c = 1.1$ nm, and space group $R\bar{3}$. The most likely structural unit is thought to comprise six molecules of the host substance linked by a hexagonal ring of H-bonded hydroxyl groups with three molecules of threefold symmetry pointing upward and the alternate three pointing downward. The downward-pointing triplet from one OH-ring interleaves with the upward-pointing triplet from an adjacent OH-ring to form a cavity or cage, the height of which is equivalent to the *c*-axis of the hexagonal cell. The cages form an infinite string, parallel to *c* by fusion of the OH-rings, and have an internal surface shape resembling that of an hourglass or a peanut shell. The crystal topography of DC is essentially the same whether or not a guest molecule is present in the cavity and only minor changes in crystal parameters have been reported for most of the DC clathrates so far studied.

The importance and versatility of inorganic cavity-containing crystalline structures have been recognized for many years. The zeolites—aluminosilicates having cavities enclosed by three-dimensional framework structures—are widely used commercially as molecular sieves in separation processes and as cracking and reforming catalysts in the petrochemical industry.

The significance of these materials has been further emphasized in recent years by the discovery and development of ZSM-5, the so-called Mobil Catalyst (*4*), a zeolite capable of converting a wide range of small oxygenated molecules (e.g., methanol, acetic acid) to a gasoline-like product in high yield, and "silicalite," a silica with zeolite-like cavity architecture capable of absorbing small organic molecules from their dilute aqueous solutions (5).

The present paper examines the sorptivity of organic clathrate-forming compounds, i.e., substances whose crystal structure involves the formation of cavities or cages which, like the zeolites, are well defined in terms of both shape and size. These "zeolite analogues" are based on Dianin's Compound and several of its adducts.

EXPERIMENTAL

Preparation of Dianin's Compound (DC)

DC was prepared in 50% yield by the acid-catalysed condensation of phenol and mesityl oxide according to the method of Baker et al. (*1*). Crystallization from cold ethanol gave the ethanol adduct as chunky, colorless prisms, mp 167°C (Ref. *1*, 165–166°C).

Preparation of Unsolvated Dianin's Compound (US/DC)

(a) The unsolvated material (empty cavities) was prepared from the ethanol complex by sublimation (150°/0.1 mm) and gave colorless hexagonal rods, mp 159–160°C (Ref. *1*, 156°C).

(b) The ethanol adduct was dissolved in hot 2 *N* sodium hydroxide and US/DC was precipitated by treatment of the solution with carbon dioxide, according to the method of Baker et al. (*1*). The product, obtained in 90% yield, had mp 159–160°C (Ref. *1*, 159–160°C).

Preparation of DC Adducts

Adducts of DC were conveniently prepared with a range of organic solvents according to the following example.

US/DC (40 mg) was dissolved in pure dry methanol (500 mg) with minimal warming. Crystallization was allowed to take place slowly by standing the clear solution at room temperature. The product was separated and dried by vacuum filtration on sintered glass to give the methanol adduct as colorless, fine hexagonal needles, mp 162–163°C (Ref. *1*, 155–156°C). In the cases where solvents with high boiling points were used, the crystalline products were washed on the filter with small amounts of water.

Adducts prepared for the present study are described in Table 1.

TABLE 1

		Guest content[a]	
Adduct	mp (°C)	wt-%	Molecules/cavity
Methanol/DC	162–163	3.8	2
Ethanol/DC	167	5.1	2
Pyridine/DC	161	8.2	2
Triethylamine/DC	161–162	6.0	1
Diethylamine/DC	165	6.1	1
Acetic acid/DC	162	9.8	2

[a] Guest content determined by vapor-phase chromatography as described in the text.

Vapor-Phase Chromatography

Concentrations of components of solvent mixtures were determined quantitatively by means of Perkin-Elmer Series 800 Gas Chromatograph equipped with a flame ionization detector and a column of Porapak-Q. Instrument settings (oven temperatures, flow rates, etc.) were adjusted to suit the particular substance, and the detector response for each was calibrated by direct injection of the pure material.

Guest solvent content of the various DC adducts was determined by heating the crystalline material at 200°C for 20 s in the coil of a CDS Pyroprobe (Chemical Data Systems, Inc., Oxford, Pennsylvania) attached to the inlet port of the gas chromatograph. Guest solvent, liberated by the melting of the crystalline adduct, was flushed into the chromatographic system and determined quantitatively as above.

"Postcolumn" Technique

Sorption studies from the vapor phase were carried out by using a short column (50 mm × 3 mm i.d.) packed with 1 g of the sorbent under investigation and inserted in the chromatograph oven between the exit of the main column and the flame ionization detector. Pure solvents and solvent mixtures were injected into the system in the usual manner and the effluent stream was analyzed quantitatively at the detector. In this way, changes in vapor composition attributed to sorption in the "postcolumn" could be evaluated directly.

RESULTS AND DISCUSSION

Although DC readily forms adducts on crystallization from its solutions in a variety of solvents, little has been reported concerning the ability of molecules of suitable size and shape, in either liquid or vapor state, to penetrate into the vacant cavities of the host material while the latter is in the solid crystalline form.

If it is assumed that penetrability factors governing passage of a guest molecule *into* the host cavity are similar to those operating for a guest molecule *leaving* the cavity, then the work of MacNicol et al. (*6*) describing the closed nature of the cavities of clathrates based upon DC is relevant here. These authors also demonstrated (*7*) that the case structure of the thia-analogue of DC prevents the escape of the volatile dimethyl mercury, even under conditions of reduced pressure over several days. Further evidence of the low permeability of the cavities of crystalline DC is found in the earlier work of Baker et al. (*1*) in which, as a routine procedure, adducts were dried at 100°C/0.1 mm for several hours without apparent loss of the guest solvent.

Results obtained recently in this laboratory (*8*) have confirmed by thermogravimetric analysis that, for a wide range of guest species, adducts of DC suffered little loss in weight at termperatures below those of their melting points.

Barrer and Shanson (*9*) have shown, however, that sorption by DC of a range of substances in the gas phase is possible. These authors claim that such sorption involves occupation of the cavities and show (in their Fig. 3b) that there is no apparent hysteresis in the sorption–desorption isotherm for neopentane (for example), thereby implying that even a molecule as bulky as neopentane has apparently little difficulty in passing into and out of the host cavities.

Barrer and Shanson invoked cavity absorption to explain their data. The sharp increase reported in the sorption of argon and xenon as a result of mild ball milling could perhaps equally well be attributed to an increase in surface (noncavity) adsorption brought about by the creation of many new surfaces. Steric constraints, similar to those suggested by Barrer and Shanson to explain the data of their Table 1, could still operate if the sorption were of the surface, noncavity type.

If movement into and out of host cavities were restricted, it might be expected that a guest substance already accommodated in a cavity would be shielded from interaction with substances outside the cavity. For example, chemical reactions through cavity boundaries should be difficult if not impossible to carry out. Hoffman et al. (*10*) have reported that glycerol, when included in a DC cavity, was rendered inert to oxidative attack by both hydrogen peroxide and lead tetraacetate. Similarly, sorbitol and D-glucose were not oxidized by periodic acid, but were in fact attacked by hydrogen peroxide and lead tetraacetate. (An alternative explanation for these results could involve stereochemical constraints imposed upon such guest substances accommodated within the clathrate host cavities.)

Thus it was appropriate to examine the sorption behavior of DC and several of its adducts toward simple organic molecules. Of particular interest in this laboratory are those substances, e.g., alcohols and volatile fatty acids, which may be produced as liquid fuels or liquid fuel precursors via the fermentation of biomass.

Sorption of Methanol and Ethanol

Both methanol and ethanol are readily accepted as guest species when US/DC is crystallized from its solutions in these solvents. Under the usual conditions of crystallization (see Experimental) the methanol adduct was found to contain two molecules of the guest for each cavity, with one molecule probably residing in each of the two "subcavities" (Fig. 1). Similarly, the ethanol adduct was found to contain two molecules of the alcohol per cavity. Weight loss data presented by Baker et al. (*1*) have suggested that each cavity is capable of accommodating three molecules of methanol.

To investigate the possibility of a guest molecule gaining access to a vacant cavity where the host substance was in the solid crystalline form, US/DC was shaken with aqueous ethanol for an extended period and the alcohol concentration of the supernatant was monitored as a function of time. No change in alcohol concentration was detected even after an exposure period of 12 h at room temperature. A similar result was obtained for methanol.

However, in another series of experiments, US/DC was exposed to a stream of nitrogen containing methanol vapor at 120°C. After 15 min, examination of the host crystals by the pyrolysis/chromatographic technique indicated that methanol had been taken up by the sorbent to the extent of ~2% by weight, corresponding to approximately one molecule of the alcohol per DC cavity. The alcohol content was not decreased when the sorbent was heated in a stream of dry nitrogen at 120°C for several hours, suggesting that the sorbed methanol was either in the host cavities or firmly attached to the outside surfaces of the crystalline host. The experiment was repeated with ethanol instead of methanol, and a similar result was obtained.

Some indication that the sorption of the two alcohols had taken place *in* the cavities rather than on the outside surfaces of the crystal was provided by the observation that when methanol vapor was passed through a bed containing the ethanol/DC adduct, no methanol was retained. Similarly, no ethanol was sorbed when its vapor was passed through a bed containing the methanol/DC adduct.

These results also suggest one alcohol is unable to displace the other from

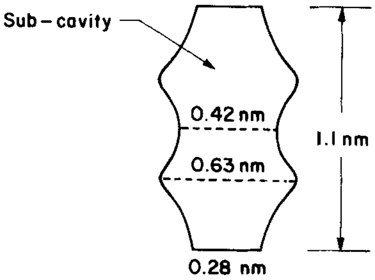


FIG. 1. Schematic drawing of cavity in Dianin's Compound. From Cook et al. (*12*).

its position in the cavity, even though, when crystallizing from an equimolar mixture of the two alcohols, the DC host exhibited a sixfold preference for the inclusion of ethanol rather than methanol (*11*).

By the use of the "postcolumn" techniques, a more convenient modification of the above, it was demonstrated that US/DC was capable of stripping ethanol from water in the vapor phase. For example, the ethanol concentration of an aqueous solution was reduced from 10% (v/v) to 1% (v/v) after one pass through a short postcolumn containing US/DC at 120°C.

The ability of the US/DC sorbent to exhibit some degree of selectivity was demonstrated when an equimolar mixture of ethanol and butan-2-ol was passed through a short postcolumn at 120°C. Examination of the effluent stream showed that both alcohols had been partially taken up, with preference shown to the butan-2-ol. Results are summarized in Table 2.

Sorption of Organic Acids and Bases

In a series of experiments similar to those described above for the alcohols, US/DC was found to be unable to sorb acetic acid from its dilute aqueous solution in the liquid phase. However, when aqueous acetic acid (10% v/v) was passed through a column containing US/DC at 120°C, sorption of 90% of the acid in the vapor stream was shown to occur.

The organic base triethylamine gave an unexpected result. When US/DC

TABLE 2

Sorbent	Feed	Mode of contact	Contact time	T (°C)	Sorption
US/DC	Aqueous ethanol (10% v/v, liquid)	Batch	12 h	20	Nil
US/DC	Aqueous methanol (10% v/v, liquid)	Batch	12 h	20	Nil
US/DC	Methanol (vapor)	Stream	15 min	120	Sorbent contains 20% ethanol
US/DC	Ethanol (vapor)	Stream	15 min	120	Sorbent contains 2% ethanol
EtOH/DC	Methanol (vapor)	Stream	15 min	120	Nil
MeOH/DC	Ethanol (vapor)	Stream	15 min	120	Nil
US/DC	Aqueous ethanol	Postcolumn		120	Effluent contains 1% EtOH
US/DC	Ethanol/butan-2-ol (equimolar, vapor)	Postcolumn		120	2° alcohol preferred

was shaken with a dilute aqueous solution of the amine, the base concentration of the supernatant was reduced considerably (as evidenced by both chromatographic and pH measurements). The possibility of explaining this result in terms of chemical reaction between the amine (basic) and the phenolic hydroxyl groups (acidic) of the DC host was discounted since (a) infrared spectral examination of the sorbent after treatment indicated no change in the hydroxyl stretching region of the spectrum and (b) it was possible to prepare the crystalline adduct of triethylamine and DC from a solution of the host in the pure solvent base. When the adduct was melted and the triethylamine guest liberated, the unsolvated host was recovered unchanged (*10*).

SORPTION BY DC ADDUCTS

The results of MacNicol (*6*) and Barrer (*9*), together with those presented above, suggest that some form of access is possible through the cavity walls of the solid crystalline host compound. The possibility was thus explored that the sorption of compounds could be influenced by guest substances already present in the cavities. Consequently, the sorption of acetic acid was examined for a number of adducts containing organic bases and that of organic bases was studied for the DC adduct of acetic acid.

Sorption of an Acid

As described above, acetic acid was not sorbed from the liquid phase by US/DC. However, when the host cavities were occupied by the base pyridine (2 molecules/cavity) and by triethylamine (1 molecule/cavity), sorption of acetic acid from dilute aqueous solution occurred from the liquid phase. The extent of sorption (2.1) and 0.17 mmol acid/g adduct, respectively) did not correspond to any stoichiometric scheme for salt formation. Where the guest species was diethylamine (containing one molecule/cavity), no detectable sorption of acid from the liquid phase was recorded.

On the other hand, each of the base-containing DC adducts examined in the present work was shown to sorb acetic acid from the vapor phase, but no systematic stoichiometric relationship could be established.

A typical result for acetic acid sorbed form vapor phase by a base adduct of DC is shown for pyridine/DC in Fig. 2.

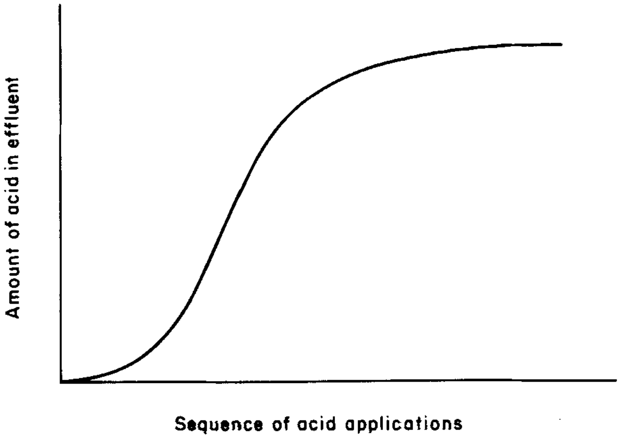


FIG. 2. Sorption of acetic acid by pyridine/DC adduct.

Sorption of a Base

The effect of an acid occupant of the DC host cavities on the sorption of an organic base from its aqueous solution was evaluated by adding an amount of acetic acid/DC adduct to a dilute solution of triethylamine in water. Titrimetric analysis of the supernatant after 1 h indicated that the base had been sorbed to an extent greater than when the host cavities were unoccupied. The increase in base sorption corresponded approximately to the amount of acetic acid present in the DC adduct. A summary of the results obtained is presented in Table 3.

CONCLUSIONS

1. Unsolvated Dianin's Compound and at least some of its adducts are capable of sorbing organic molecules.
2. In the examples studied, the possibilities for sorption are greatly enhanced when the sorbate is in the vapor phase rather than in the liquid phase.
3. The ability of DC adducts (when the cavities are occupied) to sorb certain organic substances suggests that sorption need not be restricted to the "in-cavity" type.

4. For the acids and bases examined, the influence of cavity occupants on the sorption of other species appears to have a qualitative rather than a stoichiometric affect.

TABLE 3

Sorbent	Feed	Mode of contact	Contact time (h)	T (°C)	Sorption
US/DC	Aqueous acetic acid (10% v/v, liquid)	Batch	3	20	Nil
US/DC	Aqueous acetic acid (10% v/v, vapor)	Postcolumn		120	Effluent contained 1% acid
US/DC	Aqueous triethylamine (5% v/v, liquid)	Batch	3	20	7.5 mmol base/g
Pyridine/DC	Aqueous acetic acid (10% v/v, liquid)	Batch	3	20	2.1 mmol acid/g
Triethylamine/DC	Aqueous acetic acid (10% v/v, liquid)	Batch	3	20	0.17 mmol acid/g
Diethylamine/DC	Aqueous acetic acid (10% v/v, liquid)	Batch	3	20	Nil
Pyridine/DC	Aqueous acetic acid (10% v/v, vapor)	Postcolumn		120	Effluent contained no acid
Triethylamine/DC	Aqueous acetic acid (10% v/v, vapor)	Postcolumn		120	Effluent contained no acid
Diethylamine/DC	Aqueous acetic acid (10% v/v, vapor)	Postcolumn		120	Effluent contained no acid
Acetic acid/DC	Aqueous triethylamine (5% v/v, liquid)	Batch	3	20	8.8 mmol base/g

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REFERENCES

1. W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving, and J. H. Wild, *J. Chem. Soc.*, p. 2010 (1956).
2. A. Goldup and G. W. Smith, *Sep. Sci., 6,* 791 (1971).
3. J. L. Flippen, J. Karle, and I. L. Karle, *J. Am. Chem. Soc., 92,* 3749 (1970).
4. C. D. Chang and A. J. Silvestri, *J. Catal., 47,* 249 (1977).
5. E. M. Flanigen et al., *Nature, 271,* 512 (1978).
6. D. D. MacNicol, A. D. U. Hardy, and J. J. McKendrick, *Ibid., 256,* 344 (1975).
7. R. J. Cross, J. J. McKendrick, and D. D. MacNicol, *Ibid., 245,* 146 (1973).
8. K. J. Harrington, Submitted for Publication.
9. R. M. Barrer and V. H. Shanson, *Chem. Commun.* p. 333 (1976).
10. H. L. Hoffman, Jr., G. R. Breeden, Jr., and R. W. Liggett, *J. Org. Chem., 29, 3440 (1964).*
11. K. J. Harrington, Submitted for Publication.
12. J. S. Cook, R. G. Heydon, and H. K. Welsh, *J. Chem. Soc., Faraday Trans. 2, 70*(9) 1591 (1974).

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