Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Selective Clathration of Aliphatic Alcohols by Dianin's Compound

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

To cite this Article Harrington, Kevin J.(1982) 'Selective Clathration of Aliphatic Alcohols by Dianin's Compound', Separation Science and Technology, 17: 12, 1443 — 1450
To link to this Article: DOI: 10.1080/01496398208055632
URL: http://dx.doi.org/10.1080/01496398208055632

SEPARATION SCIENCE AND TECHNOLOGY, 17(12), pp. 1443–1450, 1982-83

Selective Clathration of Aliphatic Alcohols by Dianin's Compound

KEVIN J. HARRINGTON

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

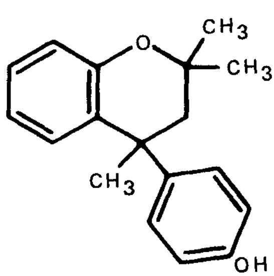
Abstract

Dianin's Compound (4-*p*-hydroxyphenyl-2,2,4-trimethylchroman) has been shown to demonstrate a marked selectivity when it forms clathrates from binary alcohol solutions. The relationship between solvent composition in solution and in the crystalline adduct was found to be linear in all but one case. The degree of selectivity was expressed quantitatively as the "preference index." Results obtained indicated that the molecular shape of a potential guest plays a dominant role in the formation of Dianin's Compound adducts.

INTRODUCTION

The ability of organic clathrates and other inclusion compounds to bring about subtle separations in organic systems has long been recognized, and a number of comprehensive reviews on the subject have appeared in recent years (*1–3*).

One such substance which continues to attract considerable attention is 4-*p*-hydroxyphenyl-2,2,4-trimethylchroman (Dianin's Compound) (*4*):



Dianin's compound

Dianin's Compound (DC) has been shown to form clathrates with many organic solvents (*5, 6*), and several of these complexes have been the subject of crystal structure analysis (*7*). The cavity formed by the crystalline host compound comprises six molecules which form a cage having the internal shape of an hour glass.

The ease of synthesis of DC and its various analogues, together with its relatively simple crystal architecture, have made it an attractive model for the study of geometric factors considered to be important in the formation of stoichiometric inclusion compounds (*8–12*). Observations based upon such studies have led to the formation of a new strategy for the design of inclusion compounds (*13*).

The selectivity with which guest molecules are accommodated within the cavities of clathrating species has created much interest in the exploitation of DC in separation technology.

The Concept of Accommodation Factor (AF)

Where one guest molecule is accommodated in each cage, the molar ratio of host to guest is six to one. The data of Baker et al. (5), covering some 54 DC adducts, show molar ratios varying from 2:1 (i.e., 3 molecules per cavity) for methanol to 9–17:1 (i.e., $\ll 1$ molecule per cavity) for decalin as guest. In many cases a value of 6:1 was obtained in accordance with the crystal structure later determined by Flippen et al. (*7*).

Low values may be interpreted as being due to one cavity providing accommodation for more than one guest molecule, whereas high values for the host to guest ratio (>6) have been explained by assuming that some cavities contain no guest molecule (*6*). When clathrate formation takes place from a solution of host in a vast excess of solvent guest (as is the usual case), it would seem reasonable to assume that all cavities formed on crystallization would have an equal opportunity to include a guest molecule, provided that the presence of a guest molecule in one cavity did not influence the inclusion capabilities of neighboring cavities. It may be that, for an adduct possessing a high host:guest ratio, more than one cavity is involved with each guest molecule or that the guest is not being accommodated *within* the cavities, but rather in the intercavity crystal spaces, or perhaps a combination of both.

The implication that guest molecules may not be entirely contained (protected?) by a cage raises the interesting possibility of involving such "partially protected" guest species in chemical reactions with a high degree of specificity, perhaps approaching that of an enzyme. The data of Hoffman et al. (*14*) concerning both the qualitative and quantitative oxidation of carbohydrates when clathrated with DC, and the selective aromatic substitution of anisole while contained, at least partially, within a cyclodextrin complex, as described by Breslow and Campbell (*15*), may lend support to this possibility.

A convenient relationship for clathrates involving DC has been put forward by Goldup and Smith (*6*) who defined an "accommodation factor"

$$AF = \frac{6}{H/G}$$

where H/G is the observed molar ratio of host to guest substances. AF is therefore equal to the number of guest molecules present for each cavity.

Recent work in this laboratory has been concerned with the ability of solid crystalline DC to sorb low molecular weight alcohols, acids, and bases (*16*), and has sought to investigate factors relevant to their formation as adducts with the DC host.

The present paper, therefore, describes results obtained from investigations designed to characterize the behavior of DC when clathrated with a range of alcohols under both competitive and noncompetitive conditions.

EXPERIMENTAL

Preparation of Dianin's Compound

DC was prepared from the acid-catalyzed condensation of phenol and mesityl oxide according to the method of Baker et al. (*5*). Treatment of a hot solution of DC in 2 *N* NaOH and CO_2 gave the unsolvated product (US/DC) as colorless rods, mp 159–160°C (Ref. 5, 159–160°C).

Preparation of DC Clathrates

Clathrates were formed in all cases by dissolving DC (40 mg) in pure solvent (0.5 g) or in solvent mixtures (0.5 g total). The mixtures were warmed gently to effect solution and were allowed to crystallize slowly on standing at room temperature. The resulting crystalline products were separated and dried by vacuum filtration on a sintered glass filter. Where solvent mixtures were involved, care was exercised when the solutions were warmed to avoid loss by evaporation of the more volatile component.

Analysis of Guest Composition

Guest content of the various adducts was determined by heating each sample at 200°C for 20 s in the coil of a CDS Pyroprobe (Chemical Data Systems, Oxford, Pennsylvania) attached to the inlet port of a Perkin-Elmer Series 800 Gas Chromatograph. The flame ionization detector response for each guest was determined by calibration with the pure solvent (*16*).

RESULTS AND DISCUSSION

The Clathration of Simple Aliphatic Alcohols

Noncompetitive Conditions

DC was dissolved in each of a range of pure aliphatic alcohols, and the adducts so obtained were analyzed as described above. From the data, values of AF were calculated and are presented in Table 1.

As might be expected, smaller molecules with little or no branching tend to be accommodated more easily (AF $>$ 1) than are larger or more bulky molecules. Differences between the values of AF shown in Table 1 and the expected whole numbers are due possibly to the effect of rate of formation of the clathrate as noted by Goldup and Smith in their studies on hydrocarbon clathration (*6*).

Competitive Conditions

It was of interest to examine whether the above accommodation characteristics could be reproduced when US/DC was forced to form adducts in the

TABLE 1

Characteristics and Accommodation Factors for Some DC/Alcohol Clathrates

Clathrate	mp (°C)	Guest weight (%)	AF
DC/methanol	162–163	3.8	1.98
DC/ethanol	167	5.1	1.88
DC/propan-1-ol	163	6.9	1.99
DC/propan-2-ol	164–166	6.9	1.99
DC/butan-1-ol	162–164	4.1	0.93
DC/butan-2-ol	162–163	4.5	1.02
DC/*t*-butanol	162	4.4	1.0

presence of more than one potential guest substance, i.e., in a competitive situation. The host compound was therefore dissolved in a number of different solvent pairs (with methanol common to each) over a range of relative solvent concentrations, and the adducts were allowed to crystallize in the usual manner. The values of AF for each guest component of the clathrate were determined, From these data, accommodation factors (relative to methanol) were calculated and were plotted against the concentrations (relative to methanol) of the solvent components of the binary mixtures from which clathration had taken place.

Figure 1 shows results obtained for methanol/ethanol mixtures, and is typical of the linear relationship found for all examples studied, with the exception of that for the system methanol/*t*-butanol.

For such linear relationships the slope of the line is numerically equal to the "preference index," i.e., in the case of Fig. 1, the slope of 6 indicates that from an equimolar solvent mixture of methanol and ethanol, DC forms a clathrate which exhibits a sixfold preference for ethanol over methanol. Table 2 lists the relative accommodation factors for the competitive and noncompetitive situations.

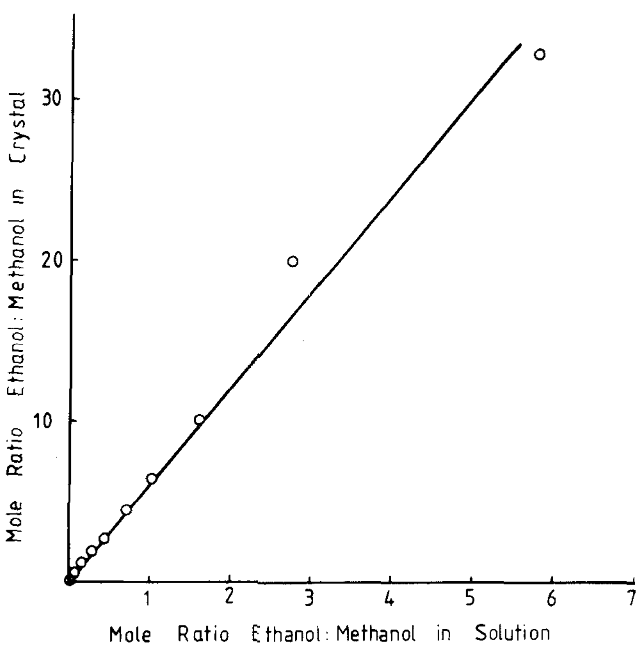


FIG. 1.

TABLE 2

Accommodation Factors (relative to methanol) of Clathrates Formed from Single Solvents and Binary Solvent Mixtures

	AF (relative to methanol)	
Binary solvent mixture	Noncompetitive	Competitive (Preference Index)
Ethanol/methanol	0.95	6.0
Propan-1-ol/methanol	1.01	2.5
Propan-2-ol/methanol	1.01	2.3
Butan-1-ol/methanol	0.47	1.4
Butan-2-ol/methanol	0.52	0.3
t-Butanol/methanol	0.51	1.6
Acetic acid/methanol	1.47	2.0

The relationship obtained from the solvent system *t*-butanol/methanol was nonlinear and is shown in Fig. 2. Direct measurement from the graph shows, however, that when DC was crystallized from an equimolar binary mixtuure of the two alcohols, the preference index is 1.6 in favor of *t*-butanol.

In a series of experiments with DC and a range of hydrocarbon solvent mixtures, Goldup and Smith (*6*) have reported results similar to those above. For example, they found that the isomeric solvents *n*-heptane and 3-methylhexane were equally incorporated into DC adducts from pure solutions, but that the linear hydrocarbon was preferred (fourfold) when the adduct was formed from the mixed solvents.

CONCLUSIONS

DC has been shown to demonstrate a marked selectivity in the formation of clathrates with alcohols when crystallized from binary solvent mixtures. For each of the alcohols up to C_4 examined in the present work, all except butan-2-ol were preferred over methanol, thus providing a further illustration of the importance of guest shape as discussed by Goldup and Smith (*6*) in their work with hydrocarbon guest solvents.

As was reported for the hydrocarbons (*6*), clathrates formed from binary alcohol mixtures accommodate guest substances in a ratio proportional to that of the components in the solutions from which clathration had taken place.

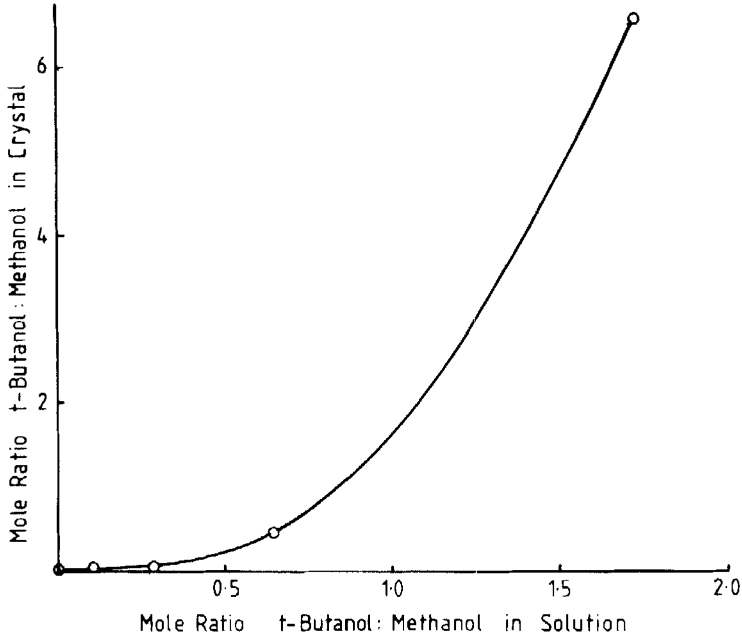


FIG. 2.

Acknowledgments

The skilled assistance of Miss Catherine Kennedy in the preparation and analysis of these materials is acknowledged with thanks.

REFERENCES

1. E. C. Makin, *Sep. Sci. 9*(6), 541 (1974).
2. D. D. MacNicol, J. J. McKendrick, and D. R. Wilson, *Chem. Soc. Rev., 7*(1), 65 (1978).
3. E. J. Fuller, in *Encyclopedia of Chemical Processing and Design,* Vol. 8, Dekker, New York, 1979, p. 333.
4. A. P. Dianin, *J. Soc. Phys. Chim. Russ., 46*, 1310 (1914).
5. W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving, and J. H. Wild, *J. Chem. Soc.,* p. 2010 (1956).
6. A. Goldup and G. W. Smith, *Sep. Sci. 6,* 791 (1971).
7. J. L. Flippen, J. Karle, and I. L. Karle, *J. Am. Chem. Soc., 92*, 3749 (1970).
8. D. D. MacNicol, *J. Chem. Soc., Chem. Commun.,* p. 836 (1969).
9. D. D. MacNicol, A. D. U. Hardy, and J. J. McKendrick, *Nature, 256*, 343 (1975).

10. A. D. U. Hardy, D. D. MacNicol., J. J. McKendrick, and D. R. Wilson, *Tetrahedron Lett.*, p. 4711 (1975).
11. A. D. U. Hardy, J. J. McKendrick, and D. D. MacNicol, *J. Chem., Soc., Chem. Commun.*, p. 355 (1976).
12. A. D. U. Hardy, D. D. MacNicol, J. J. McKendrick, and D. R. Wilson, *Ibid.*, p. 292 (1977).
13. D. D. MacNicol and D. R. Wilson, *Ibid.*, p. 494 (1976).
14. H. L. Hoffman, Jr., G. R. Breeden, Jr., and R. W. Liggett, *J. Org. Chem., 29*, 3440 (1964).
15. R. Breslow and P. Campbell, *Bioorg. Chem., 1,* 140 (1971).
16. K. J. Harrington and C. P. Garland, *Sep. Sci. Technol., 17*(11), 1339 (1982).

Received by editor April 6, 1982