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The Compressibilities of Liquid Phase Host-Guest Systems

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Abstract. The compressibilities of seven liquid phase, macrocyclic host-guest systems were determined at approximately 25 °C and 3.4×10^7 Pa. Each two-component system consisted of a cyclodextrin, a calixarene, or a crown ether as host and an appropriate solvent as guest. In each case studied, the host-guest system was found to be less compressible than the pure solvent, with the differences ranging from ∼2 to ∼18% of the magnitudes of the pure solvent compressibilities. These findings have enabled us to better understand how strong, ambient pressure, intermolecular host–guest interactions influence the compressibility of solutions. Both inclusion and solvation contribute.

Key words: Cyclodextrin, calixarene, crown ether, compressibility, host-guest.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP. 82230 (2 pages).

1. Introduction

Compressibility, the change in volume of a substance upon application of pressure, is a fundamental physical property of fluids which has both practical and theoretical implications for the chemist. From a utilitarian point of view, research in the area of fluid compressibility may lead to advances in shock absorbing devices, refrigerants, or hydraulic systems. In particular, there is considerable demand for liquids having unusually high compressibilities. Perhaps more importantly, however, compressibility studies can contribute to our understanding of the intermolecular forces which govern the properties of pure liquids and solutions. N. S. Isaacs describes liquid compressibility as being "determined by the balance between attractive and repulsive potentials [1, p. 65]." The understanding and control (through judicious selection of reagents) of these intermolecular forces is central to both inclusion science and the rational design of highly compressible liquids.

Traditionally, compressible liquid investigations have been focused on small organic molecules, binary mixtures of small organic molecules, and compounds known to have high compressibilities [2–9]. Very little has been reported, however, on the compressibilities of liquid phase, macrocyclic, host-guest systems [10–13]. It seems plausible, given favorable conditions, that pressure driven host-guest

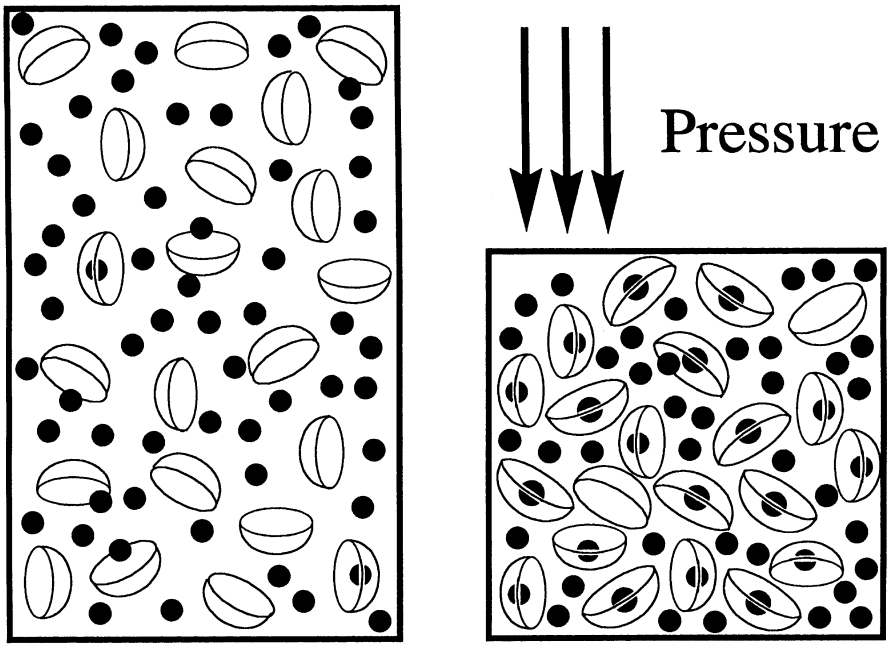

Figure 1. Schematic diagram of pressure driven host–guest complexation.

complexation could result in unusually high, bulk compressibility of the host-guest solution. An ideal system is illustrated schematically in Figure 1.

Several rigid cylindrical and cup-shaped container molecules with permanent void spaces are now either available commercially or readily synthesized via published procedures. These host molecules can form inclusion complexes with small guest molecules (often solvents) which are sterically and/or electronically well suited to reside in the cavity [14–19]. In an ideal system for attaining high compressibility, a low host-guest affinity would result in little complex formation at ambient pressures, but elevated pressures would force inclusion and a concomitant reduction in volume. Associated requirements would appear to be that the host molecule does indeed maintain a cavity within its structure, and, that under the experimental conditions chosen, the cavity of interest is sufficiently empty to accommodate one or more additional guest molecules.

At least two favorable scenarios for attaining high compressibility through inclusion complexation are plausible. The first is the pressure driven inclusion of guest molecules whose size and shape are compatible with the host molecule, but whose electronic and chemical properties afford little attraction to the host molecule. The second is the pressure driven inclusion of guests which are chemically and electronically compatible with the host, but are slightly too big to occupy the cavity at ambient pressures. Unfortunately, host molecules may be acquired, either by synthesis or upon purchase, with some guest molecules already in the cavity.

Ideally, this situation would be avoided because it precludes the simplest complexation reactions, ones in which the host goes from being completely empty to being completely full, which should have the greatest potential for high compressibility. In practice, however, a completely vacant cavity is difficult to achieve in the solid state and even more difficult to achieve in solution.

In this paper we will describe the results of compression experiments involving seven liquid phase, host-guest systems. The macrocyclic host molecules were selected because of their permanent cavities, their ready availability, and their importance in the field of supramolecular chemistry. Solvents were selected both to maximize host solubility and to facilitate pressure driven inclusion by serving as guests of appropriate size. Although strong, attractive, intermolecular forces must already be present in these systems at ambient pressure, the extent to which host-guest inclusion is complete or might be facilited by elevated pressures is unknown. Simple compression studies are a first logical step toward answering these important questions.

2. Experimental

2.1. Apparatus

The high pressure apparatus used in these experiments (Figure 2) was built with stainless steel components purchased from the High Pressure Equipment Company (Erie, Pennsylvania, USA). All components were rated to withstand pressures of at least 1.03×10^8 Pa and were packed with the optional teflon packing. The high pressure apparatus consists of a piston style pressure generator in series with a cross connector which attaches it to the inlet valve (1), the pressure transducer, and the experimental pressure chamber. Valves 2 and 3 are used to isolate the pressure chamber from the rest of the system. A capillary of known internal diameter is mounted, vertically, in series with Valve 3. Pressures were measured using an OMEGA PX605-20KGI cable style pressure transducer and an OMEGA DP41E High Performance Indicator.

The capillary for volume change measurements was made of TRUBORE tubing from Ace Glass Incorporated. The published inner diameter of the tubing was 0.1600 ± 0.0010 cm. The inner diameter of the capillary was verified experimentally and found to be 0.1605 cm with a standard deviation (σ_{n-1}) of ± 0.0003 cm.

The volume of the pressure chamber, V_{pc}, was determined to be 8.71 cm^3 with a standard deviation (σ_{n-1}) of ± 0.12 cm^3. This value was determined using experimental ΔV values and published compressibilities [20, 21] for four common solvents which served as standards: deionized water, methylene chloride, 1, 2-dichloroethane, and chloroform.

The components of the high pressure apparatus were assembled so that the fluid intake line, drive axis of the pressure generator, and pressure transducer were parallel to the bench top, while the high pressure chamber and TRUBORE capillary were perpendicular to the bench top (Figure 2). All components were secured to

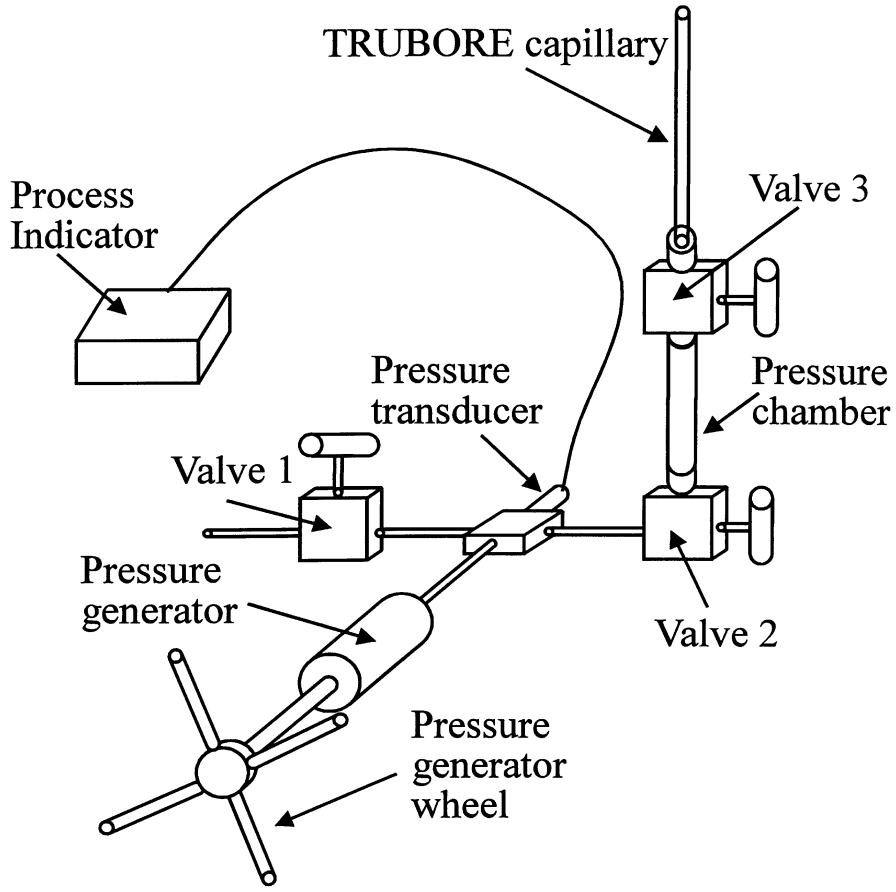

Figure 2. High pressure apparatus.

a supporting frame for stability. The high pressure chamber and capillary were arranged vertically to minimize the entrapment of air or solvent vapor within the system [2, 22].

2.2. MATERIALS

α-Cyclodextrin and β-cyclodextrin were purchased from Fluka Chemika-BioChemika in partially hydrated forms and used as received. Heptakis (2, 3, 6-tri-O-methyl)-β-cyclodextrin was purchased from Sigma Chemical Company and used as received. The calixarene (5, 11, 17, 23-tetra-*t*-butyl-25, 26, 27, 28-tetrabenzyloxy-calix[4]arene) was prepared from 4-*tert*-butyl-calix[4]arene (Aldrich Chemical Company, Inc.) according to the procedure of Gutsche et al. [25]. The crown ether, 18-crown-6, was 99% pure grade from Aldrich Chemical Company, Inc. and was used as received. No special procedures were employed to ensure that these host molecules were free

of guest molecules prior to experimentation. The structures of the host molecules are given in Figure 3.

Methylene chloride and 1,2-dichloroethane were certified A.C.S. grade from Fisher Scientific and used as received. The methylene chloride was stabilized with cyclohexene ($<$0.5%). Dimethyl sulfoxide was certified grade from Fisher Scientific and was used as received. The chloroform was certified ACS grade from Fisher Scientific and contained ethanol ($\sim$0.75%) as a stabilizer. While the chloroform was used as received for the calixarene experiment, the ethanol stabilizer was removed for the 18-crown-6 experiment. The ethanol was removed by passing the chloroform through a column of activated, neutral aluminum oxide. Gas chromatography was used to verify complete removal of the ethanol. Deionized water having a resistance of 1 MΩ was used in the α-cyclodextrin compression experiment, whereas deionized water having a resistance of 18 MΩ was used in the heptakis (2, 3, 6-tri-O-methyl)-β-cyclodextrin compression experiment.

2.3. General procedure

Although a variety of methods for quantifying compressibility and compression are commonly encountered in the literature [1, 9], we chose to determine and report percent compression [20, 21], which is the percent change in fluid volume as the fluid is compressed from ambient pressure to an elevated pressure.

$$\text{Percent compression} = \frac{\Delta V}{V_0} * 100$$

where ΔV = change in volume and V_0 = volume at ambient pressure. For convenience, we monitored expansion rather than compression. The volume change, which accompanied expansion, was determined from the fluid height change in a capillary of known inner diameter. Further details concerning the experimental procedure can be found in the supplementary material.

3. Results and Discussion

The compositions of the seven host-guest solutions, the experimental conditions for compression, and the % compression values are summarized in Table I. Because of solubility differences, the host concentrations vary considerably from system to system. To facilitate meaningful comparisons we have included, for each system: (1) the percent decrease in percent compression relative to pure solvent and (2) the percent decrease in percent compression relative to pure solvent normalized to a 1 M solution of host.

The percent compression data presented in Table I is quite precise, with standard deviations ranging from 0.01 to 0.08 for percent compression values in the 1.38 to 3.19 range. The standard deviations represent from 0.4 to 2.9% of the values determined. In each case studied, the host-guest system was found to be less

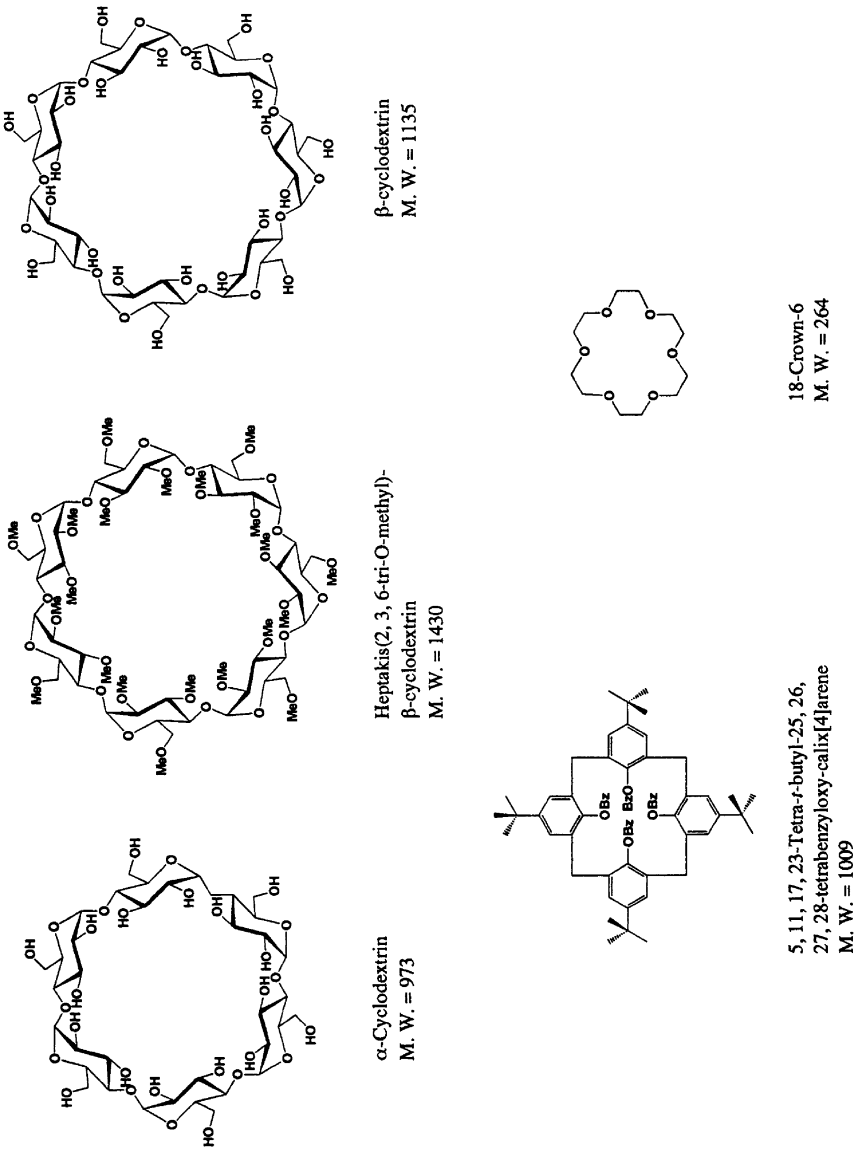

Figure 3. Host molecules used in this investigation.

Table I. Compressibilities of seven liquid-phase, macrocyclic host–guest systems at approximatly 25 °C.

Host–guest system	Applied pressure (Pa)	$\Delta V/V_0 \times 100$	# of trials	(σ_{n-1})	Experimental $\Delta V/V_0 \times 100$ of solvent	Published $\Delta V/V_0 \times 100$ of solvent	% decrease[a]	% decrease normalized to 1 M[b]
0.08223 M α-CD in Water	3.447×10^7	1.49	4	0.01	1.56	1.57 ref. [20]	4.5	54.7
0.0840 M Heptakis-(2, 3, 6-tri-O-methyl)-β-CD in Water	3.447×10^7	1.44	8	0.04	1.56	1.57 ref. [20]	7.7	91.6
0.3084 M β-CD in DMSO	3.447×10^7	1.38	9	0.04	1.66	–	16.9	54.7
0.159 M Calixarene* in CH_2Cl_2	4.054×10^7	3.13	7	0.08	3.32	3.30 ref. [21]	5.72	36.0
0.0497 M Calixarene* in $ClCH_2CH_2Cl$	4.054×10^7	2.69	9	0.03	2.74	2.70 ref. [21]	1.82	36.7
0.0730 M Calixarene* in stabilized $CHCl_3$	4.054×10^7	3.19	1	–	3.32 (stabilized chloroform)	–	3.92	53.6
1.14 M 18-Crown-6 in un-stabilized $CHCl_3$	4.054×10^7	2.76	3	0.01	–	3.35 ref. [21]	17.6	15.4

*5, 11, 17, 23-tetra-*t*-butyl-25, 26, 27, 28-tetrabenzyloxy-calix[4]arene.

[a] $= \dfrac{\text{\% compression of pure solvent} - \text{\% compression of host–guest system}}{\text{\% compression of pure solvent}} \times 100$

[b] $= \text{\% decrease} \times \dfrac{1\text{ M}}{\text{Molarity of host}}$.

compressible than the corresponding pure solvent, with the differences ranging from about 2 to 18% of the magnitudes of the pure solvent % compressions. Although highly compressible host-guest combinations have not yet been found, these results have led us to a better understanding of the intermolecular forces which determine the compressibilities of such systems.

In general, for liquid systems, there is a clear inverse relationship between the strength of cohesive intermolecular interactions and the magnitude of the compressibility [1, 2]. Although the nature of the forces involved may vary from one system to another, this relationship holds true for pure liquids, liquid mixtures, and solutions of molecular and ionic solids. The concentrations, polarities, shapes, and sizes of the molecules involved can all influence the compressibility. Arguments based on intermolecular interactions have been used successfully to explain the high compressibilities of fluorocarbons [2] as well as the low compressibilities of hydrogen bonded solvents and ionic solutions [1, 2].

When considering the compressibilities of macrocyclic host-guest systems, the intermolecular forces associated with inclusion and solvation are of utmost importance. For purposes of this discussion, *included* solvent molecules are understood to interact, primarily, with the interior of the host and are therefore separated from the continuum of solvent molecule interactions in the bulk of solvent. Correspondingly, interactions between solvent molecules and the exterior of the host are classified as solvation. Solvent molecules which are included in shallow hosts, or interact near the host's rim, might participate in solvation while being partially included.

In general, the low compressibilities observed in this study must be attributable to one, or a combination, of the following factors. (1) The pressures applied in these experiments may have been too low to achieve the desired effect. (2) Through a literature search on the host molecules used in this study, it seems probable that the attractive forces between some of the selected host molecules and their corresponding guests are strong enough to facilitate inclusion at ambient pressure. If this is indeed the case and the cavities are at least partially filled at ambient pressure, the potential for pressure driven inclusion and high compressibility is limited. (3) Solvation of the host and host-guest complex are, perhaps, the most important factors. The addition of solute, particularly to water, can increase the order of the solvent causing a decrease in compressibility [1,4,13]. The ordered solvent around each solute particle is rigid in character and therefore not very compressible. It has been suggested that the compressibility of ordered solvent is negligible in some systems, and that solution compressibility therefore corresponds to the amount of free solvent undergoing compression [1,13]. With these three relationships in mind, the host-guest systems will be discussed individually.

3.1. α-CYCLODEXTRIN IN WATER

The first system, α-cyclodextrin (α-CD) and deionized water, is the best understood. α-CD is known to crystallize from water in three different forms, with each α-CD

molecule containing at least one, but not more than three, water molecules [23, 24]. The structure of α-CD in aqueous solution, at ambient pressure, is believed to closely resemble a crystalline form which has two included water molecules. An examination of CPK models suggests that at least six water molecules could theoretically occupy the α-CD cavity. Szejtli also suggests six as the "number of water molecules taken up by the [α-CD] cavity", [19, p. 34] but his meaning is unclear. It seems reasonable to propose that the application of pressure to an aqueous α-CD solution could cause an increase in the number of included water molecules.

The α-CD/water system is one of only a handful of host-guest systems for which some compressibility data are already in the literature. Nomura et al. [13] have determined the adiabatic compressibility of α-CD using ultrasonic methods and have also estimated the amount of water bound to α-CD in aqueous solution. While we had some reservations about making comparisons between Nomura's adiabatic compressibilities and our own % compressions, compressibility values extrapolated from Nomura's work seem to be consistent with our current findings. They estimate that α-CD has 21.3 waters of hydration.

Concluding, the α-CD system has been instructive albeit not highly compressible. Its failure to exhibit unusual compressibility at 3.447×10^7 Pa is attributable to both a high degree of inclusion at ambient pressure and, probably more importantly, solute induced organization of water. Its 21.3 waters of hydration [13] are understood to be ice-like in their rigidity and not very compressible. It is also possible that a pressure of 3.447×10^7 Pa is insufficient to induce pressure driven inclusion.

3.2. HEPTAKIS(2, 3, 6-TRI-O-METHYL)-β-CYCLODEXTRIN IN WATER

Heptakis (2, 3, 6-tri-O-methyl)-β-cyclodextrin differs from its unsubstituted counterpart in two significant ways. The first is its high solubility in water (17 g/100 mL compared to 1.85 g/100 mL for unsubstituted β-cyclodextrin). The second is a deeper cavity capable of accommodating larger or more numerous guest molecules. CPK models suggest that at least 15 water molecules could theoretically fit into the cavity of heptakis (2, 3, 6-tri-O-methyl)-β-cyclodextrin (compared to 11 proposed by Szejtli for unsubstituted β-cyclodextrin [19]). The potential for pressure driven inclusion is apparent.

It is necessary to speculate on why the compressibility of the heptakis (2, 3 6-tri-O-methyl)-β-cyclodextrin/water system is lower than that of pure water. As with the α-CD system, ordering of water molecules in the solvation sphere is probably a very important factor. Another possibility is that the hosts' affinity for water is already too strong at ambient pressure. In general, the water molecules inside cyclodextrin cavities are high in energy compared to water molecules in bulk solvent. This high energy arises because the water molecules in the cavity are limited in their abilities to form extended hydrogen bonded networks [19,

p. 108]. The water molecules included in a β-cyclodextrin are understandably lower in energy than those included in an α-cyclodextrin because they have more neighboring water molecules. β-cyclodextrins may, therefore, on a percent basis, be more completely filled with water than α-cyclodextrins under ambient conditions.

3.3. β-CYCLODEXTRIN IN DIMETHYL SULFOXIDE

The compressibility of the β-cyclodextrin (β-CD)/dimethyl sulfoxide system is 17% smaller than the compressibility of pure dimethyl sulfoxide. This unusually low compressibility can, most likely, be attributed to the high concentration of the solution used, the large size of β-CD, and the strong attractive interactions which occur between DMSO and the polar functional groups of the host. A large percentage of the DMSO molecules in solution must be part of the β-CD solvation sphere and, in that case, are already highly ordered and "compressed".

3.4. 5, 11, 17, 23-TETRA-*t*-BUTYL-25, 26, 27, 28-TETRABENZYLOXY-CALIX[4]ARENE AND SMALL CHLOROCARBONS

The following three systems investigated in this work employed 5, 11, 17, 23-tetra-*t*-butyl-25, 26, 27, 28-tetrabenzyloxy-calix[4]arene as host and three small chlorocarbons, dichloromethane, chloroform, and 1, 2-dichloroethane, as solvents and as guests. The host was selected because it retains its cone conformation in solution [25] and the chlorocarbons were selected because of their ability to solubilize 5, 11, 17, 23-tetra-*t*-butyl-25, 26, 27, 28-tetrabenzyloxy-calix[4]arene.

Complexation reactions between chloroform and some members of the calixarene family are well known [14, p. 73; 26]. Although our host molecule is structurally different from those mentioned in the literature and should bind small chlorocarbons less strongly because of its small ring size and bulky *t*-butyl substituents, the formation of host-guest complexes at ambient pressure is quite likely. An examination of CPK models suggests that methylene chloride, chloroform, and 1,2-dichloroethane are all small enough to occupy the "upper rim" cavity (*t*-butyl groups) of 5, 11, 17, 23-tetra-*t*-butyl-25, 26, 27, 28-tetrabenzyloxy-calix[4]arene and could even be included between the "lower rim" benzyloxy groups in certain conformations.

We therefore conclude that our inability to observe unusually high compressibility for the 5, 11, 17, 23-tetra-*t*-butyl-25, 26, 27, 28-tetrabenzyloxycalix[4]arene systems can most likely be attributed to the cavities already being filled with small molecules at ambient pressure.

3.5. 18-CROWN-6 IN CHLOROFORM

The compressibility of the 18-crown-6/chloroform system is 18% smaller than the compressibility of pure chloroform. This unusually low compressibility can be attributed to high host concentration and strong attractive forces between host

and guest (solvent). These attractive forces are most likely strong dipole-dipole interactions between the acidic chloroform proton and the electron rich crown ether core.

It is worth mentioning that this is not the first compressibility study involving a crown ether system. In the late 1970's Høiland and coworkers [10, 11] found that the addition of crown ethers to aqueous alkali metal ion solutions rendered the partial molal volumes and isentropic partial molal compressibilities independent of salt concentration. This observation was explained in terms of the crown ether "shielding" the cation from strong solvation interactions. Cation induced solvent electrostriction was thus minimized. Later, Yamada and coworkers [12] investigated the effect of pressure on *t*-butylammonium cation complexation by 1, 3-xylyl-18-crown-5 in methanol. They found that complexation was promoted by pressure, with the natural logarithm of the association constant increasing approximately linearly from 0-150 MPa. Complexation of *t*-butylammonium cation to 1, 3-xylyl-18-crown-5 in methanol is accompanied by a volume decrease, while complexation of alkali metal cations to small crown ethers in water is accompanied by a volume increase.

4. Conclusions

The compressibilities of seven liquid phase, macrocyclic host-guest systems were determined at approximately 25 °C and 3.4×10^7 Pa. In each case studied, the host-guest system was found to be less compressible than the pure solvent, with the differences ranging from $\sim$2 to $\sim$18% of the magnitudes of the pure solvent compressibilities. These results reveal significant, cohesive, intermolecular interaction between the hosts and their solvent guests, which is pronounced at ambient pressure. Solvation must be an important factor, because failure to achieve pressure driven inclusion does not, by itself, readily account for the large observed decreases in compressibility relative to pure solvents.

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