Derived thermodynamic properties of Dianin's inclusion compound, with and without guests

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Abstract. This paper describes some derived thermodynamic properties for Dianin's compound (4-p-hydroxyphenyl-2,2,4-trimethylchroman) in its unsolvated form and in its ethanol and carbon tetrachloride clathrate forms. Room-temperature densities for all three materials ($\rho = 1.170 \pm 0.004, 1.223 \pm 0.005, 1.262 \pm 0.005$ g cm^{-3}, respectively) and sound velocities along the c-axis for the unsolvated form and the ethanol clathrate ($v_T = 2.01 \times 10^3$, 2.06×10^3 m s^{-1} and $v_L = 3.18 \times 10^3, 3.11 \times 10^3$ m s^{-1}, respectively) were measured. The heat capacity at constant strain, C_ε, Debye temperatures and Grüneisen parameters for unsolvated Dianin's compound and its ethanol and CCl$_4$ clathrates have been calculated from experimental data. The latter thermodynamic property shows that the presence of the guest in the host lattice increases the deviation of the Grüneisen parameter from its harmonic value.

1. Introduction

Inclusion compounds are a multi-component form of condensed matter in which one molecular species forms a host lattice that accommodates the other (guest) molecular species. Clathrates are one subcategory of inclusion compounds; in clathrates the guest species is enclathrated in a cage formed by the host lattice. (Channel compounds form another major category of inclusion compounds.)

Although most clathrates require the guest molecules to stabilize the open structure of the host lattice, this is not always the case. The clathrate commonly known as Dianin's compound (4-p-hydroxyphenyl-2,2,4-trimethylchroman, **1**), after its discoverer [1], is stable with or without the guest species. The host lattice is made up of groups of six molecules of **1** attached through hydrogen bonding of the phenolic groups. Relative to

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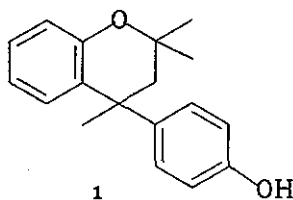
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the a, b-plane of this hexameric ring, the molecules point alternately up and down, and the hexameric units stack on top of each other along the c-axis. This gives hour-glass shaped cages, capable of accommodating small molecular guests [2]. The relatively strong hydrogen bonding is responsible for the stability of the host lattice even in the absence of guests.

For both the ethanol and CCl_4 clathrates of Dianin's compound, virtually all the cages are occupied by guest molecules. The guests maintain their molecular integrity and have considerable freedom of motion within the cage; they are not chemically bonded to the host lattice. When ethanol is the guest species, it is included as a hydrogen-bonded dimer, with one molecule occupying each half of the cage [2]. For CCl_4 as the guest species, one chlorine atom occupies the position at the waist of the cage, leaving the other half of each cage empty [3]. Relative to the unoccupied cages, it is known that at low temperatures the ethanol guests cause the lattice parameters along the c-axis to increase and those along the a-axis to decrease, while CCl_4 guests have little effect on c but cause a to increase [3, 4].

Recent information concerning the heat capacity [5], structure [2, 3], thermal expansion [3, 4] and elastic constants [6] of Dianin's compound and its ethanol and CCl_4 clathrates, now makes it possible to assess the effect of the presence and type of guest molecular species on the derived thermodynamic properties of a molecular clathrate, namely the conversion from the (measured) isobaric heat capacity, C_p, to (the more theoretically important) constant strain heat capacity, C_ε; the calculation of the Grüneinsen parameter; the calculation of the Debye temperature.

These calculations are important for a number of reasons. First, the availability of the required data for this system will provide answers to the following questions. Is the exceptionally linear temperature dependence of C_p for Dianin's compound and its clathrates also observed in C_ε, and perhaps therefore related to the glass-like thermal properties (especially thermal conductivity) observed in these [7] and other clathrates [8]? What are the Debye temperatures for this molecular solid system, with and without the guest species? What is the effect of the guest species on derived properties such as the Grüneisen parameter?

For molecular solids, it is relatively rare to have available all the data required to carry out the calculations of derived thermodynamic properties. The only additional items of information required to carry out the analysis for this system were the densities of the solids and sound velocities; the results of these measurements are reported here. To our knowledge, this is the first example of a clathrate system for which extensive data are available both with and without guest species in the cage.

2. Experimental details

Dianin's compound in its unsolvated form, and as its ethanol and CCl_4 clathrates, was prepared as described earlier [5]. Single crystals were grown from the solvent/guest at room temperature; for the unsolvated species, single crystals were grown from decanol.

The densities of single crystals were measured using a calibrated pycnometer, matching the crystal density with aqueous KI solutions to which a small amount of surfactant had been added.

Sound velocities were measured using a standard ultrasonic pulse method [9] applied along the crystallographic c-axis. Lithium niobate transducers (36° Y-cut for the longitudinal mode and X-cut for the transverse mode) were used. To maintain good coupling

between the transducers and sample, silicon grease and paraffin wax were used for the longitudinal and transverse modes respectively. The pulses were generated and received by a Matec Pulse Modulator and Receiver (Model 6600, Matec Inc., Warnick, R.I.). The apparatus was tested first by measuring the velocity of sound of Harshaw NaCl crystals; the velocities for $T = 300$ K were $(4.62 \pm 0.05) \times 10^3$ m s^{-1} and $(2.46 \pm 0.05) \times 10^3$ m s^{-1} for the longitudinal and transverse modes, respectively, and can be compared with the respective literature values [10] of 4.57×10^3 m s^{-1} and 2.46×10^3 m s^{-1}. Velocity of sound measurements were carried out for the unsolvated Dianin's compound and for the ethanol adduct. (The crystals of the CCl$_4$ adduct were too small for these measurements.)

3. Results

The measured densities (ρ) of unsolvated Dianin's compound, its ethanol adduct, and its CCl$_4$ adduct, at 23 °C, were, respectively: 1.170 ± 0.004, 1.223 ± 0.005, 1.262 ± 0.005 g cm^{-3}. These can be compared with the results of x-ray structural determinations [2, 3, 11] which, when corrected for thermal expansion [3, 4], give 1.168, 1.225, and 1.260 g cm^{-3}, respectively.

The transverse sound velocities (v_T) for the ethanol adduct and unsolvated Dianin's compound were, respectively, 2.06×10^3 and 2.01×10^3 m s^{-1}. The corresponding longitudinal mode velocities (v_L) were 3.11×10^3 and 3.18×10^3 m s^{-1}.

4. Discussion

4.1. Comparison of elastic constants with and without guests

From the present experimental results it is possible to derive directly the elastic constants c_{33} and c_{44} for this lattice, with and without ethanol guest molecules, since, for hexagonal symmetry [9]

$$c_{33} = \rho v_L^2 \tag{1}$$

and

$$c_{44} = \rho v_T^2. \tag{2}$$

We find c_{33} to be 1.2×10^{10} N m^{-2}, with or without the guest. However, c_{44} is sensitive to the presence of the guest: it is 5.2×10^9 N m^{-2} with ethanol in the host lattice, and 4.7×10^9 N m^{-2} for the unoccupied host lattice. This 10% increase in c_{44} with the ethanol molecules present shows that the guests stiffen the lattice against shear in the a, b-plane.

4.2. Heat capacity

The heat capacities reported [5] for Dianin's compound and its ethanol and CCl$_4$ clathrates were the heat capacities of the material in equilibrium with its saturated vapour, C_{sat}. This is related to the isobaric heat capacity, C_p, as follows:

$$C_{sat} - C_p = (\partial p/\partial T)_{sat}[(\partial H/\partial p)_T - V]. \tag{3}$$

For these solids, C_p is closely approximated by C_{sat}, even at room temperature.
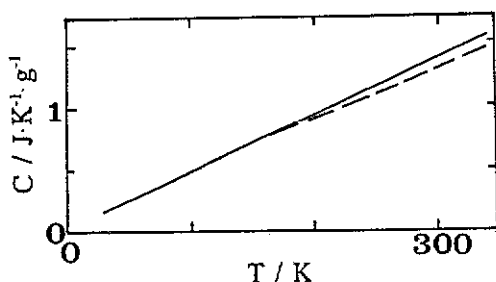
Figure 1. The heat capacity at constant pressure (C_p, ——) and at constant volume (C_v, - - -) for the ethanol adduct of Dianin's compound.

More important than C_p, at least from the point of view of comparison with solid state theory, is C_v, the isochoric heat capacity. Although this is usually related to C_p as:

$$C_p - C_v = V\alpha_V^2 T/\chi^T \tag{4}$$

where $\alpha_v = V^{-1}(dV/dT)_p$ is the volume thermal expansion coefficient and $\chi^T = -V^{-1}(dV/dP)_T$ is the isothermal compressibility, equation (4) is strictly true only for isotropic materials. As Dianin's compound and its clathrates are trigonal, clearly this is not the case here.

For an anisotropic crystal, C_p and C_v are related to the heat capacities at constant stress, C_σ, and at constant strain, C_ε. For the present purposes, the condition of constant stress means constant pressure, so $C_p = C_\sigma$, and [12]

$$C_p - C_v \approx C_p - C_\varepsilon = C_\sigma - C_\varepsilon = VT(c_{ijkl}^T \alpha_{ij} \alpha_{kl}) \tag{5}$$

where c_{ijkl}^T is the isothermal elastic constant tensor and α_{ij} is the thermal expansion tensor.

Clearly the usable form of equation (5) will depend on the symmetry of the crystal under consideration. We have shown [6] that, from the perspective of the elastic properties of Dianin's compound, their trigonal symmetry may be closely approximated as hexagonal. Although the form of equation (5) is the same for both trigonal and hexagonal symmetry, we will treat the thermal properties throughout this paper according to hexagonal symmetry for consistency. This is most important for the elastically derived properties (see later); however, the differences between the hexagonal and trigonal elastic constants are very small [6]. For either trigonal or hexagonal symmetry, equation (5) becomes

$$C_p - C_\varepsilon = VT[2(c_{11} + c_{12})\alpha_a^2 + 4c_{13}\alpha_a\alpha_c + c_{33}\alpha_c^2] \tag{6}$$

where the Voigt notation is used.

Using the measured values of C_p [5], thermal expansion [3, 4] and (hexagonal) elastic constants [6], C_ε has been calculated from equation (6) for the ethanol adduct of Dianin's compound; the results are shown in figure 1. C_p is very nearly linear in temperature from about 40 K to just above room temperature; the correction for $p - V$ work makes C_ε less than C_p, up to a few per cent at room temperature. However, even C_ε is quite linear in temperature. Although full elastic constants are not known for either unsolvated Dianin's compound or its CCl$_4$ adduct, the similarity of the sound velocities suggests that the ethanol values for c_{ij} could be used to calculate C_ε for these compounds; under that assumption, C_ε for unsolvated Dianin's compound and its CCl$_4$ adduct both look

Table 1. The smoothed values of C_p and C_ε for Dianin's compound and its ethanol and carbon tetrachloride adducts, based on the values from [5]. All values are in $J\,K^{-1}\,g^{-1}$.

T(K)	Dianin's compound		Ethanol adduct		CCl$_4$ adduct	
	C_p	C_ε	C_p	C_ε	C_p	C_ε
30	—	—	0.152	0.152	—	—
50	0.220	0.220	0.255	0.253	0.217	0.216
75	0.335	0.333	0.370	0.367	0.333	0.331
100	0.442	0.438	0.486	0.480	0.435	0.431
150	0.658	0.648	0.717	0.703	0.650	0.641
200	0.878	0.862	0.948	0.924	0.862	0.848
250	1.095	1.064	1.176	1.136	1.072	1.038
300	1.315	1.254	1.401	1.330	1.282	1.196
340	1.487	1.396	1.583	1.480	—	—

very similar to the results for the ethanol adduct shown in figure 1. Smoothed values of C_p and C_ε are selected temperatures are presented in table 1 for all three materials.

A similar effect (linear heat capacity over a wide temperature range) was observed [13] for both the monomer and the polymer of 2,4-hexadiyne-1,6-diol-bis(p-toluene sulphonate). There the linear heat capacity was attributed to the dominance of the stretching vibrational modes which contribute as $C_p(\text{str}) \propto T^1$. Unfortunately, the assignment of the vibrational modes has not been carried out for the Dianin system so it is not possible to assess the contributions of internal vibrational modes to the heat capacity. However, Dianin's compound and its adducts are molecular solids and one could expect many contributions from internal vibrational modes to the heat capacity (for example, it is known from IR [14] and Raman [15] studies of Dianin's clathrates that there are more than 100 distinct vibrational frequencies ranging from $<40\,\text{cm}^{-1}$ to $>3000\,\text{cm}^{-1}$); these are responsible for the remarkably linear temperature dependence. (It is interesting to note that the polymer of 2,4-hexadiyne-1,6-diol-bis(p-toluene sulphonate) has an unusual temperature dependence to its thermal conductivity that has been attributed to the scattering of acoustic phonons by low-energy optic phonons [16]; the thermal conductivity of Dianin's compound and its ethanol adduct show similar behaviour [7]. However, the 'glass-like' thermal conductivity does not exclusively imply truly linear heat capacity; tetrahydrofuran clathrate hydrate is a case in point [8, 17]. The linear temperature-dependence observed in the heat capacity of glasses at low temperatures has been ascribed to a tunnelling mechanism [18]. While this is unlikely to be a consideration here, the high density of vibrational frequencies in the energy range of a few Kelvin to a few hundred Kelvin, which give the linear heat capacity observed here, may be important in the mechanism of 'glass-like' thermal conductivities in these and other molecular solids [7, 19].

4.3. Debye temperatures

Particularly for the analysis of our thermal conductivity results [7], it is important to determine the Debye temperature, θ_D, for these clathrates. (Herein we use the recommended [20] superscripted θ_D notation to denote the property from which θ is
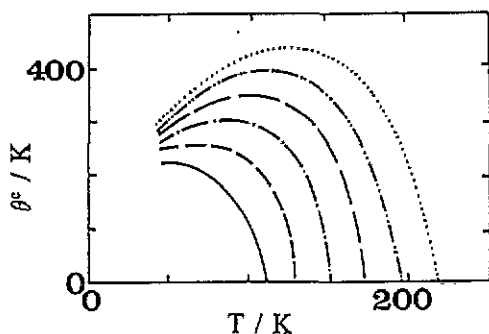
Figure 2. The calorimetric Debye temperature, θ^c, for unsolvated Dianin's compound, calculated with various values of n, the number of subgroups in the Dianin molecule; $n = 5$, (——); $n = 6$ (- - -); $n = 7$ (– · – · –); $n = 8$ (– –); $n = 9$ (– · · – · · –); $n = 10$ (· · ·).

derived: θ^c from calorimetric data, θ^{cl} from elastic constant data.) Although θ^c is well-specified for monatomics, this is not the case for molecular solids. Put simply, the problem is this: how does one decide the maximum number of degrees of freedom available? Ideally, the vibrational assignment is complete, internal vibrational contributions to C_e can be subtracted and the θ^c analysis can be carried out on the remaining contribution to C_e treating the lattice as rigid units of molecules. Even if the vibrational assignment is not available (as it is not for Dianin's compound), in some molecular crystals the internal vibrations and external vibrations (translational and librational motions of molecules or molecular groups) are well-separated energetically and can be treated separately [21].

The internal and external vibrational modes of Dianin's clathrates are not well separated. However, it is clear that many of the internal modes are at very high frequency and therefore contribute negligibly to the sub-ambient heat capacity. Another way to state this is that Dianin's molecule, concentrating on the unsolvated compound first, can be considered to consist of several subgroups, each of which can contribute its 'external' motion. In this representation higher-frequency internal modes are ignored. Taking into account the crystal structure [11], steric hindrance, ^{13}C NMR T_1 relaxation information [22], recent ^{2}H NMR data [23] and barriers to reorientation in other molecular solids [24], it is possible to distinguish six subgroups of the Dianin's molecule: the phenolic group; three methyl groups; the chroman moiety; the phenolic phenyl ring. As there is no observable gap in the vibrational spectrum, this assignment is, of necessity, rather arbitrary, and arguments also could be put forward for five or seven subgroups, although six seems most reasonable. On this basis, values of θ^c as a function of temperature for n from 5 to 10 (n is the number of subgroups) have been calculated from C_e data for unsolvated Dianin's compound; the results are shown in figure 2. All the curves show the same parabolic shape. At lower temperatures, by analogy with other solids [20], θ^c should increase slightly.

For the ethanol adduct of Dianin's compound the heat capacity data extends to lower temperatures; analogous plots of θ^c as functions of temperature for the ethanol and CCl_4 clathrates are given in figures 3 and 4, respectively. (Although here the guest molecules also contribute to C_e the high ratio of host to guest makes this contribution well within the uncertainty in the assignment of the number of contributing subgroups of the host lattice.) Again, all the curves show similar parabolic behaviour. The decrease at the
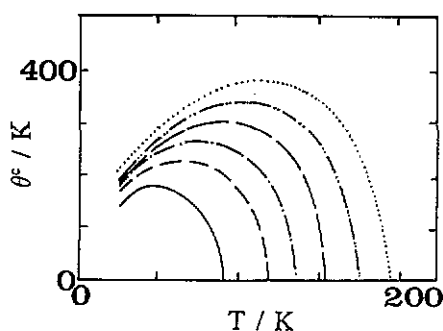
Figure 3. The calorimetric Debye temperature, θ^c, for the ethanol adduct of Dianin's compound, calculated with various values of n, the number of subgroups in the Dianin molecule; $n = 5$, (——); $n = 6$ (---); $n = 7$ (– · – · –); $n = 8$ (--); $n = 9$ (– · · – · · –); $n = 10$ (· · · ·).
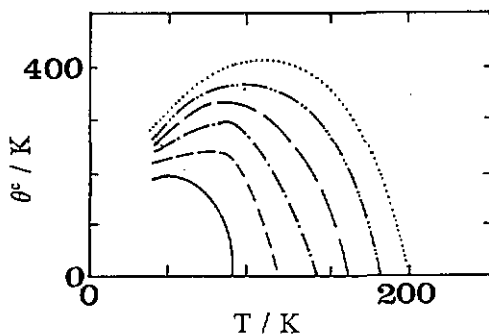

Figure 4. The calorimetric Debye temperature, θ^c, for the carbon tetrachloride adduct of Dianin's compound, calculated with various values of n, the number of subgroups in the Dianin molecule; $n = 5$, (——); $n = 6$ (---); $n = 7$ (– · – · –); $n = 8$ (--); $n = 9$ (– · · – · · –); $n = 10$ (· · · ·).

higher temperature in figures 2, 3 and 4 is due to the increasing contribution of the vibrational modes and anharmonic effects to the heat capacity [21].

It is worth noting that all θ^c curves for the unsolvated Dianin's compound and its ethanol and CCl$_4$ adducts (figures 2, 3 and 4) tend towards convergence in the low temperature region at values between 150 K and 200 K.

The Debye temperature also can be determined from the velocity of sound measurements [25]:

$$\theta^{el} = (h/k_B)(3N_0 n\rho/4\pi M)^{1/3} v_m \tag{7}$$

where h is Planck's constant, k_B is Boltzmann's constant, N_0 is Avogadro's number, n is the number of subgroups in the molecule, ρ is the density, M is the molecular mass and v_m is the sound velocity averaged over all directions of polarization and propagation. For the purposes of using our direct velocity of sound measurements, we use v_m as

$$v_m = (3)^{1/3}(v_L^{-3} + 2v_T^{-3})^{-1/3}, \tag{8}$$

which implies elastic isotropy, since the elastic constants were measured only along the

c-axis. For the unsolvated Dianin's compound, its ethanol adduct and its CCl_4 adduct, using $n = 6$ for all cases (the contribution of the guests to n will change the values by less than 2%), the values of θ^{el} from this method are 165 K, 171 K and 173 K respectively. (The sound velocities for the CCl_4 adduct were assumed to be the same as for the ethanol adduct for this calculation.)

Since this use of equation (7) applies only to elastically isotropic materials, this rough estimate of θ^{el} for the measured velocities along the *c*-axes would be justified only in the absence of other data, as for the unsolvated Dianin's compound. For the ethanol adduct of Dianin's compound, there is sufficient information to calculate θ^{el} from the full set of elastic constants. Equation (7) can be re-written [25] as

$$\theta^{el} = \frac{h}{k_B}\left(\frac{9N}{4\pi V}\right)^{1/3}\left[\int\int\left(\frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3}\right)\frac{d\Omega}{4\pi}\right]^{-1/3} \tag{9}$$

where N is the number of subgroups per unit cell, and V is the unit cell volume. Applying the harmonic series method after Alers [26], equation (9) becomes

$$\theta^{el} = (h/k_B)(9N/4\pi V)^{1/3}\rho^{-1/2}J^{-1/3} \tag{10}$$

where J can be expressed directly in terms of the elastic constants. Using the measured elastic constants for the ethanol adduct of Dianin's compound, θ^{el} from this method was found to be 186 K. The difference between this result and the value of 171 K derived from the direct velocity of sound measurements shows the slight elastic anisotropy in this system. The best test of θ^{el} is whether or not it reproduces the limiting low-temperature value of the heat capacity as this result is independent of the number of subgroups. The limiting value of C_ϵ/T^3 as $T \to 0$ derived from the elastic constant data for the ethanol adduct is 6.4×10^{-6} J K^{-4} g^{-1}, which compares favourably with the experimental value of $(9 \pm 2) \times 10^{-6}$ J K^{-4} g^{-1}.

The differences in the values of θ for the ethanol adduct as calculated from different methods reflect a number of factors. The difference between the θ^{el} values from elastic constants and mean sound velocities is likely to reflect the fact that the sound velocities were measured along the *c*-axis. From the Brillouin scattering results [6] it is known that for this direction the longitudinal sound velocity is the lowest observed and the transverse sound velocity also is low, giving the (observed) lower θ^{el}. Also, from the temperature-dependence of θ^c, one would expect, based on results for other solids, that θ^c would increase below about 25 K, making the θ_0^c value closer to θ^{el}.

4.4. Grüneisen parameter

One of the main purposes of our investigations of clathrates is to understand the role of the guest species in thermal properties. To that end, we have examined the thermal expansion of unsolvated Dianin's compound, and its ethanol and CCl_4 adducts [3, 4]. We found that the presence of the guest species increases the thermal expansion, and the presence of two (ethanol) guest molecules per cage increases the thermal expansion relative to one guest (CCl_4) molecule per cage.

For the *i*th mode with frequency ω_i, the Grüneisen parameter, γ_i, is defined as [27]

$$\gamma_i = -\partial\ln\omega_i/\partial\ln V \tag{11}$$

and for the overall lattice,

$$\gamma = \sum_i \gamma_i C_{v,i}\Big/\sum_i C_{v,i} \tag{12}$$

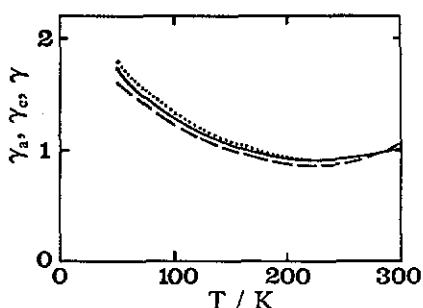where γ is the overall Grüneisen parameter, $C_{v,i}$ is the contribution of the *i*th mode to

Figure 5. The Grüneisen parameters γ (——), γ_a ($\cdots$) and γ_c (———) for the ethanol adduct of Dianin's compound.

the heat capacity, and the sum is over all normal modes. The importance of the Grüneisen parameter to the discussion here is that γ, like the coefficient of thermal expansion, is zero for a lattice with perfect harmonic interactions.

There is insufficient information to calculate the Grüneisen parameter from equation (12) for Dianin's compound and its adducts. However, for a hexagonal (or trigonal) crystal, the volumetric thermodynamic Grüneisen parameter can be written in terms of the Grüneisen parameters perpendicular and parallel to the c-axis, γ_a and γ_c, respectively [26]:

$$\gamma = (2\chi_a^S \gamma_a + \chi_c^S \gamma_c)/\chi^S \tag{13}$$

where χ^S is the bulk adiabatic compressibility, χ_a^S and χ_c^S are respectively the adiabatic compressibilities perpendicular and parallel to the c-axis, defined as

$$\chi_a^S = (c_{33} - c_{13})/[(c_{11} + c_{12})c_{33} - 2c_{13}^2] \tag{14}$$

and

$$\chi_c^S = (c_{11} + c_{12} - 2c_{13})/[(c_{11} + c_{12})c_{33} - 2c_{13}^2] \tag{15}$$

and γ_a and γ_c are defined as

$$\gamma_a = V[(c_{11} + c_{12})\alpha_a + c_{13}\alpha_c]/C_p \tag{16}$$

and

$$\gamma_c = V(2c_{13}\alpha_a + c_{33}\alpha_c)/C_p \tag{17}$$

where c_{ij} in equations (14) to (17) are the adiabatic elastic stiffnesses.

The results of the calculation of γ_a, γ_c and γ for the ethanol adduct of Dianin's compound are shown in figure 5. For these calculations it was assumed that the elastic constants are independent of temperature. Although the elastic constants of unsolvated Dianin's compound are not known, from the velocity of sound results it is not unreasonable to expect them to be close to those of the ethanol adduct; under this assumption, γ_a, γ_c and γ for the empty Dianin's compound have been calculated, and the results are
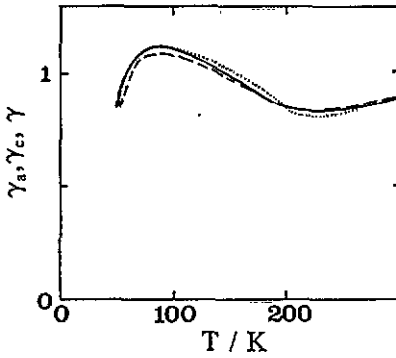
Figure 6. The Grüneisen parameters γ (——), γ_a (· · · ·) and γ_c (– – –) for unsolvated Dianin's compound.
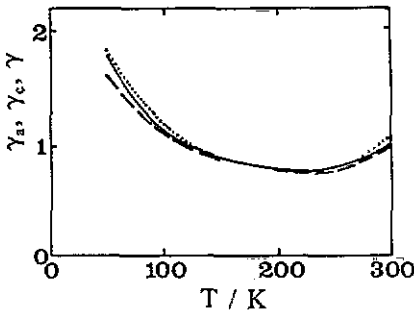
Figure 7. The Grüneisen parameters γ (——), γ_a (· · · ·) and γ_c (– – –) for the carbon tetrachloride adduct of Dianin's compound.
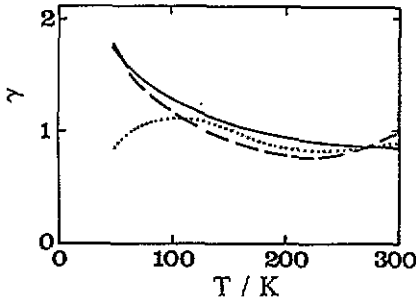

Figure 8. The overall Grüneisen parameter, γ, for unsolvated Dianin's compound (· · · ·), and its ethanol adduct (——) and CCl_4 adduct (– – –).

shown in figure 6. Given the similarity of the sound velocities of the ethanol adduct and unsolvated Dianin's compound, one might reasonably expect that the elastic properties of the CCl_4 adduct would be similar. With this assumption, γ_a, γ_c and γ for the CCl_4 adduct have been calculated; these are shown in figure 7. For direct comparison, the temperature dependence of γ for all three materials is shown in figure 8.

For non-metallic solids, the Grüneisen parameter generally is of the order of unity [20], and this is the case here. From figure 8, it can be seen that the Grüneisen parameters for the ethanol and CCl_4 adducts are very similar to one another between 50 K and 300 K. (Based on the error in the thermal expansion, we know γ to within about $\pm30\%$.) In contrast with many solids in which γ tends to zero as the temperature decreases [20], it is found here that γ increases for both the ethanol and the CCl_4 adduct as the temperature drops. The more usual (opposite) trend is observed for the unsolvated Dianin compound. A similar effect was noted for the Grüneisen parameter of tetra-hydrofuran clathrate hydrate in comparison with hexagonal ice [28]. The present results appear to be the first direct comparison of the Grüneisen parameter of a clathrate with and without its guest species.

Although this increase in γ at low temperatures is rare, it is not without precedent; similar behaviour has been observed [29] in solid CO and attributed [20] to the existence [30] of low-frequency librational modes. If, in adducts of Dianin's compound, there are low-frequency optic modes associated with motion of the guest molecules in the cages, as has been proposed in the mechanism of enhanced thermal resistance in clathrate hydrates [19], these modes may be the source of the anharmonicity that gives rise to the unusual low-temperature dependence of γ observed here.

An increase in γ with decreasing temperature has been observed also in some amorphous materials, and attributed in part to the linear temperature dependence of the heat capacity [20]. Although this may be a factor in the Dianin clathrates, it is not the total determinant, as the heat capacity is quite linear both with and without guests in the case, yet γ has very different temperature dependences for these different cases. Almost certainly it is the enhancement of the thermal expansion due to the presence of the guest that is responsible for the increased low-temperature Grüneisen parameter in the ethanol and CCl_4 clathrates of Dianin's compound relative to the empty lattice.

5. Conclusions

Thermodynamic properties have been derived from experimental thermal properties of unsolvated Dianin's compound and its ethanol and CCl_4 adducts. The constant strain heat capacity, C_ε, is found to be remarkably linear over a wide temperature range, consistent with a large number of optic modes spread over a wide frequency range. From heat capacity, velocity of sound and elastic constants, we determined the Debye temperatures (θ_0^ε, θ_0^{el}) to be (170 ± 20) K for all three compounds. The Grüneisen parameter shows an increased deviation from its harmonic value when guests are present in the cages.

Acknowledgments

References

[1] Dianin A P 1914 *J. Russ. Phys. Chem. Soc.* **46** 1310
[2] Flippen J L, Karle J and Karle I L 1970 *J. Am. Chem. Soc.* **92** 3749
[3] Abriel W, du Bois A, Zakrzewski M and White M A 1990 *Can. J. Chem.* **68** 1352
[4] Zakrzewski M, White M A and Abriel W 1990 *J. Phys. Chem.* **94** 2203
[5] White M A and Zakrzewski M 1990 *J. Incl. Phenom. Molec. Recog. Chem.* **8** 215
[6] Zakrewski M, Mróz B, Kiefte H, White M A and Clouter M J 1991 *J. Phys. Chem.* **95** 1783
[7] Zakrewski M and White M A 1991 unpublished
[8] White M A 1987 *J. Physique Coll.* **48** C1 565
[9] Truell R, Elbaum C and Click B B 1969 *Ultrasonic Methods in Solid State Physics* (New York: Academic)
[10] Simmons G and Wang H 1971 *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook* 2nd edn (Cambridge, MA: M I T)
[11] Cameron T S, Linden A, Abriel W, Zakrzewski M and White M A 1991 unpublished
[12] Kitaigorodsky A I 1973 *Molecular Crystals and Molecules* (New York: Academic)
[13] Engeln I J 1980 *Polym. Sci. Polym. Phys. Edn* **18** 2227
[14] Gilson D F R 1962 *PhD Thesis* University of British Columbia
[15] Brooker M 1988 private communication
[16] Wybourne M N, Kliff B J and Batchelder D N 1984 *Phys. Rev. Lett.* **53** 580
[17] White M A and MacLean M T 1985 *J. Phys. Chem.* **89** 1380
[18] Cahill D G and Pohl R O 1988 *Ann. Rev. Phys. Chem.* **39** 93
[19] Tse J S and White M A 1988 *J. Phys. Chem.* **92** 5006
[20] Barron T H K, Collins J G and White G K 1980 *Adv. Phys.* **29** 618
[21] Leadbetter A J 1965 *Proc. R. Soc.* A **287** 403
[22] Ripmeester J A 1983 *J. Incl. Phenom.* **1** 87
[23] Bernhard T, Zimmerman H and Haeberlen U 1990 *J. Chem. Phys.* **92** 2178
[24] Parsonage N G and Staveley A K 1978 *Disorder in Crystals* (Oxford: Clarendon)
[25] Anderson O L 1965 *Physical Acoustics* vol III B (New York: Academic) p 43
[26] Alers G A 1965 *Physical Acoustics* vol III B (New York: Academic) p 27
[27] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (New York: Holt, Rinehart and Winston)
[28] Tse J 1987 *J. Physique Coll.* **48** C1 543
[29] Gill E K and Morrison J A 1966 *J. Chem. Phys.* **45** 1585
[30] Voitovitch E I, Tolkachev A M, Manzhelii V G and Gavrilko V G 1971 *Ukr. Fiz. Zh.* **16** 1217