Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Sang-Ok Lee [a], Kenneth D. M. Harris [a], Peter E. Jupp [b], Laurent Elizabe [a] & Steven Swinburn [a]

[a] School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K.

[b] School of Mathematical and Computational Sciences, University of St Andrews, St Andrews, Fife, KY16 9SS, U.K.

Version of record first published: 24 Sep 2006

To cite this article: Sang-Ok Lee, Kenneth D. M. Harris, Peter E. Jupp, Laurent Elizabe & Steven Swinburn (2001): Probing Host-Guest Interaction Energies in Solid Inclusion Compounds from Experimental Studies of Competitive Inclusion, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 517-525

To link to this article: http://dx.doi.org/10.1080/10587250108023730

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 517-525
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Probing Host-Guest Interaction Energies in Solid Inclusion Compounds from Experimental Studies of Competitive Inclusion

SANG-OK LEE[a], KENNETH D.M. HARRIS[a], PETER E. JUPP[b], LAURENT ELIZABE[a] and STEVEN SWINBURN[a]

[a]*School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K. and* [b]*School of Mathematical and Computational Sciences, University of St Andrews, St Andrews, Fife KY16 9SS, U.K.*

(Received September 24, 1999)

An approach to assess host-guest interaction energies in solid inclusion compounds with tunnel host structures is described, based on experimental studies of competitive inclusion of two different types of potential guest molecules $X(S)_qX$ and $X(S)_rX$ ($q \neq r$) within the host tunnel. The proportions (m and $1-m$) of the two types of guest molecule included within the host tunnel depend on the proportions (γ and $1-\gamma$) of the two types of guest in the external "pool" of potential guest molecules and the relative "affinities" (χ and $1/\chi$) of the host tunnel for including the two types of guest. Expressions linking χ, m and γ can be applied to determine χ directly from experimental measurements of m for inclusion compounds prepared with different values of γ. The value of χ depends on the intermolecular interaction energies *per unit length of tunnel* for the two types of guest molecule, and χ may be expressed in terms of the host-guest interaction energies for the spacer units S and the end-groups X, and the guest-guest (X···X) interaction energy. Preliminary experimental results for urea inclusion compounds containing binary mixtures of α,ω-dibromoalkane guest molecules are presented.

Keywords: solid inclusion compounds; host-guest interaction energy; mathematical modelling; urea tunnel structure

INTRODUCTION

In solid inclusion compounds [1] with tunnel host structures (typified by urea inclusion compounds [2]), the spatial distribution and orientation of the guest molecules is usually highly constrained, allowing different types of guest molecules to be introduced in a geometrically controlled manner within the same host structure. These materials therefore provide a good opportunity for systematic investigations of intermolecular interactions, in which different functional groups can be constrained to interact in geometrically controlled ways. For example, as recognized by Hollingsworth [3,4], experimental measurements of the relative numbers of different types of end-group interaction between guest molecules in host tunnel structures may lead to fundamental information on the relative preferences for interactions between different types of functional groups.

Recently, we developed a stochastic model [5] to understand intermolecular interactions in solid inclusion compounds, considering the general case of tunnel host structures containing binary mixtures of guest molecules X–R_1–X and X–R_2–Y in known proportions (where X and Y are different end-groups and R_1 and R_2 are appropriate spacer blocks). The analysis focused mainly on the different types of guest-guest interaction (X···X, X···Y, Y···X and Y···Y) that may exist between adjacent guest molecules within the host tunnel, and methods to assess the energies of these interactions were developed. Two approaches ("sequential" and "simultaneous" models) for constructing the guest substructure in the inclusion compound were considered, and are specified in reference 5.

In this paper, we describe a similar approach to understand energetic properties of tunnel inclusion compounds (Figure 1) containing binary mixtures of guest molecules, with particular interest in host-guest interaction. We focus on competitive inclusion of two different types of

FIGURE 1 Schematic illustration of a tunnel inclusion compound containing guest molecules of two different types A and B.

guest molecule that have the same end-groups but different chain lengths [$X(S)_qX$ and $X(S)_rX$ ($q \neq r$), where X is the end-group (e.g. CH_3, halogen) and S is the spacer unit (e.g. CH_2, CH)]. We consider a single host tunnel, under the assumption that the guest molecules in different tunnels in the real inclusion compound behave essentially independently of each other.

MATHEMATICAL BACKGROUND

We consider that the two different types of guest molecule are introduced competitively into the host tunnel from an external "pool" in which the proportions of the two potential guest molecules may be controlled experimentally. If the two types of guest molecule have the same end-groups X, the guest-guest interaction (X···X) is the same for each pair of adjacent guest molecules within the host tunnel, and guest-guest interaction therefore plays no part in the competitive inclusion of the two types of guest molecule. The proportion m_i of guest molecules of type i (with $i = 1, ..., N$) inside the host tunnel can be shown to approximate to:

$$m_i \approx k_p \chi_i \gamma_i , \tag{1}$$

where γ_i is the proportion of molecules of type i in the external pool of potential guest molecules, χ_i depends on the relative affinity of the host tunnel for including guest molecules of type i, and k_p is a constant. The "affinity" of the host tunnel for a given type of guest molecule depends on the energy of the inclusion compound (host-guest plus guest-guest interaction energies) per unit length of tunnel. For a binary mixture ($N = 2$) comprising two types of guest molecules A and B, equation (1) leads to:

$$\frac{m_A}{m_B} \approx \frac{\chi_A \gamma_A}{\chi_B \gamma_B} = \chi \left(\frac{\gamma_A}{1 - \gamma_A} \right), \tag{2}$$

where we define $\chi = \chi_A/\chi_B$ (note: $\gamma_B = 1 - \gamma_A$). As $m_B = 1 - m_A$, we obtain:

$$m_A \approx \frac{\gamma_A \chi}{1 + \gamma_A (\chi - 1)} . \tag{3}$$

This equation can be derived using either the sequential model or the simultaneous model for constructing the guest substructure. Equation (3) allows χ to be determined directly from experimental measurements of m_A for a set of inclusion compounds prepared for different (known) values of γ_A. Clearly χ has the properties of an equilibrium constant $\{B\} \rightleftarrows \{A\}$,

where {A} denotes a given length of host tunnel occupied by guest molecules of type A and {B} denotes the same length of host tunnel occupied by guest molecules of type B.

INTERACTION ENERGIES

We now relate χ to the intermolecular interactions for a family of inclusion compounds comprising a particular type of host tunnel structure containing binary mixtures of guest molecules A [$X(S)_{n_A}X$] and B [$X(S)_{n_B}X$] with the same end-groups X, the same spacer units S, and different lengths ($n_A > n_B$). The distance taken up by a guest molecule of type A along the host tunnel is denoted c_A and the distance taken up by a guest molecule of type B along the host tunnel is denoted c_B. We make the following assumptions:

[a] the energy of interaction between a spacer unit S and the host tunnel is a constant (α) and is independent of the number (n_i) of spacer units, the type of end-groups, the position of the spacer unit within the guest molecule, and the position of the guest molecule along the host tunnel;

[b] the energy of interaction between an end-group X and the host tunnel is a constant (β) and is independent of the type and number of spacer units, and the position of the guest molecule along the host tunnel;

[c] the energy of interaction (X···X) between the end-groups of two adjacent guest molecules is a constant (δ) and is independent of the identities of the guest molecules and the position of the pair of adjacent guest molecules along the host tunnel;

[d] each guest molecule adopts its ground-state conformation, and all guest molecules of a given type have the same intramolecular potential energy;

[e] the host tunnel structure is the same irrespective of the proportions and distribution of the two different types of guest molecule within it, and we subsequently do not consider the energy of the host structure.

For a given pair of end-groups (X···X), the total interaction energy (host-guest plus guest-guest) is $\eta = 2\beta + \delta$. The energy term α is characteristic of the type of spacer unit S and the type of host tunnel, and the energy term η is characteristic of the type of end-group X and the type of host tunnel. Thus, $\alpha = \alpha_{S,H}$ and $\eta = \eta_{X,H}$ (note: $\beta = \beta_{X,H}$ and $\delta = \delta_X$). The total interaction energies for single guest molecules of types A and B in the inclusion compound are:

$$E_A = n_A \alpha_{S,H} + \eta_{X,H} \quad \text{and} \quad E_B = n_B \alpha_{S,H} + \eta_{X,H} . \tag{4}$$

To assess the relative "affinity" of the host tunnel for the two different types of guest molecule, we require to consider energies per unit length of tunnel rather than energies per guest molecule. The "unit length of tunnel" is conveniently taken as the periodic repeat distance (c_h) of the host tunnel structure. Thus, the total interaction energies per unit length of tunnel for guest molecules of types A and B are:

$$\bar{E}_A = \frac{c_h}{c_A} [n_A \alpha_{S,H} + \eta_{X,H}] \quad \text{and} \quad \bar{E}_B = \frac{c_h}{c_B} [n_B \alpha_{S,H} + \eta_{X,H}] . \tag{5}$$

In principle, c_A and c_B may be determined from diffraction studies of the inclusion compounds containing only guest molecules of type A ($\gamma_A = 1$) and only guest molecules of type B ($\gamma_A = 0$) respectively. It has been found experimentally [6–8] and shown mathematically [9] that, for a family of inclusion compounds, each comprising a single type of guest $X(S)_{n_i}X$ within the same host tunnel structure, the periodic repeat distance (c_i) of the guest molecules is usually approximated by a linear relationship:

$$c_i \approx f n_i + g . \tag{6}$$

In this expression, f can be interpreted as the distance taken up along the tunnel by each spacer unit S, and g can be interpreted as the distance taken up along the tunnel by a pair of end-groups X···X. As an example, for incommensurate urea inclusion compounds containing $Br(CH_2)_nBr$ guest molecules, single crystal X-ray diffraction studies [8] give $f \approx 1.26$ Å and $g \approx 5.50$ Å. As f is characteristic of the spacer units and g is characteristic of the end groups, we may write $f = f_S$ and $g = g_X$.

We now consider the physical interpretation of χ, and its relation to the energetic properties of the inclusion compound. In our model, there is one energy state ($\bar{E}_A$) for guest molecules of type A and one energy state ($\bar{E}_B$) for guest molecules of type B. Thus, with the interpretation of χ as an equilibrium constant:

$$\chi = \exp\left(\frac{-(\bar{E}_A - \bar{E}_B)}{kT}\right) \tag{7}$$

with [from equations (5) and (6)]:

$$\bar{E}_A - \bar{E}_B \approx \left(\frac{c_h}{(f_S n_A + g_X)(f_S n_B + g_X)}\right)(\alpha_{S,H} g_X - \eta_{X,H} f_S)(n_A - n_B) . \quad (8)$$

Equations (7) and (8) may be used to extract information on the energy terms from values of χ determined experimentally using equation (3).

APPLICATIONS

We now consider the application of the methodology described above to determine energetic properties of inclusion compounds from experimental data. The experimental data comprise pairs of values of m_A and γ_A for inclusion compounds containing binary mixtures of guest molecules A and B, and measurements of c_A and c_B (from diffraction studies of inclusion compounds containing only guest molecules of type A and only guest molecules of type B respectively) from which f_S and g_X may be estimated.

First, we consider crystal growth of a number N_k of inclusion compounds ($k = 1, ..., N_k$) with the same host tunnel structure and the same type of guest molecules A [$X(S)_{n_A}X$] and B [$X(S)_{n_B}X$], but for different (known) values of γ_A between 0 and 1. Experimentally, γ_A represents the proportion of potential guest molecules of type A in the crystallization solution. For each of the N_k inclusion compounds, the proportion m_A of guest molecules of type A included within the host tunnel is determined experimentally, and the set of values $\{(\gamma_A,m_A)_k\}$ should conform to equation (3) with the same value of χ for all members of the set. The ability of equation (3) to fit the full set of data $\{(\gamma_A,m_A)_k\}$ is a good test of the validity of our model. The value of χ depends on the type of spacer unit S, the type end-group X, the host tunnel structure (H) and the values of n_A and n_B. Thus, $\chi = \chi_{S,X,H}(n_A,n_B)$.

This procedure can be repeated for other pairs of guest molecules within the same family $X(S)_{n_i}X$ for the same host tunnel structure (H). Thus, we consider N_p pairs of guest molecule types (labelled $j = 1, ..., N_p$), each representing a different pair of values of n_A and n_B. For each pair (j), the value of $\chi_{S,X,H}(n_A,n_B)_j$ can be obtained as described above. Our model provides the link between experimentally derived values of $\chi_{S,X,H}(n_A,n_B)_j$ and energetic properties of the inclusion compounds. However, from fitting our model [equations (7) and (8)] to values of $\chi_{S,X,H}(n_A,n_B)_j$ for sets of inclusion compounds containing binary mixtures of guest molecules from the family $X(S)_{n_i}X$, only $\alpha_{S,H}g_X - \eta_{X,H}f_S$ can be determined and we

cannot obtain values of the separate energy terms $\alpha_{S,H}$ and $\eta_{X,H}$. An approach that does allow $\alpha_{S,H}$ and $\eta_{X,H}$ to be determined separately is described elsewhere [10].

EXPERIMENTAL

Urea inclusion compounds containing binary mixtures of α,ω-dibromoalkane [$Br(CH_2)_nBr$; n = 7 to 12] guest molecules were prepared from commercially available reagents using the following method. A mixture of urea (1 g, 1.665 mol) and two different α,ω-dibromoalkanes (total number of moles fixed at 0.002 mol for all preparations) were dissolved in methanol in conical flasks at 50 °C. For each pair of α,ω-dibromoalkane guests, several binary mixtures were considered, with different mole fractions in solution (γ_A). All solutions were then cooled simultaneously in an incubator to 30 °C over a period of 3 hours to allow crystallization to occur. The crystals were collected and washed with a small amount of 2,2,4-trimethylpentane to remove any α,ω-dibromoalkane molecules adsorbed on their external surfaces. For all samples, the crystals had the long hexagonal needle morphology characteristic of conventional urea inclusion compounds. Powder X-ray diffraction confirmed that the samples were conventional urea inclusion compounds, with no detectable amounts of the "pure" crystalline phases of α,ω-dibromoalkanes or urea.

For each sample of urea inclusion compounds prepared, gas chromatography (GC) was used to assess the ratio (m_A:m_B) of the two different types of guest within the inclusion compound. Samples for GC analysis were prepared by dissolving a small amount (*ca.* 10 mg) of the crystals in methanol (1 cm^3). The GC data were recorded using a Carlo Erba GC 8000 Series (8130) instrument, with a BPX5 (15 m × 0.53 mm) megabore column, a gas flow of 10 kPa and a temperature program rising from 80 °C to 340 °C at 10 °C per minute. Reference samples containing known amounts of the α,ω-dibromoalkanes were also studied to establish a calibration. For each urea inclusion compound sample, the quantity m_A was determined from quantitative analysis of the peaks for the two α,ω-dibromoalkane guest molecules in the GC data.

RESULTS

Analysis of our experimental measurements of $\{(\gamma_A,m_A)_k\}$ for binary mixtures of α,ω-dibromoalkane guest molecules [$Br(CH_2)_{n_i}Br$; n_i = 7 to

12] in the conventional urea tunnel structure shows that equation (3) fits the data well for all 15 pairs $(n_A,n_B)_j$ of guest molecules considered [n_A = 8, ..., 12; n_B = 7, ..., n_A–1]. Representative results from these studies are shown in Figure 2. The values of $\chi(n_A,n_B)$ obtained by fitting our model to

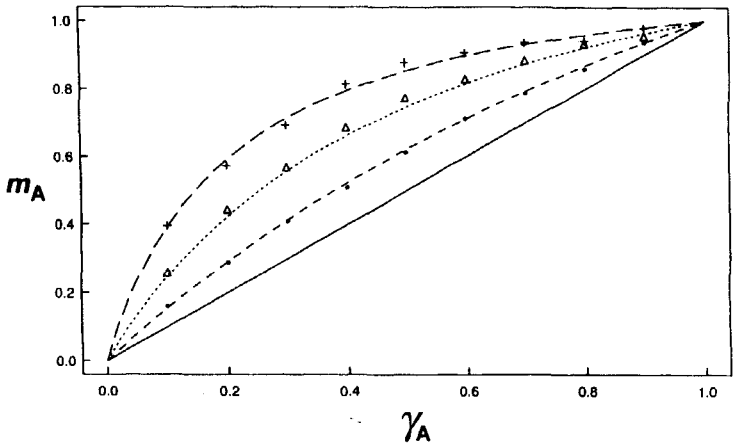

FIGURE 2 Plots of m_A *versus* γ_A for binary mixtures of guest molecules $Br(CH_2)_{n_A}Br$ and $Br(CH_2)_{n_B}Br$ ($n_A > n_B$) in the conventional urea tunnel structure: • symbols represent data for n_A = 10, n_B = 9; Δ symbols represent data for n_A = 10, n_B = 8; + symbols represent data for n_A = 10, n_B = 7.

the combined set of data shown in Figure 2 are: $\chi(10,7)$ = 5.78; $\chi(10,8)$ = 2.93; $\chi(10,9)$ = 1.64. The curves shown in Figure 2 are those obtained by putting these values of χ in equation (3), which clearly provides a good description of the experimental data. As expected intuitively, the value of $\chi(n_A,n_B)$ increases as the difference between n_A and n_B increases (with $n_A > n_B$). The straight solid line (which corresponds to $m_A = \gamma_A$) has been added as a guide to the eye, and would represent the situation (χ = 1) in which the host tunnel structure has the same affinity for including both types of guest molecule.

The value of $\alpha_{S,H}g_X - \eta_{X,H}f_S$ determined [using equations (7) and (8)] from the data shown in Figure 2 is -3.53×10^4 Å J mol^{-1} [with an approximate 95 % confidence interval of $(-3.65,-3.41) \times 10^4$ Å J mol^{-1}].

For comparison, the value of $\alpha_{S,H}g_X - \eta_{X,H}f_S$ estimated [11] for α,ω-dibromoalkane/urea inclusion compounds on the basis of calculations using standard potential energy parameterizations [12,13] is -4.2×10^4 Å J mol^{-1}. The comparatively close agreement between the experimentally derived and computed estimates of $\alpha_{S,H}g_X - \eta_{X,H}f_S$ is noteworthy, particularly in the light of the fact that the potential energy parameterization was not specifically optimized with respect to α,ω-dibromoalkane/urea inclusion compounds.

A detailed discussion of the full set of experimental results obtained for binary mixtures of α,ω-dibromoalkane guest molecules in the urea host tunnel structure will be given in a forthcoming publication [14].

Acknowledgements

We are grateful to the University of Birmingham and CVCP for financial support.

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