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Experimental Determination of Interaction Energies in a Porous Molecular Solid

Sang-Ok Lee,[†] Kenneth D. M. Harris,[*,†] Peter E. Jupp,[‡] and Lily Yeo[†]

School of Chemistry, University of Birmingham
Edgbaston, Birmingham B15 2TT, United Kingdom
School of Mathematics and Statistics
University of St. Andrews, St. Andrews
Fife KY16 9SS,United Kingdom

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To derive a fundamental rationalization of the structural properties of molecular solids, it is essential to understand the intermolecular interactions that govern the observed molecular packing arrangements. However, while chemists have considerable intuitive understanding of preferred intermolecular interaction motifs, derived both from observing recurrent structural motifs in known crystal structures and from computational studies of intermolecular interaction strengths, there is a paucity of direct quantitative experimental information on intermolecular interaction energies. In this contribution, we apply a method for estimating interaction energies in tunnel inclusion compounds[1,2] directly from experimental investigations of the competitive co-inclusion of binary mixtures of potential guest molecules. In general, tunnel host structures provide a good opportunity for systematic studies of intermolecular interactions, as different types of guest molecule are constrained to interact with the host structure and with each other in geometrically controlled ways.[2−4]

Our experimental studies of competitive co-inclusion focus on the formation of inclusion compounds containing two different types of guest molecule $X(Sp)_{n_i}X$ and $X(Sp)_{n_j}X$, within the same host tunnel structure. The guest molecules have the same types of end-group (X) and spacer unit (Sp), but different chain lengths n_i and n_j ($n_i > n_j$). For each pair of guest molecule types (i, j), the inclusion compound is prepared for several different values of the proportion of $X(Sp)_{n_i}X$ molecules in the crystallization solution (denoted by γ_i) and in each case we measure experimentally the proportion of $X(Sp)_{n_i}X$ guest molecules in the inclusion compound (denoted by m_i). Thus, our experimental data comprise several values of (γ_i, m_i) for each pair of guest molecule types (i, j). Clearly, the values of (γ_i, m_i) indicate the relative extent of uptake of the two different types of guest molecule within the host tunnel structure, which in turn depends on the interaction energies within the inclusion compound.

We have previously developed a mathematical model[5−7] that provides a framework for establishing relationships between certain structural aspects of tunnel inclusion compounds and the interaction energies within them (host−guest and guest−guest interactions), including the case[7] of competitive co-inclusion of two different types of guest molecule $X(Sp)_{n_i}X$ and $X(Sp)_{n_j}X$. In the present work, we apply, for the first time, our methodology for determining interaction energy terms directly from experimental measurements of the type described above. For these studies, we focus on urea inclusion compounds[2,8−11] containing α,ω-dibromoalkane $[Br(CH_2)_nBr]$ guest molecules.[12,13] The host structure in urea inclusion compounds[14,15] comprises a hydrogen-bonded arrangement of urea molecules, which contains linear, parallel tunnels (diameter ∼5.5−5.8 Å).

As derived elsewhere,[7] for a tunnel inclusion compound prepared under conditions of competitive co-inclusion of guest molecules i and j, values of γ_i and m_i are related by

$$\frac{m_i}{m_j} \approx \left(\frac{\gamma_i}{\gamma_j}\right) \exp\left(\frac{(\alpha g - \eta f)\, c_h}{f^2}\,\frac{1}{kT}\left(\frac{1}{n_i + \phi} - \frac{1}{n_j + \phi}\right)\right) \qquad (1)$$

where $m_j = 1 - m_i$ and $\gamma_j = 1 - \gamma_i$. In this expression, α is the average interaction energy between a spacer unit Sp and the host tunnel, and

$$\eta = 2\beta + \delta \qquad (2)$$

where β is the average interaction energy between an end-group X and the host tunnel, and δ is the average interaction energy (X···X) between two adjacent guest molecules in the tunnel. The length (c_i) of tunnel occupied by a guest molecule of type i usually obeys a linear relationship

$$c_i \approx f n_i + g \qquad (3)$$

(which may be established from appropriate diffraction studies[7]), and we define

$$\phi = g/f \qquad (4)$$

Physically, f can be interpreted as the distance taken up along the tunnel by each spacer unit Sp, and g can be interpreted as the distance taken up along the tunnel by each pair of end-groups X···X. The periodic repeat distance of the host structure along the tunnel direction is denoted c_h. Taking logarithms of eq 1 gives

$$Y_{ij} = \log\left(\frac{m_i}{m_j}\right) - \log\left(\frac{\gamma_i}{\gamma_j}\right) \approx \theta\, x_{ij}, \qquad (5)$$

where

$$\theta = \frac{(\alpha g - \eta f) c_h}{f^2}\,\frac{1}{kT} \qquad (6)$$

and

$$x_{ij} = \frac{1}{n_i + \phi} - \frac{1}{n_j + \phi} \qquad (7)$$

For each pair (i, j) of guest molecule types, we obtain N_{ij} experimental measurements (denoted by y_{ijk}; $k = 1, ..., N_{ij}$) of Y_{ij}. Fitting these values of y_{ijk} as a function of x_{ij} (eq 5) allows θ to be estimated and hence allows the interaction energy term $\alpha g - \eta f$ to be determined. The mathematical procedures developed for the fitting procedure are described elsewhere.[16]

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[*] To whom correspondence should be addressed: Telephone: +44-121-414-7474. Fax: +44-121-414-7473. E-mail: K.D.M.Harris@bham.ac.uk.

[†] University of Birmingham.

[‡] University of St. Andrews.

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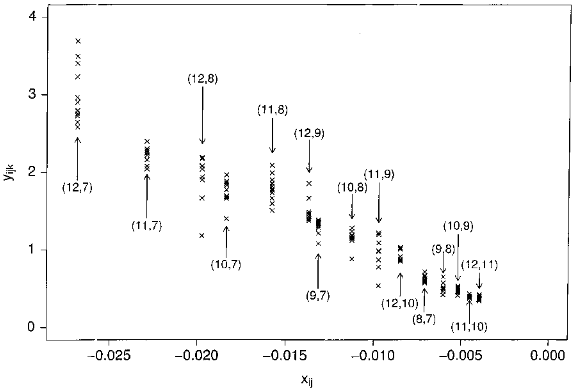

Figure 1. Plot of experimental measurements y_{ijk} *versus* x_{ij} for mixtures of guest molecules $Br(CH_2)_{n_i}Br$ and $Br(CH_2)_{n_j}Br$ within the urea tunnel structure. The values in parentheses are (n_i, n_j).

In this contribution, we report the first application of this methodology, to determine the interaction energy term $\alpha g - \eta f$ for $Br(CH_2)_nBr$/urea inclusion compounds, and we compare the results to the corresponding information derived from computational studies. In terms of its physical interpretation, we emphasize that $\alpha g - \eta f$ *is* proportional to $\alpha/f - \eta/g$ [specifically, $\alpha g - \eta f = fg(\alpha/f - \eta/g)$], which represents the average change in energy per unit length of tunnel obtained by substituting a spacer unit in place of an adjacent pair of end-groups, as discussed in more detail in ref 7. We note that the analysis presented here does not provide separate values for the energy terms α and η, although a strategy that does allow separate values of α and η to be determined (from measurements of $\alpha g - \eta f$ for a wider series of inclusion compounds) has been established, and is described in ref 7.

Our experimental data[17] comprise 15 pairs of guest molecule types (i, j), with between 9 and 13 separate measurements of (γ_i, m_i) in each case, covering the full range of γ_i between (but not including) 0 and 1. In total, we have 143 measurements y_{ijk} for 15 different values of x_{ij}, as shown in Figure 1 (a striking feature of Figure 1 is that the range of values of y_{ijk} for a given value of x_{ij} is roughly proportional to $-x_{ij}$, and this observation plays an important role in the analysis of data, as described in detail in ref 16). From analysis[16] of the data shown in Figure 1, θ is estimated to be −112.1, with 95% confidence interval (−114.7, −109.5). To determine $\alpha g - \eta f$ from our estimate of θ, we require values of temperature T (313 K; averaged over the crystallization experiment), f and c_h. Single-crystal X-ray diffraction results for $Br(CH_2)_nBr$/urea inclusion compounds[7,12,15,18] lead to $f \approx 1.26$ Å and $g \approx 5.50$ Å (thus $\phi \approx 4.37$) and $c_h \approx 11.06$ Å. Thus, we obtain $\alpha g - \eta f \approx -10.01$ Å kcal mol^{-1}, with 95% confidence interval (−10.24, −9.78) Å kcal mol^{-1}.

Computed values[19] of the average host−guest interaction energy $\langle E_{hg} \rangle$ are shown in Figure 2, confirming the expected[28,29] linear relationship [$\langle E_{hg} \rangle = \alpha n + 2\beta$] between $\langle E_{hg} \rangle$ and n. Analysis of Figure 2 leads to $\alpha \approx -3.70$ kcal mol^{-1} and $2\beta \approx -9.15$ kcal mol^{-1}. Our computational estimate of δ is +0.93 kcal mol^{-1}, and thus $\eta \approx -8.22$ kcal mol^{-1}. Using $f \approx 1.26$ Å and $g \approx 5.50$ Å as above, we obtain $\alpha g - \eta f \approx -10.00$ Å kcal mol^{-1}, with 95% confidence interval (−14.42, −5.57) Å kcal mol^{-1}.

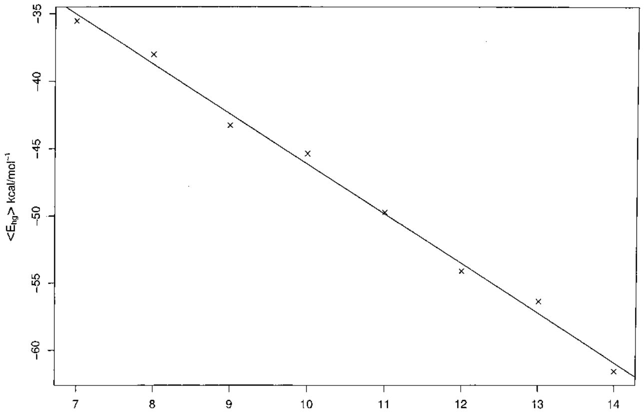

Figure 2. Computed values of $\langle E_{hg} \rangle$ versus n for $Br(CH_2)_nBr$/urea inclusion compounds.

The strategy applied here represents a novel approach for obtaining information on intermolecular interaction energies directly from experimental measurements. The excellent agreement[30] between our experimentally and computationally derived estimates of $\alpha g - \eta f$ supports both the validity of our model for analysis of the experimental data and the validity of the potential energy parametrization used in the computational work. We are currently extending the application of this method to a wider range of binary mixtures of guest molecules in urea inclusion compounds and other tunnel host structures. Given the wide-ranging importance of understanding intermolecular interactions in molecular solids, there is a very real prospect that the development of direct experimental approaches for establishing quantitative information on intermolecular interaction energies, such as the method demonstrated in this paper, will make significant future impact in this field.

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(17) Urea inclusion compounds containing binary mixtures of guest molecules $Br(CH_2)_{n_i}Br$ and $Br(CH_2)_{n_j}Br$ [n_i = 8, ..., 12; n_j = 7, ..., n_i − 1] were prepared as follows. Urea (1 g; 0.0166 mol) and two different $Br(CH_2)_nBr$ guests (total of 0.002 mol in all cases) were dissolved in methanol at 50 °C. For each of the 15 pairs (i,j) of guest molecule types, between 9 and 13 separate crystal growth experiments were carried out using different mole fractions γ_i (across the full range from 0 to 1) of the two guest molecules in the crystallization solution. For a given pair (i,j), all solutions were cooled simultaneously to 30 °C over 3 h, allowing crystallization to occur under identical conditions in each case. The crystals were collected and washed with a small amount of 2,2,4-trimethylpentane. For each sample, the mole fractions (m_i and m_j) of the two different types of guest molecule within the inclusion compound were determined by gas chromatography [Carlo Erba GC 8000 series (8130); BPX5 (15 m × 0.53 mm) megabore column].

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(19) Our computational studies of host−guest interaction in $Br(CH_2)_nBr$/urea inclusion compounds (n = 7, ..., 14) considered a single $Br(CH_2)_nBr$ guest molecule within the urea tunnel structure. Because of the incommensurate relationship between the host and guest structures in $Br(CH_2)_nBr$/urea inclusion compounds,[13,15,20−24] the guest molecules within a given tunnel sample all values of z-coordinate within the unit cell of the host structure. We therefore computed the host−guest interaction energy (E_{hg}) as a function of the position (z) of the guest molecule along the tunnel. Full details of the procedure adopted for these calculations (which used a standard potential energy parametrization[25,26] based on the atom−atom summation technique) are described (applied to a different system) elsewhere.[27] The average host−guest interaction energy $\langle E_{hg} \rangle$ for the incommensurate system was determined by averaging $E_{hg}(z)$ over all positions z of the guest molecule along the tunnel. The guest−guest interaction energy δ was estimated (using the same potential energy parametrization) for a pair of $Br(CH_2)_nBr$ molecules constrained to approach each other in the linear trajectory dictated by the tunnel structure.

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(30) In statistical terms, the agreement between the results from our computational study and the analysis of our experimental data can be assessed by determining a 95% confidence interval for the difference in the mean values of $\alpha g - \eta f$ obtainable from the two approaches. This 95% confidence interval is determined[16] to be (−4.43, +4.42) Å kcal mol^{-1}. Since the value 0 (i.e., zero difference between the results from the two approaches) lies well inside this interval, we conclude that there is excellent agreement between the two methods.