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Gas Complexes

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Supramolecular Solid–Gas Complexes: A Thermodynamic Approach

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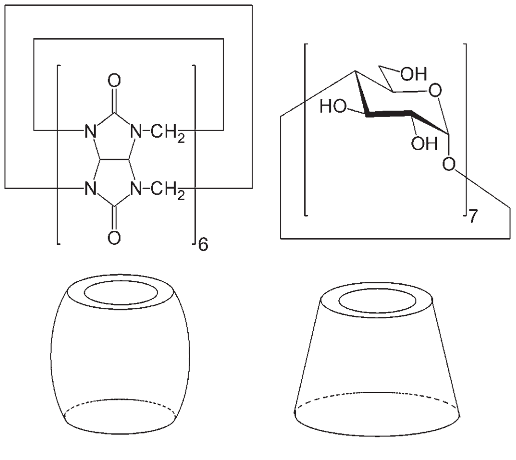
The reversible binding of gases by solid materials is of great interest for modern technologies concerning gas separators, sensors, and storage devices for use in fuel cells. Since the first studies of Cramer and Henglein[1] on the complexation of gases by α-cyclodextrin in aqueous solution, a range of inclusion complexes with gases has been investigated. Recently, various macrocyclic receptors were proposed as suitable molecular containers for different gases.[2] Nevertheless, the rules governing the selectivity of gas–receptor interactions and the thermodynamic stability of gas complexes are still poorly understood. Day et al. found that cucurbit[*n*]urils are able to form complexes with various gases at atmospheric pressure,[3] while Atwood and co-workers have shown the possibilities of gas encapsulation by substituted calixarenes.[4] The main research trends in the supramolecular chemistry of gases were analyzed by Rudkevich et al.[2a,b] In some cases it was possible to determine the thermodynamic quantities of gas-inclusion processes. Cram et al.[5] as well as Rebek and co-workers[6] measured the stability constants and reaction enthalpies for the complexation of CH_4 and Xe by self-assembling cavities in $CDCl_3$ by using ^{1}H NMR and ^{129}Xe NMR spectroscopic methods. Gorbatchuk et al.[7] calculated the Gibbs free energies for the formation of a complex between solid calixarenes and gaseous organic compounds from adsorption isotherms. The results on the thermodynamics of the binding of molecular oxygen by Co^{II} complexes and protein molecules (hemoglobin, myoglobin, etc.) in solution were reviewed by Martell and co-workers.[8] Although adsorption microcalorimetry[9] and variable-temperature FTIR spectroscopy[10] were successfully applied for the study of the interactions between gases and porous inorganic materials (zeolites etc.), it is not clear from the literature whether such methods are suitable for the investigation of macrocyclic ligand complexes. Furthermore, the interpretation of the results may be difficult because of incomplete equilibrium between gaseous and solid phases as a result of the undefined capacity of the surface as well as the possibility of changes in the crystal structure in the course of the reaction.[8] To date, no direct methods seem to have been adapted to determine of thermodynamic parameters for the complexation of gases by solid macrocyclic receptors.

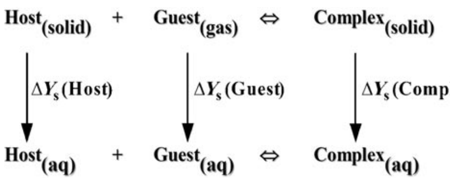
The chemical reactions, which are difficult to study in an experiment, can be described on the basis of Born–Haber-type thermodynamic cycles.[11] Thus, Gox and Schneider have obtained the thermodynamic parameters of the complexation between [2.2.2.]cryptand and alkali-metal salts in the solid state by using the corresponding data in solution.[12a] Danil de Namor et al. calculated from solution data "the standard enthalpies of coordination" corresponding to the complexation process of calixarene derivatives with metal salts in which the reactants and product are in their solid state.[12b] Herein we demonstrate and discuss the application of an indirect "solution" approach to investigate gas inclusion in solid macrocyclic ligands by using examples of the typical 1:1 complexation equilibria between solid cucurbit[6]uril (**1**), β-cyclodextrin (**2**, Figure 1), and the volatile *n*-alkylamines propylamine (**3**), butylamine (**4**), pentylamine (**5**), and hexylamine (**6**).



1 **2**

Figure 1. Chemical and schematic structures of cucurbit[6]uril (**1**) and β-cyclodextrin (**2**).

The principle of the approach is as follows: The equilibria for the complexation in solution and at the solid–gas interface are related to the Gibbs free energies (*G*), enthalpies (*H*), and entropies (*S*) of the reaction participants in solution (solid host, gaseous guest, and "solid–gas" complex) through a thermodynamic cycle represented by Scheme 1.



Scheme 1. Thermodynamic cycle for the calculation of solid–gas complexation equilibria.

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The thermodynamic parameters of the complexation in solution can be determined by using calorimetric, potentiometric, or spectrophotometric titrations. The Gibbs free energies of solution are calculated from solubility values according to Equation (1).

$$\Delta G_S = -2.303RT\log S \tag{1}$$

The enthalpies of solution may be obtained by using solution calorimetry or from the temperature-dependence of the solubility.

The thermodynamic parameters for the complexation of a gaseous guest by a solid host are calculated from Equation (2).

$$\Delta_r Y_{\text{solid-gas}} = \Delta_r Y_{\text{aq}} - [\Delta Y_S(\text{Complex}) - \Delta Y_S(\text{Host}) - \Delta Y_S(\text{Guest})] \tag{2}$$

$\Delta_r Y^0_{\text{solid-gas}}$ is the Gibbs free energy or enthalpy for "solid–gas" complexation, $\Delta_r Y^0_{\text{aq}}$ is the corresponding parameter for the reaction in solution (here in aqueous solution), and ΔY^0_s are the Gibbs free energies or enthalpies of solution of the reactants.

The free energies and enthalpies of the amines in solution and the solubility of cucurbit[6]uril in water at 25 °C were taken from the literature.[13,14] For many inclusion processes, an almost complete shielding of the guest (cation or molecule) in the complex from interactions with the solvent leads to an appropriate parity in the thermodynamic functions of solution (transfer) of the host (ligand) and the host–guest complex [Eq. (3)][12a]

$$\Delta Y_S(\text{complex}) \approx \Delta Y_S(\text{host}) \tag{3}$$

We have recently found that the Gibbs free energies of β-cyclodextrin–amine complexes in solution are nearly identical with that of β-cyclodextrin—amine complexes.[15] The cucurbit[6]uril–amine complexes are somewhat more soluble than that of the free host, and the assumption in Equation (3) in terms of the Gibbs free energies is not applicable. For these complexes the stability constants are calculated from Equation (2).

As has previously been accepted,[15] the enthalpies of the host (here cucurbit[6]uril) and corresponding amine complexes in solution are assumed to be in accordance with Equation (3). This equation is valid only for the inclusion complexes in which all the solvating sites of the guest molecule are coordinated by the functional groups of the host. At the same time, it allows the enthalpies and entropies for the solid–gas complexation to be estimated when appropriate experimental data on solution enthalpies (and entropies) of the complexes are not available.

As all the experiments were performed in solution, any adsorption effects at the host surfaces are lacking. Incomplete complexation or possible changes in the crystal structure during the course of the reaction (as may happen by direct measurements in heterogeneous systems) were also excluded in the study. Elemental analysis of the obtained solid complexes shows an exactly 1:1 composition.

The stability constants, reaction enthalpies, and entropies for the complexation of several amines in the gas phase by solid cucurbit[6]uril and β-cyclodextrin, as well as the corresponding data in aqueous solution are presented in Table 1. The thermodynamic parameters determined in acidic solution were recalculated for the reactions of unprotonated amines as described in the Experimental Section. The reactions in solution and under solid–gas conditions are related to the complexation of unprotonated amines.

Table 1: Thermodynamic data, log *K*, ΔH, and $T\Delta S$ for the complexation of *n*-alkylamines (Am) by cucurbit[6]uril (cuc) and β-cyclodextrin (β-CD).

Amine	log K[a]	$-\Delta H$ [kJ mol^{-1}]	298.15 ΔS[a] [kJ mol^{-1}]
		$\text{Cuc(6)}_{(aq)} + \text{Am}_{(aq)} \Leftrightarrow [\text{Cuc(6)}\subset\text{Am}]_{(aq)}$	
3	6.6 ± 0.3	62.2 ± 0.7	-24.5 ± 1.0
4	6.3 ± 0.2	77.0 ± 1.0	-41.1 ± 1.2
5	6.3 ± 0.2	78.5 ± 0.7	-42.7 ± 0.9
6	5.9 ± 0.1	74.3 ± 0.6	-40.4 ± 0.7
		$\text{Cuc(6)}_{(s)} + \text{Am}_{(g)} \Leftrightarrow [\text{Cuc(6)}\subset\text{Am}]_{(s)}$	
3	5.3 ± 0.4	118.1 ± 0.9	-87.8 ± 1.3
4	4.9 ± 0.3	136.0 ± 1.0	-108.0 ± 1.3
5	4.3 ± 0.3	140.6 ± 0.8	-116.1 ± 1.1
6	4.4 ± 0.2	140.1 ± 0.7	-115.0 ± 0.9
		$\beta\text{-CD}_{(aq)} + \text{Am}_{(aq)} \Leftrightarrow [\beta\text{-CD}\subset\text{Am}]_{(aq)}$[b]	
3	4.3 ± 0.07	1.6 ± 0.05	22.7 ± 0.5
4	4.3 ± 0.06	1.5 ± 0.15	23.1 ± 0.5
5	4.3 ± 0.06	1.6 ± 0.15	23.2 ± 0.5
6	4.6 ± 0.04	1.2 ± 0.13	25.1 ± 0.4
		$\beta\text{-CD}_{(s)} + \text{Am}_{(g)} \Leftrightarrow [\beta\text{-CD}\subset\text{Am}]_{(s)}$[b]	
3	4.6 ± 0.1	57.5 ± 0.1	-32.6 ± 0.7
4	4.5 ± 0.1	60.6 ± 0.2	-35.8 ± 0.8
5	4.3 ± 0.2	63.7 ± 0.2	-39.6 ± 0.8
6	4.4 ± 0.1	67.0 ± 0.2	-41.6 ± 0.8

[a] Mole fraction standard state. [b] Data from Ref. [15].

In the reactions of solid hosts with gaseous guests, any solvation effects are lacking and the interaction forces, as indicated by the enthalpy changes, become more favorable upon transfer of the reactions from solution to solid–gas conditions. At the same time, the reaction entropies are changed from favorable (positive) to negative values for β-cyclodextrin complexes and to more negative values for cucurbit[6]uril complexes (Table 1).

In summary, we have demonstrated that the thermodynamics for the complexation of gaseous substances by solid macrocyclic receptors can be studied on the basis of the data obtained in solution. We intend to apply this concept to the complexation of different gases and to developing new effective gas-binding systems.

Experimental Section

All amines were of the highest commercially available purity (Fluka). Cucurbit[6]uril was prepared as described previously.[16] Distilled deionized water was used throughout the experiments. pH titrations were performed by using a GLpKa analyzer (Sirius Analytical Instruments, Forest Row, UK). During the titrations the ionic strength *I* was kept constant with KCl at $I = 0.15$ M. At least a tenfold excess of the macrocyclic ligand was used for the titrations to ensure the complete formation of a complex. The potentiometric titration curves were analyzed by using software package Refinement Pro (version V1.114, Sirius Analytical Instruments, Forest Row, UK). Stability constants K_{aq,H^+} determined in acidic solution for the reaction between a protonated amine and cucurbit[6]uril ($Cuc_{(aq)} + AmH^+_{(aq)} \rightleftharpoons [Cuc \subset AmH]^+_{(aq)}$) were recalculated for the reaction of unprotonated amine ($Cuc_{(aq)} + Am_{(aq)} \rightleftharpoons [Cuc \subset Am]_{(aq)}$) according to [Eq. (4)].

$$K_{aq} = \frac{K_a(\text{complex})K_{aq,H^+}}{K_a(\text{amine})} \quad (4)$$

K_a(amine) and K_a(complex) are the protonation constants of the amine and cucurbit[6]uril–amine complex, respectively (Table 2).

Table 2: Experimental data, pK_a [K in $l\,mol^{-1}$], $-\Delta H_a$ [$kJ\,mol^{-1}$], and S [$mol\,l^{-1}$] for cucurbit[6]uril–amine complexes.

	n-propyl amine	*n*-butyl amine	*n*-pentyl amine	*n*-hexyl amine
pK_a(amine)[a]	10.61	10.67	10.72	10.78
pK_a(complex)	9.39 ± 0.03	9.09 ± 0.08	9.29 ± 0.07	9.60 ± 0.05
$-\Delta H_a$(amine)[a]	57.4	58.7	59.5	60.6
$-\Delta H_a$(complex)	9.4 ± 0.3	9.0 ± 0.5	8.4 ± 0.3	8.4 ± 0.2
log K_{aq,H^+}	5.4 ± 0.2	4.71 ± 0.1	4.84 ± 0.1	4.76 ± 0.1
$-\Delta_r H_{aq,H^+}$[b]	14.2	26.8	27.4	22.1
S(complex) × 10^4	4.2 ± 0.1	4.7 ± 0.1	4.3 ± 0.1	4.2 ± 0.1

[a] Data from Ref. [17]. [b] Data from Ref. [18]

Similarly, the reaction enthalpies in acidic solution $\Delta H_{aq,H^+}$ were recalculated for the reaction of unprotonated amine by using Equation (5).

$$\Delta_r H_{aq} = \Delta_r H_{aq,H^+} - [\Delta H_a(\text{complex}) - \Delta H_a(\text{amine})] \quad (5)$$

The calorimetric titrations were carried out using a Tronac calorimeter (Model 450, Tronac Inc. USA). The reaction enthalpies were calculated from the experimental data by published procedures.[19] Solid complexes of the amines with cucurbit[6]uril were prepared by the addition of solid cucurbit[6]uril to pure liquid amines, and heating the mixtures for two days. Afterwards the liquid amines were removed and the solids were washed with acetone and dried. Elemental analysis (%) calcd for $C_{39}H_{45}N_{24}O_{12}$ (1055.95): C 44.36, H 4.30, N 33.16, C/N 1.34:1; found: C 38.32, H 4.67, N 29.71, C/N 1.29:1; calcd for $C_{40}H_{47}N_{24}O_{12}$ (1069.98): C 44.90, H 4.43, N 32.72, C/N 1.37:1; found: C 39.04, H 4.67, N 29.42, C/N 1.33:1 calcd for $C_{41}H_{49}N_{24}O_{12}$ (1084.01): C 45.43, H 4.56, N 32.30, C/N 1.41:1; found: C 39.63, H 4.67, N 29.29, C/N 1.35:1; calcd for $C_{42}H_{51}N_{24}O_{12}$ (1098.19): C 45.94, H 4.68, N 31.89, C/N 1.35:1; found: C 39.11, H 4.75, N 28.35, C/N 1.38:1.

The solubilities of the complexes in water were determined by using a Total Organic Carbon Analyzer (TOC-5050, Shimadzu, Japan). An excess of the solid complex was added to water, equilibrated in an ultrasound bath, and then stirred in air maintained with a thermostat at 25.0 ± 0.1 °C for several days. Prior to the measurements of the total organic carbon content of the solutions they were passed through a membrane polycarbonate filter (0.2 μm).

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