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Complexation of gaseous guests by solid host
I. Quantitative thermodynamic approach for the reactions of β-cyclodextrin with amines using data in aqueous solution

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Abstract

The stability constants and reaction enthalpies for complexes of different primary, secondary and tertiary amines with β-cyclodextrin and the protonation constants of the amines in aqueous solution have been measured at 298.15 K using potentiometric and calorimetric titrations. Pronounced selectivity of the inclusion process in aqueous solution is shown. Free energies of solution of the complexes in water determined from solubility measurements appear to be nearly identical with that of β-cyclodextrin. By using a thermodynamic cycle and thermodynamic parameters of solution of the reaction participants, the Gibbs energy, enthalpy and entropy of the complexation reactions between solid β-cyclodextrin and several gaseous amines are calculated. Complex stabilities in aqueous solution and at the solid–gas interface are comparable. Unlike the equilibria in aqueous solution, the reaction enthalpies for the "solid–gas" complexation are much higher and the interactions are unfavorable in terms of the entropy changes.

Keywords: β-Cyclodextrin; Amines; Solid–gas complexation; Thermodynamic parameters; Solution; Selectivity

1. Introduction

Inclusion compounds of naturally occurring cyclodextrins with gases were firstly obtained by Cramer and Henglein in the 1950s [1]. They found that hydrocarbons, halogens, oxygen, carbon dioxide and noble gases under high pressure (7–120 atm) form stoichiometric and non-stoichiometric complexes with α-cyclodextrin in aqueous solution. Chlorine and bromine form complexes with β-cyclodextrin and iodine with γ-cyclodextrin. Nowadays molecular recognition of vaporous guests by the solid hosts is of great interest in many research and engineering areas. Encapsulation of gases by cavity-containing solid materials is crucial for developing new gas separators, sensors and storage devices for use in fuel cells [2–6]. The design of novel synthetic cavities for gas inclusion is a quickly emerging research area. Clathrates, cross-linked polymers, carbon nanotubes, dendrimers, calixarens, fullerens and cyclodextrins were proposed as suitable molecular containers for gases of different nature. Nevertheless, the driving forces of inclusion in heterogeneous systems are much less studied as compared to that in pure condensed (liquid, solid) [7–11] or gas phase [12,13]. The reaction free energies and structure–affinity relationships for inclusion of volatile organic compounds by solid calixarens have been determined by static gas chromatographic headspace analysis [14,15]. Several investigations have been performed concerning complexation of gaseous hydrocarbons, amines and alcohols by solid cyclodextrins [16–18].

In the present work, the complex formation of different primary, secondary and tertiary amines by β-cyclodextrin is studied. The reactions in water and at the gas–solid interface are related with the Gibbs free energies and enthalpies of solution of the reaction participants (solid cyclodextrin, gaseous amine and "solid–gas" complex) via a thermodynamic cycle. It makes possible thermodynamic parameters for the reactions between solid β-cyclodextrin and several gaseous amines to be determined using the data obtained in aqueous solution.

2. Experimental

All amines (Fluka) and β-cyclodextrin ("Cavasol W7", Wacker-Chemie GmbH) are of the highest purity commercially

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available. Distilled deionized water is used throughout the experiments. pH-metric titrations are performed using a GLpKa analyzer (Sirius Analytical Instruments, Forest Row, UK). Glass electrodes are standardized using Sirius-Four-Plus^{TM} procedure, which relates *operational* pH scale to *concentration* pH scale, taking liquid junction potentials and other deviations from ideal behaviour into account. An acidic solution of the amine (0.001–0.004 M) is titrated with potassium hydroxide (0.5 M). During the titrations the ionic strength I is kept constant with KCl at $I = 0.15$ M. In water the protonation equilibrium of the amine (Am) is given by

$$\mathrm{AmH^+} \Leftrightarrow \mathrm{Am} + \mathrm{H^+}$$

with

$$K_a = \frac{[\mathrm{Am}] \cdot [\mathrm{H^+}]}{[\mathrm{AmH^+}]} \tag{1}$$

In the presence of β-cyclodextrin the *apparent* protonation constant of the amine (K_a^*) is determined by the following equation:

$$K_a^* = K_a(1 + K \cdot C_{\beta\text{-CD}}) \tag{2}$$

where

$$K = \frac{[\beta\text{-CD} \cdot \mathrm{Am}]}{[\mathrm{Am}] \cdot [\beta\text{-CD}]}$$

The stability constant for β-cyclodextrin–amine complex (K, l mol^{-1}) is calculated from Eq. (3)

$$K = \frac{K_a^*/K_a - 1}{C_{\beta\text{-CD}}} = \frac{10^{-(\mathrm{p}K_a^* - \mathrm{p}K_a)} - 1}{C_{\beta\text{-CD}}} \tag{3}$$

where $C_{\beta\text{-CD}}$ is the concentration of β-cyclodextrin. At least a 10-fold excess of β-cyclodextrin was used for the titrations to ensure a complete complex formation. The potentiometric titration curves were analyzed using the software package Refinement Pro, Version V1.114 (Sirius Analytical Instruments).

The calorimetric titrations are carried out using a Tronac Model 450 calorimeter. During the calorimetric titration, a solution of β-cyclodextrin (0.015 M) is titrated continuously into 40 ml solution of amine (0.0009–0.001 M) for 1 min (burett rate 0.333 ml/min). An excess of NaOH was added to all aqueous amine solutions to suppress the protonation of amines. The measured heat after correction for all non-chemical effects depends on the number of moles and the reaction enthalpy of the β-cyclodextrin–amine complex formed during the titration. The reaction enthalpies are calculated from the experimental data by published procedures [19–21]. No change of the reaction enthalpies was detected at high pH values varying between 11 and 13.

Solid complexes of the amines with β-cyclodextrin are prepared from aqueous saturated solution of β-cyclodextrin (at 90 °C) with excess of amine by cooling. Formed residues are filtered and dried up in a vacuum exicator at room temperature (48 h). Solubility of the complexes in water is determined as follows. An excess of the solid complex is added to water, equilibrated in an ultrasound bath and then stirred in an air thermostat at 25.0 ± 0.1 °C for several days. Aliquots are removed, passed through membrane polycarbonate filter (0.2 μm) and analyzed gravimetrically by evaporating the solvent and weighing the residue. Composition of the complexes is verified by determination of the amine content by titration of the weighted samples dissolved in water with a standard solution of hydrochloric acid. The experiments are performed in triplicate.

3. Results and discussion

3.1. Selectivity of interactions between β-cyclodextrin and amines in aqueous solution

The pK_a values of the amines and stability constants of β-cyclodextrin–amine complexes in aqueous solution are given in Table 1. These data are on the molar concentration scale. The values of stability constants reported in this work are in the range of statistically expected stabilities for β-cyclodextrin complexes calculated by Connors [9]. The consideration of thermodynamic parameters for primary, secondary and tertiary amine complexes of β-cyclodextrin brings an insight into the geometrical aspects of selectivity of the host–guest complexation process. Diameters of the narrower and wider rim (0.60 and 0.65 nm, respectively) and height (0.78 nm) of the cavity for β-cyclodextrin are known from crystallographic analysis. As a comparable value for amine molecules, their approximate molecular diameter (d_m) can be estimated from the densities of pure amines at 25 °C (ρ_{25}) using Eq. (4)

$$V_m^{25} = \frac{M_r}{\rho_{25} \cdot N_A} = \frac{4}{3}\pi r_m^3; \quad d_m = 2r_m \tag{4}$$

where V_m^{25} is the volume occupied by an amine molecule at 25 °C, M_r the molar mass of the amine and r_m is the radii of

Table 1
Stability constants, log $K^{(c)}$, of β-cyclodextrin–amine complexes and pK_a values of the amines in aqueous solution at 298.15 K ($I = 0.15$ M KCl)

Amine	pK_a		log $K^{(c)}$	
n-Propylamine	10.61	10.57[a]	2.52 ± 0.07	
n-Butylamine	10.67	10.64[a]	2.57 ± 0.06	
n-Pentylamine	10.72	10.63[a]	2.60 ± 0.06	
n-Hexylamine	10.78	10.64[a]	2.87 ± 0.04	1.81 ± 0.10[b]
n-Heptylamine	10.75	10.66[a]	2.66 ± 0.03	
n-Octylamine	10.73		2.73 ± 0.03	2.62 ± 0.12[b]
n-Nonylamine	10.71		2.65 ± 0.01	
Cyclopropylamine	9.12	9.10[a]	1.69 ± 0.07	
Cyclobutylamine	10.12		2.14 ± 0.04	
Cyclopentylamine	10.76	10.65[a]	2.24 ± 0.01	
Cyclohexylamine	10.77	10.58[a]	2.76 ± 0.02	
Cycloheptylamine	11.21		3.12 ± 0.03	
Dipropylamine	11.42	11.00[a]	3.00 ± 0.10	
Dibutylamine	11.07	11.25[a]	2.37 ± 0.03	
Dihexylamine	9.42		2.41 ± 0.06	
Hexamethylenimine	11.37	11.10[a]	2.92 ± 0.03	
N-Methylcyclohexylamine	11.05		2.72 ± 0.02	
N,*N*-Dimethylcyclohexylamine	11.20		2.63 ± 0.03	
Triethylamine	10.74		2.61 ± 0.06	
Tributylamine	9.05	9.93[a]	1.85 ± 0.10	
Tripentylamine	7.43		1.47 ± 0.13	

[a] Ref. [24].
[b] Ref. [10] in phosphate buffer; pH 6.9.

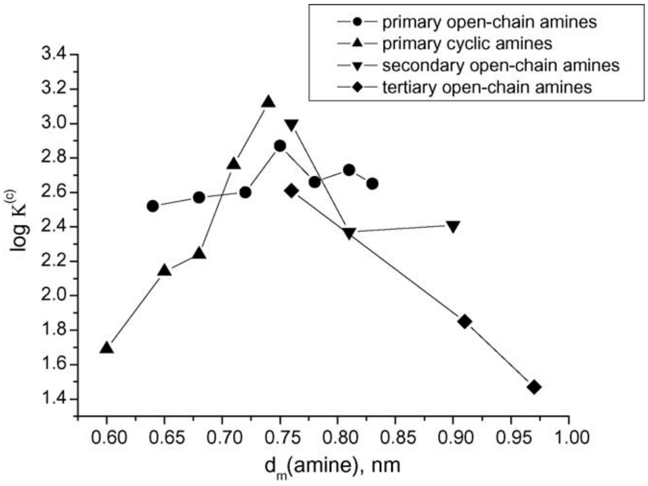


Fig. 1. Stability constants, $\log K^{(c)}$, of β-cyclodextrin–amine complexes in aqueous solution at 298.15 K as function of the molecular diameter (d_m) of the amine molecules.

amine molecule which is considered as a sphere. The suggestion about the spherical shape of amine molecules (Eq. (4)) is obviously a reasonable approximation only for primary cyclic amines and tertiary open-chain amines. Nevertheless, the pattern of selectivity derived in terms of this approximation is the same for all of the amines studied (Fig. 1). The most stable complexes are formed with the amines, which have d_m values in the range of 0.7–0.8 nm that is somewhat larger as compared to the sizes of β-cyclodextrin cavity. However, as the volume of a molecule calculated by Eq. (4) includes also so-called free volume due to non-close packed structure in the liquid state, one can conclude that the geometrical recognition between amines and β-cyclodextrin cavity is to be an important factor of selectivity in aqueous solution.

As far as the magnitudes and in some cases even the sign of the standard free energy, and especially entropy changes (not the enthalpy changes), are dependent on the standard states and the corresponding concentration scale, the choice of a suitable concentration scale for the standard state of an infinitely dilute solution is not a trivial issue. Correct comparison of the reaction driving forces in different environments (liquid solvents, gas phase) is only possible with thermodynamic parameters standardized on the mole fraction concentration scale containing no “extra” contributions that are related to the physical properties of the solvent (density, molar mass) without any connection to the reaction in solution itself. Relatively small changes of thermodynamic parameters of complexation during transfer from the gas phase to the solvent or from one solvent to another cannot be correctly compared due to these additional so-called “cratic” terms [9,22,23]. The conversion of stability constants of the complexes ($\log K^{(c)}$ in the molar (c) scale (Table 1)) and free energies of solution of amines ($\Delta G_s^{(m)}$ in the molal (m) scale [24]) to the mole fraction (m.f.) concentration scale (x) was made according to Eqs. (5) and (6):

$$\log K^{(x)} = \log K^{(c)} - \Delta\nu \log \frac{\rho_{H_2O} \cdot 10^3}{M_{H_2O}} \qquad (5)$$

Table 2
Thermodynamics of complexation of amines by β-cyclodextrin in aqueous solution at 298.15 K

Amine	$\log K^{(x)}$	$-\Delta_r H^0_{aq}$ (kJ mol^{-1})	$298.15\Delta_r S^{(x)}_{aq}$ (kJ mol^{-1})
n-Propylamine	4.3 ± 0.07	1.6 ± 0.05	22.7 ± 0.5
n-Butylamine	4.3 ± 0.06	1.5 ± 0.15	23.1 ± 0.5
n-Pentylamine	4.3 ± 0.06	1.6 ± 0.15	23.2 ± 0.5
n-Hexylamine	4.6 ± 0.04	1.2 ± 0.13	25.1 ± 0.4
Hexamethylenimine	4.7 ± 0.03	1.7 ± 0.07	24.9 ± 0.2
Dipropylamine	4.7 ± 0.10	1.5 ± 0.03	25.6 ± 0.6
Dibutylamine	4.1 ± 0.03	1.1 ± 0.07	22.4 ± 0.2
Triethylamine	4.4 ± 0.06	2.4 ± 0.35	22.5 ± 0.7

$$\Delta G_s^{(x)} = \Delta G_s^{(m)} + 2.303RT \lg \frac{10^3}{M_{H_2O}} \qquad (6)$$

where $\Delta\nu = -1$ is the algebraic sum of the stoichiometric coefficients for the reactions β-CD + amine ⇔ [β-CD ⊂ amine], ρ_{H_2O} the density (g cm^{-3}) of water at 298.15 K and M_{H_2O} is the molar mass (g mol^{-1}) of water.

Standard thermodynamic parameters for complexation of several open-chain amines by β-cyclodextrin in aqueous solution are given in Table 2. The dependence of the complex stabilities, reaction enthalpies and entropies upon the number of methylene groups in the alkyl chains of the amines is negligible. Small negative values of the reaction enthalpy and positive entropy changes can be attributed to partial desolvation of the reaction participants upon complexation without a tight binding inside of the cyclodextrin cavity. Stability constants of the complexes with primary cyclic, secondary and tertiary open-chain amines are more sensitive to the molecular structure of the amines (Table 1). The correlation of the complex stabilities with pK_a values (Fig. 2) can indicate on participation of amino groups of the amines in hydrogen bond or long-range dipole–dipole interactions with cyclodextrin cavity. Very large dipole moments of cyclodextrins in the range 2–20 D have been reported [9].

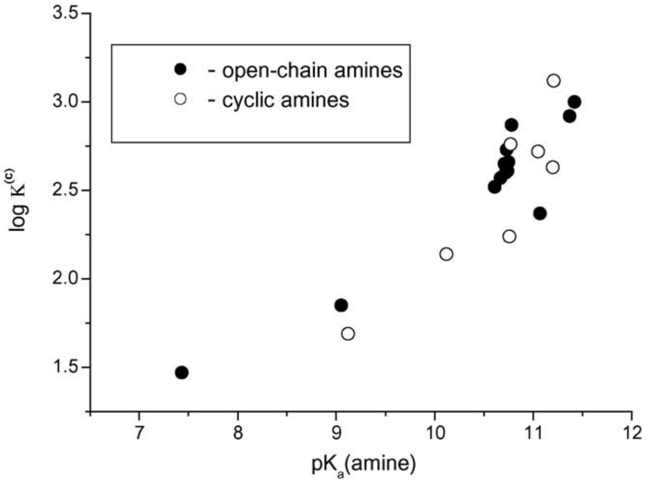
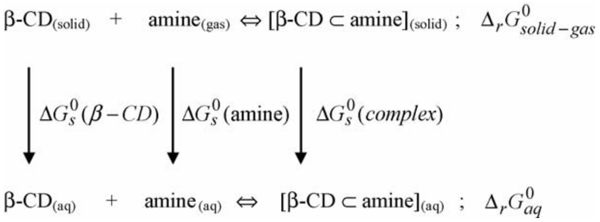


Fig. 2. Stability constants, $\log K^{(c)}$, of β-cyclodextrin–amine complexes in aqueous solution at 298.15 K as function of pK_a values of the amines.



Scheme 1.

3.2. *Quantitative determination of the thermodynamic parameters for solid–gas complexation reactions*

The thermodynamic parameters of complex formation between solid β-cyclodextrin and gaseous amines may be obtained from the thermodynamic cycle represented by Scheme 1, using Eq. (7):

$$\Delta_r G^0_{\text{solid–gas}} = \Delta_r G^0_{\text{aq}} - [\Delta G^0_{\text{s}}(\text{complex}) - \Delta G^0_{\text{s}}(\beta\text{-CD}) - \Delta G^0_{\text{s}}(\text{amine})] \qquad (7)$$

where $\Delta_r G^0_{\text{solid–gas}}$ is the Gibbs free energy for complexation reaction of gaseous amines by solid β-cyclodextrin, $\Delta_r G^0_{\text{aq}}$ the Gibbs free energy for the reaction in aqueous solution and ΔG^0_{s} are the Gibbs free energies of solution of the reaction participants in water. The analogous scheme in terms of the enthalpy and entropy changes may be written.

Free energies of solution were calculated from solubility values (*S*—solubility, expressed as m.f.) according to Eq. (8)

$$\Delta G^{(x)}_{\text{s}} = -2.303RT \lg S \qquad (8)$$

Solubility of several solid complexes, corresponding free energies of solution and the free energies and enthalpies of solution of amines from the gas phase to water at 25 °C reported by Jones and Arnett [24] are presented in Table 3. Solubility of β-cyclodextrin in water at 25 °C obtained in this work, 18.7 ± 0.3 g l^{-1}, is in agreement with the literature values [9,25,26]. Solubilities of the studied β-cyclodextrin complexes have the same order of magnitude as for β-cyclodextrin. Furthermore, the Gibbs free energies of solution of the complexes calculated from corresponding solubilities (Eq. (8)) (Table 3) appear to be nearly identical with that of β-cyclodextrin (20.1 kJ mol^{-1}):

$$\Delta G^0_{\text{s}}(\text{complex}) \approx \Delta G^0_{\text{s}}(\beta\text{-CD}) \qquad (9)$$

An appropriate parity in the thermodynamic functions of solution of the host and the host–guest complex is a consequence of fairly complete shielding of the guest from the interactions with the solvent. Introducing this assumption into Eq. (7) the following relationship is obtained:

$$\Delta_r G^0_{\text{solid–gas}} \approx \Delta_r G^0_{\text{aq}} + \Delta G^0_{\text{s}}(\text{amine}) \qquad (10)$$

The similar with Eq. (9) regularities have been obtained for thermodynamic transfer parameters of cryptand complexation with alkali, alkali earth and silver(I) ions [7]. According to Eq. (7) the determination of $\Delta_r G^0_{\text{solid–gas}}$ requires the measuring of stability constants and solubilities of the host–guest complexes in water provided the ΔG^0_{s} values for the host and the guests are known. As a first approximation the Eq. (10) may be used, also for the inclusion complexes, which are difficult to isolate from aqueous solution. Assuming that the Eq. (9) is also valid in terms of enthalpy of solution of the host and the host–guest complex, the $\Delta_r H^0_{\text{solid–gas}}$ values can be calculated according to Eq. (11)

$$\Delta_r H^0_{\text{solid–gas}} \approx \Delta_r H^0_{\text{aq}} + \Delta H^0_{\text{s}}(\text{amine}) \qquad (11)$$

Stability constants obtained from $\Delta_r G^0_{\text{solid–gas}}$ values (Eqs. (7) and (9)) are identical within the experimental and calculation errors (Table 4). Unlike the equilibria in aqueous solution, the enthalpy changes for the reactions of solid β-cyclodextrin with gaseous amines are large and the entropy changes are negative:

$$\Delta_r H^0_{\text{solid–gas}} \gg \Delta_r H^0_{\text{aq}} \approx 0 \qquad (12)$$

$$\Delta_r S^0_{\text{aq}} > 0; \quad \Delta_r S^0_{\text{solid–gas}} < 0 \qquad (13)$$

The values of $\Delta_r H^0_{\text{solid–gas}}$ and $\Delta_r S^0_{\text{solid–gas}}$ increase with the number of methylene groups in the alkyl chains of the amines (Table 4). Stability constants are comparable with the corresponding data in aqueous solution due to enthalpy–entropy compensation (Fig. 3). In the scope of the suggested assumptions (Eqs. (9)–(11)), the interactions between β-cyclodextrin and amines “without water” seems to be more strong although not favorable in terms of the entropy changes.

Table 3
Enthalpies of solution and free energies of solution of amines, solubilities (*S*) and free energies of solution of the complexes in water at 298.15 K

Amine	$-\Delta H^0_{\text{s}}(\text{amine})$[a] (kJ mol^{-1})	$\Delta G^{(x)}_{\text{s}}(\text{amine})$[a] (kJ mol^{-1})	*S*(complex) (g l^{-1})	$\Delta G^{(x)}_{\text{s}}(\text{complex})$[b] (kJ mol^{-1})
n-Propylamine	55.9 ± 0.08	−0.55 ± 0.04	19.7 ± 0.5	21.1 ± 0.1
n-Butylamine	59.0 ± 0.06	−0.12 ± 0.04	19.1 ± 0.6	21.2 ± 0.1
n-Pentylamine	62.1 ± 0.06	0.72 ± 0.04	20.5 ± 2.3	21.1 ± 0.4
n-Hexylamine	65.8 ± 0.06	0.98 ± 0.04	30.5 ± 1.7	19.7 ± 0.1
Hexamethylenimine	68.3 ± 0.05	7.31 ± 0.05	25.4 ± 2.6	20.2 ± 0.3
Dipropylamine	72.2 ± 0.10	2.60 ± 0.04	–	20.1[c]
Dibutylamine	79.0 ± 0.22	4.33 ± 0.04	–	20.1[c]
Triethylamine	70.1 ± 0.16	5.15 ± 0.04	–	20.1[c]

[a] Ref. [24].

[b] Corrected for dissociation of β-cyclodextrin–amine complexes using the data given in Table 1.

[c] $\Delta G^{(x)}_{\text{s}}(\text{complex}) = \Delta G^{(x)}_{\text{s}}(\beta\text{-CD})$.

Table 4
Thermodynamics of complexation of amines by β-cyclodextrin at the gas–solid conditions at 298.15 K

Amine	$\log K^{(x)}_{\text{solid–gas}}$ [a]	$\log K^{(x)}_{\text{solid–gas}}$ [b]	$-\Delta_r H^0_{\text{solid–gas}}$ [c] (kJ mol^{-1})	$298.15\Delta_r S^{(x)}_{\text{solid–gas}}$ (kJ mol^{-1})
n-Propylamine	4.6 ± 0.1	4.4 ± 0.1	57.5 ± 0.1	−32.6 ± 0.7
n-Butylamine	4.5 ± 0.1	4.3 ± 0.1	60.6 ± 0.2	−35.8 ± 0.8
n-Pentylamine	4.3 ± 0.2	4.2 ± 0.1	63.7 ± 0.2	−39.6 ± 0.8
n-Hexylamine	4.4 ± 0.1	4.5 ± 0.1	67.0 ± 0.2	−41.6 ± 0.8
Hexamethylenimine	3.4 ± 0.1	3.4 ± 0.05	70.0 ± 0.1	−50.7 ± 0.3
Dipropylamine	–	4.3 ± 0.1	73.7 ± 0.1	−49.2 ± 0.7
Dibutylamine	–	3.4 ± 0.02	80.1 ± 0.3	−60.9 ± 0.4
Triethylamine	–	3.5 ± 0.07	72.5 ± 0.5	−52.7 ± 0.9

[a] Calculated by Eq. (7).
[b] Calculated by Eq. (10).
[c] Calculated by Eq. (11).

A more detailed description is obtained from the analysis of electrostatic and covalent contributions to thermodynamic parameters of transfer for complexation reactions [23,27]. Electrostatic and covalent contributions to transfer enthalpy from the solid–gas conditions ($\varepsilon_{\text{gas}} = 1$) to aqueous solution ($\Delta_{\text{tr}} H^0_{\text{r}} = \Delta H^0_{\text{w}} - \Delta H^0_{\text{solid–gas}}$) can be estimated according to Eqs. (14) and (15) [27]:

$$\Delta_{\text{tr}} H^0_{\text{r,el}}(\text{solid–gas} \to W) = \Delta H^0_{\text{solid–gas}} \left(\frac{\varepsilon_{\text{gas}}}{\varepsilon_{\text{w}}} - 1 \right) \qquad (14)$$

$$\Delta_{\text{tr}} H^0_{\text{r},cov} = \Delta_{\text{tr}} H^0_{\text{r}} - \Delta_{\text{tr}} H^0_{\text{r,el}} \qquad (15)$$

These values for complexation of amines by β-cyclodextrin are presented in Table 5. In all cases the electrostatic contributions are unfavorable (positive) and increase with the number of methylene groups in the alkyl chains of the amines. Covalent contributions are negligible. Probably, any specific solute–solvent interactions are not essential. Water in this special case displays itself only as a medium for electrostatic interactions.

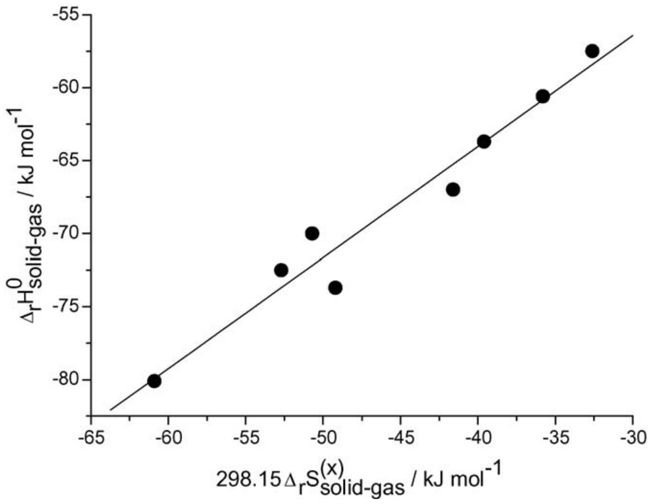


Fig. 3. Enthalpy–entropy compensation for complexation reactions of solid β-cyclodextrin with gaseous amines at 298.15 K.

Table 5
Transfer enthalpies from gas–solid conditions to water at 298.15 K for the complexation of amines by β-cyclodextrin and the corresponding electrostatic, $\Delta_{\text{tr}} H^0_{\text{r,el}}$, and covalent, $\Delta_{\text{tr}} H^0_{\text{r,cov}}$, contributions

Amine	$\Delta_{\text{tr}} H^0_{\text{r}}$(solid–gas → W) (kJ mol^{-1})	$\Delta_{\text{tr}} H^0_{\text{r,el}}$ (kJ mol^{-1})	$\Delta_{\text{tr}} H^0_{\text{r,cov}}$ (kJ mol^{-1})
n-Propylamine	55.9 ± 0.2	56.8 ± 0.1	−0.9 ± 0.3
n-Butylamine	59.1 ± 0.4	59.8 ± 0.2	−0.7 ± 0.6
n-Pentylamine	62.1 ± 0.4	62.9 ± 0.2	−0.8 ± 0.6
n-Hexylamine	65.8 ± 0.3	66.1 ± 0.2	−0.3 ± 0.5
Hexamethylenimine	68.3 ± 0.2	69.1 ± 0.1	−0.8 ± 0.3
Dipropylamine	72.2 ± 0.1	72.7 ± 0.1	−0.5 ± 0.2
Dibutylamine	79.0 ± 0.4	79.1 ± 0.3	−0.1 ± 0.7
Triethylamine	70.1 ± 0.9	71.6 ± 0.5	−1.5 ± 1.4

4. Conclusions

A quantitative approach has been described to determination of thermodynamic parameters of reactions between a solid host and gaseous guests. The Gibbs free energy, enthalpy and entropy of complexation reactions of several gaseous amines with solid β-cyclodextrin have been determined using corresponding data obtained in aqueous solution. It has been shown that solution energy of the inclusion complexes in water is nearly identical with that of β-cyclodextrin. This assumption can be used to estimate the stability of "solid–gas" complexes of β-cyclodextrin when the stability constants in aqueous solution and the Gibbs free energy of solution of the guests are known. Studies related to complexation thermodynamics of other macrocycles with different gaseous organic and inorganic substances are underway.

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