

Thermodynamic Interaction Parameters of *Tetra-n-undecylcalix[4]resorcinarenes* with Selected Solvents Studied by Inverse Gas Chromatography

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Abstract

The basic thermodynamic parameters, characterising intermolecular interactions of tetra-*n*-undecylcalix[4]resorcinarene and its octaacetate derivative with simple organic solutes, were calculated by using the inverse gas chromatography method. Free energy, enthalpy and entropy of sorption were determined.

Introduction

Calixarenes and calixresorcinarenes, the cyclic oligomers, are the products of basic or acidic condensation of aldehydes with *p*-substituted phenols or resorcinol, respectively [1–3]. This class of compounds is capable of selective interaction with inorganic and organic cations and anions, as well as neutral organic species. They found many practical applications: as chemical sensors [3, 4], selective carriers in liquid membranes [5, 6] and stationary phases for gas [7–10] or liquid (high performance) chromatography [11–20]. Resorcinarenes form solvates with many solvents [21, 22]. The crystallographic data demonstrate that in the complexation process not only van der Waals interactions are involved, but hydrogen bonds as well [23, 24].

Inverse gas chromatography (IGC) is a convenient tool for studies of specific interactions between stationary phases and solvents [25–26]. IGC allows for the assessment of the selectivity of the compounds studied as stationary phases for gas and HPLC [27–29].

The IGC experiments are similar to routine gas chromatography as far as instrumentation and methodology is concerned. The difference consists of the use of the studied compounds as stationary phases and the application of selected, well-known solutes. The accurate temperature measurements as well as precise flow regulation of the mobile phase in the chromatograph enables the exact evaluation of retention values needed for the calculations of the thermodynamic parameters associated with intermolecular interactions of the polymer studied with representative group of organic compounds.

In this work we studied tetra-*n*-undecylcalix[4]resorcinarene and its octaacetate derivative (Figure 1).

The aim of these studies was the estimation of standard thermodynamic parameters: free energies, enthalpies and entropies of sorption of the calixresorcinarenes with simple organic compounds bearing various functional groups.

Experimental

Synthesis

Tetra-n-undecylcalix[4]resorcinarene (1)

The title calix[4]resorcinarene was prepared by the condensation of the dodecyl aldehyde with resorcinol according to Aoyama procedure [30]. Yield 72% after crystallisation from acetone–hexane 1:1 v/v, and drying at 100 °C for 12 h under reduced pressure (0.1 Torr). Mp: 270 °C.

ESI/MS (chloroform, MeOH): M⁺ + H–1104.

Tetra-n-undecylcalix[4]resorcinarene octaacetate (2)

Calix[4]resorcinarene (**1**) (0.2 g) was dissolved in 25 cm³ of acetic anhydride and three drops of BF₃ were added. The reaction mixture was refluxed for 15 min. The mixture was cooled to room temperature and methanol was added to remove acetic anhydride. Yellow solid was obtained and crystallised from acetic acid. Yield: 65%. Mp: 126–128 °C.

¹H-NMR Hitachi 60 MHz, CDCl₃, TMS, δ (ppm): 6.9–7.2 (m, 2, Ar–H), 4.2 (t, 1, Ar–CH–Ar), 2.16 (s, 6, ArO(CO)CH₃), 0.8–1.6 (m, 23, –(CH₂)₁₀CH₃).

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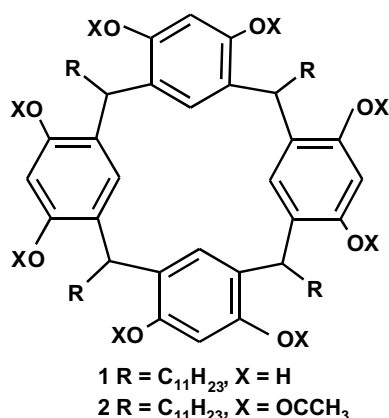


Figure 1. Chemical structure of studied compounds.

Differential scanning calorimetry (DSC) measurements

The DSC test was performed on Du Pont Instruments differential scanning calorimeter. The operating temperature was from 25 to 300 °C.

IGC experiments

The investigated calixresorcinarenes were coated on chromatographic support Chromosorb G (silanized, specific surface 0.5 m²/g; 6 g), 80/100 mesh (John–Manville) (10% w/w). The samples of resorcinarenes were dissolved in methylene chloride and solid support was added. The solvent was removed by slow evaporation during gentle stirring. The glass chromatographic column was 1.8 m in length and 3 mm internal diameter.

The Perkin–Elmer (Norwalk, CT, U.S.A.) gas chromatograph, model 900, with flame ionisation detector was used. The flow rate of the carrier gas was 25 cm³/min. Measurements were carried out in isothermal conditions at 80, 100, 120, 140 and 160 °C. The following solvents were used as the test solutes: *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methylpropanol-2, 2-methylpropanol-1, 2-butanol, acetone, ethyl acetate, ethyl ether, methylene chloride, chloroform (p.a.) from POCh – (Gliwice, Poland); *n*-decane, *n*-undecane, nitromethane (p.a), acetonitrile, pyridine (r.g.) from Reachim (Moscow, Russia).

Calculations

Specific retention volume (V_g) of solutes was calculated from experiment using the following equation [25, 26]:

$$V_g = F t_r j 273.2 / T_0 w, \quad (1)$$

where F is carrier flow rate measured at room temperature T_0 (K), t_r adjusted retention time of the solute, j is pressure correction factor, w is mass of stationary phase in the column.

All thermodynamic parameters were calculated from known expressions [25–29, 31]. Partial molar enthalpy of sorption:

$$\Delta H_s = -R[\partial V_g / \partial (1/T)], \quad (2)$$

where R is gas constant, T is column temperature (K).

Partial molar free energy of sorption:

$$\Delta G_s = -RT \ln(M_1 V_g / 273.2R) \quad (3)$$

M_1 is molecular mass of the solute.

Results and discussion

The calix[4]resorcinarenes are stable compounds in a wide range of the temperature. Figure 2 presents DSC curve for tetra-*n*-undecylcalix[4]resorcinarene. At the beginning of the curve we observed thermal effect related to the loss of solvents from which the compound was crystallised. The first effect is related to the loss of acetone (4%), the second is connected with the loss of dimethylformamide (5%) [21]. The decomposition of resorcinarene was observed above 270 °C, the stationary phases were thermally stable in the experimental conditions.

Taking into account the support surface (6 g, 2.98×10^{18} nm), surface per molecule for calix[4]resorcinarene (~ 2 nm²) from LB measurements [32], amount of the resorcinarene molecules forming the phase (3.3×10^{20}) it can be estimated that more than 200 layers were formed. The thickness of the stationary phase was evaluated as 0.3–0.4 μm, taking into account the dimensions of the unit cell (1.2–3 nm, Figure 3) from crystallographic studies [24].

Calixresorcinarene forms solvate crystals during gentle evaporation of solvent, and further heating causes loss of the solvent from crystal lattice.

Packing of solvated molecules of calixresorcinarene 1 with dimethylformamide in the crystal lattice is presented in Figure 3.

Self-organization of lipophilic tetra-*n*-undecylcalix[4]resorcinarenes involves hydrogen bonds between hydroxyl groups and van der Waals forces between long aliphatic tails. This interplay provides highly ordered

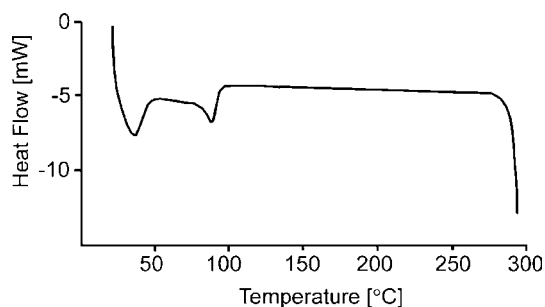


Figure 2. DSC curve of tetra-*n*-undecylcalix[4]resorcinarene.

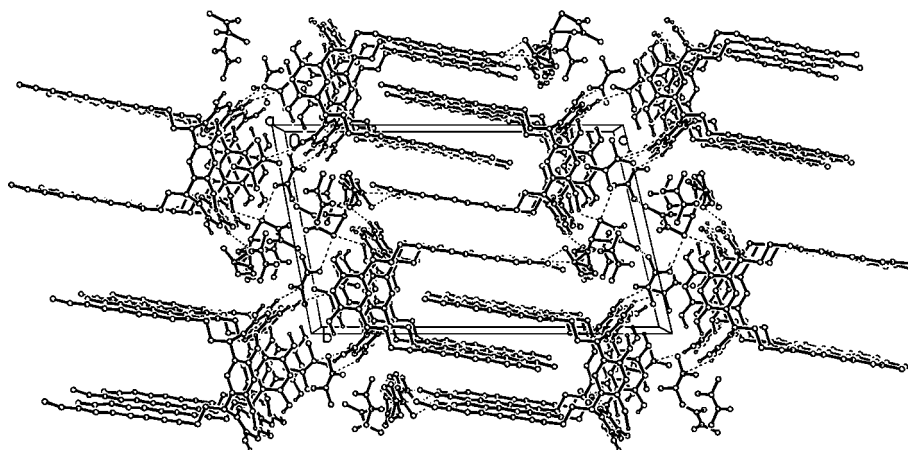


Figure 3. Packing of dimethylformamide solvate with **1** molecules in crystal lattice (hydrogen atoms are omitted).

lamellar layers in the solid state. The vacancies are formed between dimers. This porous structure enables easy solvent penetration not only within polar sites between layers but also between lipophilic vacancies formed by aliphatic chains. Easy sorption and desorption phenomena of solvents displayed by calixresorcinarenes have been used in sensors for vapours [33–35].

Partial molar free energy, enthalpy and entropy of sorption

The calculated values of ΔG , ΔH and ΔS of sorption of calixresorcinarenes with various solutes are collected in Tables 1 and 2. The parameter values related to the sorption function are similar for both tetramers. It is

worth to note that value of free energy of sorption pyridine is particularly very low.

It seems that porous structure of the calixresorcinarene **1** in the solid state favours the interpenetration of the aliphatic hydrocarbons within the network of long undecyl chains via van der Waals interactions. The nature of the octaacetate **2** is not known, but no doubt will not be the same as in case of **1** because of the lack of structuring effect of hydrogen bonding network. The possible explanation is that the acetylated form of calixresorcinarene (**2**) no longer can form hydrogen bonds like the parent compound. The calixresorcinarene **1** displays the highest affinity to acetone, nitromethane, 1-propanol and its octaacetate derivative to acetone, methanol and ethyl ether.

Table 1. Values of specific retention volume, thermodynamic function of sorption for solutes at 120 °C on undecylcalix[4]resorcinarene

Solute	V_g (cm ³ /g)	ΔG_s (kJ/mol)	ΔH_s (kJ/mol)	ΔS_s (kJ/mol K)
Hexane	1.9	16.08	-35.11	-0.130
Heptane	4.8	12.56	-37.78	-0.128
Octane	10.5	9.57	-40.40	-0.127
Nonane	20.3	7.04	-44.22	-0.130
Decane	39.3	4.54	-48.35	-0.135
Undecane	71.9	2.26	-52.05	-0.138
Methanol	0.8	22.14	-25.19	-0.120
Ethanol	1.5	18.90	-36.38	-0.141
1-Propanol	3.7	15.08	-46.36	-0.156
2-Propanol	1.6	17.82	-46.48	-0.166
1-Butanol	8.1	11.83	-42.96	-0.139
2-Methyl-1-propanol	5.5	13.10	-42.41	-0.141
2-Butanol	3.4	14.67	-43.62	-0.148
2-Methyl-2-propanol	2.1	16.25	-44.12	-0.154
Acetone	1.5	18.14	-43.52	-0.157
Ethyl acetate	2.5	15.11	-30.78	-0.117
Ethyl ether	0.9	19.01	-31.04	-0.127
Methylene chloride	1.1	17.91	-21.57	-0.100
Chloroform	2.9	13.63	-27.86	-0.106
Nitromethane	1.3	18.45	-43.17	-0.157
Acetonitrile	1.3	19.74	-32.02	-0.132
Pyridine	28.4	7.52	-28.45	-0.091

Table 2. Values of specific retention volume, thermodynamic function of sorption for solutes at 120 °C on undecylcalix[4]resorcinarene acetate

Solute	V_g cm ³ /g	ΔG_s kJ/mol	ΔH_s kJ/mol	ΔS_s kJ/mol K
Hexane	5.2	12.79	-19.85	-0.083
Heptane	12.4	9.44	-25.88	-0.090
Octane	25.5	6.67	-25.43	-0.082
Nonane	49.3	4.13	-29.36	-0.085
Decane	92.9	1.72	-29.80	-0.080
Undecane	178.9	-0.72	-29.03	-0.072
Methanol	1.3	20.48	-31.46	-0.132
Ethanol	2.1	16.45	-24.55	-0.108
1-Propanol	5.6	12.43	-22.30	-0.092
2-Propanol	2.5	13.03	-26.66	-0.109
1-Butanol	16.1	8.88	-12.70	-0.057
2-Methyl-1-propanol	11.4	9.64	-12.66	-0.059
2-Butanol	7.4	10.78	-13.05	-0.064
2-Methyl-2-propanol	3.3	13.25	-20.02	-0.088
Acetone	2.0	14.08	-31.91	-0.125
Ethyl acetate	6.0	10.91	-16.69	-0.074
Ethyl ether	1.7	15.58	-28.51	-0.116
Methylene chloride	3.9	12.00	-19.05	-0.084
Chloroform	10.5	8.22	-16.46	-0.066
Nitromethane	14.3	9.85	-12.78	-0.059
Acetonitrile	7.5	12.59	-15.05	-0.074
Pyridine	33.7	6.06	-17.53	-0.062

Presented data indicate that the quite strong interaction occurred between calixresorcinarenes and the hydrocarbons. The interaction parameter decreases from hexane to nonane. It means that longer the hydrocarbon chain, the interaction became stronger. This can be explained as hydrophobic interaction between hydrocarbons and chains connected to lower rim of calixresorcinarenes. Stronger interactions are observed for more lipophilic calixresorcinarene **2**. Rather strong interactions are observed also between calixresorcinarenes and chloroform or pyridine. Pyridine forms molecular complexes with calixresorcinarenes and their stoichiometry and crystallographic structure have been published [36, 37].

It can be rationalised in terms of calixresorcinarene orientation in stationary phase: the calix may be perpendicular or horizontal to the bed surface. The first orientation is conceivable, since the support has basic properties (pH 8.5), so the phenolic groups, slightly acidic, will have an affinity to basic surface. If the first orientation takes place we should observe lower values of interaction parameter for alcohols and higher for hydrocarbons. The second orientation is more probable, where the long hydrocarbon chains are better accessible and hydroxyl groups are engaged in association process (see Figure 3).

Conclusions

The results indicate that thermodynamic functions of sorption of simple solutes with *n*-undecylcalix[4]resor-

cinarene (**1**) differ reasonably from analogous data for its octaacetate (**2**). Tetramer (**2**) revealed lower electron affinity for majority of the solutes studied.

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