THERMAL ANALYSIS OF CALIX[4]RESORCINARENE COMPLEXES WITH SECONDARY AND TERTIARY AMINES[*]

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Abstract

Tetra-*n*-undecylcalix[4]resorcinarene forms solid adducts with secondary and tertiary amines. Thermal decomposition of these complexes was investigated by means of thermogravimetry (TG) and differential scanning calorimetry (DSC). It was found that deamination of complexes occurs as multi-step process. The stoichiometry of complexes was evaluated on the basis of TG studies and total heats of deamination were calculated from DSC measurements.

Keywords: amine, calix[4]resorcinarene, complexes, DSC, TG

Introduction

Calixresorcinarenes still attract great attention due to their multimode complexation properties. There are numerous monographs describing their synthesis, conformational dynamics, complexation abilities, thermodynamics, solid-state structures, industrial applications, and many other features [1–7]. They can serve as carriers for ion or neutral molecules in transport across liquid membranes, sensors for cations, anions and neutral species in liquid membrane electrodes [4, 6, 7], sensors for vapours of organic solvents [8–10], stationary phases for gas and liquid (high performance) chromatography [11, 12]. Their complexation and recognition abilities were investigated preferably in solutions.

Iwanek *et al.* found that tetra-methylcalix[4]resorcinarene forms complexes with primary and secondary amines with stoichiometry 1:2 or 1:4, depending on the concentration of amines in acetonitrile solutions [13, 14]. He also observed that secondary aliphatic amines formed solid adducts with methylresorcinarene in ethanol. Their stoichiometry was calculated as 1:2 on the basis of ^{1}H NMR spectra [13]. It was interesting to study stoichiometry and thermal stability of complexes of this type with lipophilic

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calix[4]resorcinarene, as they had practical applications mentioned above. We have demonstrated previously that liphophilic tetra-*n*-undecylcalix[4]resorcinarene (C11) forms crystalline solvates with a range of organic solvents. The composition and thermal stability was followed by thermogravimetric method [15]. Also the crystal structures of dioxane, dimethylformamide (DMF), and dimethylacetamide (DMA) solvates have been solved [16–18]. XRD (single crystal diffraction) analysis indicates following ligand:solvent stoichometries: dioxan 1:4, DMF 1:6, and DMA 1:5. On the other hand, TG experiments showed respectivelly stoichiometries as 1:3, 1:3 and 1:4. This discrepancy can be explained as follows: crystals for XRD measurements were immediately sealed, once picked out from solution, whereas materials for TG were dried on open air. Figure 1 presents X-ray structure of lipophilic calix[4]resorcinarene solvate with dioxane.
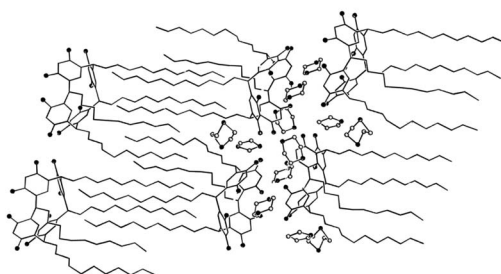

Fig. 1 X-ray structure of tetra-*n*-undecylcalix[4]resorcinarene solvate with dioxane. The hydrogen atoms are omitted for clarity. Black circles denoted oxygen atoms

Lipophilic calixresorcinarene forms molecular dimers in solid-state, in such way that four long aliphatic chains form cavity which accommodates chains of the other molecule. Van der Waals forces between long aliphatic tails provides highly ordered lamellar layers in the solid-state with interpenetrating alkyl chains and macrocyclic resorcinol units linked by hydrogen bond. The first stage of decomposition dioxane solvate can be associated with a loss of molecules placed in lipophilic parts of the crystal lattice. Inside polar parts, the host-guest interactions are stronger due to hydrogen bonding. Thus, these bonds are broken at higher temperature [15]. Thermal analysis is frequently used in the studies of molecular inclusion complexes together with structure studies [19, 20].

The aim of this work was to study solid complexes of tetra-*n*-undecylcalix[4] resorcinarene with selected secondary and tertiary amines (Fig. 2), obtained from dioxane solutions by crystallization. In particular, we were interested in the stoichiometry of these complexes and in the dynamics of their decomposition.

Experimental

Synthesis of complexes with amines

All reagents (analytical grade) were obtained from Fluka or Aldrich. The tetra-*n*-undecylcalix[4]resorcinarene was obtained by method of Aoyama [21] and

dried at 100°C. The solids of complexes were prepared according to method from [13] using dioxane as solvent. Calixresorcinarene was dissolved in boiling dioxane, and amine was added in 1:4 ratio. The precipitate was collected after slow cooling, then washed with cold dioxane. Complexes were dried at room temperature on air for one day, allowing weakly bounded solvent to evaporate.
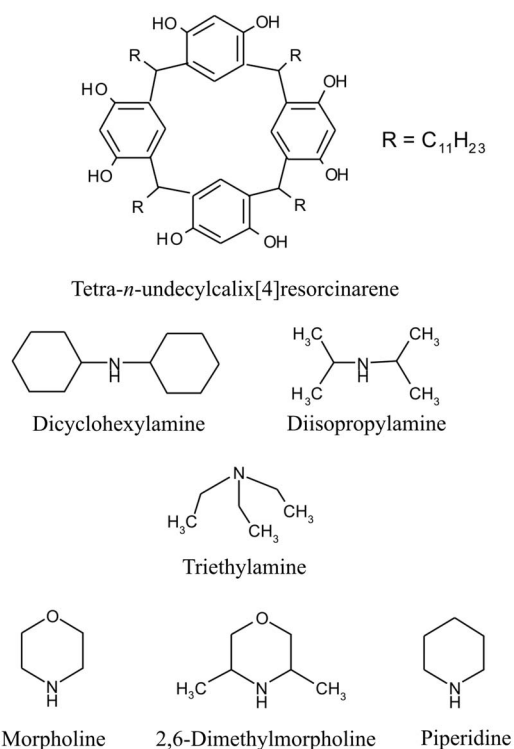

R = $C_{11}H_{23}$

Tetra-*n*-undecylcalix[4]resorcinarene

Dicyclohexylamine

Diisopropylamine

Triethylamine

Morpholine

2,6-Dimethylmorpholine

Piperidine

Fig. 2 Structures of host and guest molecules

TG and DSC measurements

Measurements were carried out using the DuPont Thermal Analyst 2100 equipped with TGA 951 and DSC 910 modules. Runs were performed at a scan rate of 10 K min^{-1} in atmosphere of argon in range of temperatures 295–550 K, below the melting point of tetra-*n*-undecylcalix[4]resorcinarene and its complexes with amines. Experimental details were as published earlier [15, 22].

Results and discussion

Figure 3 presents the most characteristic examples of TG, DTG and DSC curves for triethylamine, morpholine and 2,6-dimethylmorpholine.
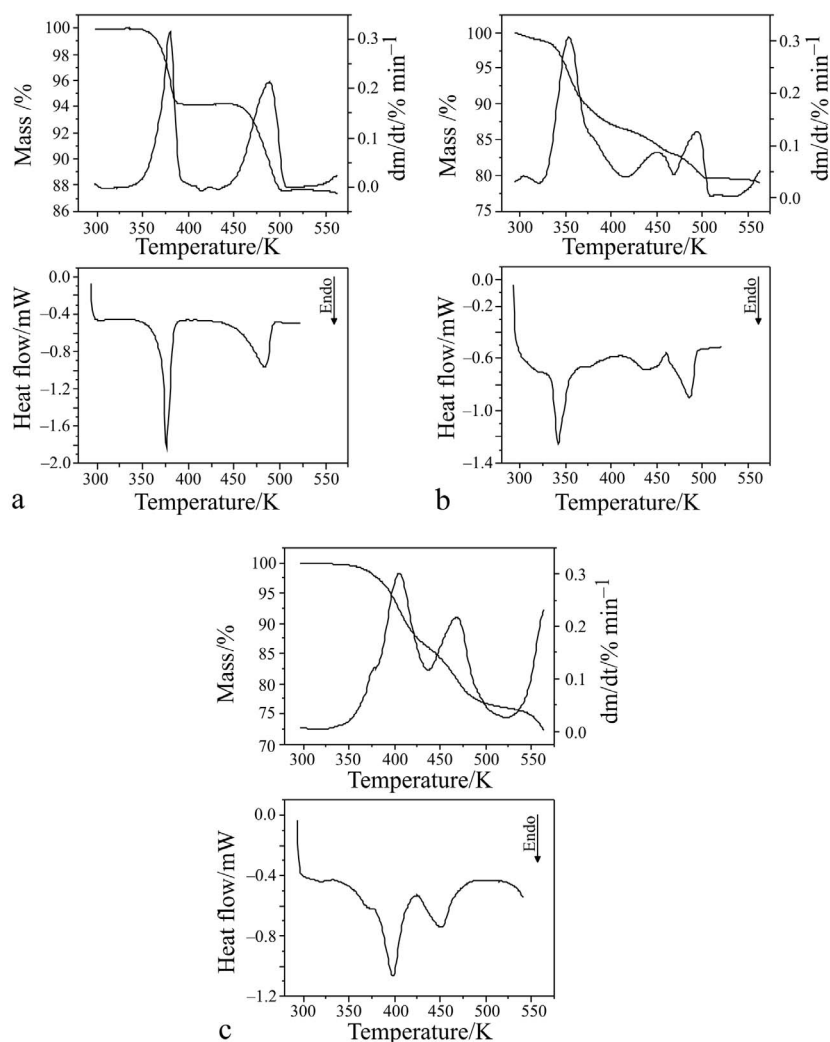
Fig. 3 TG, DTG (upper) and DSC (lower) curves of decomposition
calix[4]resorcinarene complexes with: a – triethylamine, b – morpholine,
c – 2,6-dimethylmorpholine

The shape of all curves indicates that the decomposition process of calix[4]resorcinarene complexes is complicated. In the case of triethylamine (Fig. 3a) this process occurred in two well-separated steps. In contrast, the profile of thermoanalytical curve of the calix[4]resorcinarene complexes with morpholine and dimethylmorpholine is quite different and three partially overlapping steps can be observed (Fig. 3b, c). In the case of dimethylmorpholine, two first steps overlap, forming one broad peak with inflection at 375 K, only slightly marked on DTG and

DSC curves (Fig. 3c). It is worthy to note the different dynamics of decomposition of these two morpholine complexes.

The decomposition data for calix[4]resorcinarene complexes with amines and dioxane (for comparison) are presented in Table 1.

The molar ratio of host/guest complexes was evaluated on the basis of DTG results. Partial overlapping of the peaks is probably due to complex deamination kinetics, as well as may originate from the specificity of the measurement methodology. In the calculated data this phenomenon has resulted in non-integral stoichiometry. Nevertheless, the total stoichiometry, i.e. the global number of amine molecules bonded by calixresorcinarene is always an integer quantity. This total stoichiometry of complexes was in agreement with calculated from ^{1}H NMR [13].

The lipophilic calix[4]resorcinarene forms 1:2 complexes with secondary and tertiary amines in majority of cases. The only exceptions are morpholines, which form complexes of stoichiometry 1:3. The host molecules can interact with morpholines not only with nitrogen atom, but also the oxygen atom is able to form another hydrogen bond as well to hydroxyl groups of resorcinol unit. So, the third molecule of morpholine can be accommodated in the crystal lattice.

As mentioned above, the measurements were conducted in the temperature range below the melting point of the calix[4]resorcinarene complexes. Good complementarity of the DSC and DTG peaks allows to assign the mass losses (DTG) to heat effects (DSC) determined in the particular temperature range.

Deamination process as well as desolvatation is accompanied by endothermic heat effect. Total heats of decomposition of amine complexes are always greater than this of dioxane solvate decomposition. This indicates that the amines form stronger complexes than dioxane. Thus, in the competition of amine and solvent molecules during crystallisation, the amine bonding has a priority. The DSC and DTG peaks associated with the loss of dioxane from the solvate with calix[4]resorcinarene at low temperatures (ca. 328 K) have been observed sporadically, probably as the remnant of the fourth molecule present in the dioxane solvate crystal, and released spontaneously, while dried on open air at room temperature. These observations allow us to assign very small mass losses of the complexes at low temperatures due to release of dioxane molecules. For example, the mass loss of 1.1%, during decomposition complex with diisopropylamine (Table 1), we ascribed to dioxan. Also, the small mass loss (0.5%), in the range of temperature 312–325 K, can be interpreted as solvent release in the case of complex decomposition with morpholine (Fig. 3b).

In case of diisopropylamine and triethylamine an interesting phenomenon occurs: the first deamination step is associated with higher thermal effect than that in the second deamination step. It might be that two phenomena are superimposed in this case: deamination and crystal lattice rearrangement. The explanation of this feature calls for further research. This crystal lattice reorganization has been observed in case of some calixarene and calix[4]resorcinarene solvates [23, 24].

Calixresorcinarenes, as weak phenolic acids, can form molecular associates with basic compound, such as nitrogen-containing heterocycles and amines. Although the crystal structure of amine complexes with lipophilic calix[4]resorcinarene

Table 1 Data of thermal decomposition of tetra-*n*-undecylcalixresorcinarene complexes

Guest	TG midpoint/K	DSC peak/K	Mass loss/%	Molar ratio C11:G*	Heat of desolv./deamin./J g^{-1}	Total heat of decomp./kJ mol^{-1}
1,4-dioxane	356	360	11.5	1:2	148.0	
	401	389	6.3	1:1	64.3	128.0
				1:3 total		
Dicyclohexylamine	441	433	9.6	1:0.8	9.9	
	498	477	15.2	1:1.2	40.4	260.8
				1:2 total	61.7	
Diisopropylamine	346	324	1.1	solvent	5.9	
	392	392	6.5	1:1	46.3	137.0
	492	498	6.5	1:1	40.9	
				1:2 total		
Triethylamine	380	376	5.87	1:1	88.9	
	489	484	6.63	1:1	78.1	255.7
				1:2 total		
Morpholine	342	342	12.6	1:2	127.7	
	440	439	3.6	1:0.5	19.8	234.3
	486	486	3.5	1:0.5	39.4	
				1:3 total		
2,6-Dimethylmorpholine	405	399	13.9	1:1.7	112.6	
	469	452	10.1	1:1.3	58.5	159.2
				1:3 total		
Piperidine	349	346	11.1	1:1.4	167.0	
	492	483	4.7	1:0.5	22.9	169.8
				1:2 total		

*C11 and G denotes tetra-*n*-undecylcalixresorcinarene and amine or dioxane respectively

is still unknown, one can suppose, by analogy with the solvate, that the amine molecules are hydrogen bonded with resorcinol units (Fig. 1). Stoichiometry of adducts suggests that four amines are accommodated between two calix[4]resorcinarene molecules. Two hydroxyl groups of each of host molecule are engaged in binding of two amine molecules. If this assumption is right, the partial overlapping of DSC and DTG peaks observed during deamination process can be explained, besides the possible reorganisation of the crystal lattice during thermolysis, in terms of disorder of amine molecules.

Conclusions

Calixresorcinarene forms complexes with amines with stoichiometry 1:2 in the solid-state. Higher stoichiometry (1:3) was observed for morpholines, due to the ability of oxygen atom to form hydrogen bond with host molecule.

The shapes of DTG and DSC curves have revealed multi-step process of deamination. Probably, the phenomenon of steps overlapping is associated with structural changes during deamination and partial disordering of amine molecules in polar channels in crystal lattice as well.

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References

1 C. D. Gutsche, Calixarenes, Monographs in Supramolecular Chemistry, Royal Soc. Chem., Cambridge 1989.

2 J. Vicens and V. Böhmer, Calixarenes: a Versatile Class of Macrocyclic Compounds, Kluwer, Academic Publishers, Dordrecht 1991.

3 J. Vicens, Z. Asfari and J. M. Harrowfield, Calixarenes: 50th Anniversary: Commemorative Volume, Kluwer Academic Publishers, Dordrecht 1994.

4 R. Pochini, Ungaro, ch. 4, 103 and Y. Aoyama, ch. 9, p 279 in Comprehensive Supramolecular Chemistry, Vol. 2 (Vol. Ed. F. Vögtle), Elsevier Sci. Ltd., Oxford 1996.

5 C. D. Gutsche, 1998, Calixarenes Revisited, Monographs in Supramolecular Chemistry, Royal Soc. Chem., Cambridge.

6 M. Pietraszkiewicz, O. Pietraszkiewicz and P. Prus, ch.11, p. 239, in Cyclophanes for 21th Century (Ed. H. Takemura), 2002, Research Signpost, Kerala.

7 K. Ocicka, H. Radecka, J. Radecki, M. Pietraszkiewicz and O. Pietraszkiewicz, Sens. Actuators B, 89 (2003) 217.

8 F. L. Dickert, U. P. A. Baumler and H. Stathopulos, Anal. Chem., 69 (1997) 1000.

9 F. L. Dickert, O. Hayden and E. Zenkel, Anal. Chem., 71 (1999) 1338.

10 Z. Cao, K. Murayama and K. Aoki, Anal. Chim. Acta, 448 (2001) 47.

11 O. Pietraszkiewicz and M. Pietraszkiewicz, J. Incl. Phenom. Macro., 35 (1999) 261.

12 H. Zhang, R. Dai, Y. Ling, Y. Wen, S. Zhang, R. Fu and J. Gu, J. Chromatogr. A, 787 (1997) 161.
13 W. Iwanek, R. Froehlich, M. Urbaniak, Ch. Naether and J. Mattay, Tetrahedron, 54 (1998) 14031.
14 W. Iwanek and M. Urbaniak, Tetrahedron, 57 (2001) 10377.
15 O. Pietraszkiewicz, E. Uzig, W. Zielenkiewicz and M. Pietraszkiewicz, J. Therm. Anal. Cal., 54 (1998) 249.
16 T. Borowiak, M. Mączynski, M. Pietraszkiewicz and O. Pietraszkiewicz, J. Incl. Phenom. Macro., 35 (1999) 131
17 M. Pietraszkiewicz, O. Pietraszkiewicz, W. Kolodziejski, K. Wozniak, N. Feeder, F. Benevelli and J. Klinowski, J. Phys. Chem. B, 104 (2000) 1921.
18 R. Kuzmicz, L. Dobrzycki, K. Wozniak, F. Benevelli, J. Klinowski and W. Kolodziejski, Phys. Chem. Chem. Phys., 4 (2002) 2387.
19 K. Mészáros–Szécsényi, V. M. Leovac, Ž. K. Jaćimović, V. I. Češljević, A. Kovács and G. Pokol, J. Therm. Anal. Cal., 66 (2001) 573.
20 J. Madarász, P. Bombicz, K. Jármi, M. Bán, G. Pokol and S. Gál, J. Therm. Anal. Cal., 69 (2002) 281.
21 Y. Aoyama, Y. Tanaka, H. Toi and H. Ogoshi, J. Am. Chem. Soc., 110 (1988) 634.
22 O. V. Kulikov, W. Zielenkiewicz and E. Utzig, Thermochim. Acta, 237 (1994) 333.
23 M. Perrin, F. Gharnati, D. Oehler, R. Perrin and S. Lecocq, J. Inclusion Phenom. Mol. Recognit. Chem., 14 (1992) 257.
24 J. L. Atwood, L. J. Barbour, A. Jerga and B. L. Schottel, Science, 298 (2002) 1000.