Effect of the size of calixarene macrocycle on the thermodynamic parameters of formation of inclusion compounds in guest vapor—solid host systems*

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The influence of the calixarene macrocycle size on the thermodynamic parameters of inclusion formation in organic guest vapor—solid host systems was studied in the series of *tert*-butylcalix[4]arene (**1**), *tert*-butylcalix[6]arene (**2**), and *tert*-butylcalix[8]arene (**3**). For this purpose, sorption isotherms of a guest vapor by a solid host were determined using the static method of headspace GC analysis for the systems involving calixarenes **2** and **3** in addition to the earlier obtained data for calixarene **1**. Besides, the stoichiometry and decomposition temperatures of saturated clathrates formed in these systems were determined using thermogravimetry. The compositions of some of these clathrates differ substantially from those of clathrates crystallized from a host solution in a liquid guest. For the most guests studied with the thermodynamic activity below 0.6, their uptake by calixarenes **1**—**3** changes in the series **2** < **1** < **3**. As a whole, the trend for each particular parameter of clathrates of hosts **1**—**3** (stoichiometry, guest activity at 50% saturation of the host) with increasing the size of the calixarene macrocycle is specific for each guest studied. The results obtained are useful for the estimation of receptor properties of calixarenes in quartz microbalance sensors.

Key words: guest—host inclusion compounds, clathrates, thermogravimetry, headspace GC analysis, sorption isotherms.

tert-Butylcalix[n]arenes and their derivatives belong to one of the main types of receptors in supramolecular chemistry.[1,2] The presence of a cyclic intramolecular H bond imparts a relatively rigid nonplanar conformation to their molecules, and the initial members of the series (n = 4—6) gain a "cone" conformation, which provides their ability to form clathrates with neutral organic compounds.[1,3] This property of calixarenes is used, for instance, to determine the concentration of organic compounds in air and in water using piezoelectric sensors of the quartz microbalance type.[4—7] The aimed use of solid calixarenes requires to know the structure—property relationships for inclusion compounds involving calixarenes. The macrocycle size is considered to be an important structural parameter of calixarenes, determining, to a great extent, their receptor properties. This is concluded from the analysis of the data on binding organic compounds by thin layers of calixarenes in piezoelectric sensors.[4—7] The influence of the calixarene structure on the properties of their clathrates is also often evaluated from the X-ray diffraction[1] and thermogravimetric data.[8,9]

At the same time, it is problematic to compare an information on the thermodynamic parameters of clathrates obtained for the same guest—host pairs under different conditions, including different preparation history of a host without a guest and different methods of clathrate preparation. This problem is caused by the phase transition as a result of the interaction of a guest vapor with a solid host.[10,11] Clathrate formation in these systems is characterized by a binding threshold of a guest compound depending on its thermodynamic activity.[11—14] Below this threshold, the host does not virtually sorb the guest, whereas above the threshold the uptake increases rapidly in a narrow interval of the guest activity to a level corresponding to the formation of a stoichiometric inclusion compound.[11—14] The high cooperativity of intermolecular interactions in the solid phase of clathrates is a reason for a high sensitivity of the clathrate formation process to external factors. The cooperative influence of the third component[3] and temperature[15] on the stoichiometry of

clathrate formation was observed, as well as the cooperative influence of the third component on the binding threshold of the guest vapor by the solid host.[13] The packing of host molecules without a guest in the solid phase can depend on the conditions of preparation.[10,15] These


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effects can be a reason for the absence of a binding threshold by the concentration or thermodynamic activity of the substances analyzed when using calixarenes in quartz microbalance sensors,[4,5] which can be resulted from the preparation conditions of the host thin layer on the sensor surface.

In this work, we report the results of studying the influence of the macrocycle size of *tert*-butylcalix[n]arenes on the thermodynamic parameters of binding the vapors of organic compounds by the host powder under standard conditions in the absence of secondary cooperative effects. The structure—property relationship is analyzed for *tert*-butylcalix[4]arene (**1**), *tert*-butylcalix[6]arene (**2**), and *tert*-butylcalix[8]arene (**3**), as well as for several guests: benzene, toluene, carbon tetrachloride, which cannot form strong hydrogen bonds, and chloroform, which possesses a proton-donor ability. The data on the guest thermodynamic activity for 50% saturation of the host stoichiometry obtained in this study for calixarenes **2** and **3** are compared with the data obtained earlier[12,13] under the same conditions for calixarene **1** and with the X-ray diffraction data (see Refs. 8, 16, and 17) on the stoichiometry of clathrates crystallized from a host solution in the liquid guest for some guest—host pairs studied. In addition, the "structure—property" relationships observed are compared with the data[4−6] for binding the guest vapor by thin layers of calixarenes **1**—**3** in quartz microbalance sensors.

Experimental

tert-Butylcalix[6]arene (**2**) and *tert*-butylcalix[8]arene (**3**) were synthesized as described in Refs. 18 and 19, respectively. Involatile impurities were removed by multiple recrystallization, and volatile impurities were removed by heating *in vacuo* (100 Pa) at 150 °C (calixarene **2**) and 130 °C (calixarene **3**) for 8 h. The absence of changing the white color of the calixarene powder on heating served as a criterion for complete purification of the host from involatile organic impurities. The absence of volatile impurities was checked by headspace GC analysis: methanol (3—5 mol.%) was added to a sample of the purified host, and the vapor phase was analyzed after equilibration in a hermetically closed ampule for 24 h. The content of the main host, estimated by TLC, was at least 99% in each case. The guests were purified directly before measuring by a standard procedure.[20] According to the results of GLC analysis, the content of the main substance in the guests was at least 99.5%.

To determine the sorption isotherms, equal portions (0.0700 g) of purified samples of the host with different amounts of the guests under study were stored for 72 h at 298 K in 15-mL ampules hermetically closed with gaskets of polytetrafluoroethylene film (0.2 mm thick) and silicone rubber. The study of the binding kinetics showed that the equilibrium distribution of the guest between the vaporous and solid phases in the systems under study is achieved mainly within the first 24 h. The liquid guest was sampled into small open glass ampules placed inside ampules containing the host to provide the host saturation with
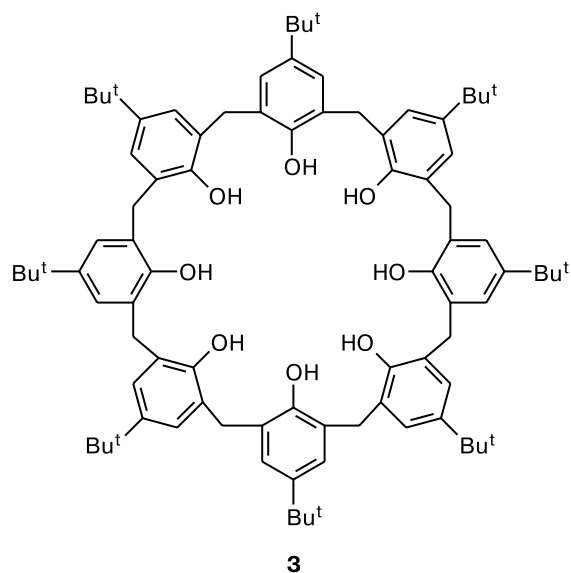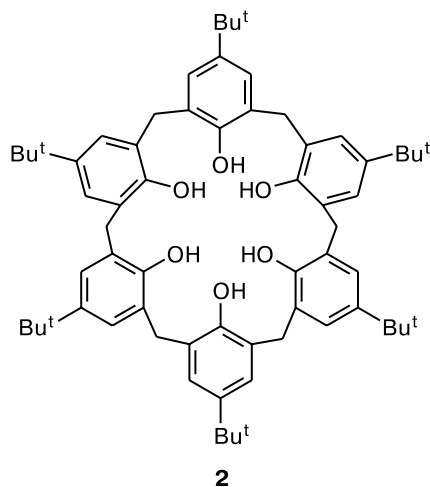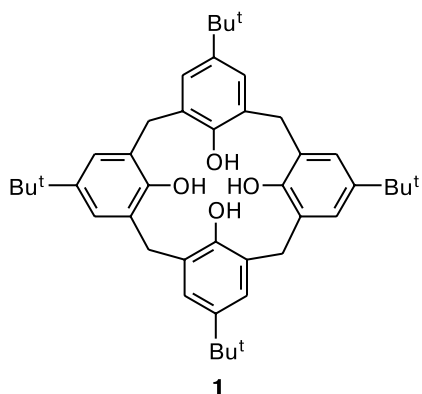
the guest from the vaporous phase only. The presence of the non-evaporated liquid guest after equilibration was monitored visually.

The thermodynamic activity of the guest was determined as its partial vapor pressure in the system (P/P_0) under approximation that the vapor of the guests is an ideal gas under the experimental conditions. This value was measured by the static headspace GC analysis at 298 K as described previously.[12] The uptake of the guest A (mole of guest per mole of host) was calculated as the difference of the total amount of the guest added to the ampule containing the host and the amount of the guest in the vapor phase of the system. The latter was calculated from the measured activity of the guest P/P_0 and its saturated vapor pressure at 298 K.[21] The accuracy of determination of the sorbate activity ranges from 5% (for $P/P_0 > 0.5$) to 10% (for $P/P_0 < 0.1$). In each case, the most part of the error is systematic and caused by the non-linear vapor sampling into a capillary column (3—5% at $P/P_0 < 0.10$) and the error of analysis of a sample of the saturated sorbate vapor (2—3%). The error of the guest uptake A determination is 5%. The sorption isotherms for the most guest—host systems were determined from two to four times. The sorption isotherms were repeatedly measured for the same host sample purified from the bound guest by drying *in vacuo* on heating as described above.

The compositions of samples of the solid host saturated with the guest vapor with the unity thermodynamic activity ($P/P_0 = 1$) at 298 K were determined by thermogravimetry using an MGDTD-17S microthermoanalyzer (Setaram) from the weight loss with the temperature increase. In this experiment, the rate of temperature increase was 4 K min^{-1}. The measurements were carried out for samples of inclusion compounds 10—15 mg in weight at an atmospheric pressure. The time of sample exposure to air, from the moment of depressurization of ampules containing the saturated guest vapor to the determination of their weight in the microthermoanalyzer, was shorter than 2 min. For samples of inclusion compounds (clathrates) of host **2** with toluene and chloroform, we checked the weight loss of the sample at room temperature (21 °C) without heating by weighing in the microthermoanalyzer for 1 h. The accuracy of determination of the guest content in an inclusion compound sample by thermogravimetry was 5%.

Results and Discussion

Sorption isotherms of guest vapors by solid calixarenes. The isotherms obtained in this work for sorption of organic vapors by solid *tert*-butylcalix[6]arene (**2**) and *tert*-butylcalix[8]arene (**3**) at 298 K are presented in Fig. 1. The sorption isotherms of the same guests by solid *tert*-butylcalix[4]arene (**1**), which have been obtained previously under comparable conditions,[12,13] are also given for comparison (see Fig. 1).

In most cases, the isotherms obtained for the sorption of organic vapors by calixarenes **2** and **3** have a binding threshold of the guest with respect to its thermodynamic activity P/P_0, below which the sorption of the guest is absent or insignificant. When the threshold activity is achieved by the guest, a cooperative increase in the uptake is observed with the further achievement of the sorp-

tion isotherm saturation corresponding to the formation of stoichiometric inclusion compounds. According to the Gibbs phase rule, the presence of a region of the host solid phase saturation with the guest in the sorption isotherms and the binding threshold of the guest with respect to its activity indicates the phase transition from the phase of the host without guest to the phase of inclusion compound.[11,12,22]

Isotherms of this type were fitted by the Hill equation[23]:

$$A = SC(P/P_0)^N/(1 + C(P/P_0)^N), \tag{1}$$

where S is the stoichiometry of the saturated clathrate, C is the sorption constant, N is the cooperativity constant, and A is the experimentally determined composition of the solid phase (mole of guest per mole of host). When fitting the sorption isotherms, we took into account the points with the guest activity $P/P_0 < 0.85$ at which no noticeable multilayer sorption at the interface occurs in the systems under study. The fitting of the obtained sorption isotherms by Eq. (1) gave two parameters with a satisfactory accuracy: the stoichiometry of the inclusion compound S and the ratio of the logarithm of the sorption constant to the cooperativity constant (lnC)/N or the activity of the guest $\alpha_{0.5S}$ at 50% saturation of the host by the guest.

$$\alpha_{0.5S} = \exp(-(\ln C)/N), \tag{2}$$

The cooperativity parameter N and sorption constant C are calculated with large errors. The values of the fitting parameters S, N, and $\alpha_{0.5S}$ are presented in Table 1 along with the stoichiometry values S obtained under the same conditions and by the same experimental method for calixarene **1**.[12,13]

Equation (1) described satisfactorily the sorption isotherms for all the systems, except for the chloroform vapor—solid host **3** system. For this system, the sorption isotherm has a more complex shape. The interval of chloroform activity $P/P_0 = 0$—0.3 includes a saturation region corresponding to the formation of clathrate with the stoichiometry 1 : 1. The further increase in the guest activity results in a cooperative increase in the guest uptake to a saturation level corresponding to the clathrate composition **3** · 8.4 CHCl$_3$. The sorption isotherm of chloroform vapors by host **3** for the guest activities $P/P_0 = 0.3$—0.83 was fitted by the Hill equation modified by the addition of a free term equal to the stoichiometry of the assumed intermediate clathrate $S_1 = 1$ (mole of guest per mole of host)

$$A = SC(P/P_0)^N/(1 + C(P/P_0)^N) + S_1. \tag{3}$$

A similar 8 : 1 clathrate (mole of CHCl$_3$ per mole of calixarene) has previously been prepared from a solution of host **3** in chloroform and studied by X-ray diffraction
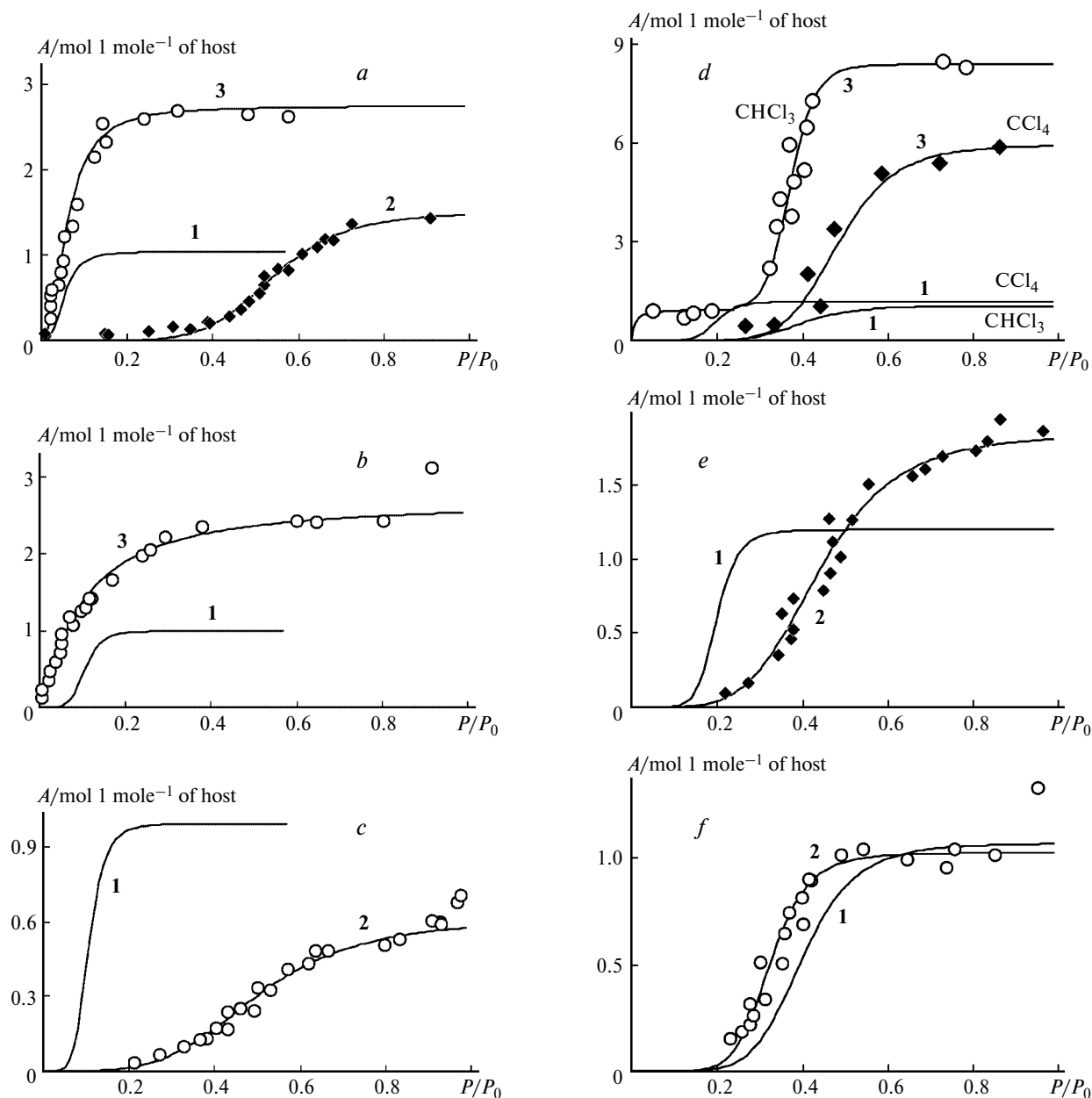
Fig. 1. Vapor sorption isotherms of organic compounds by solid *tert*-butylcalix[4]arene (**1**),[12,13] *tert*-butylcalix[6]arene (**2**), and *tert*-butylcalix[8]arene (**3**) at 298 K: C_6H_6 (*a*), $PhCH_3$ (*b*, *c*), CCl_4 (*d*, *e*), and $CHCl_3$ (*d*, *f*).

analysis.[8] An intermediate clathrate with the composition $3 \cdot 1.4\ CHCl_3$ was also observed by thermogravimetry.[8]

Composition of host—guest inclusion compounds according to the thermogravimetric analysis data. The compositions of inclusion compounds (clathrates) S_{TG} (mole of guest per mole of host) involving calixarenes **2** and **3** prepared by the saturation of the host with the guest vapor with the unity activity, $P/P_0 = 1$, were also determined by thermogravimetry. Typical TG curves for the clathrates studied are shown in Fig. 2. The results of thermogravimetric analysis including the S_{TG} value, the starting (T_1, T_3) and end (T_2, T_4) points of clathrate decomposi-

tion, and the decrease in the sample weight Δm (%) on heating are presented in Table 2 along with the published X-ray diffraction and thermogravimetric studies of the stoichiometry of the clathrates prepared by crystallization of the host solutions in the liquid guest.

The inclusion compounds of host **2** and clathrate $3 \cdot 2.6\ PhCH_3$ are stable in air at room temperature. This can be concluded from the starting point of decomposition T_1, which exceeds 40—80 °C the room temperature (18—21 °C) for these species (see Table 2). For clathrates of host **2** with chloroform and toluene, we additionally verified the stability of the clathrate in air by weighing the

Table 1. Thermodynamic parameters of the vapor sorption isotherms of organic compounds by solid *tert*-butylcalix[4]arene (**1**), *tert*-butylcalix[6]arene (**2**), and *tert*-butylcalix[8]arene (**3**), $T = 298$ K*

Calixarene	Guest	$\alpha_{0.5S}$	S	N	δ
1[a]	$CHCl_3$	0.4	1.07	6.5	0.02
	C_6H_6	0.05	1.08	2.1	0.01
	CCl_4	0.2	1.2	8	0.04
	$PhCH_3$	0.11	0.99	5.7	0.02
2	$CHCl_3$	0.32	1.02	7.3	0.04
	C_6H_6	0.54	1.50	6.4	0.02
	CCl_4	0.44	1.85	4.8	0.04
	$PhCH_3$	0.50	0.61	4.2	0.03
3	$CHCl_3$[b]	0.37	7.40	12.8	0.05
	C_6H_6	0.06	2.75	2.2	0.07
	CCl_4	0.49	5.94	7.4	0.07
	$PhCH_3$	0.10	2.69	1.2	0.05

* S is the stoichiometry of the saturated clathrate, N is the cooperativity constant, $\alpha_{0.5S}$ is the guest activity at 50% saturation of the host with the guest, and δ is the standard fitting deviation of the sorption isotherms for the shortest distances between experimental points and the curve calculated by Eqs (1) and (2).
[a] The data for host **1** were taken from the previously published works.[12,13]
[b] The fitting parameters for the sorption isotherm for the chloroform activities $P/P_0 = 0.3—0.83$ using Eq. (3). The overall stoichiometry of the clathrate of host **3** with chloroform is $S_1 + S = 8.4$.

clathrate sample in a microthermoanalyzer at a constant temperature for 1 h (21 °C). In this case, no weight decrease of the clathrate sample was detected within the experimental errors (0.04% of the sample weight). The clathrates of host **3** with chloroform and carbon tetrachloride begin to lose the guest without heating already at 18 °C. The inclusion compound $\mathbf{3} \cdot 2.6\ C_6H_6$ is also unstable. The starting point of its decomposition $T_1 = 29$ °C (see Table 2) exceeds only slightly the room temperature. An analogous instability of crystals of the $\mathbf{3} \cdot 8\ CHCl_3$ clathrate prepared from a solution of calixarene **3** in chloroform has been observed earlier.[8]

The inclusion compounds under study are characterized by two different types of behavior during heating. The most part of the clathrates, except for inclusion compounds of calixarene **2** with benzene and carbon tetrachloride, have only one decomposition step. Typical TG curves (derivatograms) with one decomposition step of clathrate obtained in this work are presented in Fig. 2, *a—c*. The clathrates $\mathbf{2} \cdot 1.58\ C_6H_6$ and $\mathbf{2} \cdot 1.64\ CCl_4$ have two decomposition steps (see Fig. 2, *d, e*) and very similar behavior on heating. The first decomposition step of these clathrates begins at temperatures lower than the guest boiling point $T_{b.p.}$ by 10 and 13 °C, respectively, and terminates at $T_2 = 123$ °C (see Table 2). This produces clathrate $\mathbf{2} \cdot 0.60\ C_6H_6$, which is stable up to $T_3 = 151$ °C, whereas clathrate $\mathbf{2} \cdot 0.26\ CCl_4$ is stable up to $T_3 = 155$ °C. Further heating results in the formation of the starting calixarene **2** containing no guest at $T_4 = 180$ °C. The two-

Table 2. Data of thermogravimetry for guest—host inclusion compounds (clathrates) prepared by the saturation of the solid host with guest vapor having the unity thermodynamic activity $P/P_0 = 1$ at 298 K[a]

Guest	**2**								**3**				
	$T_{b.p.}$	T_1	T_2	T_3	T_4	Δm (%)	S_{TG}	S^{XRD}	T_1	T_2	Δm (%)	S_{TG}	S^{XRD}
			°C							°C			
$CHCl_3$	61.2	86	200	—	—	10.6	0.97[b]		[c]	130	41.3	7.6; 7.8[8]	8[8]
C_6H_6	80.1	70	123	151	180	11.1	1.58[d]	3[17]	29	80	13.1	2.6	—
CCl_4	76.8	64	123	155	185	20.4	1.64[e]		[c]	113	41.1	6.5	—
$C_6H_5CH_3$[f]	110.6	102	192	—	—	7.0	0.79; 0.67[9]	1[16]	59	147	15.6	2.6	—

[a] The previously published data are presented for clathrates prepared by crystallization from a host solution in the liquid guest. T_1 and T_3 are the starting points of clathrate decomposition, T_2 and T_4 are the end points of clathrate decomposition, Δm is the decrease in the sample weight, S_{TG} is the stoichiometry of the clathrate according to the TG data, and S^{XRD} is the stoichiometry according to the X-ray diffraction data.
[b] The previously published value of the clathrate stoichiometry S_{TG} corresponding to the sum of the weight decrease at ~20 °C without heating (6.4 moles of guest/1 mole of host) and that in a temperature interval of 30—180°C (1.4 moles of guest/1 mole of host).[8]
[c] The decomposition of the clathrate begins at room temperature (18 °C) without heating.
[d] $S_{TG} = 0.60$ moles of guest/1 mole of host for the clathrate with the starting point of decomposition $T_3 = 151$ °C.
[e] $S_{TG} = 0.28$ for the clathrate with the starting point of decomposition $T_3 = 155$ °C.
[f] The starting point of decomposition of the clathrate $\mathbf{2} \cdot 0.67\ PhCH_3$ is $T_1 = 117$ °C, and the end point of decomposition is $T_2 = 145$ °C.[9]

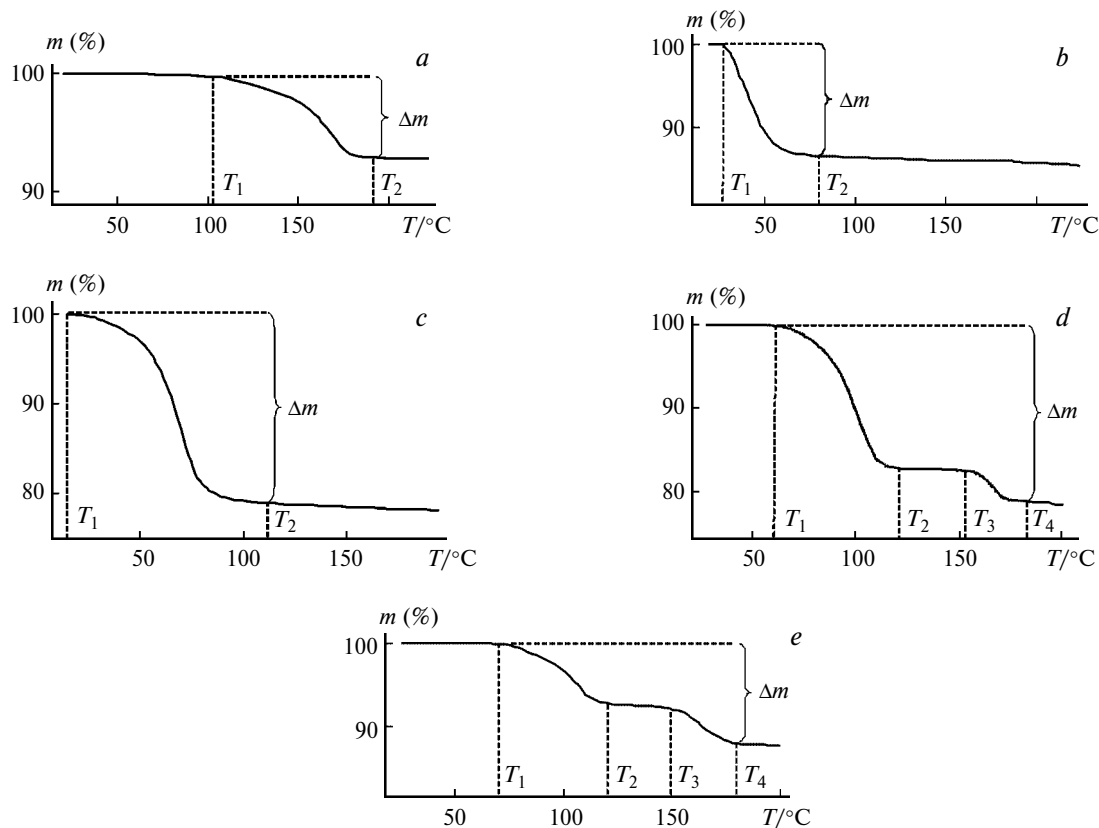**Fig. 2.** Thermogravimetric curves of decomposition of the clathrates $2 \cdot 0.79$ $C_6H_5CH_3$ (*a*), $3 \cdot 2.6$ C_6H_6 (*b*), $3 \cdot 6.5$ CCl_4 (*c*), $2 \cdot 1.64$ CCl_4 (*d*), and $2 \cdot 1.58$ C_6H_6 (*e*) prepared by the saturation of the host with guest vapor having the unity activity ($P/P_0 = 1$) at 298 K.

step decomposition of the clathrates $2 \cdot 1.58$ C_6H_6 and $2 \cdot 1.64$ CCl_4 on heating can be caused by conformational transitions of calixarene **2**, which is characterized by a "compressed cone" conformation in the solid state.[1,16,17] This conformation is very flexible in solution[1] and, perhaps, undergoes changes when losing some guest molecules in clathrates of this calixarene with a stepwise change in the packing.

A comparison of the stoichiometry values of saturated inclusion compounds S and S_{TG}, obtained by two different experimental methods in this work, shows that these values agree satisfactorily, in most cases, within the experimental errors. Exceptions are the systems involving host **2** and carbon tetrachloride and toluene for which discrepancies are 13 and 30%, respectively (see Tables 1 and 2). This can be reasoned by a relatively narrow interval of the saturation region of sorption isotherms for these systems with respect to the guest activity (see Fig. 1, *c*, *e*). This interval does not allow one to conclude unambiguously whether the complete saturation of the host was achieved at the guest activity $P/P_0 < 0.85$ or not. For higher P/P_0 values, multilayer sorption at the interface and formation of a separate liquid phase cannot be distinguished from clathrate formation based on the sorption

isotherms only. It can be assumed that for a clathrate of guest **2** with toluene, for which the thermogravimetric data show a higher content of the guest ($S_{TG} = 0.79$) than the extrapolation of the sorption isotherm does ($S = 0.61$), the amount of the bound guest increases with an increase in its activity up to $P/P_0 = 1$.

The stoichiometry values S and S_{TG} obtained in this work for inclusion compounds prepared by the saturation of the solid host with the guest vapor correspond to some published data for crystals prepared from a host solution in the liquid guest (see Tables 1 and 2). This correspondence holds for clathrates of calixarene **3** with chloroform, which have been studied previously by X-ray diffraction crystallography and thermogravimetry.[8] The published data on the stoichiometry of clathrates of host **2** with toluene obtained by thermogravimetry ($S_{TG} = 0.67$ mole of guest per mole of host)[9] and X-ray diffraction analysis ($S^{XRD} = 1$)[16] diverge substantially between each other and from thermogravimetric data obtained in this study ($S_{TG} = 0.79$, see Table 2). The crystallization temperature of the clathrates under study is not mentioned in the works,[9,16] although differences in this temperature can exert a substantial effect on the stoichiometry of a solid guest—host solid complex (clathrate)[15] and

can be a reason for the discrepancies observed. The difference in preparation conditions also can cause a considerable discrepancy between the stoichiometry values obtained for the clathrate of host **2** with benzene in the present work, $S_{TG} = 1.58$, $S = 1.50$ (see Tables 1 and 2), and the previously published X-ray diffraction data[17] for crystals grown from a benzene solution, $S^{XRD} = 3$. In the present work, this clathrate was prepared by crystallization at room temperature from a solution of calixarene **2** in benzene and was studied by thermogravimetry. The resulting clathrate has the composition ($S_{TG} = 3$) corresponding to the published S^{XRD} value determined by X-ray diffraction crystallography[17] and a lower starting point of decomposition ($T_1 = 66$ °C) than that of the clathrate obtained by the saturation of the solid host with the guest vapor (see Table 2). Meanwhile, the parameters of existence of an intermediate clathrate ($T_2 = 140$ °C, $T_3 = 148$ °C, $T_4 = 175$ °C) found in the cited[17] and our works are comparable.

The available thermogravimetric data indicate that clathrates of calixarene **1** with toluene and chloroform prepared by crystallization from a solution of the host in the liquid guest are highly stable ($T_1 = 139$ and 186 °C, respectively) and have a composition of 1 : 1.[9] According to the X-ray diffraction data, crystals of clathrates of calixarene **1** with toluene and benzene have the same composition. In both cases, these data coincide with the composition of inclusion compounds determined from the sorption isotherms of the guest vapor by the solid host at 298 K [12,13] (see Table 1).

Structure—property relationships for inclusion compounds of calixarenes 1—3. The data obtained by headspace GC analysis and thermogravimetry make it possible to obtain two parameters for each host—guest pair with an accuracy sufficient for analysis of structure—property relationships: stoichiometry of a saturated inclusion compound (clathrate) S (S_{TG}) and activity of the guest at 50% saturation of the host $\alpha_{0.5S}$ (see Tables 1 and 2). The $\alpha_{0.5S}$ value characterizes the guest—host affinity, because it is directly related to the Gibbs energy ΔG_c of clathrate formation on transferring one mole of the guest from the pure liquid to the saturated clathrate

$$\Delta G_c = RT\int_0^1 \ln(P/P_0)\mathrm{d}Y = RT\ln\alpha_{0.5S},$$

where Y is the saturation extent of the host with the guest. The right part of this equation is valid if the sorption isotherm can be fitted by Eq. (1).

Analysis of the data obtained (see Table 1) shows that the increase in the macrocycle size in the series of calixarenes results in a substantially different character of changing the activity at 50% saturation of the host with the guest ($\alpha_{0.5S}$) for different guests. For chloroform, the $\alpha_{0.5S}$ value in this series changes insignificantly: **1** ≈ **2** ≈ **3**.

For carbon tetrachloride, $\alpha_{0.5S}$ increases only on going from host **1** to host **2** and further remains almost unchanged: **1** < **2** ≈ **3**. For benzene and toluene, $\alpha_{0.5S}$ in the system with host **2** is ten- and fivefold higher than those with each of hosts **1** and **3**, respectively: **1** < **3** ≪ **2**. The lower $\alpha_{0.5S}$ value means a greater host—guest affinity.

The dependences on the calixarene macrocycle size observed for the stoichiometry S and S_{TG} of saturated clathrates in the guest vapor—solid host systems under study also differ for different guests (see Tables 1 and 2). For chloroform and toluene, S and S_{TG} vary in the series **1** ≈ **2** ≪ **3** and **1** ≈ **2** < **3**, respectively, whereas for benzene and carbon tetrachloride, they change in the series **1** < **2** < **3**. As a whole, for toluene and for the bottom part of the activity range of benzene and carbon tetrachloride, host **1** is intermediate in the sorption value A at a specified activity of the guest P/P_0 compared to hosts **2** and **3**: **2** < **1** < **3**. For chloroform with $P/P_0 < 0.6$, the sorption isotherm by solid host **1** lies a little lower than the sorption isotherm by host **2**.

The influence of the calixarene macrocycle size on the parameters of sorption isotherms of the guest vapor, which is observed in this work, differs substantially from that formed previously for binding vapors of the same organic compounds by thin layers of these calixarenes on piezoelectric sensors of the quartz microbalance type. Sensors of this type exhibit a sharp increase in the sensitivity to the guest vapor on going from host **1** to hosts **2** and **3**.[4—6] In this case, the sensitivity of a sensor (calculated per mole of host) to all the guests studied increases more than fivefold, including the sensitivity to toluene increasing by more than an order magnitude. The stoichiometry of the saturated inclusion compound of host **2** with toluene ($S = 1.3$), estimated from the sorption isotherm obtained using a quartz sensor,[4] corresponds by an order of magnitude to the values obtained in our work (see Tables 1 and 2). Hence, it can be assumed that a special behavior of the systems involving host **1** is a source of the discrepancies in the results obtained by two experimental methods. A reason can be an increase in the stability of the guest—host clathrates with a decrease in the macrocycle size. This is seen by a comparison of the starting point of clathrate decomposition T_1 for calixarenes **2** and **3** (see Table 2) and the previously published data[9] for clathrates of host **1** for toluene ($T_1 = 139$ °C) and chloroform ($T_1 = 186$ °C). It can be assumed that, unlike calixarenes **2** and **3**, for a restricted time of blowing a sensor with air having a low temperature, the thin layer of host **1** loses only a small portion of bound volatile organic compounds (guests). This results in a decrease in the sorption capacity and sensitivity of a sensor. For clathrates of host **2** with benzene and tetrachloromethane, one should take into account that relatively stable intermediate clathrates with the starting point of decomposition $T_3 \approx 150$ °C can be formed (see Fig. 2, *d, e*).

The data obtained in this work provide insight into the influence of the *tert*-butylcalix[n]arene macrocycle size on the thermodynamic parameters of interactions in the guest vapor—solid calixarene systems prepared under standard conditions, where the influence of the procedure of preparation of hosts without a guest is erased by drying *in vacuo* at decomposition temperatures of their clathrates. The results obtained are useful for predicting the behavior of the calixarenes studied in systems for odor recognition.

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