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Thermodynamic characteristics of thermal dissociation of inclusion compounds based on graphite fluorides

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Abstract Thermal dissociation processes for acetonitrile inclusion compounds based on the polymer fluorographite host matrix $C_2F_xBr_{0.01}\cdot yCH_3CN$, where $x = 0.49$–0.92, $y = 0.174$–0.285, are investigated. Thermodynamic parameters (ΔH°_{av}, ΔS°_{av}, ΔG°_{298}) for deintercalation of the compounds of the first filling step into the compounds of the second step and gaseous guest within temperature range 294–352 K were determined. The effect of the host matrix fluorination degree on the thermodynamic characteristics of the studied processes is demonstrated.

Keywords Thermal dissociation · Vapor pressure · Thermodynamic parameters · Inclusion compounds · Fluorinated graphite · Acetonitrile

Introduction

Fluorinated graphite intercalation compounds (FGIC, intercalates) form a class of layered compounds significant from the scientific and applied aspects. Investigation of these compounds properties may promote the development of clathrate formation theory for guest–host low-dimensional systems. During the recent years, much attention has been paid to the development of the scientific concept of a transition from macromolecules to nanotechnologies. In this respect, graphite and its oxidized forms are promising. In the oxidized forms of graphite, two-dimensional carbon layers are separated due to the transition of a definite amount of the matrix carbon from the sp^2 hybrid state into the sp^3 hybrid state due to the formation of covalent bonds between carbon and a heteroatom (oxygen, nitrogen, fluorine [1–6]). Different ratios of the sp^2/sp^3 states of carbon atoms in the synthesis products imply the possibility of the formation of a variety of nonstoichiometric berthollide phases possessing different properties. The effect of fluorination degree on the characteristics of synthesis products was demonstrated in the studies of graphite hydrofluorides $C_xF(HF)_\delta$ [2] and the products of graphite high-temperature fluorination $(C_xF)_n$ [3]. The properties of FGIC were studied mostly for the compounds that are stable in the air.

Fluorinated graphite intercalation compounds are layered inclusion compounds based on the polymeric two-dimensional fluorographite matrix; these compounds are built according to the guest–host principle. Fluorinated graphite intercalation compounds have a general formula $(C_2F_xHl_z\cdot yG)_n$, where $(C_2F_xHl_z)_n$ is the host component (Hl is chlorine or bromine), x, y, z are stoichiometric coefficients, and G is the guest component (organic or inorganic compound [6, 7]). Similar to graphite [8–10], depending on equilibrium conditions and the guest component nature, fluorographite matrices may form inclusion compounds of different steps of filling [6]. The effect of the matrix fluorination degree on the FGICs physicochemical properties has been studied insufficiently: investigations were carried out mainly for the compounds based on highly fluorinated matrices. For instance, it was shown in [11] with the help of tensimetric method for the samples with $x = 0.92$ and 0.96 that the processes of FGIC-1 (the 1st stage of filling, alternation of guest and host layers) equilibrium deintercalation to form FGIC-2 (the 2nd stage of filling, alternation of two host layers and one guest layer) and the gaseous guest are described, within the measurement error, by a single equation of the temperature dependence of pressure. Meanwhile, taking into account

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the layered structure of FGIC and mainly Van der Waals character of the guest-to-host interaction [6], it should be expected that a more significant decrease in the matrix fluorine content with respect to the limiting composition C_2F should cause spatial changes that would noticeably affect the macro-characteristics of the common supramolecular system. These investigations were undertaken in [12–15] where the influence of fluorine content on FGIC properties with four guests (acetonitrile, chloroform, dichloroethane, methylene dichloride) was represented. For example, article [12] showed the decrease of equilibrium vapor pressure above CH_3CN FGICs with decrease of fluorination degree x at fixed temperature (298 K). Thermodynamic properties for FGIC-1 deintercalation processes were not investigated.

In this study, we studied the effect of the composition (structure) of the C_2F_x matrix ($0.49 < x < 0.92$) on the thermodynamic characteristics of the processes of thermal deintercalation of FGIC-1 to form FGIC-2 and a gaseous guest component (Fig. 1). The guest component was acetonitrile, a compound that is rather inert with respect to the fluorographite matrix; its molecules form FGIC-1 with the simple structure of the guest layer [6]. This fact makes it easier to obtain the reliable quantitative data for inclusion compounds based on the polymer host component [16]. The error of tensimetric measurements for the case of the guest subsystem single-layer structure turned out to be comparable with the guest vapor pressure measurements error for classical inclusion compounds (for example, the compounds based on Scheffer complexes [17]).

Experimental

Synthesis of the first step of filling compounds (FGIC-1)

To obtain FGIC-1, we used FGIC-2 with acetonitrile and liquid acetonitrile. The FGIC-2 synthesis was carried out by the graphite oxidation at room temperature in several stages using the procedure of the substitution of one guest by another [6, 11, 12]. Bromine trifluoride was used as the fluorinating agent. To prevent uncontrolled interaction (explosion), 8–14% solutions of bromine trifluoride in bromine were used. The natural graphite fraction with the crystallite size 0.4 × 0.3 × 0.02 mm, purified by known procedures (ash percentage: not more than 0.13% mass) and heated at 800–820 °C was used for the synthesis. The characteristics purified graphite (according to the data obtained by means of X-ray phase analysis, Raman spectroscopy, and BET) were close to those for the highly ordered graphite. Acetonitrile was distilled above P_2O_5 (boiling point 82.1 °C). The products of FGIC-2 $C_2F_xBr_{0.01}{\cdot}y_2CH_3CN$ synthesis were identified by means of elemental analysis [12]; their composition was: $C_2F_{0.92}Br_{0.01}{\cdot}0.136CH_3CN$ (**1**), $C_2F_{0.87}Br_{0.01}{\cdot}0.136CH_3CN$ (**2**), $C_2F_{0.69}Br_{0.01}{\cdot}0.112CH_3CN$ (**3**), $C_2F_{0.49}Br_{0.01}{\cdot}0.084CH_3CN$ (**4**).

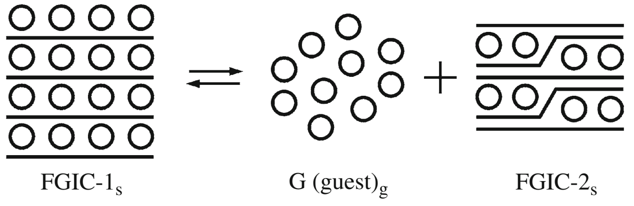

Fig. 1 Scheme of FGIC-1 deintercalation process to form FGIC-2 and gaseous guest

The FGIC-1 synthesis was carried out under the isopiestic conditions (P, $T \approx$ Const), starting from precise weighed portions of FGIC-2 (**1–4**). Saturation curves showed the effect of x on the amount of the included guest and on the rate of the transformation of FGIC-2 into FGIC-1 (Fig. 2). As the fluorine content of the matrices decreases, mass increment (Δm) was from 12 ($x = 0.92$) to 9 ($x = 0.49$) mass%. The FGIC-1 compositions according to the isopiestic data are presented in Table 1. The products of FGIC-1 synthesis were studied by tensimetry, DTA, and XPA methods.

Pressure measurement

The FGIC-1 deintercalation (dissociation) pressure was measured with a static method using membrane null-manometers of spoon type. Measurements were carried out using the conventional version of the method in which the whole membrane chamber is situated within the zone of controlled temperature. The sample thermostating and temperature measurements accuracy was ±0.05 K. The

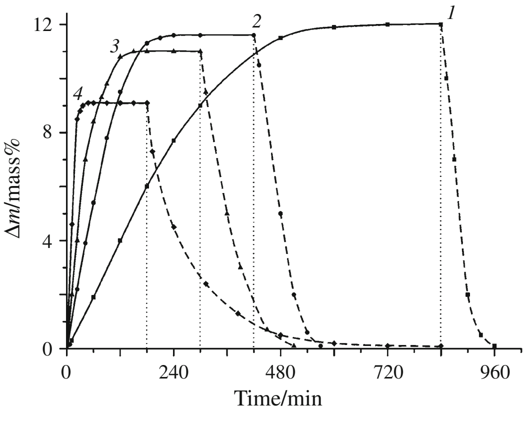

Fig. 2 Curves of FGIC-2 saturation with acetonitrile (guest vapor pressure: about 80 torr, temperature: 298.1 K) and decomposition of FGIC-1 with $x = 0.92$ (*1*), 0.87 (*2*), 0.69 (*3*), 0.49 (*4*) in the air. FGIC-2 sample weights at the start of experiment correspond with the weights of samples obtained after FGIC-1 thermal decomposition

Table 1 Chemical compositions and some properties of the 1st stage ($C_2F_xBr_{0.01}\cdot y_1CH_3CN$ = FGIC-1) and the 2nd stage ($C_2F_xBr_{0.01}\cdot y_2CH_3CN$ = FGIC-2) inclusion compounds

No.	x	FGIC-1				FGIC-2	
		y_1 (±0.009)	T_{dec}/°C (±0.4)		I_c/Å (±0.02)	y_2 (±0.006)	I_c/Å (± 0.08)
			2/° min^{-1}	7/° min^{-1}			
1	0.92	0.285	100.5	100.7	9.45	0.136	15.52
2	0.87	0.283	102.1	102.5	9.41	0.136	15.47
3	0.69	0.240	108.6	109.1	9.22	0.112	14.98
4	0.49	0.174	114.6	114.7	9.02	0.084	14.53

I_c identity period along c-axis

sensitivity of Pyrex membranes was ≈0.1 torr, the studied temperature range was 294–352 K. The weighed portions of FGIC-1 were 0.8–0.9 g, the volume of the membrane chamber was 30–40 cm^3. The approach to the equilibrium was carried out from the lower pressure by increase, similar to the case described in [11]. The time of the equilibrium vapor pressure stabilization varied from several hours to a day.

Thermal analysis

Fluorinated graphite intercalation compound-1 thermal decomposition was studied with a thermoanalytical DTA equipment which records thermal effects of phase transitions within a broad temperature (from −150 to +300 °C). FGIC-1 samples (35–40 mg) were placed in ampoules with a strangulation and a hollow in the bottom for a thermocouple. After deep cooling (with liquid nitrogen), a capillary about 0.2 mm in diameter and 30–35 mm long was pulled out. After the interval of time necessary for equilibrium establishment (20–40 h), the capillary was opened immediately before recording the heating curves. The accuracy of temperature measurement in reversible phase transitions was ±0.4°; heating rate was 2–7°/min.

X-ray phase analysis

The structural characteristics were determined at room temperature using the DRON-SEIFERT-RM4 diffractometer (CuK_a-radiation, graphite monochromator). Recording was carried out in a step-through mode within the angle range 2θ from 5° to 55°. The cells with FGIC-1 were insulated with a Teflon film 5 μm thick.

Results and discussion

Thermal and structural characteristics

During heating of the FGIC-1 samples obtained by the saturation of the weighed portions of FGIC-2 with the guest component through the gas phase, the heating curve (DTA) exhibited one endo-effect; according to the XPA data (Fig. 3), this effect corresponded to the FGIC-1 rearrangement into FGIC-2. After adding liquid acetonitrile (6–8 mL) to the cooled ampoule with FGIC-2 and keeping the mixture at room temperature for 5–14 h, two endo-effects were observed in the heating curves of the «wet» FGIC-1 samples (Fig. 4). The endo-effects at 82.1 °C corresponded to the boiling point of pure guest (the solubility is FGIC in acetonitrile is almost absent: it is less than 0.001% mass) and were taken as a reference. The maxima of the second endo-effects, within the measurement error (±0.4 °C), coincided with decomposition temperatures for FGIC-1 samples obtained by the isopiestic procedure. After heating the FGIC to a temperature not higher than 120–135 °C, cooling, adding liquid acetonitrile into the ampoule, the heating curves were multiply reproduced during repeated recording procedures. Decomposition temperature of FGIC-1 was reproduced also at different heating rates (Table 1).

Thermodynamic characteristics

The results of the measurement of equilibrium vapor pressure of the guest component for the first step of filling compounds and the saturated acetonitrile vapor are presented in Fig. 5 in the coordinates $\log p - 1000/T$. The experimental data treated using the least-squares method are described by equations $\log p = A - B/T$. Coefficients A and B are presented in Table 2.

Saturated vapor pressure of acetonitrile. The temperature dependence of acetonitrile saturated vapor pressure (Fig. 5, *curve 1*) is described by equation

$$(\log p \pm 0.003) = (7.79 \pm 0.01) - (1741 \pm 5)/T$$

The average value of the acetonitrile evaporation enthalpy, calculated from the equation, is 33.3 ± 0.1 kJ mol^{-1}, which fully corresponds to the reference data (33.22 and 32.89 kJ mol^{-1} [18]).

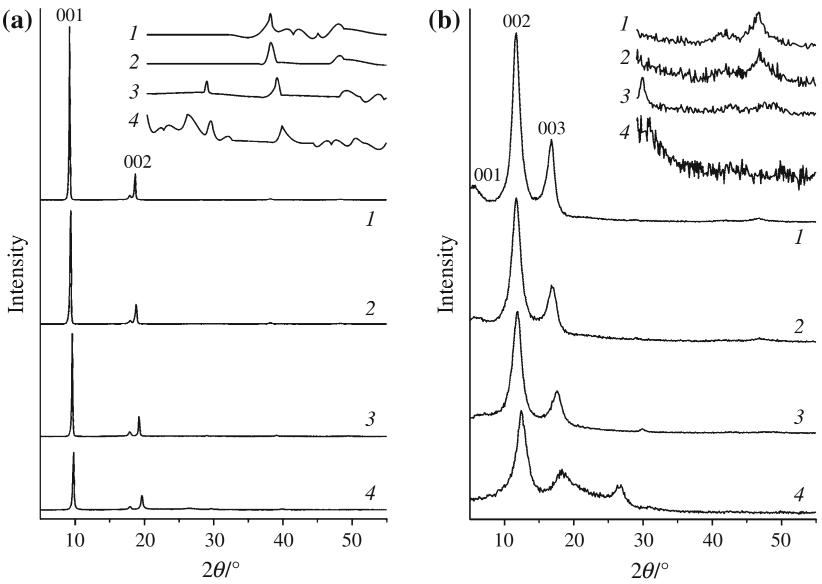

Fig. 3 FGIC-1 (**a**) and FGIC-2 (**b**) diffraction patterns

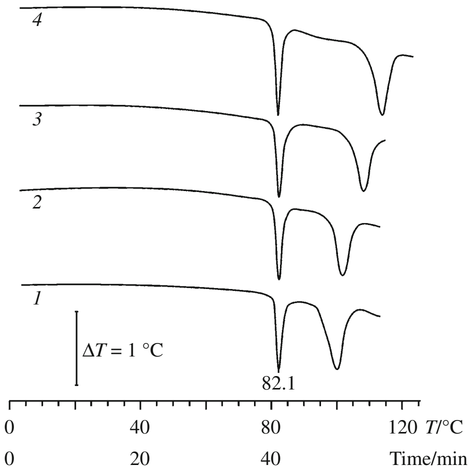

Fig. 4 Heating curves (DTA) for FGIC-1 in the slight excess of liquid acetonitrile, for FGIC-1 based on the matrices with $x = 0.92$ (*1*), 0.87 (*2*), 0.69 (*3*), 0.49 (*4*). Weighed portions of samples after endo-effects are the same as the FGIC-2 weighed portions taken for the FGIC-1 synthesis

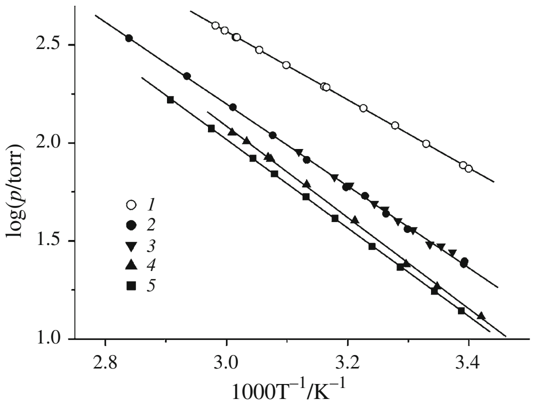

Fig. 5 Acetonitrile vapor pressure temperature dependence for pure liquid acetonitrile (*1*) and for FGIC-1 with $x = 0.92$ (*2*), 0.87 (*3*), 0.69 (*4*), 0.49 (*5*); (*p*/torr, *T*/K)

Acetonitrile vapor pressure above FGIC-1

The character of the acetonitrile vapor pressure dependencies on temperature (Fig. 5, *curves 2*–*5*) provides evidence of monovariant equilibria realized in the studied binary guest–host systems, with three coexisting phases: FGIC-$1_{\text{s.}}$, FGIC-$2_{\text{s.}}$, CH_3CN_{gas}. The differential thermal analysis data also confirm the absence of other phase transitions within the explored temperature range. Using the obtained dependencies, we calculated the changes of standard enthalpy, entropy, and the isobaric-isothermal potential for the processes of deintercalation of FGIC-1 of different compositions to form FGIC-2 and gaseous acetonitrile. These values are listed in Table 2; for 1 mol of released CH_3CN they are represented in Table 3.

Results of investigations using independent methods (DTA, XPA, and tensimetry) provide evidence of the noticeable effect of the matrix fluorination degree on the macro-characteristics of FGIC based on these matrices, namely, a decrease in fluorine content causes an increase in thermal and thermodynamic stability of FGIC-1. Thus, temperature points of phase transitions FGIC-1 → FGIC-2 corresponding to the maxima of endo-effects on heating curves are noticeably higher than the boiling point of the pure guest component and rise with a decrease in x. Acetonitrile guest vapor pressure values for FGIC-1 based on the $x = 0.96$–0.87 matrices almost coincide within the experimental error, similar to the thermodynamic parameters of their deintercalation processes. With further decrease in x, acetonitrile vapor pressure decreases noticeably, which is an evidence of these

Table 2 Coefficients for the log $p = A - B/T$ equations (p/torr, T/K) and calculated thermodynamic parameters of the FGIC-1 deintercalation processes: $C_2F_xBr_{0.01}\cdot y_1CH_3CN_s = C_2F_xBr_{0.01}\cdot y_2CH_3CN_s + (y_1 - y_2)CH_3CN_g$

No.	x	T range/K	n	A	B	$\Delta H°_{av}$/kJ· (mol FGIC-1)$^{-1}$	$\Delta S°_{av}$/JK^{-1}· (mol FGIC-1)$^{-1}$	$\Delta G°_{298}$/kJ· (mol FGIC-1)$^{-1}$
1	0.92	290–352	11	8.47(6)	2090(18)	5.96(3)	16.0(1)	1.21(1)
2	0.87	294–330	10	8.41(15)	2069(47)	5.82(13)	15.6(4)	1.19(1)
3	0.69	292–360	9	9.07(8)	2328(24)	5.70(6)	15.1(1)	1.09(1)
4	0.49	299–354	10	8.78(2)	2255(8)	3.89(1)	10.2(1)	0.86(1)

The $\Delta G°_{298}$ values are calculated from experimental dependencies of vapor pressure from temperature

n number of measurements

Table 3 Thermodynamic parameters of $C_2F_xBr_{0.01}\cdot y_1CH_3CN$ (FGIC-1) deintercalation calculated for 1 mol of CH_3CN in gas phase

No.	x	$\Delta H°_{av}$/kJ· (mol CH$_3$CN)$_g^{-1}$	$\Delta S°_{av}$/JK^{-1}· (mol CH$_3$CN)$_g^{-1}$	$\Delta G°_{298}$/kJ· (mol CH$_3$CN)$_g^{-1}$
1	0.92	40.0(2)	107(1)	8.10(6)
2	0.87	39.6(9)	106(3)	8.07(6)
3	0.69	44.5(5)	118(1)	9.24(6)
4	0.49	43.2(1)	113(1)	9.52(2)
5	CH_3CN	33.3(1)	94.00(3)	5.31(3)

For $CH_3CN_{liq} \rightarrow CH_3CN_g$ process

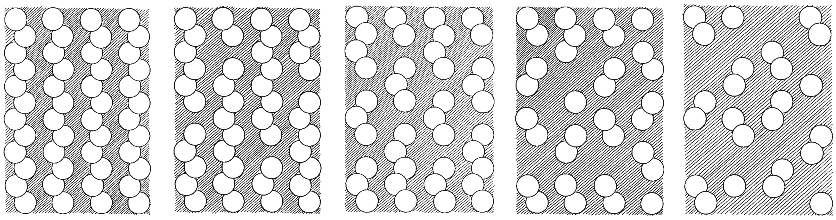
$x = 1.00$ $x = 0.92$ $x = 0.84$ $x = 0.69$ $x = 0.49$

Fig. 6 Scheme of possible changes in the sizes and shapes of cavity channels for the host matrix with decrease in the amount of fluorine atoms in it (*light circles*)

compounds stability increase. The structural characteristics are also sensitive to changes in fluorine content (Table 1): passing from the matrix with $x = 0.92$ to $x = 0.49$, identity periods for FGIC-1 decrease by 0.4 Å, for FGIC-2 by 1 Å, which substantially exceeds the measurement error.

To discuss the revealed dependencies, we used the model proposed by Bulusheva, Okotrub, and Yudanov as one of the most favorable (from the viewpoint of energy) version of fluorine distribution over the fluorographite monolayer of the cluster having the composition $(C_2F_1)_n$ [19]—Fig. 6 ($x = 1.00$). One can see in the Figure that the «removal» of fluorine (in a random manner) from the limiting composition matrix changes the interlayer space architecture: as x decreases, the relief of the fluorographite layer becomes more complicated and its “effective surface” increases. In the equilibrium state, guest molecules included in the interlayer space should occupy, taking into account the changing force field, the positions that are most favorable in energy with respect to each other and the nearest surrounding matrix fragments. In our case, the packing factor is accompanied (with a decrease in x) by a decrease in the stoichiometric coefficients y and identity periods along the direction of the c-axis of crystallites, that is, by the realization of the closest packing of the two subsystems (guest and host). Contraction of the layers with a decrease in fluorine content of the matrix leads to an increase in the role of intermolecular interaction of the host–guest type and, as a consequence, to an increase in thermal and thermodynamic stability of the compounds.

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