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The relationship between properties of fluorinated graphite intercalates and matrix composition

Part 5. Intercalates with acetone

D. V. Pinakov · V. A. Logvinenko · G. N. Chekhova · Yu. V. Shubin

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Abstract Inclusion compounds (intercalates) of fluorinated graphite matrix with acetone ($C_2F_xBr_z \cdot y(CH_3)_2CO$, $x = 0.49$, 0.69, 0.87, 0.92, $z \approx 0.01$) were prepared by guest substitution from acetonitrile to acetone. The kinetics of the thermal decomposition (the first stage of filling → the second stage of filling) was studied under isothermal conditions at 292–313 K. The relationship of the host matrices structure with inclusion compounds thermal properties and kinetic parameters is discussed.

Keywords Inclusion compounds · Intercalates · Fluorinated graphite · Isothermal kinetics · Thermal stability

Introduction

In the articles [1–4], the fluorinated graphite intercalation compounds (FGICs) with common formula $C_2F_xBr_z \cdot y_iG$ (where $x = 0.49$–0.92, $z = 0.008$–0.010, y_2 and y_1 are number of guest component per 2 atoms of graphite for the second and the first stage of filling, respectively) were investigated by physicochemical methods. Acetonitrile and low-molecular chlorinated hydrocarbons (chloroform, dichloroethane and methylene dichloride) were used as included components. It was determined that the number of included guest molecules in FGIC decreased with decrease of matrix fluorination degree. It was shown by the determination of effective activation energies that kinetic stability is nearly similar for different x with the same guest for FGICs with CH_3CN and $CHCl_3$ [1, 2] but trends to increase with decrease of fluorination degree for intercalation compounds with 1,2-dichloroethane and methylene dichloride [3, 4]. At the same time, referring to DTA method results, thermal stability considerably increased with decrease of matrix fluorination degree from 0.92 to 0.49—as for acetonitrile compounds, as for compounds with chlorinated hydrocarbons [1–4]. Topochemical mechanism for deintercalation processes of FGICs with acetonitrile is complicated—it changes from reaction on phase boundary to diffusion which increases its influencing factor with decrease of matrix fluorination degree [1]. Chloroform FGIC with $x = 0.92$ had a short initial step of phase boundary reaction which gradually disappeared with x decrease [2]. Deintercalation mechanism of FGICs with $C_2H_4Cl_2$ had only diffusive nature, and diffusive hindrance also increased with decrease of fluorination degree [3]. Methylene dichloride FGICs had complicated mechanism [4] as compounds with acetonitrile. The increase of diffusive interactions influence (and decomposition rate with x decrease) correlates with interlayer space decrease in clathrate systems: from 9.47 to 9.02 Å for the first stage FGICs (FGIC-1) with acetonitrile [1], from 10.03 to 9.61 Å for chloroform FGICs [2], from 10.28 to 9.80 Å with dichloroethane [3], from 9.82 to 9.32 Å for inclusion compounds with methylene dichloride [4]. The decomposition reaction rate is maximal for compounds with $x = 0.92$ for all these guest components. At the same time FGIC-1 of the least fluorinated matrix ($x = 0.49$) have the highest formation rate among investigated matrices; that can be the result of interlayer interactions decrease and of the host–guest interaction increase with decrease of fluorine content in our matrices (Tables 1, 2).

D. V. Pinakov (✉) · V. A. Logvinenko ·
G. N. Chekhova · Yu. V. Shubin
Nikolaev Institute of Inorganic Chemistry, Siberian Branch
of Russian Academy of Sciences, Ac. Lavrentyev Ave. 3,
Novosibirsk-90 630090, Russia
e-mail: pinakov@che.nsk.su

Table 1 Elemental composition and stoichiometry of $C_2F_xBr_z{\cdot}y_2CH_3COCH_3$ (the second stage inclusion compounds) by elemental and gravimetric analyses

No	Elemental analysis				Gravimetry
	Found elements/mass%			The second stage inclusion compound formula x (±0.01), z (±0.003), y_2 (±0.011)	Values of y_2 (±0.011)
	C (±0.50)	F (±0.30)	Br (±0.30)		
1	57.41	36.47	1.67	$C_2F_{0.92}Br_{0.010}{\cdot}0.097CH_3COCH_3$	0.097
2	58.55	35.31	1.71	$C_2F_{0.87}Br_{0.010}{\cdot}0.094CH_3COCH_3$	0.094
3	63.32	31.14	1.71	$C_2F_{0.69}Br_{0.009}{\cdot}0.073CH_3COCH_3$	0.073
4	69.85	24.70	1.70	$C_2F_{0.49}Br_{0.008}{\cdot}0.064CH_3COCH_3$	0.064

Table 2 FGIC-1 $C_2F_xBr_z{\cdot}y_1CH_3COCH_3$ properties

No	The first stage inclusion compound stoichiometry		Decomposition maximum (DTA)/°C (±0.4)	E_a (kJ/mol of the first stage compound)
	Δm/mass% (±0.2)	FGIC-1 formula y_1 (±0.015)		
1	14.7	$C_2F_{0.92}Br_{0.01}{\cdot}0.218CH_3COCH_3$	102.5	49.9
2	14.3	$C_2F_{0.87}Br_{0.01}{\cdot}0.209CH_3COCH_3$	105.1	59.0
3	14.2	$C_2F_{0.69}Br_{0.01}{\cdot}0.176\ CH_3COCH_3$	110.5	56.1 ± 3.1
4	12.5	$C_2F_{0.49}Br_{0.01}{\cdot}0.145\ CH_3COCH_3$	118.8	58.6

Δm the samples weight increase during the second to the first stage inclusion compound transformation ($m_{\text{FGIC-2}} = 100\%$)

E_a activation energy for FGIC-1 decomposition to FGIC-2 and gaseous $(CH_3)_2CO$

To continue research work of FGICs physicochemical properties, we investigated these compounds with acetone to obtain such relationship between $(CH_3)_2CO$ FGICs properties and host matrix composition. Acetone has low boiling point (329.3 K) which makes it convenient for laboratory work with its FGICs at a room temperature. These compounds were studied to investigate the influence of guest molecules nature as well as the influence of guest component boiling point and molecular sizes. Fluorinated graphite inclusion compounds with acetonitrile and chlorinated hydrocarbons have the same character of all parameters dependencies from matrix fluorination degree. Acetone molecule has its own symmetry C_{2v}, its sizes are 4.06 and 6.64 Å in minimal and maximal projections. Acetone molecule dipole moment is about 2.8 D at 298 K [5] which allows the synthesis of its compounds by the way of guest substitution [1–4, 6] to be possible. The capability of $(CH_3)_2CO$ FGICs for thermoanalytical investigations at a room and adjacent temperatures was anticipated as well. $(CH_3)_2CO$ saturation vapour pressure is about 26.7 kPa at 295.15 K [7], boiling point is 329.4 K. It allows making thermal investigations of FGIC-1 with acetone: their decomposition temperatures, due to previous experiments with less volatile guests [1–3], should be much lower than matrix destruction temperatures (500–600 K [8, 9]). In this work, the fluorinated matrices of common formula $C_2F_xBr_z$ with different fluorine contents were chosen as host components as insufficiently explored in the clathrate formation processes.

Experimental

Synthesis of FGICs with acetonitrile was thoroughly described in [1]. These compounds, stable in storage [9, 10], were used as source components for preparation of FGICs with acetone. Purified by known technology acetone [11] had melting point 178.7 K and boiling point 329.3 K.

Intercalates with acetone were synthesized by isopiestical method by the scheme shown in [2–4] for FGICs with chloroform, dichloroethane and methylene dichloride. The weighed samples of the second stage FGICs (FGIC-2) with acetonitrile (x = 0.92, 0.87, 0.69 and 0.49) were put into hermetic reactor above liquid CH_3CN to prepare the first stage FGICs (FGIC-1), secondary they were located into hermetic reactor with liquid $(CH_3)_2CO$ for 24 h and then were covered by liquid acetone for more effective guest substitution. Sample weights were 500–600 mg, samples were inserted into weighed cylindrical cells. After primary exposition in $(CH_3)_2CO$ these samples were dried in dry N_2 flow, then they were located above liquid $(CH_3)_2CO$ to repeat their saturation process. After 3–4 saturation–decomposition cycles, referring to infrared spectra of these compounds (Fig. 1a), all CH_3CN (Fig. 1b) was substituted

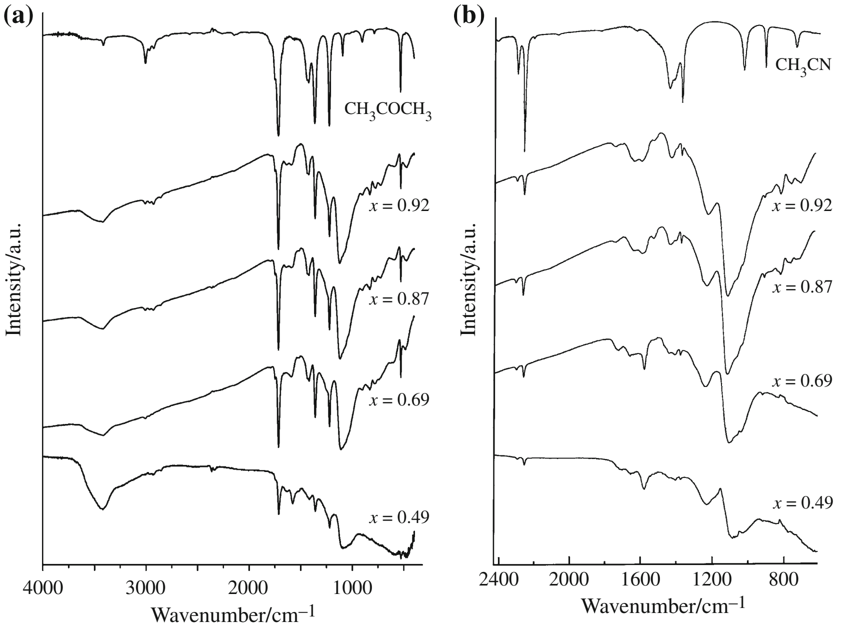

Fig. 1 Absorption IR-spectra for pure guests: acetone (**a**), acetonitrile (**b**) and their inclusion compounds based on matrices with $x = 0.92$, 0.87, 0.69 and 0.49 (spectra were obtained by Fourier spectrometer SCIMITAR FTS 2000; samples were prepared by standard technique by pressing of 3 mg samples into KBr pills)

to $(CH_3)_2CO$. Experiments allowed to determine the acetone FGIC-2 stoichiometry with good reproducibility, which follows from comparing of y_2 values obtained from elementary analysis and from gravimetric measurements (Table 1). The saturation procedure was repeated to determine the FGIC-1 stoichiometry (Table 2) and to obtain kinetic saturation curves to find out the time of full FGIC-2 saturation to FGIC-1 [1–4]. Under results of FGICs X-ray phase analysis, identity period of FGIC-1 with $(CH_3)_2CO$ was from 9.60 Å ($x = 0.92$) to 9.17 Å ($x = 0.49$), for FGIC-2 its value was from 15.57 Å ($x = 0.92$) to 14.68 Å ($x = 0.49$).

Thermal decomposition of $(CH_3)_2CO$ FGICs was explored by DTA thermoanalytical equipment [1]. The samples (30–40 mg of $(CH_3)_2CO$ FGIC-1 in small excess of liquid acetone) were placed into ampoules which had a bottlenecks and holes for thermocouples on their bottom external side. After deep cooling (liquid N_2) the capillaries (0.2 mm in diameter and 30–35 mm in length) were drawn; after equilibration (24–48 h) these capillaries were unsealed directly before DTA curves recording. Under these conditions, gas phase consisted of practically pure guest component with vapour pressure about 27 kPa [7] because FGIC s do not dissolve in $(CH_3)_2CO$. The accuracy of reversible phase transition temperature measurements was ±0.4 °C, heating rate was 3.2°/min.

The investigation of FGIC-1 thermolysis kinetics was undertaken by periodical fixing of FGIC-1 (obtained by isopiestical method) weight loss and subsequent mathematical treatment of original kinetic data (weight values from time). Temperature-controlled high-accuracy (±0.015 mg) weighing machine was applied for this research; measurements were taken under fixed temperatures (±0.2 K) in 292–313 K temperature range.

Results and discussion

Intercalates with $(CH_3)_2CO$ obtained by isopiestical method and dried in N_2 flow till constant weight had structure of FGIC-2 according to X-ray phase analysis results.

Saturation curves (dependence of FGIC-2 to FGIC-1 saturation depth from time) at 293.15 K are shown in Fig. 2. Equilibration time of saturation through gas phase

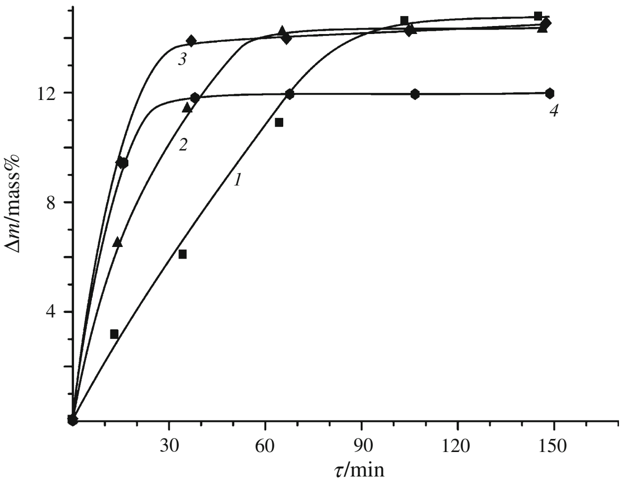

Fig. 2 FGIC-2—acetone saturation curves ($P \approx 1$ bar, $T = 295$ K) for $x = 0.92$, 0.87, 0.69 and 0.49 matrices

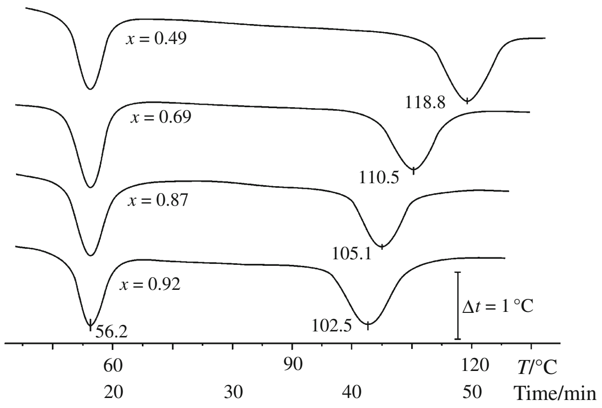

Fig. 3 DTA heating curves for acetone FGIC-1 with minor excess of free $(CH_3)_2CO$. Matrix fluorination degree (x) is specified under each curve

depended on host matrix fluorination degree and had values from 40–50 min for $x = 0.49$ to 210–240 min for $x = 0.92$.

FGIC-1 decomposition temperatures to FGIC-2 (X-ray phase analysis data) and gaseous guest had considerably higher values than the pure $(CH_3)_2CO$ boiling point (329.4 K) and increased with decrease of matrix fluorination degree (Fig. 3). FGIC-1 samples decomposition time at ambient atmosphere depended as on fluorination degree (x), as on temperature for each matrix; its values were from 70 ($x = 0.92$) to 800 min ($x = 0.49$) (Fig. 4a–d) in temperature range 292–313 K. It can also be seen that more developed surface of fluorinated graphite layers and their approaching with decrease of fluorination degree increase interactions as between guest component and graphite matrix, as between matrix layers within the scope of the whole clathrate system. These factors result in the kinetic stability increase of FGIC-1 based on less fluorinated matrices.

The experimental dependence of FGIC-1 deintercalation rate (transformation degree α from time τ) at ambient atmosphere for each temperature and matrix were processed by equation $\ln[-\ln(1-\alpha)] = n\ln(K/n) + n\ln\tau$ which comes from 2-fold logarithm of Erofeev's equation [12] with respect to Sakovich's relation [13], where n is non-dimensional value, K is generalized rate constant (s^{-1}). These equations were used by a number of researchers to investigate thermal decomposition kinetics of different compounds [14] and to research kinetics of phase and polymorphic transitions, dissolution, and adsorption processes [15]. Kinetic curves (Fig. 4) can be approximated by nearly parallel lines (Fig. 5); it can be explained by kinetic parameter n constancy for each matrix in the temperature range explored.

'Effective' activation energies found from the ln $K - 10^4/T$ dependencies line slope (Fig. 6) had values 49.9, 59.0, 56.1 ± 3.1 and 58.6 kJ/mol for FGIC-1 with $x =$ 0.92, 0.87, 0.69 and 0.49 respectively, which is considerably higher than evaporation enthalpy of pure $(CH_3)_2CO$ in explored temperature range ($\Delta H^\circ = 32.29$ kJ/mol at 300.6 K and 29.11 kJ/mol at 329.3 K [16]). These values exceed E_a for FGICs with acetonitrile (51–53 kJ/mol [1]), they are considerably higher than E_a for FGICs with

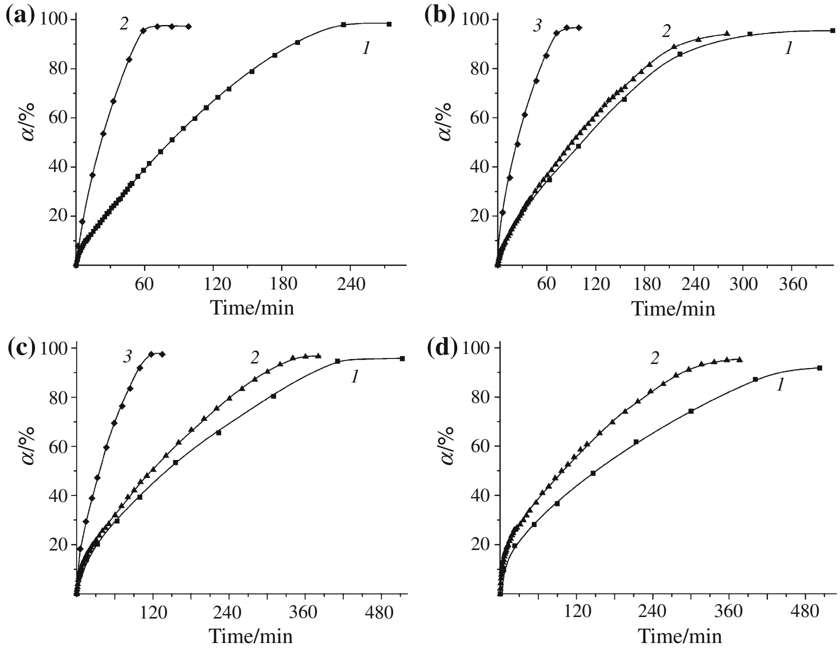

Fig. 4 Isothermal decomposition curves for FGIC-1 with acetone: **a** $x = 0.92$ at 292.3 K (*1*) and 313.2 K (*2*); **b** $x = 0.87$ at 293.2 K (*1*), 295.6 K (*2*) and 313.2 K (*3*); **c** $x = 0.69$ at 293.2 K (*1*), 296.9 K (*2*) and 313.2 K (*3*); **d** $x = 0.49$ at 293.2 K (*1*) and 299.3 K (*2*)

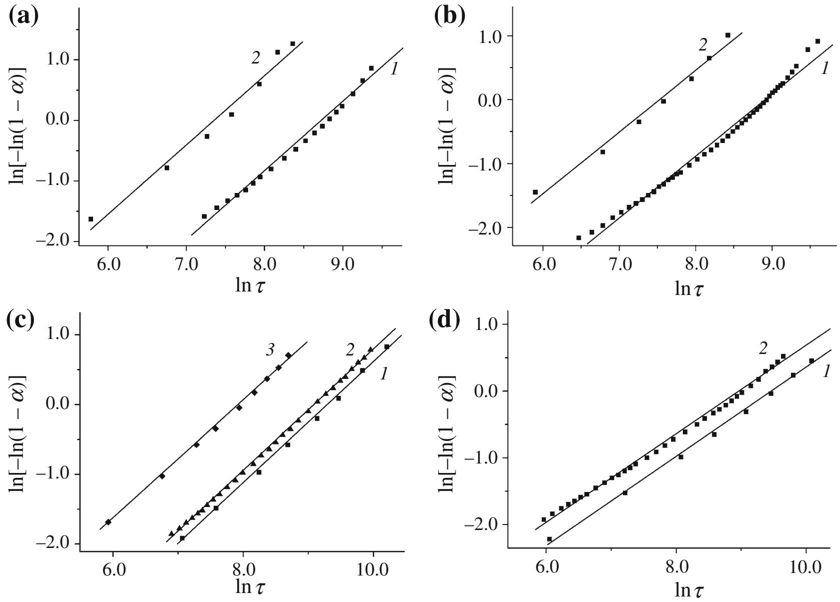

Fig. 5 Dependences of ln[−ln(1-α)] versus ln(τ, s), numbers of curves correspond to those in Fig. 4

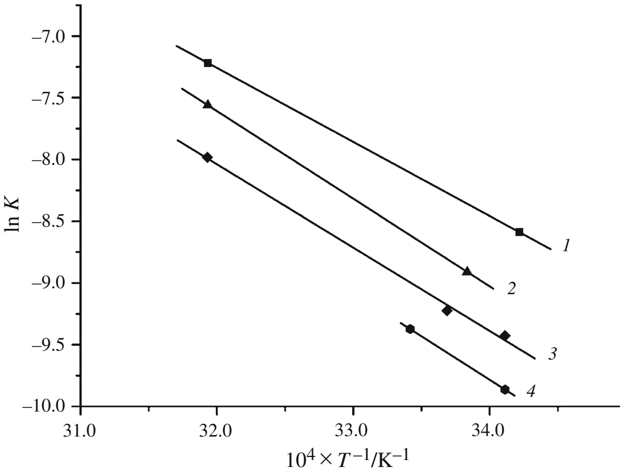

Fig. 6 Dependence of ln *K* versus 10^4/T: $x = 0.92$ (*1*), 0.87 (*2*), 0.69 (*3*) and 0.49 (*4*)

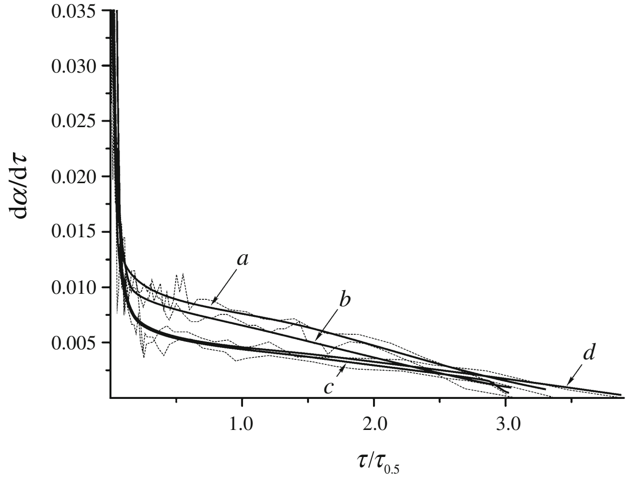

Fig. 7 Dependences of dα/dτ versus reduced time $\tau/\tau_{0.5}$: $x = 0.92$, T = 292.3 K (*a*); $x = 0.87$, T = 295.6 K (*b*); $x = 0.69$, T = 296.9 K (*c*); $x = 0.49$, T = 299.3 K (*d*)

chloroform (42–51 kJ/mol [2]) and methylene dichloride (39–51 kJ/mol [4]), but at the same time they are smaller than “effective” activation energy values for the same *x* dichloroethane FGICs decomposition (53–66 kJ/mol [3]).

To determine the mechanisms of acetone FGIC-1 deintercalation reactions under isothermal conditions, we compared dα/dτ dependences from reduced time $\tau/\tau_{0.5}$ [17]. These curves character (Fig. 7) shows, according to this reference, about explicit prevalence of phase boundary reaction mechanism for $x = 0.49$–0.92 in the temperature range explored.

Conclusions

Generalized Erofeev’s equation was applied specially to estimate decomposition kinetics parameters. This equation allowed showing the prevalence of phase boundary reaction for $(CH_3)_2CO$ FGIC-1 deintercalation practically irrespectively of matrix fluorination degree. The *n* coefficient has values of 1.14–1.15, 0.96–0.97, 0.86–0.87 and 0.66–0.67 for $x = 0.92$, 0.87, 0.69 and 0.49, respectively. According to Patrilyak [14] and Logvinenko [17], values $n > 1$ ought to correspond with kinetically controlled reactions, $n < 1$ with diffusionally controlled; graphical view of these reactions assumes the reaction mechanism on phase boundary. However, the diffusion hindrance increases with decrease of fluorination degree for $(CH_3)_2CO$ FGIC-1 deintercalation, too.

Effective thickness of guest layer (about 3.60–3.70 Å for all matrices) has considerably smaller value than minimal Van-der-Waals projection size of $(CH_3)_2CO$ molecule (4.06 Å), it denotes the close packing of guest molecules fragments in the cavities of the matrix surface. This conclusion coming from acetonitrile, chloroform, dichloroethane and methylene dichloride FGICs properties investigation [1–4] is applicable for acetone and may be similar for all types of small organic guest molecules chemically which are inert to fluorinated graphite matrices: with decrease of fluorination degree diffusive obstacles become more and more substantial, but their influence (with x change) on activation energy values is scarcely noticeable.

Analysis of the guest content dependencies from matrix fluorination degree for FGIC-2 (Table 1) and FGIC-1 (Table 2) with acetone displays guest content decrease with decrease of fluorination degree x as in previously investigated clathrates with other guest components [1–4]. For $x = 0.92$–0.87 included component content was similar within error, but for $x < 0.87$ it evidently decreased. Reversible deintercalation temperature increase with decrease of fluorination degree (Fig. 3) can be interpreted by host–guest and host–host interactions growth. FGIC-1 activation energies also tend to grow with decrease of fluorine content in carbon matrix.

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