

The relationship between properties of fluorinated graphite intercalates and matrix composition

Part 4. Intercalates with methylene dichloride

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Abstract Inclusion compounds (intercalates) of fluorinated graphite matrix with methylene dichloride ($C_2F_xBr_z \cdot yCH_2Cl_2$, $x = 0.49, 0.69, 0.87, 0.92$, $z \approx 0.01$) were synthesized by guest substitution from acetonitrile to methylene dichloride. The kinetics of the thermal decomposition (the first stage of filling \rightarrow the second stage of filling) was studied under isothermal conditions at 291–303 K. The relationship between the structure of host matrices with thermal properties and kinetic parameters of inclusion compounds is discussed.

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

Introduction

In the articles [1–3] the fluorinated graphite inclusion compounds ($C_2F_xBr_z \cdot y_1G$, where $x = 0.49–0.92$, $z = 0.008–0.010$, y_2 and y_1 —number of the guest component molecules per two C-atoms of the fluorinated graphite matrix for the second and the first stage of filling respectively) were investigated by physicochemical methods. Acetonitrile CH_3CN [1], chloroform $CHCl_3$ [2] and 1,2-dichloroethane $C_2H_4Cl_2$ [3] were used as included guest components. These molecules differ by nature, size and their own

symmetry. It was shown by recording of the saturation curves that number of the guest molecules per two C-atoms of matrix reduced with decrease of carbon matrix fluorination degree. By determination of the effective activation energies it was shown that kinetic stability is nearly similar within error for intercalates with CH_3CN and $CHCl_3$, but it has a visible increase with decrease of the fluorination degree for inclusion compounds with 1,2-dichloroethane. But at the same time thermodynamic stability of the first stage inclusion compounds evidently grows with decrease of fluorination degree from 0.92 to 0.49 both for intercalates with acetonitrile and with chlorinated hydrocarbons. The topochemical mechanism of deintercalation process for inclusion compounds with acetonitrile is complicated: it gradually changes from phase boundary reaction (the most on $x = 0.92$, where in the beginning the nucleation mechanism is observed) to diffusion ($x = 0.49$) which affects greater with reduction of matrix fluorination degree. In the case of chloroform there was no nucleation stage in deintercalation, the affect of phase boundary reaction considerably reduced with decrease of x , being minor even with $x = 0.92$. In the inclusion compounds with $C_2H_4Cl_2$ deintercalation mechanism was only diffusive, numeric affect of diffusion increased with decrease of fluorination degree. The increase of diffusion interactions contribution can be explained by reduction of interlayer space in clathrate system from 9.47 to 9.02 Å in the inclusion compounds with acetonitrile [1], from 10.03 to 9.61 Å with chloroform [2], from 10.28 to 9.80 Å for the fluorinated graphite inclusion compounds with 1,2-dichloroethane [3]. At the same time the first stage inclusion compounds of the least fluorinated matrix ($x = 0.49$) are formed with the highest rate which could be explained by the loss of host–host interactions and the increase of host–guest interactions with decrease of x .

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To continue investigations of physicochemical properties of the fluorinated graphite intercalates with chlorinated hydrocarbons, in this article the fluorinated graphite intercalates with methylene dichloride (dichloromethane, CH_2Cl_2) were investigated. Methylene dichloride has comparatively low boiling point which, however, allows to work with its intercalates based on fluorinated graphite matrices at a room temperature. The methylene dichloride molecule has its own symmetry C_{2v} , minimum and maximum projection sizes of CH_2Cl_2 molecule are 4.11 and 6.33 Å respectively. Dipole moment of the CH_2Cl_2 molecule is about 1.55 D at 298 K [4], which allows to synthesize inclusion compounds with methylene dichloride by substitution of CH_3CN to this substance [1, 2, 5] for investigation of the matrix composition influence on synthesized compounds properties. We expected the intercalates with methylene dichloride to be suitable for thermoanalytic investigations within 291–303 K temperature range. Methylene dichloride has vapour pressure about 47.4 kPa (0.474 bars) at 293.15 K, boiling point of CH_2Cl_2 is 313.9 K. It allows to make thermoanalytic investigations of the first stage inclusion compounds, because their decomposition temperatures, as reported in [1–3], are supposed to be considerably lower than the temperature of matrix destruction (500–600 K [6, 7]). In this work we chose $\text{C}_2\text{F}_x\text{Br}_z$ matrices with different fluorine content as host components, because until recently they are insufficiently explored in clathrate formation processes.

Experimental

Synthesis of layered inclusion compounds with acetonitrile was described thoroughly in [1]. It was carried out by obtaining the first stage inclusion compound of graphite with Br_2 , oxidation by the fluorinating agent (BrF_3 – Br_2 solutions) in hermetic reactor during 14–360 days with subsequent substitution of intercalated aggressive media to acetonitrile. Stable intercalates with acetonitrile [7, 8] were used as initial components for the synthesis of inclusion compounds with methylene dichloride. Refined by known technology methylene dichloride [9] had melting point 176.5 K and boiling point 313.9 K.

The inclusion compounds with methylene dichloride were prepared by isopiestic method as it was shown in [2, 3] for compounds with chloroform and 1,2-dichloroethane. Samples of the second stage inclusion compounds with acetonitrile ($x = 0.92, 0.87, 0.69$ and 0.49) were placed above liquid acetonitrile to prepare the first stage inclusion compounds, then they were transported to the hermetic reactor above liquid methylene dichloride, exposed for nearly 24 h and then filled by liquid methylene dichloride for more effective substitution of acetonitrile into new

guest molecule. Samples were about 500–600 mg, they were held by weighed cylindrical cells. After the first exposure in methylene dichloride these samples were dried for nearly 24 h in the N_2 flow, and then they were placed above methylene dichloride to saturate them again. After 3–4 cycles of saturation and decomposition, as it was shown by IR-spectra (Fig. 1a), all acetonitrile (Fig. 1b) was substituted to methylene dichloride. (Spectra were taken on Fourier spectrometer SCIMITAR FTS 2000; samples were prepared by standard method—3 mg of inclusion compound were pressed in tablets with KBr.) The new second stage inclusion compounds were saturated isopiastically again to determine the end time of saturation by stopping the mass increase [1–3]. These experiments allowed defining the stoichiometry of the first and the second inclusion compounds with methylene dichloride with a good reproducibility. It comes from comparison of stoichiometric coefficients y_2 , which were obtained from the chemical analysis data and results of gravimetric measurements (Table 1). As it comes from X-ray diffraction analysis of intercalates with methylene dichloride, identity period (I_c) of the first stage inclusion compounds was between 9.82 Å for $x = 0.92$ and 9.32 Å for $x = 0.49$, for the second stage inclusion compound—between 15.84 Å for $x = 0.92$ and 14.74 Å for $x = 0.49$.

Thermal decomposition of the first stage inclusion compounds with methylene dichloride was investigated by the homemade differential thermal analysis equipment [1]. Samples (30–40 mg of the first stage inclusion compound with slight excess of methylene dichloride) were placed to ampoules with bottleneck and the hollow for thermocouple in the bottom. After deep cooling (in liquid nitrogen) we made capillaries (≈ 0.2 mm diameter and 30–35 mm length) which were opened after equilibrium reaching (20–40 h) directly before heating curve recording. In this

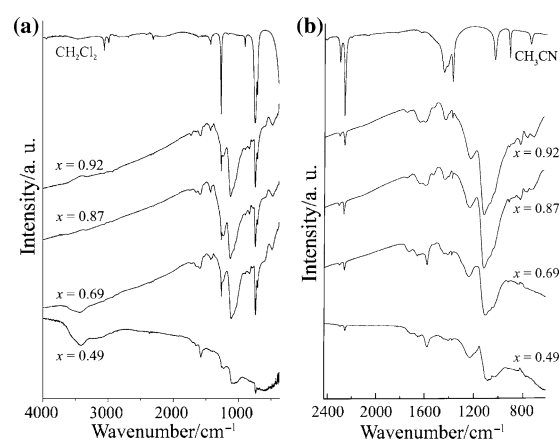


Fig. 1 IR-absorption spectra for pure guests: methylene dichloride (a), acetonitrile (b), and their second stage inclusion compounds based on $x = 0.92, 0.87, 0.69$ and 0.49 matrices

Table 1 Elemental composition and stoichiometry of $C_2F_xBr_z \cdot y_2CH_2Cl_2$ (the second stage inclusion compounds) by elemental and gravimetric analysis and their properties

No	Colour	Elemental analysis				The second stage inclusion compound formula, $x (\pm 0.01), z (\pm 0.003), y_2 (\pm 0.011)$	Gravimetry Values of $y_2 (\pm 0.011)$
		Found elements, mass. %					
		C (± 0.50)	F (± 0.30)	Cl (± 0.30)	Br (± 0.30)		
1	Yellow	49.31	34.07	14.65	1.56	$C_2F_{0.92}Br_{0.010} \cdot 0.106CH_2Cl_2$	0.106
2	Light green	50.00	32.61	15.39	1.58	$C_2F_{0.87}Br_{0.010} \cdot 0.110CH_2Cl_2$	0.110
3	Dark green	54.88	28.60	14.54	1.57	$C_2F_{0.69}Br_{0.009} \cdot 0.094CH_2Cl_2$	0.094
4	Black	62.19	23.27	12.59	1.60	$C_2F_{0.49}Br_{0.008} \cdot 0.071CH_2Cl_2$	0.071

$I_c, \text{Å}$ —identity period along c -axis. (Crystallograms were taken at room temperature on the DRON-SEIFERT-RM4 diffractometer: CuK_α -radiation, graphite monochromator on the reflected beam, scintillation detector with amplitude discrimination)

experimental method the gas phase consists of pure guest component, because inclusion compound is practically insoluble in methylene dichloride; it has vapour pressure about 47 kPa [10]. Accuracy of temperature measurement was about $\pm 0.4 \text{ }^\circ\text{C}$; heating rate was $3.2 \text{ }^\circ\text{C min}^{-1}$.

Investigations of kinetic parameters for thermal decomposition of the first stage inclusion compound were carried out by periodical fixing of the first stage inclusion compound sample weight loss. These original kinetic data were processed mathematically to calculate required values. We used thermostatically controlled analytic balance ($\pm 0.015 \text{ mg}$), measurements were taken at fixed temperatures ($\pm 0.2 \text{ K}$) from 291 to 303 K.

Results and discussion

The first stage inclusion compounds with CH_2Cl_2 obtained by isopiestic method after drying to constant mass in the dry N_2 flow transformed into the second stage inclusion compound (according to X-ray structure analysis). They

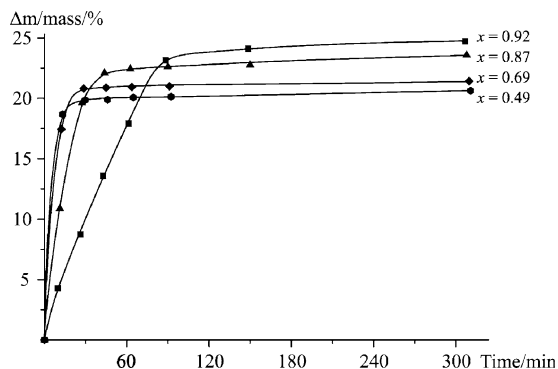


Fig. 2 Saturation curves of the second stage inclusion compound with methylene dichloride ($P \approx 1 \text{ bar}$, $T = 293 \text{ K}$) for $x = 0.92$, 0.87, 0.69 and 0.49 compounds

differed by colour—from yellow through pale green to dark green and black with decrease of fluorination degree from 0.92 to 0.49.

Saturation curves of the initial second stage inclusion compound by methylene dichloride (increase of saturation depth versus time) at 293.15 K are shown on Fig. 2. Equilibration time of satiety through gas phase depended from the matrix fluorination degree and varied from 60 min for $x = 0.49$ to 240–300 min for $x = 0.92$. Investigations of samples saturated by methylene dichloride by X-ray diffraction analysis showed the change of interplanar spacing (Table 2) in comparison with the second stage inclusion compounds and confirmed the formation of the first stage inclusion compound with one guest layer after one host layer.

Decomposition temperatures of the first stage inclusion compounds to the second stage (shown by RCA data) and gaseous guest were much higher than the boiling point of the pure guest (313.9 K) and increased with decrease of matrix fluorination degree. The formation of the individual first stage inclusion compound phases for all considered fluorination degrees is proved by the fact of their regeneration (according to RCA data) after thermal decomposition in DTA chamber, cooling and placing above methylene dichloride at a room temperature for 24 h. DTA heating curves were reproduced many times as well. The decomposition time of the first stage samples depended both on fluorination degree x and on temperature with constant x (Fig. 3a–d); it lasted from 25 ($x = 0.92$) to 130 min ($x = 0.49$) in the temperature range 292–303 K. It is obvious that more developed “surface” of graphite layers and their approach with decrease of x makes host–guest and host–host interactions stronger in the whole clathrate system, so it appears in the first stage inclusion compound stability increase with decrease of their fluorination degree.

Experimental data of decomposition degree α from time τ for each matrix at different temperatures were mapped by

Table 2 Properties of the first stage inclusion compounds $C_2F_xBr_z \cdot y_1 CH_2Cl_2$

No	Colour	The first stage inclusion compound stoichiometry		Decomposition maximum (DTA), °C (± 0.4)	E_a^b (kJ/mol of the first stage compound)
		Δm^a , mass. % (± 0.2)	Formula y_1 (± 0.015)		
1	Yellow	24.3	$C_2F_{0.92}Br_{0.01} \cdot 0.253CH_2Cl_2$	70.5	46.0 ± 3.0
2	Light green	22.5	$C_2F_{0.87}Br_{0.01} \cdot 0.244CH_2Cl_2$	79.0	47.0 ± 3.4
3	Dark green	21.3	$C_2F_{0.69}Br_{0.01} \cdot 0.209CH_2Cl_2$	86.0	39.3 ± 0.8
4	Black	20.0	$C_2F_{0.49}Br_{0.01} \cdot 0.165CH_2Cl_2$	90.9	50.7 ± 3.0

^a Δm —sample mass increase during the second to the first stage inclusion compound transformation

^b E_a —activation energy of the first stage inclusion compound decomposition reaction into the second stage inclusion compound and gaseous methylene dichloride

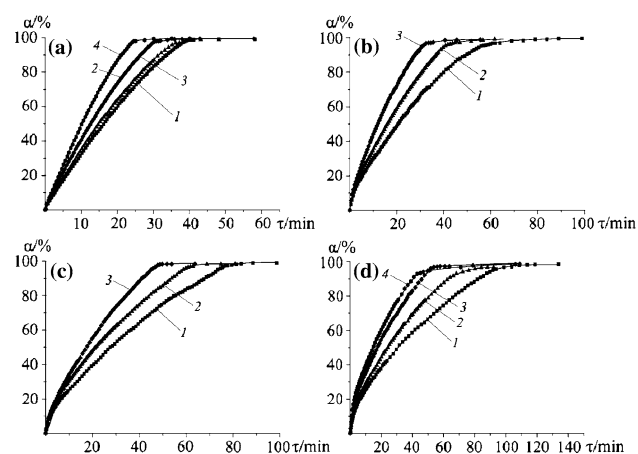


Fig. 3 Isothermic decomposition curves for the first stage inclusion compounds with methylene dichloride: **a** $x = 0.92$ at 293.3 K (1), 294.5 K (2), 297.8 K (3) and 300.3 K (4); **b** $x = 0.87$ at 292.3 K (1), 296.2 K (2) and 300.0 K (3); **c** $x = 0.69$ at 292.5 K (1), 295.7 K (2) and 299.5 K (3); **d** $x = 0.92$ at 291.9 K (1), 295.9 K (2), 299.7 K (3) and 302.6 K (4)

the equation $\ln[-\ln(1-\alpha)] = n \ln(K/n) + n \ln \tau$ (getting after taking two-fold logarithm from the Erofeev's equation [11] subject to the Sakovich's correlation [12]), where n is non-dimensional coefficient, K is generalized rate constant, s^{-1} . Equation shown above was used by many authors for kinetic investigations of both thermal decomposition of different compounds (including carbamide- n -alkanes clathrates [13]) and phase transitions, solvation and absorption [14]. Kinetic curves (Fig. 3) can be approximated by nearly parallel lines (Fig. 4), it points on the kinetic parameter n constancy in considered range of temperatures.

The “effective” activation energy (E_a) values found from line slope of $\ln K - 10^4/T$ (Fig. 5a–d) are 46.0 ± 3.0 , 47.0 ± 3.4 , 39.3 ± 0.8 and 50.7 ± 3.0 kJ/mol (per 1 mol of the first stage inclusion compound) for $x = 0.92$, 0.87, 0.69 and 0.49 respectively. It has higher value than the evaporation enthalpy of pure methylene dichloride in explored range of temperatures ($\Delta H_{vap} = 28.84$ kJ/mol at

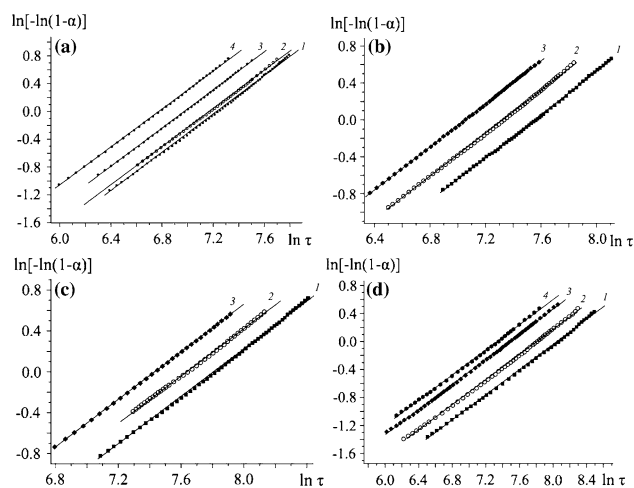


Fig. 4 Dependence of $\ln[-\ln(1-\alpha)]$ vs. $\ln(\tau, s)$. Fluorination degrees and temperatures are listed on Fig. 3

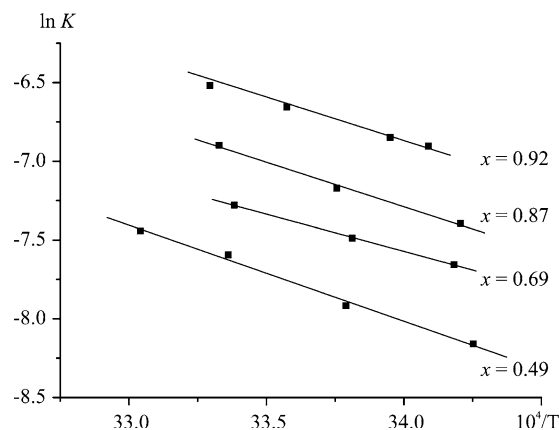


Fig. 5 Dependence of $\ln K$ vs. $10^4/T$: $x = 0.92, 0.87, 0.69$ and 0.49

298.15 K and 28.01 kJ/mol at 313.70 K [15]). These values are approximately similar to deintercalation E_a of fluorinated graphite intercalates with acetonitrile (51–53 kJ/mol [1]) and chloroform (42–51 kJ/mol [2]) based on the same matrices, but they are smaller than

“effective” activation energies of dichloroethane compounds deintercalation (53–66 kJ/mol [3]).

For determination of the first stage inclusion compound decomposition reaction mechanism in isothermal conditions we checked dependencies of $dz/d\tau$ from reduced time $\tau/\tau_{0.5}$ [15]. Analysis of these dependencies curves (Fig. 6) indicates, in accordance with the reference work, nucleation (in the beginning) and phase boundary mechanism for compounds with $x = 0.92$, prevalence of phase boundary reaction for $x = 0.87$ and 0.69 and diffusion mechanism for $x = 0.49$ in investigated temperature interval.

Conclusions

We used generalized Erofeev’s equation for the estimation of decomposition kinetic parameters. Choice of this equation allowed us to verify the change of the first stage inclusion compounds deintercalation mechanism from nucleation through phase boundary reaction to diffusion mechanism with decrease of matrix fluorination degree. Coefficient n had values of 1.37–1.38, 1.16–1.17, 1.15–1.16 and 0.89–0.90 for $x = 0.92$, 0.87, 0.69 and 0.49, respectively in $C_2F_xBr_z \cdot yC_2H_4Cl_2$ compounds. Values $n > 1$ could correspond to reaction with kinetic control, $n < 1$ corresponds to reactions with diffusion control [13, 16]. So in the case of methylene dichloride as guest component the decrease of matrix fluorination degree results in the diffusion hindrance increase as well. Sufficiently large activation energies confirm the so-called “inner diffusion”.

Effective thickness of the guest layer (about 3.8–3.9 Å for all matrices) is considerably less than CH_2Cl_2 molecule size in the minimal projection (4.11 Å), so CH_2Cl_2 molecules are distributed in the interlayer space by the principle of “the closest packing” of molecules into the cavities of relief “surface” of matrix layers. The fluorination decrease

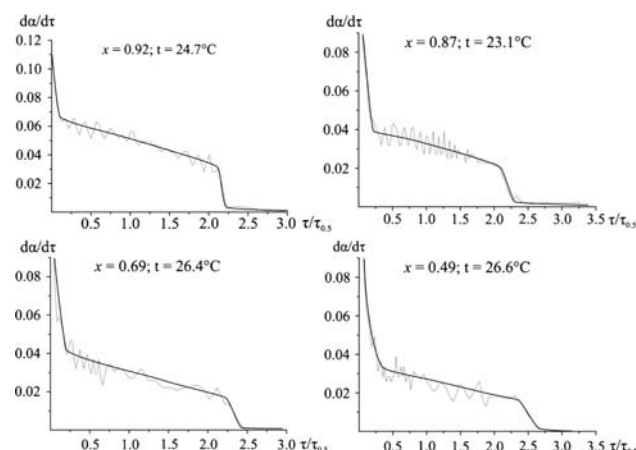


Fig. 6 Dependences of $dz/d\tau$ versus half-reaction time $\tau/\tau_{0.5}$. Fluorination degrees and temperatures are listed on figure

increases points of guest–host contacts and the strength of Van der Waals forces; these result in greater kinetic and thermodynamic stability of common intercalate system. This conclusion, which results from investigations of fluorinated graphite intercalates with acetonitrile [1], chloroform [2] and 1,2-dichloroethane [3], is applicable with CH_2Cl_2 inclusion compounds with the same fluorinated graphite matrices and has seemingly common principle: with decrease of matrix fluorination degree the diffusion obstacles become more and more considerable, although the activation energies change not much with matrix fluorination degree (x).

Analyzing stoichiometry dependencies of the second (Fig. 7) and the first (Fig. 8) stage inclusion compounds from fluorination degree x for all investigated guest molecules (CH_3CN , $CHCl_3$, $C_2H_4Cl_2$, CH_2Cl_2) we can see decrease of included molecules number with decrease of x . For $x = 0.92$ – 0.87 number of intercalated molecules was nearly constant within error, but for $x < 0.87$ it visibly tends to decrease. Dependence of the reversible first to second stage deintercalation temperatures from fluorination degree (Fig. 9) can be explained by the increase of both “host–guest” and “host–host” intermolecular interactions. With decrease of fluorination degree the increase of deintercalation temperature is observed; in all cases the first stage compound deintercalation temperatures are considerably higher than boiling points of pure guest components. Activation energies of deintercalation (Fig. 10) tend to grow with decrease of x , this tendency is evident for inclusion compounds with chloroform and 1,2-

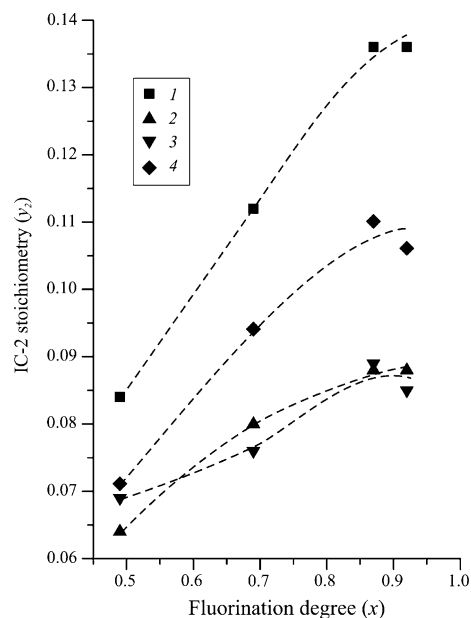


Fig. 7 Dependences of the second stage inclusion compounds stoichiometry with CH_3CN (1), $CHCl_3$ (2), $C_2H_4Cl_2$ (3) and CH_2Cl_2 (4) versus matrix fluorination degree (x)

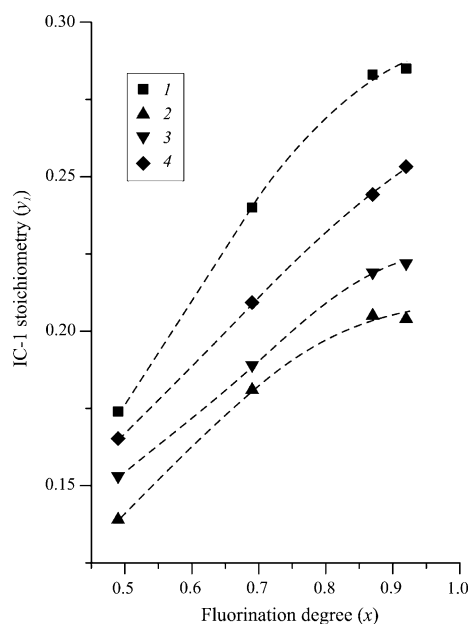


Fig. 8 Dependences of the first stage inclusion compounds stoichiometry with CH_3CN (1), CHCl_3 (2), $\text{C}_2\text{H}_4\text{Cl}_2$ (3) and CH_2Cl_2 (4) versus matrix fluorination degree (x)

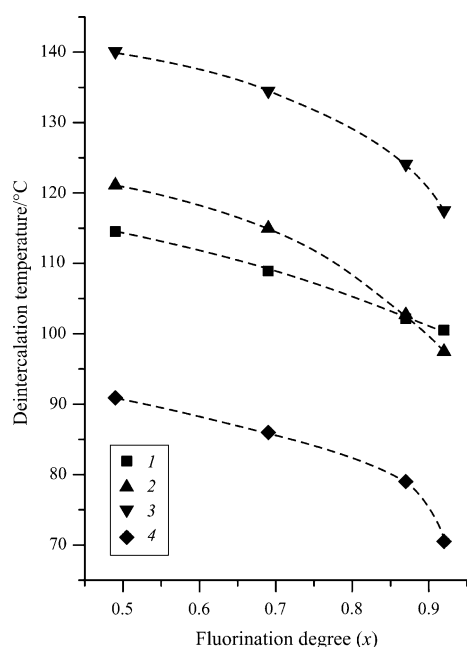


Fig. 9 Dependences of the first stage inclusion compounds reversible deintercalation temperature versus matrix fluorination degree (x): for CH_3CN (1), CHCl_3 (2), $\text{C}_2\text{H}_4\text{Cl}_2$ (3) and CH_2Cl_2 (4)

dichloroethane, not evident for compounds with acetonitrile. Compounds with methylene dichloride keep this tendency—but inclusion compound based on $x = 0.69$ matrix drops out from this dependence. It can be supposed that $\text{C}_2\text{F}_{0.69}$ matrix has such distribution of F atoms which results in lesser kinetic difficulties in comparison with

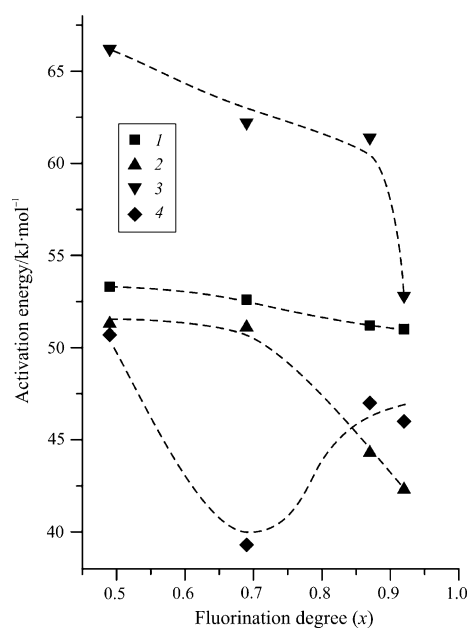


Fig. 10 Dependences of the first stage inclusion compounds reversible deintercalation activation energies versus matrix fluorination degree (x): for CH_3CN (1), CHCl_3 (2), $\text{C}_2\text{H}_4\text{Cl}_2$ (3) and CH_2Cl_2 (4)

other researched matrices during methylene chloride molecules emission to gas phase.

Looking at temperature dependences of deintercalation half reaction time ($\tau_{0.5} - T$) for all fluorinated graphite intercalates with chlorinated hydrocarbons [2, 3] (Fig. 11, half reaction time in logarithmic scale) we can see the influence of guest component boiling point and its molecular mass on the total stability of these compounds at a room temperature, as against of kinetically inert cellular inclusion compounds (for example, hydroquinone clathrates with Ar, Kr and Xe, which can be kept in unchanged state for years without decomposition to α -hydroquinone and gaseous guest [17]). Kinetic hindrances are not the

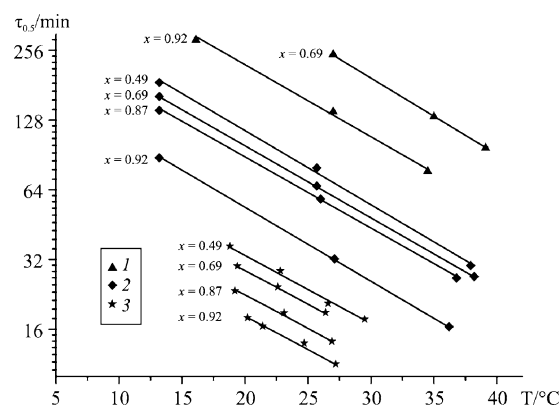


Fig. 11 Dependences of the reversible deintercalation half-reaction time $\tau/\tau_{0.5}$ versus temperature for the first stage inclusion compounds with $\text{C}_2\text{H}_4\text{Cl}_2$ (1), CHCl_3 (2) and CH_2Cl_2 (3) based on matrices of different fluorination degree

limiting factor of the first stage fluorinated graphite inclusion compounds total stability due to their layered structure—these compounds with four investigated guest components (including acetonitrile) are kinetically labile, their total stability at room temperature is determined mostly by thermodynamic properties of guest components. Unlike the first stage inclusion compounds, the second stage compounds have the structure which results in their kinetic inertness because of matrix layer deformation. It causes closure of communication lines between the interlayer space and ambient atmosphere, so open interlayer spaces transform into closed cellular chambers of host matrix. Therefore, emission of guest molecules from the first stage inclusion compounds is impossible up to the matrix destruction temperature (≈ 300 °C). Also, destruction of the guest molecules is possible at these temperatures, because guest component ought to chemically react with HF, which escapes during thermal decomposition of the C_2F_x matrix.

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