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THE RELATIONSHIP BETWEEN PROPERTIES OF FLUORINATED GRAPHITE INTERCALATES AND MATRIX COMPOSITION
Part II. Intercalates with chloroform

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Inclusion compounds (intercalates) of fluorinated graphite matrix with chloroform ($C_2F_xBr_z{\cdot}yCHCl_3$, x=0.49, 0.69, 0.87, 0.92, z=0.01) were synthesized by guest substitution from acetonitrile to chloroform. The kinetics of the thermal decomposition (the 1st stage of filling → the 2nd stage of filling) was studied under isothermal conditions at 286–311 K. The relationship between the structure of matrices intercalates with thermal properties and kinetic parameters of inclusion compounds is discussed.

Keywords: *fluorinated graphite, inclusion compounds, intercalates, isothermal kinetics, thermal stability*

Introduction

It was shown earlier [1] by DTA, XRD, determination of activation energies and decomposition mechanism that the kinetic stability of inclusion compounds series $C_2F_xBr_z{\cdot}y_1CH_3CN$ (x=0.49–0.92; y_1=0.174–0.288; z=0.008–0.010) is nearly similar within error value. But thermodynamic stability (according to DTA results at guest pressure ≈100 kPa) considerably increases with decrease of x from 0.92 to 0.49 and y_1 from 0.288 to 0.174. Decomposition of the 1st stage inclusion compound into the 2nd stage inclusion compound and gaseous guest proceeds by complex mechanism: nucleation, phase boundary reaction and diffusion. It is worth to note that decomposition topochemical mechanism is complex: it gradually changes from phase boundary reaction (the most on x=0.92) to diffusion (x=0.49), so it depends on the fluorination degree. The decreasing of fluorine atoms numbers must increase the diffusion hindrance through interlayer space because of interplanar spacing decrease from 9.47 till 9.02 Å. Nevertheless, the 1st stage inclusion compound of the least fluorinated matrix (x=0.49) is formed with the highest rate which can be explained by the loss of host-host interactions and increase of host–guest interactions with decrease of x.

Investigations of decomposition kinetics of such inclusion compounds with other organic guest molecules with different nature, shape and size have a reasonable practical value. In this work chloroform ($CHCl_3$) is used as the guest. Its molecule size is 6.44–7.14 Å [2], dipole moment is about 1.5 D [3], which allows synthesizing inclusion compounds with chloroform by other guest substitution [4].

Intercalates with chloroform appear to be suitable for thermoanalytic investigations because in the required temperature range chloroform doesn't react with fluorinated matrix. The symmetry of the chloroform molecule is similar to this for acetonitrile (C_{3v} group), but it has a different geometry which can affect to kinetic parameters and the decomposition mechanism of the 1st stage inclusion compounds for different fluorination degree.

Chloroform has vapour pressure 20.7 kPa (0.207 bar) at 293.15 K and boiling point at 334.85 K. It allows to make thermoanalytic investigations of these compounds, because their decomposition temperature is considerably lower than the temperature of matrix destruction (≈600 K [5]).

We chose fluorinated graphite matrices with different fluorine content as host components. Their formulae were defined by elemental analysis with maximum possible accuracy in [1, 6]. The 1st stage inclusion compounds with different fluorinated matrices are still insufficiently explored, mainly interplanar distances of x≈0.9 inclusion compounds were found [7].

Experimental

Synthesis of these compounds with acetonitrile is described thoroughly in [1]. It was carried out by graphite oxidation by fluorinating agent (BrF_3–Br solutions) with subsequent substitution of intercalated aggressive media to acetonitrile. Stable interca-

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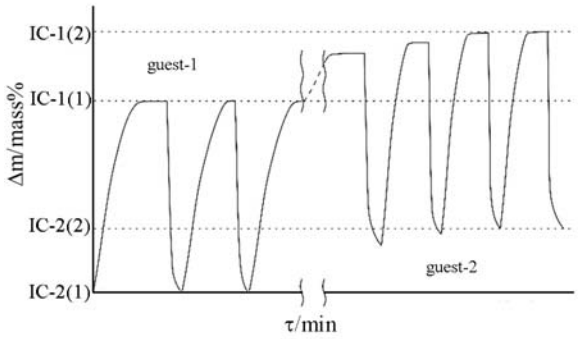

Fig. 1 Model of guest substitution in C_2F_x inclusion compounds interlayer spaces (guest-1 is acetonitrile, guest-2 is chloroform)

lates with acetonitrile [6] were used as initial components for synthesis of inclusion compounds with chloroform. Refined by known technology chloroform [8] had melting point 209.6 K and boiling point 334.8 K.

Inclusion compounds with chloroform were prepared by isopiestic method as it was shown on Fig. 1. Initial samples of the 2nd stage inclusion compounds with acetonitrile (x=0.49, 0.69, 0.87 and 0.92) were placed above liquid acetonitrile to prepare the 1st stage inclusion compounds by 'unsealing' them (IC-1(1) on Fig. 1; Fig. 2b). Then they were quickly transported to hermetic reactor above liquid chloroform, exposed for nearly 24 h and then filled by liquid chloroform for more effective substitution of acetonitrile into new guest molecule. Samples were 500–600 mg, they were held by cylindrical cells. After the first exposure in chloroform these samples were dried for 2–3 days in the N_2 flow (Fig. 2d), then they were placed above chloroform to 'unseal' and saturate them again. After 3–4 cycles of saturation and decomposition, as it was shown by IR-spectra (Fig. 3a), all acetonitrile was substituted to new guest component – chloroform (Fig. 3b). The new 2nd stage inclusion compound was saturated isopiestically again to get kinetic saturation curves – point-by-point dependences of sample mass increase from reaction time. The end of reaction was determined by reaching the plateau – stopping of mass increase during 1–2 h. These experiments allowed defining the stoichiometry of the 1st and the 2nd inclusion compounds with chloroform with good reproducibility (Tables 1, 2). It comes from comparison of stoichiometric coefficients y_2 for the 2nd stage inclusion compound (Table 1), which were obtained from chemical analysis data and results of gravimetric measurements.

Thermal decomposition of the 1st stage inclusion compound was investigated by the homemade differential thermal analysis equipment [1]. Samples (30–40 mg of the 1st stage inclusion compound and

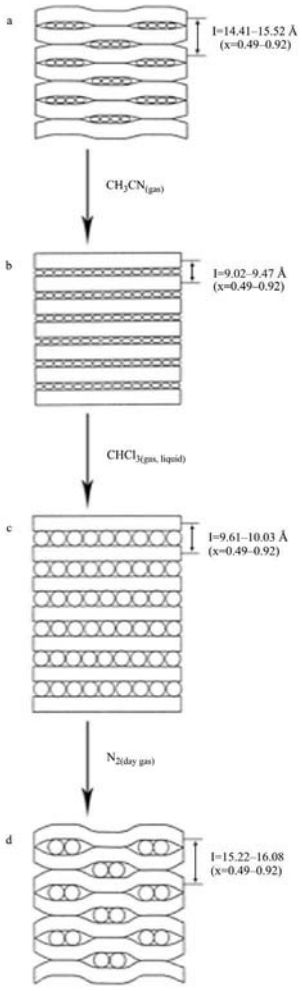

Fig. 2 Structural change model of $C_2F_xBr_z$ during acetonitrile substitution to chloroform in host matrix:
a – the 2nd stage inclusion compound with CH_3CN,
b – the 1st stage inclusion compound with CH_3CN,
c – the 1st stage inclusion compound with $CHCl_3$,
d – the 2nd stage inclusion compound with $CHCl_3$

0.05 mg of $CHCl_3$) 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 experimental method the gas phase of guest component had vapour pressure about 10 kPa [9], because inclusion compound is practically insoluble in chloroform. Accuracy of temperature measurement was about 0.4°C; heating rate was 3.2 K min^{-1}.

Investigation of the 1st stage inclusion compound thermal decomposition kinetic parameters were carried out in isothermic conditions as in [1] by periodical fixing of the 1st stage inclusion compound (which was synthesized isopiestically as it was shown above) sample mass loss. We used thermostatically

Table 1 Elemental composition and stoichiometry of $C_2F_xBr_z$ y_2CHCl_3 (the 2nd stage inclusion compounds) by elemental and gravimetric analysis and their properties

No.	Colour	Elemental analysis					Gravimetry	I_c/Å[1)] (±0.02)
		Found elements/mass%				The 2nd stage inclusion compound formula x (±0.01), z (±0.003), y_2 (±0.011)	Values of y_2 (±0.011)	
		C ±0.005	F ±0.30	Cl ±0.30	Br ±0.30			
1	yellow	47.570	33.17	17.56	1.52	$C_2F_{0.92}Br_{0.010}\cdot0.088CHCl_3$	0.088	16.08
2	light green	48.360	31.87	18.05	1.54	$C_2F_{0.87}Br_{0.010}\cdot0.088CHCl_3$	0.088	15.92
3	dark green	52.710	27.66	17.95	1.52	$C_2F_{0.69}Br_{0.009}\cdot0.080CHCl_3$	0.080	15.44
4	black	59.440	22.31	16.57	1.53	$C_2F_{0.49}Br_{0.008}\cdot0.065CHCl_3$	0.065	15.22

I_c, 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)

controlled (±0.2 K) analytical balance at different temperatures from 286 to 311 K.

Results and discussion

The 1st stage inclusion compounds (synthesized by the way shown above) were dried in the dry N_2 flow till constant mass and transformed into the 2nd stage inclusion compound (according to X-ray structure analysis) – alternation of filled by guest and empty interlayer spaces. They differed by colour and electrisation as inclusion compounds with acetonitrile [1].

Saturation curves of the initial 2nd stage inclusion compound by chloroform (increase of saturation depth *vs.* time) at 295 K are shown on Fig. 4. Equilibration time of satiety through gas phase increased with matrix fluorination degree from 8 h for x=0.49 to 72 h for x=0.92. The distinguished relation between the 1st stage formation rate and amount of fluorine in matrix is shown on Fig. 4. X-ray structure investigations of the 1st stage inclusion compounds demonstrated changing of interplanar spacings (Table 2) in comparison with the 2nd stage and confirmed the 1st stage structure with one guest layer after one host layer (Fig. 2c). Thickness of the host layer re-

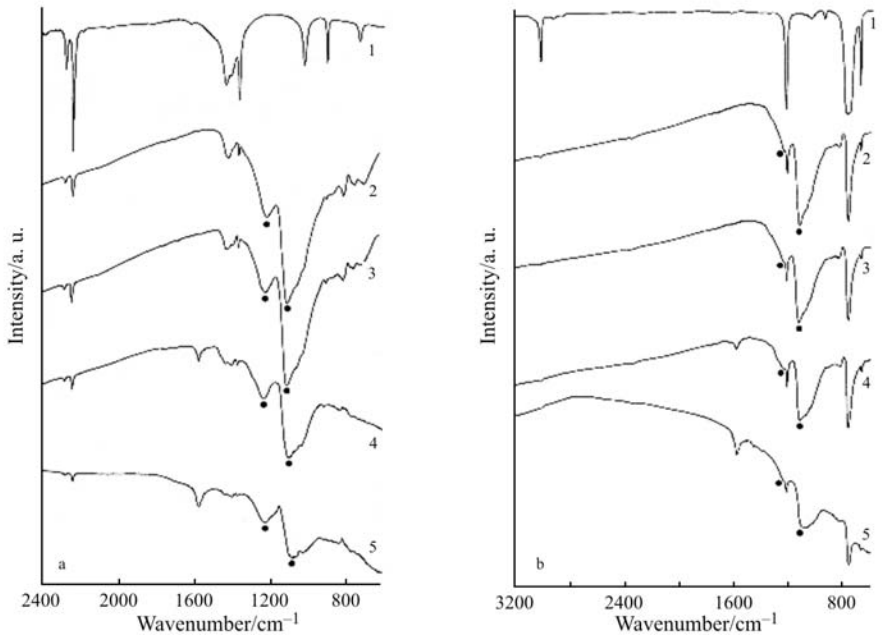

Fig. 3 IR-absorption spectra for pure guests; chloroform (a–1), acetonitrile (b–1), and their 2nd stage inclusion compounds based on x=0.92 (2), 0.87 (3), 0.69 (4) and 0.49 (5) matrices. Absorption peaks of C–F bonds in host matrix are marked by points. (Spectra were taken on Fourier spectrometer SCIMITAR FTS 2000 – 3 mg of inclusion compound were pressed in tablets with KBr.)

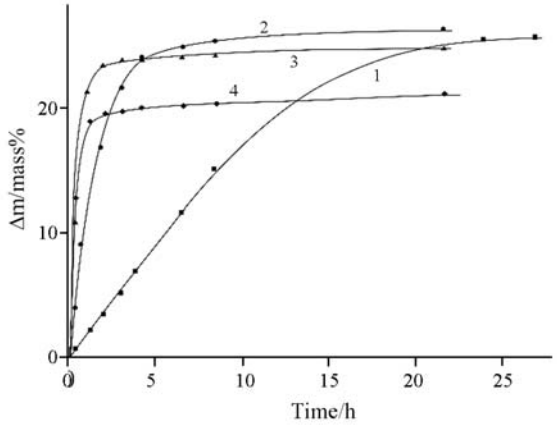

Fig. 4 Saturation curves of the 2nd stage inclusion compound with chloroform (P=1 bar, T =300.5 K) for x=0.92 (1), 0.87 (2), 0.69 (3) and 0.49 (4)

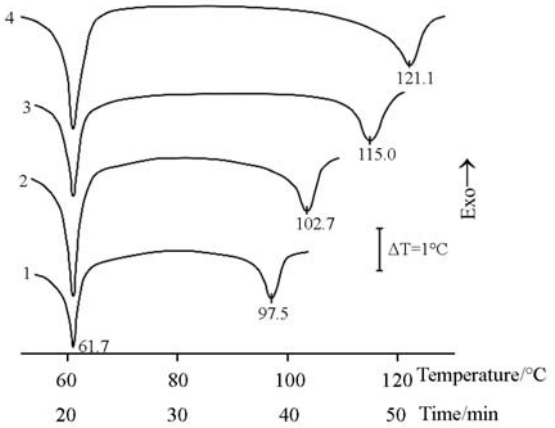

Fig. 5 Heating curves of the 1st stage inclusion compounds with little excess of liquid chloroform, for x=0.92 (1), 0.87 (2), 0.69 (3) and 0.49 (4)

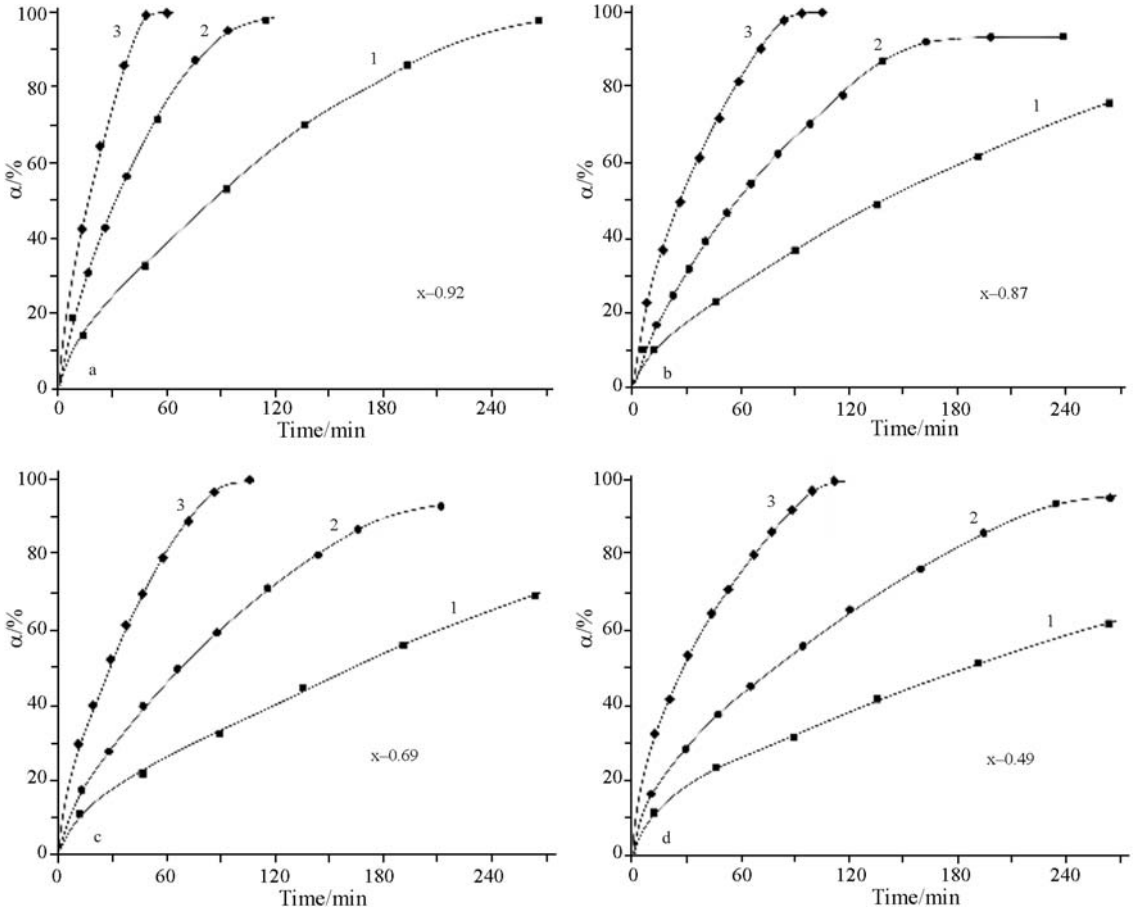

Fig. 6 Isothermic decomposition curves for the 1st stage inclusion compounds with chloroform: a – x=0.92 at 286.35 (1), 300.25 (2) and 309.35 K (3), b – x=0.87 at 286.35 (1), 299.15 (2) and 309.95 K (3), c – x=0.69 at 286.35 (1), 298.85 (2) and 311.35 K (3), d – x=0.49 at 286.35 (1), 298.95 (2) and 311.05 K (3)

Table 2 Properties of the 1st stage inclusion compounds ($C_2F_xBr_z{\cdot}y_1CHCl_3$) with chloroform

No.	Colour	The 1st stage inclusion compound stoichiometry		I_c/Å (±0.02)	Layer thickness/ Å (±0.04)		Decomposition maximum DTA/ °C (±0.4)	Activation energy[2]/ kJ mol^{-1}
		Δm/ mass% (±0.2)	Formula y_1 (±0.015)		host	guest		
1	yellow	26.6	$C_2F_{0.92}Br_{0.01}{\cdot}0.204CHCl_3$	10.03	6.05	3.98	97.5	42.3
2	light green	25.6	$C_2F_{0.87}Br_{0.01}{\cdot}0.205CHCl_3$	9.94	5.98	3.96	102.7	44.3
3	dark green	24.6	$C_2F_{0.69}Br_{0.01}{\cdot}0.181CHCl_3$	9.73	5.71	4.02	115.0	51.1
4	black	20.4	$C_2F_{0.49}Br_{0.01}{\cdot}0.139CHCl_3$	9.61	5.61	4.00	121.1	51.3

[1] Δm sample mass inrease during the 2nd to the 1st stage inclusion compound transformation.
[2] E_a activation energy of the 1st stage inclusion compound decomposition reaction into the 2nd stage inclusion compound and gaseous chloroform

duces with decrease of x (Table 2), as it was in such inclusion compounds with acetonitrile [1, 6]. Effective thickness of the guest layer is about 4 Å for all matrices (Table 2) is considerably less than $CHCl_3$ molecule size in minimal projection 6.44 Å [2]), which says about nearly closest packing of its molecules in the interlayer space by the principle of the closest occupancy [10, 11].

Decomposition temperatures of the 1st stage inclusion compounds to the 2nd stage (shown by RCA data) and gaseous guest (Fig. 5) are much higher than the boiling point of the pure guest (334.85 K) and depend on x. The formation of the individual 1st stage inclusion compound phases is proved by the fact of their regeneration (according to RCA data) after thermal decomposition in DTA chamber, cooling and

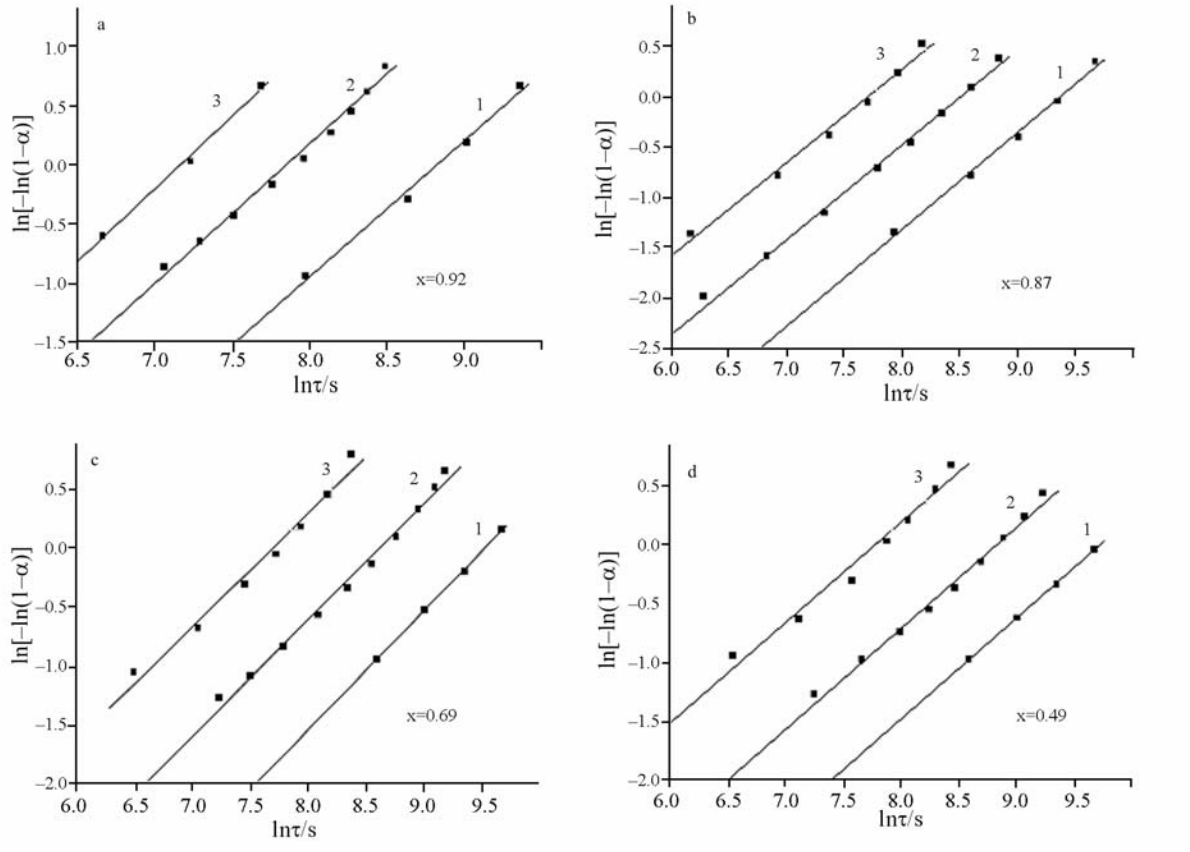

Fig. 7 Dependence of ln(τ/s) *vs.* ln[–ln(1–α] (legend on Fig. 4)

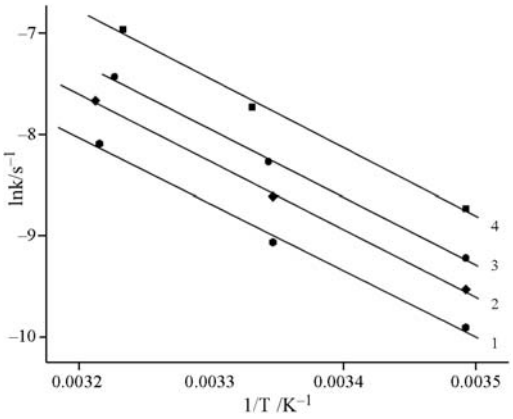

Fig. 8 Dependence of ln*k vs.* 1/*T*: *x* =0.92 (1), 0.87 (2), 0.69 (3) and 0.49 (4)

placing above chloroform at a room temperature for 30–40 h. DTA heating curves were reproduced many times as well. The decomposition time of the 1st stage compound samples (60–600 min) depended both on fluorination degree *x*, and on temperature (Figs 6a–d). It is obvious that more developed surface of graphite layers and their approach with decrease of *x* make host-guest and host-host interactions stronger and we can see it in the 1st 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 equation $\ln[-\ln(1-\alpha)]=n\ln(k/n)+n\ln\tau$ (getting after the two-fold taking logarithm from Erofeev's quation subject to Sakovich's correlation), where *n* – non-dimensional coefficient, *k* – generalized rate constant, s^{-1}. Equation shown above was successfully used by many authors for kinetic investigations of both thermal decomposition of different compounds (including carbamide-*n*-alkanes clathrates) and phase transitions, solvation and absorption [12]. Kinetic curves (Fig. 4) can be approximated by nearly parallel lines (Fig. 5), it points on the kinetic parameter *n* constancy in considered range of temperatures. Coefficient *n* had values of 1.17–1.19, 0.93–0.95, 0.97–0.99, 0.85–0.86 for *x* =0.92, 0.87, 0.69 and 0.49 respectively. Values *n*>1 considered to describe reaction with kinetic control [12, 13], *n*<1 – with diffusion control.

Activation energy (E_a) values found from line slope of ln*k*–10000/*T* are 42.3, 44.3, 51.1 and 53.3 kJ mol^{-1} (per 1 mol of the 1st stage inclusion compound) for *x* =0.92, 0.87, 0.69 and 0.49 respectively. It has higher value than evaporation enthalpy of pure chloroform in the temperature range 290–370 K (ΔH^0_{vap} =32.0–27.3 kJ mol^{-1} [14]). This value, as it was shown in [1] for inclusion compound with acetonitrile, is much more than E_a of hexagonal urea-*n*-hexane inclusion compound decomposition

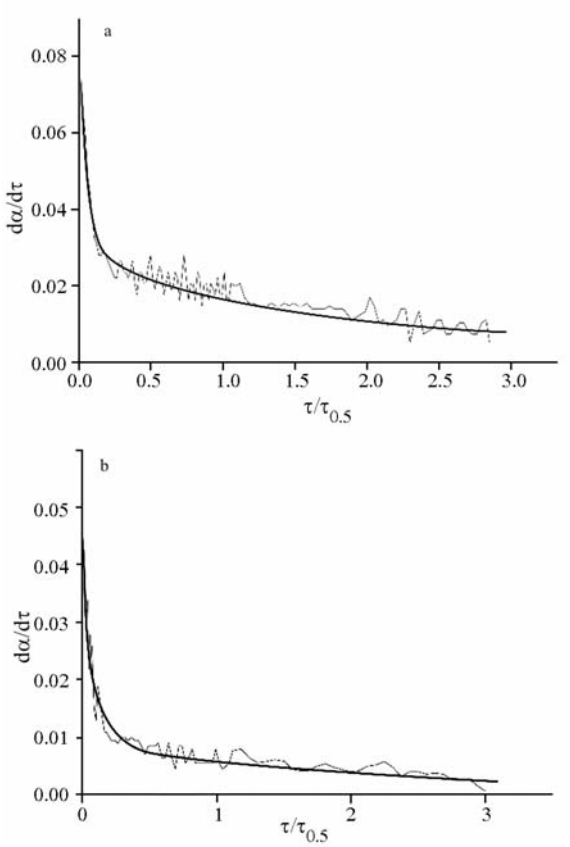

Fig. 9 Dependence of dα/dτ *vs.* reduced time $\tau/\tau_{0.5}$ for a – *x* =0.92 at *T*=300.25 K and b – *x* =0.49 at *T*=298.95 K (b)

(14.88 kJ mol^{-1} of inclusion compound $CO(NH_2)_2{\cdot}0.186C_6H_{14}$) [12] and comparable with E_a of hydroquinone-acetonitrile clathrate decomposition (48.9 kJ mol^{-1} of inclusion compound $C_6H_4(OH)_2{\cdot}0.333CH_3CN$) [13], which is sufficiently stable inclusion compound with cellular host matrix.

For determination of the 1st stage inclusion compound decomposition reaction mechanism in isothermal conditions we checked dependencies of dα/dτ from reduced time $\tau/\tau_{0.5}$ (Fig. 9) [13]. We can see two reaction stages for all matrices: on phase boundary in the beginning and then diffusion mechanism. For *x* =0.92 we have longer phase boundary stage than for other inclusion compounds which decomposition goes by diffusion mechanism from the very beginning.

Conclusions

We meaningly used generalized Erofeev's equation for the estimation of decomposition kinetic parameters. Such equation selection gave us the possibility to look after the imbedding from the reaction kinetics to the diffusion: coefficient n had values of 1.18, 0.94, 0.98, 0.86 for *x* =0.92, 0.87, 0.69 and 0.49 respectively in $C_2F_xBr_z{\cdot}yCHCl_3$; values *n*>1 correspond to

reaction with kinetic control, $n<1$ – with diffusion control. So the fluorination decrease results in the diffusion hindrance increase. Big enough activation energies confirm the so-called 'inner diffusion'.

Effective thickness of the guest layer (about 4 Å for all matrices) is considerably less than $CHCl_3$ molecule size (in minimal projection 6.44 Å), so $CHCl_3$ molecules are distributed in the interlayer space by the principle of the closest packing of molecules pieces into the cavities of relief surface of matrix layers. The fluorination decrease increases points of guest host contacts and the strength of van der Waals forces; this results in the greater kinetic stability of common intercalate system. This conclusion have a certain attitude to intercalate with acetonitrile, the imbedding from the reaction kinetics to the diffusion exists as well, although the activation energies did not change noticeably in the series [1].

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