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RELATIONSHIP BETWEEN PROPERTIES OF FLUORINATED GRAPHITE INTERCALATES AND MATRIX COMPOSITION

Part III. Intercalates with 1,2-dichloroethane

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Inclusion compounds (intercalates) of fluorinated graphite matrix with 1,2-dichloroethane ($C_2F_xBr_z{\cdot}yC_2H_4Cl_2$, x=0.49, 0.69, 0.87, 0.92, $z\approx0.01$) were synthesized by guest substitution from acetonitrile to dichloroethane. The kinetics of the thermal decomposition (the 1st stage of filling→the 2nd stage of filling) was studied under isothermal conditions at 289-313 K. The relationship between the structure of host matrices 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 in [1, 2] for the 1st stage inclusion (intercalation) compounds (IC) of fluorinated graphite with acetonitrile $C_2F_xBr_z{\cdot}y_1CH_3CN$ (x=0.49–0.92, y_1=0.174–0.288, z=0.008-0.010) and chloroform $C_2F_xBr_z{\cdot}y_1CHCl_3$ (x=0.49–0.92, y_1=0.139–0.204, z=0.008–0.010) by DTA, XRD, determination of activation energies and decomposition mechanism that kinetic stability is nearly similar within error value for all x in this range, but thermodynamic stability considerably increases with decrease of x from 0.92 to 0.49. For inclusion compounds with acetonitrile the topochemical mechanism of deintercalation process 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, reaction on phase boundary was observed only with x=0.92 in the beginning, with x=0.87 there was nearly no reaction on phase boundary, x=0.69 and 0.49 were deintercalated by diffusion mechanism only. The increase of diffusion interaction can be explained by decrease of interlayer space in clathrate system from 9.47 to 9.02 Å in the case of inclusion compound with CH_3CN [1] and from 10.03 to 9.61 Å with $CHCl_3$ [2]. At the same time the 1st 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 increase of host–guest interactions with decrease of x.

Therefore, investigation of inclusion compounds properties behaviour with larger guest molecules has a significant practical value. In this work 1,2-dichloroethane ($C_2H_4Cl_2$) is used as a guest molecule, its own symmetry is C_{2h}. Minimum and maximum projection sizes of $C_2H_4Cl_2$ molecule are 4.73 and 7.67 Å, respectively. Dipole moment of $C_2H_4Cl_2$ molecule is about 1.6 D at 298 K [3], which allows synthesizing inclusion compounds with 1,2-dichloroethane by substitution of CH_3CN to other guest component [1, 2, 4] to investigate influence of matrix composition on synthesized compounds properties. We expected intercalates of 1,2-dichloroethane to be suitable for thermoanalytic investigations within 289–313 K temperature range. Having more than two-fold difference between molecular masses of dichloroethane (98.96 g mol^{-1}) and acetonitrile (41.05 g mol^{-1}) these two guest components have nearly similar boiling points ($C_2H_4Cl_2$ – 356.95 K, CH_3CN – 355.25 K). Dichloroethane has vapour pressure about 10.6 kPa (0.106 bar) at 298.15 K. So it allows to make thermoanalytic investigations of the 1st stage inclusion compounds, because their decomposition temperatures are supposed to be considerably lower than the temperature of matrix destruction (500–600 K [5, 6]). In this work we chose $C_2F_xBr_z$ matrices with different fluorine content as insufficiently explored in clathrate formation processes.

Experimental

Synthesis of these inclusion compounds with acetonitrile is described thoroughly in [1]. It was carried out by

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obtaining the 1st stage inclusion compound of graphite with Br_2, oxidation by fluorinating agent (BrF_3–Br_2 solutions) during 14–360 days with subsequent substitution of intercalated aggressive media to acetonitrile. Stable intercalates with acetonitrile [6, 7] were used as initial components for synthesis of inclusion compounds with 1,2-dichloroethane. Refined by known technology 1,2-dichloroethane [8] had melting point 237.8 K and boiling point 356.9 K.

Inclusion compounds with 1,2-dichloroethane were prepared by isopiestic method as it was shown on Fig. 1. 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, then they were transported to hermetic reactor above liquid 1,2-dichloroethane, exposed for nearly 24 h and then filled by liquid 1,2-dichloroethane for more effective substitution of acetonitrile into new guest molecule. Samples were 500–600 mg, they were held by weighed cylindrical cells. After the first exposure in 1,2-dichloroethane these samples were dried for nearly 24 h in the N_2 flow (Fig. 1d), then they were placed above 1,2-dichloroethane to saturate them again. After 3–4 cycles of saturation and decomposition, as it was shown by IR spectra (Fig. 2a), all acetonitrile (Fig. 2b) was substituted to 1,2-dichloroethane. The new 2nd stage inclusion compounds were saturated isopiestically again to determine the end time of saturation by stopping the mass increase. These experiments allowed defining the stoichiometry of the 1st and the 2nd inclusion compounds with 1,2-dichloroethane with good reproducibility. 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.

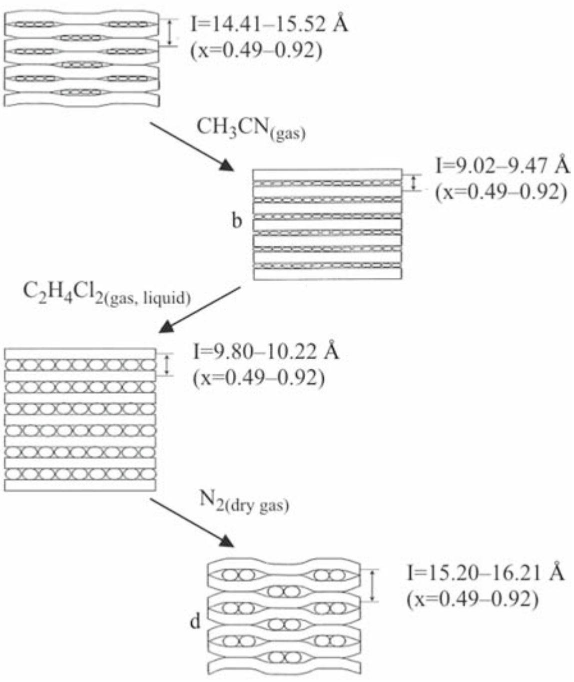

Fig. 1 Structural change model of $C_2F_xBr_z$ during acetonitrile substitution to 1,2-dichloroethane in host matrix:
a – the 2nd stage inclusion compound with CH_3CN,
b – the 1st stage inclusion compound with CH_3CN,
c – the 1st stage inclusion compound with $C_2H_4Cl_2$,
d – the 2nd stage inclusion compound with $C_2H_4Cl_2$

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 with 1,2-dichloroethane with slight excess of free guest component) 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 10.6 kPa [9], because inclusion compound is practically insoluble in 1,2-dichloroethane. Accuracy of temperature measurement was about 0.4°C; heating rate was 3.2°C min^{-1}.

Investigations of the 1st stage inclusion compound thermal decomposition kinetic parameters were carried out by periodical fixing of the 1st stage inclusion compound (which was synthesized isopiestically as it was shown above) sample mass loss. We used thermostatically controlled analytical balance (±0.015 mg), measurements were taken at fixed temperatures (±0.2 K) from 289 to 313 K.

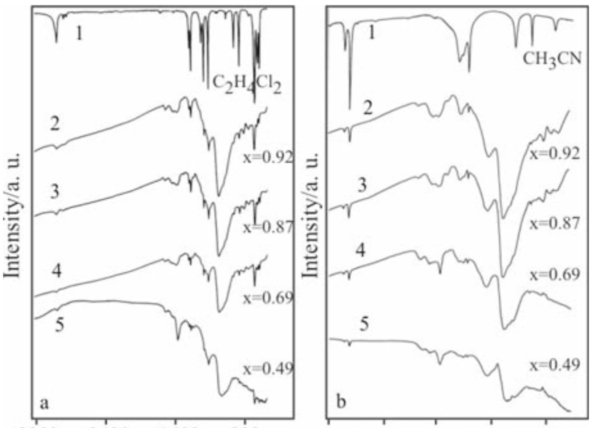

Fig. 2 IR-absorption spectra for pure guests: 1,2-dichloroethane (a-1), acetonitrile (b-1) and their 2nd stage inclusion compounds based on x=0.92 (2), 0.87 (3), 0.69 (4) and 0.49 (5) matrices. (Spectra were taken on Fourier spectrometer SCIMITAR FTS 2000; samples were prepared by standard method – 3 mg of inclusion compound were pressed in tablets with KBr.)

Table 1 Elemental composition and stoichiometry of $C_2F_xBr_z{\cdot}y_2C_2H_4Cl_2$ (the 2nd stage inclusion compounds) by elemental and gravimetric analysis and their properties

No.	Colour	Elemental analysis					Gravimetry	I_c/Å1) (±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±0.50	F±0.30	Cl±0.30	Br±0.30			
1	yellow	51.37	34.47	11.89	1.58	$C_2F_{0.92}Br_{0.010}{\cdot}0.085C_2H_4Cl_2$	0.085	16.21
2	light green	52.16	32.95	12.58	1.59	$C_2F_{0.87}Br_{0.010}{\cdot}0.089C_2H_4Cl_2$	0.089	15.98
3	dark green	56.97	28.89	11.88	1.59	$C_2F_{0.69}Br_{0.009}{\cdot}0.076C_2H_4Cl_2$	0.076	15.61
4	black	62.94	22.82	11.99	1.57	$C_2F_{0.49}Br_{0.008}{\cdot}0.069C_2H_4Cl_2$	0.069	15.20

1)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).

Table 2 Properties of the 1st stage inclusion compounds ($C_2F_xBr_z{\cdot}y_1C_2H_4Cl_2$) with 1,2-dichloroethane

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 energy2)/kJ mol^{-1} of the 1st stage compound
		Δm/mass% (±0.2)	Formula y_1 (±0.015)		host	guest		
1	yellow	26.7	$C_2F_{0.92}Br_{0.01}{\cdot}0.222C_2H_4Cl_2$	10.22	5.99	4.23	117.5	52.8
2	light green	25.6	$C_2F_{0.87}Br_{0.01}{\cdot}0.219C_2H_4Cl_2$	10.14	5.84	4.30	124.1	61.4
3	dark green	24.6	$C_2F_{0.69}Br_{0.01}{\cdot}0.189C_2H_4Cl_2$	9.99	5.62	4.37	134.5	62.2
4	black	20.4	$C_2F_{0.49}Br_{0.01}{\cdot}0.153C_2H_4Cl_2$	9.80	5.40	4.40	140.1	66.2

1)Δm – sample mass increase 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 1,2-dichloroethane.

Results and discussion

The 1st stage inclusion compounds with 1,2-dichloroethane obtained by isopiestic method after drying to constant mass in the dry N_2 flow transformed into the 2nd stage (Fig. 1d) inclusion compound (according to X-ray structure analysis). They 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 2nd stage inclusion compound by 1,2-dichloroethane (increase of saturation depth *vs*. time) at 298.15 K are shown on Fig. 3. Equilibration time of satiety through gas phase increased with matrix fluorination degree from 3.5 h for x=0.49 to 9 h for x=0.92. Investigations of samples saturated by 1,2-dichloroethane by X-ray diffraction analysis showed change of interplanar spacing (Table 2) in comparison with the 2nd stage inclusion compounds and confirmed the formation of the 1st stage inclusion compound with one guest layer after one host layer.

Decomposition temperatures of the 1st stage inclusion compounds to the 2nd stage (shown by RCA data) and gaseous guest are much higher than the boiling point of the pure guest (356.9 K) and increased with decrease of matrix fluorination degree. The formation of the individual 1st stage inclusion compound phases for all fluorination degrees from 0.49 to 0.92 is proved by the fact of their regeneration (according to RCA data) after thermal decomposition in DTA chamber, cooling and placing above 1,2-dichloroethane at a room temperature for 24 h. DTA heating curves were reproduced many times as well. The decomposition time of the 1st stage compound samples depended both on fluorination degree x, and on temperature with constant x (Figs 4a–d) and lasted from 4 (x=0.92) to 36 h (x=0.49). 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, and we can see it in

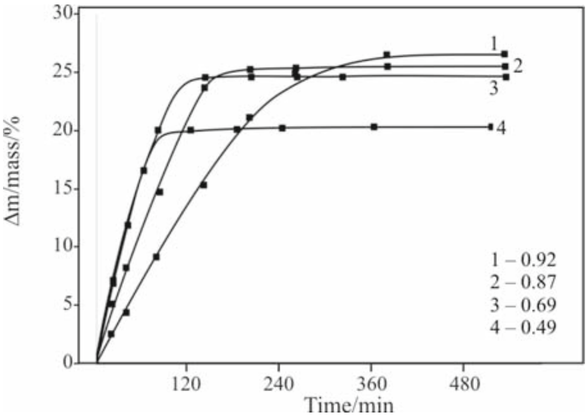

Fig. 3 Saturation curves of the 2nd stage inclusion compound with 1,2-dichloroethane (P=1 bar, T=298.15 K)

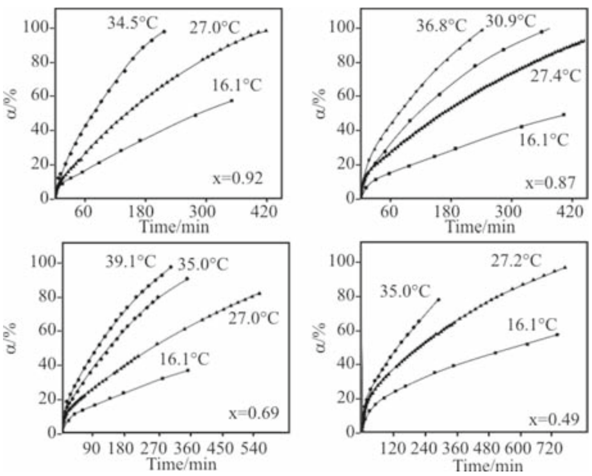

Fig. 4 Isothermic decomposition curves for the 1st stage inclusion compounds with dichloroethane. Fluorination degrees and temperatures are listed on figure

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 equation [10] subject to Sakovich's correlation [11]), 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 [12]) and phase transitions, solvation and absorption [13]. 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 0.93–0.94, 0.79–0.81, 0.71–0.72, 0.63–0.64 for x=0.92, 0.87, 0.69 and 0.49, respectively. Reaction runs under diffusion control because coefficient n is less than 1 [12, 14].

The 'effective' activation energy (E_a) values found from line slope of $\ln k-10^4/T$ (Figs 6a–d) are 52.8, 61.4, 62.2 and 66.2 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 1,2-dichloroethane in the explored range of temperatures (ΔH_{vap}=35.38 kJ mol^{-1} at 298.15 K and 32.03 kJ mol^{-1} at 356.62 K [15]). This value is much more than E_a of hexagonal urea-*n*-hexane channel inclusion compound decomposition (14.88 kJ mol^{-1} of inclusion compound $CO(NH_2)_2\cdot0.186C_6H_{14}$) [12]) and slightly more than E_a of fluorinated graphite inclusion compounds decomposition with acetonitrile (48.9 kJ mol^{-1} of inclusion compound (51-53 kJ mol^{-1} [1]) and with chloroform (42-51 kJ mol^{-1} [2]) based on the same formula fluorinated graphite matrices.

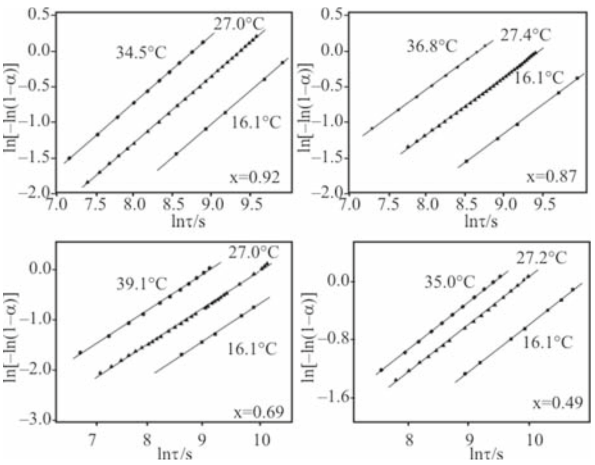

Fig. 5 Dependence of ln(τ, s) *vs*. ln[–ln(1–α)]. Fluorination degrees and temperatures are listed on figure

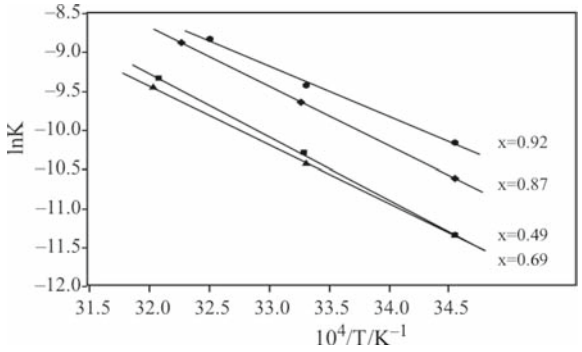

Fig. 6 Dependence of ln$K$ *vs*. $10^4/T$:x=0.92, 0.87, 0.69 and 0.49

For determination of the 1st stage inclusion compound decomposition reaction mechanism in isothermal conditions we checked dependencies of $d\alpha/d\tau$ from reduced time $\tau/\tau_{0.5}$ [14]. Analysis of these dependencies curves indicates, in accordance with the reference work, the prevalence of diffusion mechanism of deintercalation processes in the explored range of temperatures for fluorinated graphite inclusion compounds with dichloroethane for all matrices with x=0.92, 0.87, 0.69, 0.49.

Conclusions

We meaningly used generalized Erofeev's equation for the estimation of decomposition kinetic parameters. Choice of this equation allowed us to verify diffusion mechanism of the 1st stage inclusion compounds deintercalation. Coefficient n had values of 0.93–0.94, 0.79–0.81, 0.71–0.72, 0.63–0.64 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 (as it occurred with inclusion compounds of $C_2F_{0.92}Br_{0.010}$ with CH_3CN [1] and the same matrix with $CHCl_3$ [2]), $n<1$ corresponds to reactions with diffusion control. So in the case of 1,2-dichloroethane as guest component the matrix fluorination decrease 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 4.3 Å for all matrices) is considerably less than $C_2H_4Cl_2$ molecule size in minimal projection (4.73 Å), so $C_2H_4Cl_2$ 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 increases points of guest–host contacts and the strength of van der Waals forces; this behaviour results in the greater kinetic and thermodynamic stability of common intercalate system. This conclusion, which results from investigations of fluorinated graphite intercalates with acetonitrile and chloroform, is applicable with $C_2H_4Cl_2$ 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).

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