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ORIGINAL CONTRIBUTION

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Selective liquid sorption properties of hydrophobized graphite oxide nanostructures

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Abstract Hydrophilic graphite oxide (GO) of lamellar structure was prepared by oxidation of graphite; the thickness of the individual lamellae was 6.1 Å. GO was hydrophobized by *n*-alkylammonium cations, and the GO-organocomplex nanocomposites were swollen in organic solvents of various polarities (ethanol, toluene, cyclohexane, *n*-heptane) and their binary mixtures. The binary liquid composition determined the size (15–45 Å) of the lamellar GO nanostructures. Interlamellar swelling was quantitatively characterized by XRD experiments, determination of liquid sorption excess isotherms and flow microcalorimetry.

Key words Liquid adsorption – graphite oxides – swelling – microcalorimetry – nanostructures

Introduction

Graphite forms planar layers of C–C bonds of 1.44 Å length. The layers are separated by 3.39 Å. The carbon atoms are arranged in a regular, periodical manner [1–3]. The bonds holding between the layers (in the direction of *c* axis) can be broken up by strong oxidation, and hydrophilic graphite oxide of lamellar structure is generated [3–6]. According to Hofmann et al. [2–4], oxygen atoms in graphite oxide are bound to the hexagonal layers of the carbon atoms by epoxy linkages. Hydroxyl groups are also attached to the planar carbon atoms. According to Debye and Scherrer, the hexagonal layers of graphite have an aromatic structure [7]. In the course of oxidation the aromatic character is lost (Fig. 1) [8]. Hydrophilic graphite oxide readily adsorbs water or other polar liquids. As a consequence of liquid sorption, the lamellae move apart: graphite oxide exhibits one-dimensional swelling, similarly to clay minerals [2–4]. Swelling is monitored by X-ray diffraction. The (0 0 2) interference (= basal spacing d_L) varies between 6.1 and 11 Å depending upon the amount of water adsorbed, while the (hk0) interferences are invariant [3]. The C/O ratio in graphite is close to 2 : 1; according to de Boer, however, its structural formula is $C_7O_4H_2$ and the surface of the unit cell is 18.4 $Å^2/C_7O_4H_2$ unit [9]. GO is thermally unstable: when heated to 180 °C, it is converted to carbon with the concomitant liberation of CO, CO_2 and H_2O and, as shown by TEM evidence, it forms very thin lamellae [10]. The behaviour of GO is very similar to that of swelling and disaggregating montmorillonite: during water vapour adsorption, the basal spacing of the dry sample ($d_L = 6.35$ Å) increases to 7.7 Å at $p/p_0 = 0.5$ and to 11.6 Å at $p/p_0 = 1$. It readily disperses in NaOH solution ($d_L = 12.3$ Å in 0.05 N NaOH, $d_L = \infty$ in 0.01 N NaOH). Self-assembled films a few nanometers thick can be easily prepared from diluted dispersions, as the anisometric, 6.1 Å thick lamellae are capable of parallel orientation [11]. Complete disaggregation occurs when the charge density of GO layers is 0.7–2.0 charges/100 $Å^2$. Charges originate from the acidic groups [12, 13]. According to Boehm et al., –C–OH groups are also produced on

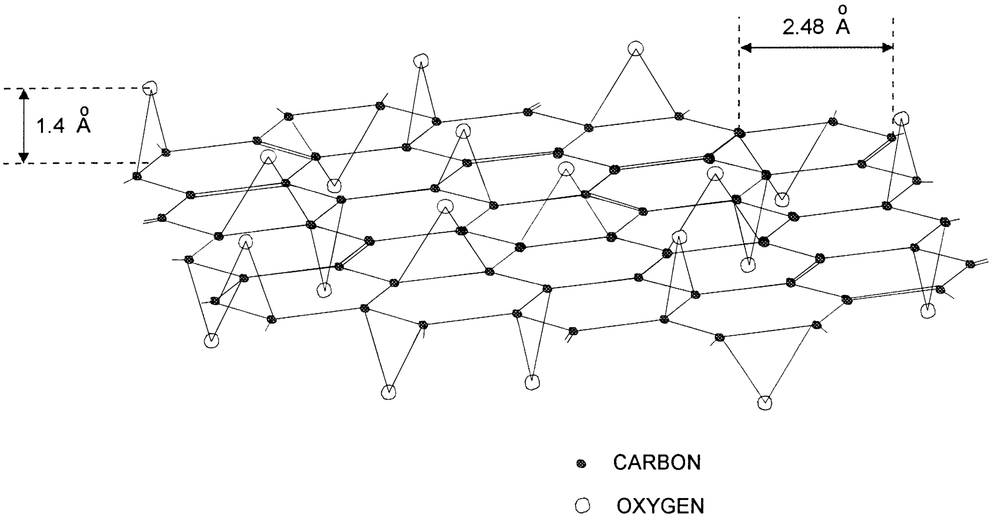

Fig. 1 Structure of graphite oxide according to U. Hoffmann

graphite lamellae in the course of oxidation. In order to account for the presence of these groups, sp^3-hybridization of C-atoms at adequate sites on the hexagonal carbon layer has to be envisaged [10, 12]. In addition, the presence of carboxyl, enol and ether groups on basal surfaces has also been demonstrated [10, 12]. The amount of acidic groups on the surfaces may be determined by titration with sodium hydroxide. The total surface ion exchange capacity reaches 3–3.5 mmol/g GO. This value is 3–4 times higher than the ion exchange capacity of montmorillonite. The cation exchange capacity of GO also makes possible the hydrophobization of lamellae by alkylammonium cations according to the principles developed for clay minerals [14–16].

We report preparation of GO from graphite by the oxidation procedure of Brodie [5], and of *n*-alkylammonium-GO derivatives with alkyl groups of various chain lengths by cation exchange reaction. Swelling of these derivatives was examined in different organic solvents and their mixtures. The adsorption capacity of hydrophobized graphite oxide in various liquids was derived from the surface excess isotherms.

Adsorption of binary liquid mixtures on solid adsorbents

If a solid adsorbent is immersed in a binary liquid mixture, the molar reduced excess amount, $n_1^{\sigma(n)}$, of component 1 per unit mass of the solid is [17]

$$n_1^{\sigma(n)} = n_0(x_1^0 - x_1)/m = n_0 \Delta x_1/m \ , \qquad (1)$$

where n_0 is the total number of moles of the liquid, x_1^0 and x_1 are the initial and equilibrium molar fractions of component 1, and m is the mass of adsorbent. The Ostwald-de-Izaguirre equation relates the adsorption excess amount and the real amount adsorbed [17]:

$$n_1^{\sigma(n)} = n_1^s x_2 - n_2^s x_1 = n_1^s - n^s x_1 = n^s(x_1^s - x_1) \ , \qquad (2)$$

where $n^s = n_1^s + n_2^s$ is the material content of the adsorption layer and $x_1^s = (1 - x_2^s) = n_1^s/n^s$ is the molar fraction of component 1 in this layer. Measured is the adsorption excess isotherm $n_1^{\sigma(n)} = f(x_1)$. The values of n_1^s and n_2^s can be obtained from the linear section of the isotherm according to Eq. (2) (Schay–Nagy extrapolation [18]). When n_1^s and n_2^s are known, $x_1^s = f(x_1)$ is calculated from Eq. (2).

The equivalent specific surface area can be calculated assuming a monolayer arrangement [19]:

$$a_{\mathrm{equ}}^s = n_1^s a_{m,1} + n_2^s a_{m,2} \ , \qquad (3)$$

where $a_{m,1}$ and $a_{m,2}$ are the cross-sectional areas of the adsorbed molecules. One can also calculate the amount $n_{1,0}^s = a_{\mathrm{equ}}^s/a_{m,1}$ which is the amount of component 1 needed to cover the surface area a_{equ}^s.

Materials and methods

Preparation of graphite oxide

Natural graphite (Kropfmühl, Bayern, Germany) was oxidized by $HNO_3/NaClO_3$ according to Brodie [5]. 10 g of graphite and 85 g of $NaClO_3$ were mixed in a flask cooled in ice; 60 cm^3 of concentrated HNO_3 was added to the mixture within 3 h with constant stirring. The mixture was then heated to 60 °C and stirred for 24 h. The solid GO sample was washed with 3 M HCl solution and with distilled water. The produced sample was filtered and dried. The entire oxidation procedure was repeated three times. The composition of GO by elementary analysis was 61% C, 35.7% O, and 3.3% H.

The cation exchange capacity (CEC) was determined in the following way: 0.5 g of GO was dispersed in 100 cm^3 of 1 M aqueous NaOH, then 100 cm^3 of 2 M NaOH in absolute ethanol were added. After stirring and shaking for 1 week, residual NaOH was titrated with 1 M HCl. The ion exchange capacity of GO was 5.5 mmole/g GO.

The specific surface are was determined by N_2 adsorption at 77 K after freeze-drying of the GO sample with an automatic sorptiometer (Gemini Micromeritics 2375). The specific surface area was determined on the basis of BET-equation.

N-alkylammonium–GO complexes were prepared in ethanol solutions of tetradecyl-, hexadecyl-, or octadecylammonium chloride by ion exchange at 50 °C for 1 week. The amount of cationic surfactant added was 1.5 CEC. The samples were washed with ethanol and dried in an oven at 50 °C. The following solvents of p.a. quality were used for further experiments: ethanol, toluene, cyclohexene and *n*-heptane. Prior to measurements, the organic solvents were dried over a 0.4 nm molecular sieve (Merck, Germany).

Adsorption experiments

Adsorption excess isotherms were determined in benzene(1)–*n*-heptane(2), ethanol(1)–cyclohexane(2) and ethanol(1)–toluene(2) mixtures by static experiments described earlier [16–19].

Flow microcalorimetry

The integral enthalpy of displacement, ΔH_{21}, was determined in an LKB 2107 flow sorption microcalorimeter (Bromma, Sweden) at 25 ± 0.01 °C. The sorption vessel was loaded with 0.3–0.5 g of adsorbent. The liquid mixture was circulated through the system at a constant flow rate of 25 $cm^3\,h^{-1}$. Measurements were made by the cumulative method with the concentration increasing in small increments.

X-ray diffractometry

The basal spacings (d_L) of the samples were determined with a Philips PW 1830 diffractometer (CuK_α radiation, $\lambda = 1.54$ Å). Dispersions of GO derivatives in binary mixtures were covered by Mylar foil (25 μm thick) to prevent evaporation of the dispersion liquids. The d_L-values were reproduced within 0.2 Å.

Results and discussions

X-ray diffraction experiments

In basal spacing of the alkylammonium derivatives (Table 1) increased from 6.84 Å (pure GO) to 18.7–20.9 Å. The orientation of alkyl chains is parallel to the surface in all three cases. The theoretical spacing for this arrangement is $d_L = 6.1 + 3 \times 4.5 = 19.6$ Å if a pseudo-three layer complex is formed (Fig. 2b) [14, 15]. For flat double layers, d_L (Fig. 2a) is $6.1 + 2 \times 4.5 = 15.1$ Å. The experimentally determined values after extraction with ethanol ($d_L =$ 14.5–15.9 Å Table 1) are obviously close to these values. The middle (third) layer of alkyl chains is desorbed from the interlamellar space in the course of extraction and *n*-alkylammonium chains lying in parallel on the surface are retained between GO layers of the dry sample (Fig. 2a) [14–16].

Various organic solvents are intercalated between the layers of GO [20, 21]. Swelling increases in the order ethanol < toluene < *n*-heptane < cyclohexane, i.e.

Table 1 Basal spacing of *n*-alkylammonium graphite oxides

GO-derivate	d_L (Å) air-dried	d_L (Å)[a]	d_1(calc.) $\alpha = 56°$ (Å)		d_L (Å) in ethanol	d_L (Å) in toluene	d_L (Å) in cyclohexane	d_L (Å) in *n*-heptane
			Monolayer	Bilayer				
GO	6.84	—	—	—	9.43	7.6	7.45	7.90
GO-C_{14}	18.7	14.50	23.16	40.22	23.5	36.8	41.0	35.7
GO-C_{16}	20.3	15.6	25.2	44.4	24.9	41.0	48.0	42.0
GO-C_{18}	20.9	15.9	27.37	48.64	25.5	42.7	47.7	44.7

[a] After extraction with ethanol and air-drying.

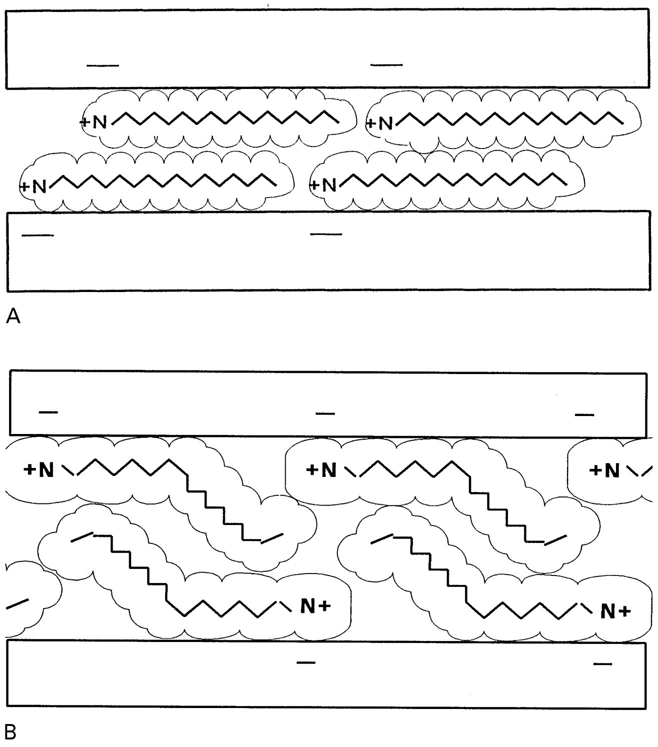

Fig. 2 (a) Dry *n*-alkylamonium GO complexes with double layer orientation. (b) Dry *n*-alkylamonium GO complexes with pseudo-three layer orientation

decreasing the polarity of the liquid solvent increases the extent of swelling. It is remarkable that there is excellent swelling in aliphatic and alicyclic solvents. The basal spacings correspond to the bilayer orientation ($d_L = 2 \times (1.27 n_c + 2.8) \sin 56^\circ + 6.1$ Å) where alkyl chains include a 56° angle with the plane of GO (Fig. 3a and b). The existence of such structures has earlier been discussed by Lagaly and Weiss in connection with X-ray diffraction studies on organo complexes of clay minerals [14, 15]. In ethanol, however, the monolayer orientation with a 56° tilting angle develops. Since the solvents studied are miscible, swelling was also investigated in binary mixtures. The interlamellar swelling of the GO-C_{18}–ammonium complex as a function of the mixing ratio $d_L = f(x_1)$ is presented in Fig. 4 for ethanol(1)–cyclohexane(2) and ethanol(1)–toluene(2). It is clearly seen that swelling is a function of the polarity of the liquid mixture. As ethanol concentration increases, the swollen bilayer structure is converted into a monolayer, where the methyl end groups of the alkyl chains touch the opposite surface (Table 1). It has also to be noted that d_L does not change significantly in pure aliphatic or cycloaliphatic medium or up to a composition of $x_1 = 0.2$–0.3, i.e. the composition of the liquid mixture in the interlamellar space, x_1^s, is nearly constant.

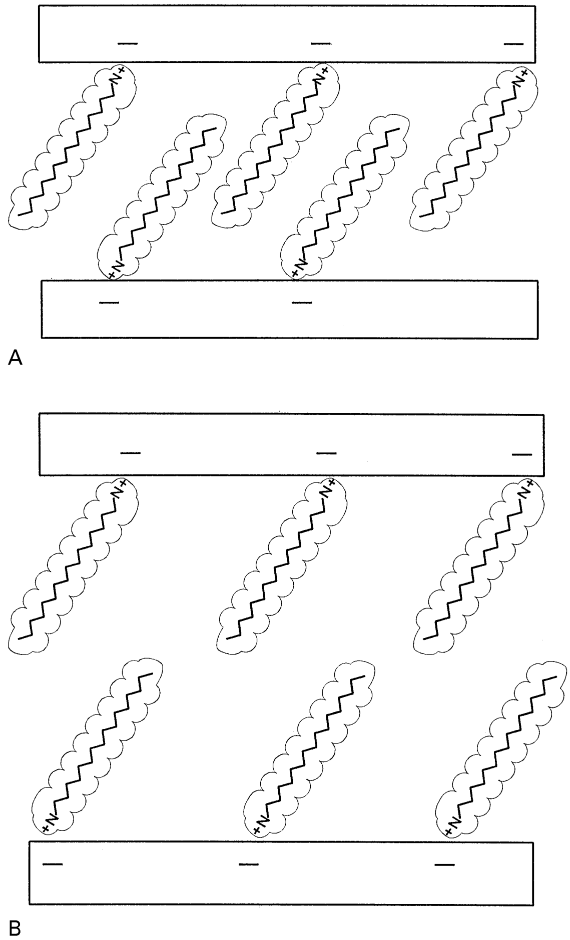

Fig. 3 Structure of alkylammonium graphite oxide with tilted chains ($\alpha = 56^\circ$): (a) monolayer orientation and (b) bilayer orientation

A similar effect was observed by Dékány et al. in earlier studies on organophilic vermiculites [22].

Liquid sorption studies

Liquid sorption excess isotherms $n_1^{\sigma(n)} = f(x_1)$ are shown in Fig. 5. The isotherm determined in benzene(1)–*n*-heptane(2) mixtures (curve 2) indicates preferential adsorption of benzene on the surface of GO. Adsorption, however, is insignificant since the intercalation of benzene is limited and adsorption takes place mainly on the external surface. The adsorption capacity calculated from the isotherm by the Shay–Nagy method [16–18] is $n_{1,0}^s = 0.6$ mmol/g which corresponds to an equivalent specific surface area of 110 m^2/g. This is 3.5 times the value of the BET surface area.

There is an abrupt change in selective adsorption when the ethanol(1)–cyclohexane(2) liquid pair is examined

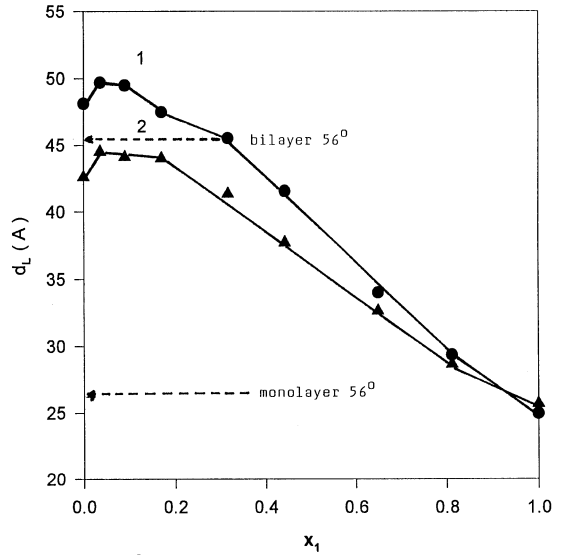

Fig. 4 Basal spacing of GO-C$_{16}$ in different liquid mixtures: (1) ethanol–cyclohexane, (2) ethanol–toluene

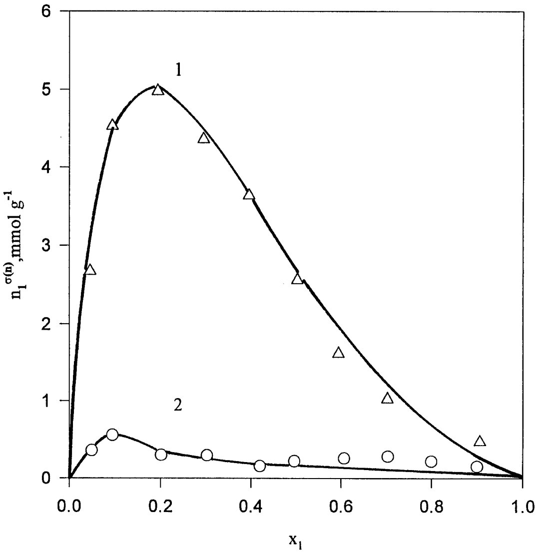

Fig. 5 Adsorption excess isotherms 1: ethanol(1)–cyclohexane(2), 2: benzene(1)–*n*-heptane(2) of GO

(curve 1 in Fig. 5). If ethanol were preferentially adsorbed on the surface of GO, the adsorption capacity is $n^s_{1,0} = 7.33$ mmol/g. The calculated equivalent specific surface area is $a^s = 7.33$ mmol/g × 120 m^2/mmol = 880 m^2/g which amounts to nearly half of the theoretical specific surface area of 1500 m^{2}g [9]. As the X-ray studies indicate a monolayer of ethanol molecules with a thickness of 9.4–6.1 = 3.3 Å, (d_L = 9.43 Å) the cross sectional area of 120 m^2/mmol is not realistic: the ethanol molecules are in contact with two GO lamellae, a cross sectional area of 2 × 120 = 240 m^2/mmol has to be used in the calculations. In such a case the calculated specific surface area is 1760 m^2/g, that is the total surface is covered with ethanol.

It has already been established by X-ray diffraction measurements that the liquid uptake by hydrophobic graphite oxide is significant. This is also indicated by the value of the adsorption capacity calculated from the surface excess isotherm (Table 2). The calculated adsorption capacity of hexadecylammonium-GO in benzene(1)–*n*-heptane(2) mixtures is 5.65 mmol/g (Fig. 6.)

The excess isotherm in ethanol(1)-cyclohexane (curve 2 in Fig. 6) is a type IV or S-shaped function (Schay–Nagy classification [17]). This is the typical shape for isotherms on hydrophobic surfaces, indicating positive adsorption of ethanol in mixtures rich in cyclohexane ($x_1 < 0.6$) and positive adsorption of cyclohexane (the value of $n_1^{\sigma(n)}$ for alcohol is negative) in mixtures rich in ethanol ($x_1 > 0.6$). The alcohol is selectively adsorbed on the hydrophobized GO surface. Ethanol is bound to free surface groups of GO by hydrogen bonds while cyclohexane solvates the alkyl chains. The adsorption capacity corresponds to a specific surface area $a^s_{\mathrm{eq}} = 820$ m^2/g which surpasses the theoretically calculated specific surface area of 1476 m^2/g, calculated from unit cell parameters [9]. At $x_1 = x_1^a = 0.6$ (azeotropic composition) [16–19] $n_1^{\delta(n)} = 0$. At this point, the composition of the interfacial phase, x_1^s, is identical with the bulk composition: $x_1 = x_1^a$. The same conclusion also follows from Eq. (2). If $n_1^\sigma = n^s(x_1^s - x_1)$, $n_1^{\sigma(n)} = 0$ for $x_1 = x_1^s$. The interfacial composition allows determination of the mosaic structure of the surface, i.e. quantification of its hydrophobicity. The surface coverage by ethanol is $\Theta_1 = n_1^s a_{m1}/a^s_{\mathrm{eq}}$. The calculated value for ethanol is 0.435 which indicates that in the middle composition range of the isotherm (x_1 = 0.2–0.8) 43.5% of the surface is covered by ethanol.

Flow microcalorimetric studies

The enthalpy of displacement was determined in ethanol(1)–cyclohexane(2) mixtures by means of the flow measuring technique. Cyclohexane was displaced by ethanol. The enthalpy isotherm $\Delta_{21}H = f(x_1)$ (Fig. 7) confirms the preferential adsorption of ethanol for x_1 = 0.1–1.0 on GO. The same is directly demonstrated by the function $d_L = f(x_1)$: the value of d_L is obviously constant from the molar fraction of $x_1 = 0.1$ to pure ethanol, i.e. there is only ethanol between the lamellae. Since it has already been proven by the analysis of the excess isotherm (Fig. 5) that the entire surface of GO participates in adsorption, the extremely large change of the enthalpy during displacement of cyclohexane by ethanol ($\Delta_{21}H_{\mathrm{total}}$ =

Table 2 Results of analysis of adsorption excess isotherms on GO and hexadecylammonium-GO

Adsorbent	n_1^s [mmol g^{-1}]	n_2^s [mmol g^{-1}]	$n_{1,0}^s$ [m^2 g^{-1}]	a_{equ}^s [m^2 g^{-1}]	V^s [cm^3 g^{-1}]
	Liquid mixture: benzene(1)–*n*-heptane(2)				
GO	0.60	—	0.60	110	0.06
GO-C_{16}	5.50	—	5.65	1077	0.551
	Liquid mixture: ethanol(1)–cyclohexane(2)				
GO	5.85	0.85	7.33	880	0.439
GO-C_{16}	6.60	4.90	15.17	1821	3.035

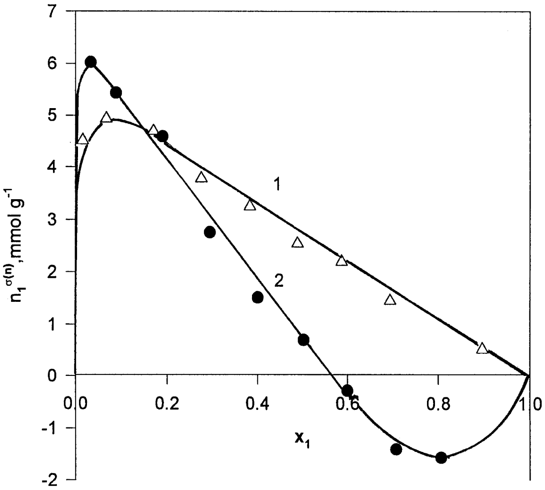

Fig. 6 Adsorption excess isotherms 1: benzene(1)–*n*-heptane(2), 2: ethanol(1)–cyclohexane(2) of GO–C_{16}

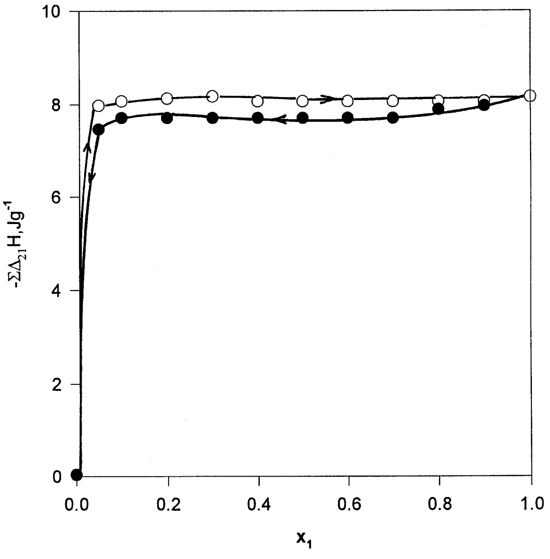

Fig. 7 Enthalpy of displacement isotherms on GO in ethanol (1)–cyclohexane(2) mixtures: (●) adsorption, (○) desorption branch

-8.171 J/g) is well accounted for. The value relative to the surface area unit is -9.28 mJ/m^2 which indicates preferential binding of ethanol on the surface. Because of disaggregation of the hydrophobic sample, flow microcalorimetry of the hydrophobized alkylammonium samples could not be carried out.

Conclusion

Compact graphite, characterized by a small specific surface area is broken up by strong oxidation and formation of graphite oxide with a polar surface and lamellar structure. Ethanol is preferentially absorbed on this surface, the adsorption capacity and adsorption enthalpy of this process have been determined. The surface of GO can be hydrophobized by alkylammonium ions. X-ray diffraction measurements indicate swelling of alkylammonium–GO complexes to be a function of both chain length and the polarity of the mixture medium. The extent of swelling can be regulated by varying the composition of the binary mixture. The alkyl chains have a tilting angle of 56°, the arrangement can vary from a monolayer to a bilayer.

Liquid sorption measurements are in agreement with the X-ray data. Thus, adsorption of benzene–heptane on hydrophilic GO takes place on the external surface only. Preferential adsorption of ethanol from ethanol–cyclohexane mixtures, however, results in the total disaggregation of GO. The ethanol–cyclohexane–GO interaction is also characterized by microcalorimetry. Hydrophobization of the surface of GO also causes total exfoliation in ethanol–cyclohexane mixtures.

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