HOST↔GUEST INTERACTION IN ACF: EPR STUDY

M. KEMPIŃSKI[1], M. ŚLIWIŃSKA-BARTKOWIAK[1], W. KEMPIŃSKI[2]
[1]*Institute of Physics, Adam Mickiewicz Uniwersity*
Umultowska 85, 61-614 Poznań, Poland
[2]*Institute of Molecular Physics, Polish Academy of Sciences*
M. Smoluchowskiego 17, 60-179 Poznań, Poland

Abstract. EPR measurements of ACF (host) filled with different liquids (guest) were performed in order to get information about the host↔guest interaction. Pristine ACF is characterized by single Lorenzian line recorded at $g = 2.0031$ value which is characteristic of carbon materials. Only very weak host↔guest interaction which lead to modified EPR spectrum of pristine ACF was found. Estimation based on the theory of EPR of small particles, gives the ACF nanocrystallites size of 1.34 nm.

1. Introduction

Activated carbon fibres (ACF) are built of nanocrystallites made up of graphene sheets (approximately three). The nanocrystallites tend to align along fibers forming slit-shaped voids [1]. Spontaneous ordering of the molecules adsorbed in the voids makes the adsorbed phase a quasi-two-dimensional system. For such a system it is possible to investigate melting-freezing processes with crystal-hexatic and hexatic-liquid transitions for near-spherical molecules adsorbed in slit-shaped pores of ACF [2]. In the two-dimensional hexatic phase every particle has on average six neighbors. The occasional five-neighbored molecule is always adjacent to one with seven close contacts.

Nonlinear dielectric effect measurements for CCl_4 and aniline in ACF (pore width 1.4 nm) show divergence at the transition confirming the hexatic phase [2]. The two parameters: the ratio of fluid-pore walls interaction/fluid-fluid interactions as well as the pore sizes are mainly responsible for existence of these transitions [3]. Electron paramagnetic resonance (EPR) of ACF filled with different fluids was measured in order to find host↔guest interaction. The experiment has been thought out as a test for spontaneous ordering of the molecules captured in the nanopores system in ACF.

2. Experimental

The experiments were carried out on pristine and liquid-filled (CCl_4, C_6H_6 and $C_6H_5NO_2$) porous ACF samples, with pores 1.4 nm wide. ACF was degased at 10^{-5} Tr vacuum pump, and then filled with appropriate liquid.

S.J. Rzoska and V.P. Zhelezny (eds.), Nonlinear Dielectric Phenomena in Complex Liquids, 387-392.

EPR spectra were obtained using a Radiopan ES/X spectrometer equipped with Oxford Instruments gas flow helium cryostat within the temperature between 4.2 ÷ 300 K. Microwave frequency was measured by microwave frequency counter with an accuracy of 5 kHz. The magnetic field was calibrated by tracking NMR magnetometer with an accuracy of 0.005 mT.

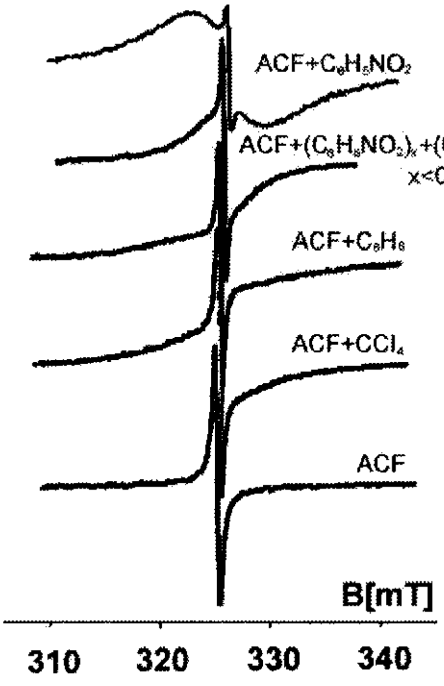

Figure 1. EPR of pristine ACF and ACF filled with different liquids.

3. Results and Discussion

3.1 EPR of ACF

In order to get information about the host↔guest interaction, EPR measurements of ACF (host) and CCl_4, C_6H_6 and $C_6H_5NO_2$ (guests) were performed. Pristine ACF is characterized by single Lorenzian line recorded at g = 2.0031 – g value which is characteristic of carbon materials (graphite $g_\perp$ = 2.0031 [4], nano-diamond g = 2.0029 [5], C_{60} fullerene g = 2.0026 [6]). *Figure 1* shows EPR spectra for pristine ACF and ACF with adsorbed liquids. When guest molecules are adsorbed in ACF voids EPR spectrum of ACF is modified – a broader component of EPR signal appears for all studied systems. There is no EPR signal from guest molecules: no charge transfer from ACF to guest molecules – no hyperfine splitting arising from interaction with nuclear spins of H or N was observed. The strongest modification of EPR spectrum of ACF was observed for ACF with $C_6H_5NO_2$ and this system will be discussed in detail.

3.2 ACF + $C_6H_5NO_2$

EPR signal of ACF with $C_6H_5NO_2$ consists of three lines (*Fig.2* and *3*). The narrow line (1) is characteristic for pristine ACF. Its g-value is equal to $g_\perp$ of graphite [4]. Its line width and g-factor are temperature independent (*Fig.3 a,b)*. Two broader components of the signal – lines (2) and (3) – are also connected with the nanographite structure of ACF. The line (2) originates from nanographite particles (host) surrounded by guest molecules captured in nanopores. Similarly to component (1), line width and g-factor are temperature independent. Broadening of the line (2), compared to (1), is caused by the shorter relaxation time of the more dense system. No Dysonian shape of EPR line is observed for each component. It means, that ACF crystallites size

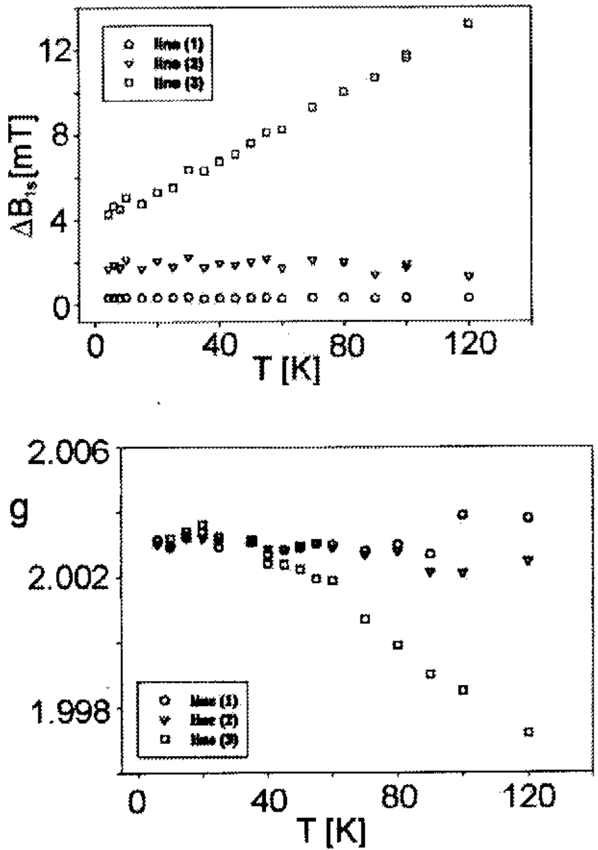

Figure 3. Temperature dependencies of: *a)* line width and *b)* g-factor.

3.3 EPR of smal carbon particles

No hyperfine splitting arising from interaction of observed paramagnetic centers with nuclear spins of H or N and Curie law observed for all components of registered EPR spectrum make possible to treat ACF as a system of nanographite particles. Such approach were proposed for fullerenes [7] and UDD (ultra dispersed diamond) [5].

There are two effects modifying the electronic properties of small particles (nanoparticles) surface effects and quantum size effects [8]. It is due to the fact that nanoparticles have discrete structure of energy levels [8,9]. There is a strong influence of the size of a nanoparticle on the g-factor value. General conclusion from the papers [8,9] is that the absolute value of the g-shift (Δg) should decrease with decreasing size of nanoparticle. The shift is described by following equation:

is lower than 3.2 μm – penetration depth of microwave field. Each of the three lines holds the Curie law (*Fig.2 b, c, d*). No hyperfine splitting from interaction with H or N nuclei together with the Curie law for all three components confirm the localization of paramagnetic centers within nanocrystallites of ACF.

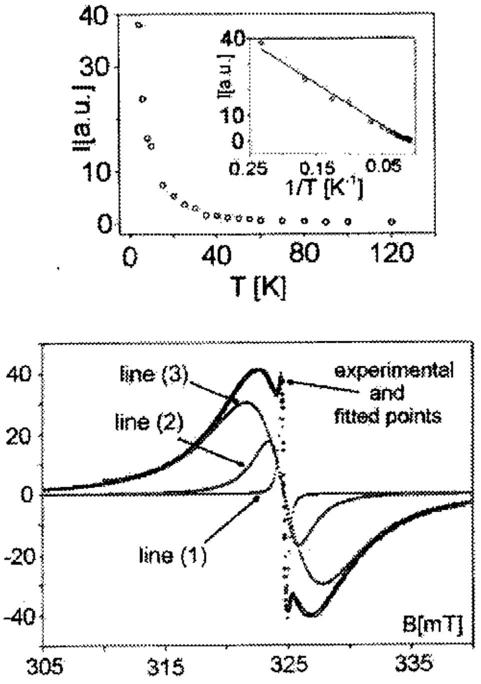

Figure 2. EPR spectrum for ACF: a) filled with nitrobenzene – fit is a sum of lines (1), (2) and (3); b) Curie law for line (1); c) Curie law for line (2); d) Curie law for line (3)

Line width and g-factor of the component (3) of observed EPR spectrum strongly depends on temperature (*Fig.3 a, b*). Such a behavior one can explain as a surface effect in ACF. Stronger instabilities of paramagnetic centers at the surface of ACF or in its larger pores appear as a temperature effect. When temperature is lowered below 20 K, both, line width and g-factor reach values characteristic for graphite nanoparticles surrounded by guest molecules captured in pores.

$$\Delta g(L) = \left[1 - \alpha \frac{a}{L}\right] \Delta g(\infty) \qquad (1)$$

$\Delta g = g - g_e$
g_e – 2.0023 (value for free electron)
$\Delta g(L)$ – g-shift of nanoparticle
α – parameter of the order of unity

a – lattice constant 0.335 nm
L – radius of a spherical particle
$\Delta g(\infty)$ – g-shift of a bulk material

EPR measurements of paramagnetic centers localized on ACF nanocrystallites in the nitrobenzene-filled ACF show g-factor shift to lower values:

$g_{\text{bulk}} = 2.0031$

$g_{\text{nanoparticle}} = 2.0029 = \bar{g}_{(2)}$

where $g_{\text{nanoparticle}} = \bar{g}_{(2)}$ is the mean value of g-factor of the line (2) (see *Fig. 3 b*).
Because of a strong temperature dependence of the width of the line (3) (*Fig.3 a*), which suggests that the line originates from the instabilities that may occur in large pores or the fibres' surface, only the g values of the lines (1) and (2) have been taken into account. Substituting these values to equation (1) it is possible to get the size of the cubic or spherical particles on which the paramagnetic centres are localised. This size is approximately 1.34 nm – ACF nanographite size [1].

4. Conclusions

Our EPR results suggest that the lines observed describe paramagnetic centers localized at nanocrystallites of ACF. There is no EPR signal from liquid molecules as has been observed. No hyperfine splitting arising from interaction of the EPR centers with nuclear spins of H or N and stronger modification for polar molecules of $C_6H_5NO_2$ leads to a conclusion that only very weak host↔guest interaction can appear in the studied systems, and van der Waals forces are significant. This result confirms our molecular simulation results [3].

The size of nanoparticles obtained in our experiment based on the theory of EPR for small particles – 1.34 nm is in good agreement with the model for structure of ACF proposed in [1].

5. References

1. Fung, A.W. P., Wang, Z. H., Dresselhaus, M. S., Dresselhaus, G., Pekala, R. W. and Endo, M. (1994) Coulomb-gap magnetotransport in granular and porous carbon structures, *Physical Review* **B49**, 17325-17335.

2. Radhakrishnan, R., Gubbins, K. E. and Śliwińska-Bartkowiak, M. (2002) Existence of Hexatic Phase in Porous Media, *Physical Review Letters* **89**, 076101-1-4.

3. Śliwińska-Bartkowiak, M., Dudziak, G., Sikorski, R., Gras, R., Radhakrishnan, R. and Gubbins, K. E. (2001) Melting/freezing behavior of a fluid confined in porous glasses and MCM-41: Dielectric spectroscopy and molecular simulation, *Journal of Chemical Physics* **114(2)**, 950-962.

4. Stankowski, J., Piekara-Sady, L., Kempiński, W., Huminiecki, O. and Szczaniecki, P. B. (1997) EPR of graphite and fullerenes, *Fullerenes Science and Technology* **5(6)**, 1203-1217.

5. Shames, A. I., Panich, A. M., Kempiński, W., Alexenskii, A. E., Baidakova, M. V., Dideikin, A. T., Osipov, V. Y., Siklitski, V. I., Osawa, E. and Ozawa, M. (2002) Defects and impurities in nanodiamonds: EPR, NMR and TEM study, *Journal of Physics and Chemistry of Solids* **63(11)**, 1993-2001.
6. Kempiński, W., Scharff, P., Stankowski, J., Piekara-Sady, L. and Trybuła, Z. (1997) EPR of fullerene ions and superconductivity in K-fullerides at low doping levels, *Physica C* **274**, 232-236.
7. Stankowski, J., Piekara-Sady, L. and Kempiński, W. (2000) EPR of fullerene molecule-derived paramagnetic center as mesoscopic conducting object, *Applied Magnetic Resonance* **19**, 539-546.
8. Buttet, J., Car, R. and Myles, Ch.W. (1982) Size dependence of the conduction-electron-spin-resonance *g* shift in a small sodium particle: Orthogonalized standing-wave calculations, *Physical Review* **B26**, 2414-2431.
9. Myles, Ch. W. (1982) Shape dependence of the conduction-electron spin-resonance *g* shift in a small sodium particle, *Physical Review* **B26**, 2648-2651.