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Study of Viscous Liquids by Spin Micro- and Macroprobe Methods at 2-mm Wave Band EPR

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Abstract. The possibility of combined application of spin microprobe and macroprobe methods at 2-mm wave band EPR in determining the viscosity of a model system is demonstrated. Such an approach widens the range of dynamic viscosity EPR measurement in condensed systems and gives one the possibility to study separately various dynamic processes in a matrix.

1. Introduction

The method of spin label and probe, in which nitroxide radical (NR) is used as a microspin reporter, is successfully used in the study of dynamic and other properties of various condensed systems [1-3], polymers and their solutions [4]. However, the interpretation of the data, obtained by this method at 3-cm wave band EPR, which is generally used for these purposes, is sometimes ambiguous. This may be stipulated mainly by a poor spectral resolution at this band and by the uncertainty of a radical hydrodynamic radius, which can vary by more than one order of magnitude, depending on the size and geometry of molecules of a matrix under study [1].

The ratio of the radical and matrix molecule sizes must also be taken into account for the correct data interpretation. If they are close, the radical can enter the crystalline cell of high-viscous matrix. As a result, its translative diffusion is almost terminated with the structural α-transition of the matrix, while its rotation diffusion remains sufficiently fast. Such a radical is pressed out into non-crystallized regions only at the temperature of the structural β-transition. If the radical is significantly larger than the solvent molecule, it can be pressed out into non-crystallized regions already in the point of the phase α-transition. As a result, the local radical concentration sharply increases, leading to the distortion of a spectrum shape, and consequently to its incorrect interpretation. Besides, the effective rotation frequency of a radical with comparatively stretched substituent, in which the intramolecular motions are possible, is changed weakly at the transition from radical to radical. This frequency seems to be defined not only by a rotation of such radicals as a whole, but mainly by the intramolecular motion of their active fragment.

If low-molecular weight liquids are analogous to Newton ones, the real high-viscous liquids are frequently resilient Maxwell substances [5]. It implies that at fast interactions of NR with its microenvironment, the latter behaves as an elastic body. The correlation time τ_c of probe rotation is therefore significantly smaller than that of mechanical relaxation of such an interaction [5]. Thus τ_c does not appear as a sufficiently informative parameter, characteristic of a dynamic process, and macro- and microscale dynamic parameters usually do not coincide [5].

Therefore, the correct interpretation of the results, obtained by using the method of spin microprobe or microlabel should be completed with the data, obtained by other appropriate methods.

Earlier we have shown [6] that the dielectric relaxation method can be used for this purpose. In this communication the other method is described, namely, the method of spin macroprobe, in which single crystalline organic metals on base of dibenzotetrathiafulvalene (DB-TTF), *bis*(ethylenedithio)tetrathiafulvalene (BEDT-TTF), tetramethyltetrathiafulvalene (TM-TTF), naphthalene and perylene ion-radical salts (IRS) as massive paramagnets are used.

2. Experimental

Single cryslalline organic metals on base of IRS were synthesized according to methods described in [7].

EPR experiments were perfomed by using a 2-mm (EPR5-01) wave band spectrometer with a superconductive magnet and H_{011} type cavity described in detail in [8-10]. Magnetic resonance parameters of IRS were also measured by using a 3-cm wave band EPR-V spectrometer. The almost spherical NR 2,2,6,6-tetramethyl-3-phenylethyl-4-oxo-piperidinyl-l-oxyl was used as a spin microprobe in the solution (1 : 10) of nujol in *tert*-butylbenzene as a model system. IRS as a spin macroprobe was introduced freely into the center of quartz capillary with the substance under study at room temperature. Then the capillary was placed into the cavity of the EPR spectrometer at T = 300 K, so that the spin macroprobe was oriented freely in an external magnetic field. In order to register the spin macroprobe reorientation this system was frozen down to T= 100 K, turned by 90° near the capillary's axis and then heated up to some temperature (in our case to about 260 K). This procedure was repeated at different temperatures. In the investigation of the model system $(DB\text{-}TTF)_3PtBr_6$ single crystals of 100x80x30 (I), 80x40x30 (II) and 50x30x30 μm^3 (III) dimension sizes and of $N = 9.8 \times 10^{26}$ m^{-3} specific bulk spin concentration and other IRS were used. The same single crystal attached to the cavity was used as an external standard. The error of the temperature setting was ±0.5 K.

3. Results and Discussion

At different EPR wave bands all IRS demonstrate a quite intensive exchange-narrowed single EPR absorption signal. Their linewidths are defined by anisotropic spin delocalization and therefore are characterized by a tensor quantity [11, 12]. An unpaired electron interacts with several heteroatoms entering the molecules of TTF group, hence the g-factor of IRS is also characterized by a tensor quantity and can vary in a wide range, depending on the crystal orientation in magnetic field [11, 12]. The magnetic parameters of some IRS with different anions^are summarized in Table 1.

Long axes of TTF molecules are arranged almost parallel to one another and are oriented under a certain angle with respect to the IRS crystalographic axes. In an external magnetic field the total dipole moment of unpaired electrons tends to be oriented along the field direction to attain the minimum energy of the spins. Provided that this disturbing force is greater than the force of dynamic friction in the sample under study, the single crystalline IRS freely hanging in the sample is oriented in the magnetic field as it is illustrated in Fig. la. The above condi-

Table 1. Peak-to-peak linewidth ΔB_{pp}, field shift dB (all in mT), and g_a component of $\boldsymbol{g}$-tensor of organic metals on the base of dibenzotetrathiafulvalene (DB-TTF), *bis*(ethylenedithio)tetrathiafulvalene (BEDT-TTF), tetramethyltetrathiafulvalene (TM-TTF), naphthalene and perylene ion-radical salts.

Organic metal	ΔB_{pp}[a]	ΔB_{pp}[b]	dB	g_{xx}
$(DB\text{-}TTF)_3PtBr_6$	0.30	0.44	27.5	2.01628
$(DB\text{-}TTF)_2PtBr_6$	0.51	0.63	26.1	2.01542
$(DB\text{-}TTF)_{033}PtBr_6$	0.62	0.93	8.6	2.00843
$(DB\text{-}TTF)_{267}SnCl_6$	0.62	2.64	0.5	2.01026
$(DB\text{-}TTF)_{25}FeCl_4$	1.65	0.93	0.2	2.01526
$(TM\text{-}TTF)_2CuBr_2$	0.82	1.12	8.4	2.01354
$(TM\text{-}TTF)_2SCN$	0.57	0.51	3.4	2.01287
$(TM\text{-}TTF)_2J$	1.35	1.50	1.5	2.01234
$(BEDT\text{-}TTF)HgCl_3$	2.01	3.73	16.4	2.01214
$(BEDT\text{-}TTF)_2CuCl_2$	2.32	4.25	14.2	2.01107
$(BEDT\text{-}TTF)_2BF_4$	2.11	3.12	11.6	2.01150
$(BEDT\text{-}TTF)HgBr_3$	1.62	2.33	5.8	2.00989
(BEDT-TTF)AgClj	3.83	7.95	0.5	2.00975
$(Naphthalene)_2PF_s$	0.07	0.18	0.0	2.00316
$(Perylene)_{1.8}PF_6$	0.05	0.15	1.2	2.00321

[a] 3-cm wave band EPR.

[b] 2-mm wave band EPR.

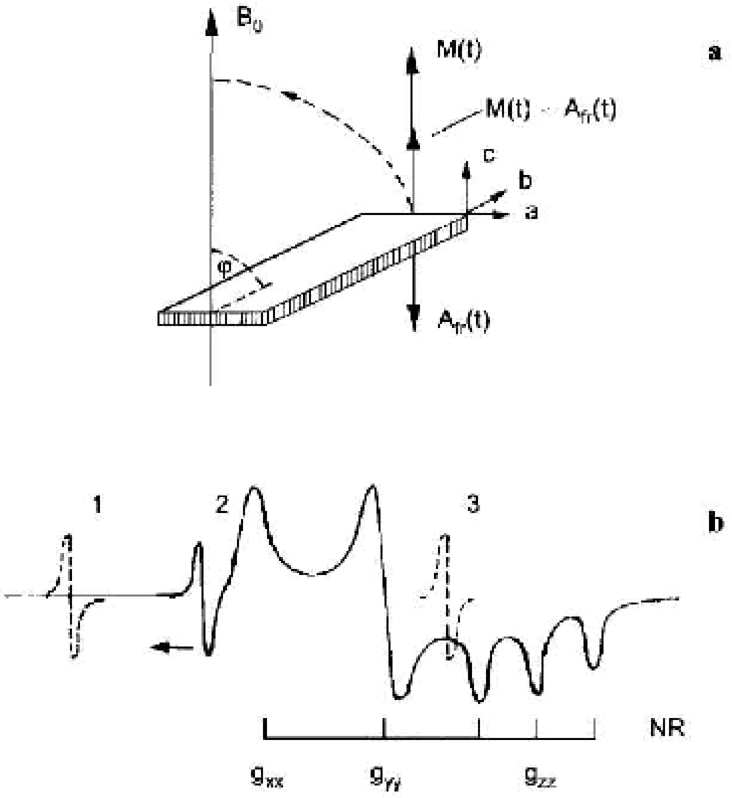

Fig. 1. *a* Schematic representation of orientation of spin macroprobe $(DBTTF)_3PtBr_6$ single crystal in an external magnetic field under ***M***(*t*) — ***A***$_{fr}$(*t*) resulting forced momentum in the heated model system, *b* a superposition of the spectra of spin macroprobe (*1-3* single lines) and microprobe (NR) in the model system registered at initial time and $T < T_g = 256$ K (3), arbitrary *t* value (*2*), and *t* ® ¥ limit at *T* » T_g (*1*).

tion was examined by us to be realized at the magnetic field higher than ~1.5 T. As the *g*-factor of IRS is the tensor value, such a reorientation process is registered directly by the shift of its EPR line d*B* (see Table 1) from the initial position *3* to lower magnetic fields into the final position *1* (Fig. lb).

This process can be applied to the study of molecular properties of IRS themselves. The total magnetization of a crystal is maximal at the parallel location of the longest *x* axis of TTF molecules in the crystal. In case of a different mutual position of IRS molecules, e.g., a parquet-like one, the apparent magnetization decreases as a function of the dihedral angle between the planes of TTF molecules in a stack. It is seen from the Table 1 that with crystals reorientation in the same medium, their EPR lines are shifted in a different manner to the lower fields due probably to different packing of the molecules in a crystal. For example, the data tabulated allows the prediction of the decrease of stacks ordering $(DB\text{-}TTF)_3PtBr_6$ ® $(DB\text{-}TTF)_2PtBr_6$ ® $(DB\text{-}TTF)_{0.33}PtBr_6$ ® $(DB\text{-}TTF)_{2.67}SnCl_6$; $(BEDT\text{-}TTF)HgCl_3$ ® $(BEDT\text{-}TTF)_2CuCl_2$ ® $(BEDT\text{-}TTF)_2BF_4$ ® $(BEDT\text{-}TTF)HgBr_3$ ® $(BEDT\text{-}TTF)AgCl_3$; $(TM\text{-}TTF)CuBr_2$ ® $(TM\text{-}TTF)_2SCN$ ® $(TM\text{-}TTF)_2J$ series and in (DB-TTF)A ® (BEDT-TTF)A ® (TM-TTF)A series.

The main characteristic of the reorientation process of the spin macroprobe is the angle (see Fig. 1a)

$$\varphi(t) = \arccos\left(\frac{\delta B(t)}{\delta B(t \to \infty)}\right), \tag{1}$$

where $\delta B(t \to \infty)$ and $\delta B(t)$ are the maximal EPR line shifts at $t \to \infty$ limit and at a current time *t*, respectively (Fig. 1b). So the spin macroprobe dynamics can be described by the following differential equation for a one-point-fixed oscillator

$$I\ddot{\varphi} + A_{\mathrm{fr}}(t) + M(t) = 0, \tag{2}$$

where $I = mb^2/12$, $A_{\mathrm{fr}}(t) = 6\pi\eta b^3\omega$ and $M(t) = NV\mu_0\mu_B B_0 \sin(\varphi)$ are the moments of inertia, friction and disturbing force, respectively; *m, b* and *V* are the mass, characteristic size and the volume of the crystal, respectively, η is the coefficient of the system dynamic viscosity, $\omega = \dot{\varphi}$ is the angular velocity of the crystal, *N* is the IRS volume spin concentration, μ_0 is the permeability for vacuum, μ_B is the Bohr magneton and B_0 is the strength of an external magnetic field. Characteristic times of such dissipative system turn in a magnetic field significantly exceed $I/(6\pi\eta b^3)$ ratio, therefore in the case of the motion on small angles Eq. (2) appears as

$$\dot{\varphi} + \tau_m^{-1}\varphi = 0, \tag{3}$$

with its solution as follows

$$\varphi(t) = \varphi_0 \exp(-t/\tau_m), \tag{4}$$

Where $\tau_m = 6\pi\eta b^3/(NV\mu_0\mu_B B_0) = \eta/\alpha$ is the mechanical relaxation time for such a process and α is a crystal constant. The latter value was determined for spin macroprobes I, II, and III to be 5.8×10^{-4}, 9.2×10^{-4} and 1.3×10^{-3} Pa, respectively.

Figure 2 demonstrates the plots of Eq. (4) for the spin macroprobe II, registered at various temperatures, whose slopes indicate τ_m value and consequently the viscosity of the system under study.

At the same time and matrix properties, the correlation time of the spin microprobe rotation can be determined from the broadening $\delta(\Delta B_i)$ of their spectral components (Fig. 1b) according to the equation [13]

$$2\tau_c^{-1} = \gamma_e \delta(\Delta B_i), \tag{5}$$

where γ_e is the gyromagnetic ratio for electron. As the broadening and shift of NR spectral components was found to be close to one another, therefore Brownian diffusion of NR is realized in this case [14].

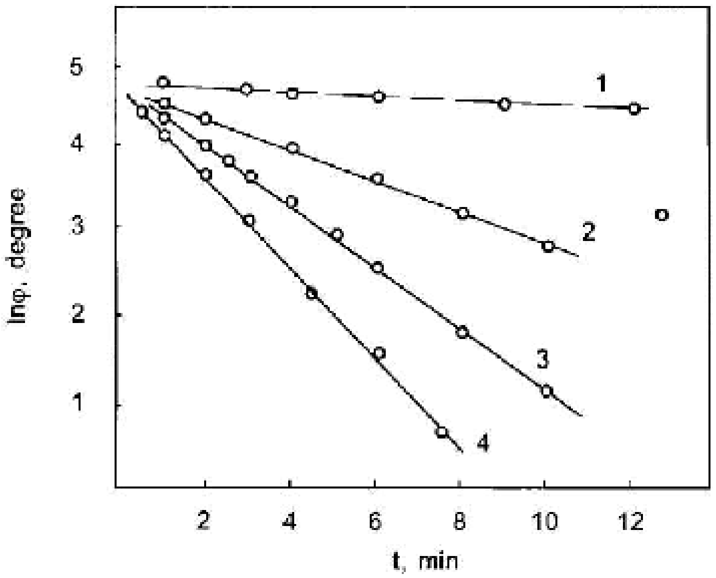

Fig. 2. Semilogarithmic plot of the angle φ of spin macroprobe turn in the model system heated up to T= 257.4 (*1*), 258.4 (*2*), 258.9 (*3*), and 262.5 K (*4*) as a function of time.

Figure 3 exhibits the Arrhenius dependence for spin microprobe Brownian rotation in the model system with correlation time $\tau_c = 4.7\times10^{-20}\exp(0.57\ \text{eV}/kT)$ s, where k is the Boltzmann constant and T is the absolute temperature. An anomalous high preexponent value, exceeding the inverted frequencies of molecular orientation oscillations in condensed phase, and the activation energy of radical rotation higher than that of a pure solvent indicate the relationship between NR mobility and a segmental mobility of nujol extented molecules $(\text{-CH}_2\text{-CH}_2\text{-})_n$, where $n > 10$. A value of η of the system under study can be calculated by using a well known Stokes's equation

$$\eta = \frac{3kT\tau_c}{4\pi r_{NO}^3}, \qquad (6)$$

where r_{NO} is the radius of the NR active fragment.

Figure 4 depicts the temperature dependence of the viscosity of the model system, determined by the method of spin microprobe for low temperatures and by the method of spin macroprobe for higher temperatures, r = 0.14 nm used for the calculation is close to the theoretical value (0.15 nm [1]) for nitroxide radical of close structure. It is evident that the data obtained by both methods are in agreement.

As it would be expected from the figure, $\eta(T)$ dependence is of activation character, is proportional to $\exp(E_a/kT)$ with E_a determined above and reflects the depinning of motion of the radical microenvironment in a glass-like matrix at $T \le 256$ K. The matrix appears as a liquid in a structural aspect but as a solid in a mechanical aspect at these temperatures. T_g = 256 K is a point of graded change of the matrix viscosity (see Fig. 4). The matrix begins melting mechani-

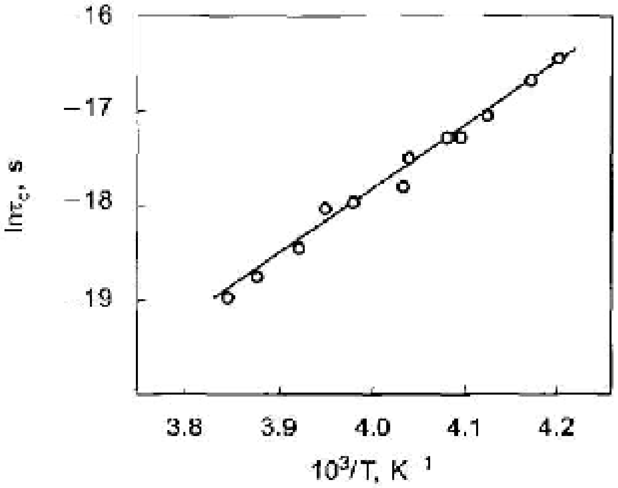

Fig. 3. The Arrhenius dependence of apparent correlation time t_c of spin microprobe rotation in the model system calculated by using Eq. (5).

cally at this temperature and gradually transforms into a viscous-flow state with the absorption of melting heat. Such a process proceeds in a limited temperature range that can be attributed to finite sizes of interacting molecules, and also to the dispersion of the length of the matrix molecules. The change of viscosity seems to have also an activation character at *T* ³ 260 K.

Extrapolating the h(*T*) dependence obtained by the method of spin microprobe to higher temperatures, one obtains h = 0.11 Pa×s at room temperature, i.e., it falls within a range of viscosity for different oils. However, such an extrapola-

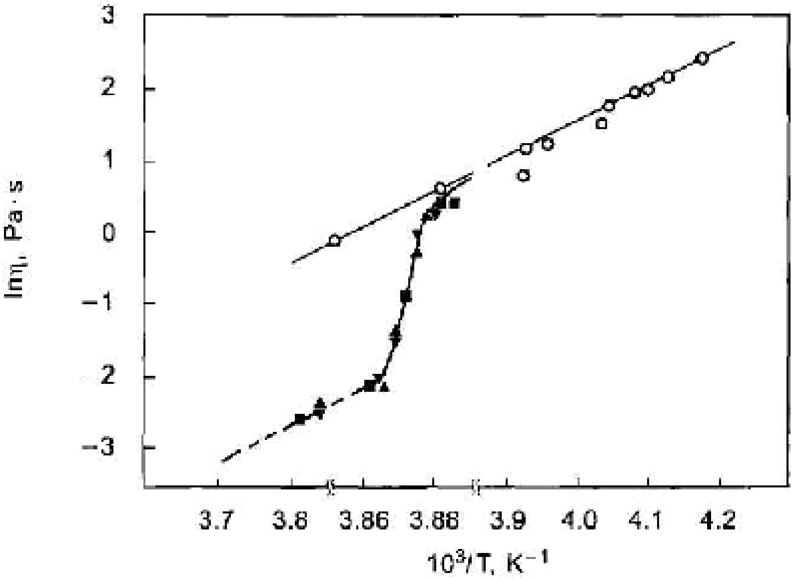

Fig. 4. Semilogarithmic dependence of dynamic viscosity h of the model system versus inverted temperature obtained by spin macroprobe (dashed points) and microprobe (open points) methods. Squares, triangles and inverted triangles are attributed to the I, II, and III macrospin probes, respectively.

tion yields $h = 5.6{\times}10^{-3}$ Pa×s, by considering the jump of $h(T)$ function at T_g shown in Fig. 4. The latter value exceeds the viscosity of cumene only by an order of magnitude and seems to be more real.

The time of the NR contact with the nearest environment t is significantly larger than t_c at $T» T_g$. On the other hand, this value is significantly smaller than the time of mechanical relaxation t_m of spin macroprobe. It implies that it becomes possible to register separately or simultaneously both elastic deformation at $t/t_c >> 1$ and a viscous flow at $t/t_m << 1$ of the same matrix at the same temperature, by using spin probes of various sizes.

4. Conclusions

Thus, the method of spin macroprobe at high magnetic fields (~5 T) successfully enriches the classic method of spin microprobe and enables a more accurate determination of dynamic viscosity in a wider temperature range. Therefore it becomes possible to characterize the mechanical losses in condensed media in a stationary regime, and to establish their glass transition point in the case of extreme mechanical losses in the system.

The dependence $t_m\ \mu\ b^3B_0^{-1}$ is derived from Eq. (4). Considering both the higher both sensitivity and magnetic field strength of the 2-mm wave band EPR spectroscopy as compared with other bands, one can conclude that the range of dynamic viscosity (and likely the other parameters as well) measurement in condensed systems is widened by at least two orders of magnitude at this band.

The high absolute sensitivity of the method can be used in the investigation of microscopic objects. One could suppose that with the sensitivity of about $5{\times}10^8$ spin/mT the signal of less then 10 mg of IRS could be registered at millimeter wave band. It implies that a linear size of the object can amount only to 2-3 mm, enabling the study of individual living cells and other microscopic objects. Besides, such a sensitivity of the method combined with the high spectral resolution allows the registration of perturbances, caused by weak intra- and interelectron interactions and the application of the method to microscopic analysis, by using IRS as specific additives, for example, in EPR tomography.

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