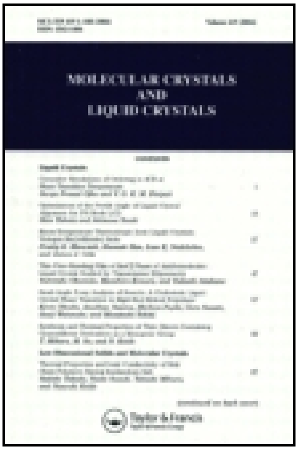

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HEXAGONAL LYOMESOPHASE OF SDS-WATER SYSTEM: ESR-SPECTROSCOPY FOR STUDY INTERMOLECULAR INTERACTION OF SPIN ZOND

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Abstract Translational diffusion of nitroxyl radical tanol was investigated by spin zond (s.z.) method in hexagonal phase and pretransitional region of SDS - Water system. Supposing the homogeneous distribution of s.z., the results obtained can be interpreted within the framework of Brownian model of translational diffusion.

INTRODUCTION

The investigation of spin zond (s.z.) intermolecular interactions controlled by translational diffusion is of great interest in lyotropic liquid crystals which are the biological membrane models. The aim of the investigation is the study of ESR-spectroscopy manifestations of spin exchange and dipolar interaction[1,2] and the division of their contributions into phase relaxation in highviscous systems by means of the including into the analysis of special line dynamic shifts[2,3].

MATERIALS AND METHODS

Sodium Dodecyl Sulphate - Water system ("Sigma",L-5750) was investigated in the range of 3 ÷ 45% mass. SDS and

$T = 30 \div 60^{o}C$ by s.z. method (s.z. - 2,2,6,6-tetramethyl-4-oxypiperidin-1-oxyl). Spin exchange constant rates $K_e \sim D_{tr}$, dipolar interaction constant rates $K_d \sim D_{tr}^{-1}$, rotational frequency values $\nu \sim D_{rot}$, values of the distance between spectral line M = 0, M = -1 (M - magnetic quantum number ^{14}N) α and s.z. order parameter S were measured. K_e and K_d were calculated by formulae

$$\Gamma = \Gamma_0 + 2/3\ K_eC + \alpha K_d \qquad (1)$$

$$(K_e - \beta K_d)C = -0.75\Gamma + \sqrt{(0.75\Gamma)^2 + 2\alpha\delta}, \qquad (2)$$

where Γ - width spectral line (M=-1), δ - spectral line dynamic shift (M=-1), α, β - constants dependent on translational diffusion model[2]. In isotropic phase ν is determined up to standard[4].

EXPERIMENTAL RESULTS AND DISCUSSION

The hexagonal phase formation under 37% SDS is fixed by the sharp increase of α (Table I), which takes place due to the origin of s.z. spectrum inhomogeneous broadening. Order parameter S is $\sim 8 \cdot 10^{-2}$ in the system

TABLE I. Values α, K_e and K_d for various SDS-systems. ($T = 30^oC$)

SDS, %mass.	$\alpha \pm 0.03$, G	K_e, $G \cdot M^{-1}$	K_d, $G \cdot M^{-1}$
3.0	16.91	102+4	---
17.5	16.40	89+2	---
30.0	16.14	61+2	---
36.0	16.17	52+1	43+4
37.0	16.46	---	---
45.0	15.81	28+1	75+5

of 45% SDS and T = 30°C. In isotropic phase the addition of SDS leads to the decreasing of α, reflecting the weakening of s.z. - water H-bound with the increasing of bound water involved with concentration SDS raise.

Γ(C) dependence for systems of 3 ÷ 36% SDS at T=30°C has the linear character (Fig. 1). Similar dependences for systems of 37 and 45% SDS in s.z. small concentration region are non-linear (Fig. 1) which reflects the averaging by spin exchange and dipolar interaction of the contribution in Γ owing to inhomogeneous broadening of spectral line.

The same effect is illustrated by the dependence of asymmetry parameter A(C) (A - ratio the positive amplitude to full one of the differential spectral line) in Fig. 2.

For systems of 36% and 45% SDS the division of contributions of spin exchange and dipolar interaction into phase relaxation was made, supposing the homogeneous s.z. concentration distribution by formulae (1) and (2), (Table I). A sharp increasing of s.z. dipolar interactions contribution is observed under the transition from 36% SDS system to 45% SDS system, while $K_e\ K_d$ = = $(2200 \pm 200)\ G^2 \cdot M^{-2}$ remains the same, that agrees with theoretical value $K_e\ K_d = 2\pi^2\gamma^2\hbar^2 = 2500\ G^2 \cdot M^{-2}$ for Brownian diffusion model.

There is $K_e/\nu = (0.32 \pm 0.03)\ M^{-1}$ for 3 ÷ 36% SDS at T = 50°C that is 5 times larger than K_e/ν for glycerin-water system (1:1). The value of K_e/ν increases by 100% for 25 - 30% SDS at 30°C for example. These results contradict well-known experimental fact that K_e/ν is constant^5. In that case K_e/ν depends only on s.z. geometry. These experimental results can be explained either by the s.z. inhomogeneous distri-

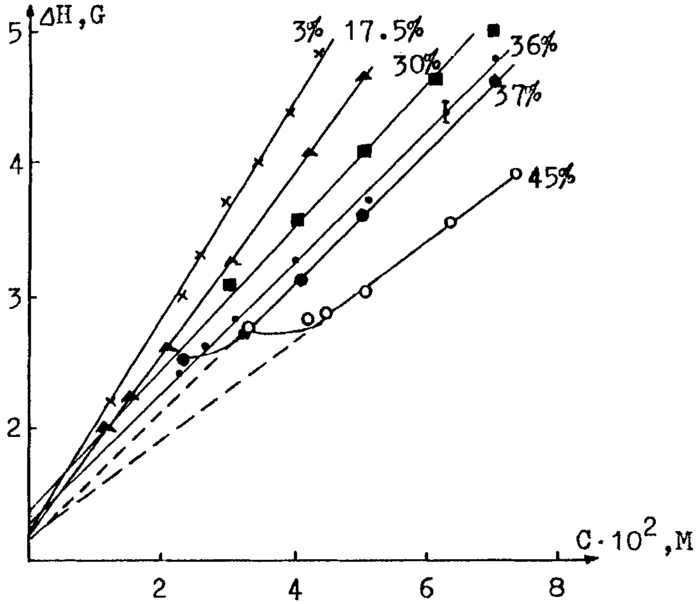

FIGURE 1. S.z. concentration dependences of ΔH (M=0) in various SDS systems (T = 30°C).

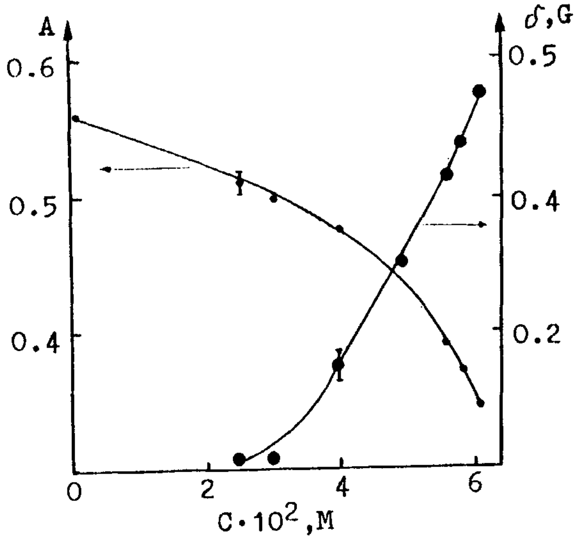

FIGURE 2. S.z. concentration dependences of δ (M=-1) and A (M=-1) in 45% SDS system (T = 30°C).

bution effect, or by the change of the character of bound between translational and rotational diffusion of s.z. in micellar systems.

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