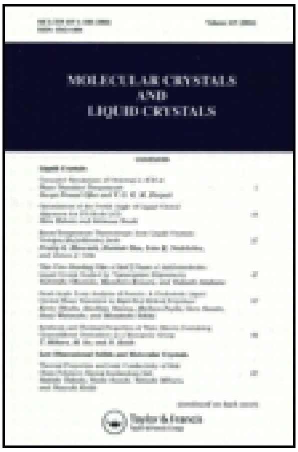

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Hydrogen-Deuterium Isotopic Effect in Lyotropic Liquid Crystals

Kirill A. Lyashenko [a] & Evgeni V. Popov [b]

[a] Institute of Industrial Ecology, Ekaterinburg, Russian Federation

[b] Ural State Technical University, Ekaterinburg, Russian Federation

Version of record first published: 04 Oct 2006.

To cite this article: Kirill A. Lyashenko & Evgeni V. Popov (1995): Hydrogen-Deuterium Isotopic Effect in Lyotropic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 265:1, 645-650

To link to this article: http://dx.doi.org/10.1080/10587259508041731

Mol. Cryst. Liq. Cryst. 1995, Vol. 265, pp. 645–650
Reprints available directly from the publisher
Photocopying permitted by license only

HYDROGEN-DEUTERIUM ISOTOPIC EFFECT IN LYOTROPIC LIQUID CRYSTALS

KIRILL A.LYASHENKO
Institute of Industrial Ecology, Ekaterinburg,
Russian Federation
EVGENI V.POPOV
Ural State Technical University, Ekaterinburg,
Russian Federation

Abstract The study of structural reconstructions in liquid crystalline phases of mesomorphic lecithin-water system due to the hydrogen-deuterium isotopic replacement was made by the positron annihilation and infrared spectroscopy methods. The changes in values of parameters of molecular interactions stipulated by such isotopic effect were obtained from the analysis of experimental and theoretical data.

INTRODUCTION

The formation of lyotropic liquid crystalline systems is stipulated by the interaction between amphiphile molecules and molecules of solvent.[1] So the investigation of structural reconstructions in amphiphile molecule ensembles due to hydrogen-deuterium replacement is an actual scientific problem.[2]

The electron-positron annihilation technique may be used as a high sensitive method of the microstructural molecular change studies because it allows the observation of a small changes in local free volume of samples. A changes in molecular ties may be observed by the infrared spectroscopy.[3,4]

Present work is devoted to the investigation of structure changes in a lecithin-water system due to the hydrogen-deuterium replacement by the electron-positron annihilation and infrared spectroscopy methods.

MATERIALS AND METHODS

The lyotropic systems were prepared from the standard 10% ethanol solution of egg lecithin produced by the Kharkov Factory of Bacterial Praparations, distilled ordinary water and chemical pure heavy water produced by the "Isotope" Association. Before samples preparing the ethanol of lecithin systems was evaporated in vacuum.

Analysis of molecular ties changes after hydrogen-deuterium replacement was carried out in lamellar phase of lecithin-water system at temperature 293 K on the infrared spectrometer UR-20.

Analysis of intermolecular free volume changes within lamellar phase, hexagonal phase and micellar solution was made by the electron-positron annihilation method on the positron life-time spectrometer. This spectrometer have time resolution of 380 ps for ^{22}Na positron source. Positron life-time spectra were calculated by POSITRONFIT program.[5]

Methods of interpretation of experimental data were written earlier.[6]

MOLECULAR TIES CHANGES

A total change (c) of system free energy F after dissolving of amphiphile molecules in a solvent is equal to:[7]

$$cF = - cF_s + cF_m + cF_e - cF_v - cF_q - cF_{st} \qquad , (1)$$

where F_s is free energy of sublimation, F_m is free energy of molecular interactions, F_e is free energy of electrostatical interactions between dissolving molecules, F_v is free energy of cavity formation in solvent, F_q is free energy of dissolving molecule mobility, F_{st} is structural free energy.

The free energy of molecular ensembles transference from ordinary water to heavy water is equal to difference (d) between equation (I) for both solvents:

$$dcF = cF\ (D_2O) - cF\ (H_2O) =$$
$$= - dcF_s + dcF_m + dcF_e - dcF_v - dcF_q - dcF_{st} \qquad .(2)$$

In the case of heavy and ordinary water with the same coefficients of surface tightening $dcF_v = 0$. Also $dcF_s = 0$ because these dissolving molecules have no easy changing protons.

A change of hydrophobic free energy F_{hp} also will not be stipulated by the electrostatical interactions (F_e) because an electrical charge is localized only in hydrophile head of amphiphile molecule.

Therefore:

$$dcF_{hp} = dcF_m - dcF_q - dcF_{st} \qquad .(3)$$

The total effect of change of Van-der-Waals interactions (F_m), mobility of molecular hydrophobic tails (F_q), structural changes (F_{st}) lead to an increasing of hydrophobic interactions in heavy water solutions in comparison with ordinary water solutions. For example, the experiments on detergents show thw following values of hydrophobic free energy for one metil group:[7]

$$cF_{hp}\ (H_2O) = 1.40\ \text{kJ/mol} \qquad (4)$$

$$cF_{hp}\ (D_2O) = 1.76\ \text{kJ/mol} \qquad (5)$$

Parameters of infrared spectra of lecithin lyotropic liquid crystals (lamellar phase) in ordinary and heavy water are presented in Table I. These data were obtained by authors.

From the Table one can see that oscillation wave number of $-CH_2-$ group decreases in heavy water. This testifies to the strengthening of C-H molecular ties in hydrophobic tails of molecules. It is interesting that the biggest change of WN takes place in deformation oscillation (I480 sm^{-1}) rather than in valent oscillation (I950 sm^{-1}) of $-CH_2-$ ties. This fact is a good evidence of structural influence of heavy water on a lyotropic ensembles of amphiphile molecules.

TABLE I Wave numbers WN (sm^{-1}) of molecular ties of lecithin lamellar phase in various solvents by the infrared spectra data

Molecular ties	Solvent	
	H_2O	D_2O
P - O - C	990	987
P = O	1260	1240
$C - CH_3$	1420	1415
$- CH_2 -$	1480	1460
$- CH_2 -$	1950	1945
$N - CH_3$	2925	2925
O - H	3550	-
O - D	-	2550

Also from the Table data we see the change of O - H ties wave number due to transference of amphiphile molecules from ordinary water (WN_h) to heavy water (WN_d) is equal to:

$$WN_h/WN_d = 1.4 \qquad (6)$$

This relation may be explained by the dynamic hydrogen-deuterium isotopic effect - change of molecular interaction velocity.

MOLECULAR FREE VOLUME CHANGE

Dependencies of obtained intensity I_a of ortho-positronium annihilation in hydrogen and deuterium systems from lecithin concentration are presented in Figure 1.

The obtained results show the biggest density of heavy water as a solvent of amphiphile molecules because

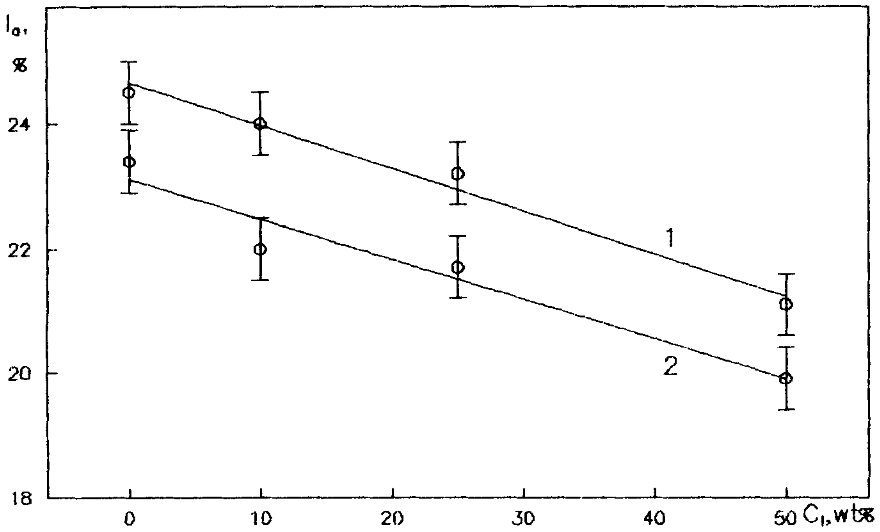

FIGURE 1 Dependencies of ortho-positronium annihilation intensity I_a from lecithin concentration C_l in ordinary water (1) and heavy water (2) solvents

I_a is proportional to sites of ortho-positronium localization in the investigated systems.

More information may be obtained from the dependencies of total free volume V_t in ordinary and heavy water systems presented in Figure 2.

In accordance with the ortho-positronium annihilation model[8] the total free volume of system characterizes a density of molecular ensembles packing. So the increasing of V_t difference between systems with ordinary and heavy water due to the increasing of lecithin concentration shows a compact packing of molecular aggregates (micelles) in deiterium system in comparison with hydrogen system. Furthermore in lamellar phase of lyotropic liquid crystal (50 wt% of lecithin in system) the ratio between total free volumes of amphiphile molecule lyotropic ensembles in ordinary water V_{th} and in heavy water V_{td} is rather and equals:

$$V_{th}/V_{td} = 1.2 \qquad (7)$$

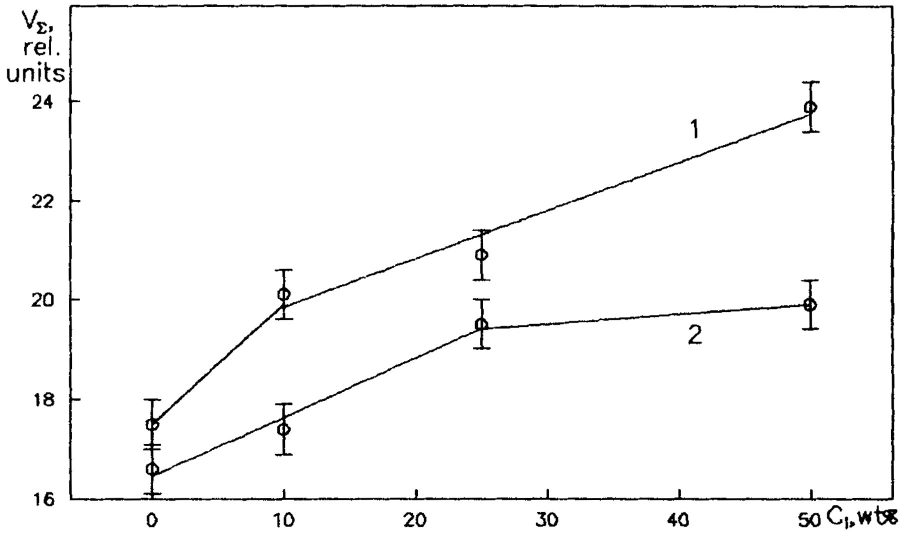

FIGURE 2 Dependencies of total free volume V_t of hydrogen (1) and deiterium (2) lecithin-water systems from the lecithin concentration C_l.

Therefore, the experimental results show that in the case of replacement of ordinary water by heavy water as a solvent of amphiphile molecules they create less quantity of molecular aggregates with more compact packing.

REFERENCES

1. G. N. Brown and J. J. Wolken, Liquid Crystals and Biological Structures (Academic Press, New York, 1979), p.20.
2. E. V. Popov, Biotronics (Higher School, Moscow, 1994), p.225.
3. H. J. Ache, Stud.Phys.Theor.Chem., 57, 318 (1988).
4. E. V. Popov, Mat.Sci. & Eng.B, 13,169 (1992).
5. P. Kirkegaard and M. Eldrup, Comput.Phys.Commun., 7, 401 (1974)
6. E.V. Popov, Mat.Chem. & Phys., 37, 97 (1994)
7. D. Oakenfull, Austr. J. Chem., 28, 715 (1975)
8. M. Eldrup, Chem.Phys., 63, 51 (1981)