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Thermodynamic Studies of Solutions of Some Alkanes Solutes on Two Monomeric Liquid Crystals Stationary Phases

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5-[4-(*p*-methoxyphenyl)-azophenyl]-2-butylthio-1,3,4-oxadiazole and 5-(4-(*p*-propoxyphenyl)-azophenyl)-2-butylthio-1,3,4-oxadiazole were used in gas chromatography at different temperatures to study the interactions and elution characteristics of some *n*-alkanes. These two liquid crystals contain the same backbone and differ in the partial replacement of the terminal alkoxy chain. The curve of the parameter 'b' in function of inverse absolute temperature shows breaks on the levels of the transition temperatures determined by DSC. Thermodynamic quantities show that these values depend to the number of alkanes carbons in these two phases liquid crystalline compounds. The transition temperatures obtained by gas chromatography are in good agreement with those found by DSC. The results are interpreted in terms of parameters 'b' and related thermodynamic quantities.

Key Words: Gas chromatography, Polarizing microscope, Liquid Crystals, Stationary phase, Differential scanning calorimetry, Mesogen.

INTRODUCTION

Liquid crystals are used as stationary phases in gas chromatography in past[1,2]. These phases can either be monomeric[3] or polymeric[4], the latter being more thermally stable. The physical and chemical properties of liquid crystal polymers have been studied by various analytical techniques[5,6]. Gas chromatography (GC) is the direct approach for the study of stationary phase properties and interactions by gas chromatography. It can provide the information on interactions between solutes and stationary phase. Smidrod and Guillet[7] used the poly(N-isopropyl acrylamide) as a stationary phase. A large number of materials have been studied and

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characterized by GC[8-12]; liquid crystalline stationary phases were widely used in analytical gas chromatography[13-15]. The thermodynamics parameters of many solutes were studied using liquid crystalline stationary phases[16,17]. Considering the measurements obtained by GC, it is possible to calculate solubility parameters of the chromatographed substances and give a thermodynamic description of the interactions of these solutes with the liquid crystalline stationary phase[18-20]. The data obtained can be used to obtain temperature-depending and more efficient stationary phases.

Bocquet and Pommier[21] showed that the values of activity coefficients are quite different in the successive domains of the liquid crystals. Seifert and Kraus[22] investigated the solution behaviour of LC phase in capillary GC and correlated the differences between partial molar free excess enthalpies at the transition temperatures with the heats of transition. Coca *et al.*[23] discussed the thermodynamics properties of 22 solutes at infinite dilution in relation with the solute-solvent (liquid crystal) interactions conditioned in an ordered degree in liquid crystal.

Judeinstein *et al.*[24] have shown the good separations of various solutes using LC phases in the solid state. These results could be explained by the important differences of their molar enthalpy of adsorption for a solid state (ΔH_a). Gareth *et al.*[25] have shown that the GC can be used to investigate the phase transition and thermodynamics of mesophases in side-chain polymeric liquid crystals. The aim of this paper is to compare the transition temperature using the parameter 'b' with those found by DSC and to study the evolution of thermodynamics values of homologous series of some *n*-alkanes in two liquid crystalline stationary phases synthesized for this work.

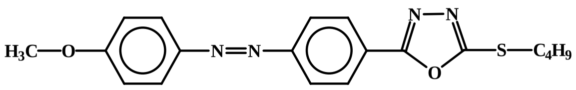
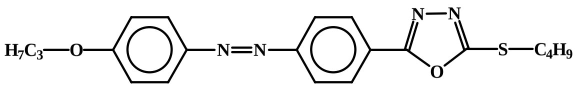
EXPERIMENTAL

A Perkin Elmer Auto System XL gas chromatograph equipped with an FID detector, split-splitless injector and a PE Nelson model 1022 integrator was used. The capillary columns are in borosilicate glass of 30 m long and 0.25 mm inner diameter. They were deactived in laboratory using the Rijks method and then coated by the static method to know the phase stationary mass impregnated on the column which is necessary for the calculation of Vg. The prepared column was then conditioned in the GC oven at a programmed temperature from 60 to 130°C using a 2°/min rate for 12 h with nitrogen carrier gas prior to use.

The nature of the mesogen phases were determined using a Leitz Laborlux 12 hot-stage polarizing microscope equipped with an electric heating device. For the two LC, the transition temperatures, from solid to nematic, then from nematic to isotropic states were determined at a 5°/min heating rate using a Perkin-Elmer differential scanning calorimeter DSC-7

TABLE-1

NAME, STRUCTURE AND TRANSITION TEMPERATURES OF THE TWO PHASES

	Name	Formula	Transition temperatures
Phase **I**	5-[4-(*p*-Methoxyphenyl)-azophenyl]-2-butylthio-1,3,4-oxadiazole		DSC: K → N : 112°C N → I :155°C GC: K → N : 110°C N → I : 157°C
Phase **II**	5-(4-(*p*-Propoxyphenyl)-azophenyl)-2-butylthio-1,3,4-oxadiazole		DSC: K → N : 111°C N → I :152°C GC: K → N : 112°C N → I : 154°C

(K: crystalline, N: nematic, I: isotropic)

TABLE-2

EXCESS MOLAR ENTHALPIES AND ENTROPIES VALUES OF *n*-ALKANES

	Phase I				Phase II			
	Nematic		Isotropic		Nematic		Isotropic	
	ΔH^E (KJ/mol)	ΔS^E (J/mol K)	ΔH^E (KJ/mol)	ΔS^E (J/mol K)	ΔH^E (KJ/mol)	ΔS^E (J/mol K)	ΔH^E (KJ/mol)	ΔS^E (J/mol K)
C13	4.15	19.61	0.40	20.12	0.53	29.27	0.25	28.55
C14	4.05	19.37	0.37	19.94	0.71	29.13	0.23	28.87
C15	4.22	18.98	0.44	19.11	0.86	29.64	0.27	29.20
C16	4.09	20.22	0.55	20.30	0.83	30.85	0.47	29.66
C17	3.74	20.27	0.47	20.23	0.77	30.52	0.19	30.21
C18	3.62	18.44	0.29	19.15	0.49	29.08	-0.09	29.90
C19	3.70	19.87	0.33	20.52	0.64	30.11	0.07	30.46

equipped with an electronic calculator. These temperatures are illustrated in the Table-1. The *n*-alkanes were purchased by Fluka (Buchs, Switzerland).

RESULTS AND DISCUSSION

The parameter 'b' is the slope of the logarithm of retention times (t'_R) of *n*-alkanes homologue series as a function of their carbon atoms number (n)[26].

$$\log (t'_R) = (b \times n) + a$$

The solute activity coefficients, at infinite dilution, γ^∞, were calculated at different temperatures from the following equation[27].

$$\gamma^\infty = 273\ R/Vg\ Ms\ P^0$$

where, Vg is the specific retention volume of the experimental *n*-alkane, calculated using the equation of Littlewood *et al.*[28]. Ms is the molecular mass of the stationary phase, P^0 is the vapour pressure of the pure gaseous solute at column temperature, calculated using the Antoine's equation and constants.

The thermodynamics molar values at infinite dilution were calculated from the following equations[29].

$$\Delta G^E = RT \ln (\gamma^\infty)$$

$$\Delta H^E = Rd(\ln \gamma^\infty)/d(1/T) = R[(\ln \gamma^\infty)T_2-(\ln \gamma^\infty)_{T1}]/(1/T_2)-(1/T_1)$$

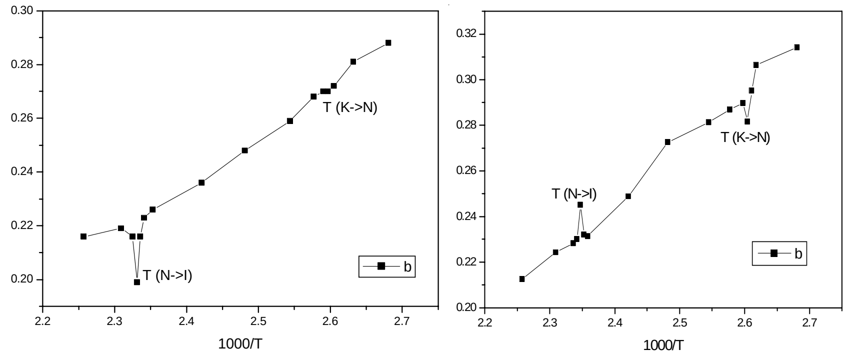
$$\Delta G^E = \Delta H^E - T\Delta S^E$$

Both the compounds exist in a nematic state. Temperatures corresponding to both solid to nematic and nematic to isotropic transitions were determined by gas chromatography on the curve showing the variations of the 'b' parameter of the *n*-alkane series in function of the inverse absolute temperature 1/T (Figs. 1a-b).

Figs. 2a-b show the logarithm of the activity coefficient of each *n*-alkane solute at infinite dilution, ln γ^∞, in function of the inverse absolute temperature 1/T. It can be observed from each curve that both transition temperatures correspond to a discontinuity of the curve.

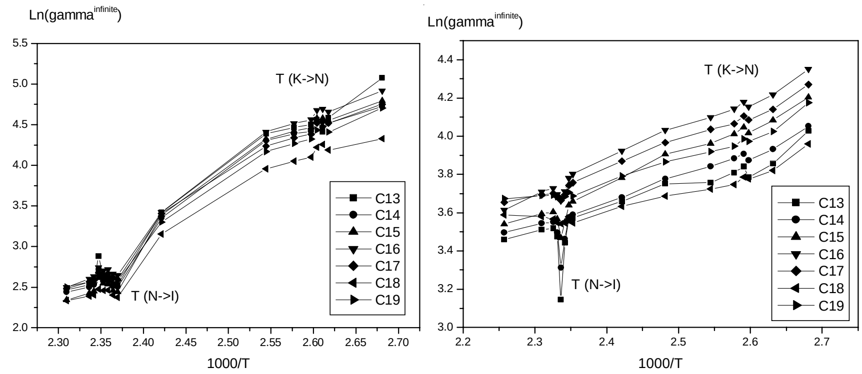
The comparison of the values of transition temperatures, obtained from reported GC and DSC (Table-1), shows that they are in good agreement. The discontinuity observed on each curve at the transition indicates that the solute molecules experience marked change in environment when they enter in a new phase. The interactions of the solutes with the stationary phase in the mesophase region differ from those in the isotropic liquid.

Further, γ^∞ in the two phases regularly decreases in the order $C_{19} > C_{18} > \cdots\cdots\cdots > C_{13}$.



(a) (b)

Fig. 1. Variation of the 'b' parameter in function of inverse absolute temperature (1/T) for (a) Phase I (b) phase II



(a) (b)

Fig. 2. Variation of logarithm of the solute activity coefficients at infinite dilution (ln γ^{∞}) in function of the inverse absolute temperature (1/T) in: (a) phase I (b) phase II

TABLE-3

FREE ENERGY DIFFERENCES VALUES ΔG^E (KJ/MOL) OF *n*-ALKANES

Alkane	Temperature (°C)											
	Phase I						Phase II					
	120	130	140	150	155	160	120	130	140	152	155	160
C13	-3.56	-3.76	-3.95	-4.15	-8.21	-8.31	-10.97	-11.26	-11.56	-11.91	-11.98	-12.12
C14	-3.56	-3.76	-3.95	-4.14	-8.16	-8.26	-10.74	-11.03	-11.32	-11.67	-12.13	-12.27
C15	-3.24	-3.43	-3.62	-3.81	-7.74	-7.84	-10.79	-11.09	-11.38	-11.74	-12.23	-12.38
C16	-3.85	-4.06	-4.26	-4.46	-8.14	-8.24	-11.29	-11.60	-11.91	-12.28	-12.22	-12.37
C17	-4.22	-4.43	-4.63	-4.83	-8.19	-8.29	-11.22	-11.53	-11.83	-12.20	-12.74	-12.89
C18	-3.63	-3.82	-4.00	-4.18	-7.90	-8.00	-10.94	-11.23	-11.52	-11.87	-12.89	-13.03
C19	-4.11	-4.31	-4.51	-4.71	-8.45	-8.55	-11.20	-11.50	-11.80	-12.16	-12.97	-13.12

The excess molar enthalpies (Table-2) in both phases indicate an endothermic effect. They are in the mesophase region greater than in the isotropic melt because the highly ordered structure in the mesophase is higher then that in the isotropic phase. Their dissolution needs more energy[30,31] and the excess molar entropies are positive (Table-2).

Table-3 shows that the free energy differences values of the *n*-alkanes are appreciable. The probable reason is that the linear alkanes offer a maximum interaction to the molecules like liquid crystals[1,2].

Conclusion

It has been shown that the gas chromatography can be used to determine the transition temperatures in liquid crystals. The observed values are in good agreement with those found by DSC. It is an efficient and convenient method to investigate the properties of solvents and the behaviour of solutes in liquid crystals. The thermodynamic molar values at infinite dilution showed an endothermic effect and are in the mesophase higher than in the isotropic region. On the other hand, the values calculated for phase I with a methoxy substituent are greater than those obtained for phase II with a propoxy group.

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