

Electrical and thermodynamical characterization of thermotropic liquid crystal

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The thermodynamic interactions, sorption properties and electrical conductivity measurements of thermotropic liquid crystalline compound, (S)-5-dodecyloxy-2-[[[4-(2-methylbutoxy) phenyl]imino]methyl]phenol (DMPIMP) are experimentally investigated in this work. The retention diagrams of trace amount of solvents such as benzene, propylbenzene, chlorobenzene were passed through the gas chromatography column loaded with DMPIMP coated on Chromosorb W. The retention diagrams of the solvents on DMPIMP were plotted by means of specific retention volumes, V_g^0 at the temperatures in K between 363 and 383 by inverse gas chromatography. Flory-Huggins liquid crystal-solvent interaction parameter, χ_{12}^∞ , equation of state liquid crystal-solvent interaction parameter, χ_{12}^* , the weight fraction activity coefficient, Ω_1^∞ and effective exchange energy parameter, X_{eff} and molar enthalpies related to the DMPIMP-solvent systems were obtained. The DMPIMP films were also characterized by means of its electrical properties depending on doping effect for the films having two different dopant concentrations such as 25 and 50 percent of tetrabutylammonium tetrafluoroborate.

(Received April 22, 2011; accepted May 31, 2011)

Keywords: Thermotropic liquid crystal, Inverse gas chromatography, Interaction parameters, Electrical conductivity

1. Introduction

Liquid crystals composed of rod-shaped molecules are still widely investigated because of use application in optoelectronic devices, prerequisites for the development of mobile communication and information processing systems [1-4].

The inverse gas chromatography (IGC) is widely used to find out physicochemical and thermodynamical parameters of the gas-liquid and gas-solid systems. In this kind of gas chromatography, the systems under investigation are used as stationary phases. Volatile substances whose interactions with the stationary phase strongly depend on the molecular structure are used as probe solutes. Low-molecular-mass liquid crystal was used as stationary phase by Kelker, in 1960s. Theoretical substantiation to apply IGC to find out thermodynamic parameters of dissolution of organic substances in the calamitic LC phases was given by Martire and co-workers [5-8].

In this study, firstly the retention diagrams of the solvents on the DMPIMP were determined at the temperatures in K between 363 and 383 by IGC. Sorption properties of a liquid crystal in liquid state can be studied at thermodynamical equilibrium region. Thermodynamic interactions of DMPIMP were determined at the studied temperatures because it was seen from the retention diagram that thermodynamical equilibrium occurred at this temperature range. Then, the molar enthalpies partial sorption, $\Delta\bar{H}_{1,s}$, partial mixing $\Delta\bar{H}_1^\infty$ and vaporization,

ΔH_v were determined. The dependence of the conductivity of the DMPIMP samples on the doping ratio and temperature were investigated.

2. Experimental

2.1. Materials and instrumentation

The DMPIMP was synthesized by the p-toluenesulfonic acid catalyzed condensation of the (S)-4-(2-methylbutoxy) aniline with the 4-dodecyloxy-2-hydroxybenzaldehyde.

The preparation procedure, spectroscopic dates and liquid crystalline properties for DMPIMP were given by us in Ref [9].

Benzene (B), Propylbenzene (PB), Chlorobenzene (CIB) and support material being Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc.

A Hewlett-Packard 5890 N gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents. The column was stainless steel tubing with 3.2 mm o.d. and 1m in length.

Tetrabutylammonium tetrafluoroborate (BF_4) as dopant and chloroform were supplied from Merck AG.

Electrical characterizations were performed on the base of dc conductivity-temperature measurements together with its variation with doping ratio. Undoped and doped samples under study were prepared by solving and

mixing of DMPIMP and dopant in chloroform with a given concentration and then pressing after solvent casting on Corning 7059 glass substrate thoroughly cleaned using analytical pipettes in air. Tetra-n-butylammonium tetrafluoroborate (BF₄) as dopant was used to prepare doped samples at a ratio of 25 and 50 %.

Aluminum electrodes were deposited by evaporation at 10⁻⁶ Torr, along the length of the glass plates, at the width of 3 mm, onto both surfaces of the samples to form a sandwich - type specimen. Contact has been performed by direct pressure of pogo contacts on the aluminum electrodes. The temperature dependence of conductivity was measured as the temperature being increased at a constant ratio as 3 °C min⁻¹.

Dark conductivity of the produced films were measured as a function of temperature using a Janis liquid nitrogen vacuum cryostat, having a thermocouple in good thermal contact with the sample. Samples were placed on top of a copper plate that is heated by a bolt heater embedded within. Temperature was recorded and controlled by Lakeshore Temperature Controller 331. Dark conductivity measurements were accomplished using a programmable Keithley 6517A digital electrometer/voltage source interfaced to a computer.

The change in the conductivity of the sample was experimentally measured under 100V constant electrical voltage. The measurements were carried out in 10⁻⁶ Torr vacuum and in the dark. The electrical conductivity of the polymer was measured in Al/ DMPIMP/A1 structure over the temperature range of 300-400 K.

2.2. Theoretical background on IGC

The specific retention volume, V_g^0 is determined experimentally from IGC measurements as follows [10-12]

$$V_g^0 = \frac{Q(t_R - t_A)J273.2}{(T_r w)} \quad (1)$$

where Q is carrier gas flow rate measured at the room temperature T_r; t_R and t_A are retention times of the solvent and air, respectively; J is pressure correction factor, w is weight of liquid crystal in the column.

According to the theories of Flory-Huggins and equation-of-state interaction parameters, χ_{12}^∞ and χ_{12}^* are defined in the Eq.(2) and Eq.(3), respectively:

$$\chi_{12}^\infty = \ln \left(\frac{273.2 R v_2}{p_1^0 V_g^0 V_1^0} \right) - \left(1 - \frac{V_1^0}{M_2 v_2} \right) - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (2)$$

where R is the universal gas constant; p_1^0 , B_{11} and V_1^0 are saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T, v_2 is specific volume of the liquid crystal, M_2 is molecular weight of the liquid crystal, respectively.

$$\chi_{12}^* = \ln \left(\frac{273.2 R v_2^*}{p_1^0 V_g^0 V_1^*} \right) - \left(1 - \frac{V_1^*}{M_2 v_2^*} \right) - \frac{p_1^0 (B_{11} - V_1^0)}{RT} \quad (3)$$

where v_2^* is specific hard-core volume of the liquid crystal and V_1^* is molar hard-core volume of the solvent.

The effective exchange energy parameter, X_{eff} in the equation of state theory is defined as follows,

$$RT\chi_{12}^* = p_1^* V_1^* \{ 3T_{1r} \ln[(v_{1r}^{1/3} - 1)/(v_{2r}^{1/3} - 1)] + v_{1r}^{-1} - v_{2r}^{-1} + X_{\text{eff}}/p_1^* v_{2r} \} \quad (4)$$

where p_1^* is characteristic pressure, v_{1r} and v_{2r} are reduced volume of the solvent and liquid crystal, respectively. T_{1r} is reduced temperature of the solvent.

The partial molar heat of sorption, $\Delta \bar{H}_{1,s}$ of the solvent sorbed by the liquid crystal is given as:

$$\Delta \bar{H}_{1,s} = -R[\partial(\ln V_g^0)/\partial(1/T)] \quad (5)$$

where T is the column temperature (K) and the partial molar heat of mixing, $\Delta \bar{H}_1^\infty$ at infinite dilution of the solvent is given as

$$\Delta \bar{H}_1^\infty = R[\partial(\ln \Omega_1^\infty)/\partial(1/T)] \quad (6)$$

where Ω_1^∞ is the weight fraction activity coefficient of solvents at infinite dilution, defined by the following equation,

$$\ln \Omega_1^\infty = \ln (273.2 R / V_g^0 p_1^0 M_1) - p_1^0 (B_{11} - V_1^0) / RT \quad (7)$$

where M_1 is molecular weight of the solvent.

Molar heat of vaporization, ΔH_v , of the solvent is related to $\Delta \bar{H}_{1,\text{sorp}}$ and $\Delta \bar{H}_1^\infty$ as follows:

$$\Delta H_v = \Delta \bar{H}_1^\infty - \Delta \bar{H}_{1,\text{sorp}} \quad (8)$$

2.3. Electrical characterization

The temperature dependence of the electrical conductivity was measured in the temperature range of 300-400 K. Electrical conductivity can be described by the exponential dependence on temperature:

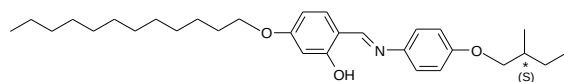
$$\sigma_D = \sigma_0 \exp(-E_a / kT) \quad (9)$$

where σ_D is the dark conductivity, E_a is the activation energy, and σ_0 the preexponential factor [13, 14]. The conductivity is obtained by measuring the current flowing through a piece of the material and using the sample dimensions to calculate σ from the equation.

Electrical characterization of the films was realized on the base of dc conductivity-temperature measurements for the films undoped and BF₄ doped with different ratios such as 25 and 50 %.

3. Results and discussion

The chemical structure and phase transition temperatures of the DMPIMP was summarized in Fig. 1. The details of preparation procedures and all spectroscopic data and liquid crystalline properties for the DMPIMP were given in Ref [9].



Cr 77.3 (32.5) SmC* 83.9 (2.5) Iso

Fig. 1. The chemical structure and phase transition temperatures of the DMPIMP.

The salicylaldehyde compound (DMPIMP) exhibits liquid crystalline properties and shows thermotropic enantiotropic mesophase. The investigations by PM showed that it exhibits smectic C* (SmC*) mesophase.

The specific retention volume, V_g^0 of the studied solvents on the DMPIMP were obtained from IGC measurements at temperatures in K between 363 and 383 using Eq.(1) Graphical results were given in Fig. 2.

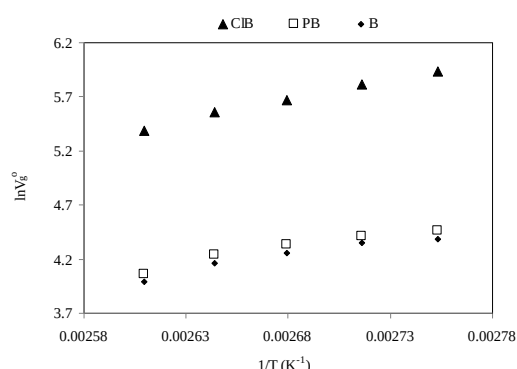


Fig. 2. Variation of specific retention volume of B, PB, ClB on DMPIMP and with the reciprocal of absolute column temperature.

The liquid crystal-solvent interaction parameters, χ_{12}^∞ and χ_{12}^* were determined from Eq.(2) and Eq.(3) and their values were given in Table 1 and Table 2, respectively.

Table 1. Flory-Huggins liquid crystal- solvent interaction parameters, χ_{12}^∞ of DMPIMP with studied solvents at various column temperatures.

t(°C)	B	PB	ClB
90	0.05	2.08	-0.06
95	-0.06	1.94	-0.09
100	-0.10	1.83	-0.11
105	-0.14	1.74	-0.16
110	-0.09	1.75	-0.14

Table 2. Equation of state liquid crystal- solvent interaction parameters, χ_{12}^* of DMPIMP with studied solvents at various column temperatures.

t(°C)	B	PB	ClB
90	0.17	2.15	0.05
95	0.08	2.00	0.01
100	0.03	1.91	-0.03
105	0.01	1.83	-0.07
110	0.06	1.83	-0.04

The values of χ_{12}^∞ greater than 0.5 represent unfavorable liquid crystal-solvent interactions while the values lower than 0.5 indicate favorable interactions in dilute liquid crystal solutions. The values of the χ_{12}^∞ parameters suggest that B and ClB are good while PB is poor for DMPIMP.

The effective exchange energy parameters, X_{eff} in the equation-of-state theory were obtained from Eq.(4) and results were given in Table 3.

Table 3. The effective exchange energy parameters, X_{eff} (J/cm³) of DMPIMP with studied solvents at various column temperatures.

t(°C)	B	PB	ClB
90	-10.54	58.40	-9.28
95	-18.12	54.70	-8.80
100	-19.72	52.38	-11.99
105	-23.65	49.56	-15.84
110	-21.20	50.57	-15.54

The higher values of X_{eff} indicate poor solubility and obtained values of X_{eff} confirm the discussion concerning χ_{12}^∞ .

The weight fraction activity coefficients of the studied solvents at infinite dilution, Ω_1^∞ were determined from Eq.(7) and results were given in Table 4.

Table 4. The weight fraction activity coefficient of solvents on DMPIMP at infinite dilution, Ω_1^∞ .

t(°C)	B	PB	ClB
90	2.79	19.42	1.93
95	2.52	16.8	1.84
100	2.42	15.23	1.80
105	2.34	13.99	1.72
110	2.46	14.10	1.76

According to Guillet [15] the solvent is good for $\Omega_1^\infty < 5$ but it is poor for $\Omega_1^\infty > 10$. The values between 5 and 10 indicate moderately good solubility. According to Ω_1^∞ values of DMPIMP, B and ClB is good solvent while PB is poor. $\Delta\bar{H}_{1,s}$ and $\Delta\bar{H}_1^\infty$ were determined from the slope of the logarithm of specific retention volume, $\ln V_g^0$, versus $1/T$ plot and from the slope of the logarithm of the weight fraction activity coefficients, $\ln \Omega_1^\infty$ versus $1/T$ plot respectively. The results were given in Table 5.

Table 5. The partial molar heat of sorption, $\Delta\bar{H}_{1,s}$ (kcal/mol), the partial molar heat of mixing, $\Delta\bar{H}_1^\infty$ (kcal/mol), molar heat of vaporization, $\Delta\bar{H}_v$ (kcal/mol) obtained by Eq. (8) and molar heat of vaporization, $\Delta\bar{H}_{VL}$ [16] (kcal/mol).

	$-\Delta\bar{H}_{1,sorp}$	$\Delta\bar{H}_1^\infty$	$\Delta\bar{H}_v$	$\Delta\bar{H}_{VL}$
B	5.4	1.8	7.2	7.4
PB	5.3	4.6	9.9	9.1
ClB	7.5	1.4	8.8	8.7

According to the values of $\Delta\bar{H}_1^\infty$, the solubility of DMPIMP in B, PB, ClB are endothermic and calculated values of molar heat of vaporization of the studied solvents, $\Delta\bar{H}_v$ (kcal/mol) are accordance with literature values.

The electrical conductivity of pure DMPIMP was measured as $8 \times 10^{-15} (\Omega \cdot \text{cm})^{-1}$ at room temperature (RT) and increased with temperature to $1.9 \times 10^{-13} (\Omega \cdot \text{cm})^{-1}$ at 85°C (Fig. 3).

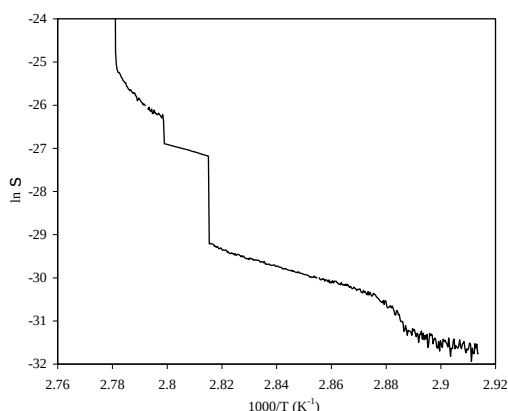


Fig. 3. Arrhenius plot of conductivity for Al / DMPIMP / Al structure.

We determined an considerable change for conductivity at starting around 75°C continuing until 85°C then observed that the logarithm of the conductivity versus inverse temperature value lies on a straight line.

The electrical properties of DMPIMP films were investigated by means of doping concentration effects also. The dark conductivities were found as $8.06 \times 10^{-13} (\Omega \cdot \text{cm})^{-1}$ and $1.27 \times 10^{-12} (\Omega \cdot \text{cm})^{-1}$ at RT, $9.71 \times 10^{-13} (\Omega \cdot \text{cm})^{-1}$ and $1.33 \times 10^{-12} (\Omega \cdot \text{cm})^{-1}$ at 75°C $9.81 \times 10^{-13} (\Omega \cdot \text{cm})^{-1}$ and $1.43 \times 10^{-12} (\Omega \cdot \text{cm})^{-1}$ at 85°C for the films having two different dopant concentrations such as 25 and 50 percent of BF_4 , respectively. After 85°C , it was observed short circuit due to the passing liquid phase of the DMPIMP films.

4. Conclusions

The IGC technique was successfully applied to determine thermodynamic properties of DMPIMP such as Flory-Huggins and hard-core polymer-solvent interaction parameters, weight fraction activity coefficients and effective exchange energy parameters at infinite dilution. The values of the parameters suggest that B and ClB are good while PB is poor for DMPIMP. According to the values of $\Delta\bar{H}_1^\infty$, DMPIMP shows endothermic solubility in studied solvents.

The transition phase of DMPIMP was determined from temperature dependent conductivity measurements at around 75 and 85°C .

We showed that the transition temperatures of DMPIMP obtained by PM were in good agreement with the ones obtained by electrical conductivity measurements and adding BF_4 dopant was positively affected on electrical conductivity of DMPIMP at least two magnitude.

Acknowledgement

This research has been supported by Yildiz Technical University Scientific Research Projects Coordination (Project Number: 2011-01-02-YULAP02).

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