J. Chem. Thermodynamics 80 (2015) 22–29

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

A new approach to study interaction parameters in cyanobiphenyl liquid crystal binary systems

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ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 12 August 2014
Accepted 13 August 2014
Available online 23 August 2014

Keywords:
Liquid crystal
Nematic
Isotropic
Phase transition
Non-random mixing
Interaction parameter

ABSTRACT

The phase transition of heptylcyanobiphenyl 7CB and pentylcyanobiphenyl 5CB liquid crystals was investigated using the differential scanning calorimetry DSC technique. Then, the phase transition of different compositions of 7CB/5CB binary mixture was studied to determine the eutectic point. The phase diagram of mentioned binary system in 7CB mole fraction of 0.45 at $T = 273.45$ K is in good agreement with that of predicted from Schroder–van Laar equation. The thermodynamic excess functions and interaction parameters were calculated to describe the phase transition physically using the non-random mixing for the first time. The P^* randomicity parameter was used to describe the phase transitions of C–N and N–I in which a small amount of P^* shows a non-random identity of C–N phase transition. Contrarily, the P^* is greater in N–I phase transition showing a random mixing process.

1. Introduction

Liquid crystals are commonly used to manufacture liquid crystal displays (LCD) screens to displays in computers, TVs, and watches [1–11]. They are also attractive materials for fundamental research because of their structural, transitional, thermal, orientational, optical, and photoacoustic properties [12,13]. Liquid crystals are composed of large asymmetric molecules which are not melted in a single stage from the anisotropic solid state to an isotropic liquid [6]. A variety of mesophases with symmetries and properties intermediate between those of a crystal and a liquid. Differences in orientational and spatial ordering of the molecules describe the mesophases. Two of more common intermediate phases between the crystal (C) and the isotropic (I) liquid are the nematic (N) and the smectic-A (A) Phases [6]. The nematic phase has the translational symmetry of a fluid but a broken rotational symmetry characterized by long-range orientational order produced by the alignment of the molecular axes along a unit vector called the director [6]. In the nematic phase, the centres of mass of the molecules are randomly positioned [6]. This is not the case in the smectic-A phase which has a layered structure with layer planes perpendicular to the director [6]. Within the layers, there is no long-range order in centers of mass position of the molecules [6].

Cyanobiphenyl (nCB) liquid crystals are the materials of interest in research due to their proto-typical thermotropic nature in nematic to isotropic (N–I) phase transition have been studied by several authors as a host material to form clay and polymer composites, solvent additives, and liquid crystal mixtures by X-ray diffraction, FTIR, optical microscopy, dielectric spectroscopy, and calorimetry techniques for several years [14–17]. Some reports can be seen on bulk pentylcyanobiphenyl 5CB and octylcyanobiphenyl 8CB to discuss the effect of anapore membranes, vycor glass, and temperature variation on (N–I) phase transition [18–20]. The phase transitions and properties of liquid crystal mixtures have been rarely investigated. Nevertheless, there have recently been several investigations on sematic-nematic phase transitions of octyloxycyanobiphenyl (8OCB)/nonyloxycyanobiphenyl (9OCB) and octylcyanobiphenyl (8CB)/ nonyloxycyanobiphenyl (9OCB) Liquid crystal mixtures to study the Mc-millan constant [21]. Regarding importance and unique proprieties of liquid crystal mixtures, we focused on 7CB/5CB mixtures phase transition and thermodynamics.

Differential scanning calorimetry, DSC, has been widely used to study the various transitions (glass transitions, crystallization, first-order and second-order transitions) of different materials; glasses, polymers, liquid crystals and *etc.* [6,22–24]. Here, we report the detailed study of activated phase transition thermodynamics of bulk heptylcyanobiphenyl (7CB), 5CB, and their different

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http://dx.doi.org/10.1016/j.jct.2014.08.010
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compositions using DSC technique. In present work, the rate kinetics and activation energy dynamics of all transitions of bulk 7CB, 5CB, and their mixtures were discussed using the Arrhenius theory. The heating rate dependence of all transitions of 7CB, 5CB, and their mixtures was investigated using the DSC technique for heating and cooling scans at five different ramp rates. A comparison was performed between thermodynamic properties and phase transition of pure 7CB, 5CB, and their mixtures to show the synergism effect. Despite many investigations dealing with mixed liquid crystals and the mixing behaviour of their binary systems, the interactions in such mixtures have not been fully understood. To our knowledge, no study has been examined on non-random mixing nature of liquid crystal. Investigating this phenomenon in systems containing liquid crystals is of a great deal of importance from both the theoretical and applied standpoints. Hence, in the present study, we investigated the nature and strength of the interactions between liquid crystal mixtures by calculating the values of parameters such as those of interaction, randomness, and size.

2. Experimental

The 5CB and 7CB were purchased from Aldrich. See table 1. The mixture samples with 15%(w/w), 30%(w/w), 45%(w/w), 60%(w/w) and 85%(w/w)7CB/5CB ratios were prepared at room temperature and were placed in an ultrasonic bath for 30 min to obtain appropriate homogeneity.

In the DSC technique, a NETZSCH DSC 200F3 model was applied to obtain different heating scan rate thermograms of (1, 5, 10, 15 and 20) $\text{K} \cdot \text{min}^{-1}$. A total of 8 mg of each sample was placed into aluminium pans (dimensions: 8 mm diameter, 0.5 mm thick) and placed in a differential scanning calorimeter along with an empty reference pan. The samples were first heated to $T = 353$ K for 7 min. and immediately quenched to $T = 173$ K. The samples were also heated from $T = (173 \text{ to } 353)$ K and then cooled to $T = 173$ K at different ramp rates. The DSC thermograms showed endothermic and exothermic peaks in heating and cooling scan rates, respectively. In the second measurement, heating and cooling of all samples gave identical results which show the reversibility of phase transition.

3. Results and discussion

3.1. Kinetics

3.1.1. Heating and cooling scans

Figure 1 shows the phase transition of bulk 7CB, bulk 5CB and mixture ratios of 15%(w/w), 30%(w/w), 45%(w/w), 60%(w/w) and 85%(w/w)7CB/5CB liquid crystals for heating and cooling at $5 \text{ K} \cdot \text{min}^{-1}$ scan rate. The C–N and N–I peaks in heating and I–N peaks in cooling are seen. The N–C phase transition is not observed in 7CB/5CB mixtures since the disordering is increased because of mixing and the phase transition cannot be observed by DSC. Overcoming this difficulty, an abrupt cooling is needed to observe the phase transition phenomenon. The Nematic phase of the binary mixture of 7CB/5CB is called the super-cooled phase. The N–I and C–N phase transitions for 7CB liquid crystals occur at higher temperatures compared to 5CB. The area of 7CB peaks is larger compared to that of 5CB. The molecular structure of the nCB liquid crystal family consists of two parts, *viz.* the head group and a hydrocarbon chain. Since the head group is identical for all family compounds, increasing intermolecular interactions were attributed to hydrocarbon chain length increase. The intermolecular interaction dependence upon the chain length of the hydrocarbon tail is explained through van der Waals attractive interactions directly dependent upon size. As mentioned above, 7CB has a greater attractive interaction compared to 5CB since its hydrocarbon tail is longer. It has the length of two methylene groups and a higher thermal energy is consequently needed to overcome this interaction in order to prompt phase transitions. The comparison is consistent with results that have been obtained from 8CB phase transitions studies [7]. Figure 1(a) and (b) show the C–N, N–I, and I–N phase transition temperatures. As can be seen in these figures, the C–N phase transition temperature of 7CB/5CB mixtures is less compared to their pure systems. According to the above noted dependence of the C–N phase transition temperature on chain length, the mixed binary system of 7CB/5CB should have a higher phase transition temperature compared to the 5CB pure system, while an inverse trend is observed which is justified by the synergism affect. In the N–I phase transition; our justification based on the chain length dependence is in agreement with data obtained that show the mixed binary system has a higher phase transition temperature compared to that of the 5CB pure system. The synergism is justified as the disordering increases because of mixing. The ordered interactions in pure states no longer exist in mixed systems resulting in a reduction in the interactions. Another reason to support our observations lies with the peak area of phase transition diagrams that indicate intermolecular interaction taken into account directly as a parameter of enthalpy change of the phase transition dependent upon intermolecular interactions. Some phase transition thermodynamic functions such as enthalpy and entropy are discussed below.

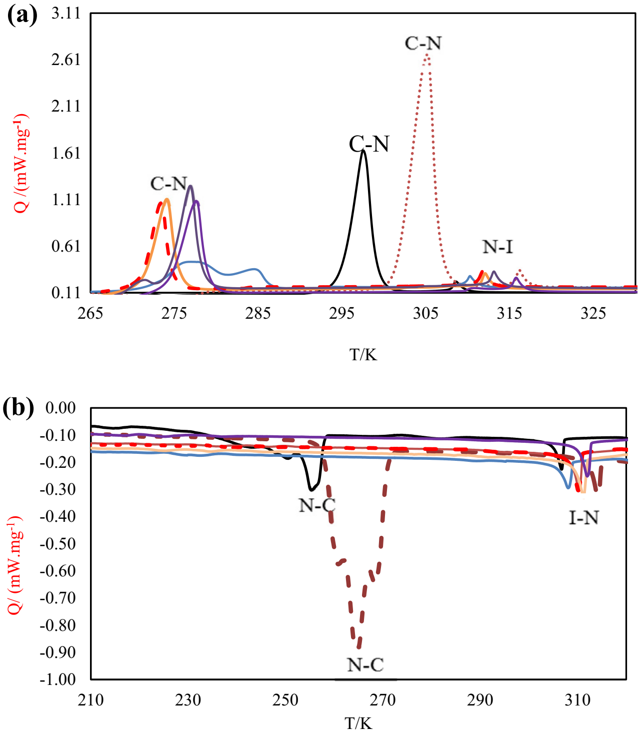

FIGURE 1. DSC thermograms phase transition of heating (a) and cooling (b) for the phase transition in heating and cooling at the 5 K·min^{-1} scan rate. (**5CB**), (**7CB**), (**15%**), (**30%**), (**45%**), (**60%**) and (**85%**) weight present of 7CB.

TABLE 1
Provenance and mass fraction purity of chemical samples studied.

Chemical name	Source	Molar mass/ $\text{g} \cdot \text{mol}^{-1}$	Mass fraction purity
Heptylcyanobiphenyl (7CB)	Aldrich	249.35	0.98
Pentylcyanobiphenyl (5CB)	Aldrich	277.40	0.98