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A non-isothermal activated kinetics of K-SmA transition of the aligned octylcyanobiphenyl

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Abstract This study explores a non-isothermal activated kinetics of the Crystalline to Smectic A (K-SmA) transition of the aligned octylcyanobiphenyl (8CB) liquid crystal. High resolution calorimetric technique was used to study the molecular motion and rearrangement of the 8CB molecules near the K-SmA transition as a function of temperature, rate, and time. In the presence of magnetic field, the transition peak was found to be shifted towards lower temperature by 0.5 K when compared with results of un-magnetized 8CB. The K-SmA transition showed a rate dependent kinetics following Arrhenius behavior where the increased shifting rate showing an increased thermal kinetics for the transition. The 8CB molecules get more aligned and more ordered that pushes the temperature of the transition towards lower temperature in the presence of magnetic field. Hence they show a temperature decrease in the peak of the transition temperature with a decrease in the enthalpy and hence needs more activation energy. This study may be useful to understand the liquid crystal behavior to upgrade liquid crystal devices (LCDs).

Keywords Alignment · Kinetics · Calorimetry · Heat capacity · Activation energy · Liquid crystal

Introduction

Liquid crystals (LCs) have always been materials of interest in research as they exhibit unique phase transitions and thermal properties those can make them useful for the applied area of the liquid crystals applications in the real world as well as in the area of pure research and science because of their specific molecular alignment when they undergo to different transitions [1–5]. Thermotropic liquid crystals at varying temperatures undergo successive phase transitions; for example, isotropic (I), nematic (N), smectic A (SmA), and crystalline (K) liquid crystal phases as temperature of the LCs changes. Nematic liquid crystals are three dimensional anisotropic fluids characterized by the average molecular direction, the so-called director n. The smectic phases are stacks of two-dimensional fluids, and characterized by the layer normal, k. The situation with k parallel to n, corresponds to the so-called smectic A (SmA) phase. Without external aligning fields the smectic A materials consist of micrometer-size domains characterized by random layer orientation. Such a material is optically opaque and mechanically looks like toothpaste, i.e., it does not flow [6]. The director and layer structure, however, can macroscopically be aligned with appropriate external fields, such as mechanical shear or magnetic field. The effect of magnetic field on the phase transitions is particularly important and interesting for study to understand the alignment of the molecules and its associated kinetics.

To simply understand the peculiar alignment behavior and its associated activated dynamics in the presence of magnetic field, calorimetric experiments were performed for the magnetized liquid crystal 4-octyl-4-cyanobiphenyl (8CB), which has a nematic phase above the SmA phase that remains at room temperature and crystalline phase above the smectic A at about 290 K in the un-magnetized form. Although, the properties of 8CB has been widely studied through various workers [7–13], but the detailed study of the crystalline to smectic A transition of the 8CB have not been found in the literature so far. Here, this report presents the non-isothermal kinetics of the

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crystalline to smectic A transition of bulk 8CB in the presence of magnetic field using calorimetric technique. Furthermore, it reports the effect of the magnetic field on the rate kinetics and the activation energy dynamics of the crystalline to smectic A transition of 8CB following Arrhenius theory. The results for the un-magnetized 8CB liquid crystal were compared to the results of the magnetized 8CB to see the clear effect of the alignment.

Experimental details

Pure octylcyanobiphenyl (8CB) liquid crystal was used to study the non-isothermal activated kinetics of K-SmA transition in the presence of magnetic field. A sample of bulk 8CB, obtained from Frinton Laboratories, having molecular weight 291.44, was degassed for about 1 h under a vacuum unit at room temperature 293 K and then used to get magnetized for study. The bulk 8CB sample was exposed to magnetic field. It consisted of cycling the samples in between smectic A and isotropic phases in the presence of a very intense magnetic field. The temperature range of this cycling was 300 to 318 K. The number of cycling was at least 50 and the intensity of the field was 0.5 T. Those cycling were needed to obtain a gel with microscopical isotropy. It was observed that in the isotropic phase, 8CB was colorless at 313 K, and looked opaque at smectic A phase from 306 *K* to the lower temperatures. But after treating these samples under magnetic effect, magnetized 8CB looked colorless even at its smectic A at room temperature 300 K. After treating sample under magnetic field, the samples underwent the calorimetric measurements to differential scanning calorimetry (DSC) with un-magnetized samples from the same batch as the magnetized ones.

The calorimetric measurements follow the method described below. A DSC (TA instruments) was used to obtain DSC thermograms of the samples (magnetized and un-magnetized bulk 8CB) at different heating scan rates of 20, 15, 10, and 5 K min^{-1}. The samples of 8CB (2.5 mg) was loaded into aluminum pans (dimensions $\sim$8 mm diameter, and $\sim$0.5 mm thick) and then passed through a high magnetic field and then placed into a DSC. The fresh magnetized sample was heated from 243 to 333 K at 20 K min^{-1} ramp rates. The respective heat flow of the sample was recorded along with temperature change during heating scans. The DSC thermograms showed well defined endothermic peaks on heating scans. The peak temperature of the transitions was taken as representative because it shows the maximum change in enthalpy. The same measurements were made for other heating ramp rates, too, using the same amount of the fresh magnetized bulk 8CB liquid crystals. Every time freshly aligned sample was used and the used samples were discarded after one use to avoid demagnetization during heating of the samples. All experimental and environmental conditions were kept identical for all runs so that a comparison of the phase transition parameters could be made to understand the rate effect on phase transitions of the sample. Same experiments were performed using same heating ramp rates for un-magnetized bulk 8CB too. All the results obtained for magnetized bulk 8CB were compared with the result found for un-magnetized 8CB liquid crystals keeping all experimental and environmental conditions identical. The rate-dependent details of un-magnetized bulk 8CB sample have been reported in our earlier publication [14]. Some other publications on the kinetic results of the 8CB can be seen in these publications [15–19]; whereas some recent alignment effect of liquid crystal with nanoparticles can be seen in the publication [20].

Results

Effect of magnetic field on heating scans

Figure 1 shows the heating scan of magnetized and un-magnetized bulk 8CB liquid crystal at 5 K min^{-1} heating ramp rate spanning the isotropic and crystal phases. Well defined endothermic peaks were found on heating scan at K-SmA, SmA–N, and N–I transitions. In the presence of magnetic field, all transitions show a little temperature shift towards lower temperature and the size of the transition peaks get smaller when compared to the results of un-magnetized results. The transitions on heating scan represent absorption of heat. The crystalline to smectic A (K-SmA) has the largest peak or enthalpy, and SmA–N has the smallest peak or enthalpy. To see clear difference between magnetized and un-magnetized results of K-SmA transition, the excess of specific heat capacity are plotted in the following figures. Figure 2 shows the excess of specific heat capacity of K-SmA or melting transition. It is clear that in the presence of magnetic field, the melting peak gets smaller than the un-magnetized sample. However, the position of the peak moves towards lower temperature by 0.5 K.

Effect of magnetic field on heating rates

A heating rate dependent study for magnetized 8CB was also performed at various heating ramp rates. Significant shift in transition temperature was observed in all transitions. This shift follows Arrhenius behavior and represents kinetics. Figure 3 shows the heating rate effect on various transitions of magnetized bulk 8CB for heating scans at different heating ramp rates varies from 5 to 20 K min^{-1}. It is clear that the magnetized sample shows a significant rate

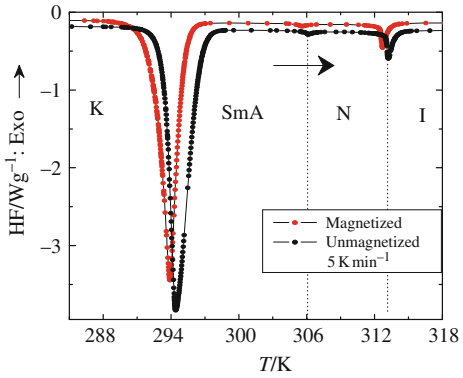

Fig. 1 Effect of magnetic field on heating scan. It is plotted as heat flow/Wg^{-1} versus temperature/K for magnetized and un-magnetized bulk 8CB liquid crystal. It shows endothermic transitions on heating at 5 K min^{-1} heating ramp rate. The *forward arrow* represents heating scans. The region K, SmA, N, and I represents crystallization, smectic-A, nematic, and isotropic state of the 8CB, respectively. For the magnetized 8CB, melting, SmA–N, and N–I transitions, at 5 K min^{-1} ramp rate, appear at ~293.9, ~305.5, and ~312.6 K, respectively. And for un-magnetized 8CB, at the same ramp rate, they appear at ~294.4, ~306.2, and ~313.2 K, respectively

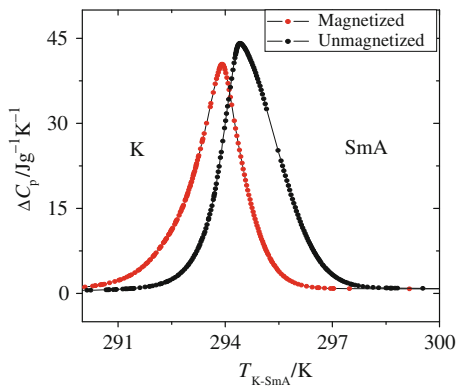

Fig. 2 The excess of specific heat capacity versus temperature plot for magnetized and un-magnetized 8CB for the K-SmA transition at 5 K min^{-1} ramp rate

effect different from the un-magnetized samples. As ramp rate increases, all transitions shift towards higher temperature. The rate of shifting in the presence of magnetic field, found to be greater than the result of un-magnetized samples. In the presence of magnetic field, the rate of shifting in the K-SmA transition is 1.26 times greater than the un-magnetized results. The rate effect on K-SmA transition can be seen clearly in the Fig. 4 which is plotted as the heat capacity of the transition versus temperature after subtracting the linear background from the obtained heat capacity of the sample. It seems that the K-SmA transition of bulk 8CB shows a rate dynamics in the presence of magnetic field. The excess specific heat capacity for the 8CB can be obtained by subtracting from the specific heat *Cp* a linear background as:

$$\Delta Cp = Cp - Cp \text{ (background)} \quad (1)$$

where *Cp* (background) is the base line and *Cp* is the specific heat capacity of the sample. The specific heat capacity/Jg^{-1} K^{-1} can be calculated by taking ratio of heat flow/Wg^{-1} and heating rate/K s^{-1}. The blow ups of such plots are shown here. It is clear from the Fig. 4 that as the heating rate increases, the K-SmA transition peak shifts towards higher temperature with an increased dynamics significantly following Arrhenius theory. The peak size and shape also changes and becomes sharper and larger but the area covered by the peak is almost same for all ramp rates and found to be independent of heating rates. The enthalpy of the K-SmA transition is 21.7 KJ mol^{-1} whereas the enthalpy of SmA–N transition is 0.10 KJ mol^{-1} and the N–I transition has intermediate enthalpy 0.54 KJ mol^{-1}.

Effect of magnetic field on activation energy

According to Arrhenius behavior [21, 22], the heating rate can be given by

$$\beta = \beta o(\exp(-\Delta E/RT)) \quad (2)$$

where β is the effective heating rate in K min^{-1}, βo a constant in K min^{-1}, ΔE the activation energy in J mol^{-1}, R the universal gas constant in J mol^{-1} K^{-1}, and T is the absolute temperature in K. This equation can also be shown as:

$$\ln\beta = \ln\beta o - \Delta E/RT \quad (3)$$

where ΔE is determined from the slope of the graph which is plotted between ln β and 1/T, and lnβo is the intercept on y axis.

K-SmA transition of the magnetized and un-magnetized 8*CB* samples follow Arrhenius behavior and indicate the required activation energy for the transitions in the form of the slope of the lines. The interesting thing found here is the slope of the lines changes in the presence of magnetic

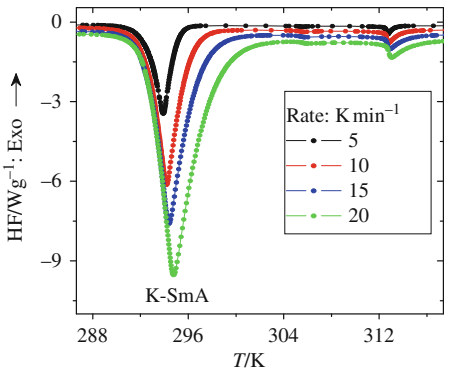

Fig. 3 Heating rate dependent plot for magnetized 8CB. Heat flow/Wg^{-1} versus temperature/K plot for heating scan for different ramp rates from 5 to 20 K min^{-1}

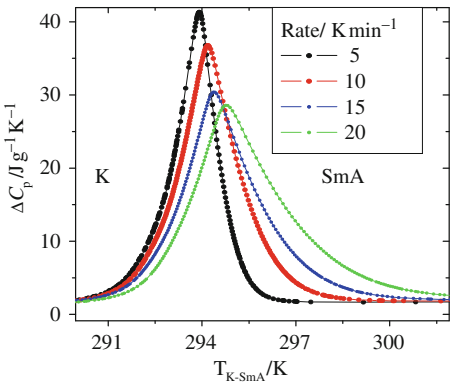

Fig. 4 Rate effect on magnetized 8CB: The excess of specific heat capacity versus temperature plot for the K-SmA transition for ramp rates from 5 to 20 K min^{-1}

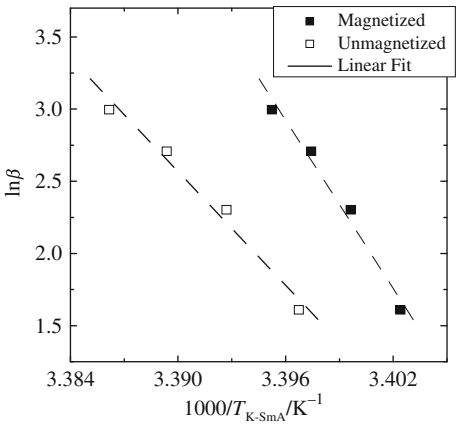

Fig. 5 A comparative semi log plot of ramp rate/K min^{-1} versus 1/*T*/K^{-1} for K-SmA transition following Arrhenius behavior for the magnetized and un-magnetized K-SmA transition of the 8CB. *Dotted lines* are linear fits. It represents negative slope due to the absorption of heat. The *errors bars* found in the transition temperature are much smaller than the symbol size. Error in the K-SmA transition temperature is found ±0.02 K

field. The slope of K-SmA transition is found to be greater than the un-magnetized sample shown in Fig. 5. The K-SmA transition shows a negative slope and negative activation due to the absorption of heat because the endothermic peaks found on heating scan shift towards lower temperature with the decrease of ramp rate. The data details for the K-SmA transition for the magnetized and un-magnetized 8CB can be seen in the Table 1.

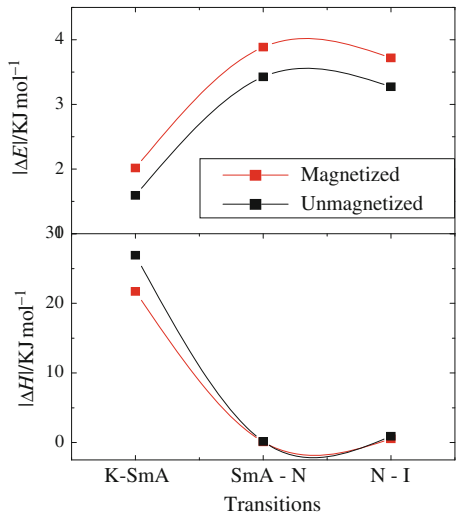

Fig. 6 *Top Panel* comparative activation energy plot; *Bottom Panel* comparative enthalpy plot for each transition of magnetized and un-magnetized 8CB. The noticeable thing is the data of the K-SmA reversed in both panels

Effect of magnetic field on enthalpy

In the presence of magnetic field, the enthalpy of the K-SmA is found to be smaller by 5.2 KJ mol^{-1} from the un-magnetized value, respectively, whereas the enthalpy of the transition calculated at different heating ramp rates is found almost same and to be independent of ramp rates following the energy conservation law.

Discussion and conclusions

Effect of magnetic field on activated kinetics

The K-SmA transition of the magnetized 8CB shows a non-isothermal activated kinetics which can be studied using the rate dependent theory of Arrhenius. Using this theory, the activation energy of molecular motion and rearrangement of the sample near the transition temperature can be calculated by Arrhenius equation. The enthalpy of the K-SmA transition decreases in the presence of magnetic field whereas the activation energy increases in the presence of magnetic field. The change found in enthalpy and activation energy indicates a relationship between the enthalpy and the activation energy of the transition. To see this relationship clearly, Fig. 6 is

Table 1 Data details for the K-SmA transition of the bulk 8CB in the presence and the absence of the magnetic field

8CB	Transition	T/K with error	ΔE/kJ mol^{-1} with error	ΔH/kJ mol^{-1} with error	ΔS/kJ mol^{-1}
Magnetized	K-SmA	293.90 (±0.02)	2.01 (±0.10)	−21.71 (±1.00)	−73.87
Un-magnetized	K-SmA	293.40 (±0.02)	1.59 (±0.10)	−26.91 (±1.00)	−91.41

plotted for all transitions observed in the bulk 8CB in the presence of magnetic field together, i.e., K-SmA, SmA–N, N–I. It is clear that in the presence of magnetic field, K-SmA transition absorbs lesser energy in terms of enthalpy (or endothermic peaks) and hence the enthalpy of the transition decreases whereas the activation energy of the respective transition increases when compared with the un-magnetized K-SmA transition. The other transitions SmA–N and N–I also show a decrease in the enthalpy and an increase in the activation in the magnetized state (although the order increase is much smaller in SmA–N and N–I transitions compared to K-SmA transition). The opposite trend of enthalpy and activation energy variation can be explained in terms of the change in the molecular alignment of 8CB liquid crystal in the presence of magnetic field. The 8CB molecules get more aligned and become more ordered in the presence of magnetic field and instead of showing a real melt at K-SmA transition, the aligned molecules of 8CB shows a kinetic melt at K-SmA transition that pushes the temperature of the transition towards lower temperature in the presence of magnetic field. Hence, they show a temperature decrease in the transition temperature showing a decrease in the enthalpy and increase in the activation energy. This type of information could lead towards understanding of the liquid crystal display (LCD) problems and solutions.

Conclusions

The non-isothermal kinetics of the K-SmA transition of the bulk 8CB was studied under the effect of the magnetic field using a rate dependent Arrhenius theory with the Calorimetric techniques. Well defined endothermic peak, found on heating scan for the K-SmA transition, shows a temperature shift towards lower temperature in the presence of magnetic field. The rate dependent study of the magnetized sample shows an increased activated dynamics following Arrhenius behavior. The temperature shifting rate of the K-SmA transition increases and shows a rate dynamics in the presence of magnetic field. The enthalpy of the transition decreases, in the presence of magnetic field, which represents the transition, absorbs less energy than the un-magnetized sample. Hence the required activation energy of the respective transition increases. This can be explained in terms of the change in alignment of the molecules of bulk 8CB in the presence of magnetic field. The molecules of the 8CB get more aligned and ordered in the presence of magnetic field, and shifts transition towards lower temperature. This effect shows a decrease in enthalpy of each transition in the presence of magnetic field and an increase in their respective activation energy.

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