

# An investigation of excess function on Binary mixtures by using Thermodynamics

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## Abstract

The binary mixture of pentylcyanobiphenyl (5CB) and onheptylcyanobiphenyl (7CB) with different ratios has been characterized by differential scanning calorimetry (DSC) to determine the phase diagrams. A simple eutectic for this system was observed. The excess functions have been calculated by utilizing the computed activity coefficient data of different composition of two compounds.

**Key words:** thermodynamic, liquid crystal, excess function and binary system

## Introduction

A lot of interest in liquid crystals came from their technological applications. One of the main properties of liquid crystals is their thermal stability and its knowledge is important because the upper limits of their applications may be governed by it. Liquid crystal materials used in the display industry are usually multi-component eutectic mixtures. In view of the thermodynamic considerations, eutectic may be defined as the heterogeneous system consisting of two or more solidus phases which are in equilibrium with a single liquidus phase and for this correspond the lowest liquidus temperature in the binary solidus-liquidus diagram of state.[1-5]

## Experimental Section

Pure 5CB, 7CB and its mixtures have been used to study the activated thermodynamics of its phase transitions. 5CB with purity 98%, Molecular weight 249.35 g/mole and 7CB with purity 98%, Molecular weight 277.40 g/mole were purchased from Aldrich. Samples with 15%(w/w), 30%(w/w), 45%(w/w), 60%(w/w) and 85%(w/w) 7CB/5CB ratios were prepared in room temperature and were put in an ultrasonic bath for 30 mins to obtain acceptable homogeneity.

## Results and discussions

The deviation from ideal behavior can best be explained in terms of excess thermodynamic Functions, which give more quantitative ideal about the nature of molecular interactions. It is given by the difference between the thermodynamic functions of mixing for a real system and the corresponding value for an ideal system at the same temperature and pressure. It is denoted by superscript E and represents the excess of a given thermodynamic property of a solution over that in the ideal solutions.

In order to know the nature of interaction between the components forming the eutectic melt, some thermodynamic functions such as excess free energy ( $G^E$ ), excess enthalpy ( $H^E$ ) and excess entropy ( $S^E$ ) were calculated using the following equations:

$$G^E = RT[X_1 \ln \gamma_1^l + X_2 \ln \gamma_2^l] \quad (1)$$

$$H^E = -RT^2[X_1 \frac{\partial \ln \gamma_1^l}{\partial T} + X_2 \frac{\partial \ln \gamma_2^l}{\partial T}] \quad (2)$$

$$S^E = -R\{X_1 \ln \gamma_1^l + X_2 \ln \gamma_2^l + TX_1 \frac{\partial \ln \gamma_1^l}{\partial T} + TX_2 \frac{\partial \ln \gamma_2^l}{\partial T}\} \quad (3)$$

The activity coefficient of a component  $i$  present in the eutectic melt is given by

$$-\ln X_i^l \gamma_i^l = \frac{\Delta_f H_i^0}{R} \left[ \frac{1}{T} - \frac{1}{T_i^0} \right] \quad (4)$$

Where  $X_i$ ,  $\gamma_i^l$ ,  $\Delta_f H_i^0$  and  $T_i^0$  are the mole fraction, activity coefficient, heat of fusion and the melting temperature of the component  $i$ ;  $R$  is the gas constant and  $T$  is the melting temperature of the eutectic. Eq. (4) is obtained by assuming the general condition of phase equilibrium for the phases and that heat of fusion is independent of temperature and the two components are miscible in all proportions in the liquid

phase only. The values of  $\frac{\partial \ln \gamma_i^l}{\partial T}$  can be calculated by taking the slope of the liquidus curve near the eutectic point in the phase diagram and using Eq. (5) which is obtained by differentiating Eq. (3):

$$\frac{\partial \ln \gamma_i^l}{\partial T} = \frac{\Delta_f H_i^0}{RT^2} - \frac{1}{X_i} \frac{\partial X_i}{\partial T} \quad (5)$$

Since the liquidus curves in the phase diagram are virtually straight lines in the region of the eutectic

composition, the value of  $\frac{\partial X_i}{\partial T}$  has been found out by measuring their slope near the eutectic point. The values of excess functions for the crystal-nematic phase transition are given table 2. The excess free energy for C-N phase transition and eutectic being negative (figure 1) suggests that there is strong interaction among the components forming the eutectic melt and weak association between like molecules. Thus, 5CB-5CB or 7CB-7CB association is weaker than that of 5CB-7CB attractive interactions. The values of  $H^E$  and  $S^E$  very much related to  $G^E$  are, respectively, a measure of excess enthalpy and excess entropy of mixing.

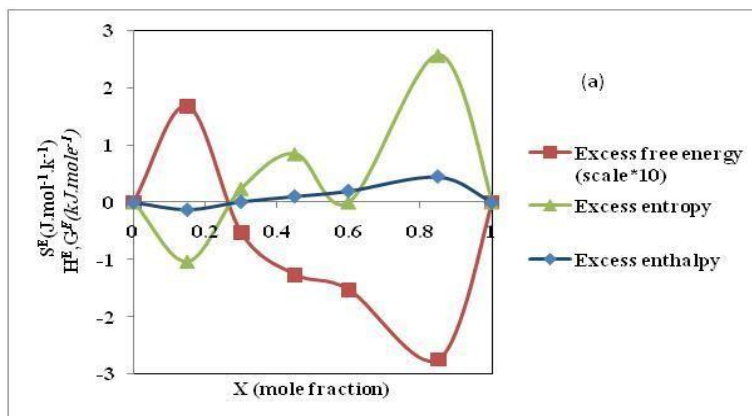


Figure1: excess function of crystal-nematic phase transition of 5CB-7CB Table1:

thermodynamics function of binary system of 5CB and 7CB

X	5CB	7CB	$\gamma_{5CB}$	$\gamma_{7CB}$	$G^E(kJ.mole^{-1})$	$S^E(J.mol^{-1}.K^{-1})$	$H^E(kJ.mole^{-1})$
0.15	0.85	0.15	0.99	2.36	0.167	-1.39	-0.12
0.30	0.70	0.30	1.08	0.77	-0.053	0.44	0.010
Eutectic	0.55	0.45	1.28	0.60	-0.126	1.05	0.103
0.60	0.40	0.60	1.67	0.54	-0.153	1.27	0.198
0.85	0.15	0.85	3.71	0.51	-0.275	2.28	0.445

**Conclusion :** The procedure proposed and applied here may be used to test the thermodynamic consistency of experimental data for the adsorption of liquid mixtures on solids. A more important application is that the consistency relationship imposes a constraint on the parameters of any model for adsorption from liquid mixtures.

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