Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

THERMODYNAMIC STUDY OF BINARY MIXTURES OF LIQUID CRYSTALS CHOLESTERYL MYRISTATE AND DODECYLOXYBENZOIC ACID

S. L. Srivastava [a] & Ravindra Dhar [b]

[a] Physics Department, University of Allahabad, Allahabad, 211 002, India

[b] Physics Department, Ewing Christian College, Allahabad, 211 003, India

Version of record first published: 24 Sep 2006

To cite this article: S. L. Srivastava & Ravindra Dhar (2001): THERMODYNAMIC STUDY OF BINARY MIXTURES OF LIQUID CRYSTALS CHOLESTERYL MYRISTATE AND DODECYLOXYBENZOIC ACID, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 79-90

To link to this article: http://dx.doi.org/10.1080/10587250108023950

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 79-90
Reprints available directly from the publisher
Photocopying permitted by license only

Thermodynamic Study of Binary Mixtures of Liquid Crystals Cholesteryl Myristate and Dodecyloxybenzoic Acid

S.L. SRIVASTAVA[a] and RAVINDRA DHAR[b]

[a]*Physics Department, University of Allahabad, Allahabad-211 002, India and*
[b]*Physics Department, Ewing Christian College, Allahabad-211 003, India*

Transition temperatures, transition enthalpies and transition entropies of the binary mixtures of Cholesteryl Myristate (ChM) and Dodecyloxybenzoic Acid (DDOBA) have been measured at different scanning rates using differential scanning calorimeter (DSC). Different mesophases have been identified by analyzing their textures under the polarizing microscope. Pure component ChM has smectic A (SmA) and cholesteric (N^*) whereas DDOBA has smectic C (SmC) and nematic (N) mesophases. Phase diagrams for this binary system have been drawn in both heating and cooling cycles. The eutectic composition of the mixture has been found to be 30±5 mole percent of DDOBA. Stability of SmA phase of ChM increases with the addition of DDOBA upto about 50 mole percent of DDOBA but decreases thereafter and completely disappears at about 78 mole percent of DDOBA. Range of SmC phase of DDOBA (~36°C) decreases rapidly with the addition of ChM and disappears at about 19 mole percent of ChM. The maximum range of N^* phase in this binary system is about 27°C in heating and 43°C in cooling. Maximum range of SmA phase in the cooling is about 52°C.

Keywords: Binary mixture; Eutectic; Cholesteryl Myristate; Dodecyloxybenzoic Acid; Thermodynamic

INTRODUCTION

Study of liquid crystal mixtures is important not only from the viewpoint of their technological applications but also from that of fundamental studies in the field of molecular interactions [1]. For example a mixture of two cholesteric compounds with opposite optical activities give rise to

materials of controllable and temperature sensitive pitch [2]. At a particular composition of cholesteric compounds with opposite optical activities exactly compensated nematic mixture is produced [3]. Mixtures of two non mesogenic compounds may give mesogenic compound [4], mixtures of nematogens may give smectics [5] and mixtures of smectogens may give nematics [6]. Mixture of smectic C (SmC) and cholesteric (N*) mesophases may give chiral SmC (SmC*) phase [7]. The phenomenon of reentrant mesophases is very common in mixtures [8,9]. Wide variety of frustrated smectic phases are also observed in mixtures [10-12].

Mixture of a nematic (N) and a cholesteric (N*) phase adopts the cholesteric texture [13,14]. These mixtures often show blue phases and that too with increased temperature range [15,16]. Nematics and cholesterics are not thermodynamically distinct and therefore they are supposed to be infinitely miscible [17]. The binary system of cholesterics and nematics are characterized by the induction of extra helical twisting which is presumably due to peculiar features of interaction between molecules of different components [18]. Consequently binary system of Cholesteryl Pelargonate (cholesteric) and Nonyloxybenzoic Acid (nematic) gives rise to SmA* phase [19-22]. In the present paper we are reporting the thermodynamic study of binary mixtures of Cholesteryl Myristate (having SmA and N* phases) and Dodecyloxybenzoic Acid (having SmC and N phases).

EXPERIMENTAL DETAILS

Pure samples of Cholesteryl Myristate (ChM) and Dodecyloxybenzoic Acid (DDOBA) were procured from Institute of Physics, Ukrainian Academy of Sciences, Kiev, Ukraina. Binary mixtures of different mole ratios were prepared by mixing the weighed out portions of pure samples. Thermodynamic study of mixtures has been done on the Differential Scanning Calorimeter (DSC) of Perkin Elmer (model DSC-7). After stabilizing the data, peak transition temperatures (T_P), and transition enthalpy (ΔH) of the mixtures have been obtained at different scanning rates between 5 ^{0}C/minute to 15 ^{0}C/minute. ΔH values are found to be almost independent of scanning rates but T_P depends linearly on the scanning rate. Extrapolated transition temperatures at the scanning rate of 0 ^{0}C/minute have been obtained by least square fit method [23,24] Uncertainty in the measurement of T_P is ± 0.1 ^{0}C whereas uncertainty in

the measurement of ΔH is about 5%. Nature of the mesophases has been identified by viewing the texture under polarizing microscope of CENSICO. The temperature of the sample under the polarizing microscope was changed by computer controlled hot stage of Instec having temperature accuracy better than ±0.01 ^{0}C.

RESULTS AND DISCUSSION

Transition temperature extrapolated at the scanning rate of 0 ^{0}C/minute for pure samples and mixtures give the phase diagram for heating and cooling as shown in Figures 1 and 2 respectively. Different mesophases as identified by texture study under the polarizing microscope are labelled in Figures 1 and 2. In the cooling cycles of the mixtures having concentration less than 50 mole percent of DDOBA, crystallization temperatures could not be recorded by DSC because crystallization process in mixtures having higher content of ChM has been found to be very slow. In these mixtures crystallization temperatures shown in the cooling phase diagram are those recorded by texture study.

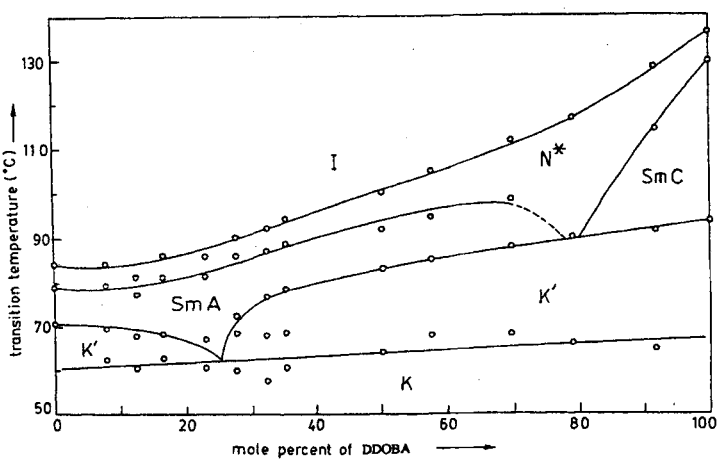

FIGURE 1 Phase diagram for the binary mixture of ChM and DDOBA in heating cycle. Dashed portion of the curve represents extrapolation.

Phase diagrams of Figures 1 and 2 show enantiotropic SmA and N* phases in ChM having phase sequence K (70.9) SmA (78.9) N* (84.3) I (84.2) N* (78.7) SmA (overnight cooling) K which agree with the literature data [25-27]. DDOBA shows phase sequence K (93.7) SmC (129.5) N (136.1) I (136.0) N (128.4) SmC (87.6) K' (69.6) K. Where I represents isotropic liquid phase, K represents crystal and K' represents mixed crystal phase. Data in parentheses represent transition temperatures in ^{0}C as determined by DSC. The melting of the mixtures from the solid phase exhibits two peaks which merge with each other at the eutectic composition of 26 mole percent of DDOBA (see Fig. 1). Near eutectic composition two melting peaks overlap, and they have been manually resolved into two curves. Their transition enthalpies have been calculated by computing the area of the curves by weight method [21]. Enthalpies of the rest of the peaks have been calculated by computer using built in software DELTA of DSC-7.

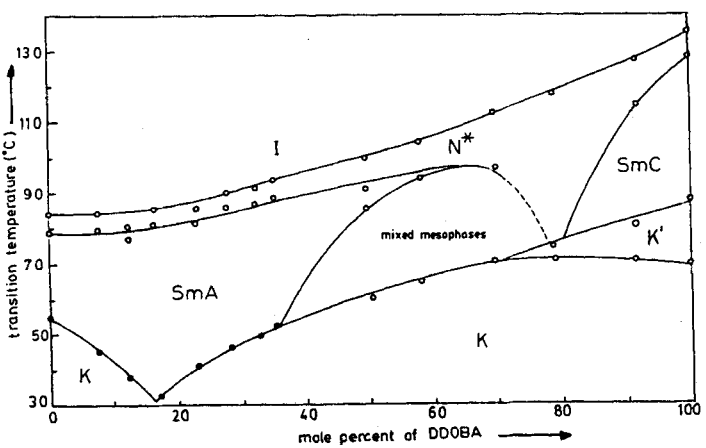

FIGURE 2 Phase diagram for the binary mixture of ChM and DDOBA in cooling cycle. Dashed portion of the curve represents extrapolation. Transition temperatures shown by ⊙ have been obtained by texture study.

Eutectic Composition

Average transition temperature of the crystal (K) to mixed crystal-mesophase (K') melt ($T_{K\text{-}K'}$) show slight increase with mole percent of DDOBA (see Fig. 1). The enthalpy ($(\Delta H)_{K\text{-}K'}$) and entropy ($(\Delta S)_{K\text{-}K'}$) of

K to K' melt increase linearly with mole fraction of DDOBA upto eutectic composition and then decrease linearly thereafter (see Figs. 3 and 4) dividing the whole mixture in two regions, one before eutectic composition and the other after eutectic composition. Least square fit plots of the data of two different regions show cross over at 35 mole percent of DDOBA. The enthalpy ($(\Delta H)_{K'\text{-meso}}$) and entropy ($(\Delta S)_{K'\text{-meso}}$) of K' to mesophase transition decrease linearly with mole fraction of DDOBA upto eutectic composition and then increase thereafter (see Figs. 3 and 4). Least square fit plots of the data of two different regions show cross over for 29 mole percent of DDOBA. From Figures 1, 3 and 4, the eutectic composition for ChM-DDOBA has come out to be 30±5 mole percent of DDOBA. The total enthalpy and entropy (sum of the K-K' and K'-mesophase) initially decreases with mole percent of DDOBA before eutectic composition but becomes almost constant after the eutectic composition (see Figs. 3 and 4).

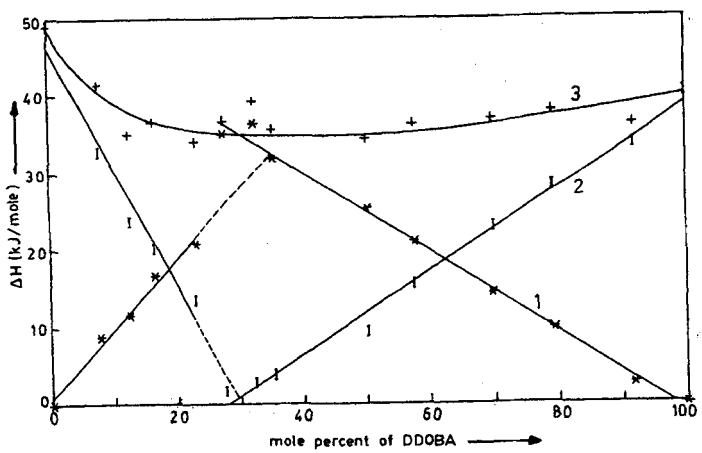

FIGURE 3 Variation of transition enthalpy (ΔH) with mole percent of DDOBA in heating. Curve 1 represents ΔH for K-K' transition, curve 2 represents ΔH for K'-mesophase transition and curve 3 represents sum of ΔH values of K-K' and K'-mesophase transitions.

The eutectic composition of the binary system has been calculated using empirical relation [28]

$$x_e = \frac{100(T_2 - T_e)}{T_1 + T_2 - 2T_e} \qquad (1)$$

where T_1 and T_2 are melting points of the lower and higher melting components of the binary mixture, T_e is the eutectic temperature and x_e is the mole percent of the lower melting component which is ChM. Equation (1) gives x_e = 75 mole percent of ChM (25 mole percent of DDOBA). Eutectic composition has also been calculated by Schroder-Van Laar equation [28,29]

$$\ln x_e = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_e}\right) - \ln f_i \qquad (2)$$

where ΔH is the crystal to mesophase transition enthalpy of ChM, R (=1.987 cal deg^{-1} $mole^{-1}$) is the gas constant and f_i is the activity coefficient. Value of f_i is 1 for ideal mixed phases [29]. Taking f_i =1, x_e comes out to be 60 mole percent of ChM which is far from the experimental value (70±5 mole percent). However molecular length of ChM is very large (almost twice) in comparison to that of DDOBA hence ChM-DDOBA mixture may not be ideal one. Assuming it to be non ideal mixture and then taking f_i=0.8, x_e comes out to be 75 mole percent of ChM which agrees with the experimental value.

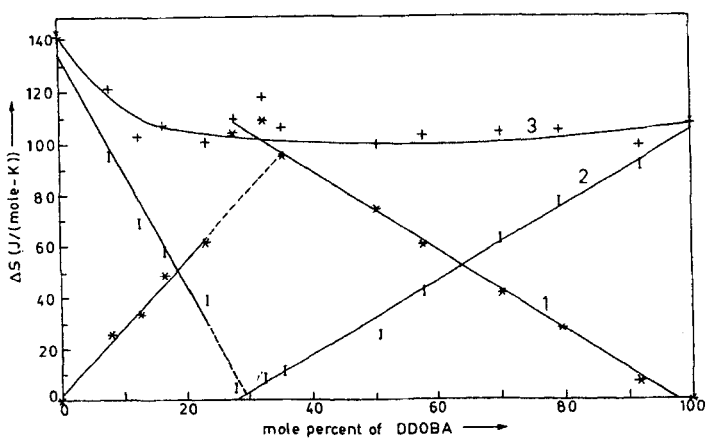

FIGURE 4 Variation of transition entropy (ΔS) with mole percent of DDOBA in heating. Curve 1 represents ΔS for K-K' transition, curve 2 represents ΔS for K'-mesophase transition and curve 3 represents sum of ΔS values of K-K' and K'-mesophase transitions.

Stability of the Mesophases

Figure 1 shows SmA to N* transition temperature (T_{AN*}) with mole percent of DDOBA. The range of the SmA phase which is 7 ^{0}C in ChM, increases with mole percent of DDOBA and becomes maximum at the eutectic composition. Above eutectic composition range of the SmA phase is almost constant upto70 mole percent of DDOBA but decreases thereafter and disappears at about 78 mole percent of DDOBA. SmA-N* transition enthalpy ($(\Delta H)_{AN*}$) and entropy ($(\Delta S)_{AN*}$) initially decrease with increase in mole percent of DDOBA and show minima at 23.1 mole percent of DDOBA which is near to eutectic composition. Above 23.1 mole percent of DDOBA, $(\Delta H)_{AN*}$ and $(\Delta S)_{AN*}$ increase with mole percent of DDOBA and show maxima for 50.3 mole percent of DDOBA. Beyond 50.3 mole percent of DDOBA, $(\Delta H)_{AN*}$ and $(\Delta S)_{AN*}$ decreases with mole percent of DDOBA and tends to be zero for 78 mole percent of DDOBA where SmA phase disappears. Both $(\Delta H)_{AN*}$ and $(\Delta S)_{AN*}$ are peculiarly high for DDOBA concentration of 50.3 mole percent which shows that stability of SmA phase is very high for this particular concentration. In the cooling cycle range of SmA phase is maximum (~52 ^{0}C) for about 17 mole percent of DDOBA (see Fig. 2). In the cooling cycle a new mesophase seems to appear between 35 and 78 mole percent of DDOBA. This mesophase appears between SmA and crystal phase. Texture of this mesophase for the unaligned samples between cross polarizers (see Fig. 5) shows simultaneous co-existence of SmA fans and dark patches. These dark patches suggest homeotropic texture resembling with those of TGBA* [30]. When this mixed mesophase is over, normal crystal texture of unaligned sample appears. The exact nature of this new mesophase can be confirmed only after the dielectric and X-ray studies.

Packing model suggested by us for the molecular arrangement in cholesteryl pelargonate (ChP)-nonyloxybenzoic acid (NOBA) binary system [21] seems to be applicable for present ChM-DDOBA system also. According to this model, two DDOBA molecules in a head to head arrangement with carboxyl group adjacent to each other forming doubly hydrogen bonds (a closed dimer of two DDOBA molecules) occupies the space between ChM molecules. Range of SmC phase of DDOBA decreases rapidly both in heating and cooling cycles (see Figs. 1 and 2) with increasing concentration of ChM and disappears completely when ChM mole percent reaches to 19 leaving wide range N* phase. SmC to N* (N for DDOBA) transition enthalpy and entropy ($(\Delta H)_{CN*}$ and $(\Delta S)_{CN*}$) also decrease with increasing concentration of ChM in

DDOBA. It seems that presence of ChM molecules (having length almost twice of the DDOBA molecules) into the matrix of DDOBA molecules increases average molecular lengths in SmC layers causing decrease in stability of SmC phase [31]. Presence of ChM molecules also reduces the dipolar interaction between DDOBA molecules responsible for the tilted SmC phase by increasing average inter molecular distances in SmC layers [6].

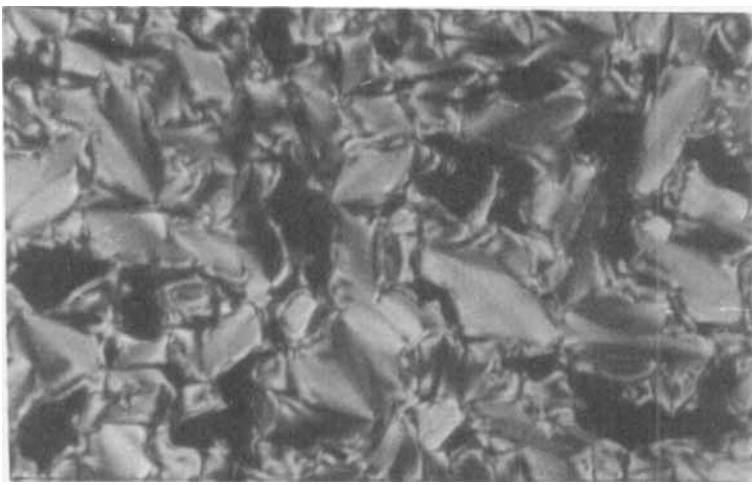

FIGURE 5 TGB A* like texture in the cooling cycle of the mixture having 50.3 mole percent of DDOBA at 68.5 ^{0}C. See Color Plate II at the back of this issue.

In ChM-DDOBA binary system, SmA phase disappears when concentration of DDOBA in ChM exceeds 78 mole percent and SmC phase disappears when concentration of ChM in DDOBA exceeds 78 mole percent, leaving wide range N* phase (~27 ^{0}C in heating and 43 ^{0}C in cooling) for the mixture having DDOBA concentration approximately 80 mole percent of DDOBA (see Figs. 1 and 2). Enthalpy and entropy for N* to I transition ($(\Delta H)_{N^*I}$ and $(\Delta S)_{N^*I}$) have been fitted on the empirical equations [21] as follows

$$(\Delta H)_{N^*I} = x_1\Delta H_1 + (1-x_1)\,\Delta H_2 + A_H[x_1\Delta H_1(1-x_1)\,\Delta H_2]^{1/2} \quad (3)$$

$$(\Delta S)_{N^*I}) = x_1\Delta S_1 + (1-x_1)\,\Delta S_2 + A_S[x_1\Delta S_1(1-x_1)\,\Delta S_2]^{1/2} \quad (4)$$

where x_I is the mole fraction of ChM, ΔH_1 and ΔS_1 are the enthalpy and entropy of N*-I transition of ChM and ΔH_2 and ΔS_2 are the enthalpy and entropy of N-I transition of DDOBA. Constants A_H and A_S are the mixing parameters and their best fit values are -0.82±0.34 and -0.76±0.35 respectively showing deviation from ideal mixing (curve 1 of Figs. 6 and 7). Finite negative values of the mixing terms of equations (3) and (4) suggests that two components of the mixture interact to produce excess disordering and destabilize N* phase as observed in several other binary systems [6,21,25]. Variation of the experimental data of $(\Delta H)_{N^*I}$ and $(\Delta S)_{N^*I}$ for ChM-DDOBA mixtures are shown in Figures 6 and 7.

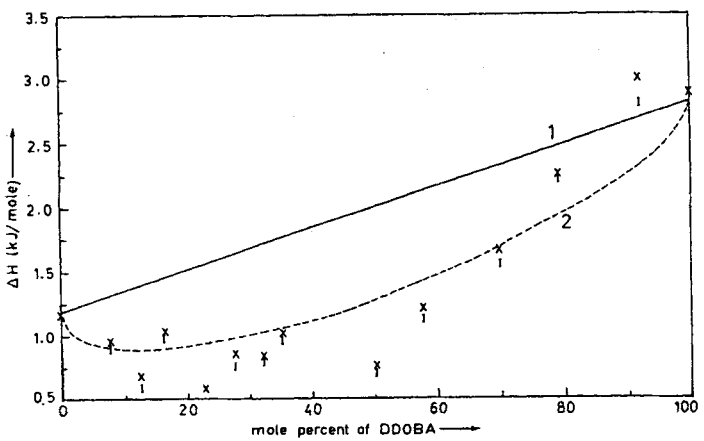

FIGURE 6 Variation of enthalpy (ΔH) for N*-I transition with mole percent of DDOBA. Curve 1 represents the theoretical plot of equation (3) with mixing parameter A_H=0 (ideal mixing) and curve 2 with A_H=-0.82. Experimental data are shown by (I) for N*-I and by (x) for I to N* transitions.

Van't Hoff equation

Van't Hoff equation [32] given by equation (5) has been applied to the ChM-DDOBA system.

$$x = \frac{\Delta H \delta T}{R T_0^2} \qquad (5)$$

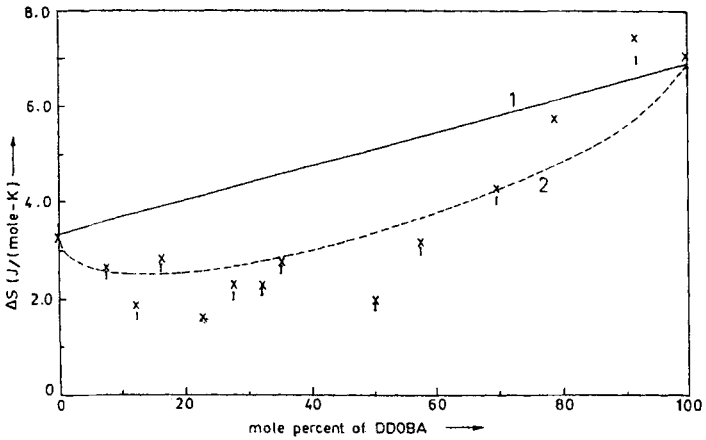

FIGURE 7 Variation of entropy (ΔS) for N*-I transition with mole percent of DDOBA. Curve 1 represents the theoretical plot of equation (4) with mixing parameter A_S=0 (ideal mixing) and curve 2 with A_S=-0.76. Experimental data are shown by (I) for N*-I and by (x) for I to N* transitions.

where x is the mole fraction of impurities added, ΔH and T_0 are the enthalpy (in cal/mole-K) and melt temperature (in K) for the pure components and δT is depression in the melt temperature for the mixture. For the mixtures having concentration of DDOBA below 26 mole percent (eutectic composition from Fig. 1), ChM has been taken as pure component whereas for the mixtures having concentration of DDOBA above 26 mole percent DDOBA has been taken as pure component. The calculated and actual impurities are given in Table 1. Table 1 shows that in ChM-DDOBA binary system as long as ChM molecules are in majority (>50%), calculated impurity is not off by more than 15% whereas when ChM molecules become in minority (<50%), calculated value deviate considerably. It seems that DDOBA molecules having length almost half of ChM molecules are better miscible with ChM and therefore Van't Hoff equation becomes applicable but ChM molecules have poor miscibility with DDOBA. Unlike the ChM-Cholesteryl Acetate system where Van't Hoff equation deviates considerably near eutectic composition [25], we find that for ChM-DDOBA system Van't Hoff equation is better applicable near the eutectic composition where alternate strata of a ChM molecule and a dimer of two DDOBA

TABLE 1 Added and calculated impurities (in mole percent) in the binary system of ChM and DDOBA.

Added impurity of DDOBA in ChM	Added impurity of ChM in DDOBA	Calculated impurity of DDOBA in ChM	Calculated impurity of ChM in DDOBA
7.8		6.5	
12.5		15.4	
16.5		13.4	
19.9		19.9	
	8.2		8.9
	20.8		13.5
	30.2		21.3
	42.3		31.3
	49.7		39.8
	64.6		54.8
	67.6		60.4
	72.2		70.0

molecules coexist. Applicability of Van't Hoff equation for eutectic composition of ChM-DDOBA system is an indication of ideal mixing.

Acknowledgement

We thank University Grants Commission, New Delhi for financial assistance under COSIST and SAP.

References

[1] E.P. Sokolova and A.Y. Vlasov, *Liq. Cryst.*, **8**, 47 (1990).
[2] J.J. Wysocki, J.E. Adams and D.J. Olechna, Liquid Crystals and Ordered Fluids, Ed. J.F. Johnson and R.S. Porter, Plenum Press, NY, (1970), p. 419 & 463.
[3] C.K.S. Nair and K.V. Ramanaiah, *Mol. Cryst. Liq. Cryst.*, **103**, 271 (1983).
[4] R. Gupta and R.A. Vora, *Mol. Cryst. Liq. Cryst.*, **106**, 147 (1984).
[5] J.M. Lohar and J.S. Dave, *Mol. Cryst. Liq. Cryst.*, **103**, 181 (1983).
[6] R. Dabrowski, B. Wazynska and B. Sosnowska, *Liq. Cryst.*, **1**, 415 (1986).
[7] D.F. Aliev, G.M. Bairamov and R.M. Cherkashina, *Sov. Phys. Crystallogr.*, **32**, 715 (1987).
[8] G. Pelzl, C. Scholz, S. Diele, H.J. Deutscher, D. Demus and H. Sackman, *Mol. Cryst. Liq. Cryst.*, **168**, 197 (1989).
[9] S. Diele, G. Pelzl, A. Humke, S. Wunsch, W. Schafer, H. Zaschke and D. Demus, *Mol. Cryst. Liq. Cryst.*, **173**, 113 (1989).
[10] G. Nounesis, C.W. Garland and R. Shashidhar, *Phys. Rev. A*, **43**, 1849 (1991).
[11] P. Patel, S. Kumar and P. Ukleja, *Liq. Cryst.*, **16**, 351 (1994).
[12] H. Richard, M. Mauzac, G. Sigaud, M.F. Achard and F. Hardouin, *Liq. Cryst.*, **9**, 679 (1991).

[13] G.S. Chilaya, Z.M. Elashvili, S.P. Ivchenko and K.D. Vinokur, *Mol. Cryst. Liq. Cryst.*, **106**, 67 (1984).
[14] Nagappa, D. Revannasidduiah and D. Krisnamurti, *Mol. Cryst. Liq. Cryst.*, **101**, 103 (1983).
[15] B. Spier and H. Stegmeyer, *Liq. Cryst.*, **9**, 1 (1991).
[16] G. Heppke, H.S. Kitzerow, D. Lotzsch and C. Papenfeb, *Liq. Cryst.*, **8**, 407 (1990).
[17] P.L. Fin and P.E. Cladis, *Mol. Cryst. Liq. Cryst.*, **84**, 159 (1982).
[18] G.S. Chilaya and L.N. Lisetski, *Mol. Cryst. Liq. Cryst.*, **140**, 243 (1986).
[19] O.D. Lavrentovich and Y.A. Nastishin, *Ukr. Fiz. Zhurn.*, **35**, 221 (1990).
[20] O.D. Lavrentovich, Y.A. Nastishin, V.I. Kulishov, Y.S. Narkevich, A.S. Tolochko and S.V. Shiyanovskii, *Europhys. Lett.*, **13**, 313 (1990).
[21] S.L. Srivastava, R. Dhar and A. Mukherjee, *Mol. Cryst. Liq. Cryst.*, **287**, 139 (1996).
[22] S.L. Srivastava and R. Dhar, *Mol. Cryst. Liq. Cryst.*, **317**, 23 (1998).
[23] K.S. Kunihisa and Y. Satomi, *Mol. Cryst. Liq. Cryst.*, **141**, 1 (1986).
[24] S.L. Srivastava, R. Dhar and M.V. Kurik, *Mol. Mat.*, **2**, 261 (1993).
[25] C.W. Griffen and R.S. Porter, *Mol, Cryst. Liq. Cryst.*, **21**, 77 (1973).
[26] S.L. Srivastava, S.K. Suri and F.M. Gouda, *Research Report*,Department of Physics, Faculty of Science, University of Gar Younis, Bengazi, Libya (1983).
[27] J.F. Johnson, R.S. Porter and E.M. Barrall, Proc. Int. Liq. Cryst. Conf. **2nd (1968)**, 169 (1969).
[28] E.C.H. Hsu, J.F. Johnson, *Mol. Cryst. Liq. Cryst.*, **27**, 95 (1974).
[29] D. Demus, Ch. Fietkau, R. Schubert and H. Kehlen, *Mol. Cryst. Liq. Cryst.*, **25**, 215 (1974).
[30] J.W. Goodby, Liquid Crystal II, Ed. D.M.P. Mingos, Springar-Berlag, Berlin (1999), p. 105.
[31] D. Coates, *Liq. Cryst.*, **2**, 63 (1987).
[32] E.M. Barrall and M.J. Vogel, *Thermochim. Acta*, **1**, 127 (1970).