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Excess refractive index studies on CSA-DMSO binary mixture showing lyophase

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Abstract Binary mixtures of ceto stearyl alcohol (CSA) and dimethyl sulfoxide (DMSO) are found to exhibit mesophase over wide range of concentrations The specific volume data, volume expansivity and refractive index variations are useful in the study of physico-chemical properties of materials. The clear measurement of transition temperature, from the isotropic liquid phase to anisotropic mesophase plays an important role in the above studies. The transition temperature studies, through refractive index variation with temperature for different concentrations, are presented in this paper. The excess refractive index variation as a function of temperature are also presented

Keywords : Lyophase, optical anisotropy, excess refractive index, Walter's equation, birefringence

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1. Introduction

The term liquid crystal signifies a state of aggregation intermediate between a crystalline solid and an isotropic liquid phase. Lyotropics can be formed by binary mixtures, of which one component may be mesogenic. Mixed liquid crystals of two compounds which are also mesogenic [1]. Ceto stearyl alcohol (CSA) is a solid mixture consisting of stearyl alcohol and cetyl alcohol. It can be extracted from sperm oil, in which the alcohols occur, or by reduction of the mixture of stearic and palmitic acids of natural fats. Ceto stearyl alcohol may either contain 90% of stearyl alcohol and 10% of cetyl alcohol or 40% stearyl alcohol and 60% of cetyl alcohol. It is in the form of white or cream flakes. The compound supplied by M/s Loba Chemie Pvt. Ltd., Bombay, was used after recrystallization in benzene solution. It showed a melting point of 53°C (±0.5°C) as observed under polarizing

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microscope. The composition of CSA used by us was determined to be 40% stearyl alcohol and 60% cetyl alcohol using Walter's equation

$$T_m = (t_1C_1 + t_2C_2)/(C_1 + C_2) \tag{1}$$

for the melting point of the binary mixtures of isomorphous substances. The melting point of cetyl alcohol and stearyl alcohol were taken as 50°C and ≈58°C respectively [2].

Ceto stearyl alcohol extracted from appropriate acids from sperm oil in the ratio 60 : 40 exhibits lyotropic mesomorphism in the pure state [3]. In this study the mesomorphism exhibited by the binary mixtures of CSA and dimethyl sulfoxide (DMSO) mixed in different concentrations is studied over a range of temperatures.

The uniaxial symmetry around the molecular axis or the director (in a nematic phase) leads to anisotropy is many physical properties such as refractive index, dielectric permittivity, magnetic susceptibility *etc.* These parameters have different values parallel to and at right angles to the molecular axis. In order to measure these quantities, samples with well-defined molecular orientation pattern is necessary. Two limiting cases arise in view of the above criteria : (i) homeotropic layers, in which the director or the molecular axis is every where perpendicular to the walls of sample holder, and (ii) a uniform planar layer in which the director or the molecular axis is parallel to one direction in the plane of the substrate [4,5]. Thus surface preparation of a substrate to get oriented sample is an important process. Excellent reviews furnishing information about the surface produced alignment of the samples are available in the literature [6–9].

2. Experimental

Using polarizing microscope attached with hot stage, the transition temperature from isotropic liquid phase to lyotropic phase for concentrations ranging from 20% to 95% of ceto stearyl alcohol in dimethyl sulfoxide are studied. The solution of ceto stearyl alcohol in dimethyl sulfoxide at a temperature about 60°C (where it is isotropic solution) is taken over a microscope glass slide and covered by a coverslip. The samples are observed under polarizing microscope with crossed polaroids. When the sample is allowed to cool slowly at the transition temperature, textures typical to the lyotropic lamellar mesophase have been observed in the binary mixtures of CSA in DMSO. The following textures have been identified from photo-micrographs. (i) The batonnets typical of lamellar phase for the concentration of 22% CSA in DMSO, (ii) small droplets with pin wheeled crosses and circular discs for the same concentration, (iii) oil streaks and tubes from the concentration of 42% CSA in DMSO, (iv) isotropic polyhedral textures for concentration 53% of CSA in DMSO, (v) focal conic textures for the concentration of 85% CSA in DMSO. Similar textures are also seen in samples of concentration range 90%, 95% of CSA in DMSO. Phase diagram of binary mixtures of CSA and DMSO is shown in Figure 1.

The temperature variation of the refractive indices of the samples were measured to an accuracy of ±0.0005. Temperatures were measured with an accuracy of ±0.1 °C using

Abbe refractometer (Toshniwal Instruments and Engineering Company, New Delhi). The principle involved in the measurement of refractive index using this refractometer is the critical angle. A few drops of the sample to be studied are placed between the illuminated

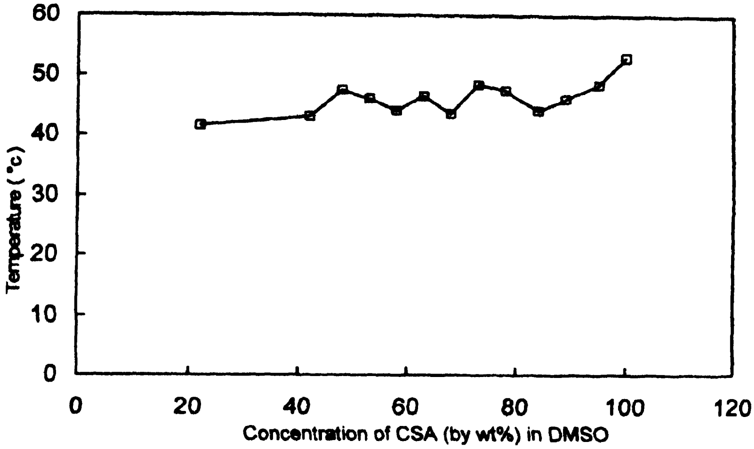

Figure 1. Phase diagram of binary mixture of CSA and DMSO; (i) below transition temperature : anisotropic mesophase (lyotropic phase), (ii) above transition temperature : isotropic liquid phase.

prisms which is maintained at the desired temperature by water circulation arrangement around the prism [10]. The lower prism of the Abbe refractometer is rubbed using fine cotton along the transverse direction of the prism gently several times till it is ensured that the oriented sample is deposited. The sample is taken in the liquid state at the higher temperature and is embedded between the two prisms. By slowly lowering the temperature the refractive index is directly measured at different temperatures.

The refractive indices along the direction of the molecular orientation and in the direction perpendicular to the molecules are identified by the known vibration directions of an external analyzer used along with the refractometer following the procedure adopted by Madhusudhana *et al* [11] and Somashekar *et al* [12]. The refractive index measured with the vibration direction parallel to the molecular axis (optic axis) of the oriented sample is denoted by n_e and the vibration direction rotated perpendicular to the direction of molecular axis is denoted by n_o. From these values the mean refractive index is calculated for the mixtures of CSA and DMSO using the relation

$$n_{\text{ave}} = \left(\frac{1}{3}\right)(n_e + 2n_o). \quad (2)$$

2.1. Optical parameters–excess refractive index :

Thermodynamic properties of mixed systems and the binary mixtures in particular containing self-associated components, exhibit deviations from ideal behavior that arise not only due to difference in molecular size and shape but also due to the hydrogen bonding between like and unlike molecules. The various physical properties of such mixtures depend on the degree of association in the pure state, the structure breaking ability of the components and the interaction due to hydrogen bonding between like and unlike molecules of the constituents [13–16]. Number of mixtures such as butyl amine, propanol, aliphatic alcohol, some alkanes in proper solvents have been studied as regards to their ultrasound velocities, specific volume, dielectric constant *etc.*, varying concentrations at different temperatures [17–20]. Densities, viscosities, dielectric constants and IR spectral studies of acetonitrile-toluene system with varying concentration and at different temperatures have been measured experimentally. These properties have been fitted to a polynomial equation [17,19]. The experimental results and excess parameters have also been calculated using the relation of the type

$$M^E = M_{\mathrm{expt}} - (C_1 m_1 + C_2 m_2) \tag{3}$$

where M^E is the excess parameter of the physical property, M_{expt} is the experimentally measured physical property, m_1 and m_2 the physical property of first and second components and C_1 and C_2 the concentration of two components.

Eq. (3) may be extended to any compound system while studying excess parameter. The binary mixtures of CSA and DMSO with varying concentrations have been taken and their refractive indices over a temperature range sufficiently above and below the transition temperature have been experimentally studied. The mean refractive index $\left(n_{\mathrm{expt}}^{\mathrm{ave}}\right)$ of each sample as a function of temperature is calculated using eq. (2). These values of $n_{\mathrm{expt}}^{\mathrm{ave}}$ are shown in Table 1 and represent the experimetnal values. Following the additive rule with the knowledge of concentrations (C_1, C_2) of constituents in each mixture, the theoretical value of the refractive index as a function of temperature is calculated. Substituting the experimental value and the calculated value of the refractive index in eq. (3), the excess refractive index (n^E) is calculated for each sample as a function of temperature and is also shown in Table 1.

3. Results and discussion

The excess refractive index plotted as a function of temperature shown in Figure 2 reveals that the excess parameter goes on decreasing with increasing temperature upto transition temperature. Then it changes sign and goes to negative minimum with further increase of temperature. This trend is observed in mixtures up to 89% by weight of CSA. At higher concentration above 90% by weight of CSA the excess refractive index remains negative but trend variation is the same as observed in the case of mixtures with lower concentration. The change of excess refractive index with concentration and temperture is in accordance with the predictions reported earlier in the case of other organic compound mixtures [13–20].

Table 1. Excess refractive indices versus temperature of mixtures of CSA and DMSO.

Conc. of CSA Wt%	34	36	38	40	42	44	46	48	50	52	54	56	58	60
100 n^{ave}_{expt}	1.4912	1.4915	1.4893	1.4882	1.4865	1.485	1.4835	1.4815	1.4795	1.4772	1.431	1.4295	1.4285	1.427
0 n^{ave}_{expt}	1.455	1.454	1.453	1.4525	1.4515	1.4505	1.4495	1.449	1.448	1.447	1.445	1.446	1.4445	1.444
42 n^{ave}_{expt}	1.4735	1.4708	1.463	1.444	1.4435	1.4425	1.442	1.441	1.44	1.439	1.438	1.4375	1.436	1.435
n^E	0.0033	0.0006	–0.0072	–0.0262	–0.0277	–0.0277	–0.0282	–0.0292	–0.0302	–0.0312	–0.0322	–0.0327	–0.0342	–0.0352
53 n^{ave}_{expt}	1.4872	1.4867	1.485	1.4833	1.48	1.481	1.478	1.437	1.435	1.435	1.4335	1.433	1.432	1.432
n^E	0.0130	0.0125	0.0118	0.0091	0.0058	0.0068	0.0038	–0.0372	–0.0392	–0.0392	–0.0407	–0.0412	–0.0422	–0.0422
58 n^{ave}_{expt}	1.4833	1.4823	1.4817	1.4797	1.4772	1.442	1.4385	1.4375	1.436	1.4345	1.4335	1.4325	1.431	1.4305
n^E	0.0073	0.0063	0.0057	0.0037	0.0012	–0.0340	–0.0375	–0.0335	–0.0400	–0.0415	–0.0425	–0.0435	–0.0450	–0.0455
72 n^{ave}_{expt}	1.4853	1.4843	1.4833	1.4817	1.4803	1.4787	1.4767	1.441	1.4365	1.434	1.431	1.4305	1.429	1.428
n^E	0.0039	0.0029	0.0019	–0.0009	–0.0011	–0.0027	–0.0047	–0.0404	–0.0449	–0.0474	–0.504	–0.0509	–0.0524	–0.0534
78 n^{ave}_{expt}	1.4853	1.4848	1.4838	1.4823	1.4800	1.4777	1.472	1.437	1.435	1.435	1.434	1.4325	1.432	1.4315
n^E	0.0021	0.0016	0.0006	–0.0009	–0.32	–0.0055	–0.0112	–0.0462	–0.0482	–0.0482	–0.0492	–0 0507	–0 0512	–0.0517
95 n^{ave}_{expt}	1.488	1.4877	1.4865	1.4852	1.4842	1.4825	1.4807	1.4782	1.4370	1.4345	1.4315	1.4290	1.4270	1.4260
n^E	–0.0014	–0.0017	–0.0029	–0.0042	–0.0052	–0.0069	–0.0087	–0.0112	–0.0524	–0.0549	–0.0579	–0.0604	–0.0624	–0.0634

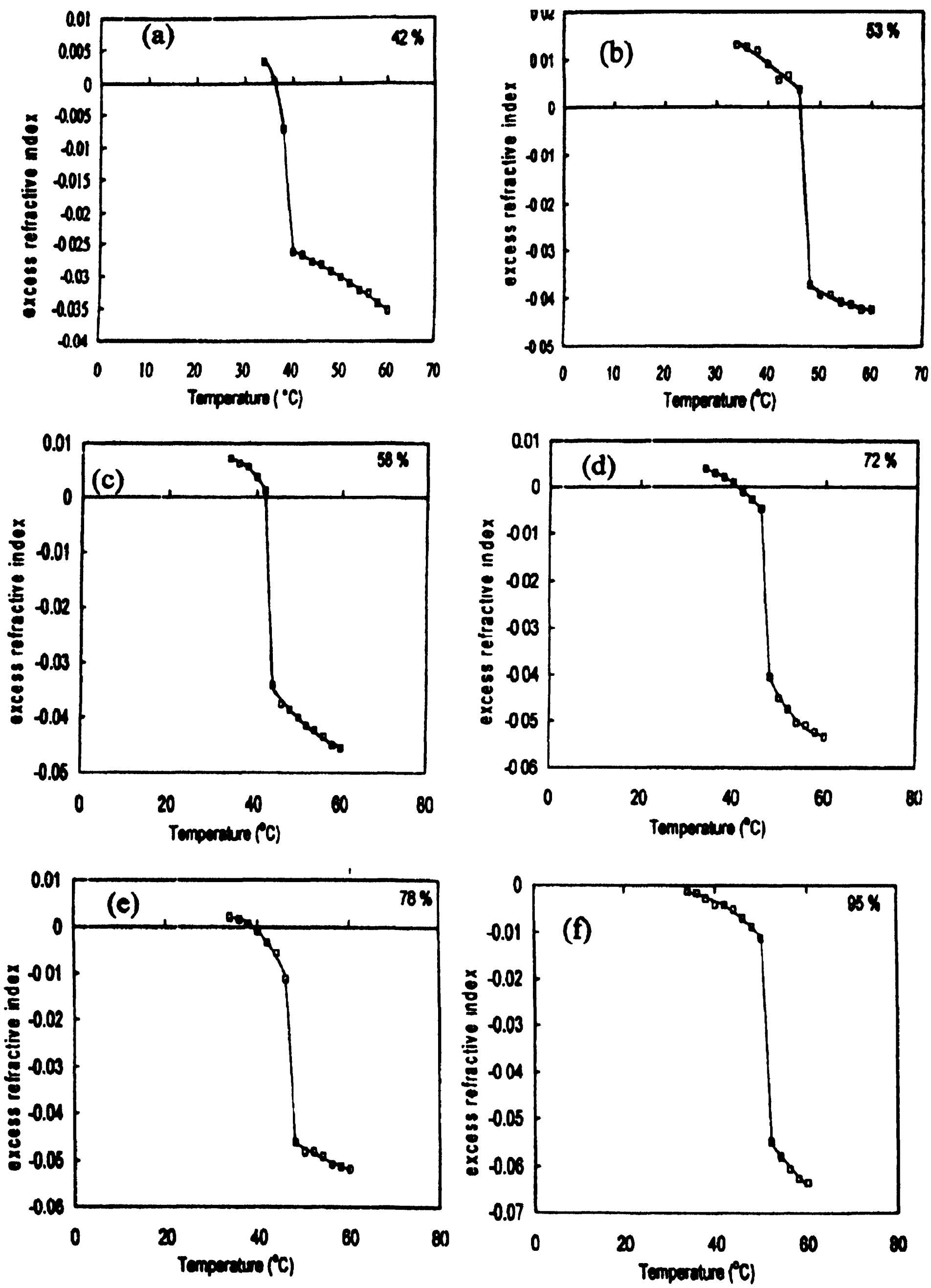

Figure 2. Temperature *versus* excess refractive index for different concentration of CSA.

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