Chapter 3

The effect of polymer and salt on the viscoelastic modes of a lyotropic discotic nematic liquid crystal

3.1 Introduction

In the previous chapter, we have described our studies on the pure CSPFO water system. CSPFO is a surfactant which forms disk like micelles in a range of concentration when dissolved in water. It is a model system to study and understand many biological phenomena. The addition of dopants like microsized particles, polymers or salts in lyotropic phases has attracted a great attention in the recent times. A small concentration of charged particles in a hyper swollen lamellar phase can destabilize the smectic order. However, it has been recently found that [1] anisotropic coherent motion of these particles along the membranes induced by an external alternating field can iron out the wrinkles in a membrane stack. This kind of hyper swollen lamellar phase finds useful applications in photonics since the interlayer spacing is of the order of visible wavelength. The addition of polymers to surfactant water system is interesting for two reasons. Firstly, these are explored with the aim of producing model systems of comparable complexity to those found in the biological systems [2]. Secondly, the solubilization power and the viscosity of polymer doped micellar system is higher than those of separate polymer and micellar solutions [3] and hence have potential applications. In a recent report, semi-flexible polymers were dissolved in a nematic solvent [4]. Polymers of sufficiently large persistence length were found to undergo a coil to rod configuration

transition at isotropic nematic transition of the medium. Also, the studies of dopants like polymer in lyotropic systems find useful applications in drug delivery. The addition of small amounts of salt is known to have profound effects [5] on the phase diagram of lyotropic systems, normally altering the transition temperature and thereby changing the temperature ranges of various phases. Occasionally, it also leads to suppressing the liquid crystalline phase [6, 7]. The salt is found to have a strong effect on the micellar solution of a non ionic surfactant [8]. The micelles grow due to increasing aggregation number as well as increased entrapped water. In the case of an ionic surfactant, doping of salt modifies both the intra- and inter-micellar interactions and therefore the structure of the aggregates.

The phase diagram of polymer doped CSPFO water system has been reported [9, 10]. Kuzma *et. al.* [9] have reported the effect of a long chain hydrophilic polymer on the phase behavior of CSPFO water system. The ternary phase diagram containing polyethylene oxide (PEO) polymer, surfactant and water shows that a lamellar phase is stable only below a certain polymer concentration, known as critical polymer concentration. This critical polymer concentration is a function of the molecular weight of polymer and is found to increase with decreasing molecular weight. For example, for a polymer having molecular weight of about 10^5, critical concentration is found to be nearly 1% for 49% (w/w) CSPFO in water. There is a concentration range near the critical concentration where on increasing the temperature one gets nematic phase, lamellar phase and then a nematic phase. Such a phase sequence in literature is referred to as reentrant nematic phase. The isotropic to nematic transition is not changed much by the addition of polymer.

The effect of salt on the phase diagram of CSPFO water system has been studied by Leaver and Holmes [6]. They have reported the effect of Cesium Chloride (CsCl) salt on the phase sequence of CSPFO water system. The discotic nematic (N_D) phase is present upto about 8% by weight CsCl although the temperature range of phase decreases. At higher temperatures there is an isotropic phase and at lower temperatures there is an extensive lamellar region. Above about 8% concentration of CsCl (by weight) there is a lamellar to isotropic transition via a two phase coexistence region. In this chapter, we report our studies on the

refractive indices and the twist viscoelastic coefficient of polyethylene glycol (PEG) and Cesium Chloride (CsCl) doped CSPFO water system. We describe our studies of the twist viscoelastic coefficient as a function of concentration of polymer and salt as well as temperature.

3.2   Experimental

The experimental setup and other details are same as that described in the previous chapter (Sec. 2.3). Polymer polyethylene glycol (PEG) of molecular weight 35,000 and CsCl were purchased from Aldrich Chemicals and used without further purification. We prepared a ternary mixture of CSPFO, PEG and water, in which water in small quantities was progressively replaced by PEG. We maintain the same concentration of the surfactant to the solution of PEG and water (45% of CSPFO (w/w) in water and PEG). Three different concentrations (0.5%, 1.0% and 2.0% (w/w)) of PEG in CSPFO were prepared. We made the CSPFO, water and CsCl sample as reported in literature [6]. Here, the concentration of CSPFO and water was maintained as 45/55 (w/w) and small quantities of CsCl was added to this mixture. We studied three different concentrations of CsCl (0.5%, 1.0% and 2.0% (w/w)) in CSPFO water system.

We have used Abbe refractometer (Carl Ziess) to measure the extraordinary and ordinary refractive indices in the N_D phase of CSPFO water system. The refractive index measurements using the refractometer are based on the internal refraction of light at the interface between the sample and the surface of an optical prism. An optical polarizer was used along with the Abbe refractometer to obtain the ordinary and extraordinary refractive indices. The accuracy of this refractometer was 10^{-3}. The refractometer had an arrangement to circulate water around the prisms to facilitate the measurements at various temperatures. We have used a water circulator (Julabo F25 HL) to maintain the temperature of the prisms upto an accuracy of 0.01^oC.

3.3 Results

We have studied the refractive indices and twist viscoelastic coefficient in the nematic mesophase of CSPFO water system. In the next subsections we describe our results on refractive indices and twist viscoelastic coefficients.

3.3.1 Refractive indices

An Abbe refractometer along with a polarizer can be used to measure the refractive indices of an uniaxial crystal [11]. Jun Li *et.al.* have used the Abbe refractometer to measure the extraordinary and ordinary refractive indices of thermotropic nematic liquid crystals [12,13]. The refractive indices of lyotropic systems have also been measured [14, 15]. We have used an Abbe refractometer with an optical polarizer to measure the values of extra ordinary and ordinary refractive indices (n_e & n_o) of CSPFO water system in N_D phase at various temperatures. The sample was sandwiched between the two prisms of Abbe refractometer and heated above N-I transition. It was then slowly cooled to N_D phase where it was aligned on the prisms homeotropically. We have measured the absolute values of n_e and n_o from which we can get the values of birefringence directly. The discotic micelles of CSPFO in water have positive diamagnetic anisotropy [16], whereas it is negative for most hydrocarbon lyotropic disks [14]. The optical birefringence for CSPFO water system very near to the phase transition was measured by Rossenblatt [17], where it was found to be positive. In Fig. 3.1 we have shown the values of n_e and n_o as a function of reduced temperature for 2% PEG doped CSPFO water system. As expected, these values decrease with increasing temperature. Fig. 3.2 shows the refractive indices for CSPFO water system doped with 2% CsCl by weight. These values of refractive indices are almost same as reported in literature for a lyotropic nematic system, Potassium Laurate/Decanol/water [14, 15].

3.3.2 Twist viscoelastic coefficient

We have shown, in Fig. 3.3, the variation of K_{22}/η with the reduced temperature for different concentrations of PEG in CSPFO-water system. We find that the twist viscoelastic
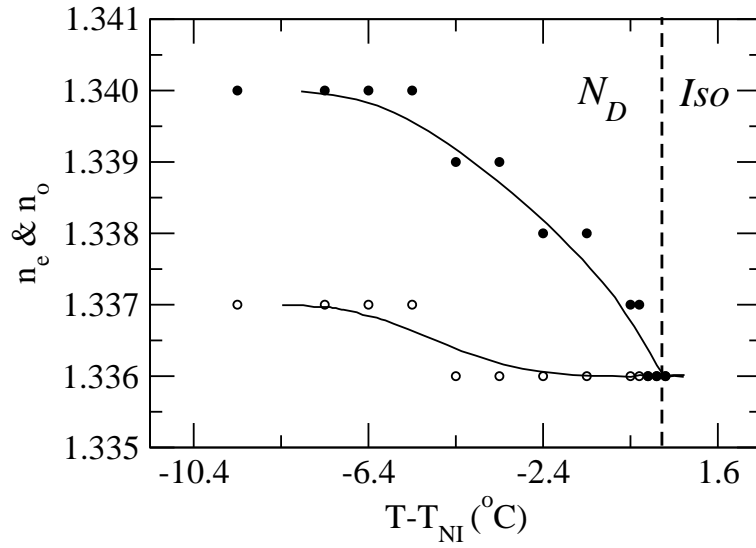
Figure 3.1: The values of n_e and n_o for 2% PEG doped CSPFO water system. Filled circles represent n_e and empty circles represent n_o. Solid lines are the cue to eyes.

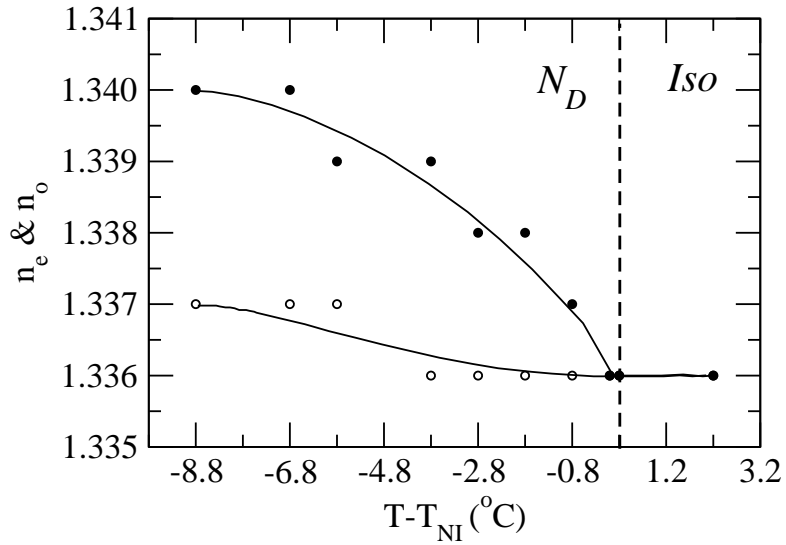
Figure 3.2: The values of n_e and n_o for 2% CsCl doped in CSPFO water system. Filled circles are for n_e and empty circles are for n_o. Solid lines are the cue to eyes.

coefficient increases as we increase the temperature in the nematic phase. Increase in the concentration of PEG at a given reduced temperature decreases the values of K_{22}/η.

The effect of CsCl salt on the viscoelastic coefficient of CSPFO water system is shown in Fig. 3.4. Again the values of K_{22}/η increase as we increase the temperature of the system in the nematic phase. The twist viscoelastic coefficient increases with the increasing concentration of CsCl in CSPFO water system. The critical concentration of CsCl, at which the nematic phase is suppressed, is 8% by weight for 50% CSPFO in water. We have performed the experiments with upto 2% of CsCl (w/w) doped in CSPFO water system. Above this concentration, transition boundaries are not sharp and a broad coexistence of nematic and isotropic phase exists.
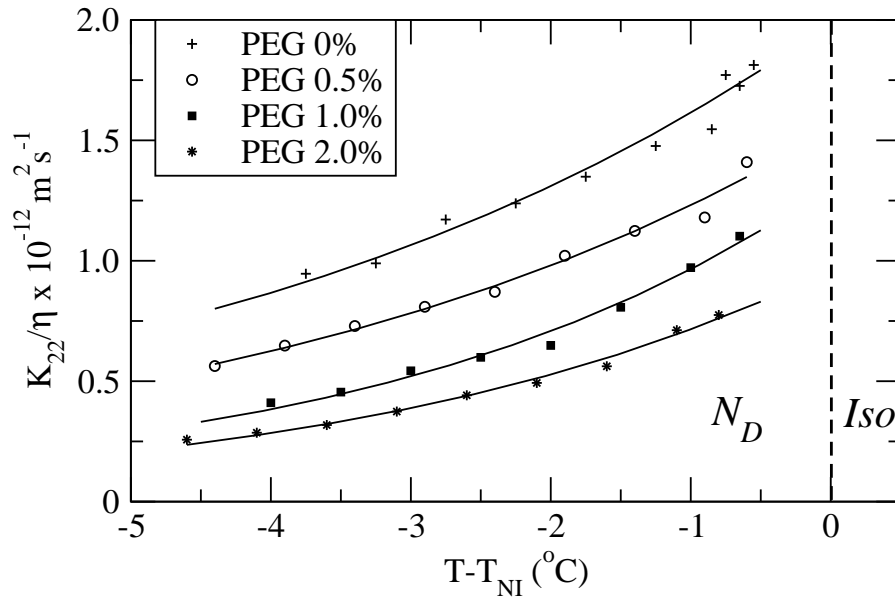

Figure 3.3: The effect of the addition of PEG on CSPFO-water system. The variation of the twist viscoelastic coefficient of CSPFO/water/PEG with the reduced temperature for various concentrations.

3.4   Discussion

We have investigated the viscoelastic behavior of CSPFO water system as we dope this system with polymer and salt. When a long chain hydrophilic polymer is added to CSPFO water system, above a critical concentration, the lamellar phase is suppressed [9]. The phase
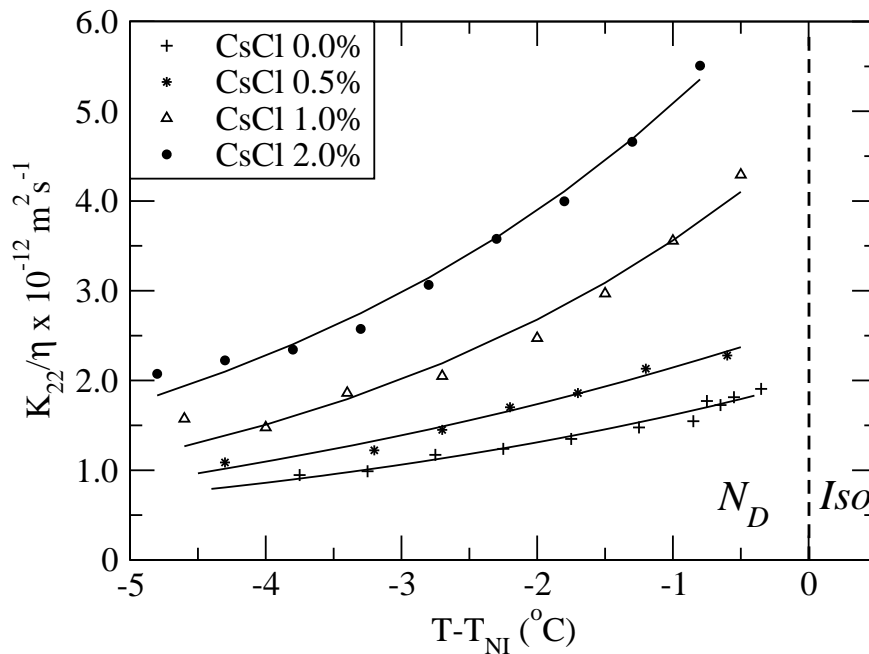
Figure 3.4: The effect of the addition of CsCl on CSPFO-water system. The variation of the twist viscoelastic coefficient of CSPFO/water/CsCl with the reduced temperature for various concentrations.

diagram of polyethylene oxide (mol. wt. 10^5) doped CSPFO water system is shown in Fig. 3.5. The polymer covers the disk like micelles and makes them more stable thereby suppressing the lamellar phase beyond a critical concentration of polymer. Our results clearly indicate that the values of K_{22}/η always increase as the temperature of the sample is increased (Fig. 3.3). With increasing concentration of PEG in CSPFO-water system, we find that the values of K_{22}/η decrease at a given reduced temperature. It is known, that the addition of polymer to CSPFO water system has negligible effect on the curvature elasticity of micellar nematic system [18]. Hence, we suggest that the addition of polymer increases the twist viscosity leading to decrease in the values of twist viscoelastic coefficient. This is in agreement with the values of viscosity for polymer doped CSPFO water system reported in literature [19].

For an ionic amphiphile like CSPFO, the surface of micelles is charged and the counterions can be either on the micelles surface or in the free solution. The addition of extra counterion (by adding CsCl salt) is expected to increase the number of counterions on mi-

celles surface. It affects the head group interactions, head group area and lowers the free energy per monomer in the micelle. Electrostatic screening reduces the coulombic repulsion between the micelles and favors the growth of larger and flatter aggregates [6]. The phase diagram of CsCl doped CSPFO water system is shown in Fig. 3.6. It can be seen that above a certain concentration of CsCl, N_D phase is absent. Fig. 3.4 shows that the values of K_{22}/η increase as a function of temperature of the sample. The addition of CsCl, increases the value of K_{22}/η at a given reduced temperature. One can conclude that the addition of CsCl may decrease the twist viscosity leading to an increase in the values of K_{22}/η. Here, it should be noted that the effect of adding CsCl on the viscoelastic coefficient is similar to that of increasing the concentration of CSPFO in the system.
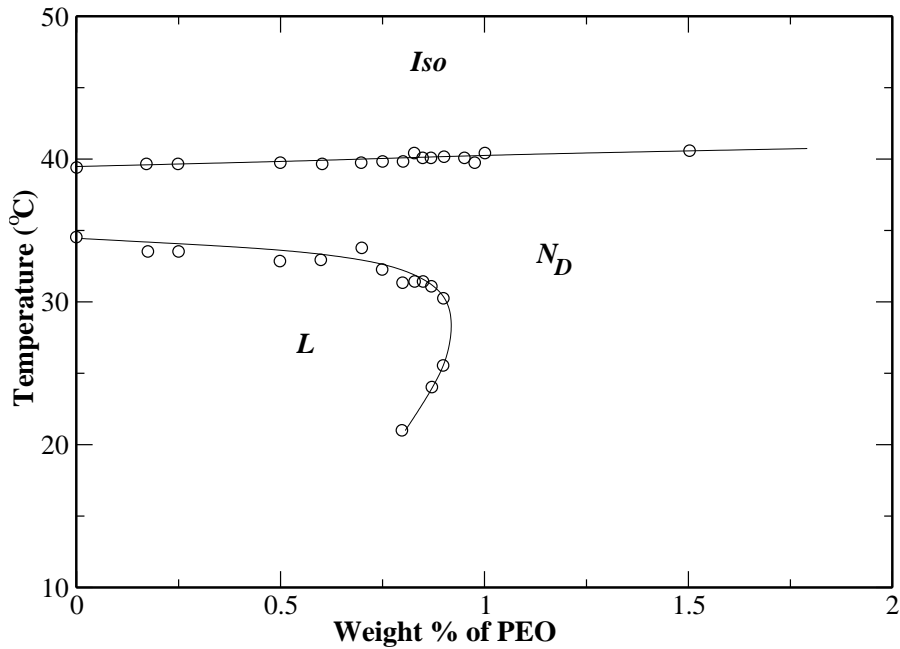

Figure 3.5: Transition temperatures of CSPFO water system as a function of water replaced by PEO; molecular weight 10^5, CSPFO concentration 49% (w/w) in water [9].

3.4.1 Estimation of activation energy

From the experimental data, we have also estimated the activation energy corresponding to twist viscosity for PEG and CsCl doped CSPFO water system. As described in the previous chapter, we used the same temperature dependence for η and K_{22} as given by Eqn. 2.8 and 2.9.
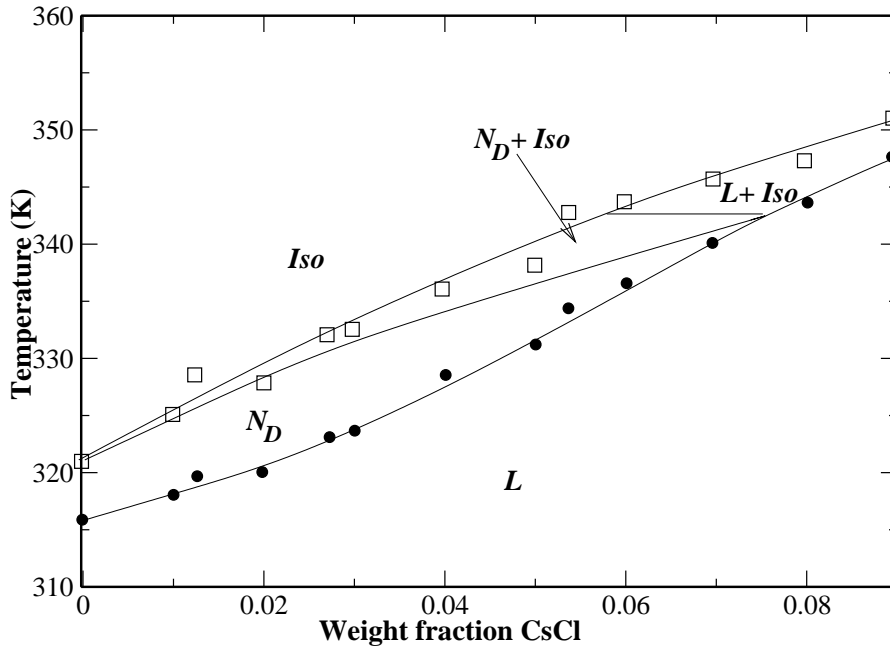
Figure 3.6: Phase diagram of CSPFO/CsCl/heavy water system for a given concentration of CSPFO/heavy water = 50% (w/w) with various amounts of CsCl. Here, *Iso* represents the isotropic, N_D represents the discotic nematic and L represents the lamellar phase [6].

Our experiments on refractive indices of CSPFO water system showed that the values of birefringence are not sensitive to the addition of small quantities of PEG. However, it has been reported that there is a small decrease in the values of birefringence for the addition of polymer of higher molecular weight taken at higher concentration [18]. We can assume that the addition of small quantities of PEG does not change the values of order parameter. Hence, to estimate the activation energy, we used the same values of order parameter reported in literature for CSPFO water system [20]. In the Fig. 3.7 we have presented the values of $ln(K_{22}/\eta S)$ as a function of temperature for 2% (w/w) PEG doped CSPFO water system. The solid line is a fit to Eqn. 2.10. The values of activation energy, for various amounts of PEG in CSPFO water system, estimated from our data are shown in Table 3.1. Though, the activation energy does not change by changing the concentration of CSPFO in water, we find that it is sensitive to the addition of PEG.

We find that the birefringence of a CsCl doped CSPFO water system is not sensitive to the small quantities of CsCl. Hence, we have taken the same values of order parameter

from literature in order to estimate the activation energy [20]. Fig. 3.8 shows the values of $ln(K_{22}/\eta S)$ as a function of temperature for 2% (w/w) CsCl doped CSPFO water system. The values of activation energy for three different concentrations of CsCl doped CSPFO water system are shown in Table 3.2. From our experiments we find that the activation energy of nematic phase of CSPFO water system increases by small amounts when PEG or CsCl is doped in small quantities.
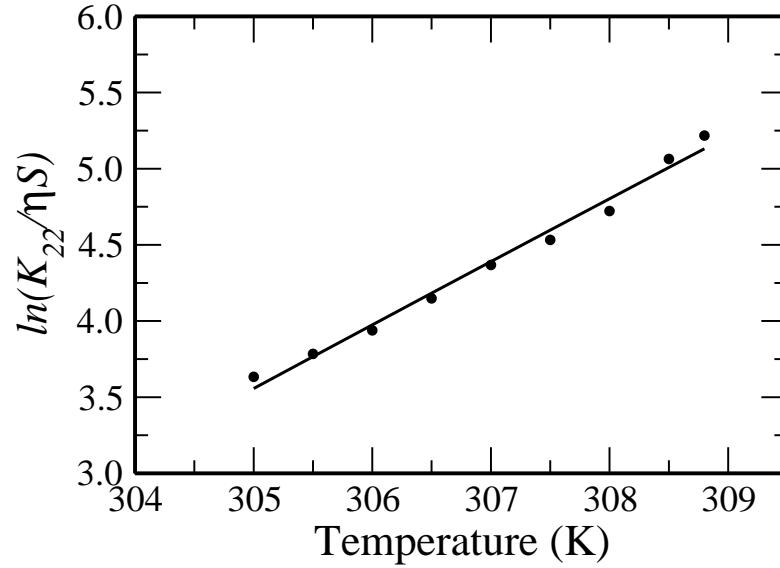

Figure 3.7: The variation of $ln(K_{22}/\eta S)$ as a function of absolute temperature for 2.0% PEG doped CSPFO water system. Solid line is the fit to Eqn. 2.10.

Table 3.1: Activation energy for PEG doped CSPFO-water system at different concentrations of PEG.

% PEG	E_a (Kcal/mole)
0	60.4 ± 2.4
0.5% PEG	64.8 ± 3.6
1.0% PEG	78.9 ± 4.7
2.0% PEG	77.5 ± 5.4

We have studied the twist viscoelastic coefficient of PEG and CsCl doped CSPFO water system as a function of temperature as well as concentration of dopants. PEG doped system
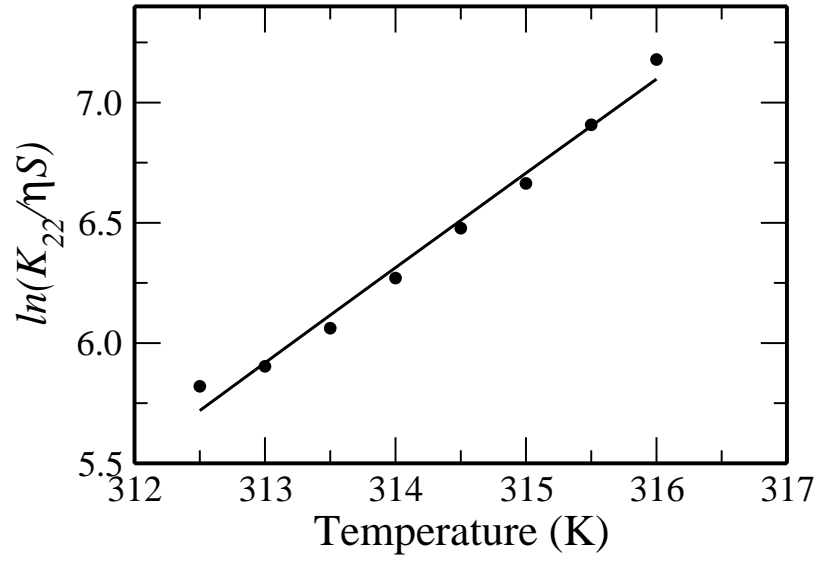
Figure 3.8: The variation of $ln(K_{22}/\eta S)$ as a function of absolute temperature for 2.0% CsCl in 45/55% (w/w) CSPFO water system. Solid lines are the fit to Eqn. 2.10.

Table 3.2: Activation energy for CsCl doped CSPFO-water system at different concentrations of CsCl.

% CsCl	E_a (*Kcal/mole*)
0	60.4 ± 2.4
0.5% CsCl	64.7 ± 3.7
1.0% CsCl	74.7 ± 6.6
2.0% CsCl	77.2 ± 3.9

has a tendency of suppressing lamellar phase while CsCl doped system has a tendency of suppressing nematic phase. We find that in the CSPFO water system, the increasing concentration of PEG decreases the values of K_{22}/η while increasing concentration of CsCl increases the values of K_{22}/η. We also find that for a given concentration of PEG or CsCl, the value of K_{22}/η in N_D phase increases with increase in temperature.

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