

# STUDIES ON CRITICAL CONCENTRATION OF LIQUID CRYSTALLINE ETHYLCELLULOSE\*

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## ABSTRACT

Critical concentrations of lyotropic liquid crystalline ethylcellulose in more than ten solvents were determined using both Abbé refractometer and polarized microscopy. Critical concentration  $C_{\text{crit}}$  of forming liquid crystal phase decreased with increasing solubility parameter  $\delta$  of solvent until approaching the  $\delta$  of polymer. Although the alcohols used as solvents had the same variation rule, the critical concentration values of their solutions were much higher, due to their excessive large hydrogen bond component of  $\delta$ . The experiments of using mixed solvents which showed good linear relation between  $C_{\text{crit}}$  and  $\delta$  also proved this rule. A technique of Transmission Optical Analysis was first used to estimate the concentration dependence of critical phase transition temperature  $T_{\text{crit}}$  of EC, and a T-C phase diagram could be drawn.

## INTRODUCTION

Since the cholesteric mesophase was found in hydroxypropyl cellulose (HPC) aqueous solution of high concentration by Werbowyj and Gray in 1976<sup>[1]</sup>, the mesophases of cellulose and its derivatives have been a field of long-standing scientific interest. There is an extensive literature on HPC, but ethylcellulose (EC) has received less attention. Both lyotropic and thermotropic liquid crystalline behaviors of EC were reported in the literatures<sup>[2-5]</sup>.

The critical concentration (hereafter  $C_{\text{crit}}$ ) is the most important behavior of lyotropic liquid crystal.  $C_{\text{crit}}$  of EC has been determined in several solvents such as m-cresol and acetic acid<sup>[6]</sup>. The main structure factors which affect  $C_{\text{crit}}$  are qualitatively considered as acidity and mole volume of solvent. In this paper,  $C_{\text{crit}}$  of EC was measured by both refractometry and microscopy. Various kinds of solvent systems were used and the relation between  $C_{\text{crit}}$  and solubility parameter of solvents are discussed. The critical phase transition temperature of EC solution was also investigated by using a technique named Transmission Optical Analysis (TOA).

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## EXPERIMENTAL

### *Materials*

The ethylcellulose studied was reagent-grade produced by Liansha Chemical Factory. The number average molecular weight was  $9.4 \times 10^3$ , as determined from the intrinsic viscosity in benzene at 25°C and the formula<sup>[8]</sup>

$$[\eta] = 2.92 \times 10^{-4} \overline{M}_n^{0.81}$$

was applied. The degree of substitution (DS) was 2.13, as calculated from elemental analysis result.

Reagent-grade solvents were used as received.

### *Solution preparation*

EC solutions over the concentration range 10—50 wt% with an interval of 2% were prepared by mixing EC with the solvent and subsequently ageing for about one month at room temperature before use. EC/methanol, EC/ethanol, EC/dioxane and EC/ethanenitrile must be aged in a refrigerator to avoid the evaporation of solvents.

### *Determination of critical concentration*

A thin layer of solution between two glass slides was placed under an OLYMPUS BHT polarized microscope at room temperature (20—30°C). The sandwich was pressured toward a direction before use. The concentration at which birefringence was just observed was defined as  $C_{\text{crit}}$ . An Abbé refractometer (Shijiazhuang Optical Instrument Factory) with a rotatable polarizer mounted on the eyepiece was used for measuring the two principal refractive indices  $n_{\parallel}$  and  $n_{\perp}$  at 30°C. Before measurements, the prism surfaces were carefully rubbed in the longitudinal direction of the prism with cotton soaked in acetone, in order to achieve macroscopic alignment of the sample molecules. An interval of 5—30 min was needed for equilibrium.

### *Determination of critical phase transition temperature*

An OLYMPUS BHT polarized microscope with METTLER FP82 hot stage, GA14 recorder and a photomonitor mounted on the eyepiece was used to record TOA curves for EC solutions. The heating rate was 1°C/min.

## RESULTS AND DISCUSSION

Fig. 1 illustrated the concentration dependence of refractive index of EC solutions in four typical good solvents which are phenol, m-cresol, acetic acid and dichoro-acetic acid. The appearance of birefringence indicated the formation of mesophase, i.e. critical concentration. Then birefringence rose with the increase of concentration

until a constant value. It is suggested that the mesophase in a biphasic system increased and subsequently became complete anisotropic phase. A droplet texture can usually be observed in this biphasic system with microscope. It can also be observed from Fig. 1 that  $n_{\perp}$  was straight line and  $n_{\parallel}$  had two kinks while the refractive indices of solvents were higher than that of EC, inversely  $n_{\parallel}$  was straight line and  $n_{\perp}$  had two kinks while the refractive indices of solvents were lower.

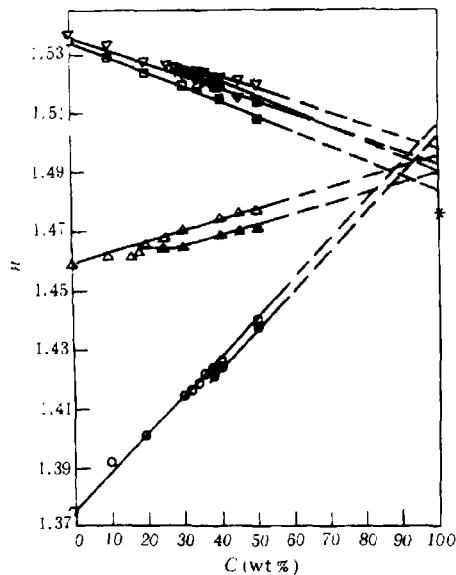


Fig. 1 Concentration dependence of refractive index for some EC solutions at 30°C in phenol ( $\nabla$ ,  $\blacktriangledown$ ), *m*-cresol ( $\square$ ,  $\blacksquare$ ), dichloro acetic acid ( $\Delta$ ,  $\blacktriangle$ ) and acetic acid ( $\circ$ ,  $\bullet$ ). The mark \* at 100% was determined using a melt casting EC film. ( $\nabla$ ,  $\square$ ,  $\Delta$ ,  $\circ$ ) for  $n_{\parallel}$  and ( $\blacktriangledown$ ,  $\blacksquare$ ,  $\blacktriangle$ ,  $\bullet$ ) for  $n_{\perp}$

The critical concentration values determined were listed in Table 1. From which it can be seen that although the results of both methods were basically consistent, the data of polarized microscopy were slightly lower than that of refractometry. It is evident that when the concentration approached critical value, the orientation of macromolecules was very easy to relax because of lower concentration and therefore lower viscosity, and also the birefringence was very weak. Because the refractometry needed relatively long determination period, while the polarized microscopy was able to catch transient birefringence, the values determined by the latter were reasonably lower than by the former. We adopted the  $C_{\text{crit}}$  from polarized microscopy in later discussion, since its data were more complete.

#### Relation between $C_{\text{crit}}$ and solubility parameter $\delta$

$C_{\text{crit}}$  is obviously affected by the properties of solvent. For example, it is well

known that the greater the polarity of acid is, the lower the critical concentration will be. But as to solubility parameter, no evident regularity was reported in the literature.

**Table 1** The comparison of the critical concentration results from polarized microscopy and Abbé refractometry

Solvent	Solubility parameter	$C_{crit}$ (PM) (%)	$C_{crit}$ (Abbé) (%)
Group 1			
Dioxane	20.2 <sup>b)</sup>	34	— <sup>d)</sup>
Acrylic acid	20.8 <sup>a)</sup>	44	46
Pyridine	21.8 <sup>b)</sup>	38	38
Acetic anhydride	21.8 <sup>b)</sup>	38	38
Acetic acid	21.9 <sup>b)</sup>	36	38
m-Cresol	22.7 <sup>b)</sup>	30	34
Ethanenitrile	24.3 <sup>b)</sup>	36	— <sup>d)</sup>
Dichloro acetic acid	24.9 <sup>a)</sup>	22	25
Formic acid	25.0 <sup>b)</sup>	30	— <sup>c)</sup>
Phenol	25.6 <sup>b)</sup>	28	30
Group 2			
Phenylamine	23.4 <sup>b)</sup>	50	50
2-Propanol	23.6 <sup>b)</sup>	50	54
Ethanol	26.3 <sup>b)</sup>	48	50
Methanol	29.5 <sup>b)</sup>	36	38

a) Calculated value according to Small's method<sup>[9]</sup>

The  $\delta$  of EC calculated is 25.7 when  $DS=2.13$

b) Literature value<sup>[9]</sup>. When  $\delta$  is not a single value, a medium value is used

c) EC/formic acid solution is too opaque to measure refractive index

d) Hard to measure because of its volatility

Fig. 2 showed some regularity on the relation between  $C_{crit}$  and  $\delta$  in EC/solvent systems. Observing as a whole, there was a tendency that the higher the  $\delta$  was, the lower the  $C_{crit}$  was. Because EC has a high  $\delta$  value of about 25.7 (to  $DS = 2.13$ ), the result implied low  $C_{crit}$  needed good solubility. EC has high cohesive energy, i.e. high hydrogen bond forces, permanent dipole interactions and also van der Waals forces. So only the solvents which also have high cohesive energy can dissolve EC

well. Perfect dissolution makes macromolecule good mobility and easier to orient, and consequently easier to form liquid crystalline phase. Solvents apparently interact with cellulosic chains in such a way as to modify considerably the potentials restricting rotations about the ether linkages<sup>[10]</sup>. Solvents effect on  $C_{crit}$  is wholly attributable to changes in molecular expansion brought about by solvent action. The larger the solvation is, i.e. the larger the molecular expansion is, the more rigid the chains become, and therefore the lower the  $C_{crit}$  will be.

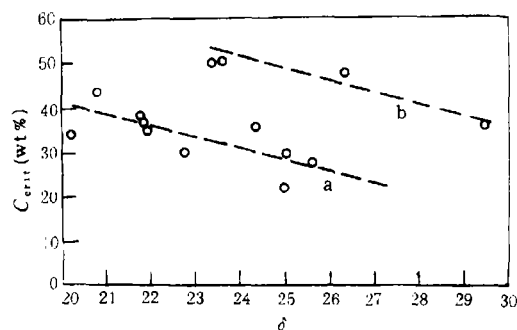


Fig. 2 Solubility parameter dependence of critical concentration for EC solutions at 30°C. Curve a for solvents in Group 1, and Curve b for solvents in Group 2

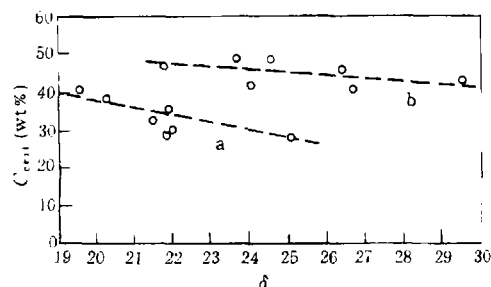


Fig. 3 Solubility parameter dependence of critical concentration for HPC solution at 30°C. Curve a for solvents in Group 1, and Curve b for solvents in Group 2 (all alcohols in it). The plots were drawn according to the literature data<sup>[7]</sup>

In fact, the solvents can be classified into two groups. All alcohols belonged to Group 2 and other solvents except few such as some amine belonged to Group 1. Each group formed a straight line in Fig. 2. They had the same variation rule, but Group 2 had much more higher  $C_{crit}$  value.  $C_{crit}$  increase with increasing the carbon number of alcohols. It is known that hydrogen bond component is more dominant in solubility parameter of alcohols than in EC or other solvents. The excess part of

hydrogen bond component do not contribute to dissolution. Therefore alcohols have relative poorer dissolution and high  $C_{crit}$ .

The plots  $C_{crit}$  vs.  $\delta$  on hydroxypropyl cellulose (HPC) can also be drawn (Fig. 3) according to the literature data<sup>[7]</sup>. A similar rule can be obtained. That may imply that the relation described above has universal sense in the cellulosic derivatives.

#### *Relation between $C_{crit}$ and $\delta$ in mixed solvents*

It is well known that  $\delta_m$  of a mixed solvent can be deduced by the relation:

$$\delta_m = V_1\delta_1 + V_2\delta_2$$

Where  $V_1$  and  $V_2$  are volume fraction of solvent 1 and 2,  $\delta_1$  and  $\delta_2$  are solubility parameter of solvent 1 and 2. Hence we can easily prepare a series of mixed solvent with considerably different  $\delta$ . A research of relation between  $C_{crit}$  and  $\delta$  can be performed by these mixed solvents.

A linear relation was shown in Fig. 4 and Fig. 5. This was another powerful fact to verify the regularity on relation of  $C_{crit}$  and  $\delta$  in EC/solvent system which have been described previously.

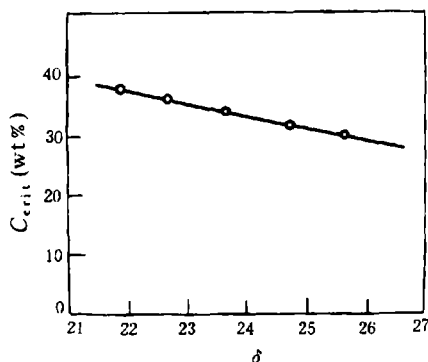


Fig. 4 Critical concentration dependence of solubility parameter for EC solutions in phenol/acetic acid mixed solvent at 30°C

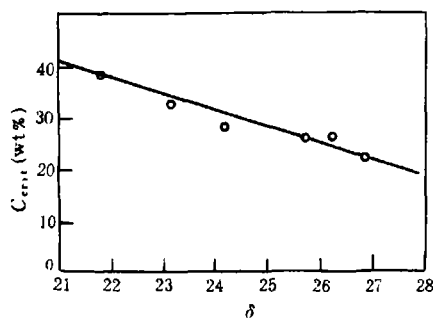


Fig. 5 Critical concentration dependence of solubility parameter for solutions in acetic anhydride/dichloro acetic acid mixed solvent at 30°C

#### *Determination of critical phase transition temperature*

On heating, the temperature at which birefringence of a polymer solution with given concentration first vanishes can be defined as critical phase transition temperature  $T_{crit}$ . An ordinary method to determine  $T_{crit}$  is by microscopy, but visual observation is hard to judge the vanishing point of birefringence. Here the Transmission Optical Analysis (TOA) technique has been used in determination.

A typical TOA curve was shown in Fig. 6. The intensity firstly fell with increasing temperature, and then became constant. The tangent point was defined as  $T_{crit}$ .

A T-C phase diagram of EC/phenol system was illustrated in Fig. 7. The diagram showed the concentration dependence of  $T_{crit}$  also can be considered as temperature dependence of  $C_{crit}$ .  $T_{crit}$  increased with concentration or  $C_{crit}$  increased with temperature. This tendency agrees with the results of other investigators<sup>[6,11]</sup>.

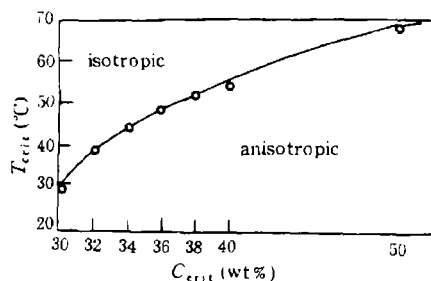
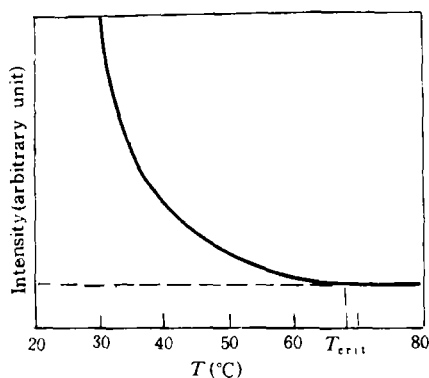


Fig. 6 A typical TOA curve for EC solutions      Fig. 7 The concentration dependence of critical phase transition temperature  $T_{crit}$  for the EC solutions in phenol

## CONCLUSIONS

The critical concentration of EC solution increased with decreasing solubility parameter of solvent. The EC/alcohols solutions had the same variation rule, but their critical concentration values were much higher than those of other solvents with similar solubility parameter. A nice linear relation of  $C_{crit}$  and  $\delta$  was shown in mixed solvent systems. Experimental results of EC showed that the critical concentration of the forming liquid crystalline phase relates to the solubility parameter of solvents.

### Keywords:

Ethyl cellulose; Lyotropic liquid crystal; Critical concentration; Solubility parameter; Transmission Optical Analysis; Phase diagram

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