

ASSOCIATION OF ETHYLENE VINYL ACETATE COPOLYMER IN DILUTE SOLUTIONS IV. SOLVENT MIXTURE AND ADDITIVE EFFECT ON C_A *

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Abstract Critical association concentration (C_A) of ethylene-vinyl acetate copolymer (EVA) in selective solvent mixtures of 1,2-dichloroethane (DCE) (polar solvent) and cyclohexane (CYH) (non-polar solvent) was investigated. DCE is a good solvent for polyvinyl acetate (PVAc) and a poor solvent for paraffin, whereas CYH is a good solvent for the paraffin and a precipitant for PVAc. Viscosities of EVA in different compositions of the solvent mixture with and without additives were measured. Viscosity results were used to determine the C_A value of the systems. It is shown that C_A was markedly dependent on the composition of the solvent mixture and concentration and structure of the additive. Solvation and competition between hydrogen bonding and micellisation were suggested for qualitative description of the changing of C_A value observed.

Keywords Polymer solution, EVA copolymer, Association, Viscosity, Additive

INTRODUCTION

Association behaviors of ethylene-vinyl acetate (EVA) random copolymer have been studied in 1,2-dichloroethane (DCE) and cyclohexane (CYH) by viscometry and dynamic laser light scattering^[1-3]. Previous works^[4] have shown that the critical association concentration (C_A) of EVA in a poor solvent of DCE exists, by which the association of EVA molecules in DCE was divided into interchain associations and intrachain associations. The C_A value increases with an increase in temperature and vinyl acetate (VA) content in EVA and a decrease in molecular weight of EVA.

The association of polymer in dilute solution is affected by many external factors such as solvent, additive, temperature and pH etc., besides the structure of the polymer. The solvent, however, is the most important one. Different solvents were usually used to investigate association phenomenon of various polymers such as homopolymers^[5, 6], block copolymers^[7, 8], water soluble polymers^[9], and ionomers^[10]. Certainly, the solvent would affect the critical association concentration of the polymer. Unfortunately, there were few works involved in critical association concentration^[11]. Lundberg *et al.*^[12-15] were unique in that their results from viscometry showed that the boundary concentration, at which interchain association transfer to intrachain association for some sulfonated ionomers, was affected by the sulfonated content of the ionomer, the other polymer added, the type of solvent and polar additives in ionomer solution. In this study, we investigated the critical association concentration of EVA random copolymer in a solvent mixture of DCE and CYH with or without some organic additives such as alcoholic or acidic additives, etc. The present systems studied in this work were based on the consideration that the crude oil is a

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mixture consisting of polar (resin-asphaltene) and non-polar (paraffin and hydrocarbon) substances, and EVA or EVA with some additives are used as pour point depressants for the crude oil and its products.

EXPERIMENTAL

An EVA sample with number average molecular weight, MWD and VA content of 16800, 1.96 and 37.5% respectively is used. The solutions of the EVA sample were prepared in a given solvent mixture of DCE and CYH with or without additives at 45°C, then filtered. Sufficient quantities of the desired solvent mixtures were prepared in volumetric flasks so as to provide stock solvent mixture supplies for the dilution of the solution. Viscosity measurements of the solution were taken with an Ubbelohde viscometer which was immersed in a constant temperature bath of 30°C $\pm$ 0.02. Repeated measurements were made until reproducible results were obtained. All alcoholic and acidic additives used were of reagent grade but the sorbitan oleate (Span80) of surfactant was of chemical grade.

RESULTS AND DISCUSSION

Solvent Effect

Figure 1 shows the reduced viscosity (η_{sp}/C)~concentration (C) relation of EVA sample in 8 different compositions (ϕ_c) of solvent mixture of DCE and CYH, where ϕ_c is the volume fraction of CYH in solvent mixture at 30°C. Obviously, the downswing in slope of $\eta_{sp}/C \sim C$ curve at the dilute regime of concentration i.e. a cross point on the curve was displayed regularly among the systems of ϕ_c equal to 0, 0.1, 0.3, 0.4, 0.7, 0.8, 1.0, except for $\phi_c = 0.6$. That is, the critical association concentration (C_A) corresponding to the cross point on the $\eta_{sp}/C \sim C$ curve^[4], at which a transition from interchain association to intrachain association occurs, increases with the decreasing of ϕ_c from $\phi_c = 0.6$ to $\phi_c = 0$ and decreases with the decreasing of ϕ_c from $\phi_c = 1.0$ to $\phi_c = 0.6$. The relation of C_A and ϕ_c is clearly shown in Fig. 2. From Fig. 2, the C_A values of EVA copolymer in various solvent mixtures are opposite to their $[\eta]$ values, i.e. $[\eta]$ value in a pure solvent of DCE or CYH is lower than in solvent mixtures, whereas the C_A value in pure solvent is higher. As we all know, DCE and CYH are marginal solvents for EVA copolymer according to their Huggins parameter^[16] (χ_1 are equal to 0.058~0.124 and 0.067~0.070, respectively), but both are also selective solvents, i.e., DCE and CYH are favorable for VA and ethylene segments in EVA respectively. Accordingly, two types of intra-association of EVA, induced by the crystallization of ethylene segments and by the induction (dipole-dipole interaction) of VA segments were

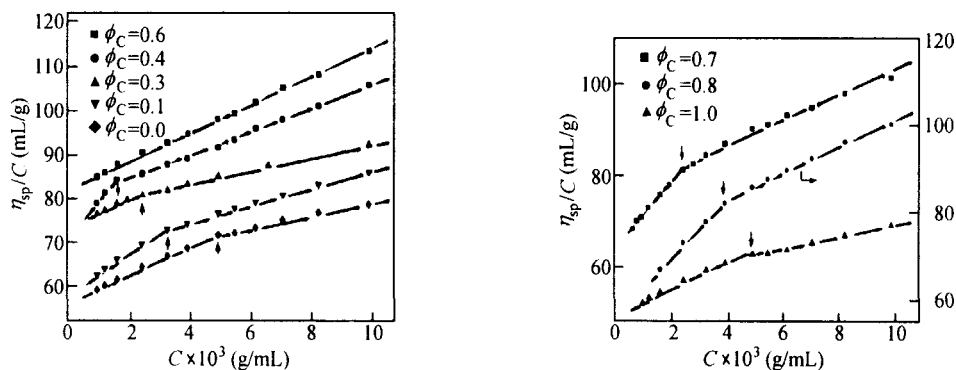


Fig. 1 Reduced viscosity (η_{sp}/C) versus concentration (C) of EVA in different composition (ϕ_c) of solvent mixture of DCE and CYH (ϕ_c is the volume fraction of cyclohexane)

considered in both solution or bulk. It makes their dimension small. Furthermore, Fig. 2 shows that the $[\eta]$ of EVA in DCE is larger than in CYH, but their C_A values are almost the same. It is well known that the VA segment in EVA molecule is a donor while the solvent of DCE is an acceptor. Therefore, hydrogen bonding (special solvation) between the carbonyl group in EVA and the methene group in DCE exists in spite of general solvation, which is similar to the intermolecular interactions of EVA and PVC^[17]. This means that the interaction of VA segments in EVA copolymer is lower than the interaction between VA segments and DCE solvent. Thus the inter-association interaction of EVA is weaker in DCE than in CYH. This is why the C_A values in DCE and CYH are kept the same, while the $[\eta]$ value of EVA in DCE is larger than that in CYH.

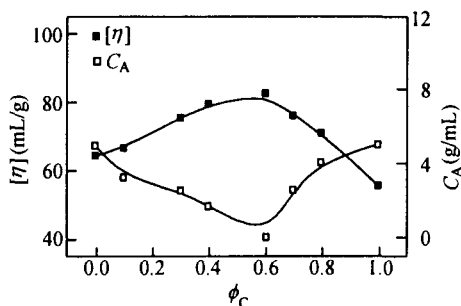


Fig. 2 Curves of C_A and $[\eta]$ versus ϕ_C of EVA sample at 30°C

Alcoholic and Acidic Additive Effect

Figure 3 shows the $\eta_{sp}/C \sim C$ relation of EVA sample in solvent mixtures of $\phi_C = 0.3$ at 30°C with and without 3000 ppm ethanol, butanol, dodecanol and octadecanol, respectively. It clearly shows that in each system the downswing of the slope of the line after the cross point on the $\eta_{sp}/C \sim C$ curve was demonstrated. The concentration corresponding to the cross point on the curves with different alcoholic additives i.e. C_A , are listed in Table 1, where δ_h represents the solubility parameter contributed by hydrogen bonding of these alcoholic additives^[18]. It is interesting to note that the C_A of the system increases with the decreasing of carbon number in the hydrocarbon (R) group of the alcoholic additives, i.e. with the increasing of hydrogen bonding (larger δ_h) of alcoholic additives. The C_A values of the systems with alcohol are larger than those of the systems without alcohol, except for the system with octadecanol. We consider that an alcoholic additive of 3000 ppm was not sufficient to change the solvent property thermodynamically, but alcohols are stronger acceptors compared with DCE, and thus there is greater solvation of VA segments by H-bonding. Octadecanol with small δ_h , however, has a long non-polar R group which is similar to a surfactant and forms a micelle or acts as "bridging" to link the other EVA chain. Obviously, micellisation or bridging are favorable to interchain association of EVA molecules. This is why for the system with octadecanol additive the C_A value (1.67×10^{-3} g/mL) is lower than that of the system (2.3×10^{-3} g/mL) without any alcoholic additive. The results above indicate that the C_A value of EVA in a solvent mixture of $\phi_C = 0.3$ with 3000 ppm alcoholic additives depends on the competition between H-bonding and micellisation.

In fact, the competition also took place in the systems with acidic additives. Table 1 also gives the C_A values of the systems with 3000 ppm acetic acid, heptonic acid, dodecanic acid and octadecylic acid, respectively, and the δ_h values of each acid. The C_A of systems with acidic additives, similar to that for systems with alcoholic additives, increases with the decreasing of carbon number in the R group of the acidic additives, i.e. the increase in H-bonding (larger δ_h) with acidic additives except for the systems with additions of dodecanic and octadecylic acid. It leads us again to consider that C_A depends on the competition between H-bonding and micellisation, i.e. H-

bonding to increase C_A and micellisation to decrease C_A . In addition, the C_A value is smaller in the system with acidic additive than that with alcoholic additive when both have the same carbon number in the R groups of the additives. It is probably due to the self-association of the acidic additives to weaken the H-bonding between the acidic additive and the EVA copolymer.

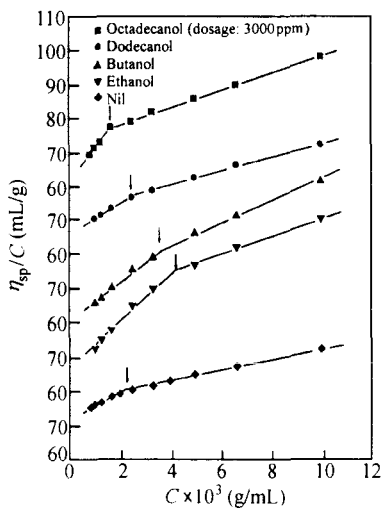


Fig. 3 η_{sp}/C versus C of EVA in solvent mixtures of $\phi_c = 0.3$ with or without 3000 ppm alcohol additives

Table 1 C_A value of EVA in solvent mixtures of $\phi_c = 0.3$ with different additives of 3000 ppm at 30°C and δ_h^* value of each additive

Additive	C_A (10^{-3} g/mL)	δ_h^* ($J^{0.5} \cdot cm^{-1.5}$)	Additive	C_A (10^{-3} g/mL)	δ_h^* ($J^{0.5} \cdot cm^{-1.5}$)
Ethanol	4.1	19.5 (18.0)	Acetic acid	3.8	13.5 (12.8)
Butanol	3.8	16.4 (14.6)	Heptonic acid	3.3	(8.32)
Dodecanol	2.6	(9.52)	Dodecanic acid	1.8	(6.67)
Octadecanol	1.7	(7.94)	Octadecylic acid	1.3	(5.88)
Nil	2.3	—	Span80	1.6	—

* δ_h^* values in () were estimated according to Eq. 7.12 of Ref. 18 ($\delta_h^* = (\sum F_i / \sum V_i)^{0.5}$)

Mixed Additive Effect

In order to further compare the effects of H-bonding and micellisation in affecting the C_A value, a typical surfactant of sorbitan oleate (Span80) was chosen. Figure 4 shows the $\eta_{sp}/C \sim C$ relation of

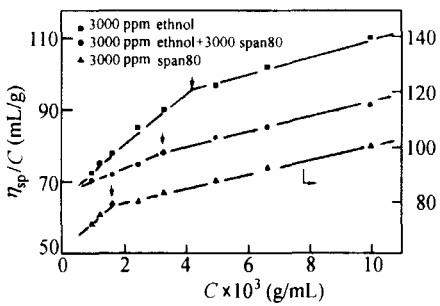


Fig. 4 η_{sp}/C versus C of EVA in solvent mixtures of $\phi_c = 0.3$ with additions of ethanol, ethanol/Span80 and Span80, respectively

EVA sample in solvent mixtures of $\phi_C = 0.3$ with additions of ethanol, ethanol/Span80 and Span80, respectively. Obviously, the C_A of EVA in solvent mixtures with the addition of Span80 or ethanol/Span80 decrease, compared with that with only ethanol additives. This indicates that micellisation due to the presence of the surfactant of Span80 impairs the H-bonding interaction. In this case EVA molecules form interchain associations.

Concentration Effect of Additive

Figures 5a and 5b show curves of the additive dosage dependence of $\eta_{sp}/C \sim C$ for EVA samples in solvent mixtures of $\phi_C = 0.3$. Both additives of ethanol and Span80 acting as H-bonding and micellisation, respectively were used. In Fig. 5a, it shows that the C_A increases as the dosage of ethanol increases, and then remains constant when the dosage of ethanol is larger than 3000 ppm. In contrast to Fig. 5b, the C_A decreases as the dosage of Span80 increases. It further indicates that additives with H-bonding (ethanol) and micellisation (Span80) are conducive to the formation of intrachain and interchain association, respectively, in solvent mixtures of $\phi_C = 0.3$.

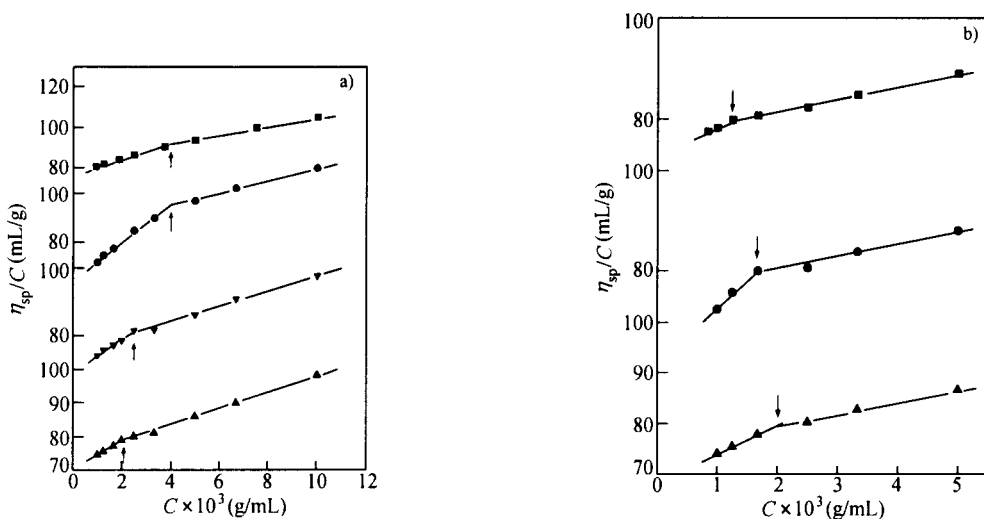


Fig. 5 η_{sp}/C versus C of EVA in solvent mixture of $\phi_C = 0.3$ with additives
a) ethanol (ppm): 500(■), 1000(▼), 3000(●), 5000(▲);
b) Span80 (ppm): 1000(▲), 3000(●), 5000(■)

CONCLUSIONS

Critical association concentration C_A , by which the association of EVA molecules in solution was divided into interchain associations and intrachain associations, decreases with an increase in the thermodynamic property of solvent mixture and is nullified in good solvent mixtures of $\phi_C = 0.6$. The decrease in C_A in the presence of small amounts of surfactant additive indicates that micellisation is conducive to the formation of intermolecular associations of the EVA in solution. Conversely, the increase in C_A in the presence of small amounts of alcoholic or acidic additives suggests that H-bonding is conducive to the formation of intrachain associations of the EVA in solution, except for some alcoholic and acidic additives with longer hydrocarbon chains, which act as surfactants. Acidic additives were found to be worse than alcoholic additives in increasing C_A . This is probably due to the self-association of the acidic additives, which weakens their H-bonding interactions.

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