

ASSOCIATION OF ETHYLENE-VINYL ACETATE COPOLYMER IN DILUTE SOLUTIONS III. CRITICAL ASSOCIATION CONCENTRATION*

Qian Jinwen (钱锦文) Li Jing (李 劲) Yang Yunsong (杨云松)
and Qi Guorong (戚国荣)

(Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China)

Abstract Association behavior of ethylene vinyl acetate (EVA) copolymer in four solvents 1, 2-dichloroethane (DCE), cyclohexane (CYH), xylene (XYL) and chloroform (CF) has been investigated by dilute solution viscometry. The critical association concentration (C_A) was determined at which the incipient decrease in slope of the $\eta_{sp}/C \sim C$ curve in solutions at the dilute regime. Our results showed that whether the C_A could exist depends on solvent property. The values of C_A in DCE increase with increasing, of temperature and vinyl acetate (VA) content in EVA and decreasing of molecular weight of EVA.

Keywords Association; Dilute solution; Viscometry

INTRODUCTION

EVA copolymer is one of the most important types of flow improver^[1] for crude oil and oil products. The efficiency of EVA copolymer as flow improver is influenced by solvent property^[2] and its incipient chain dimension in solutions^[3], besides its molecular parameters. In previous works^[4~6], we have found that association of EVA flow improver had been displayed in 1,2-dichloroethane (DCE) and cyclohexane (CYH) by viscometry and dynamic laser light scattering. It was dependent on molecular weight and VA content of EVA, the concentration of solution and thermal history of solution preparation.

The dosage of polymer in doped oils is an important factor to efficiency of polymer flow improvers^[7,8] and the concentration of polymer in solution is also a valued factor to association of polymer^[4,9,10] in solutions. Dondos et al. investigated the critical concentration of homopolymer/solvent and homopolymer-1/homopolymer-2/solvent systems by viscometry^[11,12]. In this study, the critical association con-

* This work was supported by the National Natural Science Foundation of China (No. 29474168).

Received Jun 28, 1997

centrations of a series of EVA copolymers in solutions were investigated by dilute solution viscometry.

EXPERIMENTAL

Three types of commercial EVA samples (designated as A, B, C) were used. Samples C1, C2 and C3 were prepared by fractionation from 1% benzene solution of sample C, with isopropanol as precipitant^[13]. Fractionation was carried out at $30 \pm 0.02^\circ\text{C}$. M_n and VA content of five samples [A ($M_n = 1.69 \times 10^4$, VA=29.7%), B ($M_n = 1.68 \times 10^4$, VA=37.5%), C1 ($M_n = 3.15 \times 10^4$, VA=32.7%), C2 ($M_n = 2.72 \times 10^4$, VA=31.1%), C3 ($M_n = 1.25 \times 10^4$, VA=31.5%)] were characterized by Knauer VPO instrument, Carlo Erba 1106 element analyzer and saponification value test. The EVA samples were dissolved thoroughly in given solvent at 45°C , then filtered and cooled at the measuring temperature. Viscosity measurement of the solutions was conducted in a Ubbelohde viscometer at definite temperature with deviation of $\pm 0.02^\circ\text{C}$. The reproducibility was of the order of 1%.

RESULTS AND DISCUSSION

Critical association concentration (C_A) and solvent effect

Fig. 1 shows a typical concentration dependence of the reduced specific viscosity $\eta_{sp}/C \sim C$ of sample A in 4 solvents chloroform (CF), xylene (XYL), CYH and DCE at 25°C . Straight line of $\eta_{sp}/C \sim C$ curve was obtained for CF and XYL solvents,

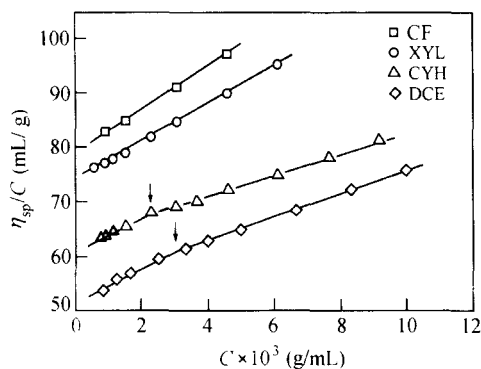


Fig. 1 Reduced viscosity (η_{sp}/C) vs concentration of sample A ($M_n = 1.69 \times 10^4$, VA=29.7%) at 25°C in chloroform, xylene, cyclohexane and 1, 2-dichloroethane

which is in normal case. Downswing in slope of $\eta_{sp}/C \sim C$ curve at certain concentration exist for solvents CYH and DCE. The incipient decrease in slope of the $\eta_{sp}/C \sim C$ curve is related to the C_A of EVA, at which the macromolecule coils start to aggregate. This result was in good agreement with previous work^[4], viz. The association of EVA exist in DCE and CYH, but not in XYL and CF. This is because the Huggins parameters χ_1 between EVA sample with VA content of 29.7% and four solvents CF, XYL, CYH and DCE are $-0.246, 0.023,$

0.070 and 0.058, respectively^[14]. Obviously, DCE and CYH are marginal solvents which cause association for the EVA samples, CF and XYL are good solvents in which EVA molecules aggregate uneasily. In the aggregating system, the decrease in slope of $\eta_{sp}/C \sim C$ curve above C_A was considered as the increase of the hydrodynamic volume being slower than the increase of the apparent molecular weight, according to the relation of $\eta_{sp}/C \propto V/M$.

VA content and molecular weight dependence of C_A

Fig. 2 shows typical plots of $\eta_{sp}/C \sim C$ of EVA sample A and B with same M_n and different VA contents in DCE at 10°C and 25°C. From Fig. 2, it is clear that the higher the VA content, the larger the C_A value despite the temperature. This means that the increasing of VA content is unfavorable to the association of ethylene segments in EVA copolymer, because DCE is a selective solvent of EVA. Fig. 3 shows typical plots of $\eta_{sp}/C \sim C$ of EVA sample C1, C2 and C3 with same VA content of different molecular weight in DCE at 25°C and the C_A values decrease with increasing of molecular weight.

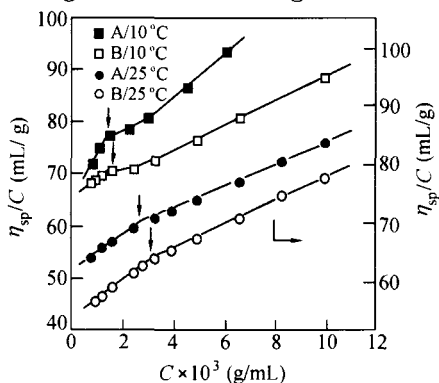


Fig. 2 η_{sp}/C VS C of sample A ($M_n = 1.69 \times 10^4$, VA=29.7%) and B ($M_n = 1.68 \times 10^4$, VA=37.5%) in DCE at 10°C and 25°C

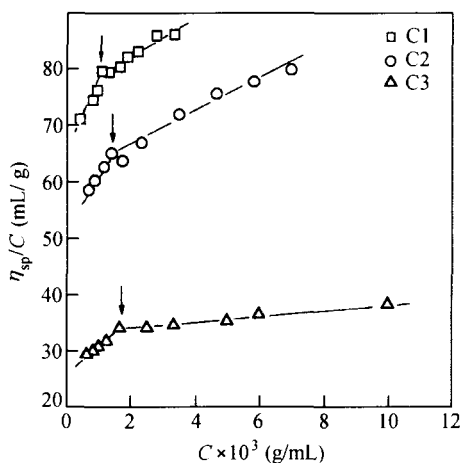


Fig. 3 η_{sp}/C VS C of sample C1, C2 and C3 in DCE at 25°C with same VA content and different M_n of 3.1×10^4 , 2.72×10^4 and 1.25×10^4 , respectively

Temperature dependence of C_A and enthalpy change of association (ΔH)

Fig. 4 shows various curves of $\eta_{sp}/C \sim C$ of sample A in DCE at 5 ~ 45°C. The downswing phenomenon of $\eta_{sp}/C \sim C$ curve indicates that association of the EVA sample exist at various temperature except for 45°C. Fig. 5 shows a plot of $\ln C_A$ versus $1/T$ of sample A in DCE at 5 ~ 35°C. A straight line was presented and from the slope of the line we obtained the ΔH of association -30.7 kJ/mol, which is lower than ΔH of micellisation (-40.4 kJ/mol) for polystyrene-block-polyisoprene

block copolymer (PS-*b*-PIP) in *n*-hexadecane given by Price^[15]. This means the thermodynamic stability is weaker in association of a random EVA copolymer than in micellisation of the PS-*b*-PIP block copolymer. In addition, the value of C_A ranges from 1.07×10^{-3} to 4.13×10^{-3} g/mL, depending on the temperature. The critical association concentration range is lower than that of CMC in the work of Price et al.^[15], which means the association of EVA random copolymer in DCE can take place in more dilute region.

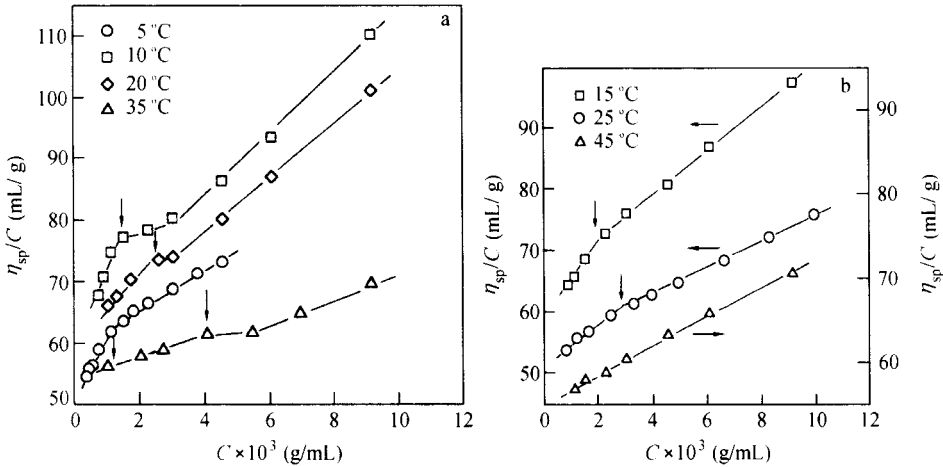


Fig. 4 η_{sp}/C vs C of sample A in DCE at 5 ~ 45 °C

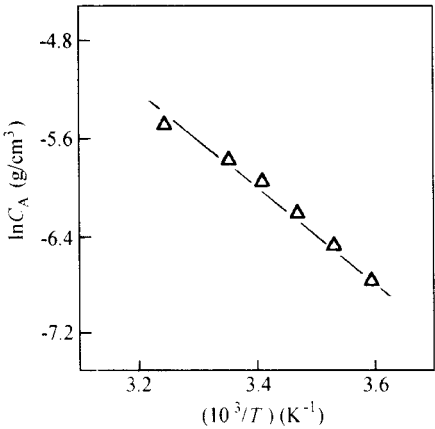


Fig. 5 $\ln C_A$ vs $1/T$ of sample A in DCE

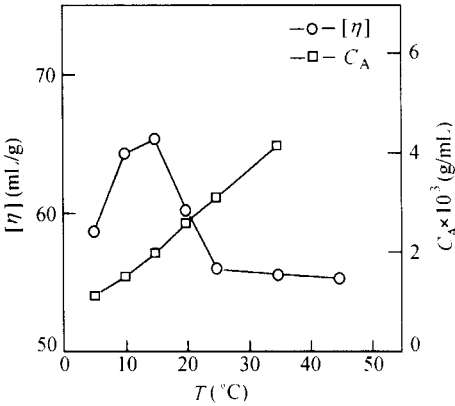


Fig. 6 $[\eta]$ vs T and C_A vs T of sample A in DCE

In dilute solution of polymers, there were two critical concentrations of C^* and C^{**} ^[16,17]. The well-known critical concentration C^* divides dilute and semi-dilute solutions and the critical concentration C^{**} which lies below C^* , separates the range of extremely dilute solutions from that of dilute solutions, viz., C^{**} is a concentration

at which the macromolecule coils start to contact^[17]. Theoretically the intrinsic viscosity $[\eta]$ represents the effective hydrodynamic volume of a polymer molecule in solutions^[18]. Thus, according to the definition of C^{**} , the system with larger $[\eta]$ should have lower C^{**} value, viz., the changes of $[\eta]$ and C^{**} with increasing of temperature should occur in opposite ways. In fact, this case was not found in Fig. 6. Fig. 6 shows the temperature dependence of C_A from Fig. 4 and $[\eta]$ ($[\eta]$ was obtained by extrapolating the points above C_A to zero in Fig. 4) of sample A in DCE. From Fig. 6, it is obvious that with increasing of temperature the C_A always goes up in spite of the changes of the $[\eta]$ values, which go up, then down and finally level off with the temperature. This change of $[\eta]$ value with temperature was also reported everywhere else^[16,18,19], which was considered to be related to the conformational transition of the polymer or the existence of UCST and LCST of the polymer-solvent systems. Therefore, the concentration related to the crossover in $\eta_{sp}/C \sim C$ curve in this binary system should be called C_A .

REFERENCES

- [1] Gilby, G.W., "Proceedings of the 2nd International Conference on Chemical in the Oil Industry", Royal Society of Chemistry, **1983**, 45, 108
- [2] Qian, J.W., Qi, G.R., Xu, Y.L., Yang, S.L., *J. Appl. Polym. Sci.*, **1996**, 60, 1575
- [3] Qian, J.W., Qi, G.R., Han, D.L., Yang, S.L., *Fuel*, **1996**, 75 (2), 161
- [4] Qian, J.W., Qi, G.R., Cheng, R.S., *Eur. Polym. J.*, **1997**, 33 (8), 1263
- [5] Qian, J.W., Qi, G.R., Fang, Z.B., Cheng, R.S., *Eur. Polym. J.*, **1998**, 34 (3 ~4), 445
- [6] Qian, J.W., Wang, S.H., Qi, G.R., Wu, C., *Macromolecules*, **1997**, 30 (11), 3283
- [7] Ei-gamal, I.M., Ei-mansey, I.M., *Erdoel kohle Erdgas Petrochem.*, **1993**, 46, 418
- [8] Sunil Kumar, M.N., *Inst. Petrol. Quart. J. Tech. Paper*, Oct.-Dec. 47, **1989**
- [9] Zhang, Y., Wu, C., Fang, Q., Zhang, Y.X., *Macromolecules*, **1996**, 29, 2494
- [10] Bodycomb, J., Hara, M., *Polym. Bull.*, **1988**, 20, 493
- [11] Dondos, A., Tsitsilianis, C., Staikas, G., *Polymer*, **1989**, 30, 1690
- [12] Pierri, E., Dondos, A., *Eur. Polym. J.*, **1987**, 23 (5), 347
- [13] Mara, K., Imoto, T., *Kolloid. Z-Z. Polym.*, **1970**, 237, 297
- [14] Dincer, S., Bonner, D.C., *Macromolecules*, **1978**, 11, 107
- [15] Price, C., Chan, E.K.M., Mobbs, R.H., Stubbersfield, R.B. *Eur. Polym. J.*, **1985**, 21, 355
- [16] Dondos, A., Papanagopoulos, D., *Makromol. Chem. Rapid Commun.*, **1993**, 14, 7
- [17] Dondos, A., Tsitsilianis, C., *Polym. International*, **1992**, 28, 151
- [18] Bohdanechy, M., Kovar, J., "Viscosity of Polymer Solutions", Elsevier-scientific, Amsterdam, **1982**
- [19] Rashid, H.V., Abubakar, S.D., *J. Polym. Sci., Part C: Polym. Lett*, **1989**, 27, 5