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INFLUENCE OF SOLVENT AND POLYMER SORT ON ANOMALOUS RHEOLOGICAL BEHAVIOR OF POLYMER SOLUTION AT HIGH DILUTION*

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Abstract: The rheological behavior of polyvinyl acetate (PVAc) in N, N'-dimethylformamide (DMF), methyl ethyl ketone (MEK), 1,2-dichloroethane (DCE), tetrahydrofuran (THF) and toluene (TOL), polystyrene (PS) in DMF, MEK, DCE, THF and cyclohexane (CYH), and random ethylene-vinyl acetate (EVA) copolymer in DCE, TOL, CYH with and without surfactant of Span80 and in the DCE/CYH solvent mixtures with surfactant of Span80 was examined at high dilution. It was shown that the extent and type of the upsweep or downsweep (anomalous rheological behavior) of the reduced viscosity-concentration curves of these different polymers at high dilution are markedly dependent on the dielectric constant of the solvent and the polarity of the polymer used. The experimental results indicated that the anomalous rheological behavior of EVA copolymer, widely used as a flow improver, is related to its efficiency in reducing viscosity and depressing pour point of crude oil and waxy solvents.

Key words: polyvinyl acetate (PVAc), polystyrene (PS), ethylene-vinyl acetate (EVA) copolymer, rheology, polymer solution, viscosity
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INTRODUCTION

Polymers in medium at high dilution have a broad range of applications nowadays. They were used as pour point depressant and viscosity reducer of crude oil and its products such as EVA and its derivatives (Sunil Kumer, 1989; Qian et al., 1996; Qian et al., 1996; Qi et al., 1992); drag reducer of water and oils, for instance, polyethylene oxide and ethylene-propylene copolymer (Choi et al., 1989; Qian et al., 1986; Interthal et al., 1985; Burger et al., 1980); flocculent of polyacrylamides for treating wastewater (Qian et al., 1992; Pelton et al., 1983; Kulicke et al., 1980) and other polymer additives in the areas of food, biochemicals, chemicals and petroleum engineering, e.g., stabilizer (Pradhan et al., 1994) etc. We have noted that these polymer functions mentioned above were exhibited in high diluted concentration region, i.e., $10^{-5} - 10^{-3}$ g/mL, and also were dependent on medium properties such as thermodynamics, polarity, pH, etc. However, it is well known that anomalous rheological behavior (ARB) of polymer solutions at high dilution usually occurs at the same concentration region of $10^{-5} - 10^{-3}$ g/mL. Thus, considering that the clarification of ARB is of great importance from the scientific and practical point of view, we were motivated to investigate further the ARB of polymer solution at high dilution.

The ARB, upsweep and downsweep of reduced viscosity (η_{sp}/C) - concentration (C), curve of polymer solution at high dilution, were influenced by various factors such as the size of capillary radius of the viscometer used (Öhrn, 1955); the extent of shaking of the solution prior to viscosity measurements (Gundiah et al., 1960; Kapur et al., 1958), shear effect or non-

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Newtonian effect of the system (Tuijnman et al., 1957), molecular weight of polymer (Pepper et al., 1959) the composition of polymer mixture (Williamson et al., 1965; Zhu et al., 1998); critical concentration (Cragg et al., 1957; Dondos et al., 1975; Dondos et al., 1983; Pierri et al., 1987; Dondos et al., 1992) and additives used (Chen et al., 1967; Lopez de Sa et al., 1988; Tadros, 1974; Dondos et al., 1988; Staikos et al., 1989; Zhu, 1995) etc. Also, many explanations of ARB were proposed. The upsweep usually was ascribed to capillary adsorption (Cheng et al., 1999; Öhrn, 1955), the change of size-shape (conformation) of the polymer chain (Gundiah et al., 1960; Kapur et al., 1958), low molecular weight (Pepper et al., 1959), strong interaction between multi-components (Williamson et al., 1965; Zhu et al., 1998) or between polymer and solvent (Zhu et al., 1998) and additive effect (Chen et al., 1967; Lopez de Sa et al., 1988; Tadros, 1974) etc.; and the downsweep was often considered to relate to the critical concentration effect or incompatibility of two polymers (Cragg et al., 1957; Dondos et al., 1975; Dondos et al., 1983; Pierri et al., 1987; Dondos et al., 1992), shear effect (Tuijnman et al., 1957), and some additives (Chen et al., 1967; Dondos et al., 1988; Staikos et al., 1989; Zhu, 1995) etc. It is, therefore, seen that the ARB of polymer solution at high dilution is a controversial issue and requires more experimental work. In this work, we investigated the dependence of the ARB of highly dilute polymer solutions of PVAc (polar polymer), PS (non-polar polymer) and EVA random copolymer (amphibious copolymer) on the solvent's dielectric constant and polymer's polarity.

EXPERIMENTAL DETAILS

1. Materials and characterization

PS and PVAc samples had M_v of 1.27×10^5 and 1.72×10^6, respectively, which were calculated from viscosity at 25℃ by M-H equations (Outer et al., 1950; Shultz, 1954), i.e., $[\eta]_{MEK} = 3.9 \times 10^{-2} M^{0.58}$, and $[\eta]_{MEK} = 1.34 \times 10^{-2} M^{0.71}$ (mL/g). EVA sample used had M_n of 16900 and vinyl acetate content of 29.7 (wt)% determined by Knaur VPO instrument and Carlo 1106 element analyzer, respectively. All solvents used were of reagent grade, the sorption oleate (Span80) of the surfactant was of chemical grade.

2. Viscometric measurements

The solutions of all samples were prepared in given pure solvents or solvent mixtures with or without additive at 35℃, and then filtered. Viscosity measurement of the solutions were conducted with an Ubbelohde type viscometer which had large efflux-time of 181.30 sec with toluene at (25 ± 0.02℃). The reproducibility of the reduced viscosity was checked and found to be within ± 1%.

3. Apparent viscosity

Apparent viscosity, η_a, of Daqing crude oil with and without EVA flow improver was measured using an NXS – 11 coaxial cylinder viscometer.

4. Pour point

The pour point, T_{pp}, of the waxy solvent with and without EVA flow improver was measured using a Bly Thermoelectric Cooling Freezing Point Tester.

RESULTS AND DISCUSSION

1. Polyvinyl acetate

Fig. 1 shows the solvent dependence of the $\eta_{sp}/C - C$ curve of PVAc in five solvents at 25℃. Each curve reveals the ARB of the upsweep at high dilution at some concentration, here called anomalous concentration, C_{ud}, at which the curve starts to deviate from the straight line at the location marked by arrow. We supposed that serious ARB of the system must be accompanied by relatively high C_{ud}. So, the C_{ud} value is a criterion for the ARB of the system. The C_{ud} and $[\eta]$ values of the PVAc in five solvents, as well as some physical parameters of each solvent, are summarized in Table 1. Unfortunately, the variation of C_{ud} values of PVAc in five solvents did not agree with the variation of the solvents' kinetic viscosity, η/ρ, and the variation of the surface tension coefficient of the solvents, α, both of which related to the flow behaviors. And also, the variation of PVAc C_{ud}

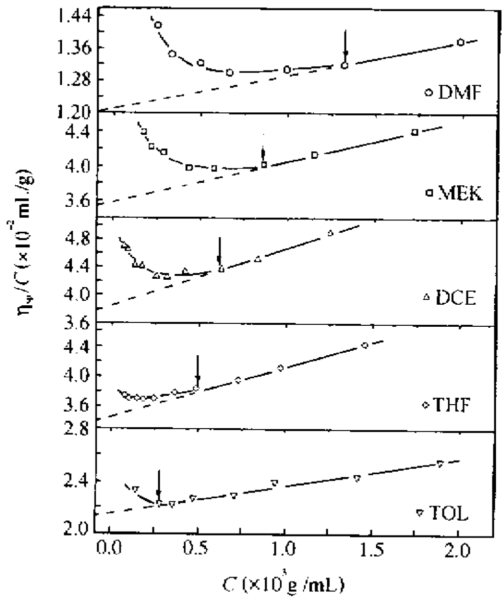

Fig.1 Solvent dependence of $\eta_{sp}/C - C$ curve for PVAc in DMF, MEK, DCE, THF and TOL

values in various solvents are independent of the intrinsic viscosity, $[\eta]$, values, which reflect the size and the shape of the polymer chain in solution (the larger the $[\eta]$, the larger the chain dimension). Therefore, neither general adsorption nor size of chain and solvent thermodynamic property can account for the ARB. Surprisingly, the C_{ud} value of the system and dielectric constant, ε, or H-bonding-polar-solubility parameter, δ_a, of the solvent in Table 1 could be linked up very well; a straight line between C_{ud} and ε is clearly shown in Fig.2. That is to say, the ARB is upsweep and preferably sensitive to solvents with larger ε for polar PVAc.

2. Polystyrene

Fig.3 shows the solvent dependence of the $\eta_{sp}/C - C$ curve for non-polar PS. At high dilution, solvents (such as DMF, MEK, DCE) with large ε could not cause the ARB of the $\eta_{sp}/C - C$

Table 1 $[\eta]$ and C_{ud} of PVAc and physical constants of solvents at 25℃

	DMF	MEK	DCE	THF	TOL	CYH
$[\eta]$(mL/g)	120	358	380	340	213	–
$C_{ud}(\times10^3$ g/mL)	1.32	0.864	0.632	0.484	0.283	–
$\eta(\times10^3$ N.S/m^2)	0.8	0.42	0.73	0.36	0.55	0.9
ρ(g/cm^3)	0.949	0.805	1.257	0.888	0.867	0.779
η/ρ(cm^2/s)	0.8430	0.5217	0.5807	0.4054	0.6344	1.1553
$\alpha(\times10^{-3}$N/m)	38	24.3	24.15	26.4	28.85	25.5
ε	31.4	17.0	10.65	7.6	2.38	2.02
δ_a(J$^{0.5}$/cm$^{1.5}$)	17.8	10.4	8.4	7.25	4.25	0

Note: a) All physical constants of solvents are from ref.(Ven Kreveln, 1990); b) Kinetic viscosity, η/ρ, was calculated from η and ρ values in Table 1 by author; c) $\delta_a^2 = \delta_n^2 + \delta_p^2$, where δ_n and δ_p are the components of hydrogen-bonding and polar solubility parameter, respectively(Ven Kreveln, 1990).

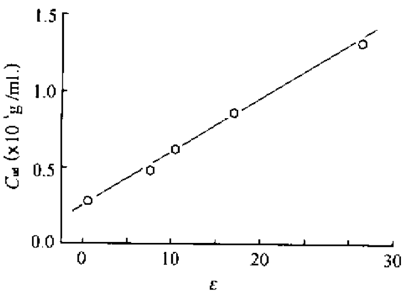

Fig.2 Variation of anomalous concentration (C_{ud}) with dielectric constant (ε) of solvent for PVAc

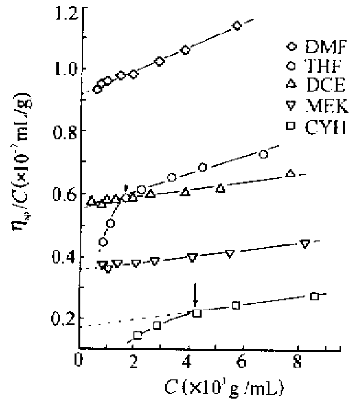

Fig.3 Solvent dependence of $\eta_{sp}/C - C$ curve for PS in DMF, MEK, DCE, THF and CYH

curve to follow a straight line. THF and CYH solvents with smaller ε cause downsweep of the $\eta_{sp}/C - C$ curve. Their C_{ud} values increase greatly as ε decreases. It means that the ARB is downsweep and selectively sensitive to solvents with lesser ε for non-polar PS.

3. Ethylene-vinyl acetate copolymer

(1) Pure solvents with and without surfactant

Fig. 4's η_{sp}/C vs C curves on the solvent and additive effects of EVA copolymer in DCE, TOL, CYH with and without nonionic surfactant of 3×10^{-3} g/mL Span80 show that at high dilution, three of the $\eta_{sp}/C - C$ curves (with filled symbols) indicate upsweep, normality and downsweep for DCE, TOL, and CYH solvents with dielectric constants of 10.65, 2.38 and 2.02 (or δ_a of 8.4, 4.25 and 0 $J^{0.5}/cm^{1.5}$), respectively. The ε effect of the ARB can be seen again clearly. Furthermore, it is very interesting to see that the ARB of EVA copolymer in DCE and CYH is same as the ARB of PVAc (polar polymer) in DCE and PS (non-polar polymer) in CYH, respectively. In other words, EVA copolymer in selective solvents could display the behavior of both polar and non-polar polymers, and could be seemingly similar to a graft or block polymer. Another three $\eta_{sp}/C - C$ curves (with hollow symbols in Fig. 4) for DCE, TOL and CYH solvents with surfactant of 3×10^{-3} g/mL Span80 showing extended upsweep, upsweep and almost normality, respectively, were obtained. The addition of nonionic surfactant to solvent could enlarge the upsweep of the $\eta_{sp}/C - C$ curve at high dilution. This is obviously due to the raising of system ε by the Span80 surfactant with both ether and ester bonds and three hydroxyls in the molecule. This surfactant effect can be found elsewhere in polymer solution with additive of ionic surfactant (Lopez et al., 1988; Tadros, 1974).

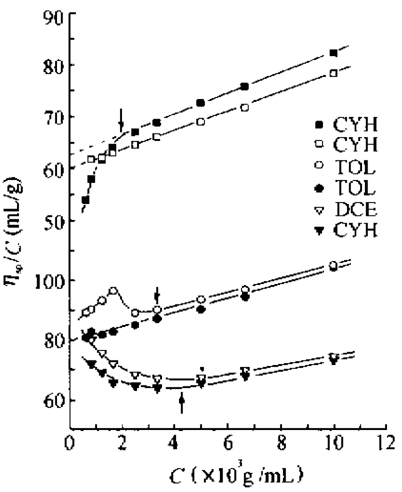

Fig. 4 Solvent and additive effects of $\eta_{sp}/C - C$ curve for EVA copolymer in DCE, TOL and CYH with (hollow) and without (solid) surfactant of 3×10^{-3} g/mL Span80

(2) Mixed solvents with surfactant

Fig. 5 shows $\eta_{sp}/C - C$ curves of EVA in DCE/CYH mixture solvents containing surfactant of 3×10^{-3} g/mL Span80, where the numbers represent the CYH volume fraction in solvent mixtures ϕ_c. Clearly, the upsweep and C_{ud} values decrease and disappear eventually as ϕ_c increases, i.e., as the ε of the mixture solvents decrease. It means again the system ε affects the ARB.

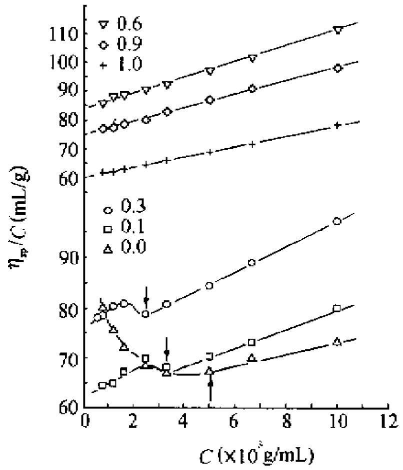

Fig. 5 Variation of η_{sp}/C with ϕ_c for EVA copolymer with DCE/CYH mixture solvents containing surfactant of 3×10^{-3} g/mL Span80

Some papers (Chatterjee et al., 1982; Dondos et al., 1975) pointed out that the interaction between polymers or conformation transition of a polymer molecule in solution could be affected by the dielectric constant of the solvent. Therefore, we believed that the dielectric property of the solvent could alter the shape of a polymer chain and the rheological behavior of polymers in solutions.

EVA copolymer is well known to be one of the most important flow improvers for oils. Surprisingly, the ARB of EVA solution at high dilution can be correlated to the rheological behavior of the oil or waxy solution doped with EVA. Fig.6 shows the solvent dependence of apparent viscosity reduction ($\Delta\eta_a\%$) of Daqing crude oil with 2×10^{-4} g/mL EVA dissolved in DCE and CYH, respectively, at different shear rates at 25℃, (here, the pure solvent effect in such system has been deducted). Table 2 gives the solvent composition (ϕ_c) dependence of C_{ud} and the variation of the pour point depression (ΔT_{pp}) in DCE/CYH mixture containing 10 (wt)% wax, 3×10^{-4} g/mL EVA and 3×10^{-3} g/mL Span 80. Fig. 6 and Table 2 clearly show that the system of EVA copolymer in DCE with ARB of upsweep ($C_{ud} = 5.1 \times 10^{-3}$ g/mL) is much better than that of the system of EVA copolymer in CYH without ARB of upsweep ($C_{ud} = 0$ g/mL) in viscosity reduction and ΔT_{pp} for Daqing crude and the waxy solvents. We consider that this is due to the different shapes of the EVA chain in DCE and CYH. Further studies regarding the effect of the chain shapes are currently underway.

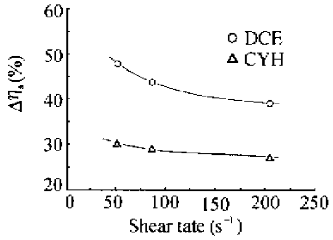

Fig.6 Solvent dependence of apparent viscosity reduction ($\Delta\eta_a\%$) of Daqing crude oil with 2×10^{-4} g/mL EVA dissolved in DCE and CYH, respectively, at different shear rate at 25℃

Table 2 The solvent composition dependence of C_{ud} and ΔT_{pp} in DCE/CYH mixture containing 10(wt)% wax, 3×10^{-4} g/mL EVA and 3×10^{-3} g/mL Span 80

ϕ_c	0.0	0.1	0.3	0.6	0.7	0.8	0.9	1.0
C_{ud}($\times 10^3$g/mL)	5.1	3.2	2.5	0	–	–	0	0
ΔT_{pp}(℃)	$\gg$70	65	24	3	2	2	2	3

CONCLUSIONS

The ARBs of PVAc, PS and EVA copolymers in solvents with different dielectric constants were investigated. It was found that the ARB of the $\eta_{sp}/C - C$ curve at high dilution could be divided into two kinds: upsweep and downsweep. PVAc (polar polymer) usually shows upsweep in its $\eta_{sp}/C - C$ curve which is sensitive to solvent with relatively large ε. PS (non-polar polymer) shows downsweep of $\eta_{sp}/C - C$ curve mainly for the solvents with smaller ε. EVA copolymer could show both upsweep and downsweep of the $\eta_{sp}/C - C$ curve in DCE with high ε and CYH with low ε, respectively. And the addition of nonionic Span80 surfactant to solution could strengthen the upsweep of the EVA / DCE system $\eta_{sp}/C - C$ curve and weaken the downsweep of the EVA/CYH system $\eta_{sp}/C - C$ curve, i.e., EVA random copolymer displays the characteristics of both polar polymer and non-polar polymer in selective solvents, respectively.

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