Studies on Pour Point Depression of EVA Polymers in Solvent Mixtures Containing Wax

J. W. QIAN, G. H. ZHOU, W. Y. YANG, Y. L. XU

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

ABSTRACT: Measurements of the change of the pour point depression (ΔT_{PP}) were performed for the wax solutions made of four solvent mixtures: ethyl acetate/hexane (EA/HEX), 1,2-dichloroethane/cyclohexane (DCE/CYH), butanone/heptane (MEK/HEP), and acetone/chloroform (AC/CF) doped with EVA polymers. The values of ΔT_{PP} increase significantly with increasing of the selective solvent EA, DCE, MEK, and AC components, for the vinyl acetate (VA) segment in EVA copolymers, in the solvent mixtures. The solvent effect of ΔT_{PP} occurring in wax solutions can also come from the solutions of EVA polymer, which were prepared by solvent mixtures with various compositions and used as parent solutions of EVA pour point depressant. From the experimental results such as the NMR of EVA macromolecules; viscosities of EVA, waxes, and their blends; and solubilities of wax with and without EVA macromolecules in the solvent mixtures, the complexation between wax molecules and ordered ethylene segment, and wax solubilization within ordered ethylene segments in EVA macromolecules are suggested for qualitative description of the observed significant variation of ΔT_{PP}. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 815–821, 2002

Key words: EVA copolymer; pour point depressant; polymer solution; selective solvent

INTRODUCTION

The solvent dependency of pour point depression of pour point depressant was reported some decades ago. Grishin et al.[1] found that the depression action of poly(methyl acrylate) (PMA) pour point depressant depends on the solvent used. In *n*-hexane, *n*-octane, isooctane, decalin, *sec*-octane, and four other solvents the PMA caused a 30–50°C decrease in the pour point, whereas in solvents such as $CHCl_3$, Et_2NH, benzene, tetralin, acetone, or MEK the PMA either caused a pour point depression of 2–5°C or was totally ineffective. Recently,[2] in a study of the effects of solvent on the action of EVA pour point depressant in wax solutions made of wax and a single solvent, it was shown that the action of EVA for the wax solutions made of various single solvents, respectively, depends greatly on the values of a interaction parameter U between wax and EVA molecules in the solutions. The system with a large variation of the pour point depression (ΔT_{PP}) was attributed to the large U-value, which was affected by the solvent. Furthermore, the solvent effect occurred not only in the wax solutions with different solvents but also in a crude oil doped with the EVA parent solutions made of various single solvents, respectively.[3] In this work, the solvent effect of pour point depression of EVA in four solvent mixtures with various compositions

was systematically examined and explained in terms of both microstates of EVA in selective solvents and macroscopic properties of the EVA/wax solutions.

EXPERIMENTAL

Samples and Solvents

Two commercial samples of ethylene–vinyl acetate copolymers (EVA), purchased from Shanghai Chemical Company, were used, designated as EVA_{30} and EVA_{38}. Their number-average molecular weight M_n (16,900, 16,800), molecular weight distribution (2.18, 1.96), and vinyl acetate (VA) content (29.7, 37.5) were characterized by membrane osmometry (Knauer membrane osmometer), SEC (Waters 150C; Waters Instruments, Rochester, MN), and elemental analysis (Carlo-Erba 1106), respectively. The polyethylene–polyvinyl acetate graft copolymer (E-g-VA) was prepared in our laboratory.[4,5] Its M_n and degree of grafting (DG) were 1120 and 14.2%, respectively. The wax was supplied by the Institute of the Refined Oil Company (Hangzhou, China) and purified by petroleum ether, which is normal paraffin with a melting temperature of 49.4°C according to its differential scanning calorimetric (Perkin-Elmer DSC-7) curve. All solvents used for the investigation were of reagent grade, and kerosene is a generally marketed product.

Measurement of NMR Spectra

Solutions of EVA_{30} with a concentration of 1 w/v % were prepared in acetone-d_6/CDCl$_3$ mixtures with volume fractions of acetone-d_6 (Φ_{AC-d6}) of 0, 0.1, 0.2, 0.3, 0.4, and 0.5, respectively. For homogenization, the solutions in sealed NMR tubes were kept for 2 days at about 45°C. All samples were completely soluble in each solvent mixture. The ^{1}H-NMR spectra were recorded with a JEOL FT-90 spectrometer (JEOL, Peabody, MA) at 25°C.

Measurement of Viscosity

Viscosity measurements of the solutions were conducted with a Ubbelhode viscometer, which was immersed in a constant-temperature bath of 30.00 ± 0.02°C. Repeated measurements were made until the reproducibility of efflux time was within 0.1 s. An extrapolation procedure from the data obtained for five concentrations of the solutions was used to evaluate intrinsic viscosity [η] and viscosity slope coefficient b in the Huggins equation.

Measurement of Solubility

The wax was dissolved in the selective solvent mixtures of DCE/CYH with different DCE contents (Φ_{DCE}) with and without 300 ppm EVA_{30} copolymer, respectively, in test tubes stirred for 24 h in a bath at 23.00 ± 0.02°C. Then 5.0 mL of a saturated wax solution was drawn out of the coexisting phase of wax and its saturated solution in the test tube and dried to a constant weight (w). The solubility (S) of the wax in a given selective solvent mixture with or without 300 ppm EVA_{30} copolymer was obtained by the equation $S = w/5$ (g/mL).

Measurement of Pour Point

The pour points (PP) of the wax systems with or without EVA pour point depressant were detected by a BLY thermoelectric cooling/freezing pour point tester. The temperature at which the sample solutions entered the tester was usually about 40°C.

RESULTS AND DISCUSSION

Effect of Solvent on ΔT_{PP} of Wax Solutions

Figure 1(a) and (b) show the variation of ΔT_{PP} of the solvent mixtures containing 10 wt % wax and 400 ppm EVA_{30} (a) and EVA_{38} (b) with $\Phi_{s,VA}$ (the volume fraction of selective solvent EA, DCE, and MEK for VA segment of EVA in EA/HEX, DEC/CYH, and MEK/HEP solvent mixtures, respectively; i.e., EA, DCE, and MEK are all good solvents for VA segment and nonsolvents for wax and ethylene segment in EVA). Clearly, ΔT_{PP} values increase drastically with increasing of EA, DCE, and MEK components in solvent mixtures, except for $\Phi_{s,VA} \leq 0.3$ [for EVA_{30} in Fig. 1(a)] and $\Phi_{s,VA} \leq 0.4$ [for EVA_{38} in Fig. 1(b)], in these cases their ΔT_{PP} values are almost zero, and also the extent of ΔT_{PP} is not the same for different selective solvents, especially those with high $\Phi_{s,VA}$ in solvent mixtures. These observations lead us to consider that the great effectiveness of EVA pour point depressant not only is mainly linked to the content of selective solvent, for VA segment of EVA, in solvent mixtures (i.e., the larger the $\Phi_{s,VA}$ in solvent mixtures, the larger the ΔT_{PP} of solvent mixtures containing wax) but also related both

types of selective solvents and VA content in EVA copolymers.

Figure 2 shows a plot of the ΔT_{PP} versus Φ_{AC} in AC/CF solvent mixtures with 10 wt % wax and 400 ppm EVA_{30}. In these solvent mixtures AC is a selective solvent (good solvent for VA segment and nonsolvent for wax and ethylene segment in EVA) and CF is not a selective solvent (good solvent for both segments in EVA). Therefore, it can be seen that ethylene segments in EVA did not dissolve well in the solvent mixtures compared with those in CF. Thus, higher AC contents in AC/CF induce larger ΔT_{PP} values. Figure 3 shows a typical ^{1}H-NMR spectrum of EVA_{30} in acetone-d_6/CDCl$_3$ solvent mixture at 25°C. The absorption bands of $\delta = 2.02$ ppm and $\delta = 1.24$ ppm are assigned to the peaks of ethylene protons and methyl protons of ethylene segment and VA segment, respectively, in the EVA chain. The areas
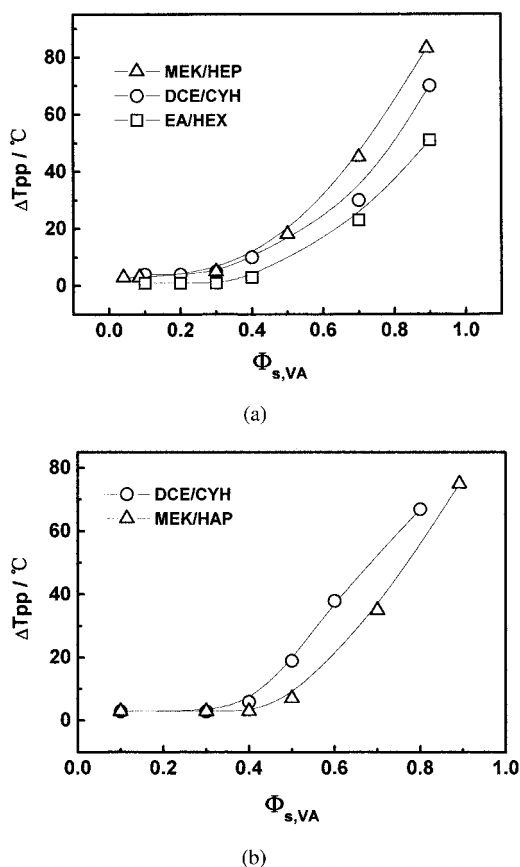

Figure 2   Change of ΔT_{PP} of the AC/CF solvent mixture containing 10 wt % wax and 400 ppm EVA_{30} copolymer with Φ_{AC}.

under the peaks of absorption bands are expressed as I_E and I_M for the ethylene segment and the methyl group in EVA, respectively; thus, the I_E/I_M ratio presents the changing of width of band of the ethylene segment in NMR spectra. Figure 4 shows the change of I_E/I_M with $\Phi_{AC\text{-}d6}$, that is, AC-d_6 volume fraction in the acetone-d_6/CDCl$_3$ solvent mixtures. The I_E/I_M ratio decreases with increasing $\Phi_{AC\text{-}d6}$; in other words, the width of the ethylene band increases with increasing $\Phi_{AC\text{-}d6}$.

Many studies[6–9] have shown that NMR bands of associated units will be broad, thus escaping detection. This means that the existence of associated ethylene segments here leads to the reduction of I_E/I_M. Thus, the ethylene segments in the nonsolvent of AC (VA selective solvent) are ordered. Moreover, the extent of ordering of ethylene segment in EVA increases with increasing Φ_{AC} in AC/CF. Compared with Figure 2, it can be seen that the larger Φ_{AC} in the AC/CF mixture results in higher content of ordered ethylene segments and, ultimately, larger ΔT_{PP}. The same phenomenon occurred for the pour point depressant of polyethylene-grafted VA. The ΔT_{PP} values of the DCE/CYH solvent mixture containing 4 wt % wax and 500 ppm E-g-VA graft copolymer are 14 and 5°C for the more-selective solvent DCE ($\Phi_{DCE} = 0.9$) and the less-selective solvent DCE ($\Phi_{DCE} = 0.1$), respectively.

Viscosity and Solubility Study of EVA/Wax Blend and Wax in DCE/CYH

Chee[10] proposed an interaction parameter U, to determine polymer 1–polymer 2 compatibility,

$$U = \frac{b_m - b}{2X_1 X_2 ([\eta]_1 + [\eta]_2)^2}$$

(a)

(b)

Figure 1   Change of ΔT_{PP} of the solvent mixtures containing 10 wt % wax and 400 ppm EVA_{30} (a) and EVA_{38} (b) copolymers with $\Phi_{s,VA}$ (the volume fraction of selective solvents EA, DCE, and MEK for VA segment in EVA in EA/HEX, DCE/CYH, and MEK/HEP solvent mixtures, respectively).
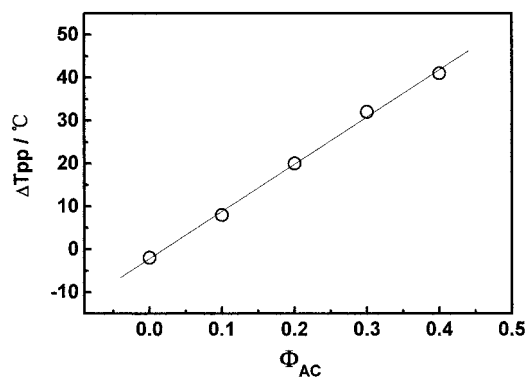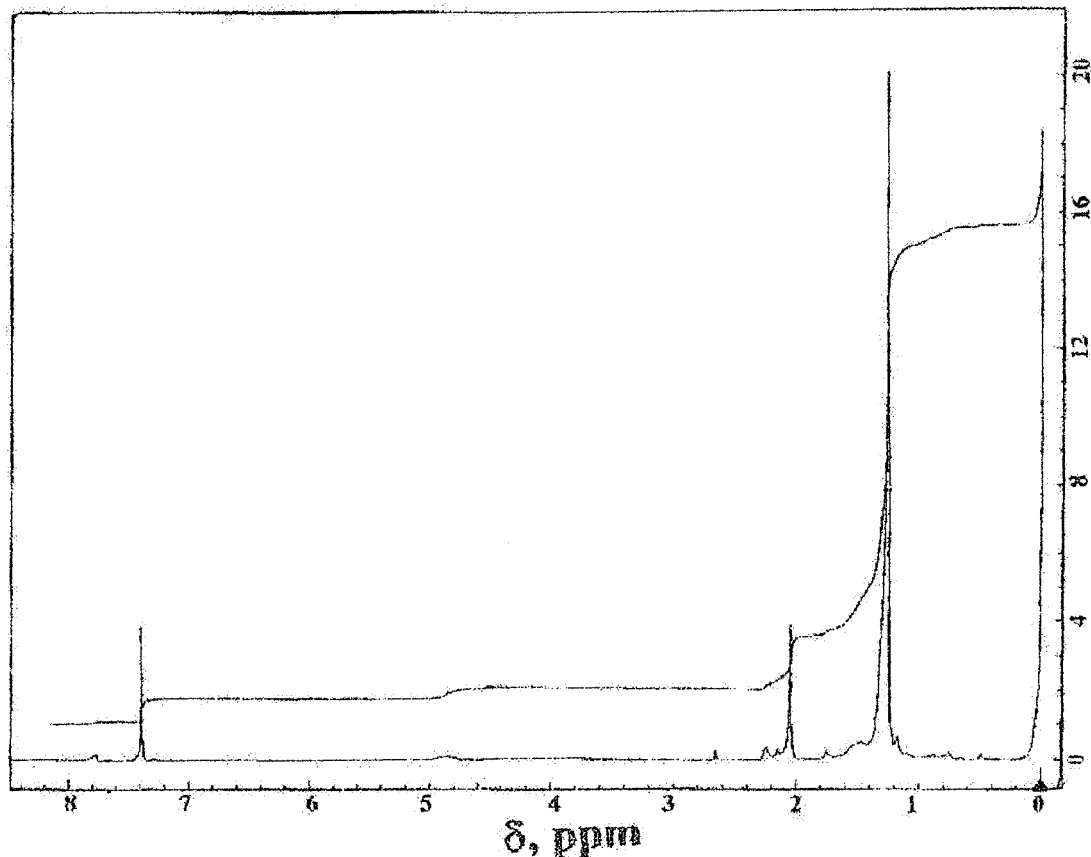
Figure 3 A typical NMR spectrum of EVA$_{30}$ copolymer in acetone-d_6/CDCl$_3$ solvent mixtures ($\Phi_{AC\text{-}[infi]d6} = 0.1$) at 25°C.

where $b = b_1X_1 + b_2X_2$, and X_1 and X_2 are the weight fractions of polymer 1 and polymer 2, respectively. The intrinsic viscosity $[\eta]$ or $[\eta]_m$ and viscosity slope coefficient b or b_m for the polymer or polymer mixture, respectively, were evaluated by the linear least-squares treatment according to
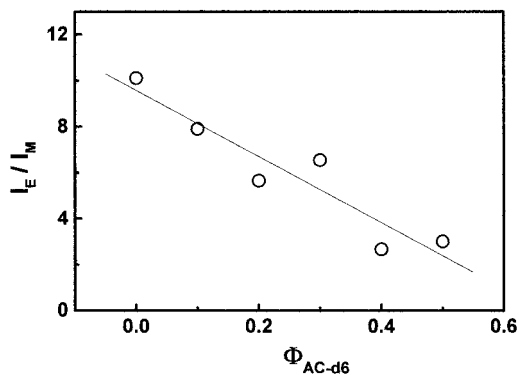
the Huggins equation. $U > 0$ signifies compatibility of two polymers, whereas $U < 0$ indicates phase separation. Figure 5 shows a curve of the U-parameter versus Φ_{DCE} in DCE/CYH solvent mixtures. This curve is similar to the curve of
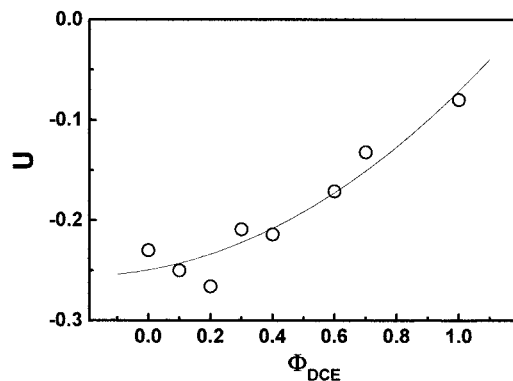

Figure 4 Change of I_E/I_M in EVA with $\Phi_{AC\text{-}[infi]d6}$ in acetone-d_6/CDCl$_3$ solvent mixture at 25°C.

Figure 5 Solvent composition (Φ_{DCE}) dependency of the interaction parameter U between EVA$_{38}$ and wax in DCE/CYH solvent mixtures at 30°C.
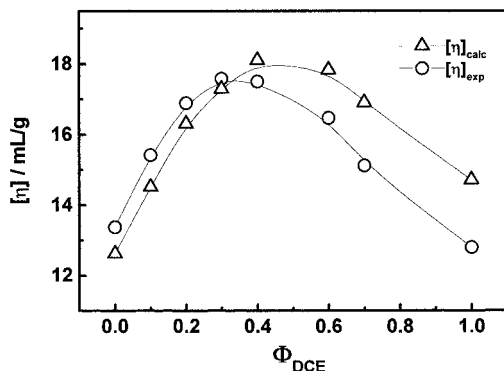
Figure 6 Variation of $[\eta]$ of EVA_{38}/wax (20/80 w/w) blend with Φ_{DCE} in DCE/CYH solvent mixtures at 30°C.

Figure 7 Variation of solubility of wax with Φ_{DCE} in DCE/CYH solvent mixture with and without 300 ppm EVA_{30} at 23°C.

ΔT_{PP} versus Φ_{DCE} in Figure 1. Therefore, the results are almost identical, whether the solvent used is a single solvent[2] or a solvent mixture; that is, the larger the Φ_{DCE} of selective solvent DCE for VA segment in EVA, the higher the U-value and the larger the ΔT_{PP}. It means that the interactions between EVA and wax in the selective solvents (DCE) of VA segments of EVA (poor solvent for ethylene segments and wax) are relatively larger than those in the selective solvents (CYH) of ethylene segments of EVA (good solvent for ethylene segments and wax).

Figure 6 shows the variation of the $[\eta]$ of EVA_{38}/wax (20/80, w/w) blend with Φ_{DCE} in DCE/CYH solvent mixtures, where the circle and triangle symbols, respectively, represent experimental and calculated value, that is, $[\eta]_{\text{exp}}$ and $[\eta]_{\text{calc}}$ according to $[\eta]_{\text{calc}} = \Sigma w_i[\eta]_i$, in which $[\eta]_i$ and w_i are $[\eta]$ and weight fraction of the component, respectively. Almost no deviations between $[\eta]_{\text{exp}}$ and $[\eta]_{\text{calc}}$ from the law of additivity exist before $\Phi_{\text{DCE}} \leq 0.4$, and the deviations between $[\eta]_{\text{exp}}$ and $[\eta]_{\text{calc}}$, $\Delta[\eta] = [\eta]_{\text{exp}} - [\eta]_{\text{calc}}$, increase with increasing Φ_{DCE}. Generally speaking, no strong interaction between two molecules exists if the additivity law holds,[11] and oppositely, compact or globular complex particles formed are considered if $\Delta[\eta] < 0$[12–17] or expanding coils attributed to strong interaction are formed if $\Delta[\eta] > 0$.[18–21] Therefore, the interaction between EVA_{38} and wax is nearly equivalent to zero when $\Phi_{\text{DCE}} \leq 0.4$, and increases with increasing Φ_{DCE} when $\Phi_{\text{DCE}} > 0.4$. This result occurs because the solvent mixtures are becoming increasingly deficient for both wax and ethylene segments in EVA_{38}.

Figure 7 shows the variation of solubilities of wax with Φ_{DCE} in DCE/CYH solvent mixtures

with and without 300 ppm EVA_{30} at 23°C. The solubilities of the wax with 300 ppm EVA_{30} are greater than those without EVA_{30}, that is, solubility of the wax increases in the presence of EVA_{30} when $\Phi_{\text{DCE}} > 0.6$. It is suspected that the interaction between wax and ordered ethylene segments in EVA molecule in solvent mixture leads to compact complexation between wax and EVA, and wax-solubilization within the ordered domain of ethylene segments. As a result, the wax distribution in the solvent mixture is nonhomogeneous, which is favorable to pour point depression of a wax solution doped with EVA pour point depressant.

Solvent Effect in EVA Parent Solution on ΔT_{PP} of Wax Solution and Kerosene-Containing Wax

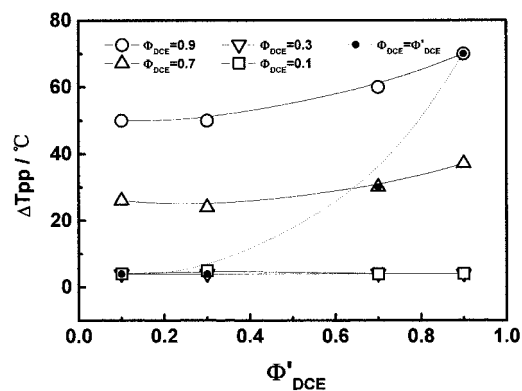Figure 8 shows the variation of ΔT_{PP} of four DCE/CYH solvent mixtures ($\Phi_{\text{DCE}} = 0.1, 0.3, 0.7,$ and

Figure 8 Variation of ΔT_{PP} of four DCE/CYH solvent mixtures ($\Phi_{\text{DCE}} = 0.1, 0.3, 0.7,$ and 0.9) containing 10 wt % wax and 400 ppm EVA_{30} with Φ'_{DCE} in EVA_{30} parent solutions used as doped solutions.

0.9) containing 10 wt % wax and 400 ppm EVA_{30} with Φ'_{DCE} (Φ' represents the composition of solvent mixture in the EVA parent solution) in the EVA_{30} parent solutions used as doped solution. For the systems in which Φ_{DCE} values are 0.1 and 0.3, the ΔT_{PP} values are equivalent and near zero, and constant with solvent composition of EVA parent solutions (Φ'_{DCE}). However, it is interesting that the variation of ΔT_{PP} of wax solutions in which Φ_{DCE} values are 0.7 and 0.9 becomes increasingly greater with increasing DCE component in EVA parent solutions (Φ'_{DCE}). This means that the EVA parent solutions with ordered ethylene segments are also favorable for ΔT_{PP} of the wax solutions in which Φ_{DCE} values are 0.7 and 0.9. The special system with $\Phi_{DCE} = 0.9$ and $\Phi'_{DCE} = 0.9$ of both wax solution and EVA parent solution, respectively, has the largest ΔT_{PP} ($\sim 70°C$). This result is attributed to the ordered structure of ethylene segments in EVA parent solution ($\Phi'_{DCE} = 0.9$), which can last longer in the wax solution of $\Phi_{DCE} = 0.9$ compared to that of $\Phi_{DCE} = 0.7$. The dotted line in Figure 8 is the same as the DCE/CYH curve in Figure 1, in which the ΔT_{PP} of the wax solution significantly increases with increasing Φ'_{DCE}, because of the same solvent compositions in both wax solution and the EVA parent solution, that is, $\Phi_{DCE} = \Phi'_{DCE}$.

Figure 9(a) and (b) show the solvent effect from parent solutions of EVA_{30} and EVA_{38}, respectively, on the ΔT_{PP} of wax–kerosene systems. Similarly as for the wax solutions in which Φ_{DCE} values are 0.9 and 0.7, in Figure 8, the ΔT_{PP} of wax–kerosene increases with increasing $\Phi'_{s,VA}$ in the EVA parent solutions, although the extent of increase of ΔT_{PP} is slightly lower.

CONCLUSIONS

The pour point depression (ΔT_{PP}) of wax solutions doped with EVA or PE-g-VA depends on the composition of solvent mixtures. The ΔT_{PP} are significantly greater in the solvent mixtures with high contents of selective solvents for VA segment in EVA such as EA, DCE, MEK, and AC. On the other hand, ΔT_{PP} values are almost zero in the solvent mixtures with low contents of the above-mentioned selective solvents. The solvent effect from the parent solution of EVA pour point depressant can also be seen from the variations of ΔT_{PP} of given wax solutions such as wax–kerosene system. Ethylene segments of EVA macro-
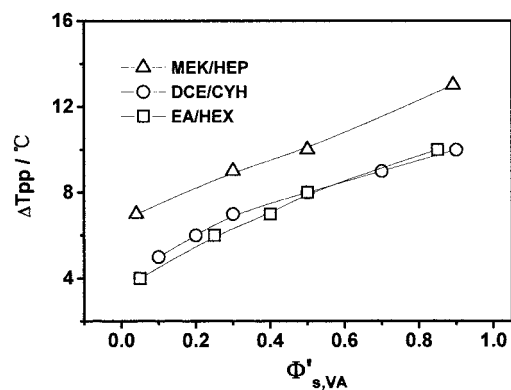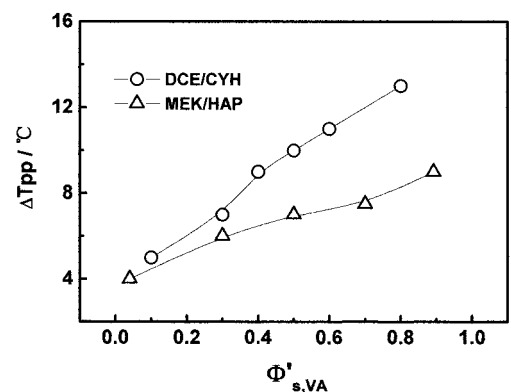
Figure 9 Variation of ΔT_{PP} of kerosene containing 10 wt % wax and 400 ppm EVA_{30} (a) and EVA_{38} (b) with $\Phi'_{s,VA}$ in EVA parent solutions made of DCE/CYH, MEK/HAP, and EA/HEX, respectively.

molecule in AC-d_6/CDCl$_3$ solvent mixtures are ordered according to NMR spectra, and the extent of ordering increases with increasing acetone-d_6 content in acetone-d_6/CDCl$_3$ mixtures. Ordered ethylene segments are favorable to the action of pour point depression of EVA pour point depressant because of the complexation between wax and ordered ethylene segments and wax solubilization within the ordered domain of ethylene segment based on low [η] of EVA/wax blend compared with the additivity law and high solubility of wax in DCE/CYH solvent mixtures with EVA, respectively.

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