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Thermodynamic analysis for the interaction of polyacrylate with wax in heptane

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Abstract

The effect of polyacrylate (PA) on wax-precipitation temperature in heptane was investigated using differential scanning calorimetry (DSC). A thermodynamic analysis for the dissolution of wax in the absence and presence of PA was conducted. Results suggested that the change in wax-precipitation temperature caused by the introduction of the additives may be regarded as an index for characterizing the interaction of polymer additives with wax. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyacrylate; Wax; Thermodynamic analysis

1. Introduction

It is well known that the flowability of waxy crude oils, diesel fuels and other base oils degrades with decreasing temperature, due mainly to the precipitation of wax and the formation of wax networks. In order to improve the low-temperature flowability of crude oils or diesel duels, polymer additives, such as vinyl acetate copolymer, acrylate copolymer and their derivatives, have been widely used as so-called pour point depressants (PPDs) [1,2]. In general, inhibition of wax crystallization has been considered to occur in the presence of PPDs by nucleation, co-crystallization or adsorption [3–5]. However, it should be pointed out that, up to now, a universal explanation for the role of PPDs has not been satisfactorily achieved. The interaction between the PPDs and the wax is still an interesting theme of scientific research at present.

The aim of the present study was to explore the interaction of wax and polyacrylate (PA), one of the widely used PPDs, with a particular emphasis on the effect of PA on the precipitation temperature of wax in organic solvent, the model oil. A thermodynamic analysis for the dissolution of wax in solvent was conducted. It was found that the change in wax-precipitation temperature may be used as an index for characterizing the interaction between wax and PPDs.

2. Experimental

Two polymers, poly(hexadecyl acrylate) (PA-16) and poly(octadecyl acrylate) (PA-18), were synthesized in our laboratory by radical polymerisation in solution, with a procedure similar to that described by Rubin [6]. The number-average molecular weight and the polydispersity were determined by high performance exclusion chromatography (GPC) to be 1.1×10^4 and 1.72 for PA-16 and 1.1×10^4 and 1.68 for PA-18, respectively.

The wax, a mixture of *n*-alkanes with a melting point of 49.4°C, supplied by the Refined Oil Company of Hangzhou, P.R. China, was purified with petroleum ether. It has a polydisperse molecular weight of 320.

A series of wax/heptane solutions were prepared by dissolving the wax in heptane at 60°C and then cooling to room temperature. These formed solutions were maintained at room temperature for about 24 h and then used as the model oil samples in the present study. The wax-precipitation temperature, T_c, of each model oil sample was measured with a Perkin Elmer DSC-7 differential scanning calorimeter with an accuracy of ±0.1°C. The sample size was about 10–20 mg. Each sample was heated from room temperature to 30°C at a rate of 100°C/min and maintained at 30°C for 5 min. Then it was cooled to −20°C at a rate of 1°C/min and the T_c value was determined automatically by computer.

The interaction of PA with wax was evaluated by measuring the change in T_c (ΔT_c) of the sample that results from the addition of PA/heptane solution into the model oil.

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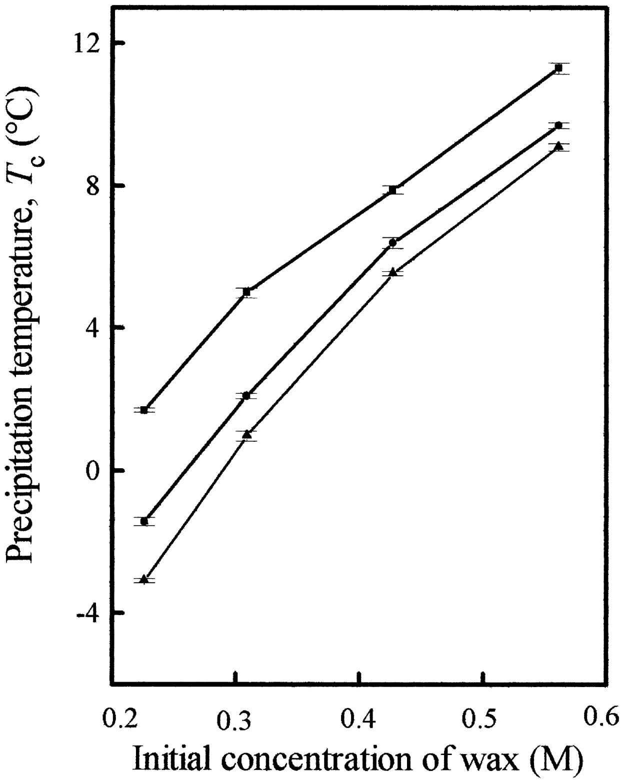


Fig. 1. The measured precipitation temperature, T_c, as a function of the initial concentration of wax in heptane (■), 1000 ppm PA-16/heptane (▲) and 1000 ppm PA-18/heptane (●) ($n = 5$, ±Sd).

The PA/heptane solution was prepared using the same procedure as that for the preparation of the model oil, as described above. The T_c of the system of PA/wax/heptane was also determined by DSC.

The conformation of PA in heptane and in the model oil was observed at 15°C with a JOEL 100CX Transmission Electron Microscope (TEM). A copper grid (used for the sample preparation for TEM), covered with a fine film of carbon was dipped into the solution. The remaining solvent was removed by evaporation or capillarity. Then the grid was placed under a TEM with a magnification of 5×10^5 to observe the PA conformation.

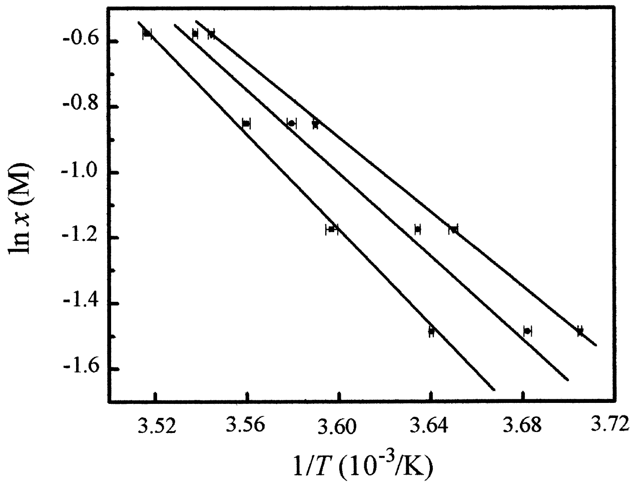


Fig. 2. The solubility, x, of wax as a function of temperature, T, in heptane (■), 1000 ppm PA-16/heptane (▼) and 1000 ppm PA-18/heptane (●) ($n = 5$, ±Sd).

Table 1
The calculated values of ΔH_d and ΔS_d for different systems

Systems	ΔH_d (kJ/mol)	ΔS_d (J/mol K)
Wax/heptane	62.8 ± 2.4	216.0 ± 8.5
1000 ppm PA-18/wax/heptane	50.6 ± 1.2	174.1 ± 3.4
1000 ppm PA-16/wax/heptane	47.6 ± 0.9	161.7 ± 3.3

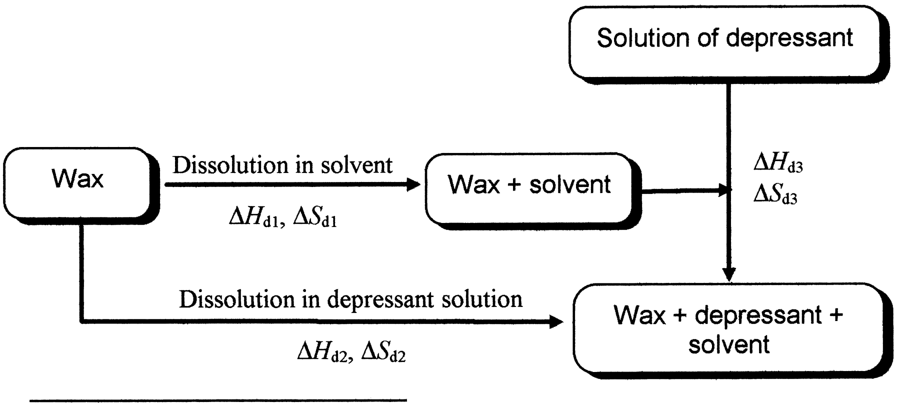
3. Results and discussion

It has been suggested that the PPDs are not good solvents for wax and that the interaction between PPDs and wax has little effect on the wax-precipitation temperature [7,8]. However, our experimental investigations show that, in the system of wax/heptane, the model oil, the wax-precipitation temperature depends strongly on the type of PA added into the system. Fig. 1 plots the measured wax-precipitation temperature, T_c, as a function of the initial concentration of wax in heptane solvent in the absence and presence of different additives, PA-16 and PA-18, respectively. The error bars in Fig. 1 represent standard deviation for five independent measurements. The typical values of the standard deviation are very small, about 0.1°C, indicating that the polymer additives play a significant role in the wax-precipitation temperature, although only a few degrees of change in T_c were observed.

Note that the precipitation of wax in solution can be considered to be as a result of the decrease in solubility of the wax with decreasing temperature. Therefore, the experimental results shown in Fig. 1 demonstrate the temperature-dependence of the solubility of wax in different solutions. In other words, if considering the quantity used for scaling the ordinate of Fig. 1 as the test temperature, T, the corresponding values read from the abscissa can be regarded as the solubility of wax at this temperature. Based on such a consideration, it can be concluded directly from Fig. 1 that the addition of PA may increase the solubility of wax in heptane at a given temperature.

Undoubtedly, the observed changes in the precipitation temperature or the solubility of wax in heptane due to the introduction of PA should be a result of the interaction between PA and wax. This can be demonstrated with the following thermodynamic analysis for the dissolution of wax in heptane.

By treating the precipitation temperature as the test temperature, T, and the concentration of wax as the solubility of wax, x, at the corresponding test temperature, the experimental data show in Fig. 1 are replotted in Fig. 2. Clearly, for each system, a good linear relationship exists



$$\Delta H_{d2} = \Delta H_{d1} + \Delta H_{d3} \qquad \Delta S_{d2} = \Delta S_{d1} + \Delta S_{d3}$$

For PA-16: ΔH_{d3} = -15.2 KJ/mol; ΔS_{d3} = -54.3 J/mol·K

For PA-18: ΔH_{d3} = -12.2 KJ/mol; ΔS_{d3} = -41.9 J/mol·K

Fig. 3. Illustration of the thermodynamic process of the dissolution of wax in PA/wax/heptane system.

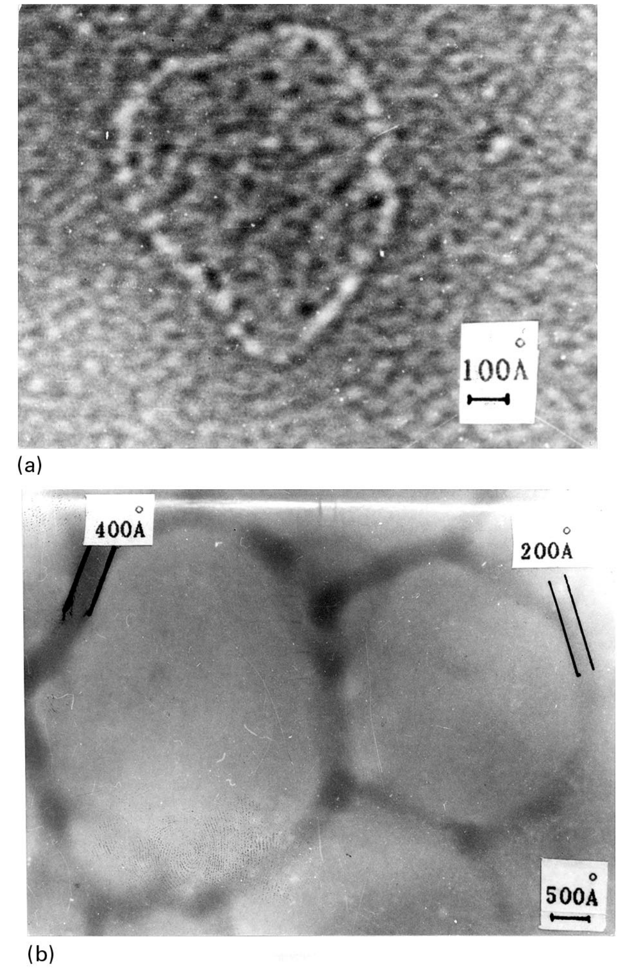


Fig. 4. Transmission electron micrograph of PA-18 in PA-18/heptane solution (a) and of (PA-18)–wax in PA-18/wax/heptane solution (b).

between $1/T$ and $\ln x$, indicating that the dissolution of wax in heptane is an ideal process. Thus, the dependence of the solubility of wax on temperature can be described according to the well-known Van't Hoff equation [9,10]:

$$\ln x = \frac{\Delta S_d}{R} - \frac{\Delta H_d}{RT} \tag{1}$$

where x is the solubility of wax at a given absolute temperature, T; R is the universal gas constant; ΔS_d and ΔH_d are the changes of entropy and enthalpy, respectively.

For each system, ΔH_d and ΔS_d are calculated by conventional linear regression analysis and the results are listed in the Table 1. From these results, some useful conclusions can be deduced.

First, both ΔH_d and ΔS_d for the wax/heptane system are positive, implying that the dissolution of wax in heptane is an endothermic process and the formed wax/heptane system tends to be disorderly. The smaller values of ΔS_d for both the additive/wax/heptane systems compared with that for the wax/heptane system signify that the systems containing the additives are more ordered.

Second, the role of PA on the dissolution of wax in heptane can be explained clearly from the analysis of the thermodynamic process shown in Fig. 3. The introduction of PA into the wax/heptane system results in negative values of ΔS_d, indicating that the degree of ordering of the system of wax/heptane is improved by PA.

In order to reveal the essence of the increase in the ordering degree of the system with the introduction of PA, PA conformations were studied using TEM. Fig. 4a and b shows the conformation of PA-18 in the solution of PA-18/heptane and the conformation of (PA-18)–wax in PA-18/wax/heptane solution containing 0.3125 M wax, respectively. Both these solutions contain the same content, 400 ppm, of PA-18. Obviously, in the PA-18/heptane solution, a vesicle-like structure is observed. The thickness of the

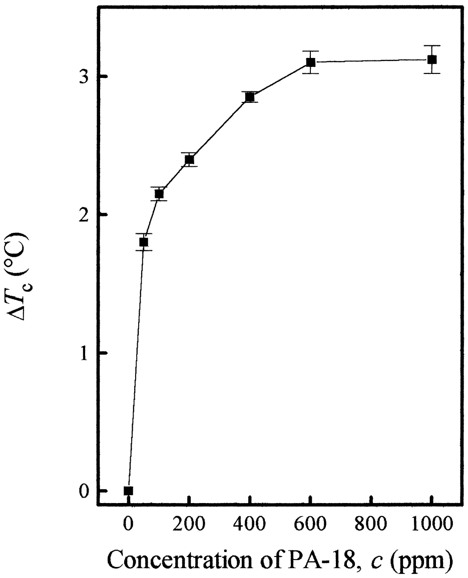


Fig. 5. Change in wax-precipitation temperature, ΔT_c, as a function of the concentration, c, of PA-18 in PA-18/wax/heptane system ($n = 5$, ±Sd).

edge of the vesicle is measured to be 23 Å which is in accordance with the calculated value, 25 Å, of the thickness of the side chain in PA-18, signifying that the formation of the vesicle-like structure results from ordered arrangement of the side chain of PA, i.e. the crystallization of the side chain. In the solution of PA-18/wax/heptane, a similar vesicle-like structure is also observed, but the thickness of the vesicle edge increases to 200–400 Å. Similar results are also observed in the PA-16 solutions. The thickening of the vesicle edge indicates that a complex is formed between PA and the wax. The complex formation must be driven by the co-crystallisation of a PA side chain with wax, a thermodynamic process with a decrease in entropy ($\Delta S < 0$). Therefore, the system of PA/wax/heptane has a higher ordering degree than that of wax/heptane.

Third, ΔH_d and ΔS_d for 1000 ppm PA-16/wax/heptane system are smaller than those for 1000 ppm PA-18/wax/heptane system, respectively. The smaller value of ΔS_d for the PA-16/wax/heptane system compared with that for the PA-18/wax/heptane system indicates that the complex of (PA-16)–wax is more ordered than that of (PA-18)–wax in heptane solution. In principle, the more ordered the complex, the more stable the system is, thus the stronger the interaction of the additive with wax. So, the interaction between PA-16 and wax is stronger than that between PA-18 and wax.

It is of interest to note that the change in T_c of wax in heptane caused by PA-16 is larger than that caused by PA-18 in each case studied, as shown in Fig. 1. Combined with the analyses above, it can be concluded that the change in T_c, ΔT_c, of wax-precipitation temperature may be considered as an index for characterising the interaction between wax and polymer additives. The larger the value of ΔT_c, the stronger the interaction is. This conclusion can also be verified by analysing the other experimental result shown in Fig. 5, a plot of ΔT_c versus the concentration, c, of PA-18 introduced into the wax/heptane system. It can be seen from Fig. 5 that with the increase in the concentration c, of PA-18, ΔT_c increases markedly. In an appropriate range of concentration of the polymer additive introduced, it can be expected that the ordering degree of the additive–wax complex would be increased with the increase in concentration of the additives. As a result, an increasing tendency in ΔT_c with the concentration of the polymer additive would be observed.

4. Concluding remarks

First of all, it should be pointed out that there have been few reports on the effect of PPDs on the precipitation temperature, T_c, of wax in solution. It is found in the present study that T_c may be a useful parameter for studying the interaction of PPDs with wax. Therefore, future work should be aimed at the validity and generality of this conclusion, in order to establish a quantitative method for describing the role of PPDs in waxy oils, diesel fuel and other base oils with the precipitation temperature of wax.

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