Cloud Points of Poly(propylene glycol) Aqueous Mixtures at Various Concentrations

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Cloud points of aqueous poly(propylene glycol) (PPG) mixtures at various concentrations of PPG are determined using the particle counting method. The average molecular weight of the PPG is 1205 $g \cdot mol^{-1}$, and its concentrations are changed from 0.01 up to 0.15 mass fraction. In this method, by slowly increasing the solution temperature, the number of particles is measured. At the temperature where a new phase appears, a sudden change in the number of particles would be observed, and this temperature indicates the cloud point for the solution. This procedure is repeated for various PPG concentration mixtures, and the cloud-point curve of the aqueous PPG mixture is determined. Also, a simple model for correlating cloud-point data is presented, and the results show a good consistency between the measured and the calculated data.

Introduction

The cloud point of a solution is the temperature at which the solution becomes two phases. This phenomenon can be observed for some components which have partial miscibility with respect to each other. The determination of the cloud point is very important from different points of view, such as designing the extraction apparatus and holding a homogeneous system at a stable condition with respect to the composition of the system species. There are several methods for cloud-point measuring, for example, visual observation,[1] turbidimetry,[2] light scattering,[3] viscometry,[4] thermo-optical methods,[5] and so on. The particle counting method is a new method for cloud-point measuring which has been introduced by Eliassi et al.[6−8] The basis of this method for cloud-point measuring is determining the number of particles in a mixture; namely, when a new phase appears in a solution, this phase arises as a large number of small particles. At this time, the solution becomes cloudy due to the scattering of the light beam passing through the solution. So, if the number of particles in a solution is measured at various temperatures, it is expected that, at the temperature where a new phase appears, a sudden change in the number of particles would be observed, and this temperature indicates the cloud point for the solution.

Experimental Section

Chemicals. Analytical grade poly(propylene glycol) with an average molar mass of 1205 $g \cdot mol^{-1}$ (PPG1205) was obtained from Merck (Germany). Double-distilled water was used for making solutions. The sample mass was measured by an electronic balance (2842, Sartorius GMBH, Germany) with an accuracy of ± 0.1 mg. The uncertainty of the mass fraction calculation was less than ± 0.0002.

Apparatus and Procedures. Figure 1 shows the diagram for the experimental setup. A laser particle counter (Spectrex Corporation, model PC-2000, US) was used for particle counting.

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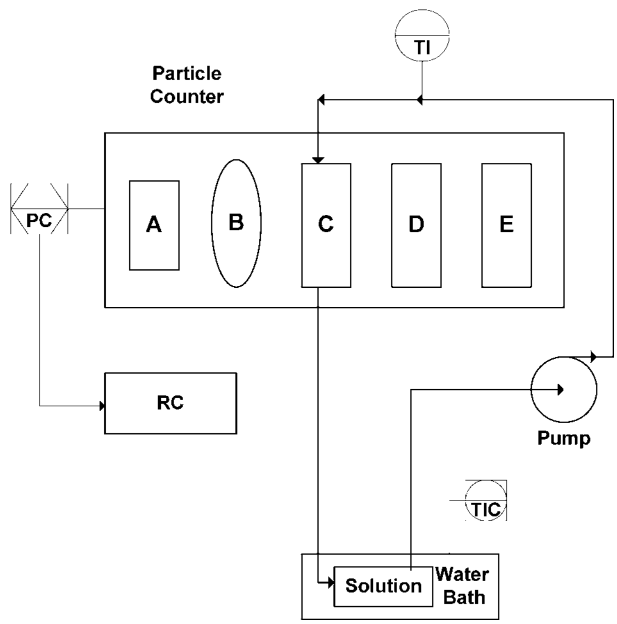

Figure 1. Schematic diagram of the used setup for determining the cloud point of PPG aqueous solutions. PC, personal computer; TIC, temperature indicator and controller; TI, temperature indicator; RC, recorder; A, photodetector; B, detector lens; C, flow cell; D, scanner; E, laser diode.

The sample compartment consists of a flow cell where PPG aqueous solution was pumped from a storage vessel kept at a constant temperature by a water bath system. The temperature of the solution was recorded at the entrance of the cell by a thermocouple with an accuracy of ± 0.1 K. The required time for determining the number of particles was 15 s. Therefore, the temperature of the water bath was changed and controlled by a thermostat with an appropriate rate to maintain the required temperature at the flow cell. At each temperature, the output of the apparatus has been sent to a PC, and finally the number of particles per cubic centimeter will be recorded by a printer.

Samples were weighed with an analytical balance with an accuracy of ± 0.1 mg. Each experiment was repeated three

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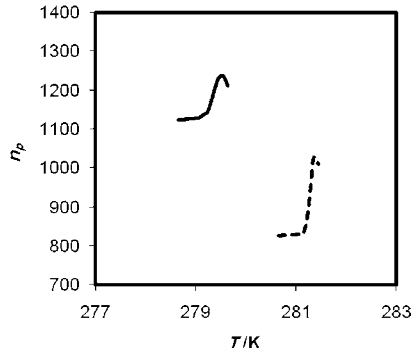

Figure 2. Number of particles per cubic centimeter (n_p) versus temperature for two different mixtures of PPG1205 + H_2O: solid line ($w_p = 0.15$), dashed line ($w_p = 0.1$). w_p is PPG mass fraction.

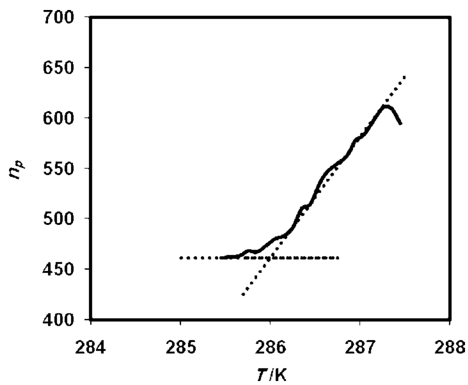

Figure 3. Number of particles per cubic centimeter (n_p) versus temperature for a mixture of PPG1205 + H_2O ($w_p = 0.01$).

times, and the reproducibility and accuracy of the measured cloud-point temperatures by statistical analysis of the obtained results was estimated as ± 0.2 K.

Figure 1 shows the schematic of the used apparatus setup for determining the cloud point of PPG aqueous solution.

Results and Discussion

Figure 2 shows the number of particles versus temperature for two different PPG1205 + H_2O mixtures. The mass fraction of PPG in one of them is 0.15 and in the other mixture is 0.1. According to this figure, on increasing the temperature of the first solution from (278.65 to 279.15) K, the number of particles is nearly constant, but at 279.15 K, a sharp increase is observed, which is due to the appearance of the first particles for the formation of a new phase. Therefore, 279.15 K is recorded as the cloud point of this mixture.

For the second mixture for which PPG mass fraction is 0.1, on increasing the temperature of the solution from (280.15 to 281.15) K, the number of particles is nearly constant, but at 281.25 K, a sharp increase is observed, which is due to the appearance of the first particles for the formation of a new phase. Therefore, 281.25 K is recorded as the cloud point of this mixture.

A similar method was repeated for two other mixtures which the mass fractions of PPG were 0.05 and 0.02. Cloud points for these mixtures were measured at (282.95 and 285.95) K, respectively.

Figure 3 shows the variation of the number of particles versus temperature for a dilute aqueous solution of PPG1205. The mass fraction of PPG in this mixture is 0.01. It can be seen that there is not a sharp and sudden increase of the number of particles for this sample. For this case, we can partition the graph to two parts. In one of them the particle changes are very slow, and in the other part the changes are faster. By passing two straight lines through these two parts, their intersection point is selected as the beginning of the sharp changes. Therefore, 286.15 K can be considered as the cloud point of 0.01 mass fraction of PPG aqueous mixture.

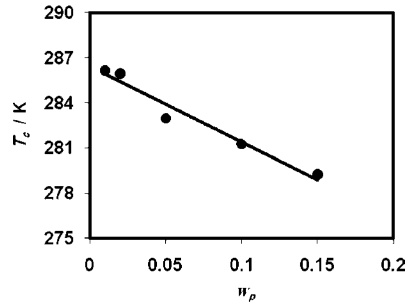

Figure 4. Cloud point (T_c) changes of aqueous solutions of PPG1205 versus w_p. The solid circles, ●, are experimental data, and solid line is obtained by eq 2.

According to the obtained results, the cloud point decreases with increasing the polymer concentration in the mixture. A simple model for cloud-point correlation can be used as follows:

$$T_c = Aw_p + B \tag{1}$$

where T_c and w_p are the calculated cloud point and PPG mass fraction in the mixture, respectively. A and B are adjustable parameters. For the PPG1205 aqueous solutions, A and B are calculated, so the following correlation is introduced:

$$T_c = -49.99w_p + 286.41 \tag{2}$$

In Figure 4, the experimental data and the calculated results by eq 2 are shown. The root-mean-square deviation (σ) is defined as:

$$\sigma = \left[\frac{\sum_{i=1}^{n}(T_{ci} - T_i)^2}{n - 1}\right]^{1/2} \tag{3}$$

where T_{ci} and T_i are the calculated and experimental cloud points, respectively, and n is the number of experimental points. The root-mean-square deviation of the calculated cloud point in respect to experimental solubility is 0.5941.

Conclusions

The effect of PPG1025 concentration on the cloud point of PPG1205 aqueous solutions was investigated by the particle counting method. The obtained results indicate that the cloud points decrease with an increase in PPG concentration. So, by increasing the PPG concentration from 0.01 up to 0.15 polymer mass fraction, the cloud point decreases from (285.95 to 279.25) K. According to the obtained results, a linear correlation can correlate the cloud points with PPG mass fraction with a good consistency, with respect to the experimental data.

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