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Cosolvent effect of alkyl acrylates on the phase behaviour of poly(alkyl acrylates)–supercritical CO_2 mixtures

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Cloud-point data to 220°C and 2000 bar are presented for ternary mixtures of poly(butyl acrylate)–CO_2–butyl acrylate (BA) and poly(ethyl hexyl acrylate)–CO_2–ethyl hexyl acrylate (EHA). The addition of either BA or EHA to the respective polymer–solvent mixtures decreases the cloud-point pressures by as much as 1000 bar and changes the pressure–temperature slope of the cloud-point curves from negative to positive which significantly increases the single-phase region. Both BA and EHA provide favourable polar interactions with the acrylate groups in the backbone of the polymer and they densify the solvent mixture. However, the effect of these cosolvents on the location of the cloud-point curves diminishes as the amount added to the solution increases. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

A cosolvent can greatly enhance polymer solubility in a given solvent due to several factors. If the solvent is highly expanded, the addition of a dense, liquid cosolvent reduces the free volume difference between the polymer and the solvent[1]. Also, if the cosolvent provides favourable physical interactions, such as polar interactions, the region of miscibility should expand[2]. Interpreting the effect of a cosolvent added to an SCF solvent is slightly more complicated since increasing the system pressure reduces the free volume difference between the solvent and the polymer and it also modulates the probability of interaction between polymer, solvent, and cosolvent segments in solution[3]. The high-pressure, polymer–SCF solvent–cosolvent studies reported in the literature show that cloud points monotonically decrease in pressure and temperature with the addition of a polar cosolvent as long as the cosolvent does not form a complex with the polar repeat units in the polymer[4–6]. In these cases, the cosolvency effect is directly related to the polar forces of attraction contributed by the cosolvent and to the increase in solvent density resulting from the addition of a liquid cosolvent to a supercritical fluid solvent.

The focus of the work presented here is the determination of the impact of butyl acrylate (BA) cosolvent on the phase behaviour of the poly(butyl acrylate) (PBA)–CO_2 system and of 2-ethyl hexyl acrylate (EHA) cosolvent on the phase behaviour of the poly(2-ethyl hexyl acrylate) (PEHA)–CO_2 system. Given that CO_2 has been considered a desirable reaction medium for free radical polymerizations[7], the phase behaviour for these ternary poly(acrylate)–monomer–CO_2 mixtures provides needed information on the regions where homogeneous polymerizations can occur in the presence of excess monomer. Rindfleisch *et al.*[8] have demonstrated that the PBA–CO_2 and PEHA–CO_2 cloud-point curves are horizontal at ~1100 bar at high temperatures. However, as the temperature is lowered the PEHA–CO_2 curve increases sharply in pressure at ~155°C and the PBA–CO_2 curve increases in pressure at ~80°C. This sharp pressure increase reflects a significant change in the interchange energy which characterizes the balance of polymer segment–CO_2 cross-interactions relative to polymer segment–segment and CO_2–CO_2 self-interactions. At high temperatures, where entropic effects are expected to dominate, the location of the cloud-point curves are fixed by the free volume difference between PBA and CO_2 and PEHA and CO_2. When BA and EHA are added to CO_2 the polarity and density of the solvent mixture are expected to increase since both of these cosolvents are dense, polar liquids. Hence, cloud-point pressures at high temperatures should be lower compared to the binary polymer–CO_2 curves and the temperature where the sharp increase in cloud-point pressure is observed should be reduced.

A small amount of binary CO_2–BA data are obtained to complement the PBA–CO_2–BA studies presented here since there are no literature phase behaviour data available on these mixtures. The primary purpose for obtaining CO_2–BA data is to determine whether CO_2 and BA form multiple phases in the pressure–temperature–composition regions explored in the PBA–CO_2–BA studies. The CO_2–BA data are fitted to the Peng–Robinson equation of state[9] and the phase behaviour for this binary solvent mixture is calculated at elevated operating temperatures and pressures. No attempt was made to obtain data on the CO_2–EHA mixture nor were calculations performed on this mixture since there are no pure component critical properties available for EHA.

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EXPERIMENTAL

Phase behaviour data were obtained with a high-pressure, variable-volume cell that has a 1.59 cm inner diameter, 7.0 cm outer diameter, and a working volume of ~28 cm^3. A 1.9 cm thick sapphire window is fitted in the front part of the cell for observation of the phases. Polymer is loaded into the cell which is subsequently purged several times at room temperature with CO_2 at 3–6 bar to remove any entrapped air. BA and EHA monomer is quantitatively transferred into the cell with a syringe and CO_2 is then transferred into the cell gravimetrically with a high-pressure bomb. The solution is compressed to the desired pressure with an internal piston displaced with water in a high-pressure generator. The pressure of the mixture is measured with a Heise gauge (Dresser Ind., model CM-108952, 0–3450 bar, accurate to within ± 3.5 bar). Because the measurement is made on the water side of the piston, a small correction (~1 bar) is added to account for the pressure required to move the piston. The temperature of the cell is measured using a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Keithley Instruments, Inc., Model 195T, accuracy ± 0.03%). The system temperature is typically maintained to within ± 0.2°C below 200°C. The mixture inside the cell is viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-024-000-55) placed against the outside of the sapphire window. Light is transmitted into the cell with a fibre optic cable connected at one end to a high density illuminator (Dolan-Jenner Industries, Inc., model 180) and at the other end to a borescope. The solution in the cell is well mixed using a magnetic stir bar activated by an external magnet beneath the cell.

Cloud points are obtained at a fixed PBA or PEHA concentration of ~5 wt.%. The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. The results obtained with this definition of the cloud point have been compared in our laboratories with results obtained using a laser light turbidity measurement where the cloud point is defined as the condition where a 90% decrease in light transmitted through the solution occurs. Cloud points obtained by both methods are identical within the reproducibility of the data. The cloud points are measured at least twice at each temperature, and are typically reproducible to within ± 5 bar at the highest temperatures. In the region where the cloud-point pressure increases very rapidly for a small change in temperature, the cloud points are reproducible to within ± 10 bar.

MATERIALS

Both polymers are obtained from Aldrich Chemical Company. The PBA has a weight average molecular weight, M_w, of 61 800 and a molecular weight polydisper-

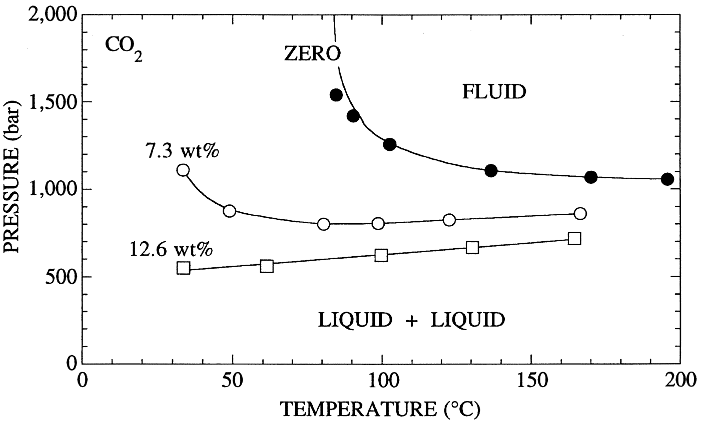

Figure 1 Impact of free butyl acrylate monomer (on a polymer-free basis) on the phase behaviour of the poly(butyl acrylate)–CO_2 system. Data for the poly(butyl acrylate)–CO_2 system were obtained by Rindfleisch *et al.*[8]

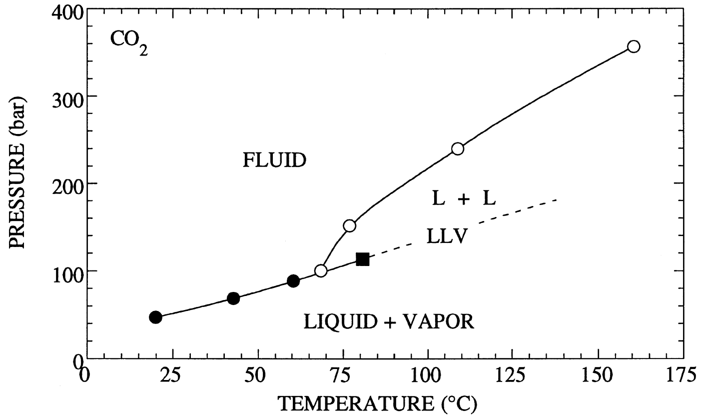

Figure 2 Impact of 32.0 wt.% butyl acrylate monomer (on a polymer-free basis) on the phase behaviour of the poly(butyl acrylate)–CO_2 system. ○, fluid → liquid + liquid transitions; ●, fluid → liquid + vapour transitions; ■, liquid + liquid → $liquid_1 + liquid_2$ + vapour (LLV) transition; - - -, suggested extension of the LLV line

sity, M_w/M_n, equal to 2.99. The PEHA has a M_w of 112 800 and a M_w/M_n equal to 2.97. Butyl acrylate and 2-ethylhexyl acrylate (99 + % purity), obtained from Aldrich Chemical Company, contain approximately 40 ppm of 2,6-di-tert-butyl-4-methyl phenol and are used as received. CO_2 is obtained from Airgas Corporation (99.8% minimum purity) and used as received.

EXPERIMENTAL RESULTS

Figure 1 shows the effect of modest amounts of BA on the cloud-point behaviour of the PBA–CO_2 system. At temperatures greater than 100°C the cloud-point curve is shifted to moderately lower pressures, more than likely due to the decrease in the free volume difference between PBA and the mixed solvent. For instance, at 150°C, the addition of ~7 wt.% BA to a PBA–CO_2 mixture lowers the cloud-point pressure from 1100 bar to 850 bar. Note that the sharp increase in the PBA cloud-point curve shifts from 85 to ~30°C with 7.3 wt.% BA added to the solution and this pressure increase is not observed at 30°C when 12.6 wt.% BA is added to the solution. In fact, the PBA–CO_2–12.6 wt.% BA curve exhibits a positive slope over the range of 30–160°C.

Figure 2 shows that adding 32 wt.% BA to the PBA–CO_2 solution significantly changes the phase behaviour. Now the cloud-point curve takes on the appearance of a typical lower critical solution temperature (LCST) boundary[10]. At 150°C the phase transition has shifted from 1100 bar in pure CO_2 to ~350 bar in a CO_2 + 32 wt.% BA mixture. The cloud-point curve intersects a liquid → liquid + vapour (LV) curve at ~65°C and 100 bar. A liquid and vapour phase coexist at pressures below this curve. Note that the LV curve switches to a liquid$_1$ + liquid$_2$ + vapour (LLV) curve at temperatures greater than 65°C. The slope of the PBA–CO_2–BA LCST curve, ~2.7 bar °C^{-1}, is approximately 40% greater than that observed for binary poly(isobutylene)–alkane mixtures reported by Zeman and Patterson[11] since, at the same temperatures and pressures, the CO_2–BA mixture is more compressible than the alkanes used in the Zeman study. PBA dissolves in pure BA even at atmospheric pressure which suggests that adding more BA to the solution will shift the intersection of the cloud-point curve with the LV curve to higher temperatures, which means that the single-phase region will increase.

Figure 3 shows parts of the CO_2–BA isotherms obtained at 75 and 35°C. The solid lines show the calculated isotherms at these temperatures using the Peng–Robinson equation of state with the critical properties of butyl acrylate[12] (T_c = 644 K; P_c = 45.4 bar; acentric factor = 0.312). Also, two fitted mixture parameters are used that account for CO_2–BA cross-interactions, k_{ij} = 0.010, and that account for non-arithmetic averaging of the covolume, $\eta_{ij} = -0.090$. Details of the type of calculations involved are found elsewhere[13]. *Figure 3* shows that very good fits of both isotherms are obtained. The calculated curves shown

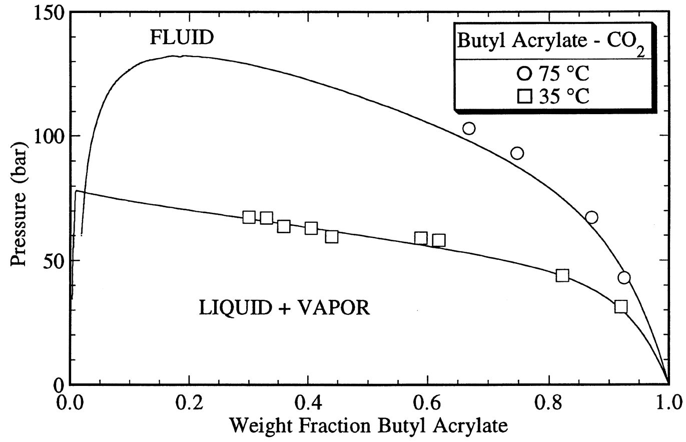

Figure 3 Phase behaviour of the CO_2–BA system determined in this study. The solid lines are calculated isotherms with the Peng–Robinson equation of state

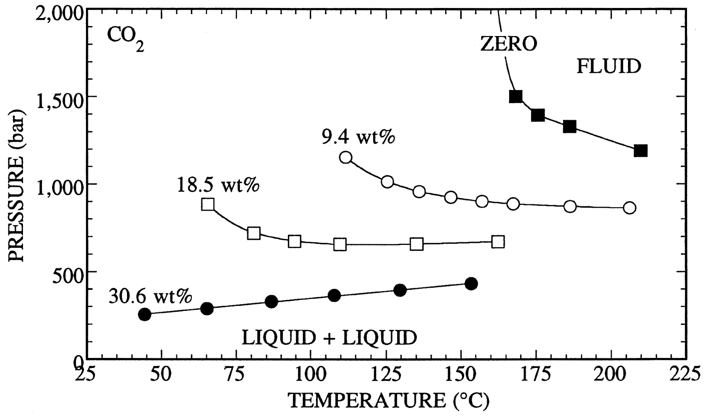

Figure 4 Impact of free 2-ethylhexyl acrylate monomer (on a polymer-free basis) on the phase behaviour of the poly(ethyl hexyl acrylate)–CO_2 system. Data for the poly(ethyl hexyl acrylate)–CO_2 system were obtained by Rindfleisch *et al.*[8]

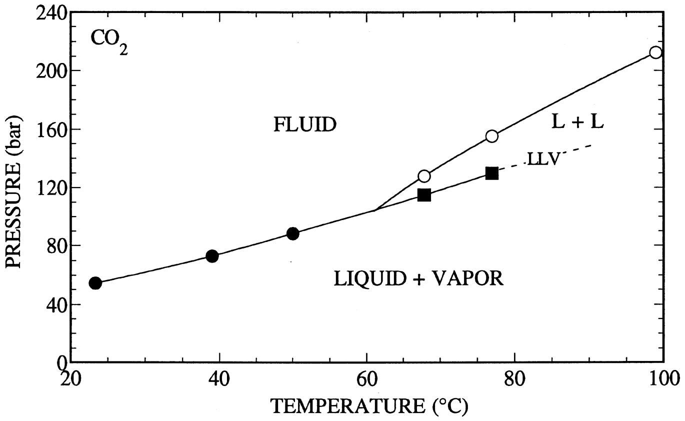

Figure 5 Impact of 41.0 wt.% free 2-ethyl hexyl acrylate monomer (on a polymer-free basis) on the phase behaviour of the poly(ethyl hexyl acrylate)–CO$_2$ system. ○, fluid → liquid + liquid transitions; ●, fluid → liquid + vapour transitions; ■, liquid + liquid → liquid$_1$ + liquid$_2$ + vapour (LLV) transitions; - - -, suggested extension of the LLV line

here and at higher and lower temperatures indicate that the binary CO$_2$–BA system does not exhibit three-phase behaviour. Therefore, the LLV line shown in *Figure 2* is a consequence of having PBA in solution. It is interesting that the calculated bubble-point curve for a binary CO$_2$–BA mixture with 32 wt.% BA virtually superposes onto the LV curve for the PBA–CO$_2$–BA system shown in *Figure 2*.

The cloud-point behaviour of the PEHA–CO$_2$–EHA system shown in *Figure 4* exhibits many of the same trends as that shown in *Figure 1* for the PBA–CO$_2$–BA system. If the 18.5 and 30.6 wt.% curves are extrapolated to 200°C, it is apparent that the impact of EHA monomer diminishes rapidly as increasing amounts of EHA are added to solution. For example, the cloud-point pressure decreases by ~350 bar with the first 9.4 wt.% EHA added to the solution, it decreases by ~200 bar with the addition of the next 9.1 wt.%, and it decreases by 150 bar with the addition of the next 12.1 wt.%. Nevertheless, the cloud-point pressure at 200°C decreases from 1250 bar to 550 bar with the addition of 30.6 wt.% EHA added to solution. Note that the temperature at which the sharp increase in the PEHA cloud-point curve occurs shifts progressively from 160°C to 100°C with the addition of the first 9.4 wt.% EHA, and it shifts further still to ~55°C with the addition of the next 9.1 wt.% EHA added to the solution. The cloud-point curve with 30.6 wt.% EHA exhibits a positive slope. The impact of EHA as a cosolvent is perhaps more impressive relative to that of BA since it is much more difficult to dissolve PEHA in pure CO$_2$ than it is to dissolve PBA.

The similarities are also apparent between the phase behaviour of the PEHA–CO$_2$–41.0 wt.% EHA system shown in *Figure 5* and the PBA–CO$_2$–32.0 wt.% BA system shown in *Figure 2*. The PEHA–CO$_2$–41.0 wt.% EHA cloud-point (LCST) curve intersects the LV curve at ~60°C and 100 bar compared to ~65°C and 100 bar for the PBA–CO$_2$–32.0 wt.% BA curve. The slope of the PEHA LCST curve is ~2.8 bar °C^{-1} compared to ~2.6 bar °C^{-1} for the PBA LCST curve in *Figure 2*. The results obtained in this study demonstrate clearly that it is possible to obtain a single phase that extends over a large temperature range at modest pressures if sufficient amounts of free acrylate monomer are added to the solution.

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