Comparison of the effect of density and hydrogen bonding on the cloud-point behaviour of poly(ethylene-*co*-methyl acrylate)–propane-cosolvent mixtures

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Cloud-point data to 170°C and 2800 bar (280 MPa) are presented for poly(ethylene-*co*-(31 mol%) methyl acrylate) at ~5 wt% in propane and in hexane and in mixtures of propane plus 5, 10, and 15 wt% hexane, hexene, methanol, ethanol, n-propanol and n-butanol. Hexane and hexene, which densify the propane, have no effect on the pressure–temperature location of the copolymer–propane cloud-point curve; however, the alcohols, which hydrogen bond to the acrylate repeat units, lower the curve by as much as 75°C. The magnitude of the temperature shift of the cloud-point curve decreases with increasing alcohol content as the acrylate units become saturated and the alcohol preferentially self-associates. Methanol is the least effective cosolvent as it self-associates more than the other alcohols at a given temperature.

(Keywords: cosolvent; cloud-point curve; hydrogen bonding)

INTRODUCTION

It is well known that the use of proper cosolvents can increase the region of miscibility of polymer–solvent mixtures[1–3]. This enhanced miscibility is even more pronounced when the cosolvent hydrogen bonds with the repeat units in the backbone of the polymer. Many researchers have studied the effect of hydrogen bonding liquid cosolvents on the solubility behaviour of polymer–solvent systems. For example, Wolf and Blaum[4] reported that small amounts of 2-butanol depressed the upper critical solution temperature (*UCST*) of a poly(methyl methacrylate) (PMMA)–chlorobutane mixture by 70°C. The lowering of the *UCST* is attributed to the formation of hydrogen bonds between butanol and the methyl methacrylate repeat units in the backbone of the polymer. However, the *UCST* increases approximately 50°C above that for PMMA in pure chlorobutane at high butanol concentrations, where butanol preferentially hydrogen bonds to itself. Rätzsch *et al.*[5] determined the effect of vinyl acetate monomer cosolvent on the phase behaviour of poly(ethylene-*co*-vinyl acetate) (EVAc)–ethylene mixtures. In the temperature range of 160–240°C they found that the cloud-point pressure was lowered by as much as 400 bar† when the amount of vinyl acetate cosolvent exactly matched the amount of vinyl acetate in the backbone of the EVAc.

Recently, Meilchen and co-workers[6,7] contrasted the effect of two different cosolvents, acetone and ethanol, on the phase behaviour of poly(ethylene-*co*-methyl acrylate) (36 mol% acrylate)–propane mixtures. Acetone, which is a polar base, does not hydrogen bond to the basic acrylate repeat unit in the copolymer. However, ethanol, which is also polar, can hydrogen bond to the acrylate repeat units. At cosolvent concentrations of less than approximately 10 wt%, both cosolvents shifted the cloud-point curves to lower temperatures and pressures, although ethanol was more effective than acetone at increasing the region of miscibility due to favourable ethanol–acrylate association. At cosolvent concentrations greater than 10 wt%, where the amount of ethanol is in excess of the amount needed to hydrogen bond to the acrylate sites, ethanol acted as a non-solvent that caused the copolymer to precipitate from solution. At high concentrations the excess ethanol preferentially self-associates, causing a large increase in ethanol–ethanol interactions relative to ethanol–copolymer interactions. In contrast, it was possible to continuously increase the one-phase region by adding up to 26 wt% acetone, which does not hydrogen bond to the acrylate repeat units.

In general, the location of the cloud-point curve is expected to be dependent on the density of the solvent or solvent mixture and the strength of the intermolecular interactions between polymer, solvent and cosolvent. The density-dependent or, equivalently, pressure-dependent strength of the solvent is a universal characteristic that can be understood by considering the following simplified expression, which shows that the internal energy of a mixture, U_{total}, is linearly related to density[8,9]:

$$\frac{U_{\text{total}}}{NkT} \approx \frac{3}{2} + A_1 \rho \int \Gamma_{ij}(r) g(r) r^2 \, dr \tag{1}$$

where $\Gamma_{ij}(r)$ is the pair potential energy of *ii*, *ij* and *jj* interactions, $g(r)$ is the radial distribution function, and

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† 1 bar = 0.1 MPa

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Table 1 Physical properties of the solvents used in these studies[28,29]

Solvent	Critical temperature (°C)	Critical pressure (bar)	Critical density (g cm^{-3})	Polarizability (cm^3 x 10^{25})	Dipole moment (debye)
Propane	96.6	42.5	0.217	62.9	0.0
Hexane	234.4	30.1	0.233	118.3	0.0

Table 2 Physical properties of the cosolvents used in these studies[28–30]

Cosolvent	Density at 20°C (g cm^{-3})	Polarizability (cm^3 x 10^{25})	Dipole moment (debye)
1-Hexene	0.6731	116.0	0.4
Methanol	0.7914	32.8	1.7
Ethanol	0.7893	51.1	1.7
n-Propanol	0.8035	69.5	1.7
n-Butaol	0.8098	87.9	1.8

Table 3 Hydrogen-bonding energy of alcohols (dimerization model)[a] using infra-red or ^{1}H n.m.r. spectroscopy methods at 25°C[14–16,22,23]

Alcohol	$-\Delta H$(dimerization) (kcal mol^{-1})	$-\Delta H$(ROH–CH$_3$COOC$_2$H$_5$) (kcal mol^{-1})
Methanol	9.3±2.5	2.5±0.4
Ethanol	7.4±2.0	2.3±0.4
n-Propanol	2.6±0.5	
n-Butanol		2.4±0.2

[a] The enthalpy of dimerization for the alcohols and the enthalpy of complexing were measured in CCl$_4$ except for the n-butanol–ethyl acetate complex which was measured in pure ethyl acetate[23]

A_1 is a constant which depends on the properties of the components in solution. Equation (1) indicates that increasing the solution density decreases U_{total} because Γ_{ij} is negative. Solute solubility, which is fixed by the difference between the total mixture energy minus the sum of the pure component energies, will increase with increasing density as long as unlike interactions are stronger than pure component interactions. Although increasing the density of a gaseous solvent can be achieved by a pressure increase or the addition of a liquid cosolvent, any density enhancement of solubility will be minimal if the gaseous solvent is already compressed to liquid-like densities.

As shown in equation (1), the pair potential energy of interaction ($\Gamma_{ij}(r)$) between solvent, cosolvent and copolymer segments has a large effect in determining the total energy of the mixture. The different contributions to Γ_{ij} can be expressed using the following approximate expression[8]:

$$\Gamma_{ij} \approx -\left(C_1 \frac{\alpha_i \alpha_j}{r^6} + C_2 \frac{\mu_i^2 \mu_j^2}{r^6 kT} + C_3 \frac{Q_i^2 Q_j^2}{r^{10} kT}\right) + \text{acceptor–donor complexing} \qquad (2)$$

where α is the polarizability, μ is the dipole moment, Q is the quadrupole moment, r is the distance between the molecules, k is Boltzmann's constant, C_{1-3} are fixed constants, and T is the absolute temperature. Induction forces are neglected here. The strength of the acceptor–donor complexing term should vary inversely with temperature if the enthalpy of interaction is independent of temperature. The location of the cloud-point curve in pressure–temperature space results from a balance of like and unlike interactions as determined by equation (2), which depends on the physical characteristics of the components in solution.

A poly(ethylene-*co*-methyl acrylate) copolymer with an acrylate content of 31 mol% (EMA$_{69/31}$) is used in this study. Although this copolymer has a fairly broad polydispersity ($M_w = 105\,000$ and $M_n = 22\,600$), Meilchen *et al.*[10] have shown that the phase behaviour is much less affected by polydispersity as compared to the acrylate content in the backbone of the polymer. The cloud-point behaviour of EMA$_{69/31}$ in propane and in hexane is compared with previous data obtained in ethane[11] and butane[12] to demonstrate the effect of increasing only the polarizability of the solvent. *Table 1* lists the physical properties of the solvents used in this study. Non-polar propane is used as the background solvent with the various cosolvents, since propane interacts only by dispersion forces and it is therefore easier to interpret which interactions fix the characteristics of the phase behaviour when a cosolvent is added.

Table 2 lists the physical properties of the cosolvents used in this study. Non-polar hexane and slightly polar 1-hexene are dense liquids that have relatively large polarizabilities. These two cosolvents are used to determine whether increasing the density of compressed propane has an effect on the location of the cloud-point curve, as suggested by equation (1). The alcohol cosolvents have densities that are similar to those of hexane and 1-hexene, but they have very large dipole moments and they can hydrogen bond both to the acrylate repeat units and to themselves. Therefore, the alcohol cosolvents contribute dispersion, polar and hydrogen bonding interactions to the pair potential energy. Since the energy of a hydrogen bond (2–10 kcal mol^{-1})[8] is about an order of magnitude larger than that of dispersion interactions (~0.5 kcal mol^{-1})[13], alcohol–acrylate and alcohol–alcohol hydrogen bonding are expected to have a dramatic influence on the location of the cloud-point curve. Infra-red and ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy studies have been performed to measure the strength of hydrogen-bonded alcohols in carbon tetrachloride[14–17] and in saturated hydrocarbons[17,18]. The exact value of the energy of hydrogen bonding is influenced by the structure chosen for the self-associated alcohols (monomers, linear/cyclic dimers, cyclic/acyclic tetramers, linear/cyclic/branched higher polymers, etc.)[16,19–21]. If the simplest structure model is assumed, the dimer model, the energy of hydrogen bonding decreases with increasing hydrocarbon chain length of the alcohol in the order of methanol > ethanol > propanol > butanol[14–16], as shown in *Table 3*. In addition to self-association, the alcohols hydrogen bond with the acrylate sites in the copolymer. Using infra-red spectroscopy[22,23] and calorimetry[23], the enthalpy of alcohol–ethyl acetate complex formation has been determined, which should be similar to the values expected for alcohol–methyl acrylate complexes. It is interesting that the strength of alcohol–ethyl acetate complex formation is essentially constant, regardless of the hydrocarbon chain length of the alcohol. As with any chemical reaction, the competition between alcohol self-association and alcohol–acrylate complex formation will be a function of the concentration of the groups in solution. The influence of alcohol concentration will be investigated in this study.

EXPERIMENTAL

Cloud-point curves are obtained using a variable-volume cell (see *Figure 1*) made of a high-nickel-alloy steel (Nitronic 50®, 7.0 cm o.d. × 1.59 cm i.d., ~28 cm^3 working volume). A sapphire window (1.9 cm o.d. × 1.9 cm thick) is fitted into one end of the cell to allow for visual observation of the cloud-point transitions. Polymer is loaded into the cell to within ±0.002 g and then the cell is purged with nitrogen followed by propane to ensure that all of the air is removed. The liquid cosolvent is injected into the cell to within ±0.002 g using a syringe, and propane is transferred into the cell gravimetrically to within ±0.05 g using a high-pressure bomb. The solution in the cell is compressed to the desired operating pressure by displacing a movable piston using water pressurized by a high-pressure generator (HIP Inc., model 37-5.75-60). The pressure within the cell is measured with a Heise gauge (Dresser Ind., model CM-108952, 0 to 3450 ± 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 (Degussa Corporation, model no. S0115-01 Platinum, $100\,\Omega \pm 0.03\%$ at 0°C, Class 1) and a digital multimeter (Keithley Instruments, Inc., model no. 195T, accuracy ±0.03%). The solution is stirred by a magnetic bar which is activated by an external magnet. The polymer solution inside the cell is viewed on a video monitor using a borescope (Olympus Corp., model F100-024-000-55) placed against the sapphire window and connected to a video camera. Light is transmitted to the borescope and into the cell with a fibre pipe connected to a high density illuminator (Dolan-Jenner Industries, Inc., model no. 180).

At a fixed temperature, maintained within ±0.2°C, the solution in the cell is compressed to a single phase. The pressure is then slowly decreased until the solution becomes cloudy. The cloud point is defined as the pressure at which the solution becomes so opaque that the stir bar in the cell can no longer be seen. Each transition, repeated at least twice, is reproducible to within ±5 bar at the highest temperatures. In the pressure–temperature region where the cloud-point pressure increases very rapidly for a small change in temperature, the transitions are reproducible to within ±10 bar. The cloud-point curves reported here are obtained at a fixed copolymer concentration of ~5 wt%, which should be close to the true mixture critical concentration[24].

Materials

The poly(ethylene-*co*-methyl acrylate) (31 mol% acrylate) was kindly donated by Dupont Corporation. Propane (CP grade, 99.0% minimum purity) was obtained from Airgas Corporation. Methanol, ethanol, propanol and butanol (all h.p.l.c. grade, 99.5% minimum purity) and hexane and 1-hexene (both 99+%) were obtained from Aldrich Chemical Company, Inc. The copolymer, cosolvents and solvents were used as-received.

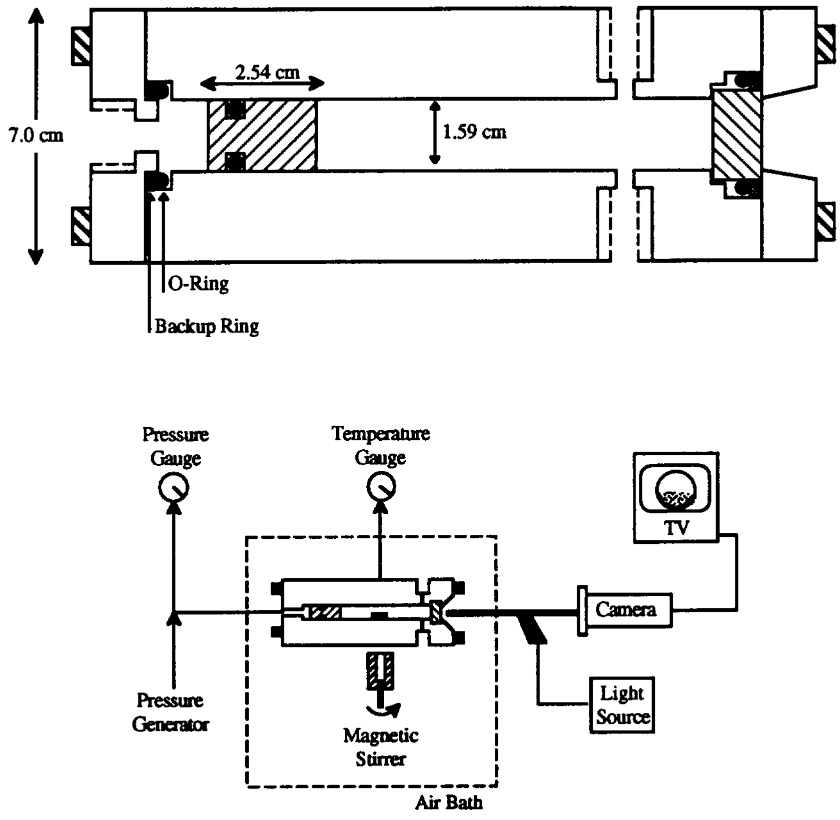

Figure 1 Schematic diagram of the experimental apparatus used to obtain high-pressure cloud-point data

RESULTS

Figure 2 shows the cloud-point curves for $EMA_{69/31}$ in ethane, propane, butane and hexane. Ethane is by far the poorest quality solvent of the four paraffins shown in *Figure 2.* Not only does ethane have the smallest polarizability, but it is also slightly less dense than any of the other paraffins at a given temperature. Therefore, it is necessary to operate at very high pressures to increase the cohesive energy density of ethane to the point at which it can dissolve $EMA_{69/31}$. Increasing the size, and hence the polarizability, of the solvent from ethane to propane shifts the cloud-point curve by as much as 1000 bar. However, the shift in the cloud-point curve is less dramatic as the molecular size of the paraffin increases from propane to hexane. At temperatures above 150°C, where polymer–polymer interactions are expected to diminish, hexane is the best of the four solvents because it has the largest polarizability and it is a liquid to temperatures of ~240°C. All of the cloud-point curves exhibit fairly large increases in pressure with decreasing temperature, which means that copolymer solubility decreases sharply regardless of the cohesive energy density of the solvent. Decreased copolymer solubility results from strong polar interactions between acrylate repeat units in the copolymer at moderate temperatures compared to non-polar dispersion and induction interactions between copolymer repeat units and the non-polar solvents. It is interesting that the cloud-point curve with hexane turns up very rapidly at temperatures near 160°C, while the cloud-point curves for propane and butane turn up less dramatically and they also extend to approximately 25°C lower temperature. Since the copolymer contains 31 mol% polar methyl acrylate repeat units, as the temperature decreases the polar interactions increase. Hexane molecules may be physically too large to interact effectively with the non-polar ethylene segments of the polymer.

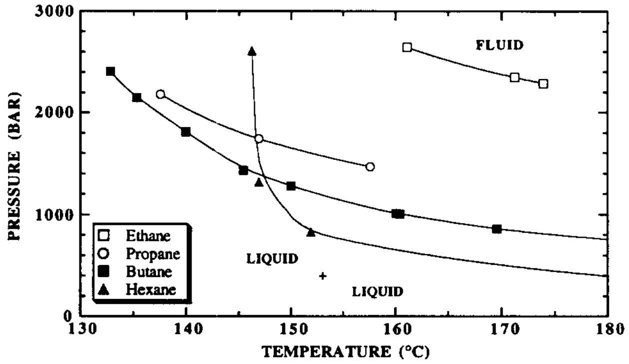

Figure 2 Comparison of the cloud-point behaviour of $EMA_{69/31}$ in ethane[11], propane, butane[12] and hexane

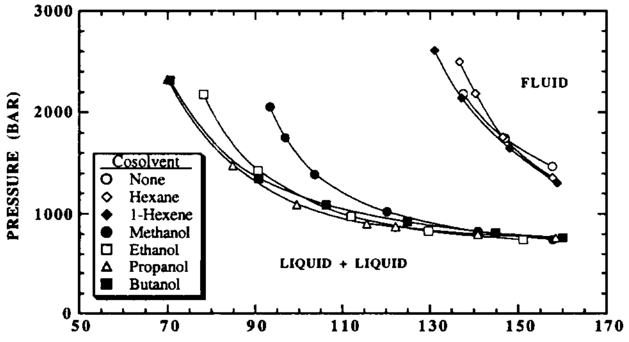

Figure 3 Effect of adding 9.5 wt% of a cosolvent on the cloud-point behaviour of the $EMA_{69/31}$–propane system

Figure 3 shows that neither hexane nor 1-hexene enhances the solubility of $EMA_{69/31}$ in propane. Both hexane and 1-hexene increase the density of propane which, based on equation (1), could have caused the $EMA_{69/31}$–propane cloud-point curve to shift to lower temperatures and pressures if copolymer–solvent and copolymer–cosolvent interactions were favourable. Perhaps it is not surprising that cosolvent density has little impact on the cloud-point curve, since the density of propane is expected to be greater than approximately 0.5 g cm^{-3} at pressures above 500 bar in the temperature range shown in *Figure 3*[25]. At high solution densities the small dipole moment of 1-hexene is expected to interact favourably with the acrylate groups in $EMA_{69/31}$; however, the effect of the dipole moment is diminished due to the large volume over which the dipole operates in 1-hexene[26].

Figure 3 also contrasts the effect of hexane and 1-hexene with that of methanol, ethanol, n-propanol and n-butanol on the location of the cloud-point curve at a constant cosolvent concentration of 9.5 wt%. Notice that the addition of an alcohol shifts the cloud-point curves significantly to lower temperatures and pressures. The enhanced miscibility of $EMA_{69/31}$ in propane–alcohol mixtures is attributed to the favourable hydrogen bonding between the alcohol and the acrylate groups in the backbone of the copolymer. At temperatures greater than 130°C, the cloud-point curves for the four alcohol cosolvents essentially superpose at approximately 500 bar lower pressure than the hexane and 1-hexene curves. The difference in the location of the cloud-point curves at high temperatures for hexane or 1-hexene *versus* the alcohol cosolvents is a result of the favourable acrylate–alcohol polar interactions as well as a small amount of acrylate–alcohol hydrogen bonding which occurs even at high temperatures.

Notice that of the four alcohol cosolvents, methanol is the least effective at increasing copolymer miscibility at temperatures below 110°C. To explain why methanol is so poor at low temperatures relative to the other alcohols, it is necessary to compare the strength of alcohol–acrylate complexing, an interaction that favours copolymer solubility, with that of alcohol self-association, an interaction that decreases copolymer solubility.

As previously mentioned in the Introduction, the alcohol dimerization energy listed in *Table 3* decreases with increasing size of the hydrocarbon chain length of the alcohol. Notice that the enthalpies of dimerization for methanol and ethanol are much larger than their respective enthalpies of complexation with ethyl acetate. Notice also that the strength of the alcohol–acetate complex, which should be similar in magnitude to an alcohol–acrylate complex, remains essentially constant, regardless of the hydrocarbon chain length of the alcohol. The data in *Table 3* suggest that the propensity for alcohol self-association increases with decreasing temperature much faster than does the propensity of forming an alcohol–acrylate complex. From the data listed in *Table 3*, it is also apparent that methanol, and to a

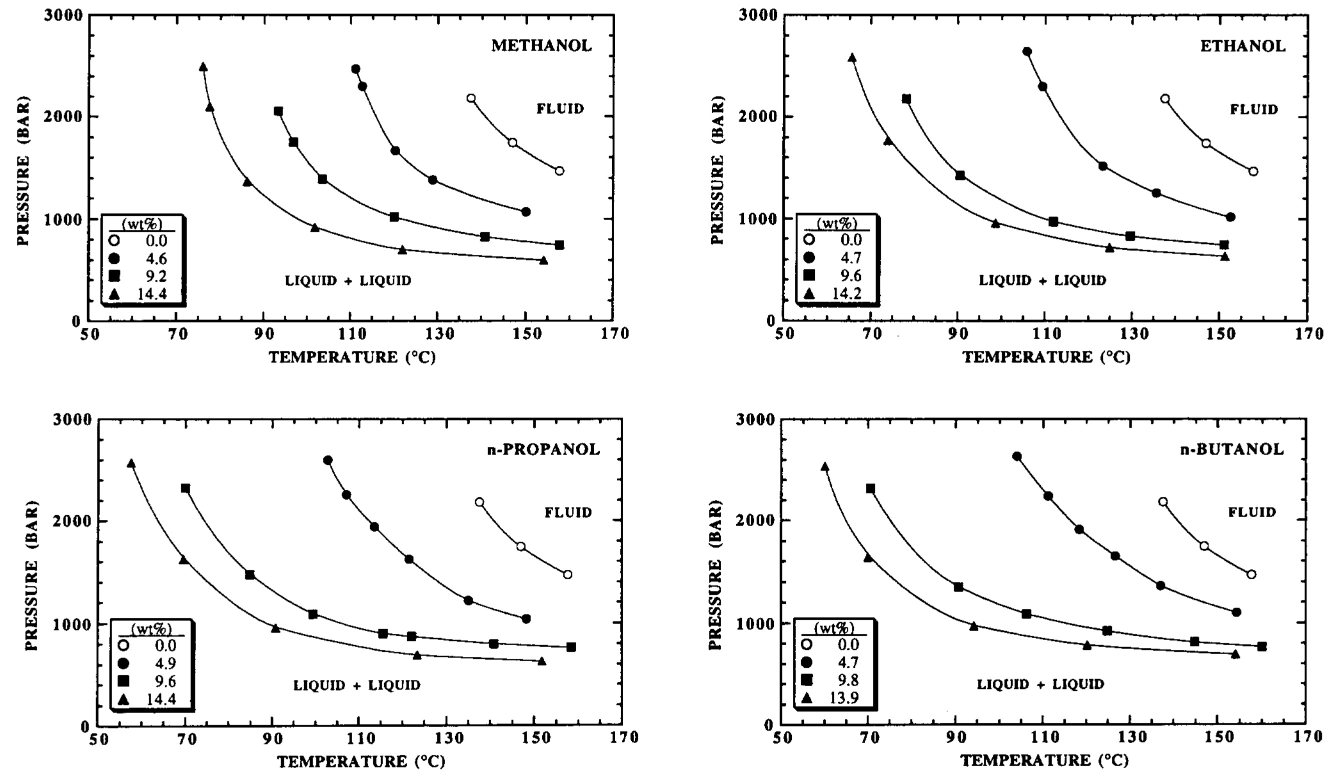

Figure 4 Effect of methanol, ethanol, n-propanol and n-butanol, in concentrations of 0.0, 5.0, 9.5 and 14.5 wt%, on the cloud-point behaviour of $EMA_{69/31}$–propane mixtures

lesser degree ethanol, self-associates more readily at low temperatures than do n-propanol and n-butanol. Therefore, the beneficial effects of methanol diminish more rapidly as the temperature is lowered than do the beneficial effects of ethanol, n-propanol or n-butanol.

Figure 4 illustrates the effect of alcohol concentrations, from 0 to 15 wt%, on the miscibility of $EMA_{69/31}$ in propane–alcohol mixtures. In general, the effect of the alcohol cosolvent on the location of the cloud-point curve becomes less pronounced with increasing amounts of cosolvent in the mixture. The reduction of the beneficial effects of an alcohol cosolvent is a direct result of the specific complexing or hydrogen bonding, which depends on the number of sites available to accept or donate a proton. $EMA_{69/31}$ becomes increasingly soluble in propane as each of the acrylate sites are complexed with alcohol cosolvent molecules. However, an increased amount of alcohol also means that the alcohol self-associates more readily, which has the negative effect of causing the solvent mixture to become more polar. Eventually, at high enough alcohol concentrations, the pair potential energy will be dominated by alcohol–alcohol interactions as opposed to copolymer–solvent or copolymer–cosolvent interactions, and the copolymer will fall out of solution.

Comparing the four graphs in *Figure 4* shows that, again, the beneficial effects of alcohol cosolvent concentration fall off inversely with the size of the hydrocarbon chain on the alcohol, which is directly related to the strength of the enthalpy of association. It should be remembered that, per mole of alcohol, a very polar hydroxyl 'head' and a non-polar hydrocarbon 'tail' are added to the solution. Methanol is the poorest of the alcohol cosolvents since, on a molar basis, it contributes the largest concentration of hydroxyl groups to the solution. Ethanol is a better cosolvent than methanol, as it contributes a hydroxyl and an ethyl chain that interact favourably with the 69 mol% non-polar ethylene repeat units in $EMA_{69/31}$. The magnitudes of the n-propanol and n-butanol effects appear to be quite similar, suggesting that increasing the hydrocarbon chain length of the alcohol beyond four carbons would have no further beneficial effect on the solubility of $EMA_{69/31}$ in solution. In fact, it could have a detrimental effect on the solubility behaviour. This speculation is corroborated by the results shown in *Figure 2*, which demonstrate that the beneficial effect of increasing the chain length of a paraffinic solvent falls off rapidly from ethane to butane. LoStracco[27] has shown that the cosolvent effects of isopropanol and tert-butanol cannot be distinguished from those of the straight-chain analogues. Evidently, for these systems the structure of the alcohol has no effect on the cloud-point behaviour.

It should be noted that Meilchen *et al.*[6,7] also report that reproducible cloud points are obtained for the $EMA_{69/31}$–propane–ethanol system at ethanol concentrations greater than 10 wt%. However, they also report the presence of a considerable amount of droplets in solution which remain undissolved regardless of pressure. They concluded that ethanol acts as a non-solvent at concentrations greater than 10 wt%, causing the copolymer to precipitate from solution. In the present study, cloud-point data are obtained for $EMA_{69/31}$ in a mixture of 15 wt% ethanol with propane. The one-phase region for this mixture was extremely bright and clear and the transitions were sharp. We conjecture that Meilchen's earlier studies were performed with an $EMA_{69/31}$ sample that was slightly contaminated with polyethylene. At temperatures below ~135°C, approximately the temperature range of Meilchen's experiments, polyethylene does not dissolve in mixtures of propane with high alcohol concentrations. Up to 10 wt% ethanol, the results from both studies are in good agreement.

CONCLUSIONS

We have shown that the addition of a dense liquid cosolvent does not affect the cloud-point behaviour of poly(ethylene-*co*-methyl acrylate) (31 mol% methyl acrylate, $EMA_{69/31}$)–propane mixtures at kilobar operating pressures. However, alcohol cosolvents dramatically lower the pressures and temperatures of the cloud-point curves, owing to hydrogen bonding between the alcohol cosolvent and the acrylate repeat units in the polymer. At high temperatures all of the $EMA_{69/31}$–propane–alcohol curves superpose, suggesting that the hydrogen bonding between alcohol–alcohol molecules and alcohol–acrylate repeat units is minimal. As the temperature is lowered, the cloud-point curves increase rapidly in pressure due to an increase in alcohol self-association, with methanol self-associating to a greater extent than the other alcohols studied. The beneficial effect of an alcohol cosolvent decreases as its concentration increases, owing to the saturation of the polar acrylate sites on the polymer and greater alcohol self-association.

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