Poly(ethylene-*co*-methyl acrylate)–solvent–cosolvent phase behaviour at high pressures

Melchior A. Meilchen, Bruce M. Hasch, Sang-Ho Lee and Mark A. McHugh*
Department of Chemical Engineering, Johns Hopkins University, Baltimore, MD 21218, USA

(Received 5 April 1991; accepted 15 July 1991)

Cloud-point data to 160°C and 2000 bar are presented showing the effect of cosolvents on the phase behaviour of poly(ethylene-*co*-methyl acrylate) (EMA) (64 mol%/36 mol%) with propane and chlorodifluoromethane (F22). Ethanol shifts the EMA–propane cloud-point curves to lower temperatures and pressures, but above ~10 wt% ethanol, the copolymer becomes insoluble. Up to 40 wt% acetone monotonically shifts the EMA–propane cloud-point curves to lower temperatures and pressures. Acetone and ethanol both shift the cloud-point curves of EMA–F22 mixtures in the same monotonic manner for cosolvent concentrations of up to 40 wt%.

(Keywords: copolymer; cosolvent; high pressures)

INTRODUCTION

Within the past 20 years there has been a great deal of effort invested in trying to understand and model the solubility behaviour of polar polymers in liquid cosolvent mixtures[1–9]. Polymer solubility is usually related to whether the cosolvent preferentially solvates or adsorbs to certain segments of the polymer chain as determined by light scattering, viscosity measurements or cloud-point measurements. The effect of preferential adsorption on improving the solubility of the polymer in solution can be quite dramatic if the cosolvent can hydrogen bond to the polymer. For example, Wolf and Blaum[9] report that ~10 mol% of 2-butanol added to poly(methyl methacrylate)–chlorobutane mixtures lowers the upper critical solution temperature by as much as 70°C. However, too much alcohol added to the solution can lead to a decrease in the solvent power of the mixture since the alcohol hydrogen bonds to itself and forms long chain structures whose length increases rapidly when the alcohol concentration exceeds ~20 mol%[10]. As the alcohol self-associates, the solvent characteristics also change as evidenced by the rapid increase in the dielectric constant of the solvent mixture[11,12]. For cosolvents which do not hydrogen bond to the polymer, more modest changes in solubility behaviour are observed. When 4-heptanone is added to PMMA–chlorobutane mixtures, the upper critical solution temperature decreases monotonically over only a 10°C range with ketone concentration[9].

Wolf and Blaum[13] have also investigated the effect of pressure on cosolvency for the polystyrene (PS)–acetone–diethyl ether system. At low pressures, high molecular PS ($M_n = 110000$) is not soluble in either liquid acetone or diethyl ether, so it is necessary to operate at elevated temperatures and pressures to dissolve high molecular weight polystyrene in either solvent. Adding acetone to PS–diethyl ether mixtures monotonically reduces the pressure needed at a given temperature to obtain a single phase.

There has also been a number of viscometric and light scattering studies on the solution behaviour of polar copolymers in liquid cosolvent mixtures[14,15]. However, only a limited number of high pressure phase behaviour studies on copolymer systems have been reported in the literature. Rätzsch and coworkers[16–18] present information on the poly(ethylene-*co*-vinyl acetate) (EVA)–ethylene–vinyl acetate system. They show that at 160°C, vinyl acetate cosolvent depresses the EVA–ethylene cloud-point pressure by as much as 400 bar and it reduces the slope of the cloud-point curve. Rätzsch and coworkers also describe the use of Flory's equation of state to calculate cloud-point curves and pressure–composition curves. Luft and Subramaniam[19] present experimental information on the effect of methyl acrylate cosolvent on the cloud-point behaviour of three poly(ethylene-*co*-methyl acrylate) copolymers of differing acrylate content dissolved in ethylene. It is difficult to interpret their data since, not only did the methyl acrylate content differ in each polymer, the polydispersity of the polymer and the molecular weight were also different. Also, Luft and Subramaniam do not present any information on the solubility of the copolymers in neat ethylene so it is not possible to interpret the effect of methyl acrylate as a cosolvent on the phase behaviour.

In this paper we present results from an experimental investigation of the effect of two cosolvents, ethanol and acetone, on the cloud-point curves of poly(ethylene-*co*-methyl acrylate) (EMA) (64 mol%/36 mol%) in propane and chlorodifluoromethane (F22). A poly-

---

*To whom correspondence should be addressed

0032-3861/92/091922-04

Table 1 Properties of propane, chlorodifluoromethane, acetone and ethanol[25]

Component	T_c (°C)	P_c (bar)	Critical density (g cm^{-3})	Dipole moment (Debye)
C_3H_8	96.7	42.5	0.217	0.0
$CHCLF_2$	96.2	49.7	0.522	1.4
$(CH_3)_2CO$	234.9	47.0	0.278	2.9
CH_3CH_2OH	243.1	63.8	0.276	1.7

disperse sample of EMA (M_w = 108 000; M_w/M_n = 4.66) and a more monodisperse sample (M_w = 91 800; M_w/M_n = 1.49) are used in this study. The properties of the two solvents and cosolvents shown in *Table 1* differ considerably. F22 has a critical temperature and pressure close to that of non-polar propane. However, F22 possesses a large dipole moment and it has a critical density which is more than twice that of propane. The more important property difference between F22 and propane is that F22 can hydrogen bond to the acrylate group in the backbone of the copolymer. Although both cosolvents, acetone and ethanol, are very polar, ethanol is expected to hydrogen bond with itself and with the basic acrylate group in the backbone of the copolymer, while acetone, which is a basic molecule, does not hydrogen bond either to itself or to the acrylate group in the copolymer. Using these two cosolvents it should be possible to ascertain the importance of polarity and hydrogen bonding on the phase behaviour.

EXPERIMENTAL

The cloud-point curves are obtained using a high-pressure, variable-volume, view cell[20-22] which is briefly described. The cell is constructed of a high nickel alloy steel (Nitronic 50, 5.7 cm OD × 1.59 cm ID, ~22 cm^3 working volume, fitted with a 1.9 cm OD × 1.3 cm thick sapphire window) that allows for very high pressure operation. It is first loaded with a measured amount of polymer to within ±0.002 g. The liquid cosolvent is transferred into the cell to within ±0.002 g using a syringe to minimize any loss due to vaporization. The gas of interest is then transferred into the cell gravimetrically to within ±0.002 g using a high-pressure bomb. The pressure of the polymer solution is measured to within ±2.8 bar using a Heise gauge. The temperature of the cell is measured to within ±0.2°C with a platinum-resistance device connected to a digital multimeter and is also maintained to within ±0.2°C. The contents of the cell are well mixed with a stir bar which is activated by an external magnet.

Cloud-point determinations are done at constant polymer concentration, which in this study is maintained between 4.0 and 5.2 wt%. The polymer-gas mixture in the cell is projected onto a video monitor using a borescope (Olympus Corporation, model D100-048-000-90) placed against the sapphire window and connected to a video camera. The cloud-point pressure, which is obtained with a reproducibility which is typically ±5 bar, is defined as the pressure at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. With the borescope-camera system, the image of the solution is enhanced and it is possible to observe when very small amounts of polymer fall out of solution which would be undetected with the naked eye.

Materials

The EMA was kindly donated by DuPont Corporation and was fractionated in our laboratory as described elsewhere[21]. Propane (CP grade, 99.0% minimum purity) was obtained from Linde Corporation and chlorodifluoromethane (99.8% minimum purity) was obtained from Matheson Gas Products.

RESULTS

EMA-F22 mixtures

Cloud-point data for the EMA-F22-cosolvent system are presented in *Figure 1*. The liquid-liquid-vapour (LLV) lines, which are expected to superpose on the vapour pressure curve of pure F22, are not shown in *Figure 1*. Since it was found that the location and slope of the P-T trace of the cloud-point curve for the EMA-F22 system was only slightly sensitive to polydispersity and molecular weight[21], the cosolvent effect of ethanol and acetone in F22 was only determined on the more polydisperse parent copolymer. As shown in *Figure 1*, the magnitude of the effect of ethanol and acetone on the EMA-F22 system is virtually identical. The addition of either cosolvent increases the single-phase region and as much as 40 wt% of either cosolvent can be added to the solution while still maintaining a single phase. Based on the observation that ethanol and ethyl acetate hydrogen bond to one another[24], it is reasonable to expect ethanol to hydrogen bond to the methyl acrylate group in the copolymer. Acetone does not hydrogen bond to the copolymer acrylate group but, assuming the behaviour of F22 is similar to chloroform, acetone is expected to hydrogen bond to F22[24].

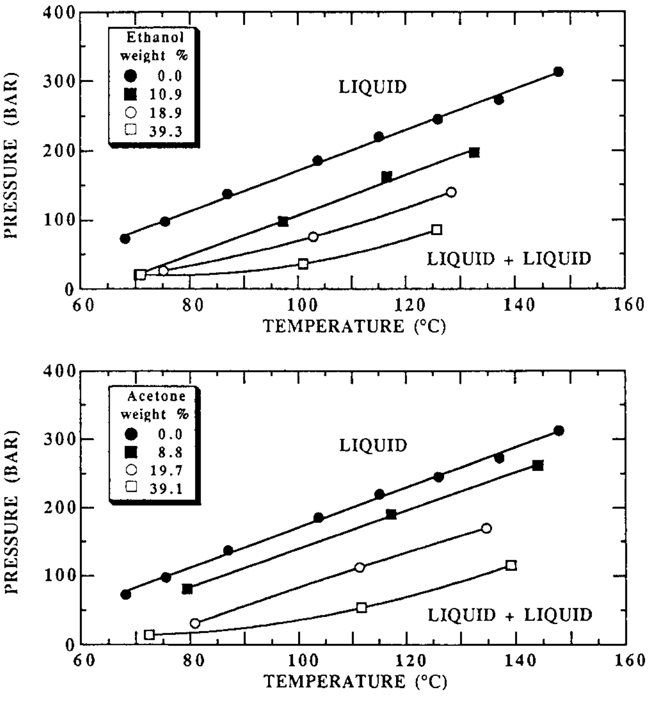

Figure 1 Effect of ethanol and acetone cosolvents on the phase behaviour of poly(ethylene-*co*-methyl acrylate)-chlorodifluoromethane mixtures. The concentration of copolymer in solution is 5.0 wt%. The copolymer has an M_w of 108 000 and an M_N of 23 200

A plausible explanation for the similar cosolvent behaviour of acetone and ethanol is that F22 moderates the effect of ethanol in two ways. F22, which is in excess relative to the copolymer concentration, competes with ethanol to hydrogen bond to the methyl acrylate group in the copolymer. F22 also hydrogen bonds to ethanol and disrupts ethanol's propensity to self-associate at high ethanol concentrations and to exhibit 'antisolvent' characteristics for this high ethylene-content copolymer. It should be noted that in F22, ethanol acts in a manner similar to acetone which improves the quality of the solvent for this polar polymer by increasing only the polarity of the solvent mixture. Unlike ethanol, F22 does not hydrogen bond to itself and, therefore, excess amounts of F22 in solution are not detrimental to its solvent capabilities.

EMA–propane mixtures

Figure 2 shows the effect of ethanol on the cloud-point curve of the EMA–propane system. Consider first the difference in cloud-point behaviour for EMA dissolved in neat propane and in neat F22. The cloud-point curve for the EMA–F22 system is at lower temperatures and as much as 1600 bar lower pressures than the cloud-point curve of the EMA–propane system. It is interesting that F22 is a better solvent for EMA than propane since the copolymer used in this study contains 64 mol% ethylene and propane dissolves polyethylene while F22 does not. Evidently there is a sufficient amount of hydrogen bonding between F22 and the methyl acrylate groups in the backbone of the copolymer to compensate for the lack of polyethylene solubility in F22. At elevated temperatures near 150°C and 300 bar, F22 is more than twice as dense as propane at the same temperature and pressures to 2000 bar. The higher density of F22 facilitates the hydrogen bonding and polar interactions with the copolymer even at temperatures as high as 150°C where F22 still exhibits a dielectric constant as high as ~4[23]. Non-polar propane is such a poor solvent for EMA that it is necessary to increase the system temperature high enough to reduce polymer–polymer interactions to make the polymer accessible to the solvent. But, at these high temperatures elevated pressures are needed to increase the density of propane to reduce the free volume difference between the polymer and solvent, and thus, make the polymer soluble in propane.

As shown in *Figure 2*, when ethanol is added to EMA–propane mixtures the cloud-point curves are shifted to lower temperatures and pressures but they remain essentially parallel. Hence, ethanol expands the region of miscibility of this copolymer in propane. Note, however, that the effect of ethanol diminishes as its concentration increases above ~2.5 wt%. For example, at a fixed pressure of ~1800 bar, 2.5 wt% ethanol decreases the cloud-point pressure by 18°C. If the concentration of ethanol is increased from 2.5 to 4.3 wt% the curve only shifts another 10°C. If the concentration of ethanol is more than doubled to 10 wt%, the cloud point curve is shifted only another 10°C. However, using the borescope–camera system, we can detect that a minute amount of polymer is present during the cloud-point determinations at 10 wt% ethanol and that this small amount of polymer remains undissolved even if the system pressure is increased 1000 bar above the cloud-point pressure at a given temperature. At ethanol concentrations greater than 10 wt%, it is still possible to obtain reproducible cloud-points, but there is now a considerably larger amount of polymer which remains undissolved regardless of pressure.

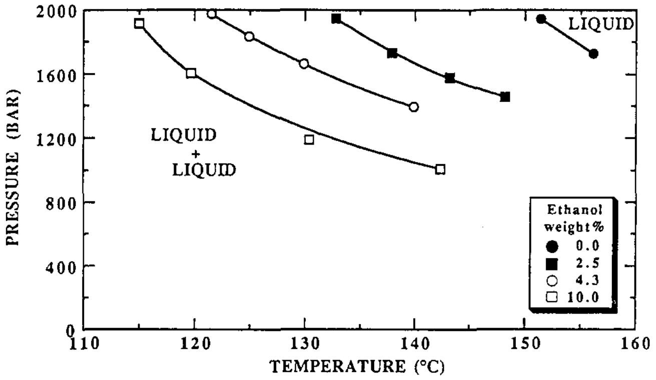

Figure 2 The effect of ethanol cosolvent on the phase behaviour of poly(ethylene-*co*-methyl acrylate)–propane mixtures. The concentration of copolymer in solution is 5.0 wt%. The copolymer has an M_w of 137000 and an M_N of 91800

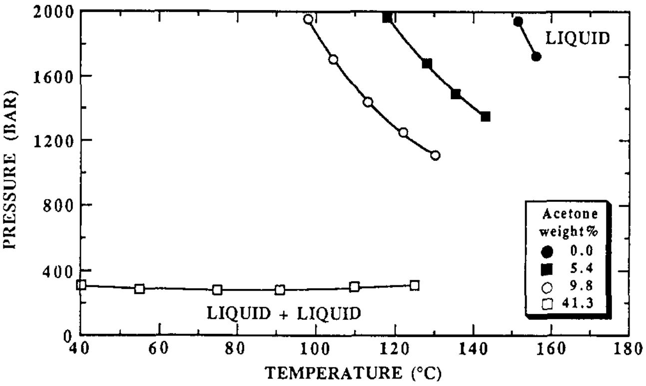

Figure 3 Effect of acetone cosolvent on the phase behaviour of poly(ethylene-co-methyl acrylate)–propane mixtures. The concentration of copolymer in solution is 5.0 wt%. The copolymer has an M_w of 137000 and an M_N of 91800

The concentration-dependent cosolvent effect of ethanol can be explained by its hydrogen-bonding tendencies. More than likely, the first amount of ethanol added to the solution exists in a monomeric form[10] which hydrogen bonds to the methyl acrylate group in the EMA. Eventually all of the acrylate sites become occupied so that as more ethanol is added to solution it will self-associate and eventually become an 'antisolvent' for this high ethylene-content copolymer.

The maximum temperature shift in the EMA–propane cloud-point curve with 10 wt% ethanol is about one half the value found for the temperature shift of the upper critical solution temperature curve for the chlorobutane–PMMA system with 10 wt% 2-butanol[9]. The difference in the magnitude of these two cases can be explained by recognizing that the copolymer used in this study is only 36 mol% methyl acrylate compared to PMMA which is a polar homopolymer. In addition, less hydrogen bonding is expected at the temperatures investigated in our study which are up to 150°C higher than those of the PMMA study.

The cloud point curves in *Figure 3* show that adding acetone to the solution shifts the cloud-point curves to lower temperatures and pressures. It initially takes twice as much acetone (5.4 wt%) compared to ethanol

(2.5 wt%) to shift the curve 20°C at a fixed pressure of 1800 bar. However, both acetone and ethanol at 10 wt% shift the EMA–propane cloud-point curve by approximately the same amount, 40°C. With acetone, however, the copolymer remains in solution even for concentrations as high as 40 wt% and we do not detect undissolved polymer above the cloud-point pressures. The effect of acetone on reducing the cloud-point temperature, or equivalently expanding the region of miscibility, is monotonic with the amount of acetone added to the solution in contrast to ethanol which exhibits a 'synergistic cosolvent' effect that reverts to 'antisolvent' behaviour at ethanol concentrations above ~10 wt%. The intermolecular forces of attraction between a methyl acrylate segment and an acetone molecule are polar and dispersion forces only, which are physical forces that do not become saturated. In contrast, the intermolecular forces of attraction between a methyl acrylate segment and an ethanol molecule include not only the physical forces found with acetone, but also a specific chemical force of attraction, hydrogen bonding, which can become saturated.

CONCLUSIONS

Polar cosolvents can increase the pressure–temperature region of miscibility of a polar copolymer dissolved in a non-polar solvent. Although a polar cosolvent increases the polarity of the mixed solvent, a larger effect is observed per mole of cosolvent if the cosolvent also hydrogen bonds to one of the groups in the backbone of the copolymer. The maximum concentration of hydrogen-bonding cosolvent that can be added to solution and still obtain a beneficial effect depends on the number of copolymer–cosolvent complexes that can potentially form in solution. Polar cosolvents, whether they hydrogen bond or not, also increase the region of miscibility of a polar copolymer dissolved in a hydrogen bonding solvent. The effect of a hydrogen bonding cosolvent is moderated in the presence of a hydrogen bonding solvent.

While it is possible to obtain a semi-quantitative description of the phase behaviour of polymer–solvent–cosolvent mixtures using a mean-field equation of state with random mixing rules[9], modelling copolymer–solvent–cosolvent phase behaviour is slightly more complicated if pure component copolymer data are not available to fit equation of state parameters. The modelling for the systems presented in this paper is addressed in a future publication.

ACKNOWLEDGEMENT

We thank the National Science Foundation for partial support of this project under grant EET-88-15629.

REFERENCES

1 Cowie, J. M. G. and McCrindle, J. T. *Eur. Polym. J.* 1972, **8**, 1185
2 Cowie, J. M. G. and McCrindle, J. T. *Eur. Polym. J.* 1972, **8**, 1352
3 Cowie, J. M. G. and McEwen, I. J. *Macromolecules* 1974, **7**, 291
4 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1983, **24**, 1449
5 Katime, I. A., Sasia, P. M. and Eguia, B. *Eur. Polym. J.* 1988, **24**, 1159
6 Blanco, M. D., Teijon, J. M. and Katime, I. A. *Eur. Polym. J.* 1990, **26**, 249
7 Palaiologou, M., Viras, F. and Viras, K. *Eur. Polym. J.* 1988, **24**, 1191
8 Viras, F. and Viras, K. *J. Polym. Sci.: Part B: Polym. Phys.* 1988, **26**, 2525
9 Wolf, B. A. and Blaum, G. *J. Polym. Sci.: Part B: Polym. Phys.* 1975, **13**, 1115
10 Prausnitz, J. M., Lichtenthaler, R. N. and Azevado, E. G. 'Molecular Thermodynamics of Fluid Phase Equilibria', 2nd Edn, Prentice-Hall, New York, 1986, ch. 10, p. 343
11 Diguet, R., Duel, R. and Franck, E. U. *Ber. Bunsenges. Phys. Chem.* 1987, **91**, 551
12 Dombro, R. A., Prentice, G. A., Westgate, C. A. and McHugh, M. A. *Fluid Phase Equil.* 1991, **1**, 221
13 Wolf, B. A. and Blaum, G. *Makromol. Chem.* 1976, **177**, 1073
14 Simionescu, C. I., Simionescu, B. C. and Ioan, S. *Macromolecules* 1985, **18**, 1995
15 Simionescu, C. I., Simionescu, B. C. and Ioan, S. *Makromol. Chem.* 1983, **184**, 829
16 Rätzsch, M. T., Findeisen, R. and Sernow, V. S. *Z. Phys. Chem.* 1980, **261**, 995
17 Wohllfarth, Ch., Wagner, P., Glindemann, D., Völkner, M. and Rätzsch, M. T. *Acta Polym.* 1984, **35**, 498
18 Browarzik, D., Rätzsch, M. T. and Wohlfarth, Ch. *Acta Polym.* 1984, **35**, 498
19 Luft, G. and Subramaniam, N. S. *Ind. Eng. Chem. Res.* 1987, **26**, 750
20 McHugh, M. A. and Guckes, T. L. *Macromolecules* 1985, **18**, 674
21 Meilchen, M. A., Hasch, B. M. and McHugh, M. A. *Macromolecules* 1991, **24**, 4874
22 Seckner, A. J., McClellan, A. K. and McHugh, M. A. *AIChE* 1988, **34**, 9
23 Uematsu, M. and Franck, E. U. *Ber. Bensenges. Phys. Chem.* 1989, **93**, 177
24 Joesten, M. D. and Schaad, L. J. 'Hydrogen Bonding', Marcel Dekker, New York, 1974, Appendix, p. 291
25 Reid, R. C., Prausnitz, J. M. and Polling, B. E. 'The Properties of Gases and Liquids', 4th Edn, McGraw-Hill, New York, 1987