

Phase behaviour studies with poly(ethylene-co-methacrylic acid) at high pressures

Sang-Ho Lee and Mark A. McHugh*

Department of Chemical Engineering, Johns Hopkins University, Baltimore, MD 21218, USA

(Received 15 April 1996; revised 30 May 1996)

Experimental cloud-point data are reported for poly(ethylene-co-3.9 mol% methacrylic acid) (EMAA_{3.9}) in ethylene, propane, butane, butene, and dimethyl ether (DME) to 250°C and 2500 bar. The cloud-point data for both EMAA_{3.9} and poly(ethylene-co-3.9 mol% acrylic acid) are virtually identical suggesting that the structural differences between these two acid copolymers does not have a significant effect on phase behaviour. Cloud-point data are presented that demonstrate the impact of methacrylic acid (MAA) content for EMAA copolymers with 0, 3.1, 3.9, and 5.4 mol% MAA in butane, butene, and DME. The region of miscibility in butane and butene decreases significantly with temperature and with increasing copolymer acid content due to dimerization of the acid groups. However, the region of miscibility in DME increases slightly with MAA content due to the cross association with the acid repeat units. Cloud-point data are reported on the impact of DME and ethanol on the phase behaviour of poly(ethylene-co-3.1 mol% methacrylic acid) (EMAA_{3.1}) in butane. At low concentrations, ethanol is a more effective cosolvent since it has two sites that can participate in hydrogen bonding with MAA. The impact of both cosolvents diminishes rapidly with increasing cosolvent concentration once all the acid sites in EMAA are saturated with cosolvent. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene-co-methacrylic acid); phase behaviour; high pressures)

INTRODUCTION

The free-radical polymerization of polyethylene and ethylene-based copolymers is normally operated in the single-phase region at temperatures ranging from 100 to 200°C and pressures as high as 2000 bar to solubilize the high-molecular weight polymers which are formed in ethylene. The pressures and temperatures needed to maintain a single phase can be exacerbated when ethylene is copolymerized with a polar comonomer and especially with a comonomer that can cross associate or self associate. A large number of studies have been conducted to determine the impact of comonomer polarity and hydrogen bonding on the phase behaviour of ethylene-based copolymers^{1–10}. Gregg *et al.*^{4,5} demonstrated that the location of the cloud-point curve is influenced by intra- and inter-polymer hydrogen bonding of polyisobutylenes with monohydroxy and dihydroxy end caps. It should be noted that the impact of the hydroxy end caps is magnified in this instance since the polyisobutylenes had molecular weights of approximately 1000. Extensive phase-behaviour studies have been performed with poly(ethylene-co-acrylic acid) (EAA) copolymers that contain up to 10 mol% acid groups in the backbone of the copolymer. Luft and Wind⁹ reported that the phase behaviour of EAA-ethylene mixtures was influenced by the dimerization of the acrylic acid groups in EAA even at 220°C. Lee *et al.*^{1,2} determined that acrylic acid content has a greater

impact on the location of the cloud-point curve than does molecular weight. Also, the location of the cloud-point is sensitive to the quality of the solvent and to temperature due to the dominant effect of the dimerization of the acrylic acid groups. Lee *et al.*¹¹ showed that the location of the cloud-point curves for EAA-butane mixtures are sensitive to small concentrations of cosolvents that are capable of hydrogen bonding with the acid groups. Reported in this paper is the effect of copolymer acid content, solvent quality, and cosolvent type for poly(ethylene-co-methacrylic acid) (EMAA) copolymers.

In the initial experiments performed in this study, the phase behaviour of EMAA_{3.9} (the subscript 3.9 represents the mol% acid in the backbone) is contrasted with that for EAA_{3.9} in ethylene, propane, butane, butene, and dimethyl ether (DME). Even though the structural difference between acrylic and methacrylic acid is modest, Rindfleisch *et al.*¹² have found that this small difference in structure can lead to a large difference in the location of the cloud-point curve for similarly related polymers, such as poly(methyl acrylate) and poly(methyl methacrylate), in weak solvents, such as carbon dioxide. The pK_a of propanoic acid (4.87) is almost the same as 2-methyl propanoic acid (4.85), which are the corresponding monomeric acids for EAA and EMAA, respectively. Spectroscopic studies show that the dimerization strengths of MAA and AA in these copolymers are also very similar (10.5–11.5 kcal mol⁻¹)^{13–16}. Table 1 lists the properties of the EMAA and EAA copolymers, and the polyethylene (PE) used in this study. The acid content of the EMAA copolymers are 3.1 (EMAA_{3.1}), 3.9

* To whom correspondence should be addressed

(EMAA_{3,9}), and 5.4 (EMAA_{5,4}) mol%. The weight average molecular weights of the parent acid copolymers are all $\sim 100\,000$. Although the molecular weight polydispersities are fairly large for these copolymers, previous studies show that the acid content has a much larger effect on the cloud-point behaviour than does molecular weight polydispersity².

Table 2 lists the properties of the five solvents used in this study. Ethylene is chosen since it is the primary solvent and reactant used in the high-pressure, free-radical copolymerization of these copolymers. Information on the impact of solvent polarizability and density is obtained by comparing the cloud-point behaviour in propane and butane. The difference between cloud-point pressures at a given temperature for EMAA in butane and in butene provides information on the impact of polar interactions and of the weak complexes^{2,19} that are expected to form between the π -electrons in butene and methacrylic acid repeat units. DME can hydrogen bond to the acid groups in the backbone of the copolymer and, therefore, comparing the phase behaviour of EMAA in DME to that in butane provides a measure of the impact of solvent-acid hydrogen bonding on the location of the cloud-point curve. In addition, the effect of methacrylic acid content on cloud-point behaviour is determined in butane, butene, and DME.

Two different cosolvents, DME and ethanol, are used with the EMAA_{3,1}-butane system. The properties of these two cosolvents are given in Table 2. DME and butane are miscible at all temperatures, above approximately 60 bar²⁰. Since DME does not hydrogen bond to itself, it should be possible to vary the concentration of DME in butane from zero to 100% and maintain a single phase at low to moderate temperatures. The cosolvent effect of DME is contrasted with that of ethanol which not only hydrogen bonds to the acid groups in the copolymer, but, it also hydrogen bonds to itself.

Table 1 Physical properties of polyethylene (PE), poly(ethylene-co-3.9 mol% acrylic acid), poly(ethylene-co-3.1 mol% methacrylic acid), poly(ethylene-co-3.9 mol% methacrylic acid), and poly(ethylene-co-5.4 mol% methacrylic acid) used in this study. The molecular weight of poly(ethylene-co-acrylic acid) and poly(ethylene-co-methacrylic acid) are based on PE standards and are correlated for the acid content of the copolymer

Polymer	Acid content (mol%)	Crystallinity (%)	M_n	M_w	M_w/M_n
PE	0.0	36.8	20 100	108 000	5.4
EAA _{3,9}	3.9	36.3	21 000	123 100	5.9
EMAA _{3,1}	3.1	36.5	16 600	102 150	6.2
EMAA _{3,9}	3.9	32.7	16 150	103 700	6.4
EMAA _{5,4}	5.4	—	13 900	69 000	5.0

Table 2 Physical properties of the solvents and cosolvents used in this study^{17,18}

Component	T_c (°C)	P_c (bar)	α ($\text{cm}^3 \cdot 10^{25}$)	μ (D)	(Proton acceptor/Donor)
Ethylene	9.2	50.4	42.3	0.0	Weak acceptor
Propane	96.7	42.7	62.9	0.0	None
<i>n</i> -Butane	152.1	38.0	81.4	0.0	None
<i>l</i> -Butene	146.4	39.7	82.4	0.4	Weak acceptor
Dimethyl ether ^a	126.8	53.0	52.2	1.3	Strong acceptor
Ethanol	240.8	63.8	51.1	1.7	Strong acceptor and donor

^a Does not self-associate, but is able to form complexes with acrylic acid groups

Interpreting which molecular interaction governs the phase behaviour of EMAA-butane-ethanol mixtures is more complex since ethanol can cross associate with the MAA groups in the copolymer and it can also self associate. Lee *et al.*¹¹ show that ethanol, by itself, cannot dissolve EAA_{3,9} and EMAA_{3,1}; therefore, pure ethanol is not expected to dissolve EMAA_{3,9}. It is also important to note that ethanol and butane are expected to form a single phase at pressures greater than 100 bar in the temperature range investigated in this study²¹⁻²⁴.

EXPERIMENTAL

Cloud points, measured at a fixed copolymer concentration of ~ 5 wt%, which is the expected maximum in the pressure-composition curve^{2,10}, are obtained using a high-pressure, variable-volume view cell described in detail elsewhere^{2,25}. Cloud-point pressures are reproducible to ± 5 bar. The lowest temperatures of the cloud-point curves presented in this work occur at either the highest operating pressure of the experimental apparatus or at the crystallization boundary.

The poly(ethylene), poly(ethylene-co-acrylic acid), and poly(ethylene-co-methacrylic acid) polymers were donated by E. I. du Pont de Nemours, Inc. Ethylene, propane, butane, 1-butene, and dimethyl ether, with minimum purities of 99%, were obtained from MG Industries and were used as received. Ethanol at a minimum purity of 99.5% was obtained from Aldrich Chemical Co. and was used as received.

RESULTS

Effect of solvent quality

Figure 1 shows that there is no significant difference in the cloud-point behaviour of EMAA_{3,9} and EAA_{3,9} in ethylene, propane, butane, butene, and DME. Evidently, the addition of a methyl group to acrylic acid does not change the magnitude of the solution interchange energy between these five solvents and the acid copolymers. Ethylene is the poorest solvent for the two acid copolymers. At temperatures greater than 180°C, pressures in excess of 1500 bar are needed to dissolve either copolymer in ethylene. At these elevated temperatures, the

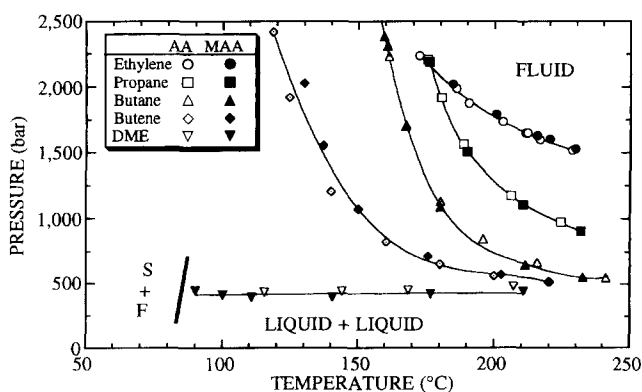


Figure 1 Comparison of cloud-point curves of ~ 5 wt% EAA_{3,9} (open symbols) and ~ 5 wt% EMAA_{3,9} (closed symbols) in ethylene, propane, butane, 1-butene, and dimethyl ether. Cloud-point curves for EAA_{3,9} in propane, butane, 1-butene, and dimethyl ether were obtained by Lee *et al.*². The cloud-point curve in DME ends at the crystallization boundary that is represented by a solid vertical line

amount of acid dimerization is reduced significantly^{16,26}, but, high pressures are needed to increase the density of ethylene before it can dissolve either copolymer.

The cloud-point curve for EMAA_{3,9} in butane is at a lower pressure than the curve in propane since butane has a larger polarizability and it has a higher density at the same temperature and pressure. The butene cloud-point curves are shifted 15–40°C lower in temperature relative to the butane curves, which is an indication of the strength of polar interactions and π -electron–acid complexing that is expected with butene and the acid groups. The high solvent strength of DME is implied by the low pressures needed to dissolve these two copolymers. DME has a lower polarizability than butane or butene, but it has a significant dipole moment and it is capable of hydrogen bonding with the acid groups in each of these copolymers.

At temperatures in excess of 200°C, the location of the cloud-point curves in Figure 1 should be fixed predominantly by nonpolar dispersion interactions. A semi-quantitative measure of the strength of the dispersion interactions of the pure solvent is the product of the solvent density, ρ_i , times the solvent polarizability, α_i ²⁷. For the arguments made here, solvent densities are calculated at the respective cloud-point pressures for each solvent using the Peng–Robinson equation of state²⁸. A single linear curve of $(\rho_i \cdot \alpha_i)$ vs temperature is obtained for ethylene, propane, butane, and butene at temperatures greater than 200°C. The slope of this curve is -0.00202×10^{-25} mol with standard deviation of 0.000758×10^{-25} mol. At lower temperatures the values of $(\rho_i \cdot \alpha_i)$ for all of the solvents deviate from this linear curve probably due to the overwhelming influence of acid dimerization on the interchange energy. Therefore, given one set of experimental data at high temperatures, it is possible to estimate high-temperature cloud-point pressures for other nonpolar solvents with EMAA_{3,9}. Not surprisingly, the values of $\rho_i \cdot \alpha_i$ for DME fall on a separate curve since DME hydrogen bonds with the acid groups in EMAA_{3,9}. It is interesting that, using the curve of $(\rho_i \cdot \alpha_i)$ for the hydrocarbon solvents, the calculated cloud-point pressure for the EMAA_{3,9}–DME system at 215°C is 1100 bar compared to the observed value of 450 bar. There are two possible reasons for the 650 bar discrepancy in calculated and observed cloud-point pressures. The densities of polar DME calculated with the Peng–Robinson equation may be too low. Or, even at 215°C, there is still some hydrogen bonding between DME and the acid groups in EMAA_{3,9} which is not accounted for with this nonpolar correlation. Since this density-polarizability correlation tool only accounts for solvent properties, it does not predict the temperature where polar interactions and acid dimerization causes the cloud-point curve to increase dramatically in pressure.

Effect of acid content

Figure 2 shows the P – T behaviour of PE, EMAA_{3,1}, EMAA_{3,9}, and EMAA_{5,4} in butane and butene. The cloud-point curves for both of these solvents appear to converge to the PE–solvent curves at temperatures in excess of 225°C where the impact of acid dimerization and polar interactions should be diminished². However, as the temperature is lowered, the EMAA–solvent cloud-point curves exhibit steep negative slopes which are a consequence of the dimerization of the acid groups

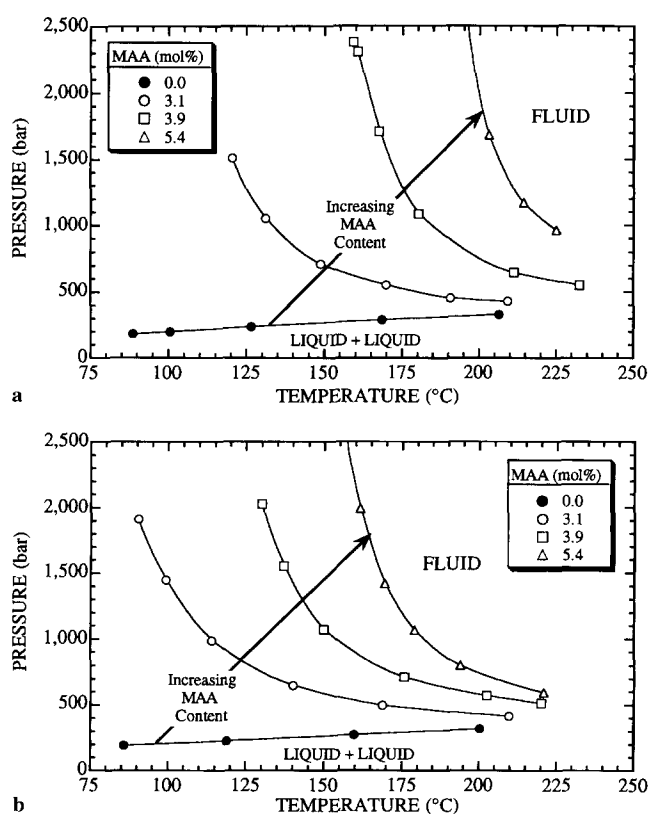


Figure 2 (a) Effect of the methacrylic acid content on the cloud-point curves for ~ 5 wt% EMAA in butane. (b) Effect of the methacrylic acid content on the cloud-point curves for ~ 5 wt% EMAA in butene

within the same EMAA chain or between chains. The EMAA–butene curves are shifted to lower temperatures compared to the curves in butane since butene is a slightly polar solvent that can also form a π -electron–acid complex in addition to interacting via dispersion and induction forces that are also operative with butane. The cloud-point curves in both solvents shift to higher temperatures with increasing acid content since the number of hydrogen bonds are proportional to acid content.

Figure 3 shows the P – T behaviour of PE, EMAA_{3,1}, EMAA_{3,9}, and EMAA_{5,4} in DME. Relative to butane and butene, DME has a smaller polarizability, a larger dipole moment, and it can hydrogen bond with the methacrylic acid repeat units. Cloud-point pressures with DME are relatively constant at approximately 400 bar over a 150°C range. In fact, it is the PE–DME curve that exhibits a negative slope with decreasing temperature. PE solidifies at temperatures below 114°C in DME so that it is not possible to extend the cloud-point curve to lower temperatures and higher pressures. At temperatures lower than 150°C, the interchange energy associated with mixing PE with DME is dominated by DME–DME polar interactions that increase with decreasing temperature and that favour phase separation. With DME the single-phase region increases as the acid content of EMAA increases due to the hydrogen bonding between methacrylic acid and DME. However, the cloud-point curves should shift to high temperatures and pressures for EMAA copolymers with high methacrylic acid content since it is not possible to dissolve poly(acrylic acid) in DME even at a temperature of 250°C.

Effect of cosolvents

Figure 4 shows the effect of DME on the cloud-point behaviour of the EMAA_{3,1}-butane system. The pressures needed to dissolve EMAA_{3,1} in butane decrease significantly when DME is added to the solution since DME hydrogen bonds with the methacrylic acid repeat units. At 120°C the addition of 5.5 wt% DME reduces the cloud-point pressure by ~700 bar. At higher temperatures, where acid dimerization is reduced^{16,26}, the impact of DME is much less. Note that pure DME is not as good a solvent as is a mixture of 38 wt% DME with 62 wt% butane. Once the methacrylic acid sites are titrated with DME, further addition of DME to the solution actually diminishes the solvent strength since DME has a smaller polarizability than butane.

The impact of DME is presented in a slightly different format in Figure 5, which shows the cloud-point pressure as a function of moles of DME sites capable of hydrogen bonding relative to the moles of acrylic acid sites in solution. A single site on one molecule of DME is assumed to interact with a single site on one acid molecule. From this figure it is evident that the initial moles of DME added to solution have the largest impact, especially at the lower temperatures where acid dimerization would be prevalent. The impact of DME essentially levels off once there are 20 times as many moles of DME sites relative to acid sites. The curves in Figure 5 terminate at pure DME solvent, which

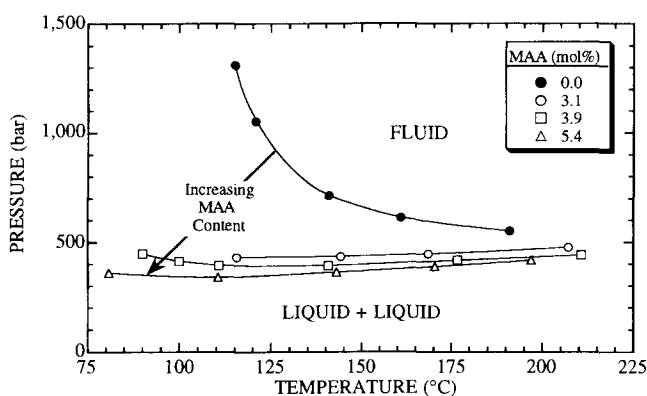


Figure 3 Effect of the methacrylic acid content on the cloud-point curves for ~5 wt% EMMA in dimethyl ether

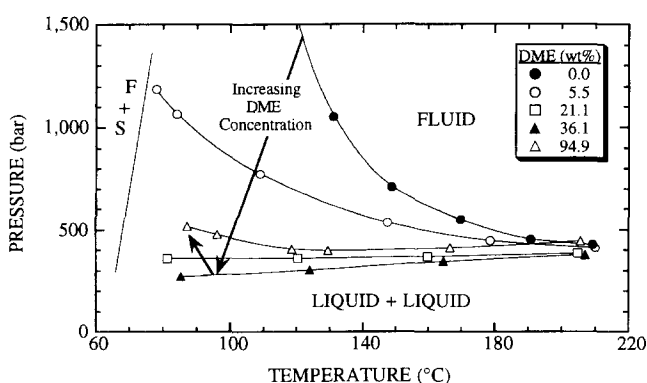


Figure 4 Effect of dimethyl ether on the phase behaviour of ~5 wt% EMAA_{3,1} in butane. The cloud-point curves end at the crystallization boundary that is represented by a solid vertical line

is 385 mol of DME sites per mole of methacrylic acid sites.

Figure 6 shows the effect of small amounts of ethanol on the phase behaviour of EMAA_{3,1}-butane mixture. Ethanol is a much better cosolvent than DME. The addition of only 1.1 wt% ethanol to the EMAA_{3,1}-butane system decreases the cloud-point pressure by 800 bar at 120°C. At ethanol concentrations greater than 10 wt%, the cloud-point curves are at very low pressures and they exhibit positive slopes. However, the cosolvent effect of ethanol diminishes more rapidly than that of DME as shown in Figure 7. In this figure the moles of ethanol sites capable of hydrogen bonding is twice the number of moles of ethanol in solution since both the hydroxy hydrogen and oxygen in ethanol can participate in hydrogen bonding with a single acrylic acid molecule. It is for this reason that ethanol, at low concentrations, is a better cosolvent than DME. Notice that the cloud-point pressures with ethanol are lower than those with DME probably due to the higher density of ethanol at these temperatures relative to DME, which is above its critical temperature.

Figure 8 shows that the phase behaviour changes quite drastically with high concentrations of ethanol. At an ethanol concentration of 15 wt% there are 62 times as many ethanol molecules as compared to methacrylic acid repeat units. Therefore, the ethanol molecules in excess of the number needed to 'saturate' the acrylic acid sites of EMAA_{3,1} are expected to self associate. At 42.4 wt%

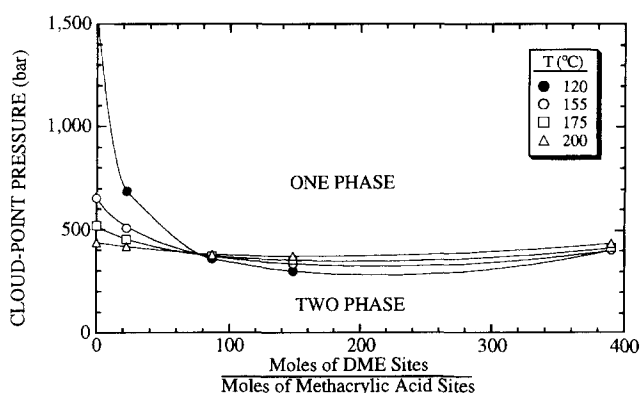


Figure 5 Change in cloud-point pressure as a function of dimethyl ether concentration. Per molecule of dimethyl ether there is one site that can hydrogen bond with methacrylic acid

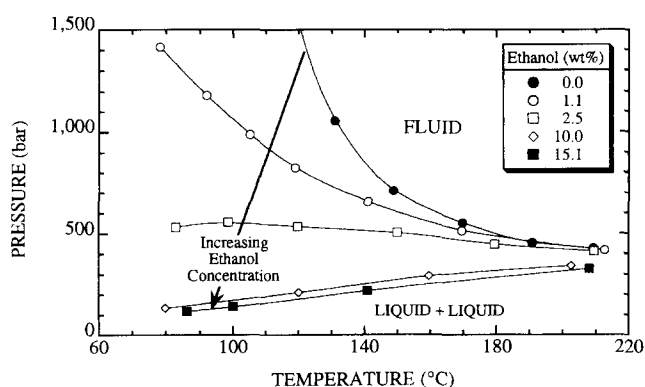


Figure 6 Effect of low concentration of ethanol on the phase behaviour of ~5 wt% EMAA_{3,1} in butane

ethanol, there are now 176 times as many ethanol molecules as compared to methacrylic acid repeat units. The cloud-point curve at this concentration exhibits a sudden increase in pressure at 115°C, which suggests that the interchange energy is now dominated by the self association of ethanol that does not favour the formation of a single phase. If the concentration of ethanol is further increased to 53.5 wt%, the cloud-point curve again exhibits a sudden increase in pressure, but now this pressure increase occurs at 160°C. At 53.5 wt% ethanol, there is a larger concentration of ethanol in excess of that needed to titrate the acid sites as compared to the 42.4 wt% solution. Since the interchange energy depends on the number as well as the strength of ethanol-ethanol associations, temperature has a large impact on the cloud-point behaviour. The trends shown in Figure 8 corroborate our finding that it is not possible to dissolve EMAA_{3,1} in pure ethanol even at 250°C and 2000 bar. It is not possible to cross plot the results in Figure 8 in a manner similar to that in Figures 5 and 6 since the acid copolymer falls out of solution at high ethanol concentrations.

CONCLUSIONS

The hydrocarbon solvents used in this study, ethylene, propane, butane, and butene could not distinguish the structural differences between EMAA and EAA since the dimerization energies of methacrylic acid and of acrylic

acid are indistinguishable and are much stronger than any other copolymer-solvent interactions. DME also could not distinguish the structural difference between these two acids probably due to the cross association energies that are expected to be similar and much stronger than any of the other possible interactions. Even though the EMAA copolymers considered in this study had as much as 94 mol% nonpolar ethylene repeat units, the region of miscibility in the hydrocarbon solvents decreases significantly with decreasing temperature and with increasing copolymer acid content. Cosolvents that cross associate with the acid repeat units dramatically increase the region of miscibility. However, the impact of the cosolvents diminishes rapidly with increasing cosolvent concentrations since there are only a finite number of acid sites that can participate in hydrogen bonding.

ACKNOWLEDGEMENTS

The authors acknowledge the National Science Foundation for partial support of this project under grant CTS-9500489. The authors also acknowledge Minna A. LoStracco who performed some of the experiments reported here.

REFERENCES

- Lee, S.-H., LoStracco, M. A. and McHugh, M. A. *Macromolecules* 1994, **27**, 4652
- Lee, S.-H., LoStracco, M. A., Hasch, B. M. and McHugh, M. A. *J. Phys. Chem.* 1994, **98**, 4055
- LoStracco, M. A., Lee, S.-H. and McHugh, M. A. *Polymer* 1994, **35**, 3272
- Gregg, C. J., Stein, F. P. and Radosz, M. *Macromolecules* 1994, **27**, 4972
- Gregg, C. J., Stein, F. P. and Radosz, M. *Macromolecules* 1994, **27**, 4981
- Hasch, B. M., Lee, S.-H. and McHugh, M. A. *Fluid Phase Equilibria* 1993, **83**, 341
- Hasch, B. M., Meilchen, M. A., Lee, S.-H. and McHugh, M. A. *J. Polym. Sci., Polym. Phys. Ed.* 1993, **31**, 429
- Meilchen, M. A., Hasch, B. M., Lee, S.-H. and McHugh, M. A. *Polymer* 1992, **33**, 1922
- Luft, G. and Wind, R. W. *Chem. Ing. Tech.* 1992, **64**, 1114
- Irani, C. A. and Cozewith, C. J. *Appl. Polym. Sci.* 1986, **31**, 1879
- Lee, S.-H., LoStracco, M. A. and McHugh, M. A. *Macromolecules* 1996, **29**, 1349
- Rindfleisch, F., DiNoia, T. and McHugh, M. A. *J. Phys. Chem.* 1996, **100**, 15581
- Earnest, T. R. Jr. and MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* 1978, **16**, 143
- Earnest, T. R. Jr. and MacKnight, W. J. *Macromolecules* 1980, **13**, 844
- Otocka, E. P. and Kwei, T. K. *Macromolecules* 1968, **1**, 244
- Buback, M. and Mahling, F. *J. Supercritical Fluids* 1995, **8**, 119
- David, R. L. 'CRC Handbook of Chemistry and Physics', 73rd edn, CRC Press, Boca Raton, FL, 1992, Chapter 9
- Reid, R. C., Prausnitz, J. M. and Polling, B. E. 'The Properties of Gases and Liquids', 4th edn, McGraw-Hill, New York, 1987, Appendix A
- Van Ness, H. C., Winkle, J. V., Richtol, H. H. and Hollinger, H. B. *J. Phys. Chem.* 1967, **71**, 5, 1483
- de Fernandez, M. E., Calado, J. C. G., Zollweg, J. A. and Streett, W. B. *Fluid Phase Equil.* 1992, **74**, 289
- Haarhaus, U. and Schneider, G. M. *J. Chem. Thermodynamics* 1988, **20**, 1121
- Brunner, E. *J. Chem. Thermodynamics* 1985, **17**, 871
- Brunner, E. *J. Chem. Thermodynamics* 1988, **20**, 273
- Brunner, E. and Hultenschmidt, W. *J. Chem. Thermodynamics* 1990, **22**, 73

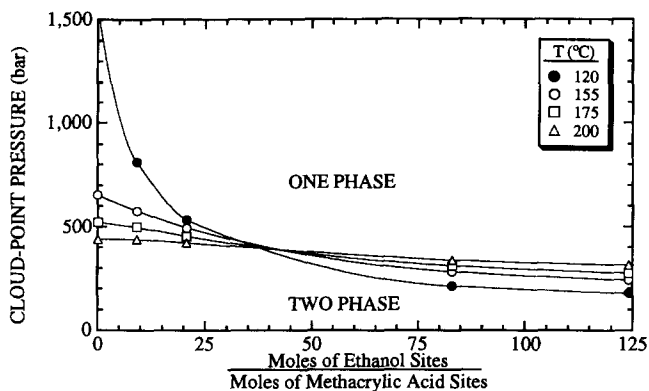


Figure 7 Change in cloud-point pressure as a function of ethanol concentration. Per molecule of ethanol there are two sites that can hydrogen bond with methacrylic acid

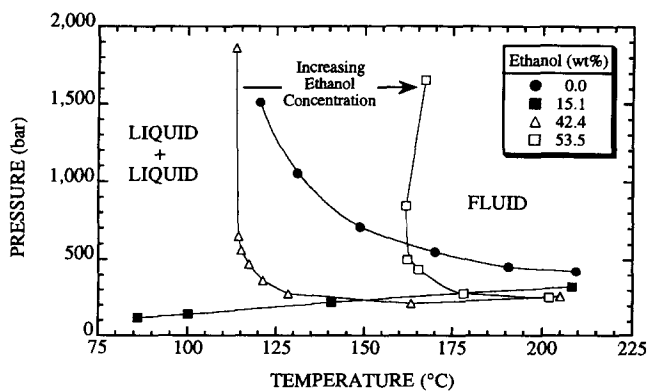


Figure 8 Effect of high concentrations of ethanol on the phase behaviour of ~5 wt% EMAA_{3,1} in butane

- 25 Meilchen, M. A., Hasch, B. M. and McHugh, M. A. *Macromolecules* 1991, **24**, 4874
- 26 MacKnight, W. J., Taggart, W. P. and McKenna, L. *J. Polym. Sci.* 1974, **46**, 83
- 27 Mertdogan, C. A., Byun, H.-S., McHugh, M. A. and Tuminello, W. H. *Macromolecules* 1996, **29**, 6548
- 28 Peng, D. Y. and Robinson, D. B. *Ind. Eng. Chem. Fundam.* 1976, **15**, 59