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PRELIMINARY SELECTION OF POLYMERIC ENTRAINERS FOR THE AZEOTROPIC DISTILLATION OF MTBE/METHANOL AND ETHANOL/WATER MIXTURES USING THE UNIFAC GROUP-CONTRIBUTION CALCULATIONS METHOD

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ABSTRACT

In this work the UNIFAC group-contribution calculations method was used to determine relative volatility in the presence of selected polymeric entrainers at different weight fractions in ethanol/water and methyl tertiary butyl ether/methanol systems. To quantify the effect of the added polymers, the ratio of relative volatility with and without the polymer was calculated. The purpose of these calculations was to identify the systems that have ratios of relative volatility distinct from unity because they may indicate polymers with the ability to break the azeotrope. This information should guide the ini-

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[*] Previous publications by the author appeared under his sub-family name of Al-Jarallah.

tial selection of potential polymers capable of breaking the azeotrope and thus save time and effort. The results of these calculations are reported. Because these polymers must be soluble in the system, solubility tests were performed and the results are reported. Comparison of these predictions with previously published experimental vapor-liquid equilibrium data for the same systems gave conflicting results: Some predictions were confirmed and others were not. Thus, the UNIFAC group-contribution calculations were not always reliable in predicting relative volatility. More accurate group-contribution methods would make the polymer design more reliable.

INTRODUCTION

Although many new separation techniques are being developed, distillation will remain the method of choice for large-scale separation of nonideal mixtures including those of azeotropic mixtures (1). Separation of such mixtures can be improved by using entrainers to break the azeotrope. These entrainers are usually low molecular weight liquids that have a boiling point that is either low (lower than the more volatile component), intermediate (between the boiling points of the components), or high (higher than the less volatile component). Upon completion of the separation and recovery of the entrainer for recycling, the distillation system will usually involve 2 or more columns (2).

A great deal of research has been conducted on entrainer selection and corresponding distillation system configuration. In the past, entrainers were selected using a trial-and-error procedure mostly based on experimental data. This procedure resulted in wasted time and resources. More recently, entrainers have been selected on the basis of their potential for producing feasible designs.

In 1991, Laroche et al. (3) presented practical solutions for choosing the best entrainers required for separating a binary azeotrope into pure components. They also suggested a feasible flow sheet of separation sequences for each entrainer. Their analysis showed that a good entrainer is a component that breaks the azeotrope and yields high relative volatilities between 2 azeotropic constituents. They used equi-volatility curve diagrams to compare entrainers.

In 1996, Widago and Seider (4) reviewed contemporary work on the separation of azeotropic mixtures. They examined the important considerations in the selection of entrainers because success in azeotropic distillation is largely determined by the choice of entrainer. They presented simple rules through the use of maps of distillation lines, in preference to residue curves, for screening the many possible entrainers. These maps are useful in the early design stages because they give specifications for the desired separations.

Group contribution calculations reported in the literature revealed a number of suitable low molecular weight entrainers (5). One possible guide for polymeric entrainer choice involves the selection of the polymeric counterparts of the low molecular weight entrainers. For example, the following entrainers were found suitable for breaking the azeotrope in the ethanol-water system: acetic acid, 2-aminoethanol, *N,N*-dimethylformamide, ethylene glycol, meso-2,3-butanediol, and morpholine. Acetic acid and ethylene glycol are already used in industry, and their polymeric counterparts, polyacrylic acid (PAA) and polyvinyl alcohol, may also be good candidates for entrainers. In this work, polymers like these are considered. These polymeric entrainers will alter the relative volatility of the components and break the azeotrope. These entrainer candidates are polymers that remain in the liquid phase and can be separated by ultrafiltration. Hence, separation can be completed with fewer columns.

Al-Amer (2000) (6) reported the experimental results of a vapor-liquid equilibrium (VLE) study of the ethanol/water and methyl tertiary butyl ether (MTBE)/methanol systems in the presence of such polymeric entrainers. He showed that some polymers have been successful in breaking the ethanol/water azeotrope while the results for the MTBE/methanol system were not conclusive. Selected data were fitted to the UNIQUAC model and a satisfactory fit was obtained and the parameters were reported.

The group contribution model should be suitable for polymer solutions. A recent review (7) presented the merits of various models for the VLE of polymer solutions. The UNIFAC-FV and the entropic-FV are more sophisticated versions of the UNIFAC, but they are not suitable for the ionic polymers that might be good candidates for the ethanol/water system (8). The UNIFAC is more commonly used in the literature than are the sophisticated versions and is suitable for use with the polymers believed to be good candidates for entrainers.

In this work, the UNIFAC group-contribution calculations method was used to calculate the relative volatility in the presence of selected polymeric entrainers at different weight fractions in the ethanol/water and MTBE/methanol systems. The aim of this calculation was to guide in the initial selection of potential polymers and thus save time and effort. The results of these calculations are reported. Because these polymers must be soluble in the system, solubility tests were performed and the results are reported. Breaking of the azeotrope can only be confirmed through experimental investigations. A sample experimental result is used to confirm the predictions from the UNIFAC calculations.

GROUP CONTRIBUTION CALCULATIONS

To get a relative ranking of the ability of the potential polymers to break the azeotrope, one can use a group contribution model. Group contribution models, such as UNIFAC, do not require a set of fitted parameters. Only the structure of the components is needed for the program to predict the VLE behavior (assuming that the group parameters are available). For the polymers investigated in this study, the group parameters were obtained from (9). These methods provide approximations and are expected to only give a qualitative indication of polymer superiority in a decreasing order.

Group contribution models allow the calculation of activity coefficients based on groups rather than on whole molecules. Calculations for a polymer can be done by selecting the proper groups for that polymer in addition to the groups for the 2 volatile components. The criterion for a useful polymer is based on the relative volatility α at the azeotropic temperature and a total pressure of 1 atm.

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 P_1^{\text{sat}}}{\gamma_2 P_2^{\text{sat}}}$$

The MTBE/methanol system has an azeotrope at 1 atm and 51.3°C with the MTBE mol fraction ≈ 0.7 (10). The relative volatility is equal to unity at the azeotrope. Using a group contribution model, the activity coefficientγ_1 is calculated for different added amounts of the selected polymers. For this system, the objective was to choose a polymer with strong interactions with MTBE and weak interactions with methanol. This situation will lead to an α_{12} value that is lower than unity. This system behavior is desired because the feed to the distillation column, which comes from the reactor, has an MTBE mol fraction close to unity. For the ethanol/water system, the azeotrope is at 1 atm and 78.2°C with the ethanol mol fraction $= 0.894$ (11). Our objective was to chose a polymer in which α_{12} was above unity.

Group Contribution Calculations for MTBE/Methanol

For the MTBE/methanol system, a list of 11 polymers was chosen for investigation (Table 1). To quantify the effect of polymer addition, we calculated the ratio of the relative volatility with and without the polymers. The calculations were done on the azeotrope (at atmospheric pressure, approximately 51.3°C, and MTBE mol fraction ≈ 0.7). Three values of polymer weight fractions were used. These values were converted to mol fraction units. The ratio of mol fractions of MTBE to methanol was kept constant at the azeotropic value (0.7:0.3).

Table 1 shows that little variation existed between the polymers, except between atactic poly(propylene) and poly(isobutene). As expected, the relative volatility decreased with the increase of polymer weight fraction. As discussed above, a lower value of relative volatility is desired for this system. Therefore, atactic poly(propylene) and poly(isobutene) were expected to give the best results, but the theoretical values must be verified experimentally.

Group Contribution Calculations for Ethanol/Water

For the ethanol/water system, the polymers must be polar to dissolve in water. Five polar polymers were chosen for study in this system. To quantify the ef-

Table 1. Ratio of the Relative Volatility of MTBE/Methanol With and Without the Polymer

	Relative Volatility at Different Weight Fractions of Polymers		
Polymer	$w = 0.01$	$w = 0.025$	$w = 0.05$
poly(2-*tert*-Butyl-1,3 butadine)	0.99	0.97	0.95
poly(5,7-Dimethyl-1,6-octadiene)	0.99	0.97	0.95
poly(2-Chloro-1,4-cis-butadiene)	0.99	0.98	0.96
Atactic poly(propylene)	0.98	0.95	0.91
poly(Isobutene)	0.98	0.96	0.92
poly(Cyclopentylethylene)	0.99	0.97	0.95
poly(Cyclohexylethylene)	0.99	0.97	0.95
poly(Ethylmethacrylates)	0.99	0.98	0.97
poly(*n*-Butyl methacrylate)	0.99	0.98	0.97
poly(Di-*n*-butyl itaconate)	1.00	0.99	0.98
poly(Oxy-1,3 phenylene)	0.99	0.98	0.97

fect of adding the polymers, we calculated the ratio of the relative volatilities with and without the polymers. The results are shown in Table 2. The calculations were done at the azeotrope (atmospheric pressure, 78.2°C, and ethanol mol fraction = 0.894). Three values of polymer weight fraction were used in the calculations. These values were converted to mol fractions based on the molecular weight of the repeat units. The ratio of mol fractions of ethanol to water was kept constant at the azeotropic value (0.894:0.106).

For this system, a ratio of the relative volatilities greater than unity is desirable. Table 2 shows that poly(ethylenimine), poly(oxymethylene), and polyethylene glycol (PEG) are expected to give the best results. As we expected, the higher the fraction of the polymer the higher the relative volatility ratio and the better potential of the entrainer to break the azeotrope. These predictions must be verified experimentally.

Table 2. Ratio of the Relative Volatility of Ethanol/Water With and Without the Polymer

	Relative Volatility at Different Weight Fractions of Polymers		
Polymer	$w = 0.01$	$w = 0.025$	$w = 0.05$
poly(Acrylic acid)	1.01	1.01	1.02
poly(Vinyl alcohol)	1.00	1.00	1.00
poly(Oxymethlene)	1.00	1.11	1.21
Polyethylene glycol	1.03	1.07	1.14
poly(Ethylenimine)	1.05	1.12	1.22

Table 3. Maximum Solubility of Polymer in Weight Percentage of Polymer

Polymer	H_2O	EtOH	MeOH	MTBE
Polyacrylamide	+, 1%	−	−	
Polycaprolactone	−		−	
Polysodium acrylate	+, 1%	−	−	
Poly(2-acryamido-2-methyl-1-propane sulfonic acid)	+, 5%	+, 17%	+, 5%	−
Polyvinyl alcohol		−	−	
Polyacrylsaeure amide	±, 0.5%	−	−	
Polyacrylsaeure nitril	−		−	
Polyethylene glycol	+, 10%	+, 12%	+, 5%	±, 0.3%
Polyacrylic acid (M.W. 2000)	+, 20%	+, 0.5%		−
Polyethylene imine	+, 20%	+, 18%		
Polypropylene adipate	−	−		
Polymethyl methacrylate	−	−	−	

+ Soluble
− Insoluble
±Partially soluble

POLYMER SOLUBILITY

The chosen polymer should be soluble in mixtures with a composition range of those usable in industrial operations. Polymers should be soluble in the entire composition range so that the possibility of polymer precipitation in the column (and the costly cleaning) is minimized in the case of unexpected composition variations.

In this work, solubility was measured in solutions prepared at low concentration, heated to 50–60°C for 2 hours, and cooled to room temperature before the solubility was determined. If found soluble, the concentration of the polymer was increased gradually until the approximate maximum solubility was found. The solubility results of the available polymers are given in Table 3 in weight percentage of the polymer. The experimental investigations designed to confirm the ability of a polymer to break the azeotrope should be done using only the soluble polymers in either system.

CONCLUSION

The predictions of good potential entrainers from Tables 1 and 2 must be verified by comparison with experimental VLE data. The results of the solubility tests (Table 3) must be used to exclude the insoluble polymers from experiments.

VLE experimental investigations were performed for the ethanol/water system with PEG, polymethyleneimine, poly(2-acrymido-2-methyl-1-propane sulfonic acid), and PAA as entrainers at different weight fractions. For the MTBE/Methanol system, only the PEG was used because it was the only soluble polymer among those available to us. The details of the experimental results are in (6). Figure 1 and Table 4 show sample results to clarify this discussion. The criteria for breaking the azeotrope can be shown graphically as the area where the xy data does not cross the x = y line and a minimum is not present in the Txy diagram. Table 4 presents the VLE data for the MTBE/methanol system with 3.3% (wt) PEG as the entrainer. The data show that an azeotrope exists at approximately 50.3°C and a methanol mol fraction of approximately 0.39 or MTBE ≈ 0.61 (barometric pressure was 0.97 bar). Based on this and the noted criteria, no polymer among those studied was found to break the azeotrope in the MTBE/methanol system. However, according to the data in Table 1, atactic polypropylene and polyisobutene (which were not available with us) should be good candidates for entrainers for this system (provided they are soluble). Thus, we recommend that the effectiveness of these polymers as entrainers be verified experimentally.

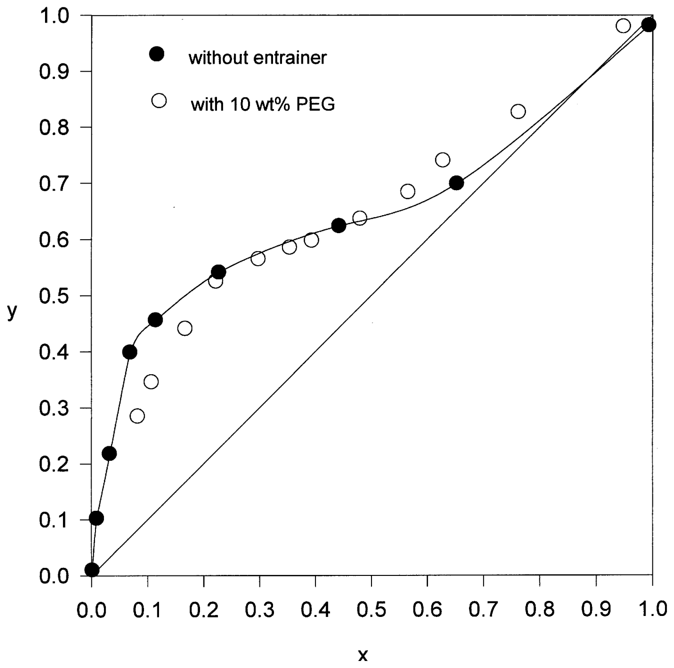

Figure 1. x-y plot for the ethanol-water system. Cases in which the azeotrope remains unbroken are represented by points on the x-y plot that do not cross the x = y line.

Table 4. VLE Data for the Methanol/MTBE System with 3.3% (wt) Polyethylene Glycol

	Methanol Mol Fraction	
Temperature °C	x	y
63.3	1.0000	1.0000
61.4	0.9199	0.9756
60.3	0.8596	0.9606
59.0	0.8051	0.9431
58.2	0.7597	0.9217
57.5	0.7414	0.8997
56.6	0.7000	0.8803
55.9	0.6435	0.8589
55.5	0.6406	0.8493
54.3	0.5923	0.8098
53.8	0.5699	0.7771
53.0	0.5436	0.7501
52.2	0.5161	0.6846
51.4	0.4712	0.5980
50.6	0.4289	0.5250
50.4	0.3999	0.4450
50.0	0.3600	0.3215
50.2	0.2998	0.2359
51.3	0.2314	0.1593

Experiments were conducted at 0.97 bar.

For the ethanol/water system, experimental investigations revealed that at least 2 polymers, 10% (wt) PEG, and 0.45% (wt) PAA can break the azeotrope for this system (6). Figure 1 shows a comparison of PEG and no entrainer on azeotrope breaking. This figure clearly shows that in the presence of PEG, the xy data did not cross the x = y line. The data in Table 2 support this result for the PEG. However, the data in Table 2 does not support the prediction that PAA can break the azeotrope. Also based on Table 2, one could reasonably predict that polyethyleneimine would be a good candidate entrainer for this system. However, the VLE data do not clearly confirm this hypothesis because the data are plotted very close to the x = y line and we cannot be sure that they did not cross it. Because the calculations were inconclusive for polyethyleneimine and the calculated results were not always consistent with experimental data, we concluded that the UNIFAC group-contribution predictions were not always reliable in predicting the relative volatility. More accurate group-contribution methods would make the polymer-design more reliable.

NOMENCLATURE

P^{sat}	saturation vapor pressure
x_i	mol fraction of component i in liquid phase
y_i	mol fraction of component i in vapor phase
α_{12}	relative volatility of components
γ_I	activity coefficient of component i

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REFERENCES

1. Fair, J.R. Inst. Chem. Eng. Symp. Ser. **1987,** *104*, 613.
2. Seader, J.D.; Henley, E.J. *Separation Process Principles;* John Wiley & Sons: New York, 1998.
3. Laroche, L.; Bekiaris, N.; Andersen, H.W.; Morari, M. Can. J. Chem. Eng. **1991**, *69,* 1302.
4. Widagdo, S.; Seider, W.D. AlChE J. **1996,** *42* (1), 96.
5. Foucher, E.; Doherty, M.; Malone, M. Ind. Eng. Chem. Res. **1991**, *30*, 760.
6. Al-Amer, A.M. Ind. Eng. Chem. Res. **2000,** *39,*10.
7. Kontogeorgis, G.M.; Fredenslund, A.; Economou, I.; Tassios, D.P. AIChE J. **1994**, *40*, 1711.
8. Kontogeorgis, G.M.; Fredenslund, A.; Tassios, D.P. Ind. Eng. Chem. Res. **1993,** *32,* 362.
9. Fredenslund, A.; Sorensen, J.M. Group Contribution Estimation Methods. In *Models for Thermodynamics and Phase Equilibria Calculations;* Sandler, S.I., Eds; Marcel Dekker: New York, 1994.
10. Alm, K.; Ciprian, M. J. Chem. Eng. Data **1980**, *25,* 100.
11. Seader, J.D.; Siirola, J.J.; Barnicki, S.D. Distillation. In *Chemical Engineer's Handbook*; Perry, R.B., Green, D., Eds.; McGraw-Hill: 1997.

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