

Demixing Pressure Measurements of Aerosol-OT in Ethane + Alcohol Solvent Mixtures

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The demixing pressures (dew point pressures) for sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in supercritical ethane + alcohol cosolvent mixtures were measured in a variable-volume view cell. The alcohols studied include methanol, 1-propanol, 1-octanol, and benzyl alcohol. The temperatures studied ranged from 40 to 100 °C with overall alcohol mass fractions ranging from 0 to 0.07. The demixing pressures for AOT (1.6 mass %) in supercritical ethane with methanol, 1-propanol, and 1-octanol were found to linearly increase with temperature. The demixing pressure was found to decrease with increasing alcohol concentration at constant temperature. The differences between methanol and propanol were resolved by calculation of the demixing solvent densities. The addition of 1-octanol decreased the demixing pressure slightly less than the addition of 1-propanol (for 3 mass % cosolvent). For benzyl alcohol as the cosolvent, the demixing pressure increased with increasing cosolvent concentration and showed a very nonlinear dependence on temperature at the highest benzyl alcohol concentration studied.

Introduction

The addition of surfactants such as sodium bis(2-ethylhexyl)sulfosuccinate (AOT) to supercritical fluid (SCF) solvents can create increased solubility of ionic and polar molecules through the formation of water-in-oil microemulsions or reverse micelles. AOT reverse micelles are thermodynamically stable aggregates of the amphiphilic surfactant, resulting in a hydrophilic headgroup region with the hydrophobic tails of the surfactant extending into a nonpolar continuous phase. AOT reverse micelles can be formed in alkane solvents even without the addition of added water, in which case they are known as “dry” micelles.¹

Cosolvents and cosurfactants such as alcohols can be used in reverse micelle systems to increase surfactant solubilities, promote aggregation, and increase water uptake. Alcohols typically having five to seven carbon atoms are most effective because they have a polarity intermediate between those of the hydrophilic short-chain alcohols and the oil-like long chain alcohols.² The alcohols act as cosurfactants by stabilizing the surfactant interface. The alkyl chains on the alcohols interact with the alkyl surfactant tails, and the hydroxyl groups interact with the polar core regions. The remaining alcohol that does not act as a cosurfactant acts as a cosolvent by dispersing into the nonpolar oil phase and altering its hydrophobicity. More hydrophilic alcohols, such as ethanol, have been shown to partition into the water core of reverse micelles.³ These effects may cause these alcohols to behave as antisolvents at certain conditions (i.e. temperature, alcohol concentration, and chain length) while behaving as cosolvents/cosurfactants at other conditions. McFann and co-workers^{2,4} reported the solubility of 0.01 M AOT in ethane with 0.5 mol % 1-octanol with water-to-surfactant ratios ranging from 0 to 19. The small addition of 1-octanol to the surfactant + solvent + water mixture was shown to appreciably reduce the pressure at which phase separation

occurs. To determine the effects of alcohol chain length on surfactant solubilities, the demixing pressures of AOT in supercritical ethane with various straight chain alcohols were measured. To investigate the effect of molecular structure of the alcohol, the effect of adding benzyl alcohol was studied. Benzyl alcohol has seven carbon atoms but has a benzene ring instead of an alkyl chain. Alcohol concentrations ranged from 0.0 to 7.0 mass %, and temperatures ranged from 40 to 100 °C. To the authors' knowledge, there are no experimental data in the literature for the demixing pressures of AOT in ethane with added methanol, propanol, or benzyl alcohol.

Experimental Section

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was purchased from Fisher Scientific (A349-500). The solvents ethane (CP grade, 99.5%, Scott Specialty Gases), methanol (99.9%, Fisher), 1-propanol (99.9%, Fisher), 1-octanol (99.9%, Fisher), and benzyl alcohol (99%, Acros Organics) were used without further purification.

The demixing pressure (or cloud point) measurements of AOT in supercritical ethane with various alcohol mixtures were performed using a high-pressure variable-volume view cell. The details of this apparatus and procedure can be found in a previous publication.⁵ For identical loadings of the pressure vessel, the demixing pressures deviated by approximately ± 2 bar. The experimental error was estimated to be ± 3 bar. The demixing pressures for 1.6 mass % AOT in ethane were found to be on average 12 bar (approximately 6.5%) lower than those reported previously.^{2,5} It has been shown in the literature² that the addition of small amounts of water can drastically increase the demixing pressure of AOT. The discrepancy in the data sets may be attributed to a lower water content in the AOT samples used in this study.

Results and Discussion

AOT in Ethane + Short Chain Alcohol Mixtures. The demixing pressures for AOT in supercritical ethane with methanol mixtures are shown in Table 1 and Figure

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Table 1. Demixing Pressure of 1.6 mass % AOT in Ethane (1) + Methanol (2)

$t/^\circ\text{C}$	demixing pressure/bar				
	$w_2 = 0.00^a$	$w_2 = 0.01$	$w_2 = 0.03$	$w_2 = 0.05$	$w_2 = 0.07$
40	153.1	141.7	129.4	128.2	127.5
50	171.8	160.1	147.2	143.2	140.5
60	189.0	177.4	163.8	158.9	151.2
80	219.5	211.1	195.6	188.2	178.5
100	246.1	239.6	224.3	215.4	203.1

^a w_2 is the overall mass fraction of methanol.

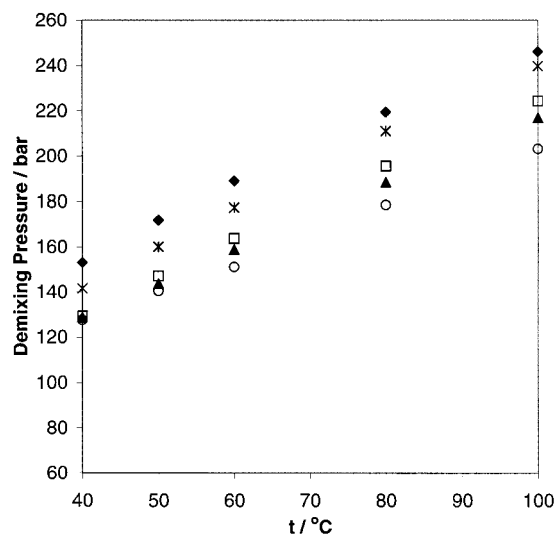


Figure 1. Demixing pressure of 1.6 mass % AOT in ethane + methanol mixtures versus temperature at several different methanol compositions: (◆) 0 mass %; (★) 1 mass %; (□) 3 mass %; (▲) 5 mass %; (○) 7 mass %. The methanol compositions are overall compositions in the mixture.

Table 2. Demixing Pressure of 1.6 mass % AOT in Ethane (1) + Propanol (2)

$t/^\circ\text{C}$	demixing pressure/bar				
	$w_2 = 0.00^a$	$w_2 = 0.01$	$w_2 = 0.03$	$w_2 = 0.05$	$w_2 = 0.07$
40	153.1	132.4	111.7	102.0	95.5
50	171.8	154.0	133.6	124.0	114.3
60	189.0	174.3	154.1	144.3	133.4
80	219.5	208.2	189.2	179.8	167.5
100	246.1	235.4	220.2	210.9	197.4

^a w_2 is the overall mass fraction of propanol.

1, and those in supercritical ethane with 1-propanol mixtures are shown in Table 2 and Figure 2. The demixing pressure increased linearly with temperature and decreased with increasing alcohol concentration. At low temperatures as the alcohol concentration increases, the relative reduction in the demixing pressure diminished. The methanol may also partition into the polar core region at a certain concentration, thereby acting to increase the demixing pressure. However, the reduction in the demixing pressure effect did not diminish as much for propanol as it did for methanol. 1-Propanol has a lower polarity that is closer to that of the surfactant interface and therefore interacts more strongly with the surfactant. However, as the temperature increased, the demixing pressure became a more linear function of the n -alcohol concentration.

The data of Ishihara et al.⁷ indicate that the ethane + methanol system exhibits a region of liquid–liquid instability (at 298 K). As one approaches an ethane mole fraction of 0.5, much larger pressures are required to achieve a single liquid phase. Unfortunately the data in the literature

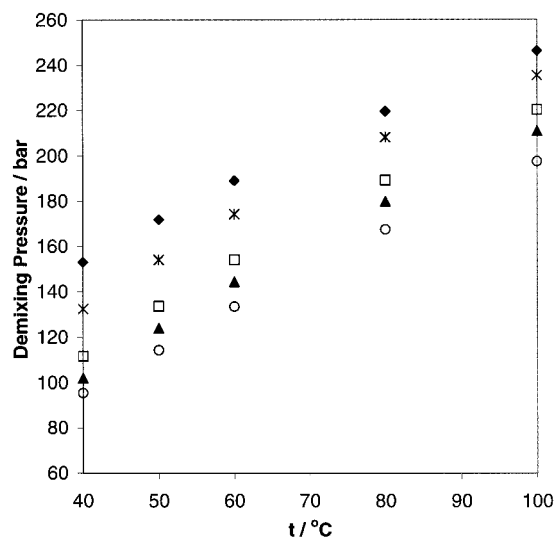


Figure 2. Demixing pressure of 1.6 mass % AOT in ethane + propanol mixtures versus temperature at several different propanol compositions: (◆) 0 mass %; (★) 1 mass %; (□) 3 mass %; (▲) 5 mass %; (○) 7 mass %. The propanol compositions are overall compositions in the mixture.

Table 3. Demixing Pressure of 1.6 mass % AOT in Ethane (1) + Benzyl Alcohol (2)

$t/^\circ\text{C}$	demixing pressure/bar		
	$w_2 = 0.00^a$	$w_2 = 0.01$	$w_2 = 0.03$
40	153.1	183.5	266.7
50	171.8	193.6	247.3
60	189.0	205.7	241.1
80	219.5	228.0	243.6
100	246.1	249.3	256.6

^a w_2 is the overall mass fraction of benzyl alcohol.

for this system⁶ at higher temperatures do not go to high enough pressures to fill out the points in the middle of the pressure–composition diagram. However, since the lattice fluid hydrogen bonding (LFHB) model¹² was found to fit the literature data^{6–8} with reasonable accuracy, it was used for extrapolation. At 50 °C, it was found that, at 8.5 mass % methanol, the extrapolated demixing pressure curve would intersect the calculated liquid–liquid solvent-phase envelope. Thus, at larger methanol concentrations, the solvent would phase separate before the AOT would fall out of solution. Therefore, demixing pressure measurements for n -alkanol concentrations > 7 mass % were not performed. However, at 100 °C, the projected curves intersect at 16.0 mass % methanol. Thus, solvent phase separation is of a smaller concern at higher temperatures. Similarly, the LFHB model predicted that propanol concentrations > ~9% will cause solvent phase separation at 40 °C.

AOT in Ethane + Benzyl Alcohol. The demixing pressures for AOT in ethane + benzyl alcohol mixtures are shown in Table 3 and Figure 3. The demixing pressure increased with increasing benzyl alcohol concentration. Benzyl alcohol has been shown to aggregate at the surfactant interface for AOT in heptane + benzyl alcohol mixtures, causing disruption of the headgroup layer.⁹ It is reasonable to assume that the presence of benzyl alcohol at the surfactant interface destabilizes the micelle structure due to steric hindrance between the phenyl group and the AOT tails. Thus, the hydroxyl group on benzyl alcohol causes it to behave as an antisolvent in this case.

The addition of 3 mass % benzene, on the other hand, was shown to decrease the demixing pressure of 1.6 mass

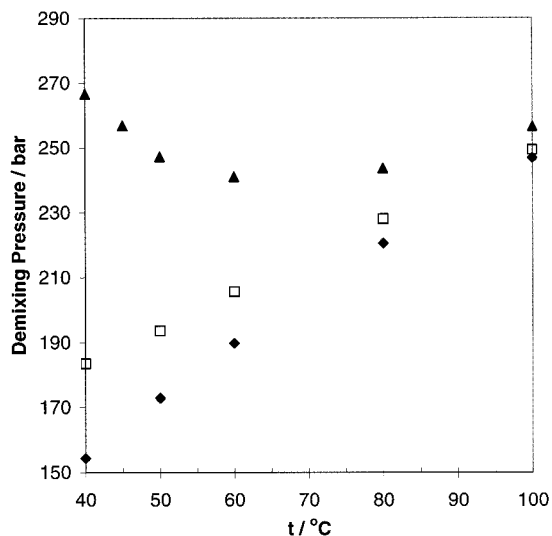


Figure 3. Demixing pressure of 1.6 mass % AOT in ethane + benzyl alcohol mixtures versus temperature at several different benzyl alcohol compositions: (◆) 0 mass %; (□) 1 mass %; (▲) 3 mass %. The benzyl alcohol compositions are overall compositions in the mixture.

% AOT in ethane by roughly 19 bar over the temperature range of interest here.⁵ It has been shown that benzene molecules aggregate in the tails of AOT (for AOT in ethane + benzene mixtures) rather than at the surfactant interface.¹⁰ Atik and Thomas⁹ suggested that benzene interacts in the surfactant headgroup region so as to produce a more compact structure.

At 3 mass % benzyl alcohol, the demixing pressure increased with decreasing temperature for lower temperatures (<60 °C) and increased with increasing temperature (>60 °C). At lower temperatures the alcohol molecules are more strongly attracted to the surfactant interface (and penetrate deeper into the tails toward the headgroups) due largely to hydrogen bonding and other attractive interactions. In the case of 3 mass % benzyl alcohol the degree of interaction at the low temperatures is strong and this results in a disruption of the interface due to the large benzene ring of the alcohol. At higher temperatures the effects of these interactions diminished so that the effect of the alcohol on the solubilization of AOT is essentially a density effect. Thus, the demixing pressure must increase with increasing temperature in order to obtain a sufficient solvent density to solubilize the AOT. The 1 mass % benzyl alcohol isopleth increases monotonically with temperature. A possible explanation for the differing behavior at this lower concentration is that the concentration of benzyl alcohol is too low to significantly affect the phase behavior. That is, the probability of alcohol–alcohol or alcohol–surfactant interactions is appreciably lower.

Comparison of All Alcohol Cosolvents. The demixing pressures for 1.6 mass % AOT in ethane + 3 mass % alcohol cosolvent mixtures are shown in Figure 4. The demixing pressures for propanol are lower than those for methanol. At lower temperatures the difference between the demixing pressures for propanol and methanol is larger due to the fact that methanol can strongly interact at the interface (i.e. some may even partition in the micelle core). The addition of 1-octanol decreased the demixing pressure slightly less than the addition of 1-propanol. The demixing pressures for benzyl alcohol as the cosolvent were larger than those for pure ethane because of the antisolvent effects of the benzene ring of the alcohol, as discussed above.

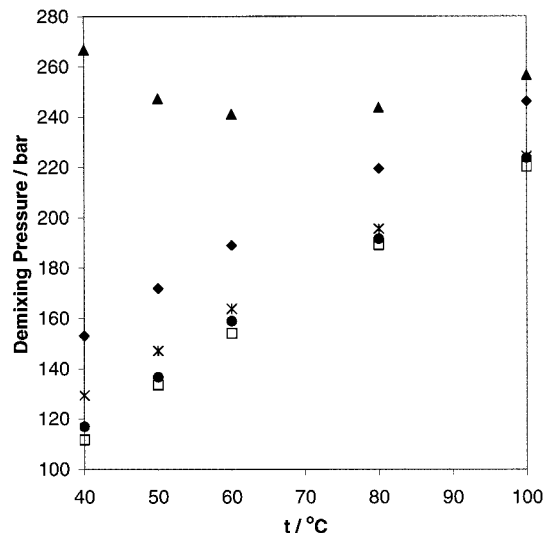


Figure 4. Demixing pressure of 1.6 mass % AOT in ethane + 3 mass % alcohol mixtures versus temperature: (◆) pure ethane; (★) methanol; (□) propanol; (●) octanol; (▲) benzyl alcohol.

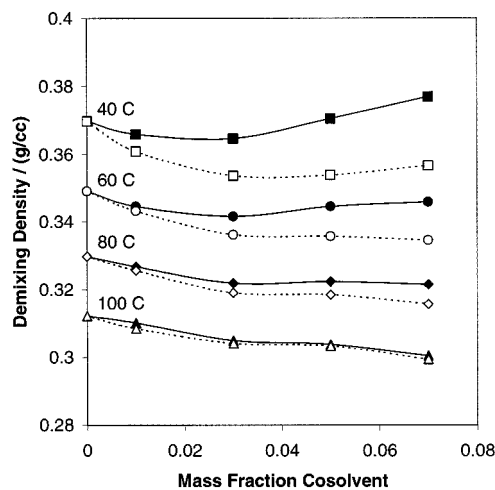


Figure 5. Demixing solvent density versus solvent composition for 1.6 mass % AOT in ethane + alcohol mixtures. Filled symbols represent the demixing densities for ethane + methanol mixtures, and open symbols are those for ethane + propanol mixtures.

Demixing Solvent Densities. The phase behavior of AOT in a low-polarity solvent has been shown to be strongly dependent on the density of the continuous-phase solvent.¹¹ To compare the effects of methanol and 1-propanol, the demixing solvent density as a function of cosolvent concentration was investigated at several temperatures. Gale et al.¹³ reported that the density required for the formation of stable AOT reverse micelles (at a given temperature) in ethane corresponded closely to that of pure ethane at similar conditions. Therefore, it was assumed that the small amount of AOT in each of the mixtures studied had a negligible effect on the solvent density. The densities were estimated using the lattice fluid hydrogen bonding model.¹² As shown in Figure 5, an addition of up to 3 mass % alcohol always causes the demixing density to decrease. However, for alcohol concentrations > 3 mass %, the demixing density increases for methanol at temperatures < 80 °C and for propanol at 40 °C. This antisolvent effect may be explained by the partitioning of alcohol into the water core, which was shown to occur for AOT in ethanol + *n*-heptane mixtures.³

The demixing densities for added 1-propanol are always lower than those for added methanol. As the temperature

increases, the difference in the demixing densities for the two cosolvents decreases. At 100 °C, the cosolvents behave nearly identically. These results can be explained by the fact that the strength of interactions decreases with increasing temperature. For both cosolvents, the demixing densities decreased with increasing temperature, which also occurred for AOT in ethane + benzene mixtures.⁵

Conclusions

The demixing pressure for AOT in ethane + short chain alcohol mixtures was found to increase with temperature and decrease with alcohol concentration. The demixing density was found to increase with increasing alcohol concentrations at sufficiently low temperatures for each short chain alcohol. 1-Propanol was found to be a better cosolvent/surfactant than methanol. The addition of benzyl alcohol had an antisolvent effect.

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