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Demixing Pressure Measurements of Aerosol-OT in Supercritical Ethane and Ethane + Benzene Mixtures

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The demixing pressures (dew point pressures) for sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in ethane and in ethane + benzene cosolvent mixtures were measured in a variable volume view cell. The temperatures studied ranged from 308 K to 333 K with benzene compositions ranging from 0 to 11.7 mass %. The demixing pressures of AOT in each solvent mixture were found to linearly increase with temperature while the demixing pressure was found to linearly decrease with increasing benzene concentration at constant temperature. It was observed that the addition of benzene to SCF ethane affects the demixing pressure of AOT primarily through its influence on the solvent density. A minimum solvent density is required to solubilize 1.6 mass % AOT, which remains constant as the solvent composition is changed at constant temperature. This demixing density was found to decrease slightly with an increase in temperature.

Introduction

Applications of supercritical fluid (SCF) solvents have continued to grow in number over the last several decades owing, in large part, to the ability to dramatically change bulk physical properties, such as density, with temperature or pressure. Unfortunately, many SCF applications that involve low critical temperature fluids are limited by the low solubilities of ionic or highly polar molecules. An alternative to increase these solubilities involves the formation of so-called water-in-oil microemulsions or reverse micelles by adding nonionic or ionic surfactants.

The solubility of surfactants in SCF solutions has gained attention in this regard since the discovery of reverse micelles and microemulsions in SCFs by Gale et al. in 1987. Since this discovery, many applications of microemulsions in SCFs have been developed including enhanced oil recovery (Carnahan et al., 1993), reactions (Matson et al., 1987; Beckman et al., 1989; Clarke et al., 1997), polymerizations (DeSimone et al., 1992), chromatographic separations (Smith et al., 1989), and others (Bartscherer et al., 1995). This paper focuses on the influence that the addition of varying amounts of benzene cosolvent has on the solubility of the surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in SCF ethane solvent (without added water). In addition to forming reverse micelles and microemulsions of water in a variety of nonpolar solvents such as alkanes, AOT also readily forms small reverse micelles in the absence of water in a variety of hydrocarbon solvents with aggregation numbers between 20 and 30 (Kotlarhyk et al., 1985).

There have been several studies on the solubility and phase behavior of AOT in pure SCF and near critical solvents (McFann and Johnston, 1991, 1993). The solubility of AOT in pure ethane and propane has been studied as a function of density in the supercritical region (Fulton and Smith, 1988; McFann, 1993). Fulton and co-workers (Fulton and Smith, 1988; Tingey et al., 1990; Jackson and Fulton, 1996) have reported AOT solubility in the liquid phase (25 °C) at the vapor pressure in a number of other pure solvents including butane, pentane, hexane, xenon, 2,2,4-trimethylpentane, isobutane, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons, and fluorocarbons. For these systems, Jackson and Fulton showed that the dielectric constant of the solvent in the UV−vis frequency range was a parameter that could be used to predict the ability of these solvents to form a microemulsion.

The solubility of AOT in a SCF with added cosolvent has not been extensively studied in the literature. A small addition of a less volatile cosolvent to a SCF solvent can increase the solubility of a solute while maintaining the favorable SCF properties (Dobbs et al., 1986). Cosolvents and cosurfactants can also be used in reverse micelle systems to increase surfactant solubilities, promote aggregation, and increase water uptake. McFann and coworkers (McFann, 1993; Johnston et al., 1989) reported the solubility of AOT in ethane with the added cosolvent octane and cosurfactant octanol. Small additions of a cosolvent to the surfactant + solvent mixture were shown to appreciably reduce the pressure required to solubilize the surfactant. The addition of a relatively nonpolar cosolvent, such as benzene, to SCF ethane could potentially influence the AOT solubility through an increase in the overall cohesive energy density of the solvent system (solubility parameter) through both energetic and increased density effects.

In this study, demixing pressures for AOT in ethane and in ethane + benzene cosolvent mixtures at temperatures ranging from 308 K to 333 K were investigated. Benzene was chosen as the cosolvent owing to its polarizability and owing to its ability to favorably interact with the nonpolar AOT hydrocarbon tails (Roberts and Thompson, 1998). The results here show that the addition of benzene cosolvent to SCF ethane decreases the demixing pressure of AOT primarily through its influence on the overall system density without observable energetic effects. The added benzene simply allows the required solvent density (for solubilization of AOT) to be achieved at a lower pressure at a given temperature.

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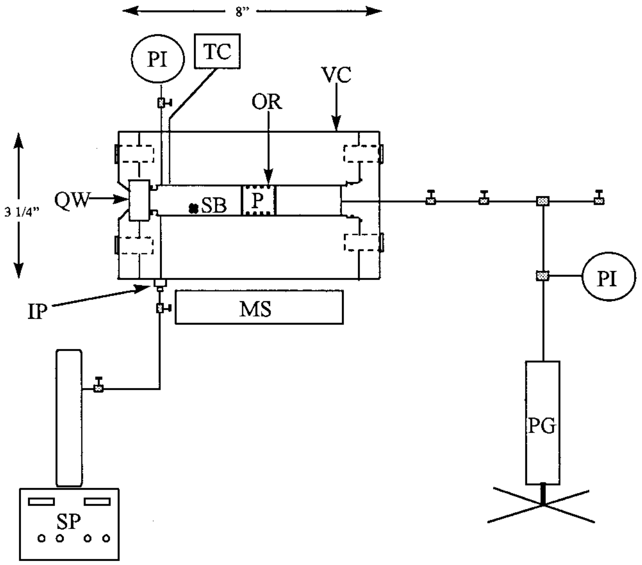

Figure 1. Experimental apparatus: IP, injection port; MS, magnetic stirrer; OR, O-ring; P, piston; PG, pressure generator; PI, pressure indicator; QW, quartz window; SB, stirbar; SP, syringe pump; TC, thermocouple; VC, view cell.

Experimental Section

Sodium bis(2-ethylhexyl) sulfosuccinate, AOT, was purchased from Fisher Scientific (A349-500). Ethane (CP grade, 99.5%) and benzene (99%) were purchased from Scott Specialty Gases and Aldrich, respectively. All materials were used without further purification.

Two different methods were used to determine the demixing pressures for the AOT + ethane + benzene system. The first method, a constant concentration method, involved measuring the demixing pressure for a fixed mixture composition at several different temperatures in a variable volume view cell apparatus. Demixing pressures at different benzene concentrations were obtained by reloading the contents of the vessel. The second method, a constant temperature method, involved measuring the demixing pressure at several different benzene concentrations at 310 K. In this case, the different benzene concentrations were obtained by subsequently injecting additional aliquots of benzene into the vessel during the experimental run. The first method establishes demixing pressure isopleths (lines of constant composition). The second method yields a variable composition isotherm.

The demixing pressure (or cloud point) measurements of AOT in ethane and ethane + benzene mixtures were performed with a high-pressure variable-volume view cell. The design of the experimental apparatus is a derivation of the design used by McHugh et al. (1991). A schematic diagram of the apparatus is shown in Figure 1. Briefly, the apparatus consists of a variable volume view cell, manual pressure generator, temperature controller, heating tape, pressure gauge, syringe pump, stir bar, and stir plate. The volume of the cell can be adjusted with the displacement of an internal movable piston. One can observe the contents of the cell by shining a light source (a flashlight or a borescope) through the quartz window on the front of the cell. A manual pressure generator (high-pressure equipment model 87-6-5) was used to manipulate the pressure in the view cell. The temperature in the cell was measured and controlled with a type E 1/16 in. thermocouple (Omega EMTSS-062G-6, Omega Engineering, Inc.) and a self-tuning PID controller (Omega CN76030) wired to a magnetic contactor (Omega MC-2-2-40-120). The thermocouple was calibrated against a NIST traceable thermometer (Omega), and the estimated accuracy is ±0.2 K. The pressure in the solvent side of the cell was measured with a digital pressure gauge (Heise 901A, Heise Precision Instruments) with an accuracy of ±0.3 bar.

Table 1. Demixing Pressure of AOT in Ethane vs Temperature

	demixing pressure/bar	
T/K	1.6 mass % AOT	3.0 mass % AOT
308	152.0	172.8
313	166.1	182.5
318	173.4	190.1
323	183.1	199.3
328	192.4	206.2
333	200.1	216.2

Cell Design. The body is constructed of 316 stainless steel. It has an outer diameter of 3 $^{1}/_{4}$ in. and a $^{7}/_{8}$ in. inner bore diameter fitted with a 1 in. outer diameter by $^{1}/_{2}$ in. thick sapphire window (Esco Products, Inc., Oak Ridge, NJ). The working volume of the cell is approximately 50 mL. The removable ends are secured by eight stainless steel bolts, and the seals between the ends and the middle section of the cell are achieved using O-rings. The piston is constructed of 304 stainless steel. The piston is 1 in. in length and has a marginal clearance with the inner bore wall. O-rings were also used to create the dynamic seal, which prevented the pressurizing fluid from contaminating the sample.

Experimental Procedure. Initially, a known amount (by mass) of AOT was added to the sample side of the view cell along with the stirring bar. In the constant composition method, an appropriate amount of benzene was delivered using a gastight syringe that was weighed before and after delivery. The desired amount of ethane was then charged to the cell with an Isco syringe pump maintained at a constant temperature and pressure. The amount of ethane delivered was determined from the difference in the volume displayed on the syringe pump controller. Using densities determined from the equation of state developed by Younglove and Ely (1987), the mass of ethane added was calculated. In the constant temperature method, once an appropriate amount of ethane was charged to the cell, subsequent amounts of benzene were delivered using an Isco high-pressure syringe pump. The cell was then heated to the desired temperature and allowed to equilibrate. The pressure was then raised well above the pressure required to achieve a clear single phase (to ensure all the surfactant was in solution). The pressure was slowly reduced until the onset of cloudiness was observed. At pressures greater than the demixing pressure, the AOT solutions are visibly clear. As the pressure is decreased, the solvent density is reduced to a point at which the solution becomes unstable and the AOT "falls out" of solution. The pressure at which AOT first begins to visibly fall out of solution is denoted as the demixing pressure. The visual observation of the demixing pressure was performed at least three times and averaged. All of the constant composition experiments were run twice (i.e., the materials were reloaded) and averaged. The demixing pressures deviated by an average of ±2 bar between the two trials. The experimental error is estimated to be ±3 bar.

Results and Discussion

AOT + Ethane System. The demixing pressures for AOT in ethane are shown in Table 1 and Figure 2. The demixing pressures for 1.6 mass % AOT in ethane between 308 K and 333 K agreed very well with the data of McFann

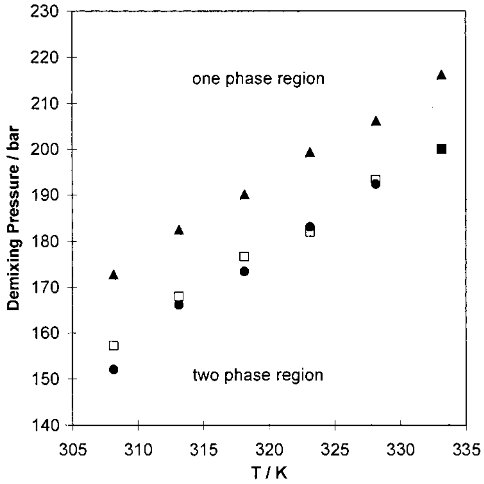

Figure 2. Demixing pressure of AOT in ethane vs temperature: (●) 1.6 mass % AOT, this study; (□) 1.6 mass % AOT, McFann (1993); (▲) 3.0 mass % AOT, this study.

Table 2. Demixing Pressure of 1.6 Mass% AOT in Ethane + Benzene Mixtures vs Temperature

	demixing pressure/bar		
T/K	1 mass % benzene	3 mass % benzene	5 mass % benzene
308	140.7	135.0	126.0
313	152.7	144.9	137.3
318	162.1	154.3	146.0
323	171.2	164.9	155.6
328	179.3	172.9	164.4
333	187.0	182.9	172.5

(1993). The average deviation from McFann's data was approximately 2 bar, which is within the uncertainty of our data. The demixing pressure isopleth for 3 mass % AOT in ethane between 308 K and 333 K was, on the average, 17 bar higher than the 1.6 mass % AOT isopleth. For both AOT compositions, the demixing pressure increased linearly with temperature with approximately the same average slope.

1.6 mass % AOT + Ethane + Benzene System. The demixing pressures for the 1.6 mass % AOT + ethane + benzene system (using the constant composition method) for benzene compositions ranging from 0 to 5 mass % are shown in Table 2 and Figure 3. All of the demixing isopleths were linear with approximately the same slope. Two experimental runs were performed for the AOT + ethane + benzene system using the constant temperature method at 310 K over a wider solvent composition range between 0 and 11.7 mass % benzene (see Table 3 and Figure 4). The maximum pressures for which vapor−liquid equilibrium can exist for benzene + ethane mixtures at 298, 313, and 333 K are ca. 40, 50, and 65 bar, respectively (Knapp et al., 1982; Kay et al., 1952; Ohgaki et al., 1976). All of the demixing pressures reported here (for benzene compositions less than 12 mass %) are thus well above the vapor−liquid equilibrium region for benzene + ethane mixtures. While we would prefer to examine a wider composition range, the composition range reported here was studied to ensure a single solvent phase for the demixing pressure measurements.

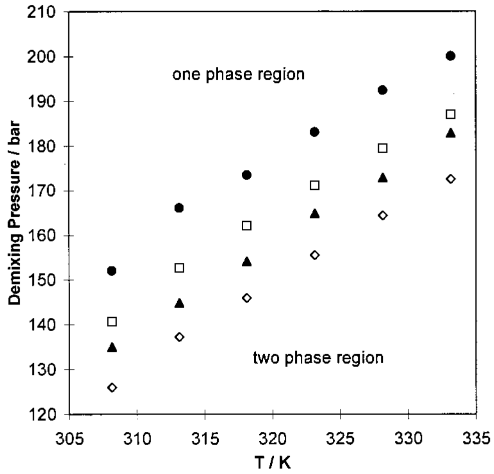

Figure 3. Demixing pressure of 1.6 mass % AOT in ethane + benzene mixtures vs temperature: (●) 0 mass % benzene; (□) 1 mass % benzene; (▲) 3 mass % benzene; (◇) 5 mass % benzene. The benzene compositions are overall compositions in the mixture.

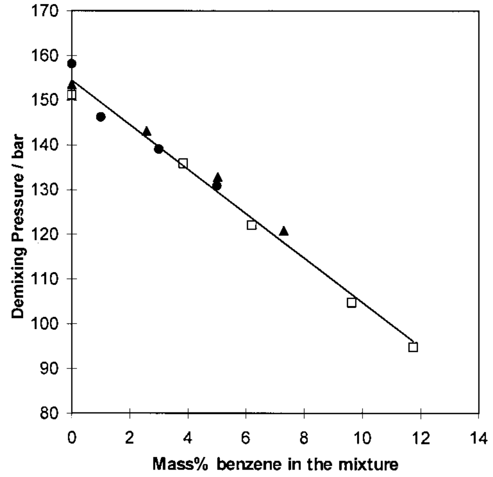

Figure 4. Demixing pressure of 1.6 mass % AOT in ethane + benzene mixtures vs benzene concentration at 310 K: (●) regressed values from constant composition method; (□) data from constant temperature method, run 1; (▲) data from constant temperature method, run 2. The solid line is a linear regression line using all of the data in Figure 4.

Table 3. Demixing Pressures for AOT in Ethane + Benzene Mixtures vs Benzene Concentration at 310 K

mass % AOT	mass % benzene	demixing pressure/bar
	Run 1	
1.60	0.00	151.2
1.54	3.83	135.9
1.50	6.21	122.1
1.45	9.64	104.7
1.41	11.74	94.9
	Run 2	
1.60	0.00	153.5
1.56	2.57	143.1
1.52	5.02	132.8
1.48	7.30	120.8

Prior to the addition of the first aliquot of benzene, the AOT composition in ethane was 1.6 mass %. Since subsequent amounts of benzene were added to the cell during each experiment, the composition of AOT decreased slightly. For the maximum benzene concentration studied, the AOT concentration was 1.41 mass %. From the data in Figure 2, the average change in demixing pressure divided by the change in AOT concentration was about 12 bar/mass % AOT. Therefore, the error introduced by assuming the AOT concentration to be constant at 1.6 mass % during the constant temperature method experiments is estimated to be 2 bar. The data from the two constant temperature runs at 310 K and values obtained by extrapolating the data in Figure 3 to 310 K are presented in Figure 4. The demixing pressure decreases linearly with

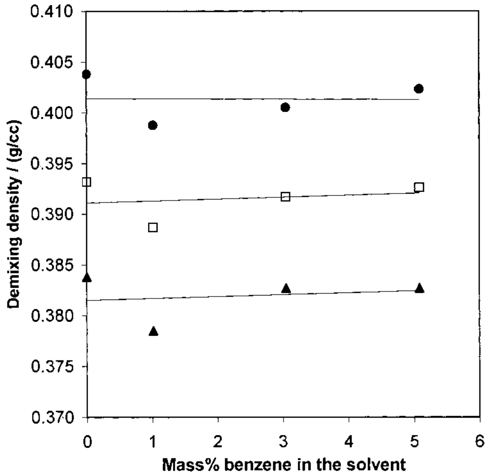

Figure 5. Demixing solvent density vs solvent composition for 1.6 mass % AOT in ethane + benzene mixtures (constant composition method): (●) 313 K; (□) 323 K; (▲) 333 K. Lines are linear regression lines fit to the data at each temperature.

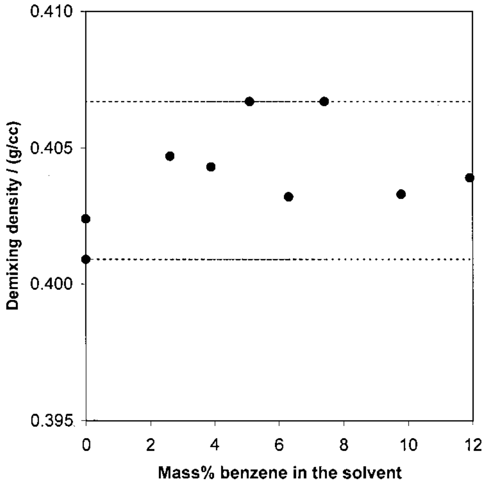

Figure 6. Demixing solvent density vs solvent composition for 1.6 mass % AOT in ethane + benzene mixtures (constant temperature method, 310 K). The dashed lines are added to illustrate that the densities span a fairly narrow range.

benzene concentration, and the results from the two experimental methods are consistent. This shows that while benzene is fairly polarizable, the demixing pressure uniformly decreases with increasing benzene concentration.

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 (Tingey et al., 1990). The demixing solvent densities were calculated for each set of experimental conditions (i.e., at each temperature, demixing pressure, and solvent composition). The densities were estimated using the Peng–Robinson equation of state with an interaction parameter (k_{12}) of 0.0493 (Knapp et al., 1982). The demixing densities for the AOT + ethane + benzene system from the constant concentration data and from the isothermal data are shown in Figures 5 and 6, respectively. Both figures illustrate that, at a given temperature, the demixing density remains constant (within the experimental error) as the solvent composition changes. This suggests that a minimum density is required to solubilize 1.6 mass % AOT at a given temperature, which is unaffected by the addition of the more polarizable benzene cosolvent. The small variations in the density data are due to the scatter in the experimental demixing pressure data.

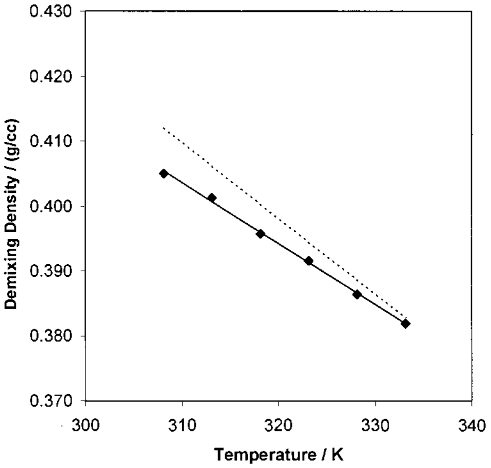

Figure 7. Average demixing density for the 1.6 mass % AOT in ethane + benzene mixtures (data from constant composition method) vs temperature. The solid line represents a linear regression of the data in this study. The dashed line represents a linear regression of the data of Gale et al. (1987) for AOT in ethane.

Both the dielectric constant of the solvent and the solvent solubility parameter (Jackson et al., 1996; Little et al., 1964) have previously been used as accurate predictors of the solubility of ionic surfactants. In this case, the solubility of AOT in the nonpolar ethane + benzene solvent mixture can be characterized simply using the mixture density.

The average demixing density at each temperature for the 1.6 mass % AOT + ethane + benzene data is plotted as a function of temperature in Figure 7. The demixing density required to solubilize 1.6 mass % AOT decreases as the temperature increases. This trend was also observed by Gale et al. (1987) for AOT in pure ethane. A linear regression line fit to the data of Gale et al. (1987) in ethane is also shown in Figure 7. The densities reported by Gale et al. were the minimum ethane densities required to form stable micelles. The decrease in solvent density with an increase in temperature suggests that the increase in thermal energy offsets the loss of ethane solvating power owing to a lower fluid density (Gale et al., 1987). The small difference between the two studies may be attributed to the fact that our densities were estimated using an equation of state whereas Gale et al. used experimentally measured values. Furthermore, a different experimental technique (visual observation of the solvation of colored dyes) was employed to measure the solubility of AOT (Gale et al., 1987).

Conclusions

The demixing pressure for AOT in ethane + benzene mixtures was found to linearly increase with temperature and decrease with benzene concentration. The solvent density required to solubilize 1.6 mass % AOT was found to be independent of the ethane + benzene solvent composition (over the solvent composition range studied) at a given temperature. The demixing solvent density was also found to decrease with increasing temperature.

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