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Phase Behavior of Reverse Aqueous Micelles
in Compressed Propane at 35°C and Pressures to 30MPa.
Solubilization of Poly(ethylene glycol)

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Abstract

Dew points were measured for reverse aqueous micelles in liquid propane at 35°C for pressures to 30 MPa. The micelles were formed by AOT or by mixtures of Brij-30 and Brij-76 with Aliquat-336. While dew-point pressures increase with water-to-surfactant ratio W_0 for AOT, they surprisingly decrease with W_0 for Brij/Aliquat-336 mixtures. Solubilities at 35°C were also measured for poly(ethylene glycol) (PEG) in reverse aqueous micelles formed by AOT in propane in the pressure range 5 to 30 MPa. Solubilities decreased with rising PEG molecular weight. PEG solubilities are mainly determined by micelle size. In the two-phase region, micelle size in compressible fluids like propane can be adjusted by varying pressure; therefore, reverse micelles may be useful for size-selective extractions for fractionation of water-soluble polymers.

Introduction

Reverse micelles are stable aggregates formed by amphiphilic molecules in apolar media, where the hydrophobic surfactant tail is in contact with the apolar solvent and the charged or uncharged hydrophilic headgroups form the polar core of the micelle. Reverse micelles are able to solubilize relatively large amounts of water in their cores. Small amounts of water are strongly bound to the headgroups. The properties of the water pool asymptotically approach those of bulk water with increasing W_0 (moles H_2O /mole surfactant). Reverse aqueous micelles can host hydrophilic molecules including biopolymers and proteins in a continuous hydrophobic medium¹⁻⁴.

Solutions containing reverse micelles have been proposed as extraction media to recover biomolecules from dilute fermentation broths^{5,6} or as a favorable micro-environment for enzymatic reactions⁷. Most previous work has been restricted to liquid hydrocarbons like iso-octane or cyclohexane at conditions remote from critical. Recently however, reverse micelle phases have been studied in supercritical and near-critical fluids which have high compressibilities. Smith and coworkers found that the anionic surfactant AOT (sodium di-2-ethylhexyl sulfosuccinate) forms aqueous micelles in supercritical and liquid ethane or propane^{8,9} as well as in the supercritical rare gases xenon and krypton^{10,11}. Smith et al.¹² showed that cytochrome-C is solubilized by reverse aqueous AOT micelles in propane at 25°C and 20 MPa. Johnston et al.¹³ reported that tryptophan is soluble at the 0.1 wt.% level in supercritical ethane using AOT with octanol as a cosolvent.

When a compressible fluid is used instead of a liquid solvent, pressure may be used at constant temperature to control the system's behavior. When an aqueous phase is in equilibrium with a compressible fluid containing AOT, W_0 rises with increasing pressure. Since W_0 is one of the major factors which affect micelle properties, pressure may be used to improve partition coefficients and selectivities for efficient

recovery of biomolecules or to optimize reaction rates of enzyme-catalyzed reactions. Variation of micelle size presents an opportunity to separate molecules according to size or molecular weight. To study the possibilities of size-selective extraction, we have measured the solubilities of poly(ethylene glycol) (PEG) with average molecular weights 1450, 3350, and 8000 g/mole in AOT reverse micelles in liquid propane at 35°C in the pressure region 5 to 30 MPa.

Daneshvar and Gulari¹⁴ recently reported that compressed carbon dioxide can be used to dissolve PEG, provided that the molecular weight is less than about 1000 g/mole. While CO₂ seems to be a suitable solvent for low-molecular-weight PEG, solubilities of heavier PEG are negligible. Our results show that for PEG molecular weights in excess of 1000 g/mole, solubilities of the order of 0.1 wt.% can be attained in compressed propane when a surfactant is supplied to establish reverse micelles.

AOT is a suitable surfactant because it aggregates readily without a co-surfactant, giving high W_0 . However, there are enzymatic reactions which cannot be performed in AOT reverse micelles. One example is the enzymatic production of L-tryptophan¹⁵. Therefore, it is of interest to investigate properties of reverse micelles using other surfactants. Little is known about the phase behavior of other surfactants in compressible fluids. Johnston et al.¹³ investigated the properties of nonionic polyoxyethylene-n-alkylethers C₁₁₋₁₄E₅ (E denotes an oxyethylene group.) and C₁₆E₁₂ (Brij-56) in supercritical ethane with octanol as a cosolvent. Although aggregation was observed, surfactant solubilities and W_0 -values were low. Beckman et al.¹⁶ used a blend of Brij 30 and Brij 52 in mixtures of ethane and propane to investigate the inverse emulsion polymerisation of acrylamide. They found that acrylamide acted as a co-surfactant. However, in their studies W_0 did not exceed 8.

Following the results of Eggers and Blanch¹⁵ in cyclohexane, we measured the phase behavior of mixtures of Brij-30 or Brij-76 and Aliquat-336 (a quaternary ammonium

salt which also acts as a co-surfactant) in liquid propane. High W_0 (approximately 20) could be obtained.

Experimental

Phase-behavior studies were conducted in a phase-equilibrium apparatus whose essentials are described elsewhere¹⁷. The fluid phase is recirculated with a magnetic pump to achieve thorough mixing and rapid equilibration. A 10-port sampling valve (Valco 10UW-HC) with two sampling loops of 1 ml volume was installed in the recirculation line on top of the equilibrium cell to allow accurate sampling of the fluid phase under process conditions. A hand-operated positive displacement pump was connected to the equilibrium cell for visual dew-point measurements. The phase-equilibrium apparatus was thermostated with a constant-temperature air bath. Temperature is measured with thermoelements to $\pm 0.2^\circ\text{C}$. Pressure is measured with two calibrated bourdon-tube pressure gauges with ranges of 20 and 75 MPa. Accuracy is estimated to be ± 0.06 MPa for pressures below 15 MPa and ± 0.08 MPa for higher pressures.

Propane was supplied by Matheson Gas (CP-grade). Brij-30 (C₁₂E₄; Sigma), Brij-76 (C₁₈E₁₀; Sigma), Aliquat-336 (tricaprylylmethylammonium chloride; Fluka), PEG-1450 (Sigma), PEG-3350 and PEG-8000 (Union Carbide) were used as received. Water was deionized using a nanopure system (Sybron/Barnstead). While AOT is often purified prior to phase equilibrium studies⁸⁻¹³, the tedious purification procedure may be unsuitable for applications; therefore, we used commercially available AOT (Fluka, 98%) for most of our measurements. However, we investigated the influence of impurities by conducting some experiments with purified AOT (Serva, 98%). Purification followed the procedure described by Ueda and Schelly¹⁸. The water content of the unpurified AOT was found to be approximately $W_0=1$ by Karl-Fischer titration. The purified AOT was essentially dry (W_0 below 0.5).

All measurements were made at 35°C and pressures between 5 and 30 MPa. The phase behavior of the propane/water/surfactant systems was studied with a synthetic method. Solid surfactants were loaded into the equilibrium cell as solutions in hexane. The solvent was then evaporated by keeping the equilibrium cell under vacuum for several hours. A known amount of water was introduced before the cell was pressurized with liquid propane. The initial pressure was higher than the expected dew-point pressure. Thus, all of the surfactants and water was solubilized in the propane phase. The one-phase system was mixed by recirculation before the pressure was isothermally reduced by the hand-operated pump until turbidity of the phase was observed. The pressure was then immediately increased until the phase appeared clear again. The reported dew-point pressures are arithmetic means of the clouding and clearing pressures which never differed by more than approximately 0.4 MPa. After some screening experiments with each system, initial system pressures could be chosen to be only slightly higher than the dew-point pressures, so that the change in system volume due to the operation of the hand pump is small compared to the volume of the equilibrium cell. Therefore, the change in molarity during an experiment was negligible when compared to the uncertainty in the system composition due to the loading procedure.

For experiments with PEG, an aqueous PEG solution was introduced into the equilibrium cell instead of pure water. Two phases were always present. When the second phase consisted primarily of PEG, the propane phase (containing reverse micelles) was not saturated with water. Thus, dew-point pressures could be measured as described above. In addition to the dew-point pressure measurements, the fluid phase was sampled at the dew-point pressure. After sampling, the pressure in the sampling loop was released by expanding the propane very slowly to atmospheric pressure through a narrow glass column filled with methanol. Then the methanol was flushed through the loop into a vial. Flushing was repeated with fresh methanol

to assure that all solute is collected. The samples were analyzed with reverse-phase HPLC for AOT and PEG on a 21.4-mm ID 25-cm column packed with Dynamax-60A 8 μm C18. A mixture of 85 vol.% methanol and 15 vol.% deionized water was used as solvent at a flowrate of 2 ml/min. Peaks were detected with a differential refractometer.

Results and Discussion

The ternary system propane-water-AOT

The system was investigated at molarities of 0.05 and 0.15 moles AOT per liter of propane solution. Consistent with the observations of Fulton et al.¹¹, the propane phase darkens from a slightly yellow color to a red-brown color but remains clear as the two-phase boundary is approached. The intensity of the color increases drastically with AOT concentration, so that the system is almost opaque for molarities higher than 0.15 M AOT. Figure 1 shows W_0 versus dew-point pressure. When the pressure is lowered below the dew-point, AOT and water precipitate to form a second phase. At higher pressures, the one-phase system is stable. However, Fulton et al.¹¹ observed upper cloud-point pressures of 137.5 and 90 MPa at 25°C and $W_0=95$ and 105, using 0.087 M AOT.

Experiments at 0.05 M AOT were conducted with purified and with unpurified AOT from different batches. Our results indicate that the impurities do not affect the phase behavior significantly. Figure 1 shows also the existence of a cross-over region for different AOT concentrations. At high W_0 , dew-point pressures decrease with rising AOT molarity, while they increase with rising AOT concentration at low W_0 .

Figure 2 compares the phase behavior at two temperatures. W_0 is plotted against the density of pure propane¹⁹ at system conditions. Lines of the same AOT molarity and different temperature seem to be parallel. At constant density, W_0 increases with rising temperature. Steytler et al.²⁰ found that W_0 decreases with rising

temperatures at constant pressure. There is no inconsistency here because density depends on both temperature and pressure.

Phase behavior is governed by intermolecular forces between the continuous-phase solvent and the hydrocarbon tails of the surfactant, and by micelle-micelle interactions^{11,21}. At constant temperature and AOT concentration, W_0 at saturation increases with rising pressure. This increase follows from enhanced attractive interactions between propane and the surfactant tails which counteract the increasing repulsive solvent penetration of the surfactant tails²¹. The increase of W_0 with rising temperatures at constant solvent density. (probably due to a lower degree of solvent penetration of the surfactant tails) leads to a decline in the radius of curvature, thereby increasing micelle size.

Micelle-micelle interactions are responsible for the observed dependence of W_0 at saturation on AOT concentration. Dynamic light-scattering studies²² show that attractive micelle-micelle interactions provide the main driving force for precipitation of surfactant and water at the phase boundary. When the pressure declines towards the phase boundary, the observed increase in the apparent hydrodynamic micelle diameter may follow from clustering of several micelles to form larger micellar aggregates. Spectroscopic probe studies¹² indicate that the properties of the aqueous micellar cores are not affected by the clustering. Thus, it seems that micelles do not coalesce and the increase in hydrodynamic diameter is due to extensive overlapping of surfactant tails. Because attractive micelle-micelle interactions become more important at higher AOT concentrations, it is not surprising that dew-point pressures rise with AOT molarity at low W_0 .

Fulton et al.¹¹ calculated Hamaker constants for AOT micelles in hydrocarbons and noble gases. For propane at 25°C and pressures below 30 MPa, the Hamaker constant decreases with rising pressure, indicating a decline in attractive micelle-micelle interactions, due to more extensive shielding by the continuous solvent. On the other

hand, the attractive interaction potential among micelles increases with micelle size. Nevertheless, the decrease of dew-point pressure with increasing AOT concentration indicates that increased repulsive micelle-micelle interactions determine the phase behavior at high W_0 .

The quaternary system propane-water-AOT-PEG

Poly(ethylene glycols) (PEG) are the simplest of the water-soluble polymers. Although they are soluble in some organic liquids, aliphatic hydrocarbons are typical nonsolvents for PEG²³. PEG is essentially insoluble in dry and water-saturated propane at 35°C. The solubilities shown in Figure 3 were obtained with the same overall molarities of AOT but different W_0 -values. At all pressures studied here, a two-phase equilibrium was observed. Because AOT partitions also into the aqueous phase²⁴, the PEG solubility plotted is that relative to the AOT concentration in the propane phase. Thus, changes in AOT solubility do not affect the results shown in Figure 3. At low pressures, where the aqueous phase is dilute, PEG concentrations rise steeply with increasing pressure, because the water uptake of the micelles increases. In this region, micelle size is mainly determined by pressure. The remaining aqueous phase becomes increasingly concentrated in PEG until the water is so strongly bound to PEG that it can no longer transfer into reverse micelles.

Upon further increase of pressure, the micelles are no longer loaded with the maximum possible amount of water. Thus, if pressure is lowered from such conditions, the unsaturated propane phase remains clear until it is saturated. This is the condition where the dew point of the propane phase and the maximum PEG solubility are observed. The decrease in PEG solubility at pressures above the dew-point pressure suggests that, perhaps, W_0 also decreases slightly due to the presence of the second phase. In agreement with other data^{12,13}, Figure 3 shows that even in compressible fluids, W_0 is the main variable which determines the degree of solubilization of hydrophilic solutes in reverse micelles.

Figure 4 shows PEG solubilities at the dew point as a function of dew-point pressure. Because rising dew-point pressures are accompanied by increasing W_0 -values, Figure 4 is equivalent to a plot of PEG solubility versus W_0 .

All experiments were carried out with overall concentrations of 0.05 moles AOT and 0.5 grams PEG per liter of equilibrium cell. One experiment with PEG-3350 was conducted with purified AOT. The observed PEG solubility does not differ significantly from that obtained with unpurified AOT.

While solubilities fall gradually with decreasing dew-point pressure for PEG-1450 and PEG-3350, for PEG-8000 there is a minimum value of pressure (or W_0) which has to be exceeded before it is readily soluble in the micellar water pool. At constant W_0 , solubilities decline with rising PEG molecular weight. These observations indicate that the phase behavior is governed by the size of the hydrophilic molecule in relation to that of the water pool.

Toward correlation of data, we relate n_{PEG} , the average number of PEG molecules/micelle, to the ratio of the mean water pool volume (V_w) to the molecular volume of PEG (V_{PEG}); n_{PEG} is obtained from

$$n_{\text{PEG}} = Y \frac{M_{\text{AOT}}}{M_{\text{PEG}}} n_{\text{AOT}} \quad (1)$$

Where Y is the solubility in g PEG/g AOT, M_{AOT} and M_{PEG} are the molecular weights of AOT and PEG, and n_{AOT} is the mean aggregation number. For $1.5 < W_0 < 20$ in iso-octane, Ueda and Schelly¹⁸ found

$$n_{\text{AOT}} = 16.1 + 6.61 W_0 \quad (2)$$

Assuming that Eq. 2 also holds for propane and higher W_0 , n_{PEG} can be calculated from Eqs. 1 and 2. For a reverse aqueous micelle formed by AOT, the hydrodynamic radius r in a variety of solvents was found²⁵ to be

$$r[\text{nm}] = 1.5 + 0.175 W_0 \quad (3)$$

Thus the radius of a dry micelle is 1.5 nm. We estimate the volume of the spherical water pool:

$$V_W [(\text{nm})^3] = \frac{4}{3} \pi (0.175 W_0)^3 \quad (4)$$

The molecular volume of PEG is approximated by

$$V_{\text{PEG}} = \frac{v_{\text{PEG}} M_{\text{PEG}}}{N_A} \quad (5)$$

where v_{PEG} is the partial specific volume of PEG in aqueous solution (0.834 ml/g²⁰) and N_A is Avogadro's number. The results shown in Figure 5 were obtained with the assumption that W_0 at saturation in the quaternary system is equal to that in the ternary propane-water-AOT mixture. Figure 5 shows that n_{PEG} increases linearly with the volume ratio V_W/V_{PEG} for all PEG solutes. Extrapolation towards dry micelles leads to $n_{\text{PEG}} \approx 3$ for PEG-1450 and 0 for PEG-3350; in addition, PEG-8000 is predicted to be insoluble in micelles with low water content. These results again indicate a size-dependent lower limit for W_0 which must be exceeded before solubilization is governed by the water-pool size. This lower limit is approximately $W_0=27$ for PEG-8000.

Further studies are needed to clarify the solubility of PEG-1450 at low W_0 . Dew points could be observed in the dry propane/AOT/PEG-1450 system, although 0.05 M AOT is

completely soluble in propane within the investigated pressure range. However, we believe that extrapolation of Figure 5 towards low V_W/V_{PEG} -ratios leads to unrealistic values for PEG-1450.

Our experiments indicate that the solubilization of PEG is governed by the size of the water pool and by interactions with the surfactant headgroups similar to those observed in studies of aqueous polymer/surfactant solutions²⁶. For PEGs with higher molecular weight, solubilities seem to increase significantly only when a certain water-pool size is exceeded. This suggests the possibility of size-selective extractions by choosing the pressure (and hence the micelle size) such that lower-molecular-weight components are readily soluble in the reverse micellar phase while solubilities of higher-molecular-weight components remain minimal.

The high calculated volume ratios V_W/V_{PEG} may be due to the assumption of a monodisperse micellar solution in Figure 5. Probably, only a fraction of the micelles solubilizes PEG (filled micelles) while the rest contains water only (unfilled micelles). For proteins and low W_0 ²⁷, it was found that a redistribution of water occurs, so that unfilled micelles become small, while W_0 increases in the filled aggregates. Nevertheless, the volume ratio includes the water contained in unfilled micelles. Although it seems possible to describe part of the system behavior with the correlation represented above, the physics of solubilization in reverse micelles are too complicated to be explained fully with such a simple picture.

The quaternary system propane-water-Brij/Aliquat-336

To study the influence of the composition of the surfactant mixture on phase behavior, initial experiments were conducted with $W_0=13$ (moles H₂O/mole surfactant mixture). While the single surfactants were not able to solubilize this amount of water, with surfactant mixtures the water uptake was sufficient to obtain a one-phase system. Figure 6 shows dew-point pressures as a function of the surfactant mixture composition. The dew-point pressure increases steeply with falling ratio of Brij-30 to

Aliquat-336 but changes in dew-point pressure are less pronounced at high Brij-30/Aliquat-336 ratios. Unfortunately, the initial water/Brij-30/Aliquat-336 liquid phase in the phase-equilibrium apparatus was too viscous to allow recirculation of propane for higher ratios. While 0.05 M dry Brij-30 is completely soluble in propane at 35°C and 5 MPa, our experience indicates that Brij-30 cannot solubilize 8 moles water/mole surfactant within our pressure range.

Figure 7 shows W_0 as a function of dew-point pressure for Brij-30/Aliquat-336 at two molarities and for Brij-76/Aliquat-336 at a fixed molarity. The molar ratio of Brij to Aliquat-336 is 1.5. Both surfactant mixtures exhibit the same phase behavior. Dew-point pressures are higher for the Brij-76 (C₁₈E₁₀) mixture than those for the Brij-30 (C₁₂E₄) mixture because the larger Brij-76 molecules require stronger attractive solvent-solute interactions. Increased surfactant concentrations lead to lower dew-point pressures, consistent with the results of Beckmann et al.¹⁶.

While the dry surfactant mixtures have low dew-point pressures, there is a steep increase in dew-point pressure when only a little water (W_0 approximately 2) is added. If W_0 rises further, dew-point pressures fall quickly and seem to approach a limiting value which is lower than the dew-point pressures of the dry systems. 25 moles water/mol surfactant mixture could not be dissolved completely in the Brij-30/Aliquat-336 reverse micellar phase. A system with 0.1 moles Brij-76/Aliquat-336 per liter of equilibrium cell and $W_0 = 20$ was also found to be in the two-phase region. In all cases a red-brown coloring of the propane phase was observed when the phase boundary was approached, consistent with the results of Beckman et al.¹⁶ for Brij-30/Brij-52 blends and with our and Fulton's et al.¹¹ observations for the AOT reverse-micellar system. When pressure was sufficiently above the dew-point pressure at constant W_0 , the system started to look turbid again, perhaps indicating upper cloud-point pressures. However, turbidity increased so slowly and gradually, that an accurate visual determination of upper cloud-point pressures was not possible.

Using Brij, the observed phase behavior is completely different from that with AOT. A reasonable explanation of our results can only be based on structural changes of the surfactant aggregates which depend on W_0 . A simple picture can be drawn, if the co-surfactant is neglected. While AOT reverse micelles are spherical because of the molecular shape of AOT²⁸, such arrangements are unfavorable for linear nonionic surfactants like Brij. Such surfactants form "hank-like" shaped aggregates in aliphatic hydrocarbons with low carbon number²⁹. A hank-like aggregate is defined by Ravey et al.²⁹ as a structure where the polyoxyethylene chains are parallel and packed "head to tail". If water is added to the dry system, water molecules start to form hydrogen bonds with the polyoxyethylene chains. Since water is not well shielded from the continuous phase in a hank-like structure, we expect an initial increase of dew-point pressure. Further addition of water promotes a gradual structural change from hank-like aggregates to lamellae with much higher aggregation numbers³⁰. In lamellae, polyoxyethylene chains and water molecules are better shielded from the hydrocarbon solvent. The gradual structural change from hank-like aggregates to lamellae might explain why dew-point pressures decrease with further increases in W_0 .

The role played by the co-surfactant is not clear. Aliquat-336 is a quaternary ammonium chloride with three aliphatic C₈-hydrocarbon chains. We expect that Aliquat-336 molecules cannot easily be located between two Brij molecules in a lamellar structure. They could be located around the cylindrical surface of the lamellar or hank-like aggregates, giving these the shape of oblate ellipsoids. However, these comments are speculations; additional investigations are necessary for achieving understanding of the observed phase behavior.

Conclusions

In the region 25 to 35°C, the phase behavior of AOT reverse micelles in liquid propane depends only slightly on temperature. W_0 increases with temperature at

constant continuous phase density. While dew-point pressures increase with AOT molarity at low W_0 , they decrease at higher W_0 .

PEG solubilities in propane are mainly determined by micelle size. When reverse micelles are formed by AOT, solubilities range from the 0.1 wt.% level for PEG-8000 to more than 0.5 wt.% for PEG-1450. PEG solubilities were correlated as a function of the ratio of the water pool volume to the molecular volume of PEG. For PEG-8000, there seems to be a lower limit of W_0 which must be exceeded before significant increases of solubility can be observed. The observed phase behavior suggests that size-selective extractions may be possible through pressure adjustment of micelle size in compressible fluids.

The phase behavior of mixtures of nonionic surfactants (Brij-30 and Brij-76) and a quaternary ammonium salt (Aliquat-336) was measured in liquid propane. Water uptake of the aggregates was as high as $W_0=20$. Surprisingly, dew-point pressures decreased with rising W_0 .

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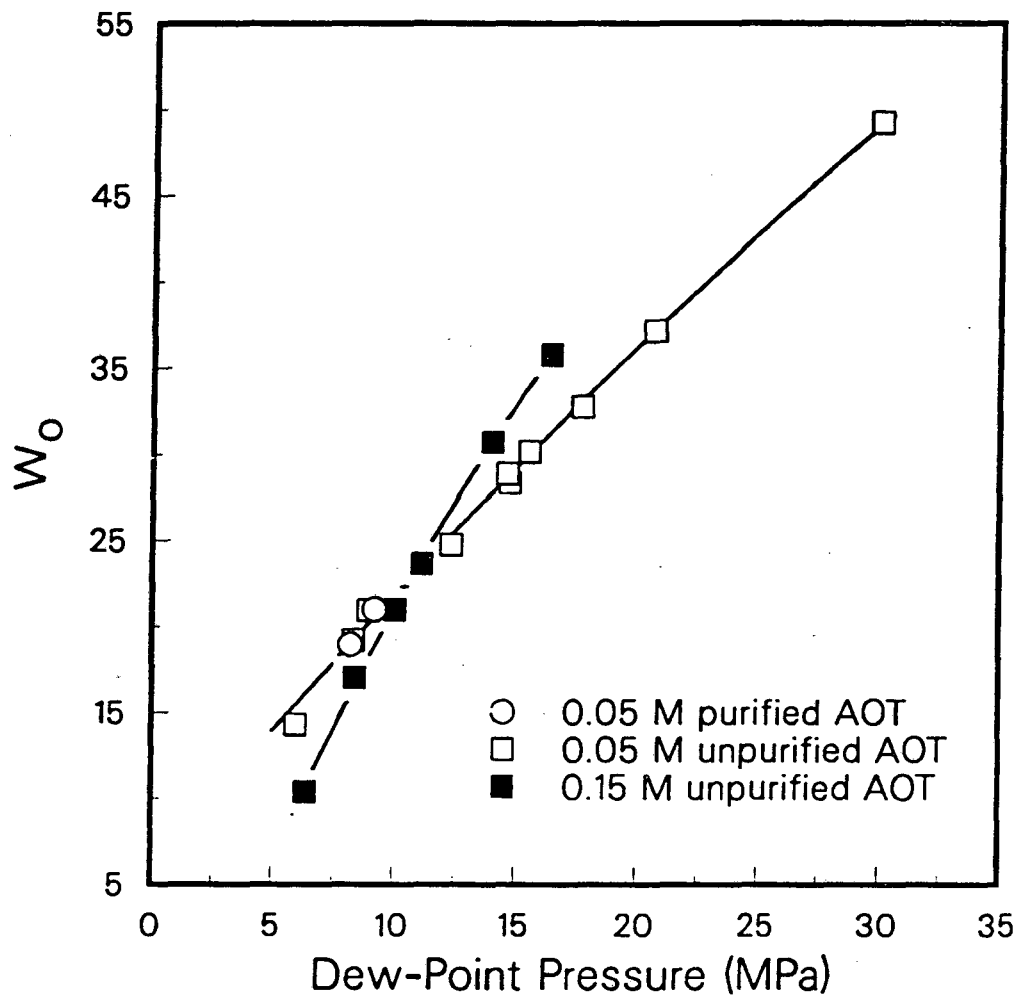
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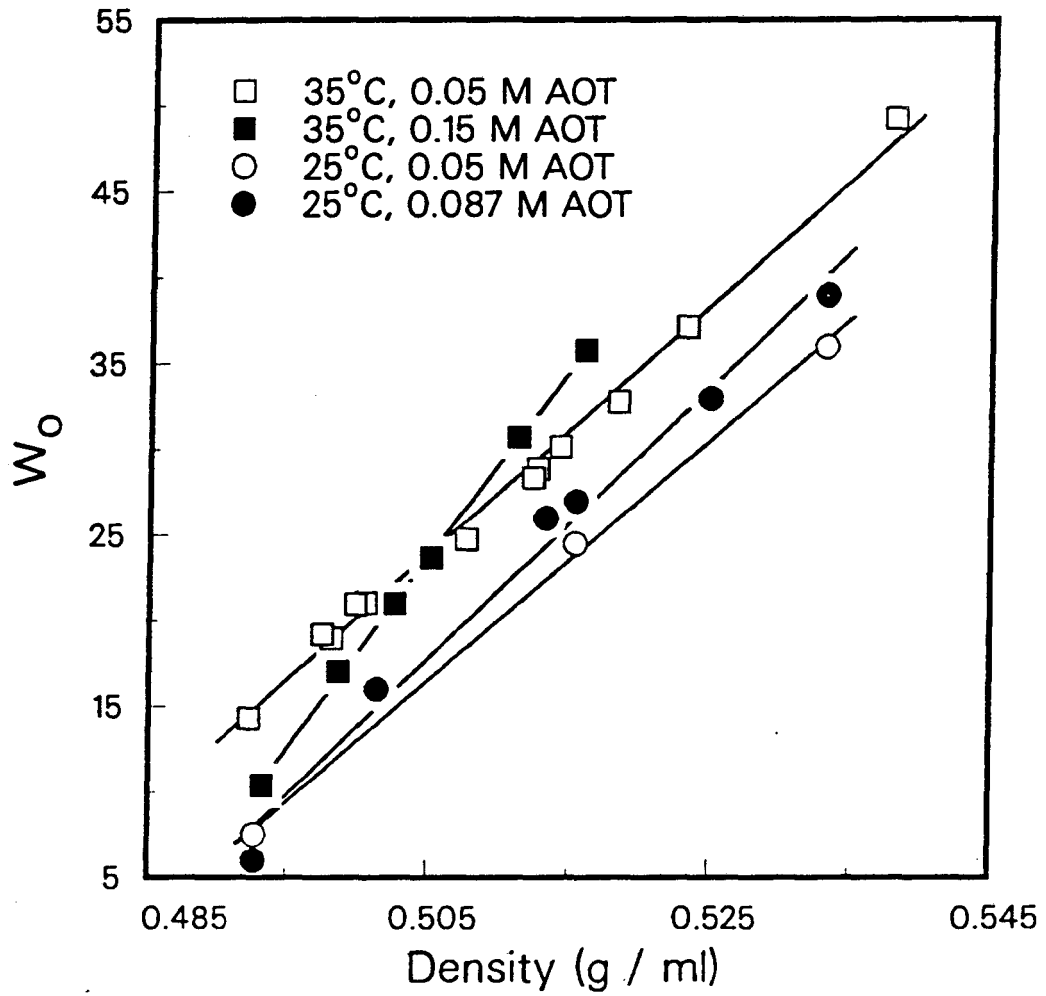
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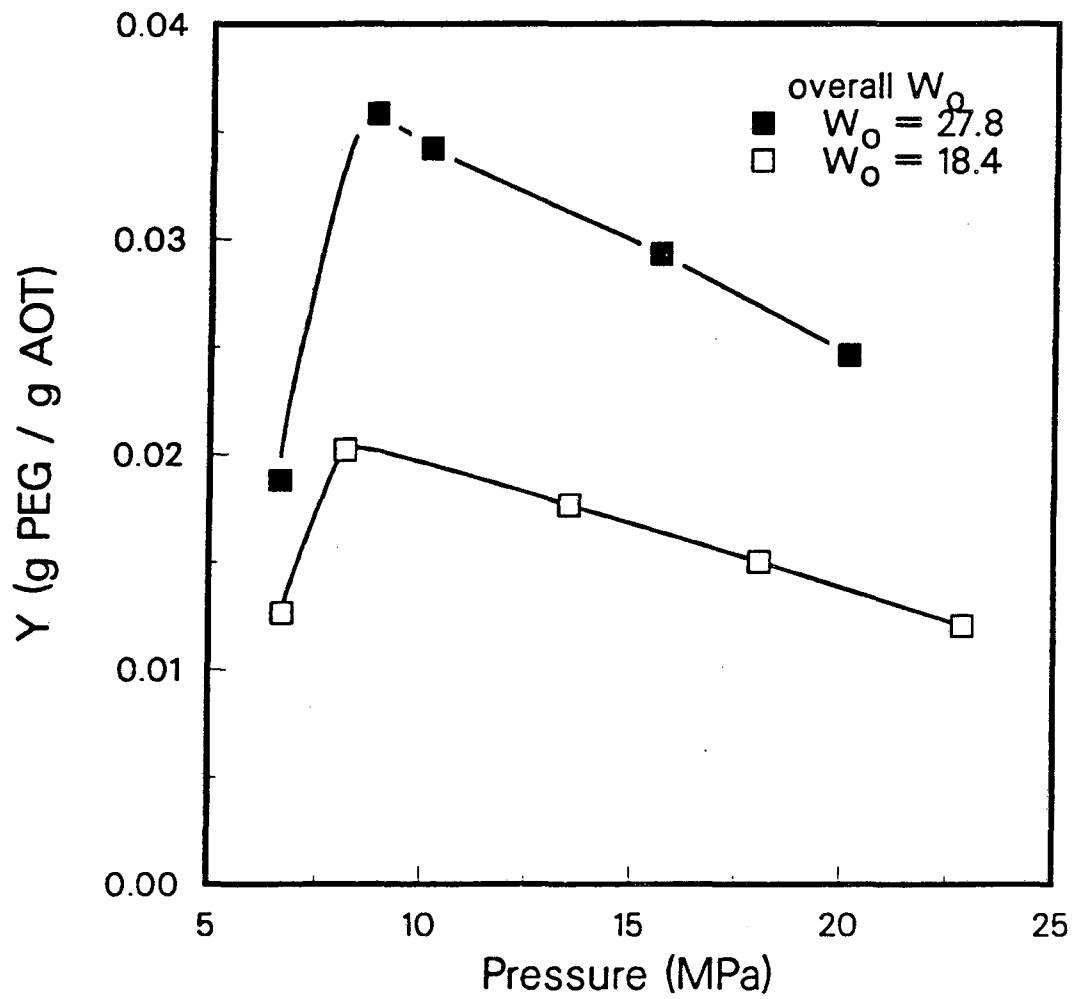
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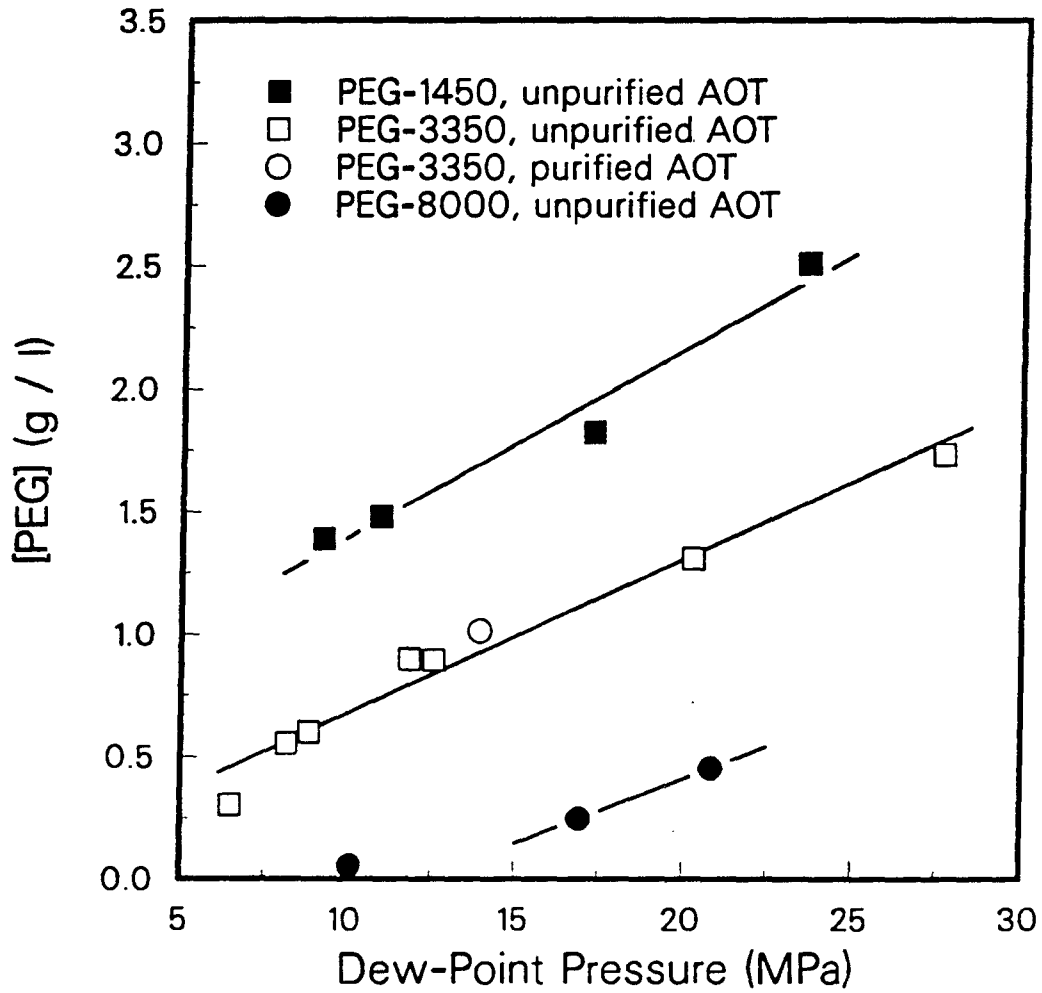
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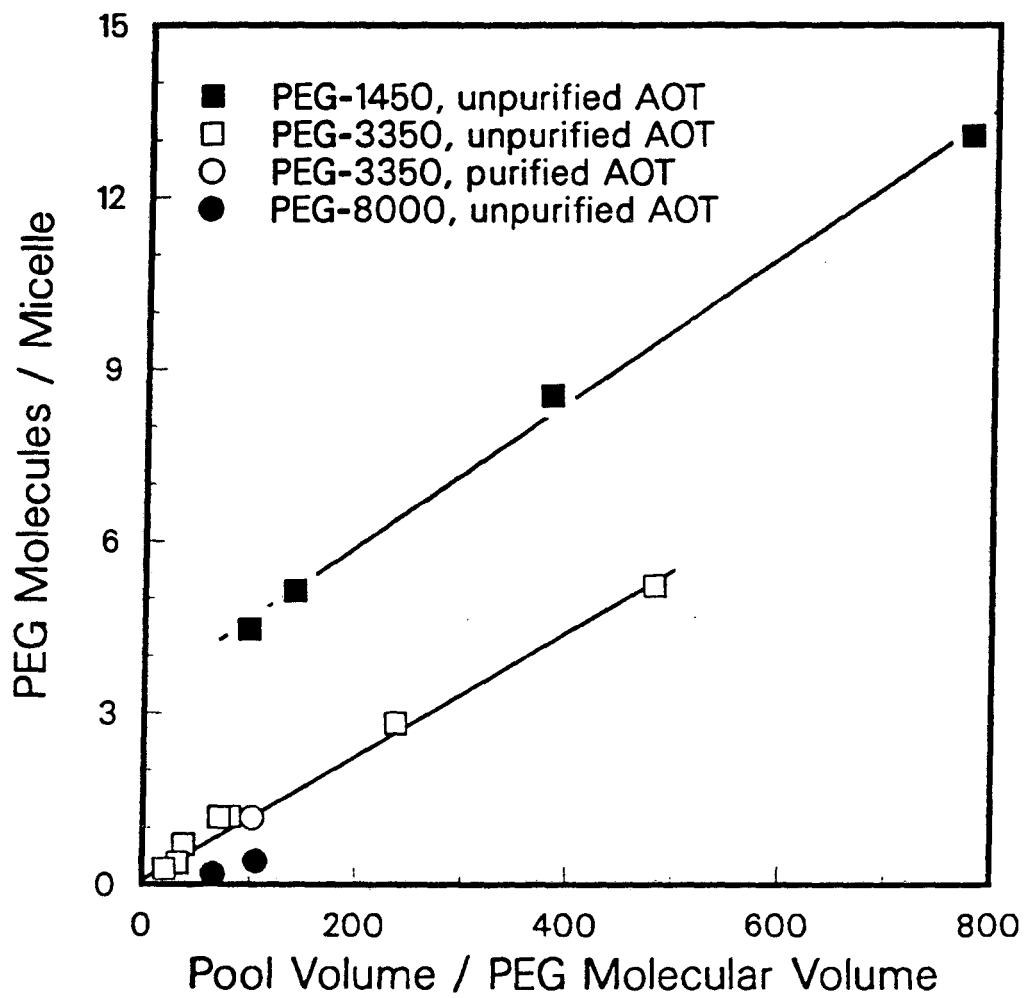
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- Figure 2 W_O at saturation versus density of pure propane¹⁹ for propane/water/AOT at 35°C and 25°C^{10,11}
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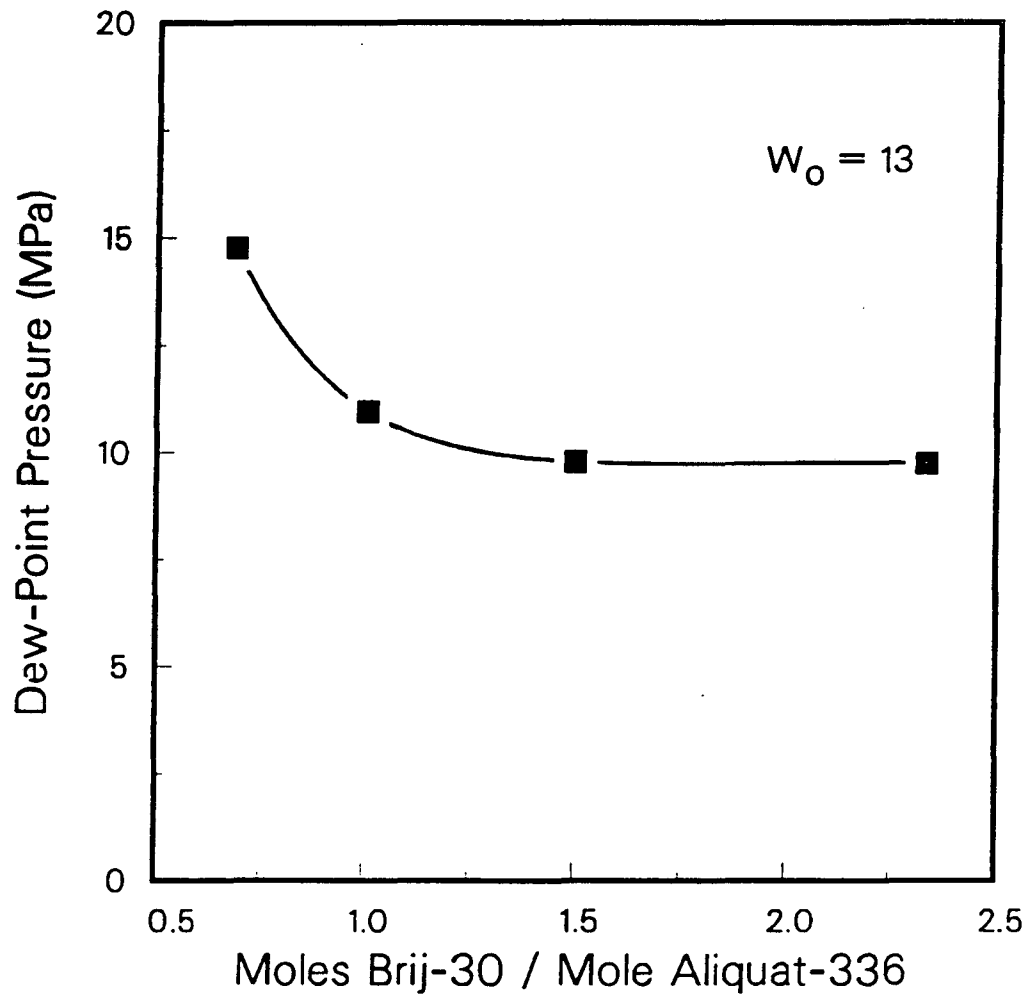


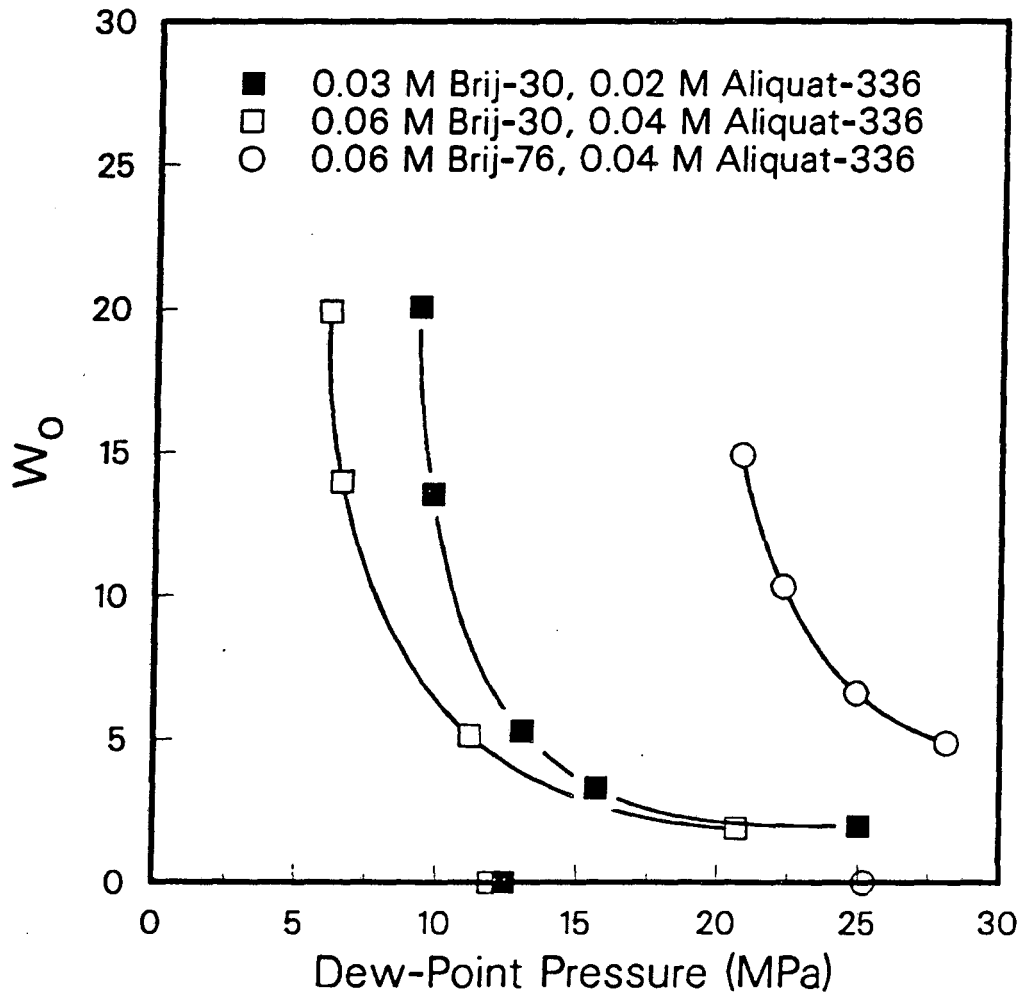












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