Influence of Methane on the Phase Behavior of Oil + Water + Nonionic Surfactant Systems

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The phase behavior of oil + water + nonionic surfactant systems has been thoroughly studied. The oil had been commonly represented by a single long-chain hydrocarbon. In this work, the influence of methane on the phase behavior of the system decane + water + 2-butoxyethanol is presented. Mixtures of methane and decane describe the oil. The methane concentrations in the oil mixture were 0, 5, and 10 wt % (respectively 0, 30, and 50 mol %). The investigated temperature range was from 278 to 365 K, and the studied pressure range was from 10 to 100 MPa. In the temperature, pressure, and methane concentration range investigated in this work, the phase transition with increasing pressure at a constant temperature was always found to be $\bar{2} \rightarrow 3 \rightarrow \underline{2}$. For the systems containing 10 wt % methane in the oil mixture the formation of gas hydrates could be observed for low surfactant concentrations and low temperatures.

Introduction

Surfactants have been suggested to be used in enhanced oil recovery to reduce the interfacial tension between the oil and the water. Ultralow interfacial tensions are usually obtained within a three-phase region where a microemulsion middle phase containing most of the added surfactant is coexisting with an excess-oil phase and an excess-water phase.[1,6]

For the optimization of the low-concentration surfactant flooding process the phase behavior of the system oil + water + surfactant has to be known. The investigation of the phase behavior of interest for the oil recovery is studied by employing model systems. These model systems contain water, a pure low-volatility hydrocarbon to represent the oil, and a surfactant or a mixture of surfactants. The results are then used to develop models for the description of the phase behavior of oil + water + surfactant systems.[1−5] However, real oils contain quite large amounts of high-volatility hydrocarbons. Therefore, the phase behavior of oil + water + surfactant systems containing a model oil consisting of only a single low-volatility hydrocarbon probably gives an incorrect picture.

In this work the influence of methane on the phase behavior of the system water + decane + 2-butoxyethanol was investigated. The mixture of decane and methane is regarded as a pseudo-component which represents the oil. The oil-to-water weight fraction α was kept constant to be equal to 0.5 (1:1). The methane concentration in the oil mixture was varied from 0 to 30 to 50 mol % (respectively 0, 5, and 10 wt %). The temperature influence was investigated in the range from 278 to 365 K and the pressure in the range from 10 to 100 MPa.

Theory

The phase behavior of oil + water + nonionic surfactant systems as a function of the temperature and the pressure has been studied thoroughly by several research groups.[1−5] The phase behavior as found for oil + water + nonionic surfactant systems is depicted in Figure 1. Figure 1a shows a tempera-
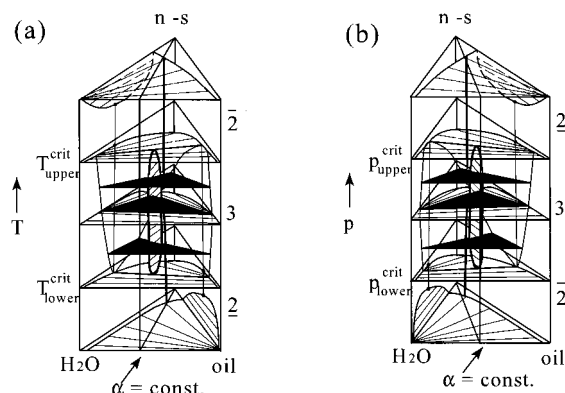

Figure 1. (a) Temperature−concentration phase prism of the oil + water + nonionic surfactant system and (b) pressure−concentration phase prism of the oil + water + nonionic surfactant system.

ture−composition phase prism. The base of the phase prism is the Gibbs phase triangle of the ternary system oil + water + nonionic surfactant. For low temperatures the surfactant is hydrophilic and a two-phase region can be observed. The lower phase consists of the water, some oil, and most of the surfactant, the upper phase is almost pure oil (denoted by Winsor I or $\underline{2}$). With increasing temperature the surfactant becomes more hydrophobic. As a result the surfactant tends to dissolve better in the oil-rich phase. For some oil + water + nonionic surfactant systems a three-phase region can be observed (denoted by Winsor III or 3). At a lower critical temperature, $T^{\text{crit}}_{\text{lower}}$, a third phase occurs. The lower aqueous phase becomes critical with a microemulsion middle phase. With increasing temperature this microemulsion phase becomes enriched in oil. At an upper critical temperature, $T^{\text{crit}}_{\text{upper}}$, the middle phase becomes identical with the upper phase. The resulting critical phase consists of oil, most of the surfactant, and some water. At higher temperatures again a two-phase region is found. A water-excess phase coexists with the upper oil-rich phase which contains most of the surfactant (denoted by Winsor II or $\bar{2}$). The influence of the pressure on the phase behavior of oil + water + nonionic surfactant systems is depicted in Figure 1b.[5] With increasing

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Behavior of Oil + Water + Nonionic Surfactant Systems

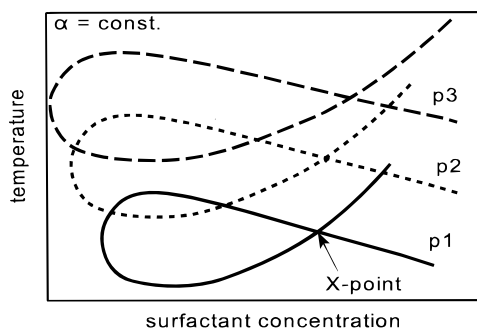*J. Phys. Chem. B, Vol. 102, No. 1, 1998* **201**

Figure 2. "Fish" diagrams of the system oil + water + nonionic surfactant at constant oil-to-water ratio α at three different pressures: $p_1 < p_2 < p_3$.

pressure the phase behavior shows the opposite evolvement than was found for increasing temperature. This means that with increasing pressure starting within a two-phase region of the type $\bar{2}$ first, a three-phase region is induced, and upon increasing the pressure further, a two-phase region of the type $\underline{2}$. Therefore, at elevated but constant pressure the three-phase temperature range is found for higher temperatures than at atmospheric pressure.

The main interest of oil + water + surfactant systems lies in the phase behavior at an oil-to-water fraction of $\alpha = 0.5$ (1:1) since at this α value the minimal interfacial tension between the water and the oil phase is commonly found. The amount of surfactant needed to solubilize the same amounts of oil and water is used to characterize the efficiency of the surfactant. The less surfactant that is needed to solubilize the same amounts of water and oil, the more efficient the surfactant is. Experiments performed at constant oil-to-water weight fractions α with varying surfactant concentration are expressed in so-called fish diagrams (Figure 2).[1] The three-phase region is described by the "body" of the fish, the one-phase region by the "tail" of the fish. The *X*-point describes the surfactant concentration needed to establish a macroscopically homogeneous phase at the given oil-to-water fraction α. Above and below the fish the occurring two-phase equilibria are situated according to the phase behavior as explained in Figure 1. The fish diagrams result from cross-sections at constant oil-to-water fractions α through the temperature−composition phase prism. By a simple mean filed calculation these fishes can be described theoretically as was shown by Kleinert[7,8] and Rudolph et al.[9] An increase of the pressure leads to a shift of the fish in the temperature−composition diagram toward higher temperatures.[5] With increasing pressure the extension of the body of the fish is enlarging. The fish diagrams of systems of water + oil + nonionic surfactant at oil-to-water weight fractions α close to 0.5 are commonly quite symmetrical to the *X*-point isotherm. The resulting fish diagrams lay horizontal and do not show an inclination. Cross sections through the temperature−composition diagram at a different oil-to-water ratio than 1:1 ($\alpha \approx 0.5$) give fish diagrams with clear inclination downward ($\alpha > 0.5$) or upward ($\alpha < 0.5$). The maximal inclination of the fish is found when the *X*-point temperature reaches the upper or lower critical temperature.[9]

Kahlweit et al.[1] investigated the phase behavior of several oil + water + nonionic surfactant systems at atmospheric pressure. The temperature range of the three-phase region is shifting toward higher temperatures and is widening up with increasing chain length of the oil. The amount surfactant needed to solubilize same amounts of water and oil is increasing with increasing oil-chain length.

The phase behavior of oil + water + surfactant systems with a light hydrocarbon (e.g. C_1 or C_3) representing the oil has scarcely been investigated. Most investigations covered the phase behavior of systems containing anionic surfactants.[6,10−12] It was found that the addition of a light hydrocarbon to a system containing a heavy hydrocarbon can inverse the sequence of the occurring coexisting phases with increasing pressure.[6,10,11]

Leung et al.[13] stated that the phase behavior of an oil + water + surfactant system containing a pure hydrocarbon of a given carbon number k can be modeled by a system containing a mixture of two hydrocarbons which have the same mean carbon number k. The fact that the pressure influence on the phase behavior of systems containing long-chain hydrocarbons is qualitatively different than the phase behavior of systems containing short-chain hydrocarbons gives reason to doubt this statement. Since life oils contain large concentrations of lighter components such as methane and ethane, it is important to investigate the phase behavior of an oil + water + nonionic surfactant system with a model oil which consists of a mixture of a volatile and a nonvolatile hydrocarbon, e.g. a mixture of methane and decane.

Experimental Section

The systems investigated consisted of 2-butoxyethanol, water, n-decane, and methane. The water used was double-distilled with a conductivity of less than 10^{-6} S cm^{-1}. The 2-butoxyethanol (C_4E_1) and the n-decane were products of Merck-Schuchardt. The methane was provided by Air Products. The stated purity of the decane was 99.5 wt % and of the methane 99.995 wt %. The decane and the methane were used without further purification. The 2-butoxyethanol was vacuum distilled and stored over molecular sieves (3 Å). After purification the purity of the 2-butoxyethanol was better than 99.8 wt % (analyzed by gas chromatography).

The experiments were carried out by applying the synthetic method. Therefore, phase transitions of samples of known and constant composition are determined visually as a function of the temperature and the pressure. The samples were prepared on a weight basis using the following equations.

$$\gamma_{\text{surfactant}} = \frac{m_{\text{surfactant}}}{m_{\text{surfactant}} + m_{\text{water}} + m_{\text{decane}} + m_{\text{methane}}}$$

$$\alpha = \frac{m_{\text{methane}} + m_{\text{decane}}}{m_{\text{water}} + m_{\text{decane}} + m_{\text{methane}}}$$

$$\beta = \frac{m_{\text{methane}}}{m_{\text{decane}} + m_{\text{methane}}}$$

The weight of the methane was determined by adding known volumes of methane at a known pressure (<0.1 MPa) and temperature. The obtained accuracy in composition on a weight fraction basis is better than ±0.004 with increasing accuracy as more methane was added. The oil-to-water weight fraction α was kept constant equal to 0.5 for all experiments. If methane was present, the oil was regarded as a pseudo-component formed by the decane and the methane. The methane weight fraction in the oil mixture increased from 0 to 0.05 and finally to 0.1 (mole fractions 0, 0.3, and 0.5). The surfactant concentration was varied from around 15 wt % to around 65 wt % of the overall composition.

The phase transitions were observed visually through two sapphire windows of a stainless steel autoclave placed in a thermostated water bath. This equipment can be used for

TABLE 1: Isopleths of the System Decane + Water + 2-Butoxyethanol (C$_4$E$_1$)^a

$\gamma_{C_4E_1}$	T/K	p/MPa	trans	$\gamma_{C_4E_1}$	T/K	p/MPa	trans	$\gamma_{C_4E_1}$	T/K	p/MPa	trans
0.163	303.83	19.51	a	0.497	332.40	40.02	b	0.594	322.71	24.51	c
	304.00	19.91	a		335.28	49.13	b		325.54	33.22	c
	307.02	30.22	a		338.23	58.33	b		325.79	33.62	c
	308.46	36.72	a		342.11	70.34	b		328.46	37.92	c
	309.82	40.52	a		345.51	81.95	b		328.64	38.82	c
	313.23	55.53	a	0.573	316.07	6.20	a		330.47	40.82	c
	316.17	68.44	a		318.97	15.31	a		322.81	15.09	d
	318.82	81.15	a		321.90	24.31	a		325.78	23.31	d
	316.16	5.20	b		324.77	33.62	a		328.49	34.82	d
	318.78	11.91	b		327.82	44.63	a		330.45	40.24	d
	322.62	23.14	b		330.75	54.03	a	0.603	315.11	16.31	c
	325.62	34.30	b		334.56	68.74	a		318.07	24.21	c
	328.47	43.93	b		337.08	78.75	a		320.94	31.02	c
	332.24	54.33	b		321.30	14.61	b		324.64	41.82	c
	334.98	61.54	b		327.74	32.92	b		327.68	49.32	c
	343.18	81.35	b		330.77	42.63	b		330.59	55.93	c
0.288	303.98	19.71	a		334.45	54.73	b		333.65	66.34	c
	304.04	19.81	a		337.01	62.24	b		336.54	75.94	c
	313.88	59.24	a		340.04	72.43	b		339.49	86.05	c
	317.89	77.65	a		343.48	85.75	b		324.71	15.09	d
	318.74	82.25	a	0.594	330.53	45.63	a		327.69	24.81	d
	320.75	92.96	a		332.28	49.83	a		330.71	33.72	d
	320.75	2.90	b		332.33	47.93	a		333.60	43.73	d
	325.47	16.61	b		334.22	56.03	a		336.47	54.53	d
	329.35	22.81	b		336.63	61.84	a		339.47	66.44	d
0.497	311.12	10.41	a		340.22	76.53	a		342.21	76.25	d
	311.24	10.21	a		340.70	77.95	a		344.35	82.75	d
	312.66	18.21	a		343.75	90.65	a	0.644	303.88	35.21	c
	314.09	17.71	a		345.32	99.66	a		306.46	49.93	c
	315.73	31.72	a		330.41	44.43	b		309.40	64.94	c
	316.17	30.32	a		332.34	45.43	b		312.32	74.54	c
	316.96	36.72	a		334.58	47.53	b		315.02	79.35	c
	319.72	45.73	a		337.25	54.73	b		315.12	82.05	c
	320.78	49.93	a		340.21	64.34	b		318.05	89.05	c
	322.60	56.83	a		340.57	67.84	b		321.00	97.86	c
	323.78	60.54	a		343.66	81.95	b		340.50	3.50	d
	325.38	67.94	a		343.76	82.05	b		341.08	5.70	d
	325.72	70.64	a		345.33	93.46	b		344.14	11.47	d
	328.58	83.75	a		317.94	14.21	c		347.17	16.81	d
	321.84	10.31	b		320.74	21.01	c		349.99	20.61	d
	328.49	28.22	b		322.67	27.52	c				

^{a} Oil-to-water weight fraction $\alpha = 0.5$ for all isopleths. $\gamma_{C_4E_1}$: weight fraction of 2-butoxyethanol; T, temperature; p, pressure; phase transitions, (a) $3 \rightarrow \underline{2}$, (b) $3 \rightarrow \bar{\underline{2}}$, (c) $1 \rightarrow \underline{2}$, (d) $1 \rightarrow \bar{\underline{2}}$.

pressures up to 100 MPa.[5] The temperatures were measured with a Pt-100 resistance thermometer connected to a resistance bridge. The temperature was kept constant within ±0.03 K. The pressure is controlled and determined by applying a dead weight gauge. The accuracy of the dead weight gauge is better than ±0.005 MPa. However, the accuracy of the phase-transition pressure is determined by the smallest pressure interval in which a phase transition could be determined. This results for the given measurements in an accuracy of the phase transition pressure of ±0.05 MPa.

During the experiments the phase transitions between a two-phase region and a three-phase or a one-phase region were determined. Therefore, a temperature was set and by variation of the pressure the phase transitions at the given temperature could be determined. To avoid metastable states the determination of the phase transitions was always performed in such a way that one of the phases vanishes.

A more detailed description of the equipment and the experimental method is given elsewhere.[5]

Results

The influence of methane on the phase behavior of the system decane + water + 2-butoxyethanol was studied as a function of the temperature and the pressure. The methane concentration

in the oil mixture was varied from 0 to 5 to 10 wt %. In Tables 1–3 the results of the measurements for the different methane concentrations are listed. The results are presented in Figures 3–7.

In Figure 3 isopleths for three different methane concentrations at a surfactant concentration of 16 wt % are depicted as an example for the other isopleths at other surfactant concentrations. For all three methane concentrations investigated here it could be observed that the three-phase region temperature range is widening up with increasing pressure. The three-phase region shifts toward lower temperatures with increasing methane concentration, and the temperature range of the three-phase region at a constant pressure decreases. For a methane concentration of 10 wt % the occurrence of a three-phase region could not be determined completely at low temperatures due to the formation of gas hydrates.

Isobaric fish diagrams have been deduced from the isopleths at different surfactant concentrations by interpolation. In Figure 4–6 the pressure influence on the phase behavior of the systems containing 0, 5, and 10 wt % methane is expressed in temperature–composition diagrams. In Figure 4 the phase behavior of the methane-free system is depicted. With increasing pressure the fish shifts toward higher temperatures, and the temperature range of the three-phase region which is described

TABLE 2: Isopleths of the System (Methane + Decane) + Water + 2-Butoxyethanol (C₄E₁)[a]

$\gamma_{C_4E_1}$	T/K	p/MPa	trans	$\gamma_{C_4E_1}$	T/K	p/MPa	trans	$\gamma_{C_4E_1}$	T/K	p/MPa	trans
0.160	287.87	8.50	a	0.498	301.33	14.31	a	0.589	311.46	28.52	c
	293.29	27.32	a		306.04	27.22	a		313.89	34.42	c
	296.30	39.42	a		309.00	38.02	a		316.81	41.02	c
	299.32	53.73	a		310.91	43.73	a		319.76	51.13	c
	303.27	73.74	a		311.95	50.33	a		322.61	59.03	c
	307.05	85.45	a		314.84	64.24	a		325.66	67.64	c
	293.54	10.91	a		320.73	94.63	a		328.39	78.55	c
	298.34	24.01	b		310.89	9.91	b		331.59	88.05	c
	304.10	42.12	b		314.89	24.01	b		333.68	97.96	c
	307.01	51.63	b		320.72	43.93	b		311.54	10.31	d
	308.93	63.74	b		323.60	51.23	b		319.65	33.22	d
	310.89	72.74	b		326.67	62.04	b		322.67	41.32	d
	313.74	78.75	b		329.61	71.24	b		325.48	52.03	d
	313.82	78.65	b		332.32	86.55	b		328.61	66.64	d
0.290	292.57	18.91	a		334.46	90.95	b		331.51	80.55	d
	293.35	20.31	a	0.551	308.52	16.41	a		333.67	91.55	d
	295.99	27.22	a		309.19	20.31	a	0.612	295.38	13.41	c
	296.45	27.92	a		312.00	29.32	a		308.56	50.33	c
	298.22	43.73	a		315.92	42.63	a		311.47	58.33	c
	300.34	49.53	a		318.85	54.43	a		315.20	69.54	c
	304.07	70.84	a		321.89	66.24	a		318.12	79.75	c
	304.10	68.64	a		325.75	84.15	a		321.06	89.05	c
	306.97	81.55	a		328.49	97.26	a		321.08	17.41	d
	307.00	87.35	a		312.01	14.31	b		324.94	30.72	d
	312.93	24.31	b		315.93	25.52	b		327.61	40.22	d
	316.66	34.82	b		318.87	35.52	b		330.71	51.43	d
	316.83	37.72	b		321.90	48.73	b		334.46	65.74	d
	319.65	47.83	b		325.56	67.43	b		339.50	85.75	d
	323.46	62.34	b	0.589	306.97	17.01	c				

[a] Oil-to-water weight fraction α = 0.5 and methane-to-decane ratio β = 0.05 for all isopleths. $\gamma_{C_4E_1}$, weight fraction of 2-butoxyethanol; T, Temperature; p, pressure; phase transitions, (a) 3 → $\underline{2}$, (b) 3 → $\underline{2}$, (c) 1 → $\underline{2}$, (d) 1 → $\underline{2}$.

TABLE 3: Isopleths of the System (Methane + Decane) + Water + 2-Butoxyethanol (C₄E₁)[a]

$\gamma_{C_4E_1}$	T/K	p/MPa	trans	$\gamma_{C_4E_1}$	T/K	p/MPa	trans	$\gamma_{C_4E_1}$	T/K	p/MPa	trans
0.167	290.46	54.03	a	0.498	310.95	87.45	a	0.589	328.25	101.46	a
	292.18	65.04	a		305.95	20.61	b		313.88	32.22	b
	295.22	82.55	a		308.42	29.52	b		315.62	35.72	b
	295.21	51.93	b		310.90	39.32	b		318.70	44.53	b
	298.16	61.94	b		315.71	59.64	b		321.57	56.33	b
	300.09	70.64	b		318.65	70.04	b		324.62	67.34	b
	304.54	93.26	b		321.51	81.45	b		326.35	81.75	b
	288.47	21.61	e		285.60	21.41	e		326.37	82.95	b
	289.45	29.12	e		287.57	42.22	e		328.30	89.75	b
	291.18	44.63	e		290.57	77.55	e		328.46	84.95	b
	293.19	65.64	e		291.55	88.35	e		304.04	13.71	c
	295.10	87.05	e	0.581	306.84	24.71	a		309.99	26.92	c
0.311	290.48	45.63	a		309.68	36.32	a		312.65	30.22	c
	293.50	61.24	a	0.551	312.74	49.43	a		309.91	20.81	d
0.290	296.39	77.05	a		314.66	58.83	a		312.67	33.62	d
	299.35	95.76	a		317.60	72.24	a	0.603	293.24	22.11	c
	303.50	27.42	b		320.59	84.45	a		296.22	31.52	c
	307.56	46.03	b		310.74	26.92	b		299.18	38.52	c
	309.86	56.23	b		314.79	368.42	b		301.24	43.33	c
	312.76	69.54	b	0.581	317.63	48.43	b		304.80	57.03	c
	316.42	87.45	b		320.58	60.24	b		304.94	53.63	c
	287.58	23.11	e		323.41	75.34	b		306.83	60.94	c
	288.53	30.32	e		324.40	83.25	b		309.63	66.44	c
	289.63	38.92	e	0.593	312.95	35.32	a		312.44	74.34	c
	290.53	46.23	e		313.86	39.22	a		315.14	80.95	c
	292.25	63.04	e		315.86	49.23	a		312.25	21.01	d
	294.24	92.05	e	0.589	318.69	60.74	a		318.05	41.02	d
0.501	296.38	19.71	a		321.61	75.64	a		321.10	57.23	d
	300.83	42.33	a		324.54	78.55	a		322.95	65.74	d
0.498	305.03	60.24	a		325.48	88.45	a		325.83	78.55	d
	308.01	73.94	a								

[a] Oil-to-water weight fraction α = 0.5 and methane-to-decane ratio β = 0.10 for all isopleths. $\gamma_{C_4E_1}$, weight fraction of 2-butoxyethanol; T, temperature; p, pressure; phase transitions: (a) 3 → $\underline{2}$, (b) 3 → $\bar{2}$, (c) 1 → $\underline{2}$, (d) 1 → $\underline{2}$, (e), gas hydrate.

by the maximal extension of the body increases slightly. The X-point temperature is also increasing slightly ($\Delta T/\Delta p \approx 0.35$ K/MPa). Figure 5 shows the phase behavior of the system containing 5 wt % methane in the oil mixture. As for the methane-free system, the fishes shift toward higher temperatures with increasing pressure. Since the fish is tilted, it is difficult
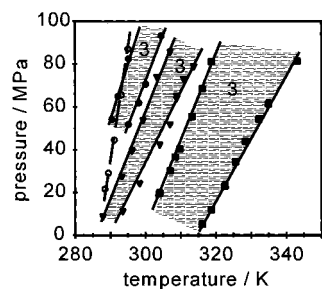
Figure 3. Typical isopleths of the system (decane + methane) + water + 2-butoxyethanol at constant oil-to-water weight fraction α = 0.5 and surfactant weight fraction γ_S = 0.16 for three different methane-to-decane weight ratios (β): ■, $\beta = 0$; ▼, $\beta = 0.05$; ●, $\beta = 0.1$ (○, gas hydrate) The lines are drawn to guide the eye; the dashed areas indicate the three-phase regions.
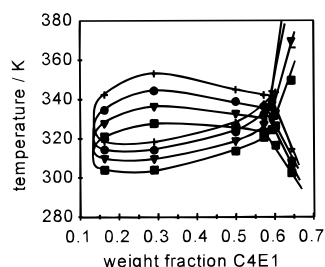

Figure 4. "Fish" diagrams of the system decane + water + 2-butoxyethanol at constant oil-to-water weight fraction α = 0.5 and constant pressure: ■, 20 MPa; ▼, 40 MPa; ●, 60 MPA; +, 80 MPa The lines are drawn to guide the eye.
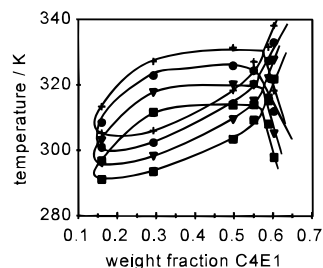
Figure 5. "Fish" diagrams of the system (methane + decane) + water + 2-butoxyethanol at constant oil-to-water weight fraction α = 0.5 and constant pressure. The methane-to-decane weight ratio is β = 0.05: ■, 20 MPa; ▼, 40 MPa; ●, 60 MPA; + 80 MPa. The lines are drawn to guide the eye.

to comment on the change of the extension in the direction of the temperature of the body of the fish with increasing pressure. However, it seems as if the width of the fish is approximately constant with increasing pressure. This can also be concluded from the slopes of the isopleths describing the phase transitions from the two-phase regions to the three-phase region. The shift of the X-point temperature with increasing pressure ($\Delta T/\Delta p \approx$ 0.29 K/MPa) is less than found for the methane-free system. The downward inclination of the fish is not changing with increasing pressure. In Figure 6 the resulting fish diagrams for a methane concentration of 10 wt % in the oil phase are depicted. Again an increase of the pressure induces a shift of the fish diagram toward higher temperatures. It seems that the width of the three-phase region is not changing with increasing pressure. The X-point temperature is not increasing as much ($\Delta T/\Delta p \approx$ 0.27 K/MPa) as for the methane-free system. The inclination of the fish diagrams is even more pronounced than for the fish diagrams containing 5 wt % methane. Again, the inclination is not changing with increasing pressure. For the methane concentration of 10 wt %, gas hydrates interfere with the occurrence of the three-phase region. The onset of the gas
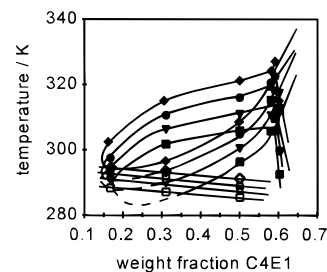

Figure 6. "Fish" diagrams of the system (methane + decane) + water + 2-butoxyethanol at constant oil-to-water weight fraction α = 0.5 and constant pressure. The methane-to-decane weight ratio is $\beta = 0.1$: ■, 20 MPa (□, gas hydrate); ▼, 40 MPa (▽, gas hydrate); ●, 60 MPa (○, gas hydrate); ◆, 80 MPa (◇, gas hydrate). The lines are drawn to guide the eye.
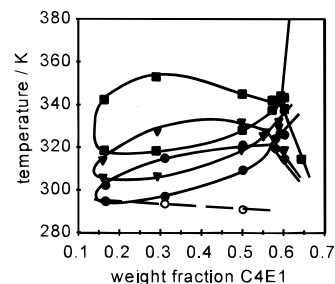

Figure 7. "Fish" diagrams of the system (methane + decane) + water + 2-butoxyethanol at constant oil-to-water weight fraction α = 0.5 and constant pressure of 80 MPa for three different methane-to-decane weight ratios β: ■, $\beta = 0$; ▼, $\beta = 0.05$; ●, $\beta = 0.1$ (○, gas hydrate). The lines are drawn to guide the eye.

hydrate formation is represented by the empty symbols. As could be expected, the gas hydrates appear at higher temperatures with increasing pressure. However, the interference of the gas hydrates with the occurrence of the three-phase region is becoming less with increasing pressure. For a surfactant weight fraction greater than 0.5 the formation of gas hydrates could not be observed.

In Figure 7 the fish diagrams for the three different methane concentrations at a pressure of 80 MPa are depicted. With increasing methane concentration the fish shifts toward lower temperatures and tilts downward. The maximal extension of the body in the direction of the temperature decreases slightly. A decrease of the X-point surfactant concentration with increasing methane concentration could not be observed. These features could be observed for all isobaric fish diagrams in the pressure range investigated.

Discussion

The addition of methane is strongly influencing the phase behavior of the system decane + water + 2-butoxyethanol. The phase behavior under the influence of the pressure is only changing quantitatively and not qualitatively compared to systems containing only decane.

In Figures 4−6 the pressure influence on the systems containing 0, 5, and 10 wt % methane are depicted. With increasing methane concentration, the three-phase region is found for lower temperatures at the same pressure (see also Figure 7). The comparison of the pressure influence on the phase behavior of the three systems is rather difficult. For the ternary system of oil + water + nonionic surfactant the upper and the lower critical temperatures are only functions of the pressure and therefore can be used to describe the influence of the pressure on the phase behavior. For the systems containing methane, the upper and lower critical temperatures are also

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functions of the methane concentration. As a result the fish diagrams show an increasing inclination with raising methane concentration. So, for example, in the system containing 10 wt % in the oil mixture, the highest point of the three-phase region coincides with the *X*-point. This makes the estimation of the upper and the lower critical temperature quite vague. Therefore, the description of the pressure influence on the phase behavior on the basis of the change of the upper and the lower critical temperature is not appropriate, and the change of the *X*-point temperature should be used instead. The comparison of the change of the determined *X*-point temperatures with increasing pressure for the three different systems shows that the influence of the pressure is slightly decreasing with increasing methane concentration. Austad et al.[6,10,11], McFann et al.,[12] and de Loos and Poot[14] found that for oil + water + surfactant systems containing volatile hydrocarbons representing the oil, the phase coexistence sequence with increasing pressure is inverted compared to the system containing nonvolatile hydrocarbons as an oil. Therefore, it can be expected that further addition of methane to the system decane + water + 2-butoxyethanol would finally lead to an inversion of the phase transition with increasing pressure at constant temperature from $\bar{2} \rightarrow 3 \rightarrow \underline{2}$ to $\underline{2} \rightarrow 3 \rightarrow \bar{2}$.

In Figure 7 the fish diagrams of the three systems containing different amounts of methane are directly compared at a pressure of 80 MPa. The picture shown is in general valid for the other investigated pressures. The *X*-point surfactant concentration is hardly changing with increasing methane concentration. It cannot be observed that the *X*-point surfactant concentration is decreasing with increasing methane concentration. However, for systems containing a single hydrocarbon, the *X*-point surfactant concentration is decreasing with decreasing chain length of the hydrocarbon.

Literature data of systems containing a single hydrocarbon of the same carbon number as the mean carbon number of the methane + decane mixture are tentatively compared with the data of this work. The data of this work are at elevated pressure due to the presence of the methane and the experimental setup. The mean carbon numbers of the methane + decane mixtures (based on mole fractions) are 7.3 ($\beta = 0.1$, $x = 0.5$) and 5.5 ($\beta = 0.05$, $x = 0.3$). Because of lack of high-pressure phase equilibrium data of oil + water + 2-butoxyethanol systems containing heptane or pentane as an oil, no direct comparison could be done. Anyhow, at atmospheric pressure the three-phase region of the system octane + water + 2-butoxyethanol is found for lower temperatures than the three-phase regions of the systems containing 5 and 10 wt % methane in the oil mixture at a pressure of 20 MPa. Even though a pressure increase results in a shift of the three-phase region toward higher temperatures, it does not seem likely that the temperature range of the three-phase region of the compared systems would agree. If the computation of the mean carbon number is based on weight fractions, the obtained mean carbon numbers are 9.5 and 9.1. The fish diagram of the system nonane + water + 2-butoxyethanol does not agree with the fish diagram of the system containing methane with a mean carbon number of 9.1. However, in this case at least the *X*-point temperature and the maximal extension of the three-phase region in the direction of the surfactant concentration could probably match. But again the lack of data at elevated pressures makes this comparison

tentative. The strong inclination of the fish diagram for systems containing methane could not be observed for systems containing pure hydrocarbons with decreasing chain length. This shows that the phase behavior of a system containing an oil mixture of a long-chain hydrocarbon and a short-chain hydrocarbon cannot be described by a system containing a one-component oil with the same mean carbon number as suggested by Leung et al.[13]

The tilt of the fishes at the oil-to-water weight fraction $\alpha = 0.5$ as it was observed for the quaternary system with increasing methane concentration was found earlier for ternary systems containing a pure long-chain hydrocarbon if cross sections are performed at oil-to-water weight fractions α higher than 0.5.[9] The clear inclination there describes the increasing hydrophobic character of the surfactant with increasing temperature. Therefore, it can be concluded that the addition of methane results in a better solubility of the surfactant in the oil phase.

Another important feature of the phase behavior of systems containing methane is the occurrence of gas hydrates. These can hinder the detection of a three-phase region. Since at higher surfactant concentrations no gas hydrates are found, the 2-butoxyethanol can be regarded to be an inhibitor for the formation of gas hydrates comparable to methanol, which is commonly used as hydrate inhibitor.

Conclusion

In this work we have shown that methane has a large influence on the phase behavior of oil + water + nonionic surfactant systems. In the range of temperature, pressure, and methane concentration investigated in this work the phase behavior was changed only quantitatively. However, for high methane concentrations ($\beta = 0.1$), gas hydrates were observed. From the observed phase behavior it can be expected that a further increase of the methane concentration would result in a qualitative change of the pressure influence on the phase behavior.

The experiments proved that the description of the phase behavior of a system containing an oil composed of a mixture of hydrocarbons by a system containing a single pure hydrocarbon with the same carbon number as the mean carbon number of the mixture is not possible if the oil mixture contains methane.

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