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Interfacial Tension of Hydrocarbon + Water/Brine Systems under High Pressure

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Interfacial tensions of 10 normal alkane + water/brine and hydrocarbon mixture + water/brine systems were measured by using a pendent drop instrument. The temperature and pressure ranges of measurements are (25 to 80) °C and (1 to 300) bar, respectively. The effects of temperature, pressure, and salt content have been studied. It was found that the interfacial tension is sensitive to temperature and salt concentration but weakly dependent on pressure and salt species.

Introduction

The interfacial tension of hydrocarbon + water/brine systems is one of the basic physical properties required for performing process calculations in petroleum, natural gas, and petrochemical industries. Although numerous surface/interfacial tension data under normal pressure and temperature have been reported in the literature (Nakahara and Masamoto, 1990; Sada et al., 1975), only a few data under high pressures and elevated temperatures were reported (Matubayasi et al., 1977; McCaffery, 1972; Jennings, 1967), and inconsistent pressure effects were observed.

There are few high-pressure interfacial tension measurements on hydrocarbon + brine systems.

For developing a generalized interfacial tension model capable of applying to reservoir engineering and other high-pressure applications, sufficient basic data are required. In this work, the interfacial tension of six pure liquid *n*-alkanes and four hydrocarbon mixtures with water/brine have been measured in the pressure range of (1 to 300) bar and temperature range of (25 to 80) °C. The effects of pressure, temperature, molecular weight of hydrocarbons, and salt species and concentration have been examined.

Experimental Section

Reagents. The purity and the source of chemicals used are listed in Table 1. Distilled water was deionized by a Model 70 ion-exchanger manufactured by Nan-Hua Medical Apparatus Corp. (China). The salt content of the seven brines prepared are given in Table 2.

Apparatus and Procedure. The JEFRI pendent drop high-pressure interfacial tension apparatus manufactured by DB Robinson Ltd. (Canada) was used in this work. The schematic flow diagram of the experimental system and the cross-sectional view of the pendent drop cell are shown in Figures 1 and 2, respectively. The maximum working range of the apparatus is 345 bar and 200 °C. The precision of measurements are as follows: pressure ±0.25%, temperature ±0.25 °C, drop dimension ± 0.01 mm. The accuracy of the calculated interfacial tension is estimated to be ±0.05 mN·m^{-1}.

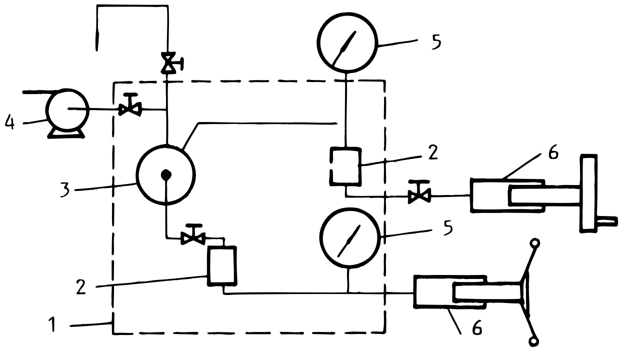

Figure 1. Schematic flow diagram of the pendent drop interfacial tension experimental system: (1) vibration-free bench; (2) sample cylinder; (3) pendent drop cell; (4) vacuum pump; (5) pressure gauge; (6) hand pump.

Table 1. Reagents Used in This Work

reagent	grade	conc/mass %	source
n-alkanes	analytical	99.0	Sigma Corp.
sodium chloride	analytical	99.5	Tang-Gu Chemical Reagents, Tianjin
magnesium chloride	analytical	≥98.0	Double-Ring Chemical Reagents, Beijing
calcium chloride	analytical	98.0	Tian-Yan Fine Chemicals, Tianjin

Table 2. Salt Content and Ionic Strength in Various Brines (t = 25 °C, P = 1.013 bar)

brine no.	salt species	salt concn/mol/L	ionic strength/mol/L
1	NaCl	0.8847	0.8847
2	NaCl + $CaCl_2$		1.1390
	−NaCl	0.4400	0.4400
	−$CaCl_2$	0.2330	0.6990
3	NaCl	0.0854	0.0854
4	NaCl	0.1716	0.1716
5	NaCl	1.8069	1.8069
6	$MgCl_2$	0.5301	1.5903
7	$CaCl_2$	0.4650	1.3950

The standard procedure used in the pendent drop method was followed, and the detailed description of the experimental procedure is given elsewhere (Cai, 1995). For checking the reliability of the apparatus and procedure applied, the interfacial tension of benzene + water was measured at 1.013 bar and 30.0 °C; the measured value (33.2 mN·m^{-1}) is in close agreement with the value of 33.0 mN·m^{-1} reported by Jennings (1967).

Results and Discussion. The interfacial tensions of six normal alkanes (hexane, octane, decane, dodecane, tetradecane, and hexadecane) with pure water and brines were measured at 25.0 and 50.0 °C under various pressures, and the results are listed in Table 3. Similar results for three (C_6 + C_{10}) binary mixtures and one (C_6 + C_{10} +

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Table 3. Interfacial Tensions of Alkane + Water/Brine Systems

a. Interfacial Tension of *n*-Alkane + Water/Brine 1/Brine 2 Systems

		H_2O		brine 1		brine 2				H_2O		brine 1		brine 2	
n-alkane	t/°C	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1} ms	*n*-alkane	t/°C	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}
C_6	25.0	36.9	50.73	36.9	53.16	38.7	53.21	C_{12}	25.0	36.9	51.97	40.4	54.18		
		109.0	50.97	109.0	53.41	109.0	53.44			105.6	52.45	109.0	54.40		
		162.2	51.18	162.2	53.65	153.6	53.83			160.5	52.79	165.6	54.37		
		215.3	51.38	220.5	53.92	220.5	54.00			215.3	53.03	225.6	55.09		
		289.1	51.71	292.5	54.16	282.2	54.24			284.0	53.31	289.1	52.85		
	50.0	40.4	48.04	38.7	50.26	43.1	50.55		50.0	40.4	49.50	38.7	51.54		
		115.9	48.22	115.9	50.54	107.3	50.79			105.6	49.69	109.0	51.79		
		165.6	48.46	165.6	50.74	157.0	51.24			162.2	49.97	158.7	52.06		
		211.9	48.80	211.9	51.97	218.8	51.38			222.2	50.30	218.8	52.43		
		290.8	48.95	289.1	51.29	289.1	51.67			284.0	50.74	289.1	52.85		
C_8	25.0	40.4	51.04	38.7	53.50			C_{14}	25.0	38.7	52.48	40.4	54.62		
		109.0	51.38	109.0	53.72					112.4	52.68	109.0	54.96		
		155.3	51.66	155.3	54.13					160.5	53.05	163.9	55.28		
		215.3	51.91	213.5	54.30					223.9	53.40	217.1	55.60		
		284.0	52.13	284.0	54.55					285.7	53.78	285.7	55.97		
	50.0	40.4	48.33	38.7	50.88				50.0	36.9	49.99	38.7	51.99		
		110.7	48.50	105.6	51.14					110.7	50.28	110.7	52.39		
		153.6	48.83	148.4	51.33					158.7	50.77	155.3	52.88		
		223.9	49.12	220.5	51.69					220.5	50.95	217.1	53.04		
		289.1	49.30	282.2	51.99					290.8	51.29	292.5	53.32		
C_{10}	25.0	43.1	51.51	40.4	53.74	38.7	53.78	C_{16}	25.0	36.9	52.91	36.9	55.05	36.9	55.07
		105.6	51.84	103.8	53.97	110.7	54.04			105.6	53.21	107.3	55.45	105.6	55.48
		160.5	52.10	155.3	54.17	160.5	54.15			162.6	53.49	158.7	55.82	150.2	55.78
		213.5	52.41	218.8	54.58	215.3	54.62			225.6	53.93	220.5	56.14	218.8	55.97
		282.2	52.65	284.0	54.82	284.0	54.93			292.5	54.26	282.2	56.46	289.1	56.43
	50.0	38.7	49.00	38.7	51.06	40.4	51.20		50.0	36.9	50.31	43.1	52.78	43.1	52.73
		98.7	49.31	112.4	51.27	105.6	51.52			110.7	50.93	110.7	53.01	105.6	53.02
		157.0	49.55	155.3	51.61	162.2	51.79			158.7	51.14	157.0	53.35	150.2	53.32
		210.2	49.84	223.9	51.88	222.2	52.00			222.2	51.37	223.9	53.68	220.5	53.72
		278.8	50.05	289.1	52.33	284.0	52.23			284.0	51.88	282.2	54.12	285.7	54.14

b. Interfacial Tension of Octane + Brine (Brine 3 to Brine 7) Systems at 25 °C

brine 3		brine 4		brine 5		brine 6		brine 7	
P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}
40.4	51.88	42.1	52.73	40.4	56.11	40.4	53.60	38.7	53.69
110.7	52.01	107.3	53.04	109.0	56.31	109.0	53.79	109.0	54.07
155.3	52.23	151.9	53.43	155.3	56.54	153.6	54.08	160.5	54.29
218.8	52.45	215.3	53.70	213.5	56.84	211.9	54.49	215.3	54.43
289.1	52.81	284.0	53.94	284.0	57.10	278.8	54.67	280.5	54.68

C_{16}) ternary mixture are tabulated in Table 4. The compositions (mole fraction) of the hydrocarbon mixtures studied were

$$\text{hexane (1) + decane (2): } x_1 = 0.3734;\ x_1 = 0.5978;\ x_1 = 0.7825$$

$$\text{hexane (1) + decane (2) + hexadecane (3): } x_1 = 0.4293,\ x_2 = 0.2518$$

Typical pressure effects on the interfacial tension are shown in Figures 3 and 4. Since the interfacial tension is weakly dependent on pressure and increases almost linearly with pressure, the measured isothermal interfacial tensions were smoothed by the following correlation:

$$\sigma = \alpha + \gamma P \tag{1}$$

where σ stands for the interfacial tension at absolute pressure P, α is a constant, and γ is a pressure coefficient $(\partial\sigma/\partial P)_T$. The regressed α and γ values for the 20 hydrocarbon + water/brine systems are given in Table 5.

The comparisons of the calculated, based on eq 1, and the reported literature values for four *n*-alkane + water systems at 25 °C (20 data points) are presented in Table 6. The absolute average deviation is 0.25 mN·m^{-1}, and the deviation slightly increases with pressure.

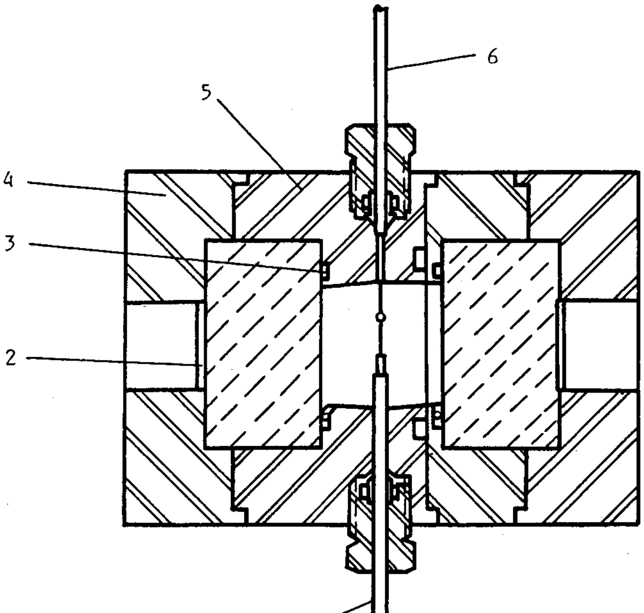

Figure 2. Cross-sectional view of the high-pressure pendent drop cell: (1) capillary tube; (2) view window; (3) sealing ring; (4) window cover; (5) main body; (6) exit tube.

Table 4. Interfacial Tension of Hydrocarbon Mixture + Water/Brine Systems

hydrocarbon mixture	t/°C	H_2O		brine 1		brine 2	
		P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}	P/bar	σ/mN·m^{-1}
hexane (1) + decane (2)	25.0	43.1	51.35	40.4	53.59	38.7	53.63
$x_1 = 0.3734$		102.1	51.53	103.8	53.98	95.7	54.00
$x_2 = 0.6266$		148.4	51.78	151.9	54.30	160.5	54.31
		217.5	52.04	215.3	54.54	217.6	54.60
		285.7	52.37	290.8	54.89	287.4	54.92
	50.0	38.7	48.30	38.7	50.99	40.4	51.04
		102.1	48.60	109.0	51.14	110.7	51.33
		151.9	48.85	155.3	51.45	148.4	51.74
		217.1	49.07	213.5	51.76	223.9	51.89
		278.8	49.40	284.0	52.07	285.7	52.15
hexane (1) + decane (2)	25.0	40.4	50.94	42.1	53.50	38.7	53.60
$x_1 = 0.5978$		103.5	51.25	102.1	53.73	102.1	53.81
$x_2 = 0.4022$		160.5	51.57	144.8	54.05	155.3	54.06
		227.4	51.81	215.3	54.35	225.6	54.34
		280.5	52.06	280.5	54.77	285.7	54.67
	50.0	42.1	48.23	43.1	50.79	42.1	50.92
		110.7	48.73	107.3	51.06	102.1	51.17
		155.3	49.00	153.6	51.36	150.2	51.44
		223.9	49.28	215.3	51.70	222.2	51.74
		287.4	49.54	287.4	52.02	282.2	52.07
hexane (1) + decane (2)	25.0	40.4	50.74	42.1	53.34	43.1	53.35
$x_1 = 0.7825$		109.0	50.98	99.1	53.54	105.6	53.71
$x_2 = 0.2175$		155.3	51.28	162.2	53.96	163.9	54.07
		211.9	51.74	225.6	54.20	225.6	54.47
		284.0	52.02	278.8	54.56	285.7	54.65
	50.0	37.0	48.25	40.4	50.55	43.1	50.47
		112.4	48.51	103.8	50.82	102.1	50.87
		160.5	48.79	160.5	51.11	160.5	51.13
		222.2	49.06	227.4	51.35	217.1	51.43
		282.2	49.36	278.8	51.66	287.4	51.75
hexane (1) + decane (2) + hexadecane (3)	25.0	34.8	51.48	43.1	53.85	40.4	53.75
$x_1 = 0.4293$		103.8	51.78	114.1	54.12	109.0	53.98
$x_2 = 0.2518$		157.0	52.04	150.2	54.37	148.4	54.29
$x_3 = 0.3189$		225.6	52.34	211.9	54.73	225.6	54.57
		278.8	52.71	285.7	55.08	278.8	55.00
	50.0	43.1	49.12	36.9	51.12	42.1	51.18
		98.7	49.47	109.0	51.40	103.8	51.50
		150.2	49.69	155.3	51.66	160.5	51.74
		225.6	49.84	222.2	52.09	218.8	52.18
		280.5	50.11	278.8	52.30	289.1	52.48

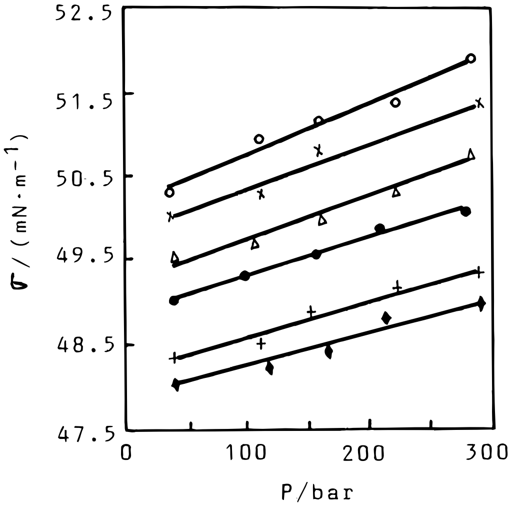

Figure 3. Pressure effect on the interfacial tension of n-alkane + water systems at 50.0 °C: (○) C_{16}; (×) C_{14}; (△) C_{12}; (●) C_{10}; (+) C_8; (♦) C_6.

Typical salt effects on the interfacial tension of n-C_8 + brine systems are depicted in Figure 5. The effect of NaCl on the interfacial tension is significant.

The effect of temperature on the interfacial tension of n-C_8 + H_2O and n-C_{16} + H_2O were studied in the temperature range (25 to 80 °C) at fixed pressures; the results are given in Table 7 and plotted in Figure 6.

Table 5. Coefficients in Eq 1 for Twenty n-Alkane + Water/Brine Systems

system	$t = 25.0$ °C		$t = 50.0$ °C	
	α/ mN·m^{-1}	$\gamma \times 10^3$/ mN·m^{-1}·bar^{-1}	α/ mN·m^{-1}	$\gamma \times 10^3$/ mN·m^{-1}·bar^{-1}
C_6 + H_2O	50.56	3.883	47.84	3.947
C_8 + H_2O	50.89	4.544	48.14	3.947
C_{10} + H_2O	51.32	4.836	48.86	4.431
C_{12} + H_2O	51.84	5.401	49.21	5.112
C_{14} + H_2O	52.18	5.446	49.80	5.252
C_{16} + H_2O	52.67	5.415	50.16	5.946
C_6 + brine 1	53.00	4.018	50.08	4.158
C_6 + brine 2	53.05	4.334	50.37	4.650
C_8 + brine 1	53.32	4.456	50.67	4.606
C_8 + brine 3	51.66	3.797		
C_8 + brine 4	52.54	5.154		
C_8 + brine 5	55.90	4.225		
C_8 + brine 6	53.36	4.855		
C_8 + brine 7	53.59	3.957		
C_{10} + brine 1	53.52	4.604	50.79	5.122
C_{10} + brine 2	53.52	4.825	51.06	4.208
C_{12} + brine 1	53.95	5.079	51.27	5.334
C_{14} + brine 1	54.38	5.571	51.86	5.317
C_{16} + brine 1	54.85	5.807	52.47	5.644
C_{16} + brine 2	54.92	5.187	52.44	5.866

Conclusions

The following conclusions can be drawn from this study: The interfacial tension of n-alkane + water/brine systems increases slightly with pressure, and an approximately linear relationship is observed. The presence of salt in the aqueous phase increases the interfacial

Table 6. Comparison of Calculated (Based on Eq 1) and Literature Reported Data[a] ($mN{\cdot}m^{-1}$) for Four *n*-Alkane + Water Systems at 25.0 °C

	$P = 50$ bar		$P = 100$ bar		$P = 150$ bar		$P = 200$ bar		$P = 250$ bar	
system	σ_{cal}	σ_{exp}	σ_{cal}	σ_{exp}	σ_{cal}	σ_{exp}	σ_{cal}	σ_{exp}	σ_{cal}	σ_{exp}
$C_6 + H_2O$	50.8	50.5	50.9	50.6	51.1	50.7	51.3	50.7	51.5	50.8
$C_8 + H_2O$	51.1	51.2	51.3	51.3	51.6	51.4	51.8	51.5	52.0	51.6
$C_{10} + H_2O$	51.6	51.6	51.8	51.7	52.0	52.0	52.3	52.1	52.5	52.2
$C_{12} + H_2O$	52.1	52.1	52.4	52.3	52.7	52.5	53.0	52.6	53.1	52.7

[a] Experimental data read from the curves in Motomura et al. (1983).

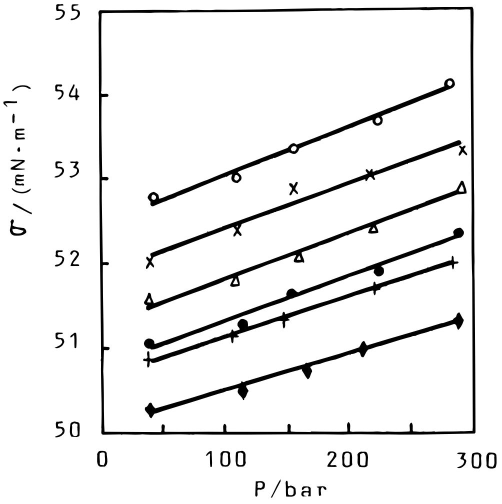

Figure 4. Pressure effect on the interfacial tension of *n*-alkane + brine 1 systems at 50.0 °C: (○) C_{16}; (×) C_{14}; (△) C_{12}; (●) C_{10}; (+) C_8; (♦) C_6.

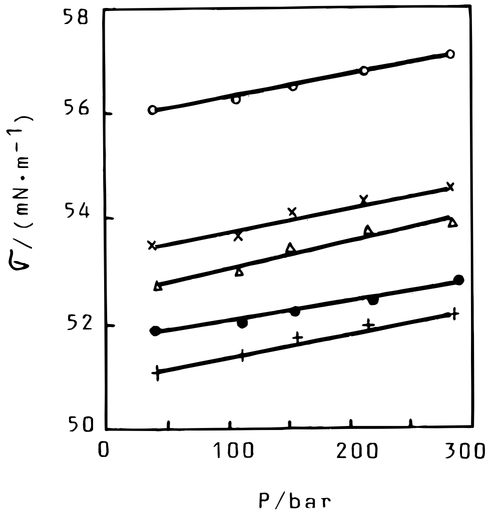

Figure 5. Salt effect on the interfacial tension of octane + brine systems at 25.0 °C: (○) brine 5; (×) brine 1; (△) brine 4; (●) brine 3; (+) H_2O.

tension. The increase depends on the concentration of the salt but is not sensitive to the salt species. The interfacial tension increases slightly with an increase in the molecular weight of the *n*-alkane.

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Table 7. Temperature Effects on the Interfacial Tension of *n*-C_8 + H_2O and *n*-C_{16} + H_2O Systems

n-C_8 + H_2O			*n*-C_{16} + H_2O		
P/bar	*t*/°C	$\sigma/mN{\cdot}m^{-1}$	*P*/bar	*t*/°C	$\sigma/mN{\cdot}m^{-1}$
40.4	25.0	51.73	36.9	25.0	52.91
	37.0	49.92		50.0	50.31
	46.0	48.81		60.0	49.37
	50.0	48.33		70.0	48.75
	58.0	47.20		80.0	47.66

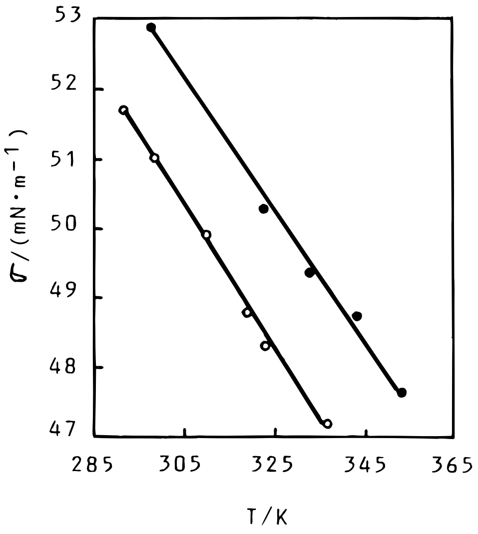

Figure 6. Temperature effect on the interfacial tension of octane + water (at 40.4 bar) and hexadecane + water (at 30.9 bar) systems: (○) C_8; (●) C_{16}.

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