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Interfacial Tension between Methane and Octane at Elevated Pressure at Five Temperatures from (274.2 to 282.2) K

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ABSTRACT: The pressure dependence of interfacial tension between methane and octane at five temperatures has been determined using the pendant-drop method. The experimental results show that the interfacial tension value decreases with the increased temperature and pressure. The higher temperature and pressure has a positive contribution on weakening the intermolecular interaction between methane and octane. The surface excess concentration for methane on octane at different temperatures and pressures and the surface free energies of adsorption for (methane + octane) were calculated and compared with the (methane + water) system. The calculated results show that methane is more preferred for the adsorption on octane than on water.

INTRODUCTION

Many engineering applications in the petroleum industry require interfacial tension data between light hydrocarbons and liquid *n*-alkanes. A series of interfacial tension experiments on hydrocarbons and *n*-alkanes have been reported.[1−7] For the interfacial properties between methane and light *n*-alkanes, Weinaug and Katz[1] measured the surface tensions of equilibrium (methane + propane) mixtures over (258.2 to 363.2) K and (0.28 to 8.48) MPa using the capillary-rise and drop-volume methods. Deam and Maddox[2] measured the (methane + nonane) interfacial tension in the temperature range from (238.7 to 297.6) K and pressures up to 10 MPa using a high-pressure pendant-drop technique. The interfacial tension data for systems between methane and butane,[3] pentane,[4] hexane,[5,6] heptane,[4,6] and decane[4] have also been reported. In addition, many theoretical methods[6,8−10] have been developed to predict the interfacial tension. But there still exists a deviation between theoretical and experimental values because of the deficiency of the corresponding data for building these theories.

Octane is an important raw hydrocarbon component in pipeline transportation from wells to the processing facilities. The interfacial tension between methane and octane under low temperature and high pressure is of importance for oil−gas transportation pipelines especially in winter or a deep sea environment, which was seldom reported as reviewed in the above literature. Additionally, the adsorption characteristics of light hydrocarbons at the gas−liquid interface of *n*-alkanes are also an important factor in petroleum industry applications. Therefore, in this work, the interfacial tension between methane and octane over (274.2 to 282.2) K was measured using the pendant-drop method. The adsorption properties of methane at the (methane + octane) interface were also investigated.

EXPERIMENTAL SECTION

Materials and Experimental Procedure. Methane with a mole fraction of 0.9999 was supplied by Beijing Beifen Gases Industry Co., Ltd. Octane of analytical grade (mass fraction of 0.999) was purchased from Beijing Chemical Reagents Corporation.

The JEFRI pendant drop high-pressure interfacial tension apparatus manufactured by D.B Robinson Corporation was used. More details of this apparatus have been described in our previous paper.[11−15] The operating temperature is controlled by three Eurotherm temperature controllers with an uncertainty of ± 0.1 K. All of the pressure gauges are calibrated using a standard RUSKA dead-weight pressure gauge with an uncertainty of ± 0.25 %.

Experimental procedures have also been described in our previous papers.[11−15] Thus, only a brief description is given below.

The pendant-drop cell and all of the connections were soaked in petroleum ether over 3 h, and this procedure was repeated prior to the loading of each new sample. The entire system was then flushed with hot distilled water and dried with compressed air and evacuated. Subsequently, methane gas was charged into one of the sample cylinders, and octane was added into another one and the pendant-drop cell. The temperature was then set to the desired value. When the system temperature was stable, methane was charged slowly into the pendant-drop cell through the bottom valve of the cell until the desired pressure was reached. The system was left at the constant temperature for more than 24 h for the liquid to be saturated with methane gas, during which period the methane was injected to maintain the system at a constant pressure value. After the pressure was stable, a methane gas bubble was introduced slowly into the pendant-drop cell through the central injection needle by a JEFRI pump. The gas bubble was swollen to the largest dimension just before it broke, and it was stabilized for about 5 min at the experimental pressure. In this way, the pendant bubble was maintained in physical equilibrium with its surroundings. Then, its profile was magnified by the microscope and recorded by a computer through the video camera. The dimensions of the bubble profile could be disposed

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automatically using the software developed by our laboratory. The interfacial tension data at different temperature and pressure conditions could be obtained by repeating the above procedures. The interfacial tension measurement was repeated three times for each operating condition. The average value was regarded as experimental data under the current operating conditions.

Calculation of Interfacial Tension. If the gas bubble is in equilibrium with its surroundings, the interfacial tension (γ) values can be calculated directly from an analysis of the stresses in the static pendant bubble, using the following equations developed by Andreas et al.[16]

$$\gamma = \Delta\rho d_e^{\,2} g/H \tag{1}$$

$$1/H = f(d_s/d_e) \tag{2}$$

where the $\Delta\rho$ is the density difference between the two phases, d_e is the unmagnified equatorial diameter of the bubble, g is the gravitational constant, and d_s is the diameter of the bubble at a selected horizontal plane at a height equal to the maximum diameter d_e. Stauffer[17] extended a more detailed table of $1/H$ as a function of d_s/d_e.

For the binary (methane + octane) system, the Patel–Teja equation of state[18] is used to calculate the density of the gas phase and liquid phase. The traditional van der Waals one-fluid mixing rules are used, and the binary interaction coefficient value is determined as 0.008 for the (methane + octane) system, which is regressed from vapor–liquid equilibrium data for (methane + octane) at (273.2 and 298.2) K measured by Kohn and Bradish.[19]

Error Analysis. If defining a parameter $\sigma = d_e^{\,2} g/H$, we can obtain the following formulation from eq 1:

$$d\gamma = \left(\frac{\partial\gamma}{\partial\sigma}\right)_{\Delta\rho} d\sigma + \left(\frac{\partial\gamma}{\partial(\Delta\rho)}\right)_{\sigma} d(\Delta\rho) \tag{3}$$

Substituting $(\partial\gamma/\partial\sigma)_{\Delta\rho} = \Delta\rho$ and $(\partial\gamma/\partial(\Delta\rho))_{\sigma} = \sigma$ into eq 3, we obtain the differential for interfacial tension:

$$d\gamma = \Delta\rho d\sigma + \sigma d(\Delta\rho) \tag{4}$$

From eq 4 the following equation for evaluating the uncertainty of the interfacial tension measurement is obtained:

$$\delta\gamma = \Delta\rho\delta\sigma + \sigma\delta(\Delta\rho) \tag{5}$$

where $\delta\sigma$ and $\delta(\Delta\rho)$ denote the uncertainties in measuring and processing the profile of pendant bubble and that of density difference determination resulting from the uncertainties in measuring temperature/pressure and the calculation error of the equation of state, respectively. The maximum uncertainty of the interfacial tension measurement for the binary (methane + octane) mixture is determined to be ± 0.40 $\mathrm{mN \cdot m^{-1}}$ by using eq 5.

■ RESULTS AND DISCUSSION

Interfacial Tension Data. We have used this device to measure the interfacial tension data of (methane + water) with the surfactant[11] and (water + octane) plus sorbitan monolaurate,[12] respectively. The accuracy of the measurement method has been verified.[11,12] According to the experimental method mentioned above, the interfacial tension between methane and octane at five temperatures ranging from (274.2 to 282.2) K and pressures from (0.1 to 8.5) MPa was measured, and the results are shown in Figure 1 and listed in Table 1.

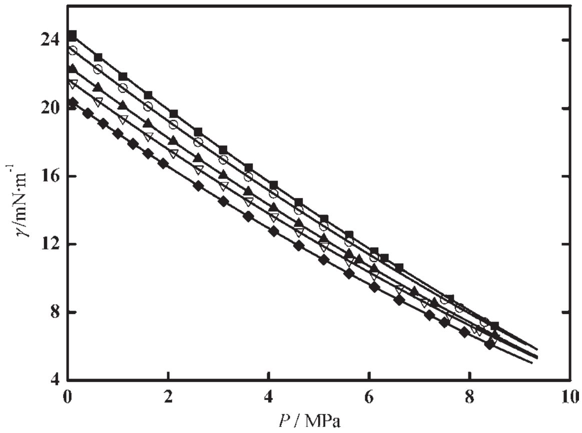

Figure 1. Variation of interfacial tension between methane and octane with pressure at different temperatures: ■, 274.2 K; ○, 276.2 K; ▲, 278.2 K; ▽, 280.2 K; ♦, 282.2 K; —, regressed line.

From Figure 1 and Table 1, it can be seen that the interfacial tension between methane and octane decreases with increasing pressure at each temperature, and higher temperature corresponds to lower interfacial tension, showing that the intermolecular interactions between methane and octane become weaker at higher temperature and pressure. The experimental interfacial tension data were also fit to be a binomial in pressure and the fitting parameters at different temperatures are listed in Table 2, which can be used for the following calculation for surface excess concentration.

Surface Excess Concentration. The surface excess concentration for methane on octane is calculated according to the common convention which places the Gibbs dividing plane such that the surface excess concentration of octane equals zero using eq 6:[5]

$$\left(\frac{\partial\gamma}{\partial P}\right)_T = -\Gamma_2^{(1)}\frac{zRT}{P} \tag{6}$$

where z represents the compressibility factor of methane at pressure P and temperature T, which is calculated using the Patel–Teja equation of state,[18] and R is the universal gas constant. $\Gamma_2^{(1)}$ is the surface excess concentration. The partial derivative in eq 6 is derived from the binomial expansions listed in Table 2. The calculated surface excess concentrations for methane on octane at different temperatures and pressures are shown in Figure 2.

From Figure 2, it can be seen that the surface excess concentration of methane on octane is greater than zero and increases with increasing pressure, meaning that methane concentration at the interface is higher than that in the bulk octane phase, and pressure has a positive effect for the adsorption of methane on octane. For investigating the difference of the adsorption of methane on polar and nonpolar liquids, we also compare the adsorption of methane on octane with water. Figure 3 shows the adsorption of methane on octane and water at 274.2 K and different pressures. It is found that the adsorption of methane on octane is higher than that on water.

Surface Adsorption Free Energy. Surface free energies of adsorption for the (methane + octane) system, ΔG, have been calculated according to eq 7,[20] where the standard state was

Table 1. Interfacial Tension between Methane and Octane at Different Temperatures and Pressures

274.2 K		276.2 K		278.2 K	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.1	24.34	0.1	23.40	0.1	22.27
0.6	22.98	0.6	22.28	0.6	21.18
1.1	21.86	1.1	21.18	1.1	20.12
1.6	20.76	1.6	20.10	1.6	19.07
2.1	19.67	2.1	19.03	2.1	18.04
2.6	18.60	2.6	17.99	2.6	17.04
3.1	17.54	3.1	16.97	3.1	16.05
3.6	16.51	3.6	15.96	3.6	15.08
4.1	15.49	4.1	14.97	4.1	14.13
4.6	14.48	4.6	14.00	4.6	13.20
5.1	13.49	5.1	13.05	5.1	12.30
5.6	12.52	5.6	12.12	5.6	11.41
6.1	11.56	6.1	11.21	5.8	11.06
6.3	11.19	7.5	8.76	6.1	10.54
6.6	10.62	7.8	8.26	6.9	9.19
7.6	8.79	8.3	7.43	7.3	8.54
8.5	7.20			8.5	6.65

280.2 K		282.2 K	
P/MPa	γ/mN·m^{-1}	P/MPa	γ/mN·m^{-1}
0.1	21.47	0.1	20.31
0.6	20.42	0.4	19.70
1.1	19.38	0.7	19.10
1.6	18.37	1.0	18.50
2.1	17.38	1.3	17.91
2.6	16.41	1.6	17.33
3.1	15.46	1.9	16.75
3.6	14.53	2.6	15.44
4.1	13.62	3.1	14.53
4.6	12.73	3.6	13.64
5.1	11.87	4.1	12.76
5.6	11.02	4.6	11.91
6.1	10.19	5.1	11.08
6.6	9.38	5.6	10.28
7.1	8.59	6.1	9.49
7.6	7.83	6.6	8.72
8.1	7.08	7.2	7.83
8.2	6.93	7.5	7.39
8.5	6.50	7.9	6.82
		8.4	6.13

Table 2. Interfacial Tension between Methane and Octane as a Function of Pressure at Different Temperatures ($\gamma = \gamma_0 + aP + bP^2$)

T	a	b
K	mN·m^{-1}·MPa^{-1}	mN·m^{-1}·MPa^{-2}
274.2	−2.339	0.0370
276.2	−2.266	0.0378
278.2	−2.201	0.0396
280.2	−2.132	0.0406
282.2	−2.062	0.0415

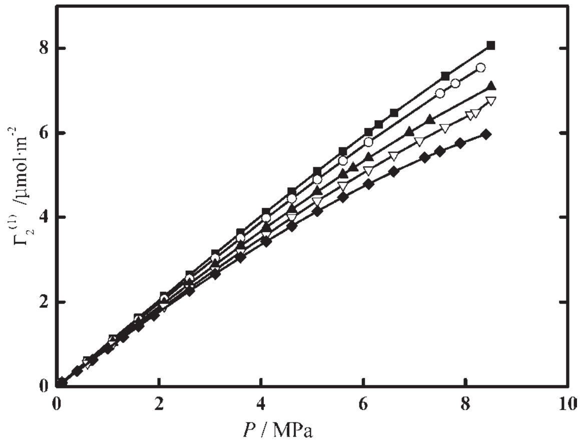

Figure 2. Surface excess concentration for methane on octane at different temperatures and pressures: —■—, 274.2 K; —○—, 276.2 K; —▲—, 278.2 K; —▽—, 280.2 K; —◆—, 282.2 K.

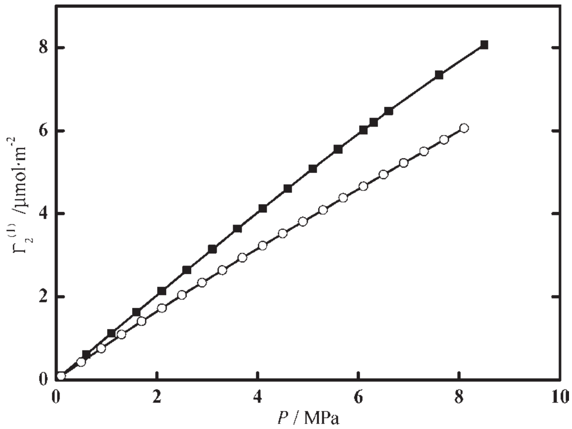

Figure 3. Adsorption of methane on octane or water at 274.2 K and different pressures: —■—, (methane + octane) system; —○—, (methane + water) system.[13]

defined as 1 atm and the gas at standard state was assumed to be an ideal gas.[21]

$$\Delta G = -RT\ln\left\{\left[\lim_{P\to 0}\left(-\left(\frac{\partial\gamma}{\partial P}\right)\right)_T\right]/0.0608\right\} \qquad (7)$$

The calculated results are listed in Table 3. It is found that the surface free energies of adsorption for (methane + octane) increase with temperature, indicating that the adsorption capacity will weaken at high temperature conditions. Compared with the (methane + water) system as shown in Table 3, the surface free energies of adsorption for the (methane + octane) system are smaller. The adsorption of methane on octane is easier than that of methane on water.

Table 3. Surface Adsorption Free Energies of Methane at Different Temperatures

T/K		274.2	276.2	278.2	280.2	282.2
ΔG/kcal·mol^{-1}	(methane + octane)	−1.991	−1.988	−1.986	−1.983	−1.978
	(methane + water)	−0.641[a]	−0.636[a]	−0.634[a]	−0.628[a]	−0.619[a]

[a] Data provided by Peng et al.[13]

CONCLUSIONS

The interfacial tension between methane and octane at different temperatures and pressures was measured using the pendant-drop method. The results show that the interfacial tension decreases with increasing pressure and temperature. The intermolecular interaction between methane and octane molecules weakens at higher temperatures and pressures. The calculated surface excess concentration and the surface free energies of adsorption for the (methane + octane) system at different conditions show that the adsorption of methane on octane is easier than that of methane on water.

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