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Measuring Surface Tension of Liquids at High Temperature and Elevated Pressure

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In this paper, an apparatus used to measure the surface tension at high temperature and elevated pressure was developed, based on the differential maximum bubble pressure method. As standard solvents, the surface tensions of methanol, ethanol, and benzyl benzoate were measured over a range of temperatures and pressures. The results were compared with the literature values, and the relative uncertainty of measurement is less than 2 %. The surface tensions of benzene, toluene, *p*-, *o*-, *m*-xylene, and the binary mixture of *p*-xylene + benzene were measured at 1.6 MPa, from (80 to 200) °C

Introduction

Surface tension is a critical parameter in the interfacial transfer process and reaction of a multiphase system. Surface tension plays a major role in processes such as distillation, absorption, extraction, analysis of bubble, and emulsion. Besides, a reaction system is usually in the gas–liquid or gas–liquid–solid phase at high temperature and elevated pressure. In these cases, interfacial mass transfer can be the rate-controlling step. So it is necessary to predict the gas–liquid mass-transfer rate. One essential requirement for such analysis is gas–liquid surface tension.

There are many methods to measure surface tensions, such as DuNouy Ring, Wilhelmy plate, capillary rise, pendant drop, and the maximum bubble pressure methods.[1] DuNouy ring, Wilhelmy plate, and capillary rise methods are widely used, but they cannot be applied at high temperature. In the DuNouy ring and Wilhelmy plate methods, it is difficult to enclose the moving parts in a hot, pressurized environment. In capillary rise, the visual observation of a liquid meniscus is not feasible at high temperature. The pendant drop and the maximum bubble pressure methods can be used at high pressures and temperatures; however, the operation of pendant drop is complicated, and the raw data are difficult to analyze. The maximum bubble pressure method can be used to measure dynamic surface tension as well as static surface tension. Further, it has the advantages of simpleness and accuracy. The differential maximum bubble pressure method is an improvement from the maximum bubble pressure method.

Therefore, the differential maximum bubble pressure method was selected, and a suitable apparatus was built. Aromatic hydrocarbons are important compounds used in production process. For example, xylene is an important chemical for phthalic acid production by liquid-phase oxidation. In the paper, the apparatus is described, and the surface tensions of five pure compounds and the binary mixture of *p*-xylene + benzene were measured at 1.6 MPa, from (80 to 200) °C.

Theory

The principle of differential maximum pressure method comes from the maximum bubble pressure method. The differential maximum pressure method using two capillaries was arranged by Sugden early.[2] Subsequently, the method was developed by others. In 1956, Cuny and Wolfp[3] derived an equation relating the differential maximum bubble pressure to surface tension σ for the case of two capillaries immersed to unequal depths

$$\sigma = \frac{1/2(\Delta p_{1,2}) + (\rho_l - \rho_g)g[(r_2 - r_1)/3 - 1/2\Delta d] + g(r_2^3 - r_1^3)(\rho_l - \rho_g)^2/(24\sigma)}{(1/r_1) - (1/r_2)} \tag{1}$$

where $\Delta p_{1,2}$ is the differential maximum bubble pressure between bubbles at each tube and Δd is differential depth between the tips of the two capillary tubes immersed to liquid. ρ_g and ρ_l are the densities of the gas and the liquid, respectively, and r_1 and r_2 are the capillary tip radius.

In this work, one calculates the value of Δd for which the second term of the numerator in eq 1 would become zero and then adjusts the capillaries so that the difference between their immersion depths Δd was equal to that value of $2(r_2 - r_1)/3$. If about 0.4 % in the surface tension is sufficient, then the third term of the numerator in eq 1 can be dropped as well.[4,5] This would make the measurement of surface tensions independent of density for practical purposes. As follows

$$\sigma = \frac{\Delta p_{1,2}}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \tag{2}$$

Experimental Section

In our laboratory, the surface tensions of binary mixtures of *o*-xylene + acetic acid, *m*-xylene + acetic acid, and *p*-xylene + acetic acid have been measured from (30 to 70) °C and at atmospheric pressure. On the basis of the previous work,[6] the apparatus for the surface tensions measurements at high temperatures and elevated pressures was designed. The apparatus was built from stainless steel. The configuration of the apparatus is shown in Figures 1 and 2. The whole apparatus in this work consists of a bubble chamber unit, a pressure measurement part, a temperature controller, a controller of gas velocity, a cathetometer, and a computer.

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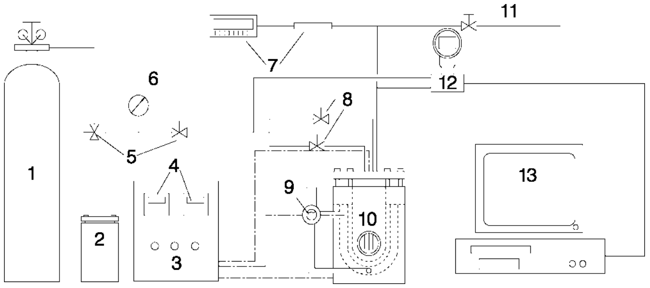

Figure 1. Schematic illustration of the apparatus: 1, N_2 cylinder; 2, high-pressure buffer; 3, switch; 4, digital meters with thermocouples; 5, cutoff valve; 6, pressure meter; 7, pressure transducer and digital meter; 8, microneedle value; 9, the heating oil; 10, high-pressure kettle; 11, vent; 12, smart differential pressure transmitter; 13, computer.

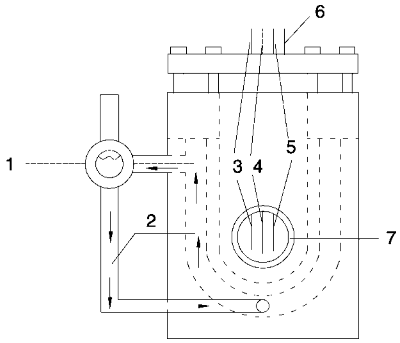

Figure 2. Schematic illustration of the bubble chamber unit: 1, the displacement of the thermocouple; 2, the heating oil; 3, large capillary; 4, thermocouple; 5, small capillary; 6, connect to pressure measurement; 7, inspection window.

Table 1. Surface Tensions of Methanol at Different Temperatures and at Atmospheric Pressure

t/C°	30.0	40.0	50.0	60.0	70.0
σ/(mN·m^{-1})	21.75	20.90	20.04	19.18	18.32
lit.[7]	21.73	20.96	20.18	19.41	18.49

Table 2. Surface Tensions of Methanol at Different Pressures and 23 °C

p/MPa	0.10	0.50	1.00	1.45
σ/(mN·m^{-1})	22.36	21.83	21.55	21.25
lit.[1]	22.33			21.20

Table 3. Surface Tensions of Benzyl Benzoate at Different Temperatures and at Atmospheric Pressure

t/°C	80.0	100.0	120.0	140.0	160.0	180.0	200.0
σ/(mN·m^{-1})	39.60	37.53	35.33	33.30	31.10	28.95	26.80
lit.[7]	39.55	37.47	35.29	33.16	31.03	28.90	26.77

To obtain data with maximum precision, the values were measured. The differential depth between capillaries was measured by a cathetometer, which was made by Shanghai Optics Apparatus with an uncertainty of ± 0.001 mm. The capillary tip radii r_1, r_2 were measured by a microscope with an uncertainty of ± 0.001 mm. They were 2.174 mm and 0.615 mm, respectively.

Pressure Measurement. The gas from the high-pressure cylinder traveled through the high-pressure buffer, pressure instrument, and microneedle valves to the bubble chamber unit. The bubble was formed at the tip of the capillary. The high-pressure buffer serves to preserve the pressure steady before the bubble chamber unit. The needle valves can be used to ensure the stabilization of the area upstream of the tubes. So, the bubble comes into being at the rate controlled at (1 to 60) bubbles per minute.

Table 4. Experimental Surface Tensions for Five Compounds at Different Temperatures and p = 1.6 MPa

	σ/(mN·m^{-1})				
t/°C	benzene	toluene	p-xylene	o-xylene	m-xylene
80.0	18.84	19.49	20.26	21.92	20.80
100.0	17.09	17.98	18.83	20.34	19.13
120.0	15.34	16.48	17.40	18.76	17.27
140.0	13.60	14.97	15.96	17.18	15.74
160.0	11.85	13.47	14.52	15.60	14.25
180.0	10.10	11.96	13.09	14.02	12.90
200.0	8.35	10.46	11.66	12.44	11.11

Table 5. Experimental Surface Tensions for the Binary Mixture of *p*-Xylene (1) + Benzene (2) at Different Temperatures and p = 1.6 MPa

	σ/(mN·m^{-1})						
	t/°C	t/°C	t/°C	t/°C	t/°C	t/°C	t/°C
x_1	80.0	100.0	120.0	140.0	160.0	180.0	200.0
0.0000	18.84	17.09	15.34	13.6	11.85	10.1	8.35
0.2000	18.3	16.82	15.34	13.86	12.39	10.91	9.43
0.4000	17.41	16.09	14.78	13.46	12.15	10.83	9.52
0.6000	17.36	16.08	14.79	13.51	12.23	10.95	9.66
0.8000	18.10	16.72	15.34	13.96	12.58	11.20	9.82
1.0000	20.26	18.83	17.39	15.96	14.52	13.09	11.66

The differential pressure was measured by an STD 120 Smart Differential Pressure Transmitter (Honeywell Corporation) with an uncertainty less than ± 0.75 Pa and with a range from (−250 to 750) Pa. In the experiment, the Smart Differential Pressure Transmitter was connected to a computer by an A/D digital transferring card. Using the computer program, not only the data can be saved automatically but also the changing curve of pressure can be displayed, and the data analysis becomes much simpler. The pressure in the bubble chamber unit was measured by a pressure transducer (Beijing West Corp.) with an uncertainty less than ± 0.01 MPa.

Temperature Control. The temperature control unit contains two major parts. As shown in the figure, the outer is the circulatory oil bath, which is used for heating the sample. The temperature was controlled by a PID temperature controller wired for direct control of the heating element. Meanwhile, two separated XMTD-808 digital meters with thermocouples provided a constant display of the temperature of the oil as well as the temperature inside the bubble chamber unit. In addition, there is a layer for heat preservation outside of the bubble

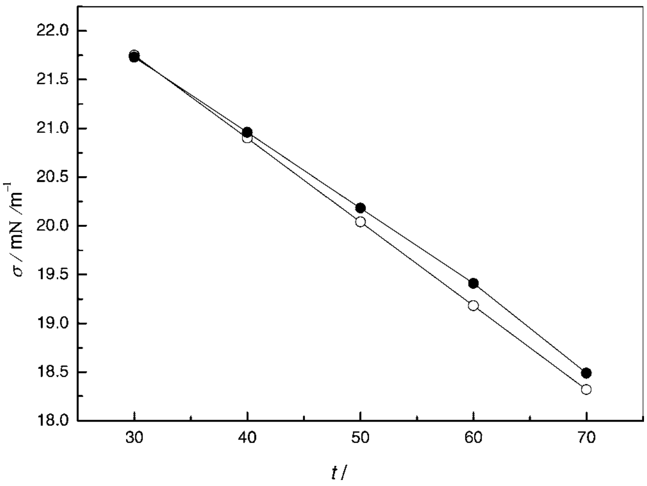

Figure 3. Surface tensions of methanol at different temperatures and at atmospheric pressure compared with literature data: ○, experimental data; ●, literature data.

Table 6. Correlation Coefficients of Compounds' Surface Tension at Different Temperatures

compound	*a*	*b*	AAD
benzene	25.83	0.08740	0.0002
toluene	25.51	0.07524	0.0003
m-xylene	28.23	0.07894	0.0002
p-xylene	27.02	0.07952	0.0001
o-xylene	26.00	0.07173	0.0072
average value			0.0016

chamber unit. The thermocouples connected with XMTD-808 digital meters were calibrated with a mercury thermometer with an uncertainty of ± 0.1 °C. The oil temperature was able to be controlled with the uncertainty of ± 1 °C. The mass of the steel provided a large heat capacity so that temperature variation in the bubble chamber unit fluctuated in the range of ± 0.1 °C from the set point.

Procedure. The measurement was carried out as follows: (a) According to Figure 1, check the apparatus; (b) clean the apparatus with distilled water and the sample. The apparatus was cleaned before each series of measurements by solvent washing and then blown dry. (c) Load the sample and open the switch. (d) The conditions of measurement were established. Then, keep the conditions for 2 h and make sure the system is in equilibrium. (e) With the microneedle valve 7 in Figure 1, adjust the bubble period. The maximum bubble pressure of the two capillaries was measured separately with the smart differential pressure transmitter (11 in Figure 1). (f) The data were transferred to a computer with a digital card. Finally, the pressure data were processed by custom software, and the surface tensions were calculated with eq 2.

Material. All chemicals used in this study were purchased from commercial suppliers. The methanol, ethanol and benzyl benzoate, benzene, toluene, and *p*-, *o*-, and *m*-xylene (>99.0 % purity) were from Tianjin Guangfu Finechemical Reagent Corp. and used for all experiments without further purification. The liquid mixtures were prepared using a BP210s balance whose uncertainty is within ± 1 mg to determine the mass of the chemicals.

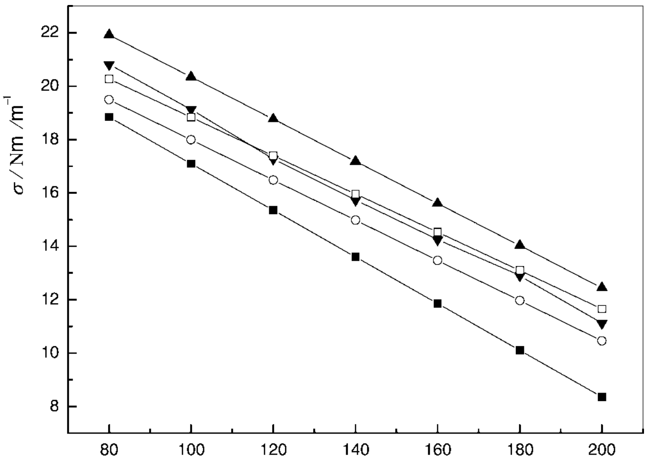

Figure 4. Surface tension of compounds as a function of temperatures and p = 1.6 MPa: ■, benzene; ○, toluene; □, *p*-xylene; ▼, *m*-xylene; ▲, *o*-xylene.

Calibration of the Apparatus. Before the experiment, the apparatus was checked using methanol, ethanol, and benzyl benzoate as standard solvents. The results compared with the data in references were listed in Tables 1, 2, and 3. By analyzing the calibration test and measuring the results, the relative uncertainty of measurement is less than 2 %.

Results and Discussion

The surface tensions of the five compounds and the binary mixture of *p*-xylene + benzene were measured and presented in the Tables 4 and 5 and Figures 3 and 4. The results were regressed with the following equation[8]

$$\sigma/(\mathrm{mN \cdot m^{-1}}) = a - bt/^\circ\mathrm{C} \qquad (3)$$

where a and b are parameters and σ is the surface tension. The regressed coefficients were provided in Table 6. The AAD means average relative deviation and is calculated from eq 4. The AAD was found to be 0.0016 for surface tensions.

$$\mathrm{AAD} = \frac{\sum_{i=1}^{N} \left| \frac{\sigma_{\mathrm{exptl}} - \sigma_{\mathrm{calcd}}}{\sigma_{\mathrm{exptl}}} \right|}{N} \qquad (4)$$

where σ = experimental values; σ_{calcd} = calculated values; and N = number of points.

Conclusion

A suitable apparatus was developed for measuring the static surface tension with the differential maximum bubble method. The configuration was described in detail. The surface tensions of benzene, toluene, *p*-, *o*-, *m*-xylene, and the binary mixture of *p*-xylene + benzene were measured at 1.6 MPa, from (80 to 200) °C. At high temperatures, the effects of pressure on the surface tension are complicated which is hard to predict. So further investigations appear to be required.

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