J. Chem. Eng. Data **2007,** *52,* 454−457

Surface Tension of *o*-Xylene + Acetic Acid and *m*-Xylene + Acetic Acid Binary Mixtures from 303.15 K to 343.15 K

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The surface tension of liquid mixtures is an important physical property in heat and mass transfer at an interface. A differential maximum bubble pressure tensiometer is described. Evaluation of the apparatus with standard chemicals had shown that the apparatus is convenient and reliable. The surface tensions of *o*-xylene +acetic acid and *m*-xylene + acetic acid were measured from 303.15 K to 343.15 K over the entire range of concentration. The data were correlated as a function of temperature and mole fraction. The average deviation is less than 1 %.

Introduction

The surface tension of liquids and solutions often has great significance in both practical and theoretical aspects. For example, it plays an important role in mass transfer processes such as distillation, extraction, and absorption by influencing the rate of mass transfer across the interface. Therefore, accurate measurements of surface tension are very important. The differential maximum pressure bubble method was suggested by Sugen[1] in 1921 and had been improved with the development of differential pressure technology. Now it has been used in a wide variety of applications with convenience and good reproduction.

Xylene is an important chemical produced for phthalic acid production by liquid-phase oxidation with acetic acid as a solvent. Therefore, the surface tensions of xylene + acetic acid mixtures are important. In our laboratory, a surface tensiometer has been concluded and evaluated based upon the principles of differential maximum bubble pressure, and the surface tensions of *p*-xylene + acetic acid had been determined. In this paper, the surface tensions of *o*-xylene + acetic acid and *m*-xylene +acetic acid were measured from 303.15 K to 343.15 K over the entire concentration. These surface tensions have not been reported so far.

Method

The relationship between differential maximum pressure and surface tension comes from the theory of maximum bubble pressure in a single capillary. Figure 1 shows a bubble being formed at the tips of two capillary tubes immersed to depths d and $d + \Delta d$. The differential maximum bubble pressure between bubbles at each tube is described as $\Delta p_{1,2}$ for tubes numbered 1 and 2. The density-related errors can be eliminated by changing the capillary arrangement. In 1956, Cuny and Wolf[2] derived an equation relating the differential maximum bubble pressure to surface tension for the case of two capillaries immersed to unequal depths:

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

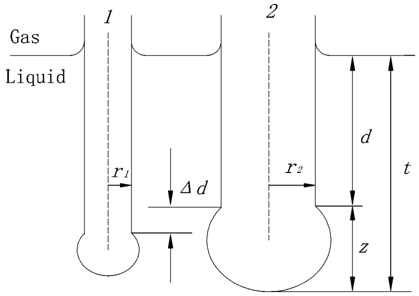

Figure 1. Illustration of the displaced capillary arrangement.

where Δd is the capillaries displacement; r_1 and r_2 are the capillary tip radii. In this work, one calculates the value of Δd for which the second term of numerator in eq 1 would become zero and then adjusts the capillaries so that the difference between their immersion depths was equal to that value of Δd. If an approximate 0.4 % of the experimental surface tensions are sufficient, the third term of numerator in eq 1 can be dropped as well.[3, 4] As follows:

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

This would make the measurement of surface tensions independent of density for practical purposes.

Experimental Section

Material. All chemicals used in this study were purchased from commercial suppliers. The *o*-xylene and *m*-xylene (> 99.0 % purity) from Tianjin Guangfu Finechemical Reagent Corp were used for all experiments without further purification. The acetic acid with > 99.5 % purity was purchased from Tianjin University Kewei Corporation. The liquid mixtures were prepared by mass using a BP210s balance accurate to within ± 0.01 mg. The average uncertainty in the mole fraction of the mixtures was estimated to be less than ± 0.0001.

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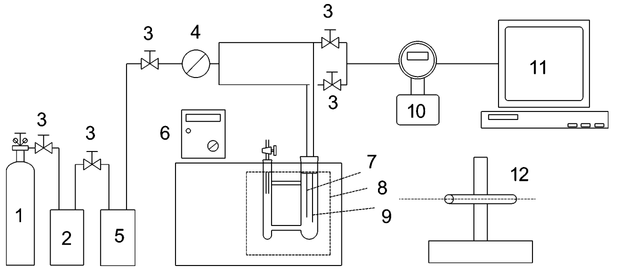

Figure 2. Schematic illustration of the apparatus: 1, N_2 cylinder; 2, high-pressure buffer; 3, micro-needle value; 4, pressure gauge; 5, low-pressure buffer; 6, constant-temperature controller; 7, small capillary; 8, inspection window; 9, large capillary; 10, smart differential pressure transmitter; 11, computer; 12, cathetometer.

Table 1. Surface Tension of Pure Reagents at Atmospheric Pressure

liquid	T/K	σ/(mN·mP^{-1}) exptl data	lit. data
water	303.15	70.70	71.40[6]
methanol	303.15	21.92	21.73[6]
ethanol	303.15	21.47	21.55[6]
p-xylene	298.15	27.80	27.76[7]
o-xylene	298.15	29.53	29.49[7]
m-xylene	298.15	28.26	28.10[7]
acetic acid	298.15	26.89	27.12[8] 27.08[9]

Experimental Apparatus. The configuration of apparatus is showed in Figure 2. The whole apparatus in this work is consisted of the pressure measurement cell, the sample tube, temperature controller, cathetometer, and flowing velocity controller. The differential pressure was measured by a STD 120 smart differential pressure transmitter by America Honeywell Corporation with an uncertainty less than ± 0.75 Pa and the range of −250 Pa to 750 Pa. Temperature was controlled by the Germany Huber's Polystat cc1 compatible control circulation baths, within ± 0.02 K of the selected value. The immersed depth of capillary can be measured by cathetometer with an uncertainty better than ± 0.001 mm, made by Shanghai

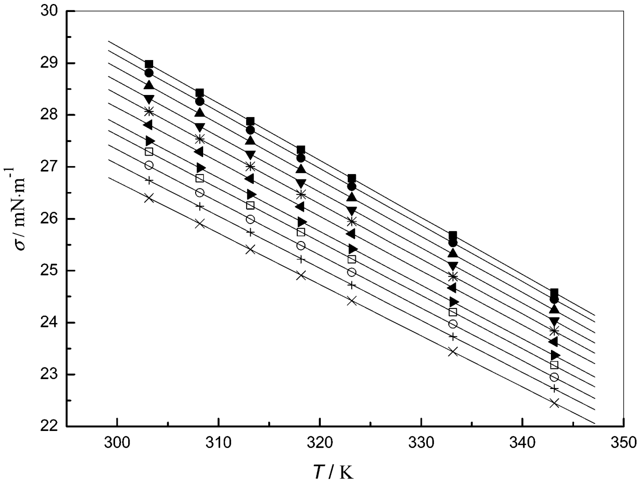

Figure 3. Surface tension of acetic acid (1) + o-xylene (2) vs temperature at various concentrations: ■, 0.0000; ●, 0.1001; ▲, 0.2001; ▼, 0.3000; *, 0.4188; left-facing solid triangle, 0.4999; right-facing solid triangle, 0.5999; □, 0.7018; ○, 0.7999; +, 0.9000; ×, 1.0000.

Table 2. Experimental Surface Tension σ for Acetic Acid (1) + o-Xylene (2)

x_1	σ/(mN·m^{-1}) T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
0.0000	28.98	28.43	27.88	27.33	26.78	25.68	24.58
0.1001	28.81	28.26	27.71	27.17	26.62	25.54	24.45
0.2001	28.56	28.03	27.49	26.94	26.40	25.32	24.24
0.3002	28.32	27.78	27.25	26.70	26.17	25.11	24.04
0.4000	28.07	27.54	27.01	26.47	25.95	24.89	23.84
0.5000	27.81	27.29	26.77	26.23	25.71	24.67	23.63
0.6213	27.50	26.98	26.47	25.94	25.42	24.40	23.37
0.7001	27.29	26.78	26.26	25.74	25.22	24.20	23.18
0.8000	27.03	26.50	25.99	25.48	24.97	23.97	22.95
0.9000	26.74	26.24	25.74	25.22	24.72	23.73	22.73
1.0000	26.40	25.91	25.41	24.91	24.42	23.44	22.45

Table 3. Experimental Surface Tension σ for Acetic Acid (1) + m-Xylene (2)

x_1	σ/(mN·m^{-1}) T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
0.0000	27.58	27.04	26.49	25.94	25.38	24.27	23.18
0.1001	27.51	26.97	26.42	25.88	25.32	24.23	23.15
0.2001	27.40	26.87	26.33	25.78	25.24	24.16	23.08
0.3000	27.30	26.77	26.24	25.69	25.15	24.08	23.02
0.4188	27.17	26.63	26.10	25.58	25.04	23.98	22.93
0.4999	27.07	26.55	26.03	25.50	24.98	23.92	22.88
0.5999	26.95	26.47	25.95	25.42	24.90	23.85	22.82
0.7018	26.87	26.36	25.84	25.32	24.76	23.74	22.72
0.7999	26.71	26.19	25.68	25.17	24.65	23.65	22.63
0.9000	26.56	26.06	25.56	25.04	24.55	23.55	22.55
1.0000	26.40	25.91	25.41	24.91	24.42	23.44	22.45

Table 4. Excess Surface Tension $\Delta\sigma$ for Acetic Acid (1) + o-Xylene (2)

x_1	$\Delta\sigma$/(mN·m^{-1}) T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
0.1001	0.0883	0.0823	0.07725	0.0822	0.0762	0.0842	0.0832
0.2001	0.0963	0.1043	0.1042	0.0942	0.0922	0.0882	0.0862
0.3002	0.1145	0.1065	0.1115	0.0965	0.0985	0.1024	0.0994
0.4000	0.1220	0.1180	0.1180	0.1080	0.1140	0.1060	0.1120
0.5000	0.1200	0.1200	0.1250	0.1100	0.1100	0.1100	0.1150
0.6213	0.1230	0.1157	0.1246	0.1135	0.1063	0.1117	0.1134
0.7001	0.1163	0.1143	0.1092	0.1042	0.0922	0.0882	0.0912
0.8000	0.1140	0.0860	0.0860	0.0860	0.0780	0.0820	0.0740
0.9000	0.0820	0.0780	0.0830	0.0680	0.0640	0.0660	0.0670

Table 5. Excess Surface Tension $\Delta\sigma$ for Acetic Acid (1) + *m*-Xylene (2)

	$\Delta\sigma$/(mN·m^{-1})						
x_1	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
0.1001	0.0481	0.0431	0.0381	0.0431	0.0361	0.0431	0.0431
0.2001	0.0561	0.0561	0.0561	0.0461	0.0521	0.0561	0.0461
0.3000	0.0740	0.0690	0.0740	0.0590	0.0580	0.0590	0.0590
0.4188	0.0842	0.0632	0.0623	0.0714	0.0621	0.0576	0.0557
0.4999	0.0799	0.0749	0.0799	0.0749	0.0799	0.0649	0.0649
0.5999	0.0779	0.1079	0.1079	0.0979	0.0959	0.0779	0.0779
0.7018	0.1181	0.1130	0.1079	0.1029	0.0537	0.0525	0.0523
0.7999	0.0739	0.0539	0.0539	0.0539	0.0379	0.0439	0.0339
0.9000	0.0420	0.0370	0.0420	0.0270	0.0340	0.0270	0.0270

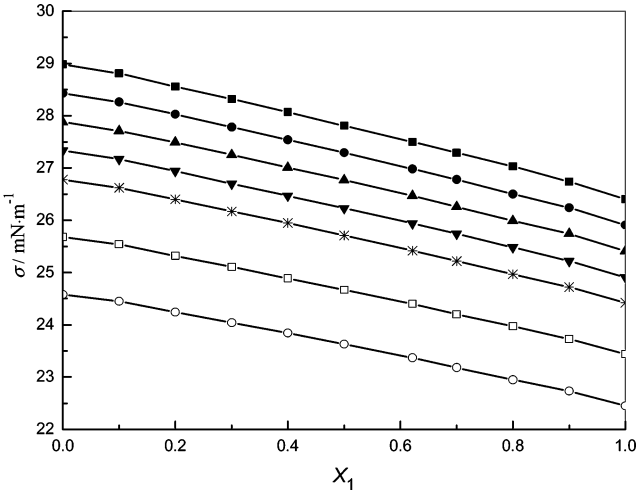

Figure 4. Surface tension at different mole fractions of acetic acid (1) + *o*-xylene (2): ■, 303.15 K; ●, 308.15 K; ▲, 313.15 K; ▼, 318.15 K; *, 323.15 K; □, 333.15 K; ○, 343.15 K.

Table 6. Surface Tension Parameter A_i and B_i (eq 3)

	acetic acid + *o*-xylene		acetic acid + *m*-xylene	
i	A_i	B_i	A_i	B_i
0	62.33	−0.1100	61.54	−0.1118
1	−5.011	0.0095	6.273	0.0169
2	0.8932	0.0014	2.037	−0.0066

optics apparatus factory. The capillary tip radius r_1 and r_2 are measured by microscope.

The apparatus has some advantages: First, the smart differential pressure transmitter is connected to a computer by an AD number transferring chip. The data were not only saved automatically by the computer's program, but also the changing curve of pressure was displayed, making data analysis much more simplified. Second, it is essential to keep a constant immersed depth during the experiment. Therefore, a U-shaped tube was used as the liquid vessel. The capillaries were immersed in one end of the tube and liquid level was adjusted from the other end, thus keeping the immersed depth constant. Third, for equilibrium surface tension, the rate of bubble formation at the tip of two capillary tubes should be equal and stable. So two pressure buffers are used to control the rate from 1 to 60 bubbles/min. In this experiment, the rate is 15 bubbles/min.[5]

Evaluation of the Apparatus. Before the experiment, the apparatus was checked using water, methanol, ethanol, and acetic acid (GC grade) as standard solvents. The evaluation data were listed in Table 1. The experimental surface tensions of water; methanol; ethanol; *p*-, *o*-, and *m*-xylene; and acetic acid are compared with the data in references in Table 1. It can be seen from the data that the experimental apparatus is reliable.

Results and Discussion

The surface tensions of *o*-xylene + acetic acid and *m*-xylene + acetic acid binary mixture system over the entire concentration from 303.15 K to 343.15 K are presented in Tables 2 and 3. The surface tensions, σ, decreased with increasing temperature for any given mole fraction of acetic acid. For a given temperature, the surface tensions of both mixtures decreased as the acetic acid component increased. Take the acetic acid + *o*-xylene binary mixture for example, Figure 3 shows the surface tensions of acetic acid + *o*-xylene as a function of temperature; Figure 4 shows surface tensions of acetic acid + *o*-xylene at different mole fraction. The results were regressed with the following equation:[10]

$$\sigma/(\mathrm{mN\cdot m^{-1}}) = \sum_{i=0}^{2} (A_i x_1{}^{i} + B_i x_1{}^{i} T/\mathrm{K}) \tag{3}$$

where x_1 is the mole fraction of acetic acid. The regressed coefficients were provided in Table 4. The average absolute deviations were found to be 0.00074 for surface tensions. AAD means average absolute deviation and is calculated from the following equation:

$$\mathrm{ADD} = \frac{\sum_{i=1}^{N} \left| \frac{\sigma_{\mathrm{exp}} - \sigma_{\mathrm{cal}}}{\sigma_{\mathrm{exp}}} \right|}{N} \tag{4}$$

where σ_{exp} = experimental values, σ_{cal} = calculated values, and N = number of points.

The excess surface tensions $\Delta\sigma$ are defined as the difference between the surface tensions of the mixture and those expected on the basis of a mole fraction average:

$$\Delta\sigma = \sigma - (\sigma_1 x_1 + \sigma_2 x_2) \tag{5}$$

The results are listed in Tables 5 and 6. They show the excess surface tensions $\Delta\sigma$ are positive for both binary mixtures.

Conclusion

A differential maximum bubble pressure tensiometer for surface tensions was established and evaluated. The surface tension data of *o*-xylene + acetic acid and *m*-xylene + acetic acid were measured from 303.15 K to 343.15 K, over the entire concentration. The deviations of apparatus are less than 1 %. The obtained data are well correlated using eq 3. The deviation is less than 1 %, so the results are reliable.

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Received for review September 5, 2006. Accepted December 10, 2006.

JE060390Q