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Interfacial Tension of Toluene + Water + Sodium Dodecyl Sulfate from (20 to 50) °C and pH between 4 and 9

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Interfacial tension of toluene + water + sodium dodecyl sulfate is reported over the aqueous surfactant concentration range of (0 to 34.68 × 10^{-5}) mol·L^{-1}, the temperature range of (20 to 50) °C, and the pH range of 4 to 9. This system is frequently used as a high interfacial tension system for liquid−liquid extraction investigations. The measurements were made by the drop-weight method, and interfacial tension values ranged from (23.1 to 38.1) mN·m^{-1}. The data show a nonlinear decrease with increasing surfactant concentration and temperature; however, there is almost a linear decrease with increasing pH. The interfacial pressure is also derived. The obtained data were correlated by empirical equations.

Introduction

Interfacial tension, defined as the work to create a unit of new surface between two immiscible fluids,[1] is an important property of liquid−liquid interfaces. This parameter affects the hydrodynamics and contact of phases for mass transfer purposes.

The data of interfacial tension are required by chemical engineers for the design of liquid−liquid contactors. For example, design of industrial extraction contactors requires knowledge of parameters such as mass transfer coefficients and the liquid−liquid interfacial area of the corresponding process. To calculate these parameters, one of the physical properties that must be known is interfacial tension.

Contaminants are usually present to an unknown extent in industrial materials. They accumulate at the interface between phases, inhibit circulation within the drops, cause hydrodynamic and adsorptive barriers to transfer across the interface, and change the pattern of drop behaviour. The interfacial tension data for pure (or clean) systems are rich in the literature; however, those with surfactants (as examples of impurity or contamination) are few.

However, the pH of aqueous solutions in contact with organic phases can alter this property. In liquid−liquid extraction, the pH of the water, used in the aqueous phases, and the solute transferred from one phase to another can provide alternatives in this case.

The temperature dependence of interfacial tension is also an important case when thermal variations are present along an extraction column or during the process.

This study presents data on interfacial tension of the phases of toluene + water, a recommended[2] and frequently used[3,4] system for liquid−liquid extraction investigations. The main specification of this system is its relatively high interfacial tension. Solutions of surfactant sodium dodecyl sulfate (SDS), as simulating industrial contaminants,[5,6] are used in contact with toluene, and the effects of temperature and pH are to be examined for each case.

The values of interfacial pressure for this system can also be obtained from interfacial tension data of the clean chemical system and that of surfactant solution.

Experimental Section

Toluene and sodium dodecyl sulfate were Merck products with purities of more than 99.5 % and 99 %, respectively, and were used as received. Laboratory-distilled water was redistilled prior to experimentation. The system of toluene + water can be considered an essentially immiscible basic binary system.[2]

The level of purity of sodium dodecyl sulfate was assessed by obtaining its critical micelle concentration in aqueous solution, using the conductometric method.[7] The conductivity was measured using a Genway 4020 conductometer, and the conductivity cell was calibrated with KCl solution. The measuring cell was immersed in a thermostat bath at 20 °C, keeping the temperature constant within ± 0.1 °C. The critical micelle concentration, obtained from the variation of specific conductivity against the concentration of SDS, is 0.00835 mol·L^{-1}, close to the value reported in the literature[7] (0.00825 mol·L^{-1}), which is obtained by this method.

Aqueous surfactant (SDS) solutions were prepared by mass using a Mettler AE-100 balance with an uncertainty of ± 0.1 mg. After preparation of the main solution, the desired next solutions were obtained by successive dilutions. The uncertainty in concentration of SDS was estimated to be within ± 0.02 × 10^{-5} mol·L^{-1}.

To adjust the pH, NaOH and HCl solutions, supplied by Merck, were used to reach the desired pH value in the aqueous phase. The measurement of pH values was performed with a Corning-M140 pH meter, having an uncertainty of ± 0.01.

The drop-weight method, which is a reproducible method and has been used by other investigators,[6,8,9] was used to determine the interfacial tension of the samples. The drop-forming device was similar to that described by Saien and Salimi.[9] The experimental apparatus is presented in Figure 1. A glass capillary (outer diameter of 4.24 mm) with a finely ground tip to give an angle of 90° between the ground face and the internal bore at the end with the edges sharp was used. The toluene phase was held in a narrow glass syringe conducted by an adjustable syringe pump (Phoenix M-CP, French) and flowed through a rigid tube to the capillary in the stagnant aqueous phase. To obtain the accurate flow rate, the syringe was initially calibrated with respect to the specified volume scale on the syringe. A very low flow rate (1 mL in 24.10 min, determined from the

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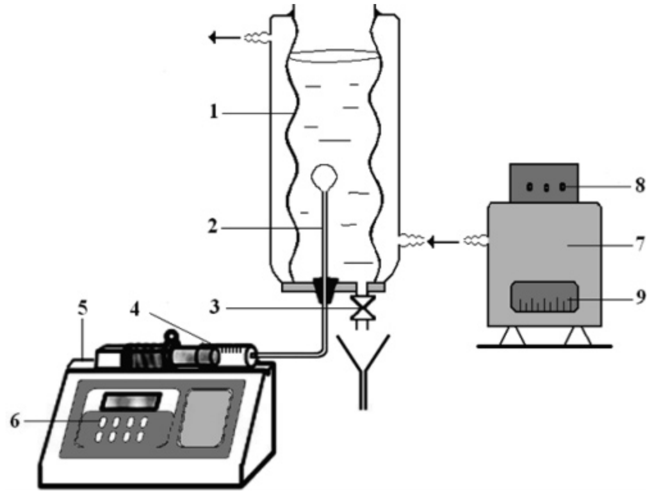

Figure 1. Schematic diagram of the apparatus for interfacial tension measurements: 1, thermostated aqueous phase container; 2, glass capillary; 3, drainage valve; 4, scaled glass syringe; 5, syringe pump; 6, flow rate adjustment and LCD display; 7, circulating thermostat; 8, temperature adjustment; 9, LCD temperature display.

Table 1. SDS Concentrations c, Phase Densities ρ, and Interfacial Tensions γ of the System

c	t	ρ_a	ρ_o	γ/mN·m^{-1}					
mol·L^{-1}	°C	kg·m^{-3}	kg·m^{-3}	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
0	20	998.21	866.84	38.1	37.8	37.5	37.1	36.8	36.5
	25	997.06	862.19	37.5	37.1	36.6	36.1	35.8	35.5
	30	995.66	857.52	36.8	36.4	36.0	35.5	35.2	34.9
	35	994.04	852.85	36.3	35.9	35.5	35.1	34.7	34.5
	40	992.22	848.15	35.9	35.5	35.1	34.7	34.4	34.1
	50	986.91	838.70	35.4	35.0	34.7	34.3	34.0	33.7
2.17×10^{-5}	20	998.21	866.84	36.5	36.2	35.8	35.5	35.2	34.7
	25	997.06	862.19	35.7	35.5	35.2	34.7	34.5	34.1
	30	995.66	857.52	34.8	34.6	34.4	34.0	33.8	33.4
	35	994.04	852.85	34.3	33.9	33.6	33.3	33.1	32.7
	40	992.23	848.15	33.8	33.5	33.2	32.9	32.7	32.3
	50	987.32	838.70	33.3	33.0	32.7	32.4	32.1	31.9
4.33×10^{-5}	20	998.20	866.84	35.0	34.8	34.4	34.0	33.7	33.5
	25	997.05	862.19	34.4	34.2	33.7	33.4	33.0	32.8
	30	995.65	857.52	33.8	33.4	33.1	32.7	32.4	32.0
	35	994.04	852.85	33.2	32.9	32.5	32.2	31.8	31.4
	40	992.21	848.15	32.9	32.4	32.0	31.7	31.4	31.0
	50	987.72	838.70	32.2	31.8	31.6	31.3	30.9	30.6
8.67×10^{-5}	20	998.20	866.84	33.1	32.8	32.7	32.3	32.1	31.6
	25	997.06	862.19	32.7	32.2	32.0	31.7	31.3	31.0
	30	995.66	857.52	32.0	31.6	31.4	31.0	30.6	30.2
	35	994.05	852.85	31.5	31.0	30.8	30.5	30.1	29.7
	40	992.21	848.15	31.0	30.5	30.2	29.9	29.6	29.1
	50	987.81	838.70	30.5	29.9	29.6	29.4	29.0	28.5
17.34×10^{-5}	20	998.22	866.84	30.6	30.2	29.9	29.5	29.2	28.9
	25	997.06	862.19	30.0	29.6	29.3	28.9	28.6	28.3
	30	995.66	857.52	29.3	29.0	28.6	28.3	27.9	27.6
	35	994.05	852.85	28.8	28.3	27.9	27.5	27.2	27.0
	40	992.23	848.15	28.3	27.8	27.3	27.0	26.8	26.4
	50	988.05	838.70	27.7	27.2	26.8	26.5	26.3	25.8
34.68×10^{-5}	20	998.23	866.84	28.3	27.8	27.3	26.7	26.2	25.8
	25	997.07	862.19	27.7	27.2	26.6	25.9	25.4	24.9
	30	995.68	857.52	27.0	26.6	26.0	25.3	24.9	24.4
	35	994.06	852.85	26.6	26.0	25.5	24.9	24.6	24.0
	40	992.24	848.15	26.1	25.5	25.0	24.4	24.1	23.6
	50	988.06	838.70	25.6	25.0	24.4	24.0	23.5	23.0

flow rate indication when calibrated by measuring the time of syringe piston movement) of the organic phase was conducted to the capillary, and drops were formed very slowly at the tip of capillary. If the flow rate and number of drops (five drops after releasing a number of drops) per the relevant measured time with a stop watch are known, then drop volume can be calculated. Each drop volume was obtained from at least three measurements of time where the maximum deviations from the average value were less than ± 0.3 %. The whole aqueous media and conducting tube were thermostated with an uncertainty of ± 0.1 °C using an adjustable safety thermostat (Optima 740, Japan).

The syringe, tube, and capillary, in contact with liquids, were thoroughly cleaned by washing with a solution of nitric acid. Then they were rinsed several times with distilled water and then with toluene. The outer surface of the capillary was cleaned, and the capillary tip was also wiped clean with a paper towel.

To determine the interfacial tension, the density of phases is required. Densities were measured at different temperatures using a density meter (Anton Paar DMA 4500, Austria) with an uncertainty of ± 0.05 kg·m^{-3}. The desired temperature is self-adjusted in this density meter with an uncertainty of ± 0.01 °C.

The experiments were carried out at different temperatures for each sample of aqueous solution, containing the corresponding pH value. New main SDS solutions were prepared for each set of experiments with a specified pH and SDS concentration and were used in successive experiments with different temperatures.

Calculation of Interfacial Tension. Considering the formation of a drop very slowly at a capillary of radius υ, the volume of liquid that eventually detaches υ is a definite function of the force tending to retain the drop on the capillary, $2\pi r\gamma$ (γ is the interfacial tension) and the buoyancy force causing detachment, $\upsilon'\Delta\rho g$, where υ' is the volume of the fully formed pendant drop and $\Delta\rho$ is the density difference between the aqueous and organic liquids (ρ_a and ρ_o). The relationship between υ and υ' has been empirically determined in a careful experimental study by Harkins and Brown[10]

$$\gamma = \frac{\upsilon\Delta\rho g}{r}\phi \tag{1}$$

where ϕ is a constant and should be obtained from the tables of Harkins and Brown,[6,10] which are correlated in an empirical equation by Drelich et al.[11]

$$\phi = 0.167 + 0.193\left(\frac{r}{\sqrt[3]{\upsilon}}\right) - 0.0489\left(\frac{r}{\sqrt[3]{\upsilon}}\right)^2 - 0.0496\left(\frac{r}{\sqrt[3]{\upsilon}}\right)^3 \tag{2}$$

To examine the performance and reliability of the method, the interfacial tension of toluene + water at 25 °C was measured (without surfactant). The measured value is the same value of 36.1 mN·m^{-1} reported in the literature.[11,12] The uncertainty in measurement results is estimated to be within ±0.1 mN·m^{-1}.

Results and Discussion

Six concentrations of SDS ranging from (0 to 34.68 × 10^{-5}) mol·L^{-1} were tested for six temperatures of (20 to 50) °C and six pH values of 4 to 9, within the estimated practical range of applications, resulting in 216 interfacial tension data. The interfacial tension data measured for the toluene + water system at various temperatures, surfactant concentrations, and pH values are listed in Table 1 along with the corresponding density of phases. The values are in the range from (33.7 to 38.1) mN·m^{-1} for a clean system and in the range (23.0 to 36.5) mN·m^{-1} for a contaminated system. Drop volumes within (288.3 to 135.7) mm^3 were generated.

Figure 2 shows the typical surfactant effects on the interfacial tension of system. At a pH value of 7 and temperature of 20 °C, for instance, the interfacial tension decreases from (37.1 to

Table 2. Interfacial Tension Parameters K_1, K_2, and K_3 (Equation 3) and the Coefficients of Determination R^2 for the System

	c/mol·L^{-1} = 0				c/mol·L^{-1} = 2.17 × 10^{-5}				c/mol·L^{-1} = 4.33 × 10^{-5}			
	K_1	$-K_2 \cdot 10^2$	$K_3 \cdot 10^4$	R^2	K_1	$-K_2 \cdot 10^2$	$K_3 \cdot 10^4$	R^2	K_1	$-K_2 \cdot 10^2$	$K_3 \cdot 10^4$	R^2
pH 4	42.09	23.86	21.05	0.9992	41.74	32.03	30.38	0.9983	38.44	20.10	15.24	0.9987
pH 5	41.93	25.18	22.62	0.9995	41.25	30.71	28.48	0.9969	38.79	23.71	19.57	0.9989
pH 6	41.81	26.96	25.43	0.9986	40.70	29.05	25.95	0.9937	38.70	25.95	23.43	0.9982
pH 7	41.76	29.45	29.01	0.9945	40.14	28.41	26.01	0.9983	38.21	25.13	22.67	0.9954
pH 8	41.62	30.73	31.05	0.9957	39.52	25.86	22.00	0.9975	37.85	24.85	21.81	0.9991
pH 9	41.12	29.39	29.38	0.9961	39.09	26.08	23.19	0.9944	38.15	28.52	26.71	0.9988
	c/mol·L^{-1} = 8.67 × 10^{-5}				c/mol·L^{-1} = 17.34 × 10^{-5}				c/mol·L^{-1} = 34.68 × 10^{-5}			
	K_1	$-K_2 \cdot 10^2$	$K_3 \cdot 10^4$	R^2	K_1	$-K_2 \cdot 10^2$	$K_3 \cdot 10^4$	R^2	K_1	$-K_2 \cdot 10^2$	$K_3 \cdot 10^4$	R^2
pH 4	36.52	19.52	14.76	0.9956	34.31	21.97	17.57	0.9975	32.15	22.81	19.29	0.9994
pH 5	36.27	20.33	15.14	0.9990	33.79	20.67	14.90	0.9952	31.50	21.51	16.86	0.9963
pH 6	36.50	22.18	16.67	0.9979	34.09	24.69	20.01	0.9941	31.21	23.33	19.52	0.9990
pH 7	36.09	22.21	17.52	0.9959	33.71	24.56	20.14	0.9944	30.52	23.80	21.43	0.9978
pH 8	36.13	24.25	20.01	0.9993	33.48	25.35	22.05	0.9956	29.39	19.60	15.86	0.9935
pH 9	35.57	23.11	17.81	0.9965	32.72	22.22	16.62	0.9981	29.43	22.65	19.81	0.9957

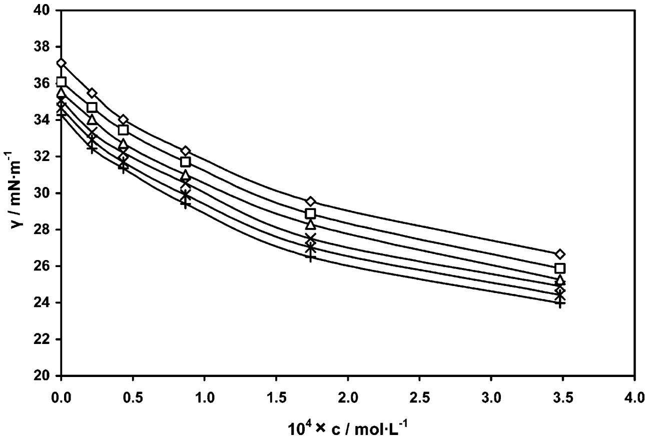

Figure 2. Interfacial tension of the system as a function of SDS concentration at pH 7 and different temperatures: ◇, 20 °C; □, 25 °C; △, 30 °C; ×, 35 °C; ∗, 40 °C; +, 50 °C.

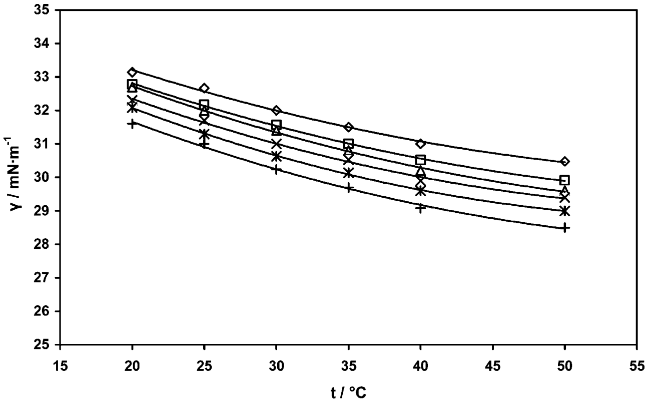

Figure 3. Interfacial tension of the system as a function of temperature at different pH values and a SDS concentration of 8.67 × 10^{-5} mol·L^{-1}. Lines represent eq 3: ◇, pH 4; □, pH 5; △, pH 6; ×, pH 7; ∗, pH 8; +, pH 9.

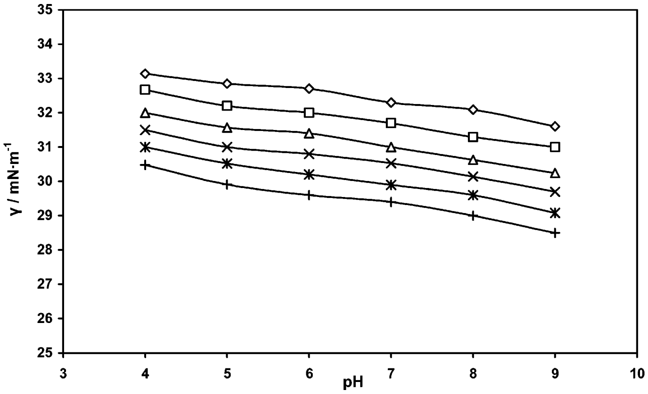

Figure 4. Interfacial tension of the system as a function of pH at different temperatures and a SDS concentration of 8.67 × 10^{-5} mol·L^{-1}: ◇, 20 °C; □, 25 °C; △, 30 °C; ×, 35 °C; ∗, 40 °C; +, 50 °C.

26.7) mN·m^{-1} by adding the surfactant. The trend of variation is nonlinear, in agreement with other works,[8,13,14] and very low amounts of surfactant cause significant reduction in interfacial tension of the system.

The increase of temperature from (20 to 50) °C results in lowering of the interfacial tension when surfactant concentration and pH are fixed. Figure 3 shows that the trend is approximately nonlinear for this system. For example, when temperature increases from (20 to 30) °C at a SDS concentration of 8.67 × 10^{-5} mol·L^{-1} and pH 7, the interfacial tension falls from (32.3 to 31.0) mN·m^{-1}, while for the temperatures from (40 to 50) °C and the same conditions, it decreases from (29.9 to 29.4) mN·m^{-1}.

The values show that interfacial tension decreases as the pH increases at a constant temperature and surfactant concentration. The change in interfacial tension is almost linear as a typical variation is shown by Figure 4. This variation can provide a large drop size produced in acidic aqueous solutions compared with basic solutions in contact with the toluene phase. It is notable that the influence of pH is much lower than that of surfactant concentration (maximum reduction of 2.6 mN·m^{-1} compared with 10.7 mN·m^{-1}, while other parameters are constant for each variation).

The results in this study were correlated by a simple second-order polynomial equation

$$\gamma/\mathrm{mN\cdot m^{-1}} = K_1 + K_2 t/°\mathrm{C} + K_3 (t/°\mathrm{C})^2 \qquad (3)$$

where K_1, K_2, and K_3 are the adjustable coefficients, obtained by fitting, whose values are listed in Table 2. The difference between calculated and experimental data was obtained in terms of the so-called coefficient of determination (R^2)[15,16]

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (\gamma_{\mathrm{cal}} - \gamma_{\mathrm{exp}})^2}{\sum_{i=1}^{N} (\bar{\gamma} - \gamma_{\mathrm{exp}})^2} \qquad (4)$$

where N, γ_{cal}, γ_{exp}, and $\bar{\gamma}$ are, respectively, the number of data used in the fit, the interfacial tension calculated by the model,

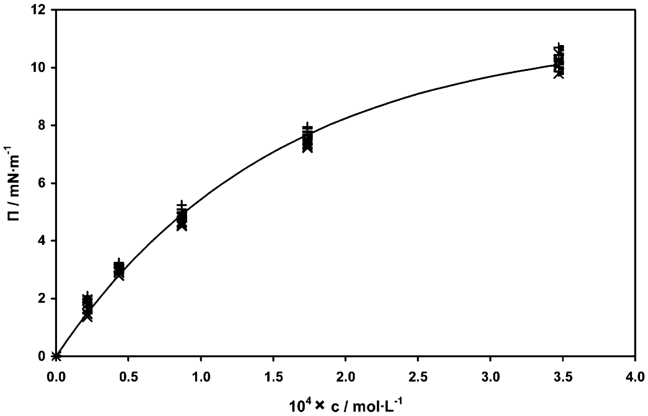

Figure 5. Variation of interfacial pressure of the system vs SDS concentration for different temperature and pH values. Line represents eq 7: −, 20 °C; ×, 30 °C; +, 50 °C.

the experimental interfacial tension, and the average of all the appropriate experimental values in the fit. The values of R^2 (0.9935−0.9995) are also given in Table 2, showing the goodness of fitting.

Using eq 3 provides a maximum deviation less than ±0.8% and an average deviation

$$\mathrm{AD} = \left[\sum_{i=1}^{N} \frac{|\gamma_{i,\mathrm{exp}} - \gamma_{i,\mathrm{cal}}|/\gamma_{i,\mathrm{exp}}}{N}\right] \qquad (5)$$

of ± 0.16 %. Figure 3 is shown as an example. The results show that both the pH and the concentration of SDS greatly influence the relationship between interfacial tension and temperature.

The interfacial pressure of surfactant solutions Π is expressed as

$$\Pi = \gamma_{\mathrm{o}} - \gamma \qquad (6)$$

where γ_{o} is the interfacial tension between clean toluene and water and γ is that of surfactant solution. The obtained interfacial pressures for this system are within (1.3 to 10.7) $\mathrm{mN{\cdot}m^{-1}}$. The results show that the interfacial pressure can be considered independent of pH and temperature, compared with the very significant influence of SDS concentration within the range used in this work. Presented in Figure 5 is the variation of interfacial pressure of the system as a function of surfactant concentration for different temperatures and pH values.

The nonlinear variation of interfacial pressure of this chemical system for the whole data can be nicely expressed through the empirical equation

$$\Pi/\mathrm{mN{\cdot}m^{-1}} = 11.23\{1 - \exp(-6.62 \times 10^{3}\, c/\mathrm{mol{\cdot}L^{-1}})\} \qquad (7)$$

By use of this equation the standard deviations were found to be less than 0.3 $\mathrm{mN{\cdot}m^{-1}}$ for 180 data points, and the mean deviation is within ± 5.9 %. The coefficient of determination for this equation is 0.9930. The lowest surfactant concentration (2.17×10^{-5} $\mathrm{mol{\cdot}L^{-1}}$) provides the maximum deviation. Figure 5 shows the agreement between measured and predicted values.

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