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Interfacial Tension between Cumene and Aqueous Sodium Dodecyl Sulfate Solutions from (20 to 50) °C and pH between 4 and 9

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Interfacial tension data obtained over the aqueous surfactant (sodium dodecyl sulfate) concentration range of (0 to 34.68 × 10^{-5}) mol·L^{-1}, the pH range of 4 to 9, and the temperature range of (20 to 50) °C are presented for the recommended chemical system of cumene and water. The measurements were made using an automatic DuNoüy tensiometer, and interfacial tension values ranged from (27.3 to 37.0) mN·m^{-1}. The data show a nonlinear decrease with increasing surfactant concentration and pH; however, there is a linear decrease with increasing temperature. The interfacial pressure was also derived. The interfacial tension and interfacial pressure values were correlated by empirical equations.

Introduction

The interfacial tension is a property that plays an important role in interphase mass and heat transfer. In liquid−liquid extraction, for example, it is a key parameter affecting the hydrodynamics and contact of phases for mass transfer purposes.

The liquid materials to be treated in the chemical industry, however, usually have a level of impurity or contamination that plays a central role in controlling the desired interfacial property in practical applications. The interfacial tension data for pure systems are rich in the literature; however, those for surfactant mixtures are few. A number of recent published works have investigated the modification of interfacial tension by surfactants in a more systematic way.[1,2] In this regard and for practical applications, measurements of interfacial tension for organic + aqueous phases in the presence of surfactants are required. The pH of solutions in contact with organic phases also alters this property. In liquid−liquid extraction, the solute transferred from one phase to another can alter the pH values.

This study presents data on the interfacial tension of the phases of cumene (isopropylbenzene) + water, a recommended high interfacial tension system for liquid−liquid extraction.[3,4] Using this chemical system has proven to be satisfactory in liquid−liquid extraction systems and avoids the use of highly flammable liquids, having flash points below 32 °C.[5] Solutions of surfactant sodium dodecyl sulfate (SDS), generally used for investigating the influence of contamination on operating conditions,[6−8] are used in contact with cumene, 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 pure chemical system and that of the surfactant solution.

Experimental Section

Cumene (>99%) and sodium dodecyl sulfate (≥99%) were Merck products and were used as received. Laboratory-distilled water was redistilled prior to experimentation. The solubility between cumene and water is very low, which is below the limits of accuracy of the chromatographic analysis.[5,9]

The level of purity of sodium dodecyl sulfate was investigated by obtaining its critical micelle concentration in aqueous solution using the conductometric method.[10,11] 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 thermostated bath at 20 °C, keeping the temperature constant within ±0.1 °C. From the variation of specific conductivity against the concentration of SDS, the critical micelle concentration obtained is 0.00833 mol·L^{-1}, close to the value reported in the literature (0.00825 mol·L^{-1}) obtained with this method.[10]

SDS solutions were prepared by mass using a Mettler AE-100 balance with an uncertainty of ±0.1 mg. After preparing the main solution, the next desired solutions were obtained by successive dilutions. An aqueous surfactant (SDS) concentration range of (0 to 34.68 × 10^{-5}) mol·L^{-1} was applied. The uncertainty in the concentration of SDS was estimated to be within ±0.02 × 10^{-5} mol·L^{-1}.

NaOH and HCl supplied by Merck were used as pH modifiers; in both cases, a concentration of 2 mol·L^{-1} was used to reach the desired pH (between 4 and 9) in the aqueous phase, and pH measurements were performed with a Corning-M140 pH meter having an uncertainty of 0.01.

The interfacial tension of the samples was measured using a PC-controlled KSV Sigma 70 tension balance that employs the DuNoüy ring-detachment method. The method is reproducible and has been used by a number of investigators.[1,12−14] The platinum ring (radius, 9.545 mm; wire radius, 0.185 mm) was thoroughly cleaned by immersion in a concentrated solution of nitric acid. Then it was rinsed with distilled water, flame dried, washed again with distilled water, and dried before each measurement. The measurements were corrected to the actual values utilizing the corrections suggested by Huh and Mason[15] to compensate for the interfacial distortion. To apply the corrections introduced into the equipment software, the density of phases was required. The temperature of the system was controlled by a Multi Temp III thermostat with an uncer-

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Table 1. SDS Concentration (*c*) and Interfacial Tension (γ) of the System

		pH					
c/mol·L^{-1}	t/°C	4	5	6	7	8	9
		γ/mN·m^{-1}					
0	20	37.0	34.5	33.1	32.4	32.3	32.1
	25	36.9	34.3	33.0	32.3	32.2	32.0
	30	36.8	34.3	32.9	32.2	32.1	32.0
	35	36.8	34.2	32.8	32.2	32.0	31.9
	40	36.7	34.2	32.8	32.1	31.9	31.8
	50	36.6	34.0	32.6	31.9	31.8	31.6
2.17×10^{-5}	20	34.9	32.7	31.5	30.8	30.7	30.6
	25	34.8	32.6	31.3	30.8	30.6	30.5
	30	34.7	32.5	31.3	30.7	30.6	30.4
	35	34.6	32.4	31.2	30.6	30.5	30.4
	40	34.6	32.4	31.2	30.5	30.4	30.3
	50	34.5	32.2	31.0	30.4	30.2	30.1
4.33×10^{-5}	20	33.4	31.3	30.4	30.0	29.9	29.8
	25	33.3	31.2	30.3	29.9	29.8	29.7
	30	33.2	31.2	30.2	29.9	29.8	29.6
	35	33.1	31.1	30.2	29.8	29.7	29.6
	40	33.1	31.0	30.1	29.7	29.6	29.5
	50	32.9	30.9	29.9	29.6	29.4	29.3
8.67×10^{-5}	20	31.5	30.1	29.3	28.9	28.8	28.7
	25	31.4	30.0	29.2	28.8	28.7	28.6
	30	31.3	29.9	29.1	28.7	28.6	28.5
	35	31.2	29.9	29.0	28.6	28.5	28.4
	40	31.2	29.8	28.9	28.5	28.4	28.3
	50	31.0	29.6	28.8	28.4	28.3	28.1
17.34×10^{-5}	20	29.5	28.7	28.3	28.1	28.0	27.9
	25	29.5	28.6	28.2	28.0	27.9	27.8
	30	29.4	28.5	28.1	27.9	27.8	27.7
	35	29.3	28.4	28.0	27.8	27.7	27.6
	40	29.3	28.4	27.9	27.7	27.6	27.5
	50	29.1	28.2	27.8	27.6	27.5	27.3
34.68×10^{-5}	20	28.9	28.3	28.0	27.9	27.9	27.8
	25	28.8	28.2	28.0	27.9	27.8	27.7
	30	28.7	28.2	27.9	27.8	27.7	27.7
	35	28.6	28.1	27.8	27.7	27.6	27.6
	40	28.6	28.0	27.7	27.6	27.5	27.5
	50	28.4	27.9	27.6	27.4	27.4	27.3

tainty of ±0.1 °C. The interfacial tension measurements were carried out at temperatures from (20 to 50) °C for each sample containing an aqueous solution at the corresponding pH value. Each reported value of the interfacial tension was an average of multiple measurements (at least eight) until the reproducibility of replicate measurements on the sample was within ±0.01 mN·m^{-1}. After the first few measurements, there is a tendency to obtain constant values. The standard deviation reported by the tensiometer increases to ±0.03 mN·m^{-1} for some multiple measurements; therefore, the uncertainty is estimated to be within ±0.1 mN·m^{-1}. New SDS main solutions were prepared for each sample used, in successive experiments with different temperatures, whereas the pH and the SDS concentration were constant.

Results and Discussion

The interfacial tension data measured for the cumene + water system at various temperatures, surfactant concentrations, and pH values are listed in Table 1. The values are in the range of (31.6 to 37.0) mN·m^{-1} for the pure system and in the range of (27.3 to 34.9) mN·m^{-1} for the contaminated system. The Table shows that an increase in the concentration of the surfactant SDS reduces the interfacial tension, regardless of temperature and pH.

Typical surfactant effects on the interfacial tension are shown in Figure 1. The trend in variation is nonlinear, in agreement with other works.[2,7,16] Low amounts of surfactants cause a significant reduction in the interfacial tension of the system, which remains nearly constant for concentrations greater than 17.34×10^{-5} mol·L^{-1}.

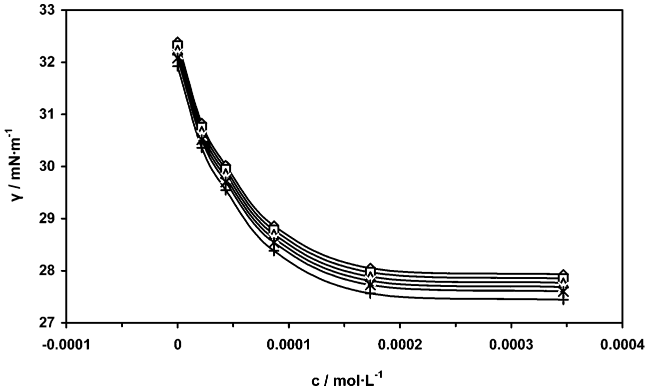

Figure 1. Interfacial tension of the system as a function of SDS concentration at different temperatures and pH 7: ◇, 20 °C; □, 25 °C; △, 30 °C; ×, 35 °C; *, 40 °C; +, 50 °C.

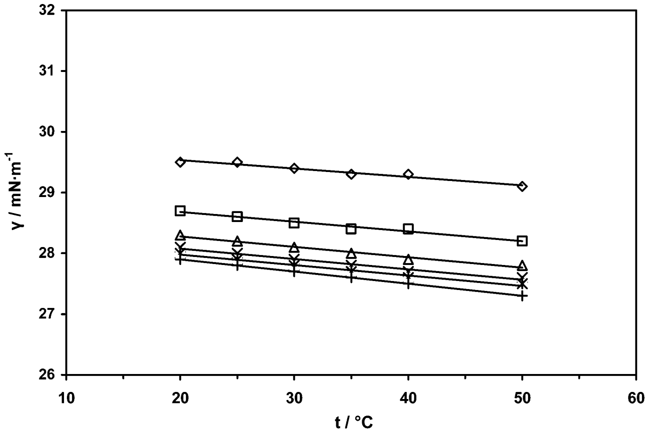

Figure 2. Interfacial tension of the system as a function of temperature at different pH values and an SDS concentration of 17.34×10^{-5} mol·L^{-1}. Lines are calculated from eq 1: ◇, pH 4; □, pH 5; △, pH 6; ×, pH 7; *, pH 8; +, pH 9.

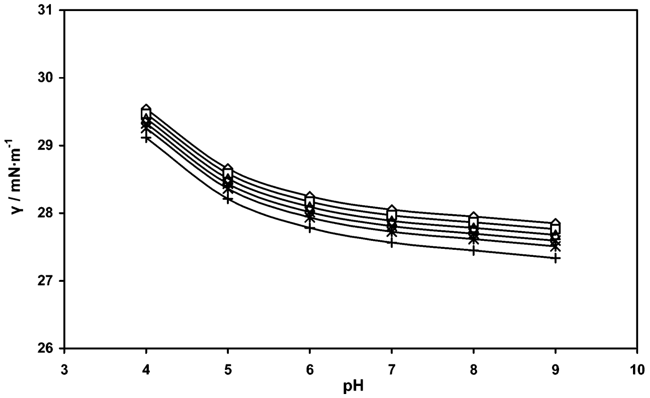

Figure 3. Interfacial tension of the system as a function of pH at different temperatures and an SDS concentration of 17.34×10^{-5} mol·L^{-1}: ◇, 20 °C; □, 25 °C; △, 30 °C; ×, 35 °C; *, 40 °C; +, 50 °C.

The increase in temperature from (20 to 50) °C results in a linear lowering of the interfacial tension when the surfactant concentration and pH are fixed, as is represented typically by Figure 2.

The values show that the interfacial tension decreases as the pH increases and the change in interfacial tension caused by a given change in pH is larger at low pH. Figure 3 shows that the trend is nonlinear. For example, when pH increases from 4 to 5, at an SDS concentration of 17.34 $\times 10^{-5}$ mol·L^{-1} and 20 °C, the interfacial tension falls from (29.5 to 28.7) mN·m^{-1}, whereas for pH from 8 to 9 and the

Table 2. Interfacial Tension Parameters K_1 and K_2 (Equation 1) for the System

c/mol·L^{-1}											
0		2.17×10^{-5}		4.33×10^{-5}		8.67×10^{-5}		17.34×10^{-5}		34.68×10^{-5}	
K_1	$K_2 \times 10^4$	K_1	$K_2 \times 10^4$	K_1	$K_2 \times 10^4$	K_1	$K_2 \times 10^4$	K_1	$K_2 \times 10^4$	K_1	$K_2 \times 10^4$
pH 4											
37.23	128.57	35.12	131.43	33.70	159.97	31.80	160.02	29.81	137.14	29.20	159.96
pH 5											
34.74	145.71	33.02	159.98	31.56	134.29	30.41	157.14	29.01	160.03	28.56	134.29
pH 6											
33.40	160.01	31.74	145.71	30.71	157.14	29.62	171.40	28.62	171.38	28.33	148.57
pH 7											
32.71	157.14	31.13	148.57	30.26	134.29	29.22	171.43	28.42	171.45	28.30	177.14
pH 8											
32.62	171.43	31.04	162.86	30.24	162.86	29.12	171.39	28.32	171.47	28.22	171.43
pH 9											
32.44	162.86	30.93	166.57	30.11	157.14	29.10	199.97	28.30	199.97	28.14	162.86

Table 3. Parameters of Equation 5 for the SDS Concentration Dependence of the System Interfacial Pressure

pH											
4		5		6		7		8		9	
m	*n*	*m*	*n*	*m*	*n*	*m*	*n*	*m*	*n*	*m*	*n*
8.22	−13 290.8	6.15	−15 457.7	5.04	−17 190.5	4.49	−18 034.1	4.43	−18 251.9	4.36	−18 400.1

same conditions it decreases from (28.0 to 27.9) mN·m^{-1}. This variation can provide an increase in the drop size produced when a highly acidic solution is used in aqueous−organic dispersions. It is notable that the influence of pH is significantly lower than that of surfactant concentration (maximum reduction of 4.9 mN·m^{-1} compared with 8.2 mN·m^{-1}) within the range used.

The experimental interfacial tension data of the system were correlated using the empirical equation

$$\gamma/\text{mN·m}^{-1} = K_1 - K_2 t/°\text{C} \tag{1}$$

which has been used by a number of investigators for interfacial tension and surface tension.[17−19] The values of K_1 and K_2, obtained by fitting, are listed in Table 2. The standard deviation, defined as

$$S = \left[\frac{\sum_{i=1}^{N}(\gamma_{\text{i,exptl}} - \gamma_{\text{i,calcd}})^2}{M - N}\right]^{0.5} \tag{2}$$

was calculated. In this equation, M and N are the number of data points and the number of adjustable parameters, respectively. The values are less than 0.1 mN·m^{-1} (0.005−0.06 mN·m^{-1}), and the mean standard deviation for 36 fitting items is 0.03 mN·m^{-1}. The results show that both the pH and the concentration of sodium dodecyl sulfate greatly influence the relationship between interfacial tension and temperature. Using eq 1 provides a maximum deviation of less than ±0.25% and an average deviation of ±0.08%. Figure 2 is shown as an example.

$$\%\text{AD} = 100\left[\sum_{i=1}^{N}\frac{|\gamma_{i,\text{exptl}} - \gamma_{i,\text{calcd}}|/\gamma_{i,\text{exptl}}}{M}\right] \tag{3}$$

The interfacial pressure of surfactant solutions, Π, is expressed as

$$\Pi = \gamma_o - \gamma \tag{4}$$

where γ_o is the interfacial tension between pure cumene and water and γ is that of the surfactant solution. Presented in Figure 4 is the variation of interfacial pressure as a function of surfactant concentration for different temperatures and pH values. The values are within (1.5 to 8.2) mN·m^{-1}. The interfacial pressure for the system can be considered to be independent of temperature; however, it is a nonlinear function of pH and surfactant concentration, with the most marked effect of the surfactant at low pH values studied.

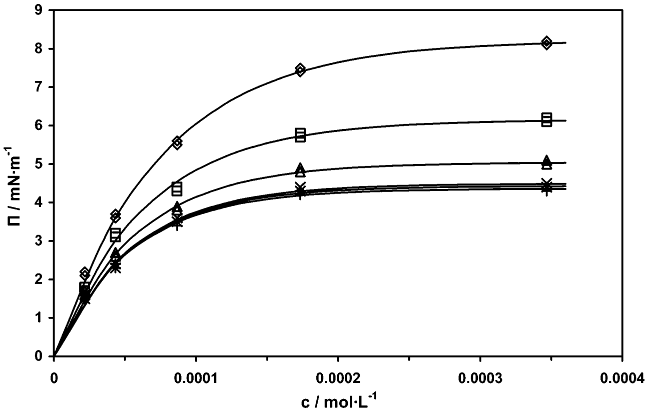

Figure 4. Variation of the interfacial pressure of the system vs SDS concentration for different temperatures and pH values. Lines are calculated from eq 5: ◇, pH 4; □, pH 5; △, pH 6; ×, pH 7; *, pH 8; +, pH 9.

The variation of the interfacial pressure of the chemical system, for each pH, was expressed through the empirical equation

$$\Pi/\text{mN·m}^{-1} = m\{1 - \exp(nc/\text{mol·L}^{-1})\} \tag{5}$$

where m and n are fitted parameters whose values are shown in Table 3. By using this equation, the standard deviations were found to be within (0.07−0.11) mN·m^{-1}, and the mean standard deviation for six fitting items is 0.08 mN·m^{-1}. The maximum and average deviations for 180 data points are within ±9.1% and ±2.2%, respectively. The lowest surfactant concentration (2.17×10^{-5} mol·L^{-1}) provides the maximum deviation. Figure 4 shows the agreement between the measured and predicted values.

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