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Interfacial Tension of Saturated Butan-1-ol + Sodium Dodecyl Sulfate + Saturated Water from 20 to 50 °C and at a pH between 4 and 9

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The liquid−liquid equilibrium interfacial tension of binary systems of saturated butan-1-ol and water has been studied over the aqueous surfactant (sodium dodecyl sulfate) concentration range of 0 to 3.48×10^{-4} mol·L^{-1} (0 to 100 ppm), the pH range of 4 to 9, and the temperature range of 20 to 50 °C. The measurements were made by the drop-weight method. No previous data were found in the literature for the effect of surfactant and pH. The experimental data show a linear decrease with increasing surfactant concentration and temperature; however, the pH reduces the interfacial tension nonlinearly. The interfacial pressure was also obtained from data. The experimental values were correlated by empirical equations.

Introduction

Interfacial tension has close connections in various areas of chemistry, biology, and unit operations. In liquid−liquid extraction, for example, it is a key parameter, affecting the hydrodynamics and contact of phases for mass-transfer purposes.

Inevitable surfactants or contaminants, having the characteristic of lowering the interfacial tension, play a central role in controlling the desired interfacial property in many practical applications. The interfacial tension data for nonsurfactant systems are rich in the literature; however, those for surfactant systems are few, and in recent years, the modification of interfacial tension with surfactant solutions has been examined more systematically.[1−3] In this regard and for practical applications, the measurements of interfacial tension for organic + aqueous phases in the presence of surfactants is 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.

The objective of this work is to measure the equilibrium interfacial tension of the saturated phases of butan-1-ol and water, a recommended low interfacial tension system for liquid−liquid extraction studies proposed by the European Federation of Chemical Engineering (EFCE),[4] in the presence of the surfactant sodium dodecyl sulfate (SDS). This surfactant is often used for investigating the influence of contamination.[5] The effects of temperature and pH are to be examined. The values of interfacial pressure for this system can also be obtained from interfacial tension data.

Experimental Section

Butan-1-ol (min 99.5%) and SDS (>99%) were Merck products and were used as received. Laboratory-distilled water was redistilled prior to experimentation. Since butan-1-ol and water are partially miscible, the phases were saturated properly at the appropriate temperature prior to experimentation. The SDS was weighed on a METTLER AE-100 balance with an uncertainty of ±0.1 mg and added to aqueous phase. The desired next solutions were obtained by successive dilutions. The uncertainty of SDS concentration was estimated to be within $\pm 0.02 \times 10^{-5}$ mol·L^{-1}.

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

Attainment of equilibrium was obtained by mild agitation of equal volumes (100 mL) of phases and leaving at rest for at least 2 h, after which a constant interfacial tension value was obtained at various times.

The interfacial tension of the samples was determined by the drop-weight method, which is a reproducible method and has been used by other investigators.[2,6,7] The drop-forming device was a glass nozzle (diameter of 1.54 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.

The butan-1-ol phase was held in a narrow glass syringe conducted by an adjustable syringe pump (Phoenix M-CP, France) and flowed through a rigid tube to the vertical nozzle in the stagnant aqueous phase. The syringe was initially calibrated with respect to the specified volume scale on the syringe to obtain an accurate flow rate. A very low flow rate (1 mL at 191-min intervals) of organic phase was conducted to the nozzle and drops were formed very slowly at the tip of the nozzle. The drop volume can be calculated by knowing the flow rate and measuring the time for release of 10 drops (after previously releasing a number of drops). Each drop volume was obtained from at least three measurements of time where the maximum deviations from the average value were less than ±0.5%. The whole aqueous media and conducting tube was thermostated with an uncertainty of ±0.1 °C using a Multi Temp III thermostat.

Densities were measured at different temperatures using a density meter (Anton Parr DMA 4500, Austria) with an uncertainty of $\pm 10^{-2}$ kg·m^{-3}. The desired temperature is self-adjusted in this density meter with an uncertainty of ±0.01 °C. Digital readings of density and temperature are shown on an liquid crystal display. The apparatus calibra-

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Table 1. SDS Concentration (*c*), Phase Densities (*ρ*), and Interfacial Tension (*γ*) of System

				γ/mN·m^{-1} at pH					
c/mol·L^{-1}	t/°C	ρ_a/kg·m^{-3}	ρ_o/kg·m^{-3}	4	5	6	7	8	9
0	20	987.43	848.06	2.06	2.02	1.96	1.86	1.72	1.50
	25	985.83	844.20	2.03	1.99	1.93	1.82	1.67	1.46
	30	984.79	841.30	1.99	1.95	1.89	1.79	1.63	1.42
	35	983.28	837.44	1.96	1.91	1.85	1.74	1.59	1.38
	40	981.37	833.72	1.93	1.88	1.82	1.71	1.55	1.34
	50	977.46	826.84	1.86	1.81	1.75	1.63	1.47	1.25
2.17×10^{-5}	20	987.49	847.72	2.04	1.99	1.93	1.83	1.69	1.48
	25	985.85	843.96	2.01	1.96	1.90	1.79	1.65	1.44
	30	984.78	841.03	1.97	1.93	1.87	1.76	1.61	1.40
	35	983.27	837.23	1.94	1.89	1.83	1.72	1.56	1.36
	40	981.34	833.61	1.90	1.86	1.79	1.69	1.52	1.31
	50	977.38	826.90	1.83	1.79	1.72	1.61	1.44	1.23
4.34×10^{-5}	20	987.54	847.38	1.99	1.96	1.90	1.80	1.66	1.44
	25	985.87	843.72	1.97	1.93	1.86	1.76	1.61	1.40
	30	984.77	840.75	1.93	1.89	1.83	1.72	1.57	1.36
	35	983.25	837.02	1.90	1.86	1.79	1.69	1.53	1.32
	40	981.32	833.51	1.86	1.82	1.75	1.65	1.49	1.28
	50	977.31	826.95	1.80	1.75	1.69	1.57	1.41	1.19
8.68×10^{-5}	20	987.66	846.70	1.96	1.92	1.86	1.75	1.62	1.40
	25	985.91	843.23	1.93	1.88	1.82	1.72	1.57	1.36
	30	984.76	840.20	1.89	1.85	1.79	1.68	1.53	1.32
	35	983.22	836.61	1.86	1.82	1.75	1.65	1.49	1.28
	40	981.27	833.30	1.82	1.78	1.72	1.60	1.45	1.23
	50	977.15	827.07	1.75	1.71	1.65	1.53	1.37	1.15
1.74×10^{-4}	20	987.88	845.34	1.86	1.82	1.75	1.66	1.51	1.30
	25	985.99	842.26	1.82	1.79	1.72	1.62	1.47	1.26
	30	984.72	839.10	1.79	1.75	1.69	1.58	1.43	1.22
	35	983.16	835.78	1.75	1.71	1.65	1.54	1.39	1.18
	40	981.16	832.87	1.72	1.67	1.61	1.50	1.34	1.13
	50	976.84	827.29	1.66	1.60	1.54	1.43	1.26	1.04
3.48×10^{-4}	20	988.33	842.62	1.66	1.61	1.55	1.45	1.31	1.10
	25	986.15	840.32	1.62	1.58	1.52	1.41	1.27	1.05
	30	984.65	836.90	1.59	1.54	1.49	1.38	1.23	1.02
	35	983.04	834.11	1.55	1.51	1.45	1.34	1.18	0.97
	40	980.95	832.02	1.52	1.48	1.41	1.30	1.14	0.93
	50	976.22	827.74	1.45	1.41	1.34	1.23	1.06	0.84

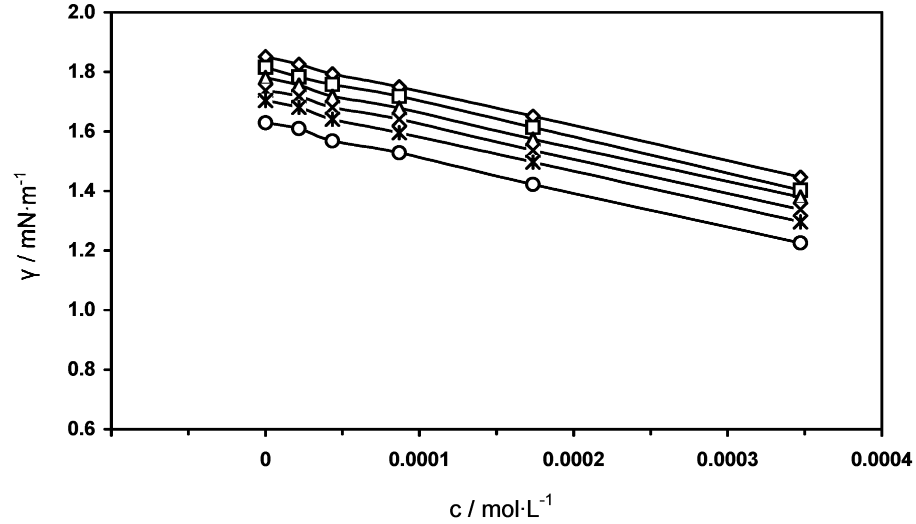

Figure 1. Interfacial tension of the system as a function of SDS concentration at different temperatures, pH = 7: ◇, 20 °C; □, 25 °C; △, 30 °C; ×, 35 °C; *, 40 °C; ○, 50 °C.

tion was performed using dry air (produced by the apparatus) and double-distilled freshly degassed water according to the instruction manual. Ultrapure water samples, supplied by the manufacturer, were used as density standards for checking calibration.

All glassware in contact with liquids was acid washed before use. The syringe, tube, and nozzle were thoroughly rinsed several times with distilled water and then with butan-1-ol phase. The nozzle tip was also wiped clean with a paper towel.

Calculation of Interfacial Tension. When a drop of liquid is formed very slowly at a nozzle of radius v, the volume of liquid which eventually detaches v is a definite function of the force tending to retain the drop on the nozzle, $2\pi r\gamma$, and the buoyancy force causing detachment, $v'\Delta\rho g$, where v', is the volume of the fully formed pendant

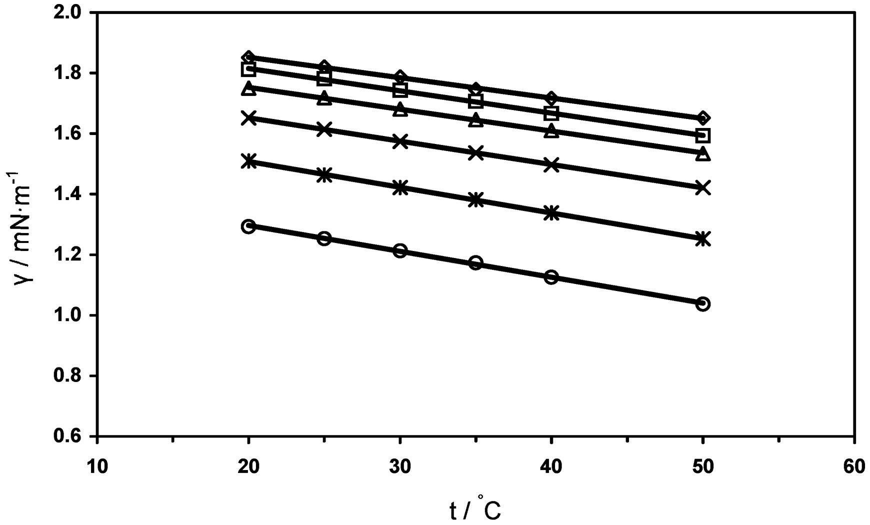

Figure 2. Interfacial tension of the system as a function of temperature at different pH values and SDS concentration of 1.74 × 10^{-4} mol·L^{-1}. Lines are calculated from eq 2: ◇, pH = 4; □, pH = 5; △, pH = 6; ×, pH = 7; *, pH = 8; ○, pH = 9.

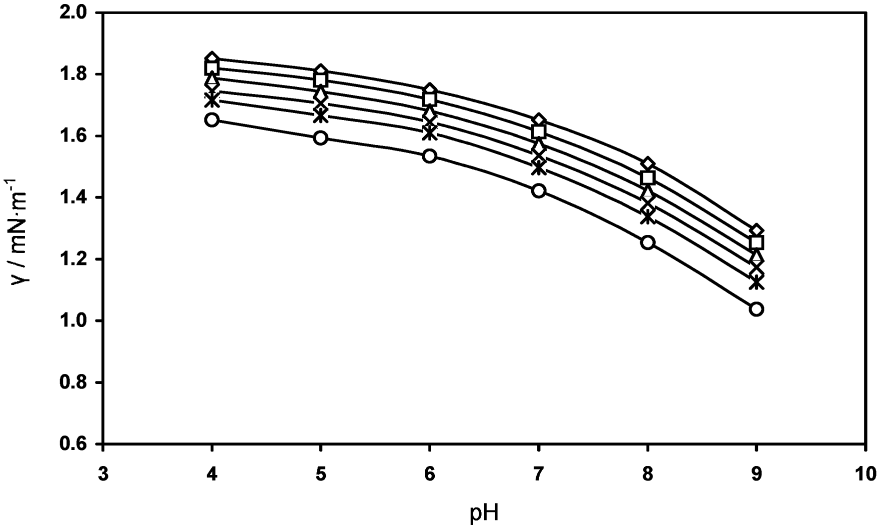

Figure 3. Interfacial tension of the system as a function of pH at different temperatures and SDS concentration of 1.74 × 10^{-4} mol·L^{-1}: ◇, 20 °C; □, 25 °C; △, 30 °C; ×, 35 °C; *, 40 °C; ○, 50 °C.

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

	c/mol·L^{-1}											
	0		2.17 × 10^{-5}		4.34 × 10^{-5}		8.68 × 10^{-5}		1.74 × 10^{-4}		3.48 × 10^{-4}	
pH	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	$K_2 \times 10^4$
4	2.19	66.57	2.18	70.57	2.13	65.43	2.10	70.57	1.99	66.57	1.80	69.43
5	2.16	70.86	2.13	67.14	2.10	70.57	2.06	69.14	1.97	74.86	1.74	66.57
6	2.10	70.86	2.08	71.14	2.04	70.57	2.00	69.43	1.90	71.14	1.70	71.14
7	2.01	76.57	1.97	72.29	1.95	75.71	1.90	74.57	1.81	77.14	1.60	73.43
8	1.88	82.29	1.86	84.29	1.82	82.29	1.78	82.29	1.68	84.00	1.48	84.00
9	1.67	82.86	1.65	84.00	1.61	82.86	1.57	84.00	1.48	86.86	1.27	85.71

drop and $\Delta\rho$ is the density difference between the liquids (ρ_a and ρ_o). The relationship between v and v' has been empirically determined in a careful experimental study by Harkins and Brown.[8] Thus

$$\gamma = \frac{v\Delta\rho g}{r}\phi \qquad (1)$$

where ϕ is a constant which is obtained from the tables of Harkins and Brown.[7,8]

To examine the performance and reliability of the method, the interfacial tension of butan-1-ol + water (each phase saturated) and butan-2-ol (Merck, min 99.5%) + water (each phase saturated) at 25 °C were measured (without surfactant). The measured values of (1.78 and 2.06) mN·m^{-1}, respectively, are in close agreement with the values of (1.8 and 2.0) mN·m^{-1} reported in the literature.[10] The differences are within ±3% of these reported values.

Results and Discussion

The interfacial tension data measured for the saturated water + butan-1-ol system at various temperatures, surfactant concentrations, and pH conditions are listed in Table 1 along with the corresponding density of phases.

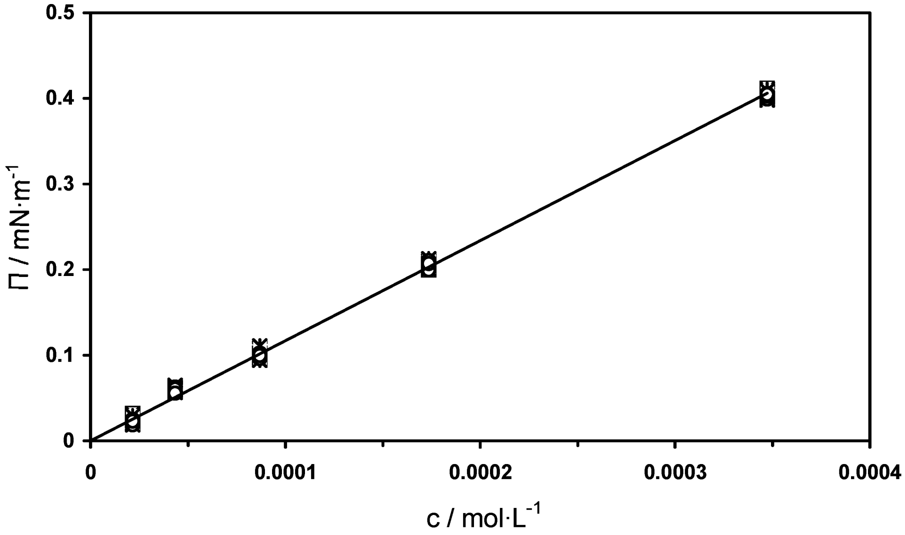

Figure 4. Variation of interfacial pressure of the system vs SDS concentration for different temperatures and pH values: ◇, 20 °C; □, 25 °C; △, 30 °C; ×, 35 °C; *, 40 °C; ○, 50 °C.

The values are in the range (0.84 to 2.06) mN·m^{-1}. The table shows that an increase in 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 increase of temperature from (20 to 50) °C also results in lowering the interfacial tension linearly when surfactant concentration and pH is fixed as is represented typically by Figure 2.

The values show that interfacial tension decreases as the pH increases; however, the change in interfacial tension caused by a given change in pH is larger at high pH. Figure 3 shows that the trend is nonlinear, for example, when pH rises from 4 to 5, at a SDS concentration of 3.48×10^{-4} mol·L^{-1} and 20 °C, the interfacial tension decreases from (1.66 to 1.61) mN·m^{-1}, whereas for the pH change from 8 to 9 and the same conditions, it falls from (1.31 to 1.10) mN·m^{-1}. This finding may give rise to a decrease in drop size produced when high alkali aqueous solutions are used in aqueous–organic dispersions. Similar variation with pH has been reported for surface tension of aqueous solutions containing surfactant.[11]

Because of the linear variation of interfacial tension with temperature, the empirical equation

$$\gamma/\text{mN·m}^{-1} = K_1 - K_2 t/°\text{C} \tag{2}$$

can be fitted to the data for each surfactant concentration and pH. This equation has been used for the surface tension of aqueous solutions under similar conditions.[11,12] By use of this equation, the maximum deviation is less than ±0.7% and average deviation is less than ±0.4%. Figure 2 is shown as an example. The values of K_1 and K_2 are listed in Table 2. The results show that both the pH and the concentration of sodium dodecyl sulfate greatly influence the relationship between interfacial tension and temperature.

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

$$\Pi = \gamma_o - \gamma \tag{3}$$

where γ_o is the interfacial tension between pure water and butanol and γ is that of surfactant solution. Presented in Figure 4 is the variation of interfacial pressure vs surfactant concentration for different temperature and pH values. The values are in the range (0.02 to 0.41) mN·m^{-1}. The interfacial pressure Π can be considered as independent of temperature and pH over the surfactant concentration range. The values show a linear dependency on surfactant concentration, giving the following trendline correlation

$$\Pi/\text{mN·m}^{-1} = 1173.5c/\text{mol·L}^{-1} \tag{4}$$

with the absolute average deviation of much less than 0.01 mN·m^{-1}. The higher deviations are for the low surfactant concentrations.

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