Surface Tension of the Ternary System Water + Acetone + Toluene

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Surface tensions and liquid densities of ternary mixtures consisting of water + toluene + acetone in the homogeneous region were determined. The pendant drop method combined with axisymmetric drop shape analysis and with an effective temperature control of the measuring cell allowed measurements of surface tension in a temperature range from (288 to 328) K and at pressure of 0.1 MPa. Liquid densities of ternary and binary mixtures of this system at the same temperature range were obtained using a vibration tube densimeter. Binary and ternary surface tensions could be predicted using ideas from the Butler model. This procedure required only surface tension data of the pure components, surface area values (obtained from molar volume), and NRTL parameters taken from the literature. Distribution of substances between bulk and surface could be analyzed using these relationships.

Introduction

The ternary system water + toluene + acetone covers a large range of polarity from the highly polar water to mildly polar acetone and nonpolar toluene. Acetone + toluene and acetone + water mixtures are miscible at all concentrations, and there is also an almost temperature-independent one-phase region of water + toluene + acetone. Furthermore, these solvents are of industrial relevance. As a liquid−liquid extraction system, water + acetone + toluene represent a model for many applications such as extraction[1−3] or distillation[4,5] processes, and even in the pharmaceutical industry such solvent systems were used to crystallize organic compounds.[6] Mass transfer processes through the interface were investigated in detail for this system.[7−11]

The measurement of surface tension is of outstanding importance in many scientific and technological areas. As a fundamental parameter, surface tension is the single most accessible experimental parameter that describes the thermodynamic state, and at least implicit, it contains information on the internal structure of a liquid interface. Apart from this theoretical interest, a detailed understanding of the behavior of a vapor−liquid interface, such as enrichment of one component in a liquid surface, is important for modeling a distillation process. On the other hand, liquid−liquid interfaces have far-reaching practical consequences in very wide areas of application. Surface tensions have been measured for a long time, and collections of experimental data for pure liquids and some binary liquid mixtures exist.[12−14] A critical review reveals that systematic investigations of multicomponent systems are rather rare,[15,16] especially those over a wide range of temperature and concentration. An increasing number of applications of microemulsions in industrial processes require considerable investigations of multicomponent systems, especially of such systems, which form microemulsions when surfactants are added. High-quality experimental data of surface and interfacial tensions also
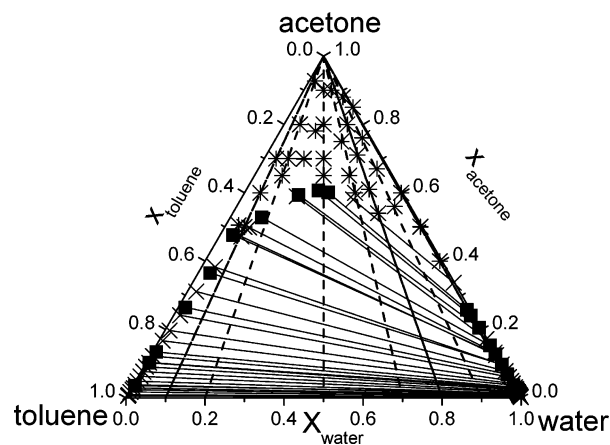
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Figure 1. Phase diagram of the system toluene + acetone + water at *T* = 293.15 K, investigated mixtures, ∗. Connected squares, ■, and crosses, ×, are experimental tie-lines obtained from the literature.[41] Dotted lines mark pseudo-binary cuts used for calculations.

form the basis for a successful modeling and for theoretical calculations of interfacial properties.[17−21] Therefore, further precise measurements are urgently needed. Because of its high flexibility and precision, the pendant drop method is the favored experimental technique to investigate both interfacial and surface tensions over several orders of magnitude. In this respect, it is superior to most other commonly used experimental methods such as Wilhelmy plate or spinning drop method.[22−25] The amount of the sample is small, and it enables the measuring of both surface and interfacial tensions with high accuracy even under high pressure.[26−28]

Experimental Section

Reagents. Both acetone ECD, tested for pesticide analysis with a purity > 99.9 % (by GC) (residue after evaporation < 0.0002 %), and toluene for pesticide residue analysis with a water content < 0.01 % and a purity of 99.8 % (Coulom assay) (residue after evaporation < 0.0005 %) were supplied by Acros

Table 1. Experimental Surface Tension σ from (288.15 to 328.15) K for Mixtures of Acetone (1) + Water (2)

	σ/mN·m^{-1}				
x_1	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15
0.0000	73.49	71.98	70.41	68.78	67.09
0.0099	62.59	61.04	59.26	58.11	57.74
0.0500	47.85	46.14	44.78	43.74	42.86
0.0999	40.32	39.07	37.88	36.87	35.71
0.1500	35.72	34.41	33.13	32.02	30.76
0.1999	33.71	32.21	30.74	29.40	28.31
0.2999	30.60	29.35	28.08	26.98	25.68
0.4000	29.19	27.98	26.78	25.47	24.23
0.4999	28.24	27.04	25.82	24.53	23.28
0.5999	27.29	26.03	24.81	23.63	22.26
0.6999	26.71	25.44	24.25	22.94	21.73
0.7999	25.78	24.51	23.20	22.02	20.90
0.8999	25.06	23.8	22.56	21.19	20.19
1.0000	24.34	23.02	21.72	20.38	19.15

Table 2. Experimental Liquid Densities ρ from (288.15 to 328.15) K for Mixtures of Acetone (1) + Water (2)

	ρ/g·cm^{-3}								
x_1	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.1	T/K = 328.15
0.0000	0.99912	0.99822	0.99706	0.99567	0.99404	0.99223	0.99023	0.98801	0.98569
0.0099	0.99490	0.99387	0.99255	0.99100	0.98916	0.98726	0.98507	0.98276	0.98029
0.0500	0.98127	0.97934	0.97721	0.97489	0.97241	0.96977	0.96673	0.96310	0.95994
0.1000	0.96581	0.96290	0.95983	0.95664	0.95333	0.94991	0.94637	0.94268	0.93887
0.1500	0.95041	0.94679	0.94305	0.93923	0.93532	0.93131	0.92721	0.92300	0.91872
0.2000	0.93561	0.93154	0.92737	0.92310	0.91878	0.91437	0.90989	0.90519	0.90064
0.3000	0.90770	0.90309	0.89835	0.89354	0.88868	0.88375	0.87876	0.87370	0.86856
0.4000	0.88477	0.87981	0.87480	0.86968	0.86453	0.85933	0.85406	0.84874	0.84331
0.5000	0.86371	0.85856	0.85335	0.84807	0.84272	0.83731	0.83185	0.82632	0.82073
0.6000	0.84583	0.84053	0.83515	0.82971	0.82422	0.81866	0.81305	0.80735	0.80160
0.7000	0.83070	0.82530	0.81980	0.81425	0.80863	0.80296	0.79722	0.79142	0.78555
0.8000	0.81804	0.81256	0.80697	0.80132	0.79562	0.78984	0.78405	0.77816	0.77220
0.9000	0.80586	0.80027	0.79460	0.78888	0.78311	0.77729	0.77140	0.76546	0.75981
1.0000	0.79565	0.79004	0.78433	0.77857	0.77276	0.76691	0.76099	0.75502	0.74898

Table 3. Experimental Surface Tension σ from (288.15 to 328.15) K for Mixtures of Acetone (1) + Toluene (2)

	σ/mN·m^{-1}				
x_1	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15
0.0000	28.90	27.76	26.77	25.72	24.27
0.1000	28.54	27.42	26.25	24.97	23.63
0.2000	27.86	26.78	25.78	24.75	23.48
0.3000	27.32	26.27	25.21	24.09	23.04
0.4000	26.98	25.87	24.88	23.74	22.70
0.5000	26.58	25.26	24.20	22.82	21.99
0.6000	25.91	24.69	23.59	22.67	21.06
0.6999	25.22	24.14	22.92	21.70	20.65
0.8000	24.68	23.46	22.51	21.34	19.95
0.9000	24.24	23.01	21.83	20.48	19.32
1.0000	24.34	23.02	21.72	20.38	19.15

Table 4. Experimental Liquid Densities ρ from (288.15 to 328.15) K for Mixtures of Acetone (1) + Toluene (2)

	ρ/g·cm^{-3}								
x_1	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15
0.0000	0.87141	0.86677	0.86212	0.85746	0.85278	0.84808	0.84337	0.83864	0.83390
0.1000	0.86662	0.86194	0.85719	0.85243	0.84766	0.84286	0.83804	0.83322	0.82834
0.2000	0.86143	0.85662	0.85177	0.84692	0.84206	0.83717	0.83223	0.82729	0.82232
0.3000	0.85560	0.85069	0.84576	0.84080	0.83583	0.83083	0.82582	0.82075	0.81567
0.4000	0.84950	0.84449	0.83943	0.83437	0.82930	0.82420	0.81906	0.81389	0.80870
0.5000	0.84216	0.83708	0.83196	0.82683	0.82164	0.81643	0.81119	0.80591	0.80059
0.6000	0.83494	0.82976	0.82452	0.81930	0.81400	0.80868	0.80332	0.79791	0.79248
0.6999	0.82667	0.82137	0.81605	0.81071	0.80529	0.79988	0.79439	0.78888	0.78331
0.8000	0.81743	0.81203	0.80658	0.80109	0.79556	0.79001	0.78439	0.77874	0.77301
0.9000	0.80756	0.80205	0.79647	0.79088	0.78521	0.77949	0.77374	0.76794	0.76208
1.0000	0.79565	0.79004	0.78433	0.77857	0.77276	0.76691	0.76099	0.75502	0.74898

Organics (Belgium) and dried over the molecular sieves Zeosorb A4/A3. The water was distilled twice.

Measuring Procedure. Densities of homogeneous liquid mixtures, needed for the surface tension evaluation by numerical solution of the Laplace equation, are determined using a vibrating tube densimeter DMA 4500 (Fa. Anton Paar) with a temperature control of $\Delta T = \pm 0.01$ K. The accuracy of the measured densities is considered to be $\Delta \rho = \pm 0.00005$ g·cm^{-3}.
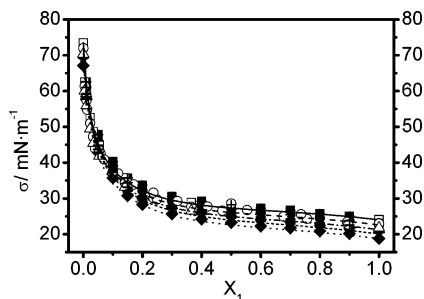
Figure 2. Experimental surface tension σ of the binary mixture acetone (1) + water (2) measured with the pendant drop apparatus. This work: ■, $T = 288.15$ K; ●, $T = 298.15$ K; ▲, $T = 308.15$ K; ★, $T = 318.15$ K; and ◆, $T = 328.15$ K. Open symbols: □, $T = 288.15$ K; ○, $T = 298.15$ K; △, $T = 308.15$ K. All are experimental surface tension values obtained from the literature[12] for comparison. Lines are model calculations according to eq 1: solid line, $T = 288.15$ K; dashed line, $T = 298.15$ K; dashed dotted line, $T = 308.15$ K; short dashed line, $T = 318.15$ K; and dotted line, $T = 328.15$ K.
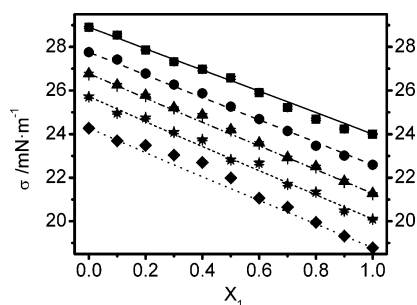

Figure 3. Experimental surface tension σ of the binary mixture acetone (1) + toluene (2) measured with the pendant drop apparatus. This work: ■, $T = 288.15$ K; ●, $T = 298.15$ K; ▲, $T = 308.15$ K; ★, $T = 318.15$ K; and ◆, $T = 328.15$ K. Lines are model calculations according to eq 1: solid line, $T = 288.15$ K; dashed line, $T = 298.15$ K; dashed dotted line, $T = 308.15$ K; short dashed line, $T = 318.15$ K; and dotted line, $T = 328.15$ K.

Table 5. NRTL Parameter Used in Determining Activity Coefficients for Water (1) + Acetone (2) + Toluene (3) in Equation 2 Obtained from the Literature[41]

component	A/K^{-1}
12	210.6
21	377.45
13	2557.3
31	1318.8
23	−301.51
32	489.2

Surface Tension. The pendant drop method combined with an Axisymmetric Drop Shape Analysis (ADSA)[29,30] was applied to determine surface tensions of homogeneous mixtures in the ternary system toluene + acetone + water. The experimental setup has been discussed in detail in previous papers.[31,32] Pendant drop profiles were extracted from drop images and analyzed by means of the ADSA software, which ensures a high-quality contour extraction and a very precise surface tension calculation by numerical solution of the Laplace equation.

The temperature inside the sample cell was kept constant to $\Delta T = \pm 0.01$ K. It was determined with a specially prepared thermistor that had been calibrated against a gallium cell to allow a temperature resolution of 0.1 mK. At a pressure of 0.1 MPa the measuring cell was saturated with sample atmosphere, and pendant drops were formed on a steel capillary. The drop images
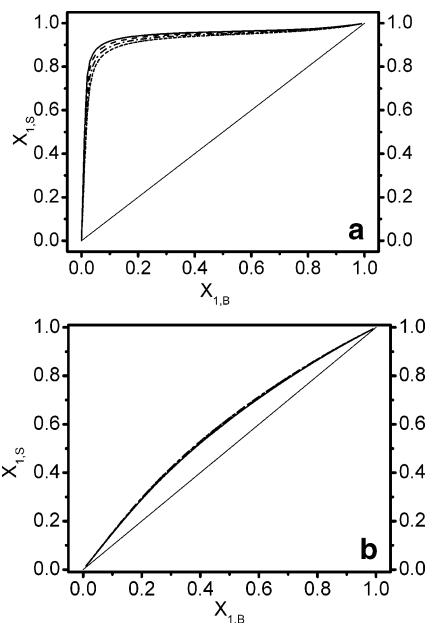

Figure 4. Calculated distribution of acetone between bulk and surface phase of the system (a) acetone (1) + water (2) and (b) acetone (1) + toluene (2). Lines are model calculations according to eq 1: solid line, $T = 288.15$ K; dashed line, $T = 298.15$ K; dashed dotted line, $T = 308.15$ K; short dashed line, $T = 318.15$ K; and dotted line, $T = 328.15$ K.
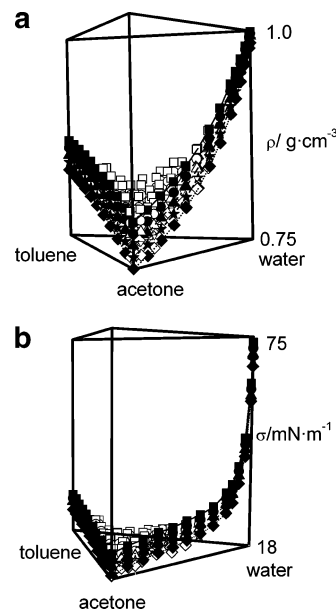

Figure 5. Experimental density ρ (a) and surface tension σ (b) of the system water + acetone + toluene at ■, $T = 288.15$ K; ●, $T = 298.15$ K; ▲, $T = 308.15$ K; ★, $T = 318.15$ K; and ◆, $T = 328.15$ K. Open symbols: □, $T = 288.15$K; ○, $T = 298.15$ K; △, $T = 308.15$ K; ☆, $T = 318.15$ K; and ◇, $T = 328.15$ K show the values for ternary mixtures inside the phase prism.

were monitored as described previously.[31,32] The accuracy of the experimental surface tension measurements is considered to be $\Delta\sigma < 0.1$ mN·m^{-1}. The reproducibility of the surface tension measurements is better than $\Delta\sigma < 0.1$ % at the 95 % confidence level, except for surface tension values of mixtures with a high amount of acetone at $T = 328.15$ K, where the reproducibility of the experimental data is $\Delta\sigma < 0.2$ % at the 95 % confidence level.

Modeling. The surface tension of a mixture can be predicted using the well-know Butler method where it is assumed
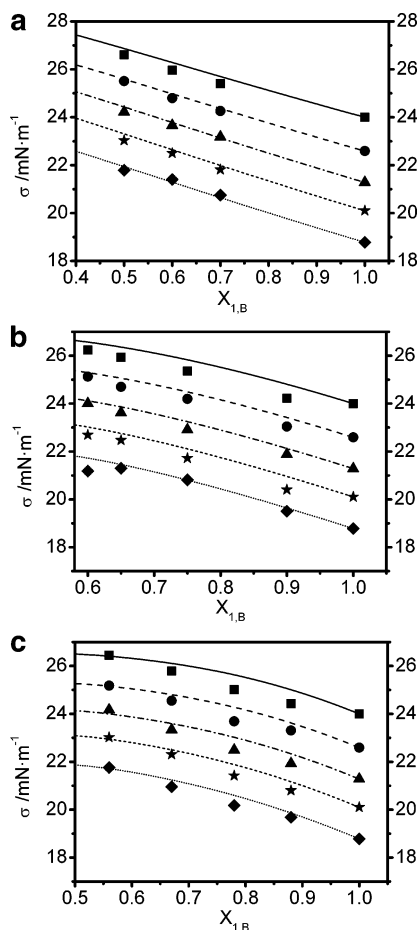
Figure 6. Experimental surface tension σ of the system water (1) + acetone (2) + toluene (3) at pseudo-binary cuts $X_3/X_1 = z = 9$ (a), $z = 3/7$ (b), and $z = 0.01$ (c) at ■, $T = 288.15$ K; ●, $T = 298.15$ K; ▲, $T = 308.15$ K; ★, $T = 318.15$ K; and ◆, $T = 328.15$ K. Lines are model calculations according to eq 1: solid line, $T = 288.15$ K; dashed line, $T = 298.15$ K; dashed dotted line, $T = 308.15$ K; short dashed line, $T = 318.15$ K; and dotted line, $T = 328.15$ K.

that the surface can be treated as a separate phase. Additionally, the nonideality of both the bulk phase and the surface phase can be described by the same activity coefficient model. This method had been applied to quite different types of systems, like non-electrolyte mixtures,[33−35] ionic solutions,[36−38] or metal-containing systems.[39,40] The surface tension of a mixture containing k components is given by

$$\sigma = \sum_{i=1}^{k} \left(\sigma_i x_{i,\mathrm{B}} + x_{i,\mathrm{B}} \frac{RT}{N_\mathrm{A} A_i} \ln \frac{\gamma_{i,\mathrm{S}} x_{i,\mathrm{S}}}{\gamma_{i,\mathrm{B}} x_{i,\mathrm{B}}} \right) \quad (1)$$

where σ_i is the surface tension of the pure component i; A_i is the surface area of molecule i; N_A denotes Advogadro's number; and $x_{i,\mathrm{B}}$ and $x_{i,\mathrm{S}}$ are the mole fractions of component i in the bulk and surface phases, respectively. The activity coefficients, γ_i, of our binary and ternary systems were calculated using the NRTL equation:

$$\frac{g^\mathrm{E}}{RT} = \sum_{i=1}^{m} x_i \frac{\displaystyle\sum_{j=1}^{m} \tau_{ij} G_{ij} x_j}{\displaystyle\sum_{l=1}^{m} G_{li} x_i} \quad \tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad \alpha_{ji} = \alpha_{ij} \quad \ln \gamma_i = \frac{\displaystyle\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\displaystyle\sum_{l=1}^{m} G_{li} x_l} +$$

$$\sum_{j=1}^{m} \frac{x_j G_{ij}}{\displaystyle\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\displaystyle\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\displaystyle\sum_{l=1}^{m} x_l G_{lj}} \right) \quad (2)$$

with parameters taken from the literature.[41] The surface area A_i is given by

$$A_i = \left(\frac{V_i}{N_\mathrm{A}} \right)^{2/3} \quad (3)$$

where V_i is the temperature-dependent molar volume of component i. The surface mole fractions of component i can be calculated by applying the standard phase-equilibrium calculation procedure. Finally, the surface tension of the mixture is represented by eq 1. This method allows the prediction of the surface tension and the surface composition based on the surface tensions of the pure components and the bulk-phase properties of the mixture.
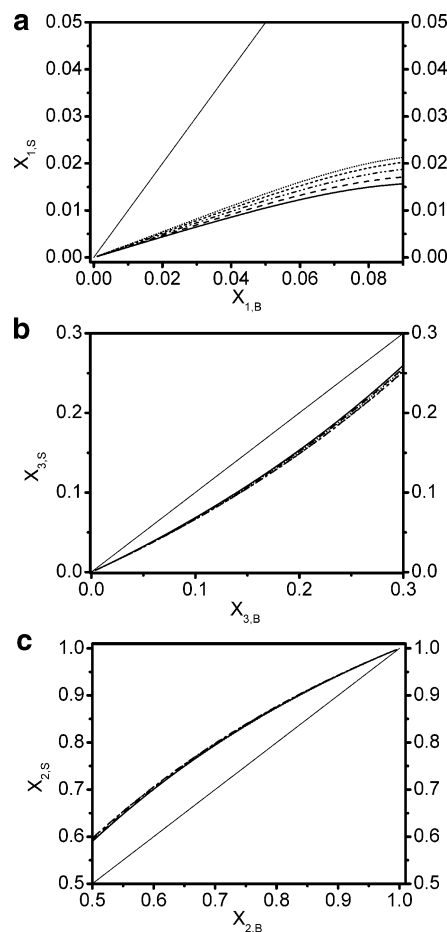

Figure 7. Calculation results of the distribution of (a) water (1), (b) toluene (3), and (c) acetone (2) between bulk and surface phase at a pseudo-binary cut of $z = 4$ using eq 1: solid line, $T = 288.15$ K; dashed line, $T = 298.15$ K; dashed dotted line, $T = 308.15$ K; short dashed line, $T = 318.15$ K; and dotted line, $T = 328.15$ K.

Table 6. Experimental Liquid Densities ρ from (288.15 to 328.15) K for Ternary Mixtures of Water (1) + Acetone (2) + Toluene (3); $z = x_3/x_1$

		ρ/g·cm^{-3}								
x_1	x_2	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15
					$z = 9$					
0.0301	0.7000	0.82717	0.82183	0.81646	0.81106	0.80565	0.80014	0.79464	0.78904	0.78340
0.0400	0.6001	0.83539	0.83015	0.82488	0.81958	0.81426	0.80889	0.80347	0.79800	0.79251
0.0505	0.5003	0.84321	0.83805	0.83288	0.82767	0.82243	0.81716	0.81185	0.80648	0.80108
					$z = 4$					
0.0150	0.9266	0.80478	0.79916	0.79354	0.78786	0.78215	0.77640	0.77059	0.76472	0.75881
0.0402	0.8000	0.81699	0.81154	0.80605	0.80051	0.79493	0.78932	0.78365	0.77792	0.77214
0.0605	0.6996	0.82690	0.82156	0.81615	0.81071	0.80523	0.79973	0.79418	0.78855	0.78289
0.0701	0.6503	0.83143	0.82613	0.82078	0.81538	0.80994	0.80447	0.79894	0.79337	0.78776
					$z = 1$					
0.0505	0.8993	0.80671	0.80112	0.79550	0.78985	0.78411	0.77834	0.77251	0.76662	0.76069
0.0994	0.8001	0.81733	0.81181	0.80628	0.80069	0.79507	0.78938	0.78365	0.77784	0.77199
0.1498	0.7002	0.82773	0.82230	0.81684	0.81134	0.80578	0.80021	0.79453	0.78883	0.78304
0.1748	0.6500	0.83293	0.82757	0.82217	0.81670	0.81119	0.80563	0.80002	0.79435	0.78861
					$z = 3/7$					
0.0699	0.9000	0.80667	0.80106	0.79543	0.78974	0.78399	0.77821	0.77236	0.76646	0.76040
0.1749	0.7499	0.82321	0.81770	0.81220	0.80662	0.80101	0.79532	0.78959	0.78376	0.77790
0.2450	0.6500	0.83470	0.82931	0.82389	0.81841	0.81289	0.80730	0.80166	0.79595	0.79019
0.2803	0.5997	0.84073	0.83542	0.83007	0.82466	0.81920	0.81368	0.80810	0.80244	0.79674
					$z = 1/4$					
0.1591	0.8010	0.81753	0.81201	0.80641	0.80076	0.79508	0.78932	0.78352	0.77767	0.77175
0.2337	0.7077	0.82841	0.82299	0.81743	0.81186	0.80624	0.80057	0.79485	0.78902	0.78318
0.3137	0.6077	0.84041	0.83507	0.82969	0.82427	0.81878	0.81322	0.80762	0.80194	0.79617
0.3677	0.5402	0.84940	0.84419	0.83893	0.83361	0.82824	0.82279	0.81729	0.81174	0.80615
					$z = 0.1$					
0.1089	0.8800	0.81733	0.81181	0.80628	0.80069	0.79507	0.78938	0.78365	0.77784	0.77199
0.2001	0.7798	0.82026	0.81474	0.80917	0.80354	0.79787	0.79213	0.78636	0.78048	0.77454
0.2998	0.6702	0.83435	0.82897	0.82348	0.81791	0.81235	0.80670	0.80102	0.79523	0.78940
0.4007	0.5593	0.84998	0.84473	0.83941	0.83404	0.82863	0.82314	0.81759	0.81197	0.80628
					$z = 0.01$					
0.1488	0.8497	0.81217	0.80659	0.80096	0.79527	0.78954	0.78375	0.77790	0.77198	0.76602
0.3965	0.5995	0.84621	0.84090	0.83554	0.83011	0.82463	0.81908	0.81348	0.80780	0.80207
0.4942	0.5007	0.86302	0.85784	0.85263	0.84733	0.84198	0.83660	0.83109	0.82555	0.81995
0.5939	0.4000	0.88307	0.87807	0.87306	0.86797	0.86280	0.85760	0.85233	0.84699	0.84158
					$z = 0.1056$					
0.4725	0.4776	0.86322	0.85804	0.85282	0.84753	0.84218	0.83678	0.83131	0.82578	0.82010
					$z = 1.4624$					
0.0891	0.7806	0.81931	0.81390	0.80838	0.80281	0.79721	0.79156	0.78586	0.78010	0.77429
					$z = 1.993$					
0.1001	0.7004	0.82741	0.82203	0.81659	0.81111	0.80559	0.80003	0.79443	0.78876	0.78303
					$z = 1.994$					
0.1005	0.6991	0.82748	0.82209	0.81667	0.81118	0.80570	0.80012	0.79451	0.78884	0.78311
					$z = 14.3034$					
0.0323	0.5057	0.84250	0.83737	0.83220	0.82702	0.82179	0.81655	0.81123	0.80589	0.80052

Results and Discussion

Mixtures of the ternary system water (1) + acetone (2) + toluene (3) in the miscible region and of the binary homogeneous systems water + acetone and acetone + toluene were systematically investigated. We determined liquid densities at nine temperatures and surface tensions at five temperatures ranging from $T = 288.15$ K to $T = 328.15$ K. Figure 1 shows the ternary phase diagram with the miscibility gap together with tie line (squares, crosses connected with solid lines) compositions at $T = 293.15$ K obtained from literature.[41] Dashed lines in the phase diagram mark the investigation strategy used to study the homogeneous region. Ratios of toluene/water were kept constant, and the amount of acetone was systematically modified with the ratio $z = x_{toluene}/x_{water} = 9, 4, 1, 3/7, 1/4, 0.1,$ and 0.01, respectively. Stars mark compositions of single samples.

Binary Mixtures. The starting point of our study was the surface tension behavior of the binary mixtures. Water and toluene are almost immiscible, so we began with liquid mixtures of acetone with water and with toluene. Experimental data of the system acetone + water are reported in Tables 1 and 2. Table 1 contains the surface tension data. The corresponding liquid densities used for the evaluation of surface tensions by ADSA are given in Table 2. Tables 3 and 4 present the corresponding data of the mixtures acetone + toluene. Figure 2 shows the results of our surface tension measurements at five different temperatures studied over the whole concentration range. For comparison, open symbols mark experimental data at $T = (288.15, 298.15,$ and $308.15)$ K taken from the literature.[12] The lines are predicted results of our modeling using eq 1 and NRTL parameters listed in Table 5. Having in mind that the modeling results are pure predictions based on surface tensions of the pure components and NRTL parameters taken from the literature,[41] the theoretical results show an excellent agreement with the experimental data. The steep decrease of the surface tension of pure water by adding a small amount of acetone could well be described with an expression based on Butler's equation.

Table 7. Experimental Surface Tension σ from (288.15 to 328.15) K for Ternary Mixtures of Water (1) + Acetone (2) + Toluene (3); $z = x_3/x_1$

		σ/mN·m^{-1}				
x_1	x_2	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15
			$z = 9$			
0.0301	0.7000	25.40	24.26	23.18	21.81	20.75
0.0400	0.6001	25.96	24.80	23.66	22.50	21.40
0.0505	0.5003	26.61	25.51	24.22	23.03	21.79
			$z = 4$			
0.0150	0.9266	24.25	23.07	21.65	20.58	19.32
0.0402	0.8000	25.09	24.01	22.78	21.61	20.61
0.0605	0.6996	25.41	24.26	22.83	21.74	21.00
0.0701	0.6503	25.78	24.48	23.33	22.21	21.10
			$z = 1$			
0.0505	0.8993	24.09	22.74	21.73	20.49	19.48
0.0994	0.8001	24.80	23.65	22.39	21.11	20.32
0.1498	0.7002	25.82	24.40	23.41	22.41	20.86
0.1748	0.6500	25.85	24.85	23.59	22.41	21.13
			$z = 3/7$			
0.0699	0.9000	24.22	23.04	21.88	20.40	19.50
0.1749	0.7499	25.36	24.20	22.91	21.72	20.81
0.2450	0.6500	25.93	24.70	23.62	22.47	21.30
0.2803	0.5997	26.24	25.13	24.00	22.69	21.18
			$z = 1/4$			
0.1591	0.8010	25.10	23.87	22.61	21.31	20.23
0.2337	0.7077	25.69	24.56	23.35	22.14	20.79
0.3137	0.6077	26.17	25.03	23.92	22.61	21.41
0.3677	0.5402	26.13	24.98	23.93	22.65	19.41
			$z = 0.1$			
0.1089	0.8800	24.43	23.31	21.93	20.80	19.68
0.2001	0.7798	25.01	23.69	22.49	21.42	20.18
0.2998	0.6702	25.79	24.55	23.34	22.31	20.96
0.4007	0.5593	26.45	25.18	24.17	23.02	21.76
			$z = 0.01$			
0.1488	0.8497	24.66	23.44	22.31	21.07	19.90
0.3965	0.5995	26.24	25.19	24.03	22.73	21.04
0.4942	0.5007	27.23	26.05	24.86	23.57	22.06
0.5939	0.4000	27.71	26.66	25.51	23.73	
			$z = 0.1056$			
0.4725	0.4776	26.97	25.73	24.62	23.39	
			$z = 1.4624$			
0.0891	0.7806	25.26	23.98	22.72	21.40	20.59
			$z = 1.993$			
0.1001	0.7004	25.66	24.49	23.30	22.04	20.98
			$z = 1.994$			
0.1005	0.6991	25.84	24.59	23.50	22.30	21.09
			$z = 14.3034$			
0.0323	0.5057	26.65	25.56	24.72	23.60	22.32

Surface tension values of acetone + toluene mixtures do not show such strong concentration dependence as depicted in Figure 3. Here, the experimental data were also compared with model calculations using eq 1. At higher temperatures, larger deviations in the experimental data were found as shown in the lowest curve at $T = 328.15$ K. At this temperature, mixtures of acetone + toluene have a rather high vapor pressure.

With the help of eq 1, we were able to describe the distribution of the mixture components between surface and bulk phase. In both binary mixtures acetone is enriched in the surface phase (see Figure 4). This effect is more pronounced in the system acetone + water as compared to the behavior in acetone + toluene mixtures. This theoretical result can be explained by the different vapor pressure difference of the pure component. The vapor pressure difference in the system acetone + water is slightly higher than that of the components in the system acetone + toluene. This can cause a different segregation behavior.

Ternary Mixtures. To provide a survey on the concentration dependence of both liquid densities and surface tensions in the ternary mixtures of the system toluene + acetone + water, the experimental data are given as 3D plots in Figure 5. Figure 5a shows liquid densities at five different temperatures, and Figure 5b depicts the corresponding results of the surface tension measurements; solid symbols represent the binary data, and open symbols represent the ternary data at the respective temperature. The steep increase of surface tension in the water-rich region results in a very asymmetric ternary surface tension area. However, both concentration and temperature dependence in this ternary system are not easy to be presented graphically. Therefore, we designed an investigation strategy (Figure 1) to prepare pseudo binary mixtures whose results can easily be drawn in a $x-y$ plot. We selected ratios of constant toluene/water composition $z = x_{\text{toluene}}/x_{\text{water}}$ with the amount of acetone systematically varying from the pure liquid to the miscibility gap. High z values characterize samples with high content of toluene, and low z values represent samples with high water content. Tables 6 and 7 summarize all experimental results for the ternary system. In Table 6 the liquid densities are given for
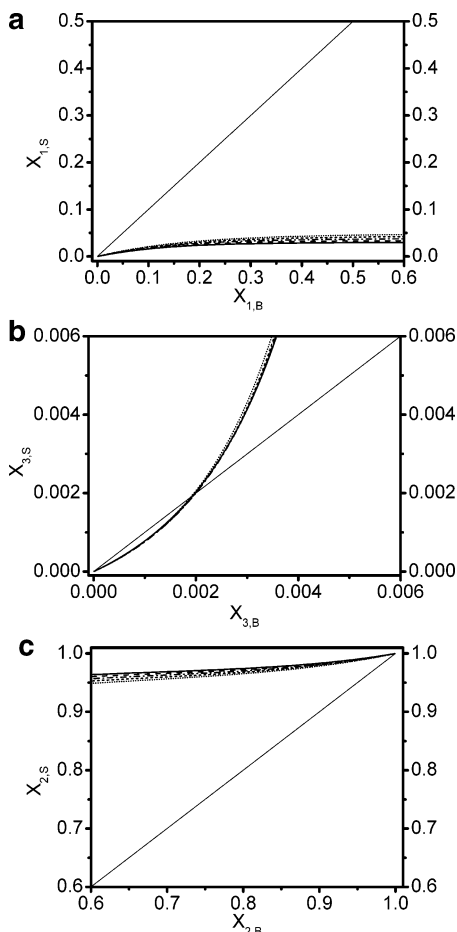
Figure 8. Calculation results of the distribution of (a) water (1), (b) toluene (3), and (c) acetone (2) between bulk and surface phase at a pseudo-binary cut $z = 0.01$ using eq 1: solid line, $T = 288.15$ K; dashed line, $T = 298.15$ K; dashed dotted line, $T = 308.15$ K; short dashed line, $T = 318.15$ K; and dotted line, $T = 328.15$ K.

Table 8. Average Relative Error, Defined by (%) = $[(\sum_{i=1}^{N}(\sigma_i^{exp} - \sigma_i^{cal})/\sigma_i^{exp})/\{N\}] \times 100$

system	T/K	points	avg relative error (%)
acetone + water	288.15	12	2.89
	298.15	12	2.53
	308.15	12	2.07
	318.15	12	1.40
	328.15	12	1.85
acetone + toluene	288.15	9	0.58
	298.15	9	0.40
	308.15	9	0.49
	318.15	9	0.74
	328.15	9	1.18
water (1) + acetone (2) + toluene (3) $z = x_3/x_1$			
$z = 9$	288.15	4	2.04
	298.15	4	0.36
	308.15	4	0.39
	318.15	4	0.67
	328.15	4	0.42
$z = 4$	288.15	5	0.97
	298.15	5	0.66
	308.15	5	0.95
	318.15	5	0.83
	328.15	5	0.77
$z = 1$	288.15	5	1.73
	298.15	5	1.44
	308.15	5	1.10
	318.15	5	1.29
	328.15	5	0.68
$z = 3/7$	288.15	5	1.53
	298.15	5	0.98
	308.15	5	0.81
	318.15	5	1.45
	328.15	5	0.81
$z = 1/4$	288.15	5	1.33
	298.15	5	0.76
	308.15	5	0.64
	318.15	5	1.28
	328.15	4	0.68
$z = 0.1$	288.15	5	1.24
	298.15	5	0.99
	308.15	5	1.20
	318.15	5	1.02
	328.15	5	0.91
$z = 0.01$	288.15	5	1.83
	298.15	5	2.08
	308.15	5	1.87
	318.15	5	0.90
	328.15	4	0.94

the ternary mixtures at nine different temperatures, and Table 7 contains the surface tensions at five different temperatures classified according to their z ratios.

To analyze and discuss the results three typical sample ratios are selected, and the experimental data are compared with the prediction. Figure 6a shows pseudo-binary mixtures with a concentration ratio $z = 9$ (i.e., a high amount of toluene), Figure 6b gives the results for the ratio $z = 3/7$, and Figure 6c represents water-rich samples with a ratio $z = 0.1$. The Butler model is able to describe the experimental data at all ratios, especially those graphs that show a clear curvature with high amounts of water.

Enrichment processes within the vapor−liquid interface can also be discussed from the results of eq 1. For all three components in a ternary mixture, we obtain the distribution between interface region and bulk phase by calculating the surface mole fraction $x_{i,S}$ for a given bulk-phase mole fraction $x_{i,B}$. A ratio of $x_{i,S}/x_{i,B} = 1$ yields no surface active enrichment/depletion and is used as a reference. Two pseudo-binary cuts at $z = 4$ and $z = 0.01$ are discussed. At a constant ratio $z = 4$ the relative enrichment of all three components are depicted in Figure 7. At all temperatures water is considerably depleted of the interface region (Figure 7a) over the whole concentration range. In contrast, acetone is always enriched in the surface region (Figure 7c), when compared with the straight line $x_{i,S}/x_{i,B} = 1$ of the neutral behavior. Toluene, having a vapor pressure between that of water and acetone, shows an interesting

enrichment/depletion behavior. At a relative high toluene concentration ($z = 4$), it could be found in the bulk phase too (see Figure 7b). Water-rich pseudo-binary cuts with a ratio $z = 0.01$ are shown in Figure 8. At a mole fraction $x_{toluene,B} = 0.002$ the enrichment/depletion behavior changes dramatically. At lower concentration toluene molecules remain in the liquid bulk phase, showing no tendency to enter the interfacial region. At higher toluene concentration ($x_{toluene,B} = 0.006$) however, the molecules seem to be enriched in the surface region (Figure 8b). In this situation water always prefers to stay in the liquid bulk phase, thus depleting the surface layer (Figure 8a). Caused by the strong repulsive interaction between water and toluene, which finally leads to demixing, at higher concentrations the toluene molecules prefer the interface region (see Figure 8b). The higher vapor pressure of acetone in comparison to toluene leads to a considerable increase of the acetone surface concentration showing a large enrichment at high acetone concentrations in the surface (Figure 8c). The enrichment behavior of ternary systems results from an interplay between the interactions in the liquid phase and the vapor pressure of the pure components.

In order to discuss the quality of the suggested model in Table 8, the derivations between the experimental data and the predicted surface tension are listed. The largest derivation was found for the system acetone + water at 288.15 K.

Conclusions

Surface tensions and liquid densities of the ternary system water + acetone + toluene versus compositions in the homogeneous region at five temperatures from $T = 288.15$ K to $T = 328.15$ K were experimentally determined using a pendant drop apparatus. Vibration tube densimeter was used to obtain liquid densities at nine temperatures from (288.15 to 328.15) K. Binary and ternary surface tensions could be well-predicted by the Butler equation. The distribution of the substances between bulk and surface could be analyzed. The selective enrichment in the surface phase for ternary systems depends strongly on the interactions and the vapor pressure of the pure components.

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