J. Chem. Eng. Data **2004,** *49,* 997−1002

Surface and Interfacial Tension of the Ternary System Heptane + Toluene + *N*,*N*-Dimethylformamide

Heike Kahl, Tino Wadewitz, and Jochen Winkelmann*

Institute of Physical Chemistry, Martin-Luther University of Halle-Wittenberg, D-06217 Merseburg, Germany

The pendant-drop method combined with axisymmetric drop-shape analysis was used to determine liquid−vapor and liquid−liquid interfacial tension of mixtures consisting of heptane (1), toluene (2), and *N*,*N*-dimethylformamide (3). The method of pendant drop with an efficient temperature control of the measuring cell allows precision measurements of surface tension and interfacial tension. Surface tensions and liquid densities of more then 20 ternary mixtures in the homogeneous region were determined at a normal pressure of 1 bar and over a temperature range from 287 K to 317 K. Inside the miscibility gap of this system, liquid densities in both liquid phases using buoyancy experiments dependent on temperature were obtained. Furthermore, the pendant-drop technique allows measurements of the interfacial tension between the two liquid phases even close to the critical solution point for the ternary mixture. The resulting interfacial tension and the density difference vs temperature up to the critical solution point could be well described using a Wegner-type expression.

Introduction

N,*N*-Dimethylformamide is well known as a selective solvent for separation processes of aromatics from paraffins.[1] Some physicochemical properties such as vapor−liquid equilibrium,[2] liquid−liquid equilibrium,[3,4] mass-transfer experiments,[5,6] and viscosities and densities[7] of *N*,*N*-dimethylformamide-containing systems are available.

The precise measurement of interfacial tensions 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 contains at least implicit 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 the 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. The selection of suitable solvents for a liquid−liquid extraction in petrochemical processing depends to a large extent on both liquid−liquid solubility and interfacial tension. Such as in tertiary oil recovery, the knowledge of phase behavior and interfacial tension is essential for an effective application of surfactants and in consideration of salinity.[8] Surface tensions have been measured for a long time, and collections of experimental data for pure liquids and some binary liquid mixtures exist.[9−11] A critical review reveals that systematic investigations of liquid−liquid interfaces are rather rare,[12,13] especially in a wide temperature and concentration range of ternary or multicomponent systems. An increased number of applications of microemulsions in industrial applications requires considerable investigations of multicomponent systems, especially such systems that form microemulsions when surfactants are added. High-quality experimental data of surface and interfacial tensions also form the basis for a successful modeling and for theoretical calculations of interfacial properties.[14−18] Therefore, further precision measurements are badly 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 the Wilhelmy plate or spinning drop.[19−22] The amount of the sample is small, and its possible to measure both surface and interfacial tensions with high accuracy even under high pressure.[23−25] Extremely low interfacial tensions in the vicinity of critical solution points[26,27] can be determined where spinning-drop measurements usually fail because of their low-temperature stability.

Experimental Section

Reagents. *N*,*N*-Dimethylformamide pa. with a purity of >99.5% (by gas chromatography (GC)) and a water content of 0.15% was supplied by Fa. Fluka and heptane pa. with a purity of >99.0% (by GC) and a water content of 0.01% and toluene pa. with a purity of >99.5% (by GC) and a water content of 0.03% were supplied by Fa. Merck, Darmstadt, Germany. All substances were dried over molecular sieves ZEOSORB A4/A3 and stored in a dark place.

Measuring Procedure and Calibration. Surface and Interfacial Tension. The experimental setup[28] to determine surface respectively interfacial tensions is discussed in detail in previous papers.[29,30] An additional dust jacket enables dust protection as well as a temperature control within the measuring cell of $\Delta T = \pm 0.002$ K over extended periods of time. The temperature inside the measuring cell was determined using a specially prepared thermistor that was calibrated against a gallium cell to allow a temperature resolution of 0.1 mK. The drop is formed on a steel capillary and illuminated by glass fiber optics aligned parallel by a light-source coupling. A special control software performs the frame-grabbing, automatic

---

* To whom correspondence may be addressed. E-mail: winkelmann@chemie.uni-halle.de. Phone: +49 3461 462090. Fax:+49 3461 462129.

10.1021/je0499566 CCC: $27.50

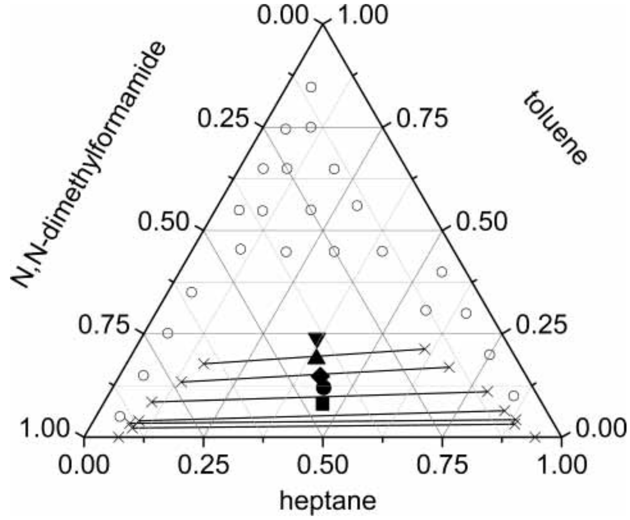

Figure 1. Localization of investigated ternary mixtures inside the miscibility gap of the system heptane (1) + toluene (2) + *N*,*N*-dimethylformamide (3) (full symbols: ■, I; ●, II; ▲, III; ▼, IV; ◆, V) and in the homogeneous region (open symbols). Experimental tie lines at 298.15 K were obtained from ref 7.

storage of the digitized drop images, and it controls both sample size and temperature. The pendant-drop profiles are extracted from the drop images and analyzed by means of the axisymmetric drop-shape analysis software,[20,31] which ensures a high-quality contour extraction and a very precise interfacial tension calculation by numerical solution of the Laplace equation. Samples are weighed to ±0.1 mg into an Erlenmeyer flask and sealed with polytetrafluoroethylene stoppers. To avoid the decomposition of *N*,*N*-dimethylformamide, the samples are kept in a dark place. For mixtures, the mol fraction is accurate to $\pm 1 \times 10^{-4}$. Details of the experimental procedure were given in a previous paper.[29] For each sample, we developed 4 different drops in this saturated atmosphere and recorded 10 images of each drop. The accuracy of the experimental surface tensions was considered to be $\Delta\sigma < 0.1$ mN/m. The reproducibility of the surface tension measurements is generally better than $\Delta\sigma = \pm 0.5\%$ at the 95% confidence level.

To measure the interfacial tension of samples with phase separation, mixtures were directly prepared in the measuring cell and equilibrated. When the temperature control shows that thermal equilibrium is reached (usually 1 h or more), the sample is stirred once again and both phases are allowed to separate. The phase separation could be followed up using the CCD camera of the pendant-drop system. Then drops of the lower phase are developed in the upper phase, and the images are recorded. The relative uncertainty, which depends on temperature and concentration, is given for each data point.

Density. The densities of homogeneous liquid mixtures, needed for the numerical solution of the Laplace equation, are determined using a vibrating tube densimeter (DMA 60, Fa. Anton Paar, with a DMA 602 measuring cell) with temperature control of ±0.01 K. For the calibration of the densimeter at each temperature, we used twice-distilled water and air. The accuracy of the measured densities in the homogeneous mixtures is considered to be $\Delta\rho = \pm 0.0001$ g·cm^{-3}.

Table 1. Experimental Surface Tension, σ, from T = 287.81 K to T = 317.86 K for Ternary Mixtures of Heptane (1) + Toluene (2) + *N*,*N*-Dimethylformamide (3) Measured with the Pendant-Drop Apparatus

			σ/mN·m^{-1}			
x_1	x_2	x_3	287.81 K	297.82 K	307.86 K	317.86 K
0.8497	0.1002	0.0501	21.04	19.78		18.26
0.7496	0.2	0.0504	21.76			18.85
0.5496	0.3998	0.0506				19.98
0.05	0.0502	0.8998	30.30	28.57		27.67
0.0497	0.1496	0.8007	29.78	29.69		27.44
0.0498	0.2515	0.6987	29.52	28.67		27.22
0.0498	0.3508	0.5994	29.85	28.39	27.59	26.99
0.1	0.75	0.15	27.39	26.42	25.38	24.41
0.1998	0.6488	0.1514	25.73	24.74	23.86	21.77
0.2917	0.5605	0.1478	24.65	23.59	22.59	21.95
0.0999	0.6504	0.2497	27.31	26.35	25.76	24.93
0.2	0.5501	0.2499	25.58	24.64	23.53	22.75
0.2994	0.4493	0.2513	23.61	23.30	22.56	21.56
0.0998	0.5482	0.352	27.28	26.14	25.65	24.53
0.1993	0.4485	0.3522	24.98	24.22	23.22	23.47
0.1	0.4553	0.4447	27.03	26.25		23.92
0.05	0.5496	0.4004	28.86	27.86		
0.0502	0.65	0.2998	28.78	27.81		
0.0497	0.7456	0.2047	28.57	27.52		
0.3997	0.4499	0.1504		22.69	21.73	21.07
0.5623	0.3071	0.1306		21.58	20.62	19.68
0.0521	0.8473	0.1006	28.26	27.17		
0.6501	0.3	0.0499	22.28			19.38
0.4498	0.4999	0.0503	23.52	22.47		20.06

The measurement of density differences between both phases in a liquid−liquid equilibrium is a much more complicated task, especially when approaching the vicinity of the critical solution point. To determine the density differences between the liquid phases, buoyancy measurements were used. The experimental setup is described in detail in previous papers.[28−30] The samples are placed inside of a temperature-controlled moveable barrel and closed with a Teflon stopper. To control the temperature, a JULABO FP 40 MH thermostat together with a thermistor is used, which enable us to keep the temperature constant to $\Delta T = \pm 0.005$ K over the measuring period. The mass of a glass vessel filled with lead was determined at several temperatures in different pure substances of known density. We used heptane, toluene, cyclohexane, and air. The cubic expansion coefficient of the glass vessel used was taken into account to calibrate the equipment.[29,30] We measured 174 reference points. The sample was filled in the barrel and brought to constant temperature. Then the mixture was stirred once again, and after phase equilibration, the mass of a load was determined in each phase. This procedure was repeated at each temperature. The accuracy of the measured densities in both liquid phases is considered to be $\Delta\rho = \pm 0.0005$ g·cm^{-3}.

Results and Discussion

Multicomponent mixtures interesting for liquid−liquid extraction consist of at least of three components. We selected a typical ternary model system for extraction: heptane + toluene + *N*,*N*-dimethylformamide. The binary miscibility gap between heptane and *N*,*N*-dimethylformamide vanishes with increasing amount of toluene in the mixture at the liquid−liquid critical point. In the miscible region of this system, 24 mixtures at four temperatures were investigated (Figure 1). Inside the miscibility gap, we selected five compositions for density measurements and for three mixtures the interfacial tension vs temperature was determined up to the vicinity of the critical point.

Experimental liquid densities, ρ, and surface tensions, σ, of the ternary mixtures at various temperatures are reported in Tables 1 and 2. Table 1 contains the surface tension data, and the corresponding liquid densities used for the evaluation of surface tension are contained in Table 2. The isothermal experimental data of density and surface tension could be well described with a cubic polynomial in

Table 2. Experimental Liquid Densities, ρ, from T = 288.15 K to T = 333.15 K for Ternary Mixtures of Heptane (1) + Toluene (2) + *N*,*N*-Dimethylformamide (3) Measured with Vibration Tube Densiometer

		ρ/g·cm^{-1}									
x_1	x_2	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K
0.8497	0.1002	0.7085	0.7042	0.6999	0.6956	0.6912	0.6868	0.6823	0.6778	0.6733	0.6686
0.7496	0.2	0.7230	0.7193	0.7150	0.7106	0.7062	0.7018		0.6927	0.6882	0.6836
0.5496	0.3998	0.7569	0.7524	0.7480	0.7436	0.7392	0.7347	0.7302	0.7256	0.7210	0.7163
0.05	0.0502	0.9348	0.9298	0.9252	0.9202	0.9150		0.9074	0.8974	0.8887	0.8835
0.0497	0.1496	0.9259	0.9208	0.9160	0.9110	0.9058	0.8999	0.8945	0.8888	0.8800	0.8751
0.0498	0.2515	0.9175	0.9123	0.9073	0.9022	0.8961	0.8907	0.8849	0.8790	0.8721	0.8670
0.0498	0.3508	0.9078	0.9026	0.8977	0.8926	0.8873	0.8819	0.8763	0.8707	0.8651	0.8596
0.1	0.75	0.8598	0.8547	0.8499	0.8446	0.8395	0.8345	0.8295	0.8246	0.8198	0.8150
0.1998	0.6488	0.8364	0.8314	0.8265	0.8214	0.8161	0.8107	0.8053	0.8000	0.7950	0.7902
0.2917	0.5605	0.8160	0.8104	0.8056	0.8004	0.7951	0.7897	0.7843	0.7790	0.7740	0.7692
0.0999	0.6504	0.8683	0.8632	0.8582	0.8523	0.8473	0.8417	0.8361	0.8305	0.8253	0.8204
0.2	0.5501	0.8477	0.8424	0.8373	0.8318	0.8249	0.8195	0.8132	0.8067	0.8003	0.7950
0.2994	0.4493	0.8273	0.8217	0.8161	0.8096	0.8082	0.7975	0.7907	0.7839	0.7773	0.7717
0.0998	0.5482	0.8733	0.8683	0.8633	0.8577	0.8526	0.8473	0.8420	0.8364	0.8316	0.8268
0.1993	0.4485	0.8526	0.8470	0.8405	0.8350	0.8292	0.8232	0.8162	0.8107	0.8054	0.8005
0.1	0.4553	0.8818	0.8769	0.8724	0.8677	0.8628	0.8577	0.8500	0.8438	0.8378	0.8328
0.05	0.5496	0.8916	0.8864	0.8811	0.8758	0.8704	0.8650	0.8596	0.8542	0.8491	0.8443
0.0502	0.65	0.8837	0.8781	0.8732	0.8680	0.8628	0.8569	0.8517	0.8466	0.8417	0.8368
0.0497	0.7456	0.8752	0.8701	0.8650	0.8602	0.8552	0.8502	0.8451	0.8403	0.8355	0.8307
0.3997	0.4499	0.7913	0.7864	0.7817	0.7768	0.7716	0.7669	0.7617	0.7564	0.7514	0.7466
0.5623	0.3071	0.7577	0.7530	0.7483	0.7436	0.7388	0.7340	0.7293	0.7246	0.7199	0.7152
0.0521	0.8473	0.8650	0.8601	0.8555	0.8510	0.8463	0.8417	0.8370	0.8323	0.8276	0.8228
0.6501	0.3	0.7394	0.7351	0.7307	0.7264	0.7219	0.7174	0.7129	0.7084	0.7038	0.6992
0.4498	0.4999	0.7752	0.7707	0.7662	0.7618	0.7573	0.7528	0.7483	0.7437	0.7390	0.7343

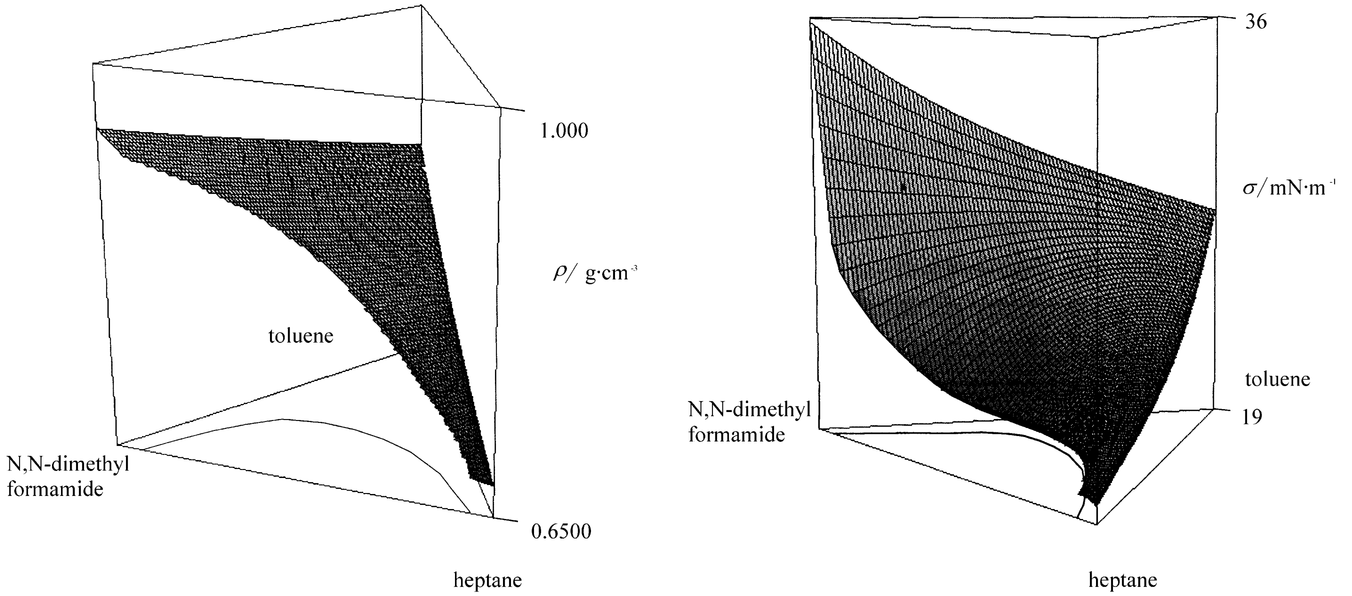

Figure 2. (a) Liquid density, ρ, of the system heptane + toluene + *N*,*N*-dimethylformamide at T = 298.15 K. The surface describes smoothed experimental data. (b) Surface tension, σ, of the system heptane (1) + toluene (2) + *N*,*N*-dimethylformamide (3) at T = 297.82 K. The surface describes smoothed experimental data.

the mol fractions of the three components. The continuous decrease of density respective surface tension from the value of *N*,*N*-dimethylformamide to those of toluene and heptane is shown at 298.15 K as a surface diagram inside the phase prism in parts a and b of Figure 2.

The influence of the formation of the ternary samples on surface tension is higher than on liquid densities. Starting from the *N*,*N*-dimethylformamide corner of the phase prism, the surface tension decreases steeper to heptane than to toluene. That could be a hint of the enrichment processes of heptane within the liquid interface.

Starting from the binary system heptane + *N*,*N*-dimethylformamide, interfacial tensions of mixtures with an increasing amount of toluene were measured. Figure 1 shows the ternary phase diagram of our system and indicates the composition of samples inside the miscibility gap.

Since the density difference between both liquid phases has a great influence on the resulting interfacial tension, derived from the pendant-drop images, bouyancy experiments were applied as described above. Close to the critical solution point, the density difference vanishes with increasing temperature (Figure 3).

Table 3 summarizes the corresponding liquid densities of five mixtures vs temperature. Since the density measurements were extended to temperatures very close to the critical solution point, the density differences should be described by the following expression

$$\Delta\rho = \rho^0\left(1 - \frac{T}{T_C}\right)^{0.325}\left[1 + A_\rho\left(1 - \frac{T}{T_C}\right)^{0.5} + B_\rho\left(1 - \frac{T}{T_C}\right)^{1.0} + ...\right] \quad (1)$$

where in addition to the classical term Wegener expansion

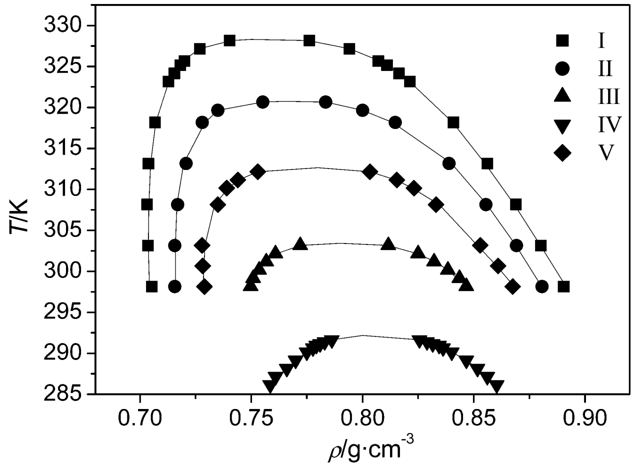

Figure 3. Experimental liquid densities, ρ, from $T = 285$ K to $T = 330$ K of the system heptane (1) + toluene (2) + *N*,*N*-dimethylformamide (3): ■, I; ●, II; ▲, III; ▼, IV; ◆, V. The densities were measured with the buoyancy method.

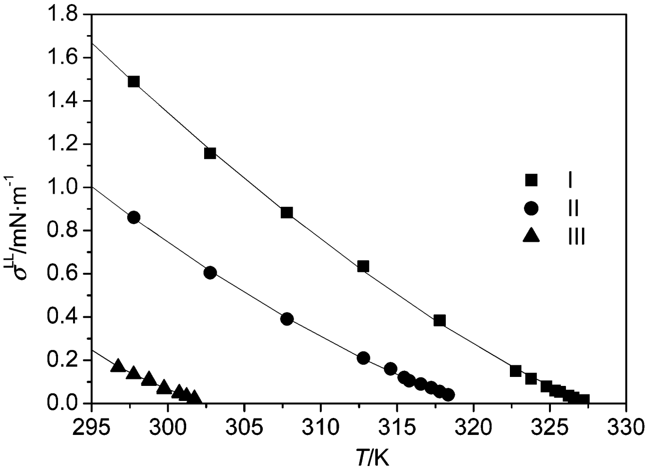

Figure 4. Experimental interfacial tension, σ^{LL}, from $T = 295$ K to $T = 330$ K for heptane (1) + toluene (2) + *N*,*N*-dimethylformamide (3) of different mixtures (■, I; ●, II; ▲, III) measured with the pendant-drop apparatus. Solid lines fitting results from eq 2 parameters σ^{0LL} and A_σ are given in Table 6.

type parameters are included. This will improve the description in the near-critical region. In eq 1, we treat ρ^0, A_ρ, and the critical temperature T_C as free parameters. B_ρ is fixed to zero. With the help of the Wegener expansion, the modeling of density differences from noncritical to near-critical regions was possible. The parameters, which were obtained by fitting our experimental data, are given in Table 4. In our model, the Wegener exponent and the critical exponent $\beta = 0.325$ were fixed, and only a single Wegener term was included.[32]

The interfacial tensions of three mixtures that were measured in the two-phase region of the system heptane + toluene + *N*,*N*-dimethylformamide in a temperature range from 295 K to the critical temperatures were presented in Figure 4.

Table 5 reported experimental interfacial tensions of three ternary mixtures together with their respective standard derivation. The experimental data can be represented by an expression similar to that for the density with Wegener expansion terms included

$$\sigma^{LL} = \sigma^{0LL}\left(1-\frac{T}{T_C}\right)^{1.26}\left[1+A_\sigma\left(1-\frac{T}{T_C}\right)^{0.5}+...\right] \qquad (2)$$

Table 3. Experimental Liquid Densities, ρ, and Density Differences, $\Delta\rho$, from $T = 298.15$ K to $T = 328.15$ K of the Two Liquid Phases for Ternary Mixtures of Heptane (1) + Toluene (2) + *N*,*N*-Dimethylformamide (3) Measured by Buoyancy Experiments

T/K	ρ^{I}/g·cm^{-3}	ρ^{II}/g·cm^{-3}	$\Delta\rho$/g·cm^{-3}
I ($x_1 = 0.4595$; $x_2 = 0.4603$; $x_3 = 0.0802$)			
298.15	0.7053	0.8905	0.1852
303.15	0.7036	0.8802	0.1766
308.15	0.7032	0.8690	0.1658
313.15	0.7038	0.8561	0.1523
318.15	0.7068	0.8409	0.1341
323.15	0.7128	0.8213	0.1085
324.15	0.7155	0.8164	0.1009
325.15	0.7182	0.8110	0.0928
325.65	0.7201	0.8071	0.0870
327.15	0.7269	0.7941	0.0672
328.15	0.7404	0.7762	0.0358
II ($x_1 = 0.4419$; $x_2 = 0.4381$; $x_3 = 0.12$)			
298.15	0.7157	0.8807	0.165
303.15	0.7157	0.8692	0.1535
308.15	0.7170	0.8555	0.1385
313.15	0.7208	0.8389	0.1181
318.15	0.7280	0.8147	0.0867
319.65	0.7350	0.8000	0.0650
320.65	0.7552	0.7835	0.0283
III ($x_1 = 0.3922$; $x_2 = 0.4182$; $x_3 = 0.1896$)			
298.15	0.7498	0.8467	0.0969
299.15	0.7509	0.8436	0.0927
300.15	0.7536	0.8384	0.0848
301.16	0.7568	0.8322	0.0754
302.15	0.7609	0.8250	0.0641
303.15	0.7721	0.8116	0.0395
IV ($x_1 = 0.3679$; $x_2 = 0.3922$; $x_3 = 0.2399$)			
298.15	0.7586	0.8603	0.1017
287.15	0.7610	0.8561	0.0951
288.15	0.7660	0.8517	0.0857
289.15	0.7700	0.8467	0.0767
290.15	0.7750	0.8401	0.0651
290.65	0.7778	0.8362	0.0584
290.95	0.7793	0.8344	0.0551
291.15	0.7810	0.8316	0.0506
291.40	0.7830	0.8290	0.0460
291.65	0.7862	0.8256	0.0394
V ($x_1 = 0.4215$; $x_2 = 0.4314$; $x_3 = 0.1471$)			
298.15	0.7290	0.8675	0.1385
300.65	0.7282	0.8609	0.1327
303.15	0.7279	0.8529	0.1250
308.15	0.7350	0.8330	0.0980
310.15	0.7390	0.8231	0.0841
311.15	0.7440	0.8154	0.0714
312.15	0.7530	0.8033	0.0503

Table 4. Parameters ρ^0, A_ρ, and T_C Describing the Liquid Densities in Equation 1 of the System Heptane (1) + Toluene (2) + *N*,*N*-Dimethylformamide (3) where $\beta = 0.325$ and $\Delta = 0.5$

sample	ρ^0/g·cm^{-3}	A_ρ	T_C/K
I	0.427 ± 0.003	−0.173 ± 0.022	328.31 ± 0.02
II	0.420 ± 0.004	−0.266 ± 0.044	320.73 ± 0.01
IV	0.417 ± 0.009	−0.439 ± 0.101	312.64 ± 0.05
III	0.391 ± 0.011	−0.534 ± 0.214	303.42 ± 0.03
IV	0.284 ± 0.006	1.842 ± 0.190	292.19 ± 0.03

The critical temperature T_C was obtained from density parametrization above, and the parameters σ^{0LL} and A_σ were fitted to experimental data. The resulting parameters are given in Table 6.

Figure 4 shows the good quality of fitting to the experimental data of interfacial tensions in a wide temperature range starting from room temperature and extending up to the critical region. The increase of interfacial tension vs

Table 5. Experimental Interfacial Tension, σ^{LL}, from T = 297.754 K to T = 327.234 K between the Two Liquid Phases for Ternary Mixtures of Heptane (1) + Toluene (2) + *N*,*N*-Dimethylformamide (3) Measured with the Pendant-Drop Apparatus

T/K	σ^{LL}/mN·m^{-1}
I ($x_1 = 0.4595$; $x_2 = 0.4603$; $x_3 = 0.0802$)	
297.75	1.490 ± 0.010
302.76	1.157 ± 0.003
307.79	0.883 ± 0.004
312.79	0.635 ± 0.002
317.78	0.384 ± 0.003
322.77	0.150 ± 0.005
323.78	0.115 ± 0.006
324.77	0.078 ± 0.005
325.34	0.060 ± 0.002
325.67	0.053 ± 0.01
326.22	0.036 ± 0.004
326.56	0.027 ± 0.005
327.23	0.014 ± 0.004
II ($x_1 = 0.4419$; $x_2 = 0.4381$; $x_3 = 0.12$)	
297.75	0.861 ± 0.005
302.77	0.605 ± 0.002
307.79	0.390 ± 0.002
312.80	0.210 ± 0.005
314.57	0.160 ± 0.004
315.47	0.120 ± 0.004
315.79	0.105 ± 0.003
316.55	0.090 ± 0.003
317.22	0.073 ± 0.004
317.79	0.055 ± 0.005
318.33	0.040 ± 0.003
III ($x_1 = 0.3922$; $x_2 = 0.4182$; $x_3 = 0.1896$)	
296.74	0.168 ± 0.005
297.74	0.134 ± 0.004
298.75	0.110 ± 0.007
298.76	0.104 ± 0.060
299.75	0.072 ± 0.002
299.76	0.065 ± 0.030
300.75	0.050 ± 0.004
300.76	0.045 ± 0.020
301.22	0.035 ± 0.004
301.73	0.023 ± 0.006

Table 6. Parameters, σ^0 and A_σ, Describing Interfacial Tension (Equation 2) for Heptane + Toluene + *N*,*N*-Dimethylformamide

sample	σ^{0LL}/mN·m^{-1}	A_σ/mN·m^{-1}
I	26.332 ± 1.225	0.405 ± 0.186
II	19.022 ± 0.696	0.919 ± 0.184
III	13.367 ± 1.949	3.761 ± 1.662

temperature becomes flatter at higher amounts of toluene. In direction to the critical end point, the interfacial tension is close to zero.

Conclusions

Surface tensions of the three-component system heptane + toluene + *N*,*N*-dimethylformamide vs compositions in the homogeneous region at four temperatures were measured with a high-precision pendant-drop apparatus. The pendant-drop apparatus is suitable for estimating interfacial tensions in systems with liquid−liquid-phase separation. Interfacial tensions of the ternary system inside the miscibility gap were measured. With density differences obtained by buoyancy experiments, the measurement of interfacial tension could be extended up to the critical region. In the vicinity of the critical solution, temperature density differences and interface tension can be described very well. Thus, simultaneous measurements of interfacial and surface tension in ternary model systems for liquid−liquid extraction can extend the so-far modest database and will be very valuable for checking theoretical approaches such as molecular simulation or density gradient theories.

Literature Cited

(1) Hradetzky, G.; Hammerl, I.; Bittrich, H. J. *Selective Solvents Data on Dimethylformamide-N-methylcaprolactam-N-methylpyrrolidine*; Physical Science Data 31; Wehner, K., Kisan, W., Eds.; Elsevier: Amsterdam-Oxford-New York-Tokyo, 1989.

(2) Wichterle, J. Liquid−Vapor Equilibrium. XXXV. Vapor-Liquid Equilibriums in the System Heptane-Toluene-*p*-Xylene and in the Systems Heptane-Toluene-Extractive Agent. *Collect. Czech. Chem. Commun.* **1965**, *30*, 3388−3398.

(3) Paschke, A.; Bittrich, H. J. Study of Liquid−Liquid Mass-Transfer Kinetics by the Single-Drop Method. *Wiss. Z. THLM* **1989**, *31*, 693−702.

(4) Surovy, J.; Dojcansky, J.; Bafrncova, S. Some Information on Calculating the Liquid−Liquid Equilibrium of Ternary Systems. An Improvement of Prediction of Liquid−Liquid Equilibrium in Ternary Systems from Binary Equilibrium Data. *Collect. Czech. Chem. Commun.* **1982**, *475*, 1420−1432.

(5) Paschke, A. Simultaneous Mass Transfer of Heptane and Toluene into a Selective Solvent. *Chem. Eng. Process.* **1993**, *32*, 201−207.

(6) Müller, O.; Winkelmann, J. Static Light Scattering Measurements along a Critical Decomposition Line of a Ternary Liquid Mixture. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1999**, *60*, 4453−4459.

(7) Paschke, A.; Novotna, A.; Winkelmann, J. Viskosität und Dichte im System Heptan-Toluen-*N*,*N*-Dimethylformamid zwischen 20 und 35 °C. *Chem. Tech.* **1993**, *45*, 167−173.

(8) Flemming, P. D.; Vinatieri, J. E.; Glinsmann, G. R. Theory of Interfacial Tensions in Multicomponent Systems. *J. Phys. Chem.* **1980**, *84*, 1526−1531.

(9) Wohlfarth, Ch.; Wohlfarth, B. Numerical Data and Functional Relationships in Science and Technology. In *Surface Tension of Pure Liquids and Binary Liquid Mixtures*; Lechner, M. D., Ed.; New Series Group IV Physical Chemistry; Landoldt-Börnstein Springer: Heidelberg, 1997; Vol. 16.

(10) Jasper, J. J. Surface Tension of Pure Liquid Compounds. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841−1009.

(11) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere: New York, 1989.

(12) Wielebinski, D.; Findenegg, G. H. Measurement of Interfacial Tension in Simple Two-Phase Ternary Systems along an Isothermal Linear Path to the Critical Point. *J. Phys. Chem.* **1984**, *88*, 4397−4401.

(13) Nagarajan, N.; Gasem, K. A. M.; Robinson, R. L., Jr. Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions of CO_2 + Hydrocarbon Systems. 6. CO_2 + *n*-Butane + *n*-Decane. *J. Chem. Eng. Data* **1990**, *35*, 228−231.

(14) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*; MacGraw Hill: New York, 2001.

(15) Kahl, H.; Enders, S. Calculation of Surface Properties of Pure Fluids Using Density Gradient Theory and SAFT-EOS. *Fluid Phase Equilib.* **2000**, *172*, 27−42.

(16) Kahl, H.; Enders, S. Interfacial Properties of Binary Mixtures. *Phys. Chem. Chem. Phys.* **2002**, *4*, 931−936.

(17) Wadewitz, T.; Winkelmann, J. Density Functional Theory: X-ray Studies of Pure Fluid Liquid/Vapour Interfaces. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3335−3343.

(18) Winkelmann, J. The Liquid−Vapor Interface of Pure Fluids and Mixtures: Application of Computer Simulation and Density Functional Theory. *J. Phys.: Condens. Matter* **2001**, *13*, 4739−4768.

(19) Rotenberg, Y.; Boruvka, L.; Neumann, A. W. Determination of Surface Tension and Contact Angle from the Shapes of Axisymmetric Fluid Interfaces. *J. Colloid Interface Sci.* **1983**, *93*, 169−183.

(20) Cheng, P.; Li, D.; Boruvka, L.; Rotenberg, Y.; Neumann, A. W. Automation of Axisymmetric Drop Shape Analysis for Measurements of Interfacial Tensions and Contact Angles. *Colloids Surf.* **1990**, *43*, 151−167.

(21) Anastasiadis, S. H.; Chen, J. K.; Koberstein, J. T.; Siegel, A. F.; Sohn, J. E.; Emerson, J. A. The Determination of Interfacial Tension by Video Image Processing of Pendant Fluid Drops. *J. Colloid Interface Sci.* **1987**, *119*, 55−66.

(22) Girault, H. H. J.; Schiffrin, D. J.; Smith, B. D. V. The Measurement of Interfacial Tension of Pendant Drops Using a Video Image Profile Digitizer. *J. Colloid Interface Sci.* **1984**, *101*, 257−266.

(23) Wiegand, G.; Franck, E. U. Interfacial Tension between Water and Nonpolar Fluids up to 473 K and 2800 bar. *Ber. Bunsen−Ges. Phys. Chem.* **1994**, *98*, 809−817.

(24) Dittmar, D.; Oei, S. B.; Eggers, R. Interfacial Tension and Density of Ethanol in Contact with Carbon Dioxide. *Chem. Eng. Technol.* **2002**, *25*, 23−27.

(25) Dittmar, D.; Eggers, R.; Kahl, H.; Enders, S. Measurement and Modeling of the Interfacial Tension of Triglyceride Mixtures in Contact with Dense Gases. *Chem. Eng. Sci.* **2002**, *57*, 355−363.

(26) Kreuser, H. Untersuchung von Kritischen und Nicht-Kritischen Phasengrenzen in Binären Flüssigen Mischungen mit Mischungslücke. Ph.D. Thesis, University of Cologne, 1992.

(27) Mainzer, T. Diploma Work, University of Cologne, 1994.

(28) Wadewitz, T. Flüssige Grenzphasensysteme: Struktur, Optische und Grenzflächeneigenschaften. Ph.D. Thesis, University of Halle Wittenberg, 1999.

(29) Kahl, H.; Wadewitz, T.; Winkelmann, J. Surface Tension of Pure Liquids and Binary Liquid Mixtures. *J. Chem. Eng. Data* **2003**, *48*, 580−586.

(30) Kahl, H.; Wadewitz, T.; Winkelmann, J. Surface Tension and Interfacial Tension of Binary Organic Liquid Mixtures *J. Chem. Eng. Data* **2003**, *48*, 1500−1507.

(31) Lahooti, S.; Del Rio, O. I.; Neumann, A. W.; Cheng, P. Axisymmetric Drop Shape Analysis (ADSA). *Surfactant Sci. Ser.* **1996**, *63* (Applied Surface Thermodynamics), 441−507.

(32) Greer, S. C.; Moldover, M. R. Thermodynamic Anomalies at Critical Points of Fluids. *Annu. Rev. Phys. Chem.* **1981**, *32*, 233−265.

Received for review January 24, 2004. Accepted April 29, 2004. The financial support of Deutsche Forschungsgemeinschaft (Wi 1081/6 and 11) is gratefully acknowledged.

JE0499566