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Liquid–liquid equilibrium, heat capacity and turbidity of binary solution nitrobenzene + *n*-pentadecane

Yimin Guo [a], Aiqin Shi [b], Jingjing Xie [b], Zhiyun Chen [b], Tianxiang Yin [b], Weiguo Shen [a,b,*]

[a] *Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China*
[b] *School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China*

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ABSTRACT

The liquid–liquid coexistence curve, the isobaric heat capacity per unit volume and the turbidity for the binary solution of nitrobenzene + *n*-pentadecane have been measured at various temperatures. The upper consolute mole fraction x_c of nitrobenzene and the upper consolute temperature T_c of the binary solution were determined to be $x_c = 0.696$ and $T_c = 307.298$ K, respectively. The values of the critical exponents related to the width of the coexistence curve, the heat capacity, the osmotic compressibility and the correlation length were deduced and found to be in good agreements with that of the 3-D Ising universality. With the heat capacity data the asymmetric behavior of the diameter of the coexistence curve was studied in terms of the complete scaling theory. The critical amplitudes related to the above four quantities were used to calculate the universal scaling ratios and to confirm their theoretical predictions.

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1. Introduction

Measurement of liquid–liquid equilibrium data is necessary not only for chemical engineering design but also for providing insight into the interactions, fluid structures and particularly the universal critical phenomena in the liquid solutions. It is well known that the critical exponents are universal, while the critical amplitudes are system-depended; however some combinations of the critical amplitudes of different thermodynamic properties may possibly have universal values as predicted by theories [1–3]. In recent years, the asymmetric behavior of the diameter of the coexistence curve in the critical region has been discussed by the newly developed “complete scaling theory” [4–6], which mixed both the dependent and independent physical fields into the scaling fields. Further tests of the complete scaling theory and the universality of the critical amplitude ratios are of interest.

It has been pointed out that two liquid solution samples prepared with nominally the same compositions may exhibit much different upper/lower consolute temperatures due to the sensitivity of the consolute point to trace impurities, such as the moisture introduced during the process of preparation of the samples. Therefore, the precision of measurement of the coexistence curve by the “cloud point” method using multiple samples may be subjected to systematic error. By contrast, the determination of the refractive indices in each of the coexisting phases of a single sample of a binary solution may be a better way to study the critical behaviors related to the coexistence curve.

Nitrobenzene is an important basic organic intermediate, which can form partially miscible mixtures with alkanes. The refractive index of nitrobenzene is significantly larger than that of alkanes, which enhances the precision in determination of the liquid–liquid equilibrium with the refractive index method. Moreover, the binary solutions of nitrobenzene + alkanes also have upper consolute temperatures in a range which is convenient for making measurements of the critical properties of the coexistence curve, the heat capacity, the osmotic compressibility and the correlation length.

In this work, we report the liquid–liquid coexistence curve, isobaric heat capacity, and turbidity for the binary solution of nitrobenzene + *n*-pentadecane. The critical exponents and the universal ratios of critical amplitudes are deduced to test the theoretical predictions. The asymmetric behavior of the diameter of the coexistence curve is discussed in the framework of the complete scaling theory.

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* Corresponding author at: Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China.

E-mail address: shenwg@lzu.edu.cn (W. Shen).

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2. Experimental

2.1. Chemicals

The suppliers, purities, and methods of drying and storing the liquids used in this work can be found in Table 1.

2.2. Measurement of coexistence curve

The refractive indexes of two coexisting phases were measured on a home-built instrument based on the "minimum deviation" technique [7,8]. A He-Ne laser with a wavelength λ of 632.8 nm was used as a light source. The standard uncertainty in the measurement of the refractive index was about 0.0001. The mole fraction, x_c of nitrobenzene at the consolute point of the binary mixture was identified with the mole fraction of the mixture which made the volumes of liquid above and below the meniscus equal, a condition which was determined visually. The standard uncertainty in determination of x_c was about 0.001 [8,9]. A sample with the upper consolute composition was then prepared in a rectangular fluorescence cell linked with an Ace-thread connector and sealed by a Teflon plug. The sample cell was placed in a water bath with a temperature stability of ±0.002 K. The standard uncertainty and the reproducibility in measurement of the temperature were about 0.02 K and 0.002 K, respectively. By variation of the temperature, a whole coexistence curve was determined using only one sample. The experiment was carried out in a sealed sample cell with vapor in equilibrium with liquid. Because the vapor pressure was low, its change with temperature had a negligible effect on the coexistence curve.

Table 1
Suppliers, purities, dried and stored methods of chemicals.

Chemical name	Supplier	Purity, mass fraction	Method of drying and storing
Nitrobenzene	Alfa Aesar	0.99[a]	Dried with 0.4 nm molecular sieves then stored in a desiccator over P_2O_5
n-Pentadecane	Alfa Aesar	0.99[a]	

[a] Provided by the supplier.

2.3. Measurement of isobaric heat capacity per unit volume

The temperature dependence of the isobaric heat capacity per unit volume at the upper consolute composition was measured using a differential scanning calorimeter, Micro DSC III (Setaram, France) based on the Tian-Calvet's principle with two calibration liquids of *n*-heptane and 1-butanol. The detailed description of the apparatus and the measurement procedure can be found in previous articles. [10,11] The background noise of Micro DSC III was less than ±0.2 μW, and the temperature stability was better than ±0.002 K. The measurements were carried out in the down scanning model with the scanning rate being selected as 0.1 K $\cdot$min^{-1}. The standard uncertainty of the heat capacity per unit volume was about 0.014 J $\cdot$cm$^{-3}\cdot$K^{-1}.

2.4. Measurement of turbidity

The apparatus and the method for the turbidity measurement have been described in the previous work [12]. A brief introduction

Table 2
Coexistence curves of temperature against refractive index (T, n), temperature against mole fraction (T, x), temperature against volume fraction (T, ϕ), temperature against dimensionless molar density (T, $\hat{\rho}$) and temperature against dimensionless partial molar density (T, $\hat{\rho}x$) for {x nitrobenzene + (1-x) *n*-pentadecane}, T_c = 307.298 K. Refractive indexes n were measured at wavelength λ = 632.8 nm and pressure p = 0.1 MPa. Mole fraction, volume fraction, dimensionless molar density, and dimensionless partial molar density are denoted by x, ϕ, $\hat{\rho}$ and $\hat{\rho}x$, respectively. Subscripts "U" and "L" relate to the upper and lower phases, respectively.[a]

T/K	n^U	n^L	x^U	x^L	ϕ^U	ϕ^L	$\hat{\rho}^U$	$\hat{\rho}^L$	$\hat{\rho}x^U$	$\hat{\rho}x^L$
307.294	1.4748	1.4797	0.679	0.715	0.439	0.481	0.982	1.021	0.667	0.730
307.290	1.4743	1.4802	0.676	0.718	0.435	0.485	0.978	1.025	0.660	0.736
307.287	1.4738	1.4807	0.672	0.721	0.431	0.489	0.974	1.029	0.654	0.742
307.283	1.4734	1.4810	0.669	0.723	0.427	0.492	0.970	1.032	0.649	0.746
307.276	1.4729	1.4815	0.665	0.727	0.423	0.496	0.966	1.036	0.642	0.753
307.272	1.4727	1.4817	0.663	0.728	0.422	0.497	0.965	1.037	0.640	0.755
307.264	1.4723	1.4822	0.660	0.731	0.418	0.502	0.961	1.041	0.634	0.761
307.253	1.4719	1.4826	0.657	0.734	0.415	0.505	0.958	1.044	0.629	0.766
307.235	1.4713	1.4833	0.652	0.738	0.409	0.511	0.953	1.050	0.621	0.775
307.214	1.4708	1.4839	0.648	0.742	0.405	0.516	0.949	1.055	0.615	0.783
307.190	1.4702	1.4846	0.643	0.747	0.400	0.521	0.944	1.060	0.607	0.791
307.159	1.4696	1.4852	0.638	0.750	0.395	0.526	0.939	1.065	0.599	0.799
307.117	1.4691	1.4858	0.634	0.754	0.390	0.531	0.935	1.070	0.592	0.806
307.066	1.4682	1.4866	0.626	0.759	0.382	0.538	0.927	1.076	0.580	0.816
307.014	1.4676	1.4872	0.620	0.762	0.377	0.542	0.922	1.080	0.572	0.823
306.944	1.4669	1.4879	0.614	0.766	0.371	0.548	0.916	1.086	0.563	0.832
306.866	1.4663	1.4887	0.609	0.771	0.365	0.554	0.911	1.092	0.554	0.842
306.776	1.4657	1.4894	0.603	0.775	0.360	0.560	0.906	1.097	0.546	0.850
306.660	1.4648	1.4904	0.594	0.780	0.351	0.568	0.898	1.105	0.533	0.862
306.509	1.4641	1.4913	0.587	0.785	0.345	0.575	0.892	1.112	0.523	0.873
306.308	1.4631	1.4926	0.577	0.792	0.335	0.585	0.883	1.122	0.509	0.888
306.096	1.4621	1.4938	0.566	0.798	0.326	0.594	0.874	1.130	0.495	0.902
305.778	1.4611	1.4952	0.555	0.805	0.316	0.604	0.864	1.141	0.480	0.918
305.373	1.4600	1.4969	0.542	0.813	0.304	0.617	0.854	1.153	0.463	0.938
304.888	1.4587	1.4986	0.526	0.821	0.291	0.629	0.842	1.165	0.443	0.957
304.165	1.4574	1.5008	0.509	0.830	0.277	0.644	0.829	1.181	0.421	0.981
302.920	1.4554	1.5042	0.480	0.844	0.254	0.668	0.808	1.204	0.388	1.017
301.895	1.4543	1.5065	0.461	0.853	0.241	0.683	0.795	1.220	0.367	1.041
300.925	1.4535	1.5085	0.446	0.861	0.230	0.696	0.785	1.233	0.351	1.061
299.944	1.4526	1.5104	0.430	0.867	0.218	0.707	0.775	1.246	0.333	1.081
298.929	1.4518	1.5122	0.414	0.873	0.207	0.719	0.765	1.258	0.316	1.098
297.898	1.4513	1.5140	0.401	0.879	0.199	0.729	0.757	1.269	0.304	1.116

[a] Standard uncertainties u are $u(p)$ = 10 kPa, $u(T)$ = 0.02 K, $u(T_c)$ = 0.05 K, $u(T_c - T)$ = 0.003 K, $u(n)$ = 0.0001, $u(x)$ = 0.002, $u(\phi)$ = 0.003, $u(\hat{\rho})$ = 0.001 and $u(\hat{\rho}x)$ = 0.002.

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