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Heat capacity anomalies of associated liquid–alkane mixtures near the liquid–liquid critical point

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ABSTRACT

The isobaric heat capacity for a set of critical binary mixtures composed by an associated liquid and an alkane was measured near the liquid–liquid critical point. From a careful analysis of experimental data, nonuniversal quantities such as critical temperatures and critical amplitudes were obtained. To obtain microscopic parameters that may characterise the critical behaviour of the studied systems, the critical amplitude of the correlation length was determined via *two-scale factor universality*. Useful insights into the influence of the molecular structure of the alkanes as well as the self-associating capability of the polar liquid on the aforementioned nonuniversal quantities are obtained.

1. Introduction

The anomalous behaviour of first and second-order derivatives of the thermodynamic potential near liquid–liquid critical points has been the subject of many studies. In particular, attention has been focused on the study of the isobaric heat capacity, whose critical behaviour can be expressed in terms of the following expression:

$$C_pV^{-1}(T) = B + Et + \frac{A^{\pm}}{\alpha}t^{-\alpha}, \tag{1}$$

where $C_pV^{-1}(T)$ denotes the heat capacity per unit volume, signs + and − refer to the homogeneous and heterogeneous region, respectively, and $t = |T - T_c|/T_c$ (with T_c being the critical temperature) reads for the dimensionless temperature critical deviation; the power-law term in the right hand side of Eq. (1) represents the critical contribution to C_pV^{-1}, which is characterized by the critical amplitude $A^{\pm}$ and the (universal) critical exponent $\alpha = 0.110$, while the remaining terms describe the background contribution. Despite critical amplitudes are nonuniversal (i.e., system-dependent) quantities, the ratio A^+/A^- is universal ($A^+/A^- \approx 0.53$ for the universality class of the three-dimensional Ising model) [1,2].

From a microscopic viewpoint, in the critical region the system is composed by clusters of fluctuating composition which become bigger the closer to T_c. The mean size of such clusters is quantified by the *correlation length* ξ, which diverges to infinity at the critical point like [1,2]:

$$\xi = \xi_0^{\pm}t^{-\nu}, \tag{2}$$

where $\nu \approx 0.63$ and $\xi_0^{\pm}$ denote system-dependent critical amplitudes. Hence, clearly, $\xi_0^{\pm}$ can be regarded as an indicator of the microscopic structure of the system at near-criticality. This quantity can be determined directly from a number of experimental techniques [3–5], or in an indirect way from the *two-scale factor X*, a dimensionless universal parameter that relates the critical amplitudes of both ξ and C_pV^{-1} *via*:

$$X = A^{\pm}(\xi_0^{\pm})^3/k_B, \tag{3}$$

where k_B is the Boltzmann constant and $X \approx 0.019$ [6]. This way, Eq. (3) provides a link between the nonuniversal critical behaviour of C_pV^{-1} and the microscopic features of the system.

The thermodynamics of binary mixtures composed by an associated liquid and an alkane have been extensively studied in the last 20 years [7–15]. The paradigm of such systems are alcohol–alkane mixtures, characterized by the strong self-association of the alcohol *via* hydrogen bonding. Large H-bonded structures in solution make alcohols to present a high degree of non-randomness, resulting in a highly nonideal thermodynamic behaviour [7–13].

In light of this, it is our aim to study the influence of the association capability on the critical behaviour of the isobaric heat capacity. To this end, measurements of C_pV^{-1} at near-criticality for a set of binary systems composed by an associated liquid and a series of alkanes were carried out using differential scanning

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calorimetry (DSC). Liquids with distinct self-association capabilities, namely, ethanol, 2-(2-ethoxyethoxy) ethanol, and benzonitrile, were selected. Ethanol shows the strongest association capability since the predominant interaction is hydrogen bonding. 2-(2-Ethoxyethoxy) ethanol also exhibits quite strong self-association, though lower than that of ethanol because of the presence of two oxygen atoms per molecule, which makes it to present a certain polar, non-associated nature. As for benzonitrile, its structure, characterized by a highly polar group bonded to an aromatic ring, favours short-range, antiparallel orientation of dipoles; this directional interaction has been shown to produce relatively weak association effects [16]. As regards the second component, alkanes with both distinct size and branching, namely, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-undecane, *n*-tridecane and 2,2,4-trimethylpentane (isooctane), were selected with a view to evaluate the influence of the alkane molecular structure on critical behaviour.

2. Experimental

2.1. Materials and procedure

Ethanol (purity > 99.5% in mass) was supplied by Merck, *n*-hexane (purity > 99.5%), *n*-heptane (purity > 99.5%) and *n*-octane (purity > 99.5%) by Fluka; 2-(2-ethoxyethoxy) ethanol (purity > 99.0%), benzonitrile (purity > 99.9%), isooctane (purity > 99.8%), *n*-nonane (purity > 99.0%), *n*-undecane (purity > 99.0%) and *n*-tridecane (purity > 99.0%) by Aldrich, and *n*-undecane (purity > 99.0%) by Sigma. Their purities were checked by gas chromatography (g.c.). All chemicals were degassed in an ultrasonic bath and dried with molecular sieves prior to use. Preparation of mixtures was carried out on the basis of reported literature values for the critical mole fraction x_c [11,14,17,18]; when not available, x_c was calculated by interpolation or extrapolation of the existing data. They were prepared under a nitrogen atmosphere by means of a Mettler AE-240 balance (with an uncertainty of $\pm 1 \times 10^{-5}$ g) and vigorously stirred prior to placement into the measuring cells. Uncertainty in mole fraction is quoted to $\pm 1 \times 10^{-4}$. Current uncertainty in x_c (i.e., ±0.01) seems to be small enough to establish general tendencies (as it is the aim of this work). As a matter of fact, it was recently shown [19] that, at most, such an uncertainty results in a 8% variation in A^+. Values for x_c from this work together with corresponding literature data are listed in Table 1.

2.2. Isobaric heat capacity per unit volume

A Setaram Micro DSC III differential scanning calorimeter was used to determine C_pV^{-1}. Detail information on the apparatus and the experimental methodology was presented in previous work [20,21]. A scanning rate of 0.01 K min^{-1} was used, affording a reproducibility of ±0.005 J K^{-1} cm^{-3}, which became slightly worse in the nearness of the critical point because of difficulties associated to experimentation in the critical region. Data in the two-phase region were significantly less reliable, since the calorimeter design precluded stirring. The temperature was measured to within ±0.002 K with a platinum resistance thermometer. The use of DSC for determining A^+ near the liquid–liquid critical point has been analysed in previous works [19–25]; the small scanning rate is the key point for obtaining reliable results. Calibration was made against two substances of known heat capacity (*viz.* 1-butanol and toluene) [26], whereas their densities, needed to obtain C_pV^{-1}, were obtained from [27,28].

Table 1
Experimental critical mole fractions for the studied binary systems.

System	x_c	Source
2-(2-Ethoxyethoxy) ethanol + hexane	0.3191	[14]
2-(2-Ethoxyethoxy) ethanol + heptane	0.3539	[14]
2-(2-Ethoxyethoxy) ethanol + octane	0.4131	[14]
2-(2-Ethoxyethoxy) ethanol + nonane	0.4440	Interpolated from [14]
Benzonitrile + octane	0.4689	[17]
Benzonitrile + isooctane	0.4650	[18]
Ethanol + undecane	0.6672	Extrapolated from [11]
Ethanol + tridecane	0.7082	[11]

3. Results and discussion

Figs. 1–3 show the $C_pV^{-1}(T)$ lambda curves for the binary systems under study. Experimental data were fitted to Eq. (1) using three approaches. All data (both in the homogeneous and heterogeneous regions) are included in approach (a), α is fixed to its accepted value, and T_c, B, E, A^+ and A^- are the fitting parameters. In approach (b) only the data of the homogeneous phase are

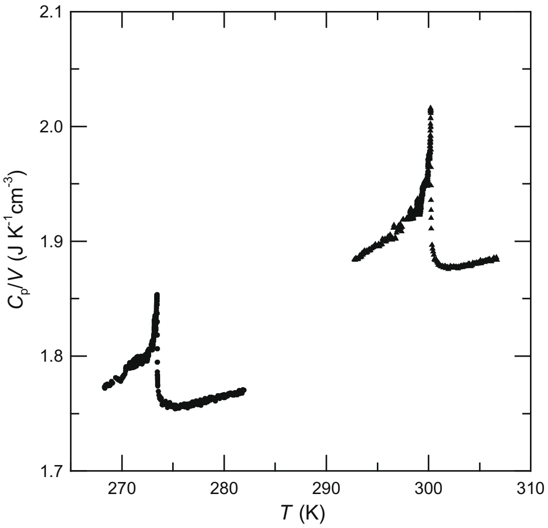

Fig. 1. Heat capacity per unit volume C_pV^{-1} of ethanol + (●) undecane, and (▲) tridecane in the critical region.

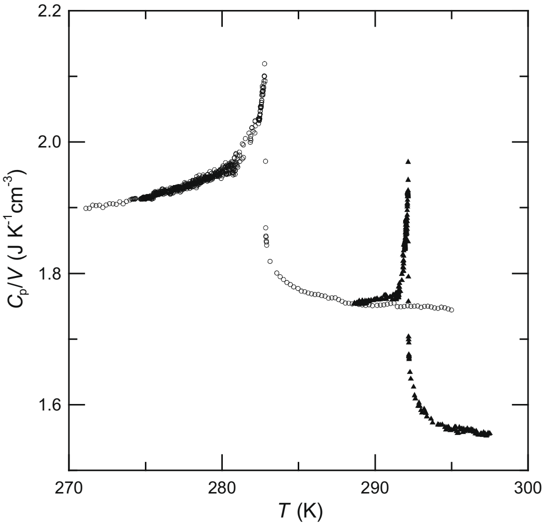

Fig. 2. Heat capacity per unit volume C_pV^{-1} of benzonitrile + (○) octane, and (▲) isooctane in the critical region.