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INFLUENCE OF CHEMICAL STRUCTURE ON CRITICAL PARAMETERS FOR DIMETHYL CARBONATE+ALKANE SYSTEMS

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In order to study the dependence of non-universal critical quantities on the molecular structure, heat capacities per unit volume for the dimethyl carbonate+(heptane, octane, nonane, decane or tridecane) critical mixtures near their upper consolute point are measured. The data are obtained at atmospheric pressure as a function of temperature in the homogeneous and heterogeneous regions by means of a differential scanning calorimeter. The exponent and amplitudes that characterises the observed critical anomaly are determined from experimental data, being their values coherent to previous results; in addition, the critical amplitudes of the correlation length was calculated from critical amplitudes using the universality of the two-scale factor. The influence of the alkane length on the critical temperature and heat capacity critical amplitude are analysed.

Keywords: *n-alkane, critical phenomena, dimethyl carbonate, critical temperature, heat capacity, two-scale factor universality*

Introduction

The thermodynamic properties of dialkyl carbonate+alkane binary systems have been extensively studied in last years [1–9]. Due to the polar character of dialkyl carbonates and the non-polarity of alkanes, these systems often present liquid–liquid equilibria. At experimental conditions close to the critical point, long-range concentration fluctuations appear [10] that produce some thermodynamic quantities, as isobaric heat capacity per unit volume C_pV^{-1}, to have an anomalous behaviour. This property exhibits near the critical point a divergence according to:

$$C_pV^{-1}=B+Et+(A^{\pm}/\alpha)t^{-\alpha} \quad (1)$$

where $t=|T-T_c|/T_c$, T_c denotes critical temperature and B, E and A^+, A^- and α are fitting parameters. The minus sign denotes the heterogeneous phase and the plus one, the homogeneous. The first two terms in Eq. (1) represent the background contribution, important far away from the critical point. The third term is the critical contribution, characterised by the amplitude $A^{\pm}$ and the exponent α, which is a system-independent, universal quantity. Its value was yielded both from theory and experiments showing a very good agreement between both sources. At present its accepted value is α=0.110 [10, 11]. On the other hand, although the ratio A^+/A^- is also an universal quantity (A^+/A^-=0.53 for binary liquid mixtures), the amplitudes are not universal and depend on the microscopic characteristics of the system.

The theory of critical phenomena relates the anomaly in C_pV^{-1} to that of the correlation length ξ. This quantity is a measure of the width of the range over which the concentration varies and in homogeneous phase near the critical point it follows the next potential law:

$$\xi=\xi_0^+t^{-\upsilon} \quad (2)$$

where ξ_0^+ is the critical amplitude of the correlation length. The above cited relation between C_pV^{-1} and ξ follows from the universality of the two-scale factor, a dimensionless parameter defined as:

$$X=A^+(\xi_0^+)^3/k_B \quad (3)$$

where k_B is the Boltzmann constant. The value of this parameter for binary liquid mixtures is X=0.019 [12]. Therefore, once A^+ is known, ξ_0^+ can be calculated from Eq. (3) and the non-universal critical behaviour of C_pV^{-1} can be related to a particular, microscopic characteristic of the system.

In this work, C_pV^{-1} was measured for the critical binary mixtures of dimethyl carbonate+(heptane, octane, nonane, decane or tridecane) systems by means of a differential scanning calorimeter in order to study the dependence of non-universal critical quantities on the microscopic details of the systems. From these experimental data, the critical amplitudes A^+ and the critical temperature T_c were determined. With a view on obtaining some information about the microscopic details that could have influence on critical amplitudes, from A^+ values, ξ_0^+ were calculated by means of Eq. (3). Finally, basing on these results, critical amplitude and critical temperature dependencies *vs*. the carbon number of the alkane are analysed and interpreted from a microscopic point of view.

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Experimental

Materials and methods

Dimethyl carbonate, nonane and tridecane (purity>99%) were supplied by Aldrich, heptane and octane (purity>99%), were obtained from Fluka and decane (purity>99%) from Sigma. Their purity was checked by gas chromatography (GC). In order to avoid the presence of moisture traces, all chemicals were stored under molecular sieves from Sigma. Also, the liquids were degassed in an ultrasonic bath prior to use. Mixtures were prepared in a nitrogen atmosphere, using a Mettler AE-240 balance accurate to within $\pm 1\cdot 10^{-5}$ g, and vigorously stirred prior to insertion into the measuring cells. Uncertainty in mole fraction is quoted in $\pm 1\cdot 10^{-4}$.

The critical mole fractions and critical temperatures for the systems dimethyl carbonate+(heptane, octane, nonane, decane or tridecane) have been obtained from [1], being the reported value directly measured or obtained from interpolation or extrapolation from these data (Table 1). Uncertainty in x_c was quoted less than 0.001 for interpolated or directly measured critical mixtures and less than 0.005 for extrapolated ones. Besides, because of the known influence of impurities on the critical temperature of the mixture [13], T_c were experimentally determined from turbidity measurements, verifying that this value agreed with that from calorimetry.

Isobaric heat capacities per unit volume C_pV^{-1} were obtained by using a Setaram micro DSC III differential scanning calorimeter. The experimental methodology for this type of calorimeters has been described in a previous work [14]. The scanning method at the rate of 0.01 K min^{-1} was used to perform the measurements. This rate afforded a reproducibility of ±0.02 mW in the signal and the accuracy in the C_pV^{-1} measurements was estimated to be ±0.005 J K^{-1}g^{-1}cm^{-3}. This value decreases when we approach to the critical point, due to the difficulties inherent to experimentation in the critical region. The procedure was less reliable in the two-phase region, as the calorimeter design did not allow the mixture to be stirred. The temperature was measured to within ±0.002 K with a platinum resistance thermometer. The accuracy of this type of measurements (DSC) for determination of A^+ near the liquid–liquid critical point has been shown in previous works [15, 16]. 1-Butanol and toluene were used as calibration liquids, their C_pV^{-1} were obtained from literatures [17–19].

Results and discussion

Fitting procedures

Figure 1 shows C_pV^{-1} values obtained for the binary critical mixtures dimethyl carbonate+(heptane, decane or tridecane). In order to obtain the parameters that appear in Eq. (1), experimental data were fitted following three different approaches. In approach (a), α was fixed to its accepted value α=0.110 and the values of homogeneous and heterogeneous phases were used to obtain T_c. This value was essentially the same than that obtained from turbidity measurements. In approach (b) α is fixed, T_c was set to the value obtained in approach (a), and only the values of the homogeneous phase were used to obtain B, E and A^+. Finally, in approach (c), the information of the homogeneous region was used, T_c was also fixed, and the experimental value of α was obtained. The method (b) is the most precise for the determination of the fitting parameters, since the less accurate information in the heterogeneous region used in the approach (a) makes it a less trustworthy method. The approach (c) presents the same characteristics than (b), but, since α is not fixed, correlation between parameters appears, fact that makes approach (c) less reliable. Since this approach gives the

Table 1 Critical mole fractions and critical temperatures for the systems dimethyl carbonate+alkane

System	x_c	T_c/K	Source
Dimethyl carbonate+heptane	0.586	267.458	
Dimethyl carbonate+octane	0.621	274.174	extrapolated
Dimethyl carbonate+nonane	0.653	280.564	
Dimethyl carbonate+decane	0.667	287.266	[20]
Dimethyl carbonate+undecane	0.710	292.371	interpolated
Dimethyl carbonate+dodecane	0.738	297.82	[1]
Dimethyl carbonate+tridecane	0.756	302.876	interpolated
Dimethyl carbonate+tetradecane	0.783	307.61	[1]*
Dimethyl carbonate+hexadecane	0.814	316.21	

*These systems have not been analyzed in this work due to their high critical temperatures, but their critical coordinates have been used to make the estimations (interpolations and extrapolations)

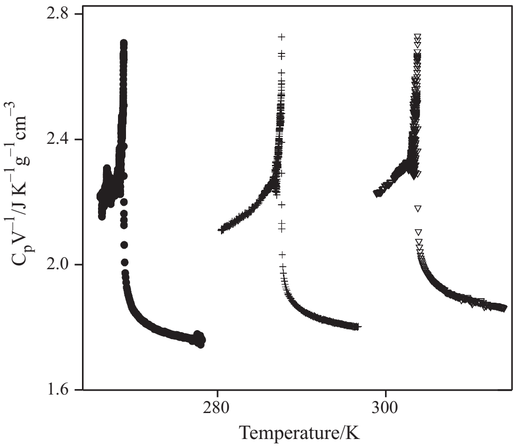

Fig. 1 Heat capacity per unit volume C_pV^{-1} of dimethyl carbonate+alkane: ● – heptane, + – decane and ▽ – tridecane in the critical region along an isobaric path

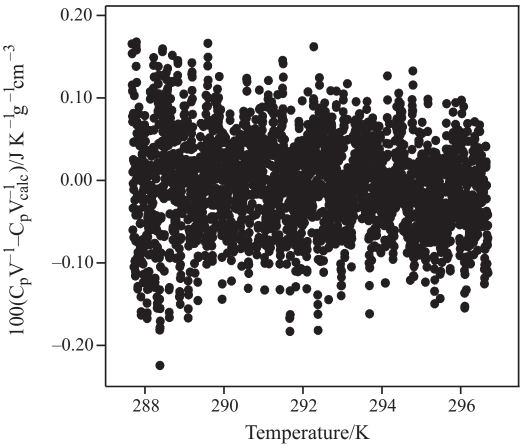

Fig. 2 Residuals for the heat capacity per unit of volume for the dimethyl carbonate+decane critical mixture in one-phase region calculated from Eq. (1)

experimental value of α, a value close to the accepted one for this critical exponent shows that the data are accurate and therefore, the value obtained for A^+ (the main aim of this fitting procedure) should be correct. Figure 2 presents the relative deviation of experimental data from the fit obtained in approach (b) for the dimethyl carbonate+decane critical mixture; random values are observed, which indicate the reliability of the fitting procedure.

Table 2 shows the values of the coefficients as well as the standard deviations of the fits to Eq. (1). This table gives also the values ξ_0^+ obtained from Eq. (3). These results reveal the precision and reliability of the experimental values, since the experimental critical exponents present values very near to the theoretical one. Although critical temperatures are higher than those obtained from literature (Table 1), the dimethyl carbonate+decane system presents a very good coherence between experimental value of its critical amplitude A^+=0.0263 J K^{-1} cm^{-3}, and the literature one, A^+=0.0249 J K^{-1} cm^{-3} [20], fact that confirms the reliability of the methodology used in the heat capacity amplitude determination.

Figures 3 and 4 show the dependencies of A^+ and T_c on the length of the alkane for dimethyl carbonate+alkane systems. It must be noted that, in addition

Table 2 Fitting parameters of Eq. (1) and standard deviations *s* for dimethyl carbonate-alkane critical mixtures

Fit	B	E	A^+	A^-	α	s	ξ_0^+	T_c
				Dimethyl carbonate+heptane				
(a)	1.427	0.94	0.0258	0.0496	fixed	0.03		
(b)	1.39	$4\cdot10^{-5}$	0.028		0.113	0.003		268.873
(c)	1.417	$7\cdot10^{-5}$	0.0262		fixed	0.007	0.215	
				Dimethyl carbonate+octane				
(a)	1.502	2.3	0.0247	0.0475	fixed	0.05		
(b)	1.50	$7\cdot10^{-4}$	0.026		0.111	0.005		275.387
(c)	1.485	$8\cdot10^{-4}$	0.0263		fixed	0.004	0.215	
				Dimethyl carbonate+nonane				
(a)	1.523	1.2	0.0241	0.0464	fixed	0.03		
(b)	1.47	$1.2\cdot10^{-4}$	0.027		0.113	0.002		281.670
(c)	1.468	$6\cdot10^{-6}$	0.0274		fixed	0.002	0.212	
				Dimethyl carbonate+decane				
(a)	1.475	1.75	0.0243	0.0468	fixed	0.04		
(b)	1.46	0.02	0.026		0.110	0.004		287.600
(c)	1.450	$6\cdot10^{-2}$	0.0263		fixed	0.002	0.215	
				Dimethyl carbonate+tridecane				
(a)	1.609	–1.5	0.0218	0.0420	fixed	0.05		
(b)	1.52	$1.5\cdot10^{-3}$	0.026		0.109	0.004		303.772
(c)	1.515	$5\cdot10^{-4}$	0.0266		fixed	0.003	0.214	

B, *E*, A^+ and A^- are in J K^{-1} cm^{-3} and ξ_0^+ in nm. The fixed value of α is 0.110

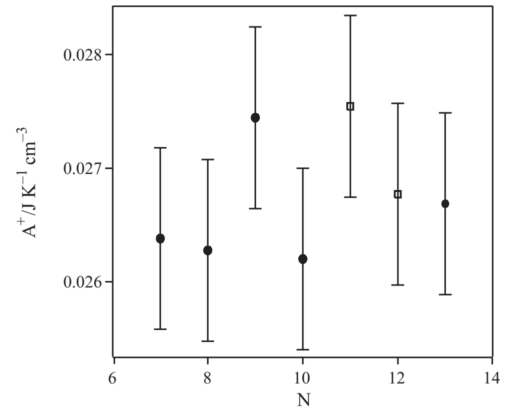

Fig. 3 Critical amplitudes A^+, as a function of the length of the alkane chain (n). □ – literature data [21] for dimethyl carbonate+(undecane or dodecane) critical mixtures

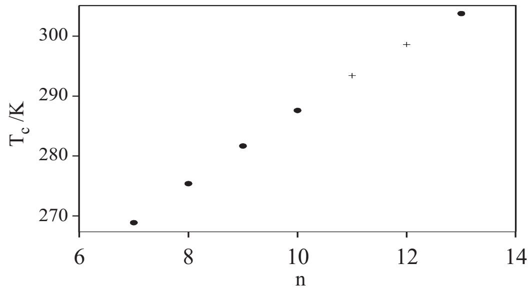

Fig. 4 Critical temperature as a function of the length of the alkane chain (n). + – Literature data [21] for dimethyl carbonate+(undecane or dodecane) critical mixtures

to the data obtained in this work, these figures show data for dimethyl carbonate+undecane and dimethyl carbonate+dodecane critical mixtures, reported in a previous work [21]. Critical amplitude A^+ does not exhibit any dependence against carbon number of the alkane within the experimental uncertainty; As regards to T_c, it increases as carbon number increases in an almost linear way. Since, through Eq. (3) A^+ is related to correlation length, quantity which can be connected to the average interaction diameter [22], it can be concluded that it is not affected by the increment of alkane length, fact which can be ascribed to the longer range of the dipolar interaction between carbonate molecules than that of dispersive interactions between alkane molecules; the former is not significantly affected by an increment in the alkane chain, which makes A^+ not to vary. As for T_c dependence *vs.* carbon number, it follows from the fact that, as alkane length is higher, attractive interactions between its molecules become higher, whereas interactions between alkane and carbonate ones remain almost unchanging; therefore, forces between like molecules increase as regards to those between unlike ones, which makes phase separation to take place easier.

Conclusions

The behaviour of C_pV^{-1} for the critical mixtures of dimethyl carbonate+alkane systems was studied in order to improve the knowledge about the critical behaviour of liquid binary mixtures near a critical demixing point. The dependencies of the critical quantities A^+ and T_c *vs.* the carbon number of the alkane are analysed: A^+ does not show, within the experimental uncertainty, any clear dependency *vs.* the carbon number of the alkane. On the other hand, T_c shows an almost linear positive dependency *vs.* the carbon number. These tendencies can be ascribed to the long-ranged dipolar interaction between carbonate molecules and to the stronger interactions that appears between alkane molecules as the alkane length increases.

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