



# Thermodynamic properties of cyclohexane–methanol liquid mixture from shear viscosity measurements



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## ABSTRACT

The binary liquid mixture cyclohexane–methanol has an upper critical point at a mass composition of 27.5% of methanol and critical temperature  $T_c = 319.608 \pm 0.234$  K. The shear viscosity and density of this system have been carried out as a function of temperature, under atmospheric pressure, over the composition range along the coexistence curve above the transition temperature. From these experimental data values, various thermodynamic parameters, namely, Gibbs energy ( $\Delta G$ ), enthalpy and entropy activation parameters  $\Delta H$  and  $\Delta S$ , the excess molar volume ( $V^E$ ), excess Gibbs energy ( $\Delta G^E$ ), viscosity deviations ( $\Delta \eta$ ) and the activation energy ( $E_{av}$ ) have been calculated and fitted to Redlich–Kister equation. Furthermore, in the one-phase region just above  $T_c$  of the critical binary fluid, the viscosity measurements yield to an enhancement as expected for Ising criticality with a crossover to regular behavior. The regular background is obtained by interpolation from the measurements at non-critical concentrations. The viscosity has been also correlated with the equation of Grunberg–Nissan, Hind et al., Katti–Chaudhri, Heric–Brewer, McAllister, Auslander and Acree–Jouyban.

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## 1. Introduction

Researches on the physico-chemical properties of liquid–liquid mixture have attempted to understand the thermodynamic behavior and transport properties. In previous papers [1–6], we have reported experimental data on macroscopic properties such as densities, viscosities, refractive indexes and specific electrical conductivities for water–isobutyric acid, water–triethylamine and water–1,4-dioxane binary liquids. From these results, it was found out that there exist specific interactions between the components and the results were influenced by intermolecular association in the medium.

In this paper, we have reported the shear viscosity ( $\eta$ ) and mass densities ( $\rho$ ) data for the binary mixture of cyclohexane–methanol separated into two liquids phases at temperature below its critical temperature  $T_c$ . Since methanol is known to be very hygroscopic and cyclohexane is a non-polar, unassociated molecule, inert hydrocarbon possessing globular structure [7], the choice of (cyclohexane–methanol) for such measurements deserves comment. In the perfectly selected mixture, the densities of the pure fluids would be very close to each other to reduce gravitational effects. In addition, the critical temperature  $T_c$  would be willingly

realized and sufficiently different from the freezing and boiling temperatures of the pure components to allow measurements over a reasonably large temperature range. The cyclohexane–methanol system, which implies a compromise of the requirements listed above, has been studied previously by several works [8–13]. For a better understanding of the physico-chemical properties and the molecular interaction between the components of the mixture binary, density and viscosity are measured in the neighborhood of the critical temperature  $T_c$ , at different temperatures in the single-phase region ( $T > T_c$ ), under atmospheric pressure, along the coexistence curve for methanol mole fraction in the temperature range (321.15–325.15 K). Critical temperature is identified visually in our laboratory to  $T_c = 319.608 \pm 0.234$  K at the critical composition  $C_c = 27.5\%$  of methanol mass fraction [14]. We have investigated the excess molar  $V^E$ , the excess Gibbs energies of activation ( $\Delta G^E$ ), the shear viscosity deviation ( $\Delta \eta$ ) for the system (cyclohexane–methanol) and determined the activation parameters  $\Delta H$  as well as  $\Delta S$  from shear viscosity data over the entire range of mole fraction of methanol at different temperatures on single homogenous phase. These results have been correlated by Redlich–Kister equation. The variation of these properties thermodynamic in terms of the temperature and composition were created to help us understand the nature of interactions between the molecules of the two liquids. This work will also provide a test of various semi-empirical equations to correlate viscosity of binary

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### Nomenclature

$T_t$	Transition temperature (K)
$T_c$	Critical temperature (K)
$t$	Reduce temperature
$E_a$	Activation energy ( $\text{J mol}^{-1}$ )
$\Delta G$	Gibbs energy of activation ( $\text{J mol}^{-1}$ )
$\Delta G^E$	Excess Gibbs energies ( $\text{J mol}^{-1}$ )
$\Delta H$	Enthalpy of activation ( $\text{J mol}^{-1}$ )
$\Delta H^E$	Excess enthalpy of activation ( $\text{J mol}^{-1}$ )
$\Delta S^E$	Excess entropy of activation ( $\text{J mol}^{-1}$ )
$\Delta S$	Entropy of activation ( $\text{J mol}^{-1}$ )
$V^E$	Excess molar volume ( $\text{cm}^3 \text{mol}^{-1}$ )
$V_m$	Molar volume ( $\text{cm}^3 \text{mol}^{-1}$ )
$N_A$	Avogadro's number [ $6.023 \times 10^{23}$ ] molecules/mol
$h$	Planck constante [ $6.624 \times 10^{-27}$ erg s/molecule, $6.624 \times 10^{-25}$ g mm <sup>2</sup> /(s molecule)]
$R$	Gas constant
$x$	Mole fraction
$x_c$	Critical mole fraction
$C_c$	Mass fraction
$M$	Molar mass
Greek letters	
$\rho$	Mass density
$\eta$	Dynamic viscosity
$\beta, \Delta$	Critical exponents
$A_i$	Coefficient parameters

mixtures. The types of used relations are those of Grunberg–Nissan, Hind et al., Katti–Chaudhri, Heric–Brewer, McAllister, Auslander and Acree–Jouyban.

## 2. Materials and methods

The cyclohexane and methanol were purchased from Prolabo without any further purification. All mixtures were prepared from weighed amounts of the pure components. The weight is performed by using an electronic balance with a resolution of  $10^{-3}$  g. The cell, in which the cyclohexane and methanol were mixed together, was immersed in a thermally stabilized water bath with thermal regulation in the order of  $10^{-3}$  K over hours. The temperature was measured by using a quartz thermometer giving a resolution of  $\pm 10^{-3}$  K (Table 1).

### 2.1. Density measurement

The mass density of the samples were measured by means of an Anton Paar digital oscillating U-tube densitometer (model DMA 4500) and samples were observed with a reproducibility of  $\pm 2 \times 10^{-5}$  g cm<sup>-3</sup>. The apparatus has been calibrated by using the published density values in Ref. [15,16].

### 2.2. Viscosity measurement

The kinematic viscosities of the cyclohexane–methanol mixtures were measured with an Ubbelohde viscometers suspended in

**Table 1**

A brief summary of the purity of the used materials.

Compound	CAS registry number	Formula	Supplier	Mass fraction purity
Cyclohexane	110-82-7	C <sub>6</sub> H <sub>12</sub>	Prolabo	0.998
Methanol	67-56-1	CH <sub>4</sub> O		

a thermostatically controlled water bath at the required temperature. The viscometer was calibrated using viscosity values taken from published values [17]. An average of four or five sets of flow times were taken for each liquid and liquid mixture. The measured values of kinematic viscosities were converted into dynamic viscosities  $\eta$  after multiplication by the density. The flow–time measurements were made with an electronic stopwatch having a precision of the order of 0.01 s (Table 2).

## 3. Theoretical background and coexistence curves

Phase transitions in fluids that are driven by short-range interactions belong to the Ising universality class. However, the simple power laws involving the universal critical Ising exponents are valid in only the asymptotic region near the critical point [29,30].

In binary mixtures, the parameter  $M$  can be chosen as the difference  $M_{u,l} = y_{u,l} - y_c$  of the composition difference of one component between the upper (u) or lower (l) phases of one component and its critical value  $\beta$ . The superscripts (u) or (l) refer to the phase above or below the meniscus in the earth's gravity field. We write the reduced temperature as  $t = 1 - T/T_c$ . The composition  $y$  of one component can be written as [2,31]

$$y_{u,l} = y_c \pm Bt^\beta(1 + b_1t^\Delta + E_yt^\omega) \quad (1)$$

The sign  $\pm$  corresponds to the phases upper (u) or lower (l).

In Eq. (1), the fraction  $y_c$  is the critical composition,  $B$  is the coexistence curve amplitude,  $b_1$  is the first order correction to scaling amplitude and  $E_y$  is the amplitude. The  $y_c$ ,  $B$ ,  $b_1$  and  $E_y$  are adjustable. The exponent  $\beta$  has either been free or fixed at the theoretical value 0.325 for the system “cyclohexane–methanol”. The exponent  $\omega$  was forced to equal unity,  $\omega = [05, 1]$ . The exponent  $\Delta$  was set to the value 0.5.

In the region not too far from the critical point, power series corrections to the asymptotic power laws may suffice. Then, the prediction for the existence curve involves a power law near critical temperature,  $T_c$ , with the exponent plus non-analytical corrections [32–34] far from  $T_c$ , the whole enabling the composition difference on one composition between the upper (u) and lower (l) phases involving the reduced temperature,  $t$ , can be described by the following equation:

$$|y_l - y_u| = Bt^\beta(1 + b_1t^{0.5} + b_2t + \dots) \quad (2)$$

**Table 2**

Comparison of experimental densities ' $\rho$ ' and viscosities ' $\eta$ ' of pure components with available literature values at  $T = 313.15, 318.15$  and  $323.15$  K and  $p = 101.32$  kPa.

Compounds	T (K)	$\rho$ (g cm <sup>-3</sup> )		$\eta$ (mPa s)	
		Experimental	Literature	Experimental	Literature
Cyclohexane	313.15	0.75941	0.75965 [18] 0.75971 [19]	0.6987	0.6980 [19] 0.7060 [20]
	318.15	0.75460	0.7539 [21]	0.6394	0.6536 [22]
	323.15	0.74976	0.74990 [18] 0.75011 [19]	0.5842	0.59778 [18] 0.6045 [22]
Methanol	313.15	0.77289	0.7729 [23] 0.7726 [24]	0.4501	0.4515 [23] 0.448 [24]
	318.15	0.76809	0.7668 [23] 0.7676 [25]	0.4247	0.4233 [23] 0.4130 [25] 0.4194 [26]
	323.15	0.76324	0.7627 [23,27] 0.76267 [28]	0.4010	0.3950 [23,27]

\* Standard uncertainties ( $u$ ) are  $u(\rho) = 0.00005$  g cm<sup>-3</sup>,  $u(T) = 0.01$  K,  $u(p) = 0.05$  kPa and the combined expanded uncertainty is  $u_c(\eta) = 0.005$  mPa s (level of confidence = 0.95,  $k = 2$ ).

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