



# Densities and viscosities of binary and ternary mixtures of cyclohexanone, 1,4-dioxane and isooctane from $T = (288.15 \text{ to } 313.15) \text{ K}$

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## ABSTRACT

Densities and viscosities of binary and ternary mixtures of cyclohexanone, 1,4-dioxane and isooctane have been measured at temperatures from 288.15 K to 313.15 K and over the entire composition range, under atmospheric pressure. From these binary data, the excess molar volumes have been determined and then fitted to Redlich–Kister equation to determine the appropriate coefficients. This work also provides a test of the Grunberg and Nissan equation for correlation the dynamic viscosities of binary mixtures with mole fractions. The interaction parameters for this equation,  $G_{12}$  were negative for all binary mixtures at different temperatures over entire range of composition which attributed to decreasing the strength of interaction between unlike molecules in mixture.

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## 1. Introduction

Mixtures of solvents are often used in chemistry to modify molecular environment in order to modulate processes such as chromatographic separation, organic synthesis, and reaction kinetics and protein folding [1]. In industrial practice, viscosities of solutions (meaning homogeneous products of dissolution of solids or gases in liquids) and fluid mixtures (meaning homogeneous mixtures resulting out of mixing of two or more fluids) are often needed for the design of the different unit operations and processes involved. In order to get information about the interaction about solvent molecules, physical properties of binary mixtures, such as viscosity are often studied.

While it will be ideal to measure the viscosities of the solutions and mixtures at the conditions of interest, constraints on the availability of time, facilities and expertise, often force the designer to use an estimated value. There are many methods available in the literature for the estimation of the viscosity of solutions and mixtures [2–7].

For estimating thermodynamic excess properties (excess volume, excess enthalpy, and excess free energy) of multicomponent solutions, there are proposed semi-empirical equations [8–10]. There are also a number of equations and methods for evaluating deviation of thermodynamic properties in multicomponent systems, such as Redlich–Kister equation [11], for binary systems and Cibulka [12], Singh [13], Nagata and Sakura [14] equations, for ternary systems.

In this work, to continue and extend our previous studies [15,16] of interactions in liquid mixtures, we focus on the viscosity and volumetric measurements of the binary and ternary mixtures of cyclohexanone, 1,4-dioxane and isooctane at  $T = 288.15 \text{ K}$  to  $313.15 \text{ K}$  and over the whole composition range for the liquid region and at ambient pressure. Cyclohexanone is useful in organic synthesis and used as precursor to Nylon 6,6 [17]. Dioxane is used as a stabilizer for trichloroethane for storage and transport [18] and isooctane (2,2,4-trimethylpentane) is the standard for 100 points on the octane rating scale, it is an important component of gasoline which used in large proportions to increase the knock resistance of the fuel [19].

This type of study is important because the viscosity of liquids mixtures provide information that is required to solve chemical engineering problems related to heat transfer, mass transfer and fluid flow.

The work will provide a test of the Grunberg and Nissan [20] interaction model correlating the kinematic viscosities of binary liquid mixtures with mole fractions. Viscosity deviations and the excess molar volumes of the binary mixtures were correlated using the Redlich–Kister's equation and the fitting parameters are calculated.

## 2. Experimental

### 2.1. Materials

Extra pure cyclohexanone (mass fraction purity > 0.99 Merck), 1,4-dioxane, (mass fraction purity > 0.99 Merck), and isooctane (mass fraction purity > 0.995 Merck) were used. The purities of

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all the chemicals were checked by gas Chromatography using a semi capillary methyl silicon column (outer diameter 530  $\mu\text{m}$ ). The solvents were degassed by ultrasound and dried over molecular sieves (Sigma Union Carbide, 0.4 nm). See table 1a.

## 2.2. Apparatus and procedures

The mixtures for the measurement of densities and viscosities were prepared with certain mole fractions. In order to prevent any probable interference by air, all the properties were measured simultaneously. All binary and ternary mixtures were prepared by mass; the mass measurements were made using an electronic balance (AB 204-N Mettler) accurate to  $\pm 0.01$  mg. The uncertainty in mole fractions is estimated to be lower than  $\pm(2 \times 10^{-4})$ . Densities were measured by an Anton Paar DMA-58 vibrating tube densimeter. Before each series of measurements, the densimeter was calibrated with bidistilled and deionized water and dry air at atmospheric pressure. By the means of Ubbelohde-type viscometer through a Schott-Gerate AVS 450 viscosity measuring system kinematic viscosity,  $\nu$ , of all mixtures was measured. The temperatures control of the capillary was provided by a Schott-Gerate CT 1650 thermostatic bath maintained to  $\pm 0.01$  K. Cell constant was determined separately with pure solvents and bidistilled-deionized water. The uncertainties of the density and viscosity measurements were  $\pm 2 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}$  and  $\pm 2 \times 10^{-4} \text{ mPa}\cdot\text{s}$ . Data processing and curve fitting were made by minitab version 15 and Sigma plot version 9-01. The details of the methods and techniques of the measurements have been described earlier [14–16].

## 3. Results and discussion

Tables 1 and 2 list the experimental kinematic viscosities and densities of the three pure solvents and their 27 binary and 33 ternary mixtures, along with their compositions expressed as mole

fractions ( $x_i$ ), at different temperatures. As can be seen in table 1, the agreement between our reported values and the literature for pure components is well. The viscosity deviations,  $\Delta\eta$ , for binary and ternary mixtures were determined using the equation:

$$\Delta\eta = \eta_{\text{mix}} - \sum_i^N (\eta_i x_i), \quad (1)$$

where  $\eta_{\text{mix}}$  is the viscosity of the mixture;  $\eta_i$  is the absolute viscosity of pure component  $i$ ;  $x_i$  is the mole fraction of component  $i$ ; and  $N$  is the number of components in the mixture. The viscosity deviations for three binary mixtures are depicted in figures 1–3.

The viscosity deviations for binary mixtures were fitted to a Redlich–Kister equation. In this equation,  $\Delta Q_{ij}$  (viscosity deviation) and  $A_p$  (fitting coefficients) can be obtained by the least-squares method for each isotherm (table 3).

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^M A_p (x_i - x_j)^p, \quad (2)$$

where  $\Delta Q_{ij}$  is the viscosity deviation or any other properties deviations,  $x$  is the mole fraction,  $A_p$  is the fitting parameter, and  $M$  is the degree of the polynomial expansion.

The excess molar volume  $V_m^E$  can be calculated from:

$$V_m^E = \sum \left( \frac{1}{\rho} - \frac{1}{\rho_i} \right) x_i M_i, \quad (3)$$

where  $\rho$  is the density of mixture and  $x_i$ ,  $M_i$  and  $\rho_i$  are mole fraction, molar mass and density of pure components, respectively. This quantity is fitted to a Redlich–Kister-type equation showed above in equation (2), in which  $V_m^E$  is used as  $\Delta Q_{ij}$ . The fitting coefficients  $A_p$  for binary mixtures at various temperatures along with the corresponding determination coefficients ( $R_{\text{sq}}$  values) are depicted in table 4.

The dependence of  $V_m^E$  on temperature and composition can be explained as a balance between positive and negative contributions. The positive contributions come from dispersion forces and weak dipole-dipole interaction between unlike molecules. The negative contribution results from specific interactions including charge transfer and structural contributions of the geometrical fitting of one component into another due to a difference in molar volumes. Figures 4–6 demonstrate the comparison of our calculated values for the molar excess volumes,  $V_m^E$ , in binary mixtures

**TABLE 1a**  
Sample provenance and purity.

Component	Source	Mass fraction purity
Cyclohexanone	Merck	0.99
1,4-Dioxane	Merck	0.99
Isooctane	Merck	0.995

**TABLE 1**  
Densities  $\rho$  and viscosities  $\eta$  of pure components at several temperatures.<sup>23–26</sup>

Component	T/K	$10^{-3} \rho / \text{kg}\cdot\text{m}^{-3}$		$\eta / \text{mPa}\cdot\text{s}$	
		This work	Literature	This work	Literature
Cyclohexanone	288.15	0.9537		2.5990	
	293.15	0.9495		2.3318	
	298.15	0.9452	0.9418 <sup>23</sup> , 0.9420 <sup>27</sup> , 0.94215 <sup>28</sup>	2.1016	2.0205 <sup>23</sup> , 2.229 <sup>27</sup> , 1.819 <sup>29</sup>
	303.15	0.9403	0.9374 <sup>27</sup>	1.9045	1.799 <sup>27</sup>
	308.15	0.9357	0.9365 <sup>23</sup> , 0.9328 <sup>27</sup>	1.7338	1.5849 <sup>23</sup> , 1.635 <sup>27</sup>
	313.15	0.9311		1.5842	
1,4-Dioxane	288.15	1.0391		1.4381	
	293.15	1.0337		1.3111	
	298.15	1.0281	1.02792 <sup>28</sup> , 1.0280 <sup>24</sup>	1.2023	1.1770 <sup>24</sup>
	303.15	1.0223	1.0222 <sup>25</sup>	1.1065	1.0937 <sup>25</sup>
	308.15	1.0170		1.0219	
	313.15	1.0106		0.9477	
Isooctane	288.15	0.6962		0.5439	
	293.15	0.6921		0.5125	
	298.15	0.6883	0.6878 <sup>26</sup> , 0.6879 <sup>27</sup> , 0.6875 <sup>29</sup>	0.4844	0.492 <sup>27</sup> , 0.496 <sup>29</sup>
	303.15	0.6842	0.6837 <sup>26</sup> , 0.6836 <sup>27</sup>	0.4586	0.4360 <sup>27</sup> , 0.466 <sup>27</sup>
	308.15	0.6796	0.6801 <sup>26</sup> , 0.6793 <sup>27</sup>	0.4216	0.441 <sup>27</sup>
	313.15	0.6755	0.6754 <sup>26</sup>	0.4130	0.3910 <sup>27</sup>

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