



Effect of temperature and composition on the density, refractive index, and excess quantities of binary mixtures of 2,4,6,8-tetramethyl-2,4,6,8-tetraethenylcyclotetrasiloxane with aromatic hydrocarbons

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ABSTRACT

Density and refractive index were determined for the binary mixtures containing 2,4,6,8-tetramethyl-2,4,6,8-tetraethenylcyclotetrasiloxane (D_4^{VI}) and aromatic hydrocarbons (ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene) at five temperatures (288.15, 298.15, 308.15, 318.15, and 328.15) K and atmospheric pressure by a DMA4500&RXA170 combined system. The density and refractive index correlations for these systems were tested by an empirical second order polynomial and by the Lorentz–Lorenz equation. Excess molar volumes were calculated and correlated by the Redlich–Kister equation and the Legendre polynomials. The values of the volume expansivity (coefficient of thermal expansion) of pure chemicals and four binary solutions were estimated from temperature dependence of densities. Values of partial excess volumes at infinite dilution for these four binary systems at different temperatures were calculated either from the adjustable parameters of Redlich–Kister smoothing equation or the Legendre polynomials. The deviations in refractive index were calculated and correlated by the Redlich–Kister polynomial expansions. The molar refractions were calculated from the Lorentz–Lorenz equation. The deviations in molar refractions were calculated and correlated by the Redlich–Kister polynomial expansions. Factors affected these excess quantities were discussed. The results obtained indicate that the excess molar volumes, the deviations in refractive index and the deviations in molar reactions at each temperature are negative. The system $\{D_4^{VI}(1) + o\text{-xylene}(2)\}$ exhibits the maximum negative deviations from ideality among these four systems, which is the result of multiple factors such as the partial interstitial accommodation effect, the steric hindrance, the size of molecule and the instantaneous dipole-induced dipole interactions.

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1. Introduction

In recent years, with the gradual depletion of oil resources and their fast rising prices, some synthetic rubbers initiated from oil or natural gas resources will gradually be replaced by silicone rubbers since the latter does not depend on the oil or natural gas resources at all. On the other hand, since the structural parameters of the Si–O bond, such as its length and angle, are quite different from that of C–C, C=C or triple bond, therefore, compared with other synthetic polymers, silicone based polymers possess incomparable physical and chemical properties such as excellent resistance to oxygen, ozone, and ultraviolet light. Among all the industrialized silicone intermediates, 2,4,6,8-tetramethyl-2,4,6,8-tetraethenylcyclotetrasiloxane (D_4^{VI} , CAS RN: 2554-06-5) is currently one of the most important intermediates and its annual consumption is ranked in the second place in silicone industry. The

molecule structure of D_4^{VI} is presented in figure 1. The most significant application of D_4^{VI} is that they can be used produce the matrix for various silicone oils, rubbers or silicone resins, which is achieved through copolymerization with octamethylcyclotetrasiloxane (D_4) or other monomers conducted in bulk or in the solution. The presence of vinyl groups as substituents along the siloxane polymer chain is crucial to the vulcanization of silicone elastomers, whether the elastomer is peroxide cured or whether the elastomer is cured through the Pt-catalyzed hydrosilylation reaction between a silanehydride crosslinker and the vinyl groups.

Cyclosiloxanes form a series of non polar compounds and they can dissolve completely in aromatic hydrocarbons, therefore, some special silicone polymers are prepared by means of solution polymerization and these solvents are selected as the reaction media. Among these solvents, ethylbenzene and xylene isomers are preferred due to their low toxicity relative to benzene or toluene. These four solvents are also of great importance in the petrochemical industry, because they are the main basis for the manufacture of many organic compounds.

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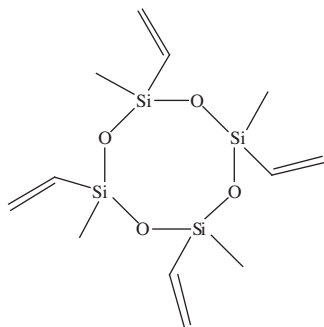


FIGURE 1. Structure of 2,4,6,8-tetramethyl-2,4,6,8-tetraethenylcyclotetrasiloxane.

TABLE 1
Sample table.

Chemical name	Source	Final mole fraction purity	Analysis method
Ethylbenzene	Alfa Aesar	0.999	GC ^b
<i>o</i> -Xylene	Alfa Aesar	0.999	GC ^b
<i>m</i> -Xylene	Alfa Aesar	0.999	GC ^b
<i>p</i> -Xylene	Alfa Aesar	0.999	GC ^b
D_4^{VIa}	Guangdong Xibo	0.995	GC ^b

^a $D_4^{VI} = 2, 4, 6, 8$ -tetramethyl-2, 4, 6, 8-tetraethenylcyclotetrasiloxane.

^b Gas–liquid chromatography.

It is known that the mixing of different compounds gives rise to properties such as volume, enthalpy and entropy of mixing, which reflect the extent of the deviations from non-ideality. The excess properties are necessary for the design and calculation of the chemical engineering process involving substance separation, heat transfer, mass transfer and fluid flow [1]. The information about the excess properties of liquid mixtures containing D_4^{VI} and aromatic compounds, and their dependence on composition and temperature are very important fundamental data for their applications in the separation fields. To date, many studies have been focused on binary or ternary systems consisted of Ionic Liquids (ILs) or H-bond containing chemicals such as alcohols with non-polar or polar solvents [2–7]. With these studies, some important factors responsible for the positive or negative deviations from ideality for binary polar–polar or non-polar–polar systems have been discussed. However, a survey of the literature shows that very few reports have ever been made on the excess quantities for binary solutions of cyclosiloxanes with aromatic hydrocarbons.

To conduct research on excess quantities of binary mixtures of cyclosiloxane with aromatic hydrocarbons and to investigate the interactions that take place between solute–solute, solute–solvent, and solvent–solvent for binary non-polar systems, here we measured the densities and the refraction index for the binary systems of D_4^{VI} with aromatic hydrocarbon (ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene) at $T = (288.15, 298.15, 308.15, 318.15, \text{ and } 328.15) \text{ K}$ and atmospheric pressure. The volume expansivity (α), excess molar volume (V_m^E), molar refraction (R_m), the deviations in refractive index (Δn_D) and the deviations in molar refraction (ΔR_m) for these four binary systems were calculated and further correlated with the Redlich–Kister equation and the Legendre polynomials.

2. Experimental

2.1. Chemicals and materials

The material, 2,4,6,8-tetramethyl-2,4,6,8-tetraethenylcyclotetrasiloxane (D_4^{VI}), was obtained from commercial sources and purified

TABLE 2

Values of experimental density (ρ) and refractive index (n_D) of the pure liquid components and literature values at $T = (293.15 \text{ or } 298.15) \text{ K}$ and atmospheric atmosphere.

	$\rho / \text{g} \cdot \text{cm}^{-3}$		n_D	
	Exp.	Lit.	Exp.	Lit.
D_4^{VI} ^a	0.98765	0.9875 [8]	1.43415	1.4342 [12]
Ethylbenzene	0.86255	0.86255 [9]	1.49297	1.49304 [13]
<i>o</i> -Xylene	0.87567	0.87557 [10]	1.50257	1.50262 [14]
<i>m</i> -Xylene	0.85983	0.85980 [11]	1.49444	1.49455 [15]
<i>p</i> -Xylene	0.85662	0.85670 [11]	1.49298	1.49312 [14]

^a Literature values for D_4^{VI} provided at $T = 293.15 \text{ K}$. Standard uncertainties u are $u(T) = 0.01 \text{ K}$, the combined expanded uncertainties U_c are $U_c(\rho) = 0.00005 \text{ g} \cdot \text{cm}^{-3}$, and $U_c(n_D) = 0.00004$.

by a vacuum distillation method. Ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene were provided by Alfa Aesar. All chemicals above were dried with molecular sieves of $4 \cdot 10^{-10} \text{ m}$ and filtrated through a filter ($0.45 \mu\text{m}$). The purities of these chemicals were confirmed by a gas–liquid chromatography (table 1). Before use, all chemicals were degassed in an ultrasonic bath. The density and the index of refractive measurements for all solvents conducted at $T = (293.15 \text{ or } 298.15) \text{ K}$ are listed in table 2 and compared with those in the literature [8–15].

All of the binary solutions were prepared in airtight stopped glass bottles to prevent evaporation. Masses of these samples were determined by weighing on an analytical balance (Sartorius, model BS 224S, $\pm 0.1 \text{ mg}$). The uncertainty in the determination of the molar fraction basis and the volume fraction basis are about 0.0001.

2.2. Density and refractive index measurements

The density and refractive index values of pure components and their mixtures at different temperatures were automatically analyzed at atmospheric pressure by a DMA4500&RXA170 combined system (Anton Paar) with a density uncertainty of $\pm 0.00005 \text{ g} \cdot \text{cm}^{-3}$ and a refractive index uncertainty of $\pm 0.00004 n_D$. The combined system was calibrated periodically with ultra-pure water and dry air [16]. Two integrated Pt 100 platinum thermometers ($u_r(T) = 0.01$) together with Peltier elements provide an extremely precise thermostating of the sample. The estimated uncertainty of V_m^E is about $0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$. The uncertainty in the calculation of the deviations in refractive index Δn_D , the molar refraction R_m and the deviations in molar refraction ΔR_m were estimated to be 0.00004 , $0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $0.001 \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively.

3. Results and discussion

3.1. Volume expansivity of pure components

The temperature dependence of experimental densities for the four binary systems studied is presented in table 3 and graphically shown in figure 2. One can observe that the density decreases as both temperature and D_4^{VI} composition in the systems increase.

The volume expansivity (coefficient of thermal expansion), α , defined by equation (1), can be calculated from the density–temperature dependence,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (1)$$

If an elemental transformation is performed on the right-hand term in equation (1), then this equation can also be expressed as $-(\partial \ln \rho / \partial T)_p$. When $\ln \rho$ is plotted against temperature and fitted by a straight line, the correlation coefficients (R^2) and standard

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