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The density, refractive index, and thermodynamic behaviour of binary mixtures of 1,3-Diethenyl-1,1,3,3-tetramethyldisiloxane with aromatic hydrocarbons

Lijiao Yu, Hong Dong*, Chuan Wu*, Yindi Zhang

Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China

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ABSTRACT

Density and refractive index were measured for the binary mixtures composed of 1,3-Diethenyl-1,1,3,3-tetramethyldisiloxane and aromatic hydrocarbons (methoxybenzene, ethylbenzene, chlorobenzene, fluorobenzene and nitrobenzene) at five temperatures (283.15, 288.15, 293.15, 298.15, and 303.15) K and atmospheric pressure by a DMA4500&RXA170 combined system. Excess molar volumes were calculated and correlated by the Legendre polynomials. The isobaric coefficients of thermal expansion and excess isobaric coefficients of thermal expansion of five binary solutions were estimated from temperature dependence of densities. Values of partial excess volumes at infinite dilution and excess refraction indices for these five binary systems at different temperature were calculated from the adjustable parameters of the Legendre polynomials. The molar refractions were calculated from the Lorentz–Lorenz equation. Factors affected these excess quantities were discussed.

1. Introduction

As one of the most important chemicals, 1,3-Diethenyl-1,1,3,3-tetramethyldisiloxane (DETMDS, CAS RN: 2627-95-4) is widely used in the silicone industry and its structure is shown in figure 1. It is a kind of active siloxane containing silicon–vinyl bond and thus plays an important role in synthesizing vinyl terminated silicone oil, rubbers or silicone resins. The presence of vinyl groups is crucial to the vulcanization of silicone elastomers, whether the elastomer is peroxide cured or whether the elastomer is cured through the Pt-catalysed hydrosilylation reaction between a silicon hydride crosslinker and the vinyl groups.

Siloxane 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. Information about the physical properties of the pure liquids and the liquid mixtures containing aromatic hydrocarbons and their dependence on composition and temperature is very important basic information required for extraction and separation processes in petrochemical industry [1]. From a practical point of view, liquid mixtures containing organo-silicon compound and aromatic hydrocarbons seem to be very interesting.

Knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in the design process (flow, mass transfer, or heat transfer calculations) of many chemical and industrial processes [2]. The information about thermodynamic and optical properties of liquid mixtures containing DETMDS and aromatic compounds, and their dependence on compositions and temperature are very important fundamental data for their applications in the separation fields. But a literature review on thermodynamic and optical properties of binary mixtures containing siloxane and aromatic hydrocarbon reveals that the databases are limited. As a continuation of our previous research on thermodynamic and optical behaviour of binary mixtures composed of organo-silicon compound and organic liquid mixtures [3,4], the present article is focus on thermodynamic and optical properties of binary mixtures composed of DETMDS and the substituted monocyclic aromatic liquids.

In an effort to investigate molecular interactions between five monocyclic substituted aromatics and DETMDS, here we measured the densities and the refraction index for these five binary systems, namely, DETMDS with methoxybenzene, ethylbenzene, chlorobenzene, fluorobenzene and nitrobenzene, at $T = (283.15, 288.15, 293.15, 298.15$ and $303.15)$ K and atmospheric pressure. Isobaric coefficients of thermal expansion (α), excess molar volumes (V_m^E), excess refractive index (n^E) and molar refractions (R_m) for these five binary systems were calculated and further correlated.

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* Corresponding authors. Tel.: +86 571 28867861; fax: +86 571 28865135.
E-mail addresses: donghong1686@hotmail.com (H. Dong), chaunwu@yahoo.com (C. Wu).

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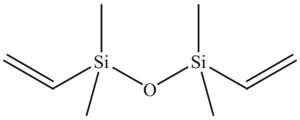

FIGURE 1. Structure of 1,3-Diethenyl-1,1,3,3-tetramethyldisiloxane.

TABLE 1
Sample description.

Chemical name	CAS registry number	Source	Mass fraction purity[a]	Mass fraction of water[b]
Methoxybenzene	100-66-3	Sigma	0.999	0.0004
Ethylbenzene	100-41-4	Alfa aesar	0.999	0.0004
Chlorobenzene	108-90-7	Sigma	0.999	0.0003
Fluorobenzene	462-06-6	TCI	0.999	0.0005
Nitrobenzene	98-95-3	Acros	0.999	0.0006
1,3-Diethenyl-1,1,3,3-tetramethyldisiloxane	2627-95-4	Shanghai Huazhirun	0.996	0.0005

[a] Determined by gas chromatography (GC).
[b] Measured by Karl Fischer moisture titrator.

2. Experimental

2.1. Chemicals and materials

DETMDS was obtained from Shanghai Huazhirun Chemical Industrial Company Ltd. and purified by a vacuum distillation method. Methoxybenzene and chlorobenzene were provided by Sigma. Ethylbenzene was provided by Alfa Aesar. Fluorobenzene was provided by TCI, and nitrobenzene was provided by Acros. All chemicals above mentioned were dried with molecular sieves of dimension 4×10^{-10} nm and filtrated through a filter (0.45 μm). Their mass fraction purities (table 1) were determined by a gas chromatograph equipped with a HP-5 column and a flame ionisation detector (FID). Water content in the organic solvents listed in table 1 was measured with the Karl–Fischer (K–F) moisture titrator (KF-1, Shanghai Anting Scientific Instrument Factory, China) and reagents for Karl Fischer titration were purchased from Aladdin Reagents (Shanghai) Co., Ltd. Before use, all chemicals were degassed in an ultrasonic bath. The density and the index of refractive measurements for all solvents conducted at $T = (293.15 \text{ or } 298.15)$ K are listed in table 2 and compared to those in the literature [5–14].

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, ±0.1 mg). The uncertainty in the determination on the mole fraction basis and the volume fraction basis are about 0.0001.

TABLE 2
Experimental densities (ρ) and refractive index (n_D) of the pure liquid components and literature values at $T = (293.15 \text{ or } 298.15)$ K and atmospheric atmosphere.

	$\rho/\text{g} \cdot \text{cm}^{-3}$		n_D	
	exp	lit	exp	lit
Methoxybenzene	0.98932	0.98917[5]	1.51460	1.5143[6]
Ethylbenzene	0.86258	0.86258[7]	1.49301	1.49304[8]
Chlorobenzene	1.10116	1.10114[9]	1.52168	1.5219[10]
Fluorobenzene[a]	1.02496	1.0225[11]	1.46284	1.4629[12]
Nitrobenzene	1.19820	1.19864[13]	1.54992	1.5499[10]
1,3-Diethenyl-1,1,3,3-tetramethyldisiloxane[b]	0.81292	0.811[14]	1.41236	1.4123[14]

Standard uncertainties: in temperature $u(T) = 0.01$ K, in density $u(\rho) = 1 \times 10^{-5}$ $\text{g} \cdot \text{cm}^{-3}$, and in refractive index $u(n_D) = 4 \times 10^{-5}$. The combined expanded uncertainty ($k = 2$) for density are $Uc(\rho) = 2 \times 10^{-5}$ $\text{g} \cdot \text{cm}^{-3}$, and for refractive index $Uc(n_D) = 8 \times 10^{-5}$ (95% level of confidence).
[a] Density values for fluorobenzene was provide at $T = 293.15$ K.
[b] All values for 1,3-Diethenyl-1,1,3,3-tetramethyldisiloxane was provide at $T = 293.15$ K.

2.2. Density and refractive index measurements

The density and refractive index values of pure components and their mixtures at different temperatures were automatically analysed at atmospheric pressure by a DMA4500&RXA170 combined system (Anton Paar) with a density uncertainty of ±0.00001 $\text{g} \cdot \text{cm}^{-3}$ and a refractive index uncertainty of ±0.00004 n_D. The combined system was calibrated periodically with ultrapure water and dry air [3]. Two integrated Pt 100 platinum thermometers ($u_r(T) = 0.01$) together with Peltier elements provide an extremely precise thermostatting of the sample. The constancy of the temperature was ±0.05 K. The estimated uncertainty of V_m^E is about $0.004 \text{ cm}^3 \cdot \text{mol}^{-1}$. The uncertainties in the calculation of the excess refractive index n^E, and the molar refraction R_m were estimated to be $(0.00004 \text{ and } 0.006) \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively.

3. Results and discussion

3.1. Thermodynamic properties

3.1.1. Excess molar volume

Densities of the pure components and their binary mixtures with DETMDS are used to determine the excess molar volumes V^E given in table 3 by

$$V_m^E = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2, \tag{1}$$

where x_i, ρ_i, and M_i represents the mole fraction, the density, and the molar mass of the pure component, respectively, while ρ represents the density of the mixture.

The composition dependence of V_m^E can be represented by the Legendre polynomials $L_k(x_1)$ [15] equation:

$$\begin{aligned} V_m^E &= x_1 x_2 \sum_{i=0}^{n} a_k L_k(x_1) \\ &= x_1 x_2 \left[\begin{array}{l} a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1) + a_3(20x_1^3 - 30x_1^2 + 12x_1 - 1) \\ + a_4(70x_1^4 - 140x_1^3 + 90x_1^2 - 20x_1 + 1) \end{array} \right], \end{aligned} \tag{2}$$

where x_1 is the mole fraction of DETMDS, a_i is the adjustable parameter.

Legendre polynomials have the valuable characteristic that for a continuous series of observations (infinite) the values of the coefficients do not change as the number of terms in the series increased [16].

When Legendre polynomials are used to correlate the excess molar volume, their parameters are obtained by the least squares fit method and the results are listed in table 4. The following equation is used to calculate the standard deviations $\sigma(Y)$:

$$\sigma(Y) = \left[\frac{\sum_i^n (Y_{exp} - Y_{cal})^2}{n - m} \right]^{1/2}, \tag{3}$$

where n is the total number of experimental points for each data set and m is the number of coefficients in equation (2). In the present work, the standard deviations between experimental values and the calculated ones for excess molar volume (V_m^E) and the excess refraction index n^E are evaluated using equation (3). The standard deviations of V_m^E for all the binary mixtures are also presented in table 4.

To exhibit the trend of V_m^E with the mole fraction of DETMDS, the excess molar volumes of these five binary systems at different temperatures are graphically presented in figure 2. Similarly, the