J. Chem. Thermodynamics 76 (2014) 45–55

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermophysical properties of binary mixtures of triethoxysilane, methyltriethoxysilane, vinyltriethoxysilane and 3-mercaptopropyltriethoxysilane with ethylbenzene at various temperatures

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

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

ARTICLE INFO

Article history:
Received 18 July 2013
Received in revised form 1 March 2014
Accepted 2 March 2014
Available online 22 March 2014

Keywords:
Organosilicon
Excess molar volume
Thermal expansivity
Molar refraction

ABSTRACT

The density and refractive index were determined for binary mixtures of triethoxysilane, methyltriethoxysilane, vinyltriethoxysilane and 3-mercaptopropyltriethoxysilane with ethylbenzene at different temperatures (T = 288.15, 298.15, 308.15, 318.15 and 328.15 K) and atmospheric pressure using a DMA4500&RXA170 combined system. The excess molar volume (V_m^E), partial excess volume at infinite dilution ($\bar{V}_i^{E,\infty}$), isobaric coefficient of thermal expansion (α), excess squared refraction indices [$(n^2)^E$], Lorentz–Lorenz molar refraction (R_m) and the deviation in molar refraction (ΔR_m) have been calculated using this data. The results have been incorporated into the Redlich–Kister equation and used to estimate the binary interaction parameter and standard deviation. In addition, the excess molar volume (V_m^E) was calculated and correlated using the Legendre polynomials. The value of partial excess volume at infinite dilution ($\bar{V}_i^{E,\infty}$) for these binary systems at different temperatures was calculated from either the adjustable parameters of Redlich–Kister smoothing equation or the Legendre polynomials. The isobaric coefficient of thermal expansion (α) of the binary systems was estimated using the temperature dependence of the densities. The results indicate that the excess molar volumes, excess squared refraction indices and the deviations in molar refractions at each temperature were negative. These phenomena are a result of a number of factors including: the partial interstitial accommodation effect, disruption in the orientational order of the pure components and steric structure.

1. Introduction

Alkoxysilanes are an important class of chemicals in the silicone industry and have been widely used for many applications including: functional materials; silane coupling agents and modifying agents for zeolite nanoparticle supported catalysts. Trialkoxysilanes have the general structure R′Si(OR)$_3$ (where R = alkyl group and R′ = hydrocarbon chain bearing a specific terminal functional group (such as vinyl, epoxy or mercapto group)) [1]. Alkoxysilanes and similar silicon containing compounds are currently the subject of extensive research due to the need for "green" technology in the metal-finishing and the adhesive industries [2]. The use of hydrolysable alkoxy groups to functionalise these compounds is beneficial to improve the physical properties of composite materials such as: filled and reinforced resins; filled elastomers; caulks for adhesion of metal and glass; and resin-coated and painted metal. When used in glass-reinforced plastics, a particularly notable improvement on the materials performance has been achieved [3]. In addition, these compounds also play important roles in the fabrication of organosilicon polymers by exploiting the hydrolysable alkoxy groups present in their structures.

Siloxanes are soluble in aromatic hydrocarbon solvents, therefore the preparation of specialised silicone polymers using solution polymerization use these solvents as a reaction medium. In addition to using siloxanes in solution polymerization, they also function as primers or adhesive promoters when dissolved in a solvent along with other constituents such as silane coupling agents or the transesterification products of a silane coupling agent. Among the aromatic solvents used, ethylbenzene is preferred due to its low toxicity compared to benzene and toluene. For various applications it is fundamental to collect data on the thermophysical properties of liquid mixtures containing organosilicon and

* Corresponding authors. Tel.: +86 571 28867861; fax: +86 571 28865135.
E-mail addresses: donghong1686@hotmail.com (H. Dong), catalyst88@163.com (C. Wu).

http://dx.doi.org/10.1016/j.jct.2014.03.003
0021-9614/

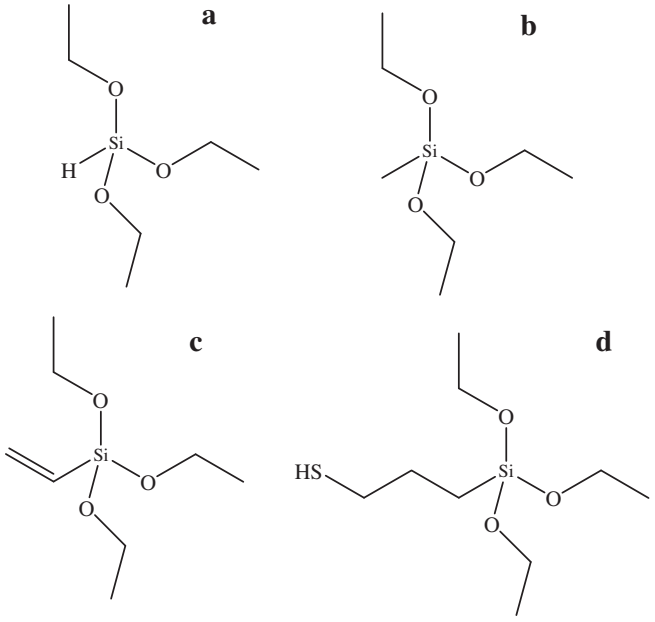

FIGURE 1. Structures of organosilicon compound: (a) triethoxysilane; (b) methyltriethoxysilane; (c) vinyltriethoxysilane; (d) 3-mercaptopropyltriethoxysilane.

aromatic compounds and their dependence on composition and temperature. However, a survey of the literature shows that very few reports have been made on the thermophysical properties of binary solutions of organosilicon compounds and aromatic hydrocarbons. In a continuation of our previous research on binary liquid mixtures composed of organosilicon compounds and organic solvents [4,5], we now report the thermophysical properties of binary mixtures of triethoxysilane, methyltriethoxysilane, vinyltriethoxysilane and 3-mercaptopropyltriethoxysilane with ethylbenzene. The densities and the refractive index for these binary systems at different temperatures $T = (288.15, 298.15, 308.15, 318.15$ and $328.15)$ K and atmospheric pressure were measured. In addition, the isobaric coefficient of thermal expansion (α), excess molar volume (V_m^E), excess squared refraction indices $(n^2)^E$, molar refractions (R_m) and the deviations in molar refraction (ΔR_m) for these binary systems were calculated and further correlated using this data.

2. Experimental section

2.1. Chemicals

Triethoxysilane, methyltriethoxysilane, vinyltriethoxysilane and 3-mercaptopropyltriethoxysilane were purchased from the Qufu Chengguang Chemical Company Ltd. and purified using vacuum distillation. The structures of triethoxysilane, methyltriethoxysilane, vinyltriethoxysilane and 3-mercaptopropyltriethoxysilane are shown in figure 1. Ethylbenzene was purchased from Alfa Aesar and used with no further purification. All chemicals were dried using 4 Å molecular sieves and filtered (0.45 μm) prior to use. The purity of the chemicals was determined by (gas + liquid) chromatography using a HP-5 column and a flame ionisation detector (FID) (see table 1). All chemicals were degassed using an ultrasonic bath prior to use. The density and refractive index were obtained for all solvents at the temperatures, $T = (293.15$ or $298.15)$ K and are compared with those reported in the literature (table 2) [6–12]. The binary solutions were prepared in airtight-stoppered glass bottles to prevent evaporation. The mass of the samples were determined using an analytical balance (Sartorius, model BS 224 S, ±0.1 mg). The uncertainty in the determination of the molar fraction basis and the volume fraction basis was about 0.0001.

2.2. Density and refractive index measurements

The density and refractive index of the pure components and their mixtures at different temperatures were automatically analyzed at 100.705 (±0.020) kPa (Weather bureau of Hangzhou) using a DMA4500&RXA170 combined system (Anton Paar) with a density uncertainty of ±0.00001 $g \cdot cm^{-3}$ and a refractive index uncertainty of ±0.00004 n_D. The combined system was calibrated periodically using ultra pure water and dry air [4]. Two integrated

TABLE 1
Sample description.

Chemical name	CAS registry number	Source	Mass fraction purity	Analysis method
Ethylbenzene	100-41-4	Alfa	0.990	GC[a]
Triethoxysilane	998-30-1	Qufu Chengguang	0.991	GC[a]
Methyltriethoxysilane	2031-67-6	Qufu Chengguang	0.996	GC[a]
Vinyltriethoxysilane	78-08-0	Qufu Chengguang	0.997	GC[a]
(3-mercaptopropyl)triethoxysilane	14814-09-6	Qufu Chengguang	0.995	GC[a]

[a] (Gas + liquid) chromatography.

TABLE 2
Experimental densities (ρ) and refractive index (n_D) of the pure liquid components and literature values at $T = 293.15$ or 298.15 K and 100.705 ± 0.020 kPa.

	ρ/g · cm^{-3}		n_D		Temperature/K
	exp.	lit.	exp.	lit.	
Ethylbenzene	0.86259	0.86258[6]	1.49299	1.49304[7]	298.15
Triethoxysilane	0.88982	0.874[8]	1.37445	1.3751[9]	298.15
Methyltriethoxysilane	0.88962	0.877[10]	1.38068	1.3838-67[10]	298.15
Vinyltriethoxysilane	0.90477	0.9036[11]	1.39664	1.3966[11]	298.15
3-Mercaptopropyltriethoxysilane	0.98406	0.9325[12]	1.43772	1.4331[12]	293.15

Standard uncertainties: in temperature $u(T) = 0.01$ K. The combined expanded uncertainty ($k = 2$) for density are $Uc(\rho) = \pm 2 \cdot 10^{-5}$ g · cm^{-3}, and for refractive index $Uc(n_D) = \pm 8 \cdot 10^{-5}$ (95% level of confidence).