Density, viscosity and excess molar volume of binary mixtures of tri-*n*-octylamine + diluents (*n*-heptane, *n*-octane, *n*-nonane, and *n*-decane) at various temperatures

Sheng Fang [a,*], Xiao-Bo Zuo [a], Xue-Jiao Xu [a], Da-Hai Ren [a,b]

[a] College of Food Science and Biotechnology Engineering, Zhejiang Gongshang University, Hangzhou 310035, China
[b] Department of Chemical & Biomolecular Engineering, Clarkson University, Potsdam, NY 13699-5705, USA

ABSTRACT

Densities (ρ) and viscosities (η) for binary mixtures of tri-*n*-octylamine (TOA) + *n*-heptane, TOA + *n*-octane, TOA + *n*-nonane, and TOA + *n*-decane are determined at *T* (283.15, 293.15, and 303.15) K and atmospheric pressure. The excess molar volume is calculated from the density data and is correlated by a Redlich–Kister type equation. The excess molar volume is negative for all the four systems. The results show that the volume accommodation effect is predominant in these systems. The Grunberg & Nissan equation and Fang & He equation for binary mixtures are used to correlate the experimental viscosity data. The Fang & He equation gives an average absolute deviation (*AAD*%) of 0.8% for TOA with alkane mixtures, better than that of 3.8% given by the Grunberg & Nissan equation.

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1. Introduction

Multi-component mixtures are frequently applied as media for various chemical and industrial processes. The knowledge of physical and chemical properties for multi-component mixtures has significance in chemical engineering industry because of their necessity in the design of effective processes [1,2]. Also, the experimental physical–chemical properties of binary mixtures are always helpful to understand the intermolecular interactions in a solution, or to analyze the performance of semi-theoretical models for representing the experimental data [3–7].

Tri-*n*-octylamine (TOA) is frequently used as a good tertiary extractant in many processes for the purification and separation of inorganic acids and metal ions [8–10]. Because of its high viscosity, TOA needs to be diluted with a non-polar diluent when applied in a real solvent extraction process. It is believed that the addition of non-polar solvent to TOA confers primarily a suitable viscosity and density to the organic phase. For example, TOA diluted in heptane or octane was used for the extraction of propionic acid [11,12], glycolic acid [13], succinic acid [14], gold(I) [15], tin(IV) [16], etc. When nonane or decane was used as diluents, it could

be used to extract cobalt(II) [17], Mo(VI) [18], monocarboxylic acids [19], etc. A suitable extractant-diluent system may be affected by many factors, such as solvent effect, temperature, distribution coefficient, extraction rate, etc. Therefore, physical–chemical properties, such as density and viscosity for the solution of TOA with dilutions [20–25] will be beneficial for the study of synthetic effect of dilutions in extraction, the design and simulation of extraction process. Until now, many papers have already been devoted to the experimental determination of viscosities and/or density of various alkylamines with different organic solvents [20–28]. However, no measurements have been reported on both densities and viscosities for TOA with *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane at different temperatures.

As a continuing study of measurements and modeling of physical–chemical properties for extractant mixtures [29–34], here, we present new measurements of densities and viscosities for the binary mixtures of TOA with *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane over the entire range of compositions at *T* (283.15, 293.15, and 303.15) K and atmospheric pressure. According to the experimental densities, the excess molar volume V^E are calculated and used to discuss the possible interactions between TOA and alkanes. Furthermore, the experimental viscosities for TOA with alkanes that can be characterized as size-asymmetric mixtures are used to test the performance of two one-parameter

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* Corresponding author. Tel.: +86 571 88071024 8578.
  E-mail address: fszjgsu@gmail.com (S. Fang).

viscosity equations, the Fang & He equation [30] and the commonly used Grunberg & Nissan equation [35].

2. Experimental section

2.1. Materials

The anhydrous grade n-heptane and n-decane were obtained from Sigma–Aldrich, while the analytical grade n-octane and n-nonane were obtained from Aladdin Chem. Co. Ltd (Shanghai, China). The claimed mole fraction purity for these chemicals was greater than 99%. These alkanes were used after single distillation. Tri-n-octylamine with mole fraction purity greater than 98% was obtained from Sigma–Aldrich. The tri-n-octylamine sample was dried over 4A molecular sieves prior to use. Complete specification of chemical samples is also listed in table 1. The purity of all samples was ascertained by comparing the values of their measured densities and viscosities with their literature values at 298.15 K. The determined densities and viscosities of pure components agree well with literature values and are given in table 2. The ultra-pure water with resistivity of 18.2 MΩ · cm was used for density checking and viscosity calibration, which was produced by a Barnstead Nanopure Diamond UV/UF water treatment system.

Binary mixtures were prepared by mass in airtight stopper glass bottles. The masses were recorded on a Mettler analytical balance with a precision of 0.01 mg. Care was taken to avoid evaporation and contamination during mixing. The uncertainty in the mole fraction was estimated to be within 0.0001.

2.2. Apparatus and procedure

The densities of pure liquids and their binary mixtures were measured by using an Anton Paar digital vibrating glass tube densimeter (model DMA 5000, Austria). The temperature of the measurement cell can be controlled automatically and within ±0.005 K for a certain value. The performance of the apparatus was checked with dry air and freshly degassed ultra-pure water everyday before routine measurements. The uncertainty of the digital vibrating glass tube densimeter is stated by the manufacturer as ±5.0 · 10^{-6} g · cm^{-3} in the density range of 0 to 3 g · cm^{-3}. The uncertainty of density measurements of pure liquids and binary mixtures in this study was estimated to be ±1.0 · 10^{-5} g · cm^{-3}.

The kinematic viscosities (v) of mixtures were measured by using series Ubbelohde type viscometers with different capillaries in diameter. The Ubbelohde viscometer was filled with experimental samples and placed vertically in a thermostatic water bath (model DF-02, Fangao Scientific, China) maintained constant to ±0.01 K for about 20 min to make the thermal fluctuations in the viscometer minimized. In order to minimize the evaporation loss during viscosity measurement, the viscometer's limb was closed using a rubber stopper with a small plastic tube which was open to the atmosphere. An electronic digital stopwatch with readability of ±0.01 s was used for the flow time measurements. The dried and thoroughly cleaned viscometer was calibrated at every experimental temperature with

TABLE 2
The experimental density (ρ) and viscosity (η) of pure substance at temperature T = 298.15 K and atmospheric pressure and compared with bibliographic data.

Compound	T/K	ρ/g · cm^{-3}		η/mPa · s	
		Exptl	Lit.	Exptl	Lit.
Tri-n-octylamine	298.15	0.80726	0.8084[a]	8.392	8.325[a]
			0.80746[b]		
			0.80701[c]		
n-Heptane	298.15	0.67978	0.6797[d]	0.397	0.396[d]
			0.67975[e]		0.392[e]
n-Octane	298.15	0.69855	0.69857[e,f]	0.510	0.514[e]
			0.69858[g]		0.5123[f]
n-Nonane	298.15	0.71395	0.71405[h]	0.667	0.669[i]
			0.713834[i]		0.664[j]
n-Decane	298.15	0.72622	0.726174[i]	0.858	0.860[i,k]
			0.7262[l]		0.858[m]

Standard uncertainties u are $u(T)$ = 0.001 K for density measurement, $u(T)$ = 0.01 K for viscosity measurement, and the combined expanded uncertainty U_c is $U_c(\rho)$ = 0.00001 g · cm^{-3}, $U_c(\eta)$ = 0.003·η with 0.95 level of confidence ($k \approx 2$).
[a] Reference [36].
[b] Reference [20].
[c] Reference [22].
[d] Reference [34].
[e] Reference [37].
[f] Reference [38].
[g] Reference [39].
[h] Reference [40].
[i] Reference [41].
[j] Reference [42].
[k] Reference [43].
[l] Reference [44].
[m] Reference [45].

freshly boiled ultra-pure water [46]. The calibrating and measuring procedure has been described elsewhere [32]. The dynamic viscosity (η) for each mixture composition was obtained from the product of the kinematic viscosity (v) and the corresponding density (ρ) of the sample, in terms of $\eta = \rho \cdot v$. Measurements were repeated at least three to four times for each solution and temperature. The combined uncertainty of the viscosity measurement was estimated to be ±0.3%.

3. Results and discussion

3.1. Experimental data

Table 3 presents the experimental density, ρ, and viscosity, η, of binary systems {x_1 TOA + (1 − x_1) n-heptane}, {x_1 TOA + (1 − x_1) n-octane}, {x_1 TOA + (1 − x_1) n-nonane}, and {x_1 TOA + (1 − x_1) n-decane} at T (283.15, 293.15, and 303.15) K and atmospheric pressure. It can be found that the addition of alkanes into TOA largely reduces the viscosity of systems. On the other hand, the effect caused by temperature upon density and viscosity is similar, namely, a decrease in the value of density or viscosity when the temperature increases. However, high temperatures may lead to big evaporation losses of alkanes and also reduce the efficiency of exothermic extraction processes [47,48].

TABLE 1
Provenance and purity of the chemicals used in this study.

Chemical name	CAS #	Source	Initial mole fraction purity	Purification method
Tri-n-octylamine	1116-76-3	Sigma–Aldrich	>0.98	No
n-heptane	142-82-5	Sigma–Aldrich	>0.99	Single distillation
n-octane	111-65-9	Aladdin Chem.	>0.99	Single distillation
n-nonane	111-84-2	Aladdin Chem.	>0.99	Single distillation
n-decane	124-18-5	Sigma–Aldrich	>0.99	Single distillation