Densities and viscosities of ten binary and ten ternary regular solution systems at 308.15 and 313.15 K

Sepehr Hamzehlouia, Abdul-Fattah A. Asfour *

Environmental Engineering, University of Windsor, Windsor, Ontario, Canada N9B 3P4

A B S T R A C T

The densities and kinematic viscosities of binary and ternary regular mixtures containing cyclohexane, m-xylene, chlorobenzene, cyclooctane and decane were measured over the entire composition range at 308.15 K and 313.15 K, respectively. The experimental results were used to test the predictive capability of the six viscosity models available in the literature; namely, the generalized McAllister three-body interaction model, the pseudo-binary McAllister model, the group contribution (GC-UNIMOD) model, the generalized corresponding states principle (GCSP) model, the Allan and Teja correlation and the Grunberg and Nissan law of viscosity. The percentage average absolute deviation (%AAD) was employed as the criterion for comparing the predictive capabilities of the aforementioned models. The experimental pure component data obtained in the present study agreed well with the corresponding literature values at both designated temperatures. The model testing results showed that the generalized McAllister showed the best predictive capability resulting in the lowest %AADs; viz., 3.3 and 3.7 at 308.15 K and 313.15 K, respectively.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Viscosity is a physical property that describes the flow resistance of simple fluids. The knowledge about viscosity has a significant value in different engineering and industrial applications; viz., heat transfer, mass transfer and pipeline design.

Viscosity value is a strong function of temperature. In the case of multi-component systems, the viscosity value is also dependent on the composition of the mixture. Therefore, temperature and composition are the major factors in viscosity models for liquid mixtures. In general the absolute viscosity of a liquid mixture can be expressed as a function of temperature, composition, absolute viscosities of the pure components constituting the mixture, and equation constants. Eq. (1) represents the general absolute viscosity function:

$$\mu_m = f(T, x_1, x_2, ..., x_{n-1}, \mu_1, ..., \mu_n, C_1, ..., C_n). \tag{1}$$

The behavior of the liquid solutions is heavily affected by the present intra-molecular forces; viz., van der Waals' forces and hydrogen bonding, in the system between the molecules of the different components constituting the liquid system. In order to address the abnormal liquid behavior in the case of diffusion, Asfour [1] classified liquid mixtures into three main categories; viz., (i) n-alkane solutions, (ii) regular solutions, and (iii) associated solutions. This led to the successful development of models for predicting diffusion coefficients. Later, Asfour et al. [2] successfully extended the classification to the prediction of viscosities in liquid mixtures.

The little knowledge we currently have about the structure of the liquids and the intermolecular forces has prevented researches from the development of theoretical models for predicting the viscosities of liquid mixtures.

Various attempts throughout the 20th century failed to develop a reliable model on theoretical grounds for predicting the viscosities of liquid mixtures. In general, the viscosity models presently available in the literature are classified into two main categories; viz., predictive and correlative. While the predictive models employ the pure component properties and molecular parameters, the correlative models require costly and time-consuming experimental data.

In the present study, six viscosity models available from the literature, four predictive and two correlative, have been selected and their predictive capabilities have been tested using the experimental and pure component data obtained during the course of the present study. The experimental data, volumetric and viscometric, were obtained for the pure components as well as for all the binary and ternary liquid mixtures of cyclohexane, m-xylene, cyclooctane, chlorobenzene, and decane over the entire composition range at both designated temperatures; 308.15 and 313.15 K. The viscosity models tested are: (i) the generalized McAllister three-body interaction model, (ii) the pseudo-binary McAllister

---

* Corresponding author. Tel.: +1 519 253 4232x2514.
  E-mail address: asfour@uwindsor.ca (A.A Asfour).

model, (iii) the group contribution (GC-UNIMOD) model, (iv) the generalized corresponding states principle (GCSP) model, (v) the Allan and Teja correlation, and (vi) the Grunberg and Nissan law of viscosity; while the former four models are predictive in nature, the latter two are correlative.

The data reported as result of the present study represent addition to the literature and can be used not only for testing the present models, but also can be used for the development and testing of future models.

2. Experimental

2.1. Materials

The pure components used in the present study are classified into two major categories; viz., (i) the components used to constitute the liquid mixtures, and (ii) the components used in calibrating the density meter. The components used to constitute the systems in the present study are: cyclohexane, m-xylene, cyclooctane, chlorobenzene and decane. The compounds used in calibrating the density meter are: benzene, ethyl benzene, 1-heptanol, 1-hexanol, 1-decanol, double-distilled water, octane, and heptane. All the chemicals used in the present study were purchased from Aldrich–Sigma and Fluka. The chemicals employed were of the highest quality; viz., 99+%. The double-distilled water was prepared in the laboratory.

The fluids used in calibrating the viscometers were purchased from Cannon Instrument Company. These were N0.4, N0.8, N1.0, and N2.0.

The manufacturers' stated purities of both categories of chemicals were greater than 99%. The purities were verified by gas chromatography (GC). An HP 5890 gas chromatograph equipped with an FID and HP1 (crossed linked methyl silicon gun) with the dimensions of 30 m (long)×0.53 mm (diameter) and 2.65 μm (film thickness) was employed in order to verify the purities. The purities as determined by gas chromatography exceed the purities stated by the manufacturers. Table 1 reports the stated purities of the chemicals and the purities as determined by gas chromatography.

2.2. Preparation of the liquid systems

The binary and ternary liquid systems were prepared gravimetrically using a Mettler HK 160 electronic balance with a reported precision of $\pm 1 \times 10^{-7}$ kg. The samples were placed in glass vials fitted with Tuf-Bond discs (Teflon/silicon) and aluminum seals in order to minimize evaporation. The procedure for the preparation of the liquid mixtures was thoroughly described by Asfour [1] in detail.

2.3. Density measurements

An Antoine-Paar density meter (model DMA 60/602) with a stated precision of $\pm 1.5 \times 10^{-6}$ g.cm^{-3} was employed for measurement of the density of the pure components and the binary and ternary liquid solutions. The density meter was placed in a wooden temperature controlled chamber where temperature fluctuations were limited to ± 0.5 K. The design of the chamber and temperature control were described in detail by Asfour [1]. The temperature inside the DMA 602 measuring cell was controlled by a Haanke N4 circulating unit. The density meter measuring cell's temperature was monitored by means of an Omega digital thermometer equipped with an ITS-90 calibrated platinum probe. The temperature accuracy of the probe is better than ± 0.01 K. The pure compounds (and mixtures) were injected to the density meter unit using 2 mL syringes. The samples remain in the measuring cell until the system reaches thermal equilibrium. The density meter readings were then taken and substituted into Eq. (2) which is a three parameter equation provided by the manufacturer and is given by

$$\rho = \frac{AT^2}{1-BT^2} - C \tag{2}$$

where ρ is the density value of the sample calculated in kg/L, and A, B and C are the adjustable parameters obtained by fitting the densities of the compounds used for calibration to Eq. (2) at 308.15 and 313.15 K. T is the average oscillation period of the ten readings reported by the density meter in seconds.

2.4. Viscosity measurements

The kinematic viscosities of the pure components, binary, and ternary liquid mixtures over the entire composition range were measured using six Cannon-Ubbelohde glass capillary viscometers manufactured by Cannon Instruments Company. Three of the viscometers employed were of the size B25 covering the viscosity range of $(0.5–2) \times 10^6$ m^2.s^{-1}. The other three viscometers were of the size B50, covering the viscosity range of $(0.8–4 \times 10^6$ m^2.s^{-1}). The viscometers were placed in a CT-1000 constant temperature bath where the bath temperature fluctuations are controlled to within ± 0.01 K. The bath temperature was continuously monitored using an Omega digital thermometer equipped with an ITS-90 calibrated platinum probe with a temperature uncertainty of better than ± 0.01 K. The procedure was repeated three times for each sample at both designated temperatures. The deviation of the measured efflux times should not exceed 0.1%. The average efflux time values were substituted into Eq. (3), a two-parameter equation provided by the manufacturer and is given by,

$$\nu = Et - \frac{F}{t^2} \tag{3}$$

where ν is the kinematic viscosity of the sample in m^2.s^{-1}, E and F are adjustable parameters obtained by fitting the viscosity measurement data for the standard viscosity fluids with accurately known kinematic viscosities into Eq. (3), and t is the average time efflux in seconds.

3. Results and discussions

Table 2 reports the densities and the kinematic and absolute viscosities of the pure components that were employed in constituting the liquid mixtures investigated in the present study and their comparison with their corresponding values available from the literature at 308.15 K and 313.15 K. There is good agreement between the two sets of data.

Tables 3 and 4 summarize the density, kinematic viscosities and absolute viscosity values of the binary and ternary sub-systems of the quinary system: cyclohexane (1)+m-xylene (2)+cyclooctane (3)+chlorobenzene (4)+decane (5) over the entire composition range at both designated temperatures; 308.15 K and 313.15 K.

Table 1
Gas chromatography analysis results for the pure components.

Compound	Manufacturer	Stated purity mol%	GC analysis mass %
Chlorobenzene	Sigma–Aldrich	99.8	99.8
Nitrobenzene	Sigma–Aldrich	99+	99.5
m-Xylene	Sigma–Aldrich	99+	99.4
Decane	Sigma–Aldrich	99+	99.8
Benzene	Sigma–Aldrich	99.9	99.9
Ethyl benzene	Sigma–Aldrich	99.8	99.9
Cyclooctane	Aldrich	99+	99.7
Cyclohexane	Aldrich	99+	99.7
1-Decanol	Aldrich	99+	99.4
1-Hexanol	Fluka	99+	99.98
1-Heptanol	Fluka	99+	99.4