

Densities and Kinematic Viscosities of Ten Ternary Regular Liquid Systems at 293.15 and 298.15 K

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Densities and kinematic viscosities of the ternary subsystems of the following regular quinary system: toluene (1) + octane (2) + ethylbenzene (3) + tetradecane (4) + hexadecane (5) were measured over the entire composition range at 293.15 K and 298.15 K. The viscosity deviations from a mole fraction-averaged viscosity of the mixture were calculated from the absolute viscosity data. All the viscosity deviations are negative. The viscosity data reported herein were utilized for testing the predictive capabilities of McAllister model and Grunberg-Nissan equation. The overall % AAD in the case of McAllister model is 1.3% as compared to 3.1% in the case of Grunberg-Nissan equation.

Introduction

Viscosity is a transport property the knowledge of which is essential in many engineering applications which involve heat transfer, mass transfer and fluid flow. Unfortunately, reliable viscometric data on liquid mixtures at different temperatures are very scarce in the literature.

The present work is part of a continuing program in our laboratory that aims at providing a viscosity database consisting of a quinary regular system and all of its corresponding quaternary, ternary and binary subsystems at different temperature levels. The pure components of the selected quinary system are of the nonassociating type with significant differences in shape and structure, i.e., toluene (1) + octane (2) + ethylbenzene (3) + tetradecane (4) + hexadecane (5). These data are required for their own value as well as for use in the development and critical testing of various predictive viscosity models. To the best of our knowledge, similar data for the systems considered in this study have not been reported before.

This study reports the viscometric and volumetric data of the ternary regular subsystems of the above named quinary system at 293.15 K and 298.15 K. The viscometric data include: viscosity as a function of composition, comparison of experimental viscosities with those reported with several different equations, and the excess viscosity. Volumetric data include: the dependence of density on composition.

Experimental Section

Procedure. The pure component densities and kinematic viscosities were measured first at the stated temperatures. Next, ternary mixtures over the entire composition range were prepared and their densities and kinematic viscosities were measured.

Materials. The individual components used in preparing the systems under investigation and chemicals used for density meter calibration were supplied by Aldrich Chemical Co. These are: toluene, benzene, ethylbenzene, octane, decane, tetradecane, hexadecane, and carbon tetrachloride. The purity of the all of the above liquids were stated by

the manufacturer to be higher than 99%. The results of a chromatographic test of reagent purity, using a 5 m × 0.53 mm methyl silicone capillary column and a flame ionization detector (FID) confirmed the stated purities.

Preparation of Solutions. All solutions were prepared by mass using a Mettler HK 160 electronic balance with a stated precision of $\pm 2 \times 10^{-7}$ kg. To avoid evaporation losses, the solutions were prepared according to procedures described earlier by Asfour (1979).

Density Measurements. The densities of the pure liquids and ternary mixtures were measured at (293.15 ± 0.01 K) and (298.15 ± 0.01 K) using an Anton Paar digital precision density meter (model DMA 60/602) which has a stated precision of $\pm 1.5 \times 10^{-5}$ kg/L. The density meter is enclosed in a controlled temperature wooden box. The temperature fluctuations inside the wooden box were kept within ±0.1 K. The density meter is connected to a Haake N4-B circulator fitted with a calibrated platinum temperature sensor (IPTS-68). The temperature fluctuations within the density meter measuring cell were kept within ±0.01 K. All temperatures were checked by an Omega electronic thermometer fitted with a calibrated platinum probe (ITS-90) with an accuracy of ±0.005 K. The electronic thermometer's readings confirmed those of the N4-B circulator with no observed difference in the second decimal place of the temperature reading. For operating temperatures below the laboratory temperature, the instrument was coupled with a refrigeration unit. The refrigerating circulator is a Lauda RMT-20. The density was determined by the following three-parameter equation, which was suggested by the density meter manufacturer:

$$\rho = \frac{A\tau^2}{1 - B\tau^2} - C \quad (1)$$

where ρ is the density and τ is the period of oscillation indicated by the density meter. The numerical values of the three parameters were determined at 293.15 K and 298.15 K using the measured densities of the compounds shown in Table 1, the densities (kg/L) of which were obtained from the literature at 293.15 K and 298.15 K. The density range of these calibration liquids covers the density range of interest.

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Table 1. Calibration Data for the Density Meter

compound	$\rho/\text{kg L}^{-1}$		data source
	293.15 K	298.15 K	
hexane	0.659 25	0.654 71	TRC Tables, 1988
heptane	0.683 75	0.679 46	TRC Tables, 1988
octane	0.702 67	0.698 62	TRC Tables, 1988
decane	0.730 12	0.726 35	TRC Tables, 1988
toluene	0.866 9	0.862 20	TRC Tables, 1988
benzene	0.879 0	0.873 66	TRC Tables, 1988
double-distilled water	0.998 234 3	0.997 07	Perry, 1984
carbon tetrachloride	1.594 0	1.584 45	Timmermans, 1950

Error analysis showed that the maximum fluctuation in density meter readings would result in an uncertainty of less than 1.5×10^{-4} kg/L in the measured density value. Also, a temperature variation of ± 0.01 K would result in an uncertainty of approximately $\pm 3 \times 10^{-6}$ kg/L in the measured density.

Viscosity Measurements. Kinematic viscosity measurements were performed by using a set of five Cannon-Ubbelohde viscometers with a stated precision of $\pm 0.1\%$. The set consists of two viscometers of sizes 25 A (range of $(0.5-2.0) \times 10^{-6}$ m² s⁻¹), two of size 50 B (range $(0.8-8) \times 10^{-6}$ m² s⁻¹), and one of size 75 J (range $(1.6-8.0) \times 10^{-6}$ m² s⁻¹). The range of the viscosities of the investigated systems used in this study varied from 0.55 to 4.5×10^{-6} m² s⁻¹. Kinematic viscosities were obtained from the measured efflux time, t , and the equation

$$v = Et - \frac{F}{t^2} \quad (2)$$

where E and F are calibration constants. The two constants were determined by using calibration standards purchased from Cannon Instrument Company. The range of standards covers the viscosity range of interest. The Cannon-Ubbelohde viscometers were placed in a Model CT-1000 temperature-controlled bath, purchased from Cannon Instrument Company. The temperature was controlled within ± 0.01 K by using a silicon oil as a bath medium. The unit was connected to external refrigerating circulator for measurements below the laboratory temperature. To monitor the temperature inside the bath, a DP95 digital RTD thermometer (ITS-90) supplied by Omega Corporation was used. The stated accuracy of the RTD thermometer is ± 0.005 K. An electronic stopwatch accurate within ± 0.01 s was used for measuring efflux time.

Results and Discussion

The pure component densities and kinematic viscosities measured in this study were compared with the corresponding values from the TRC data tables. As shown in Table 2, the agreement between the obtained values and densities and kinematic viscosities reported in the literature is excellent.

The experimental densities and kinematic viscosities are listed in Table 3 as well as the calculated absolute viscosity values, and the viscosity deviations from a mole fraction-averaged viscosity of the mixture ($\Delta\eta$). The viscosity deviation is defined as

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (3)$$

In the above equation, η is the absolute viscosity, x is the component mole fraction, and subscript i stands for pure component " i ". As it can be seen from Table 3, the values of $\Delta\eta$ are always negative.

Table 2. Pure Component Densities and Kinematic Viscosities and Their Comparison with Literature Values at 293.15 and 298.15 K

compound	$\rho/\text{kg L}^{-1}$		$10^6\nu/\text{m}^2 \text{ s}^{-1}$	
	exp	lit.	exp	lit.
$T = 293.15 \text{ K}$				
toluene	0.8669	0.866 9	0.6789	0.6747
octane	0.7026	0.702 6	0.7736	0.7758
ethylbenzene	0.8672	0.867 0	0.7804	0.7800
tetradecane	0.7628	0.762 55	3.069	3.061
hexadecane	0.7735	0.773 53	4.4880	4.492
$T = 298.15 \text{ K}$				
toluene	0.8622	0.862 3	0.6438	0.6378
octane	0.6986	0.698 62	0.7319	0.7352
ethylbenzene	0.8628	0.862 5	0.7334	0.7367
tetradecane	0.7592	0.759 20	2.753	2.771
hexadecane	0.7700	0.769 94	3.965	4.008

Table 3 reports the experimental kinematic viscosity values of the mixtures investigated in the present study at 293.15 K and 298.15 K. For each viscosity value, the corresponding efflux time was the average of three measurements with a repeatability better than $\pm 0.1\%$. The maximum expected error is less than $\pm 3 \times 10^{-10}$ m²/s.

The experimental viscosity data reported in Table 3 were used to validate the techniques proposed by Asfour et al. (1991), Nhaesi and Asfour (1998), and Nhaesi and Asfour (1999) for predicting the McAllister viscosity three-body model parameters from pure component properties. The extended McAllister three-body model (Chandramouli and Laddha, 1963) is given by the following form:

$$\begin{aligned} \ln \nu_m = & x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + x_3^3 \ln \nu_3 + 3x_1^2 x_2 \ln \nu_{12} + \\ & 3x_1^2 x_3 \ln \nu_{13} + 3x_2^2 x_1 \ln \nu_{21} + 3x_2^2 x_3 \ln \nu_{23} + \\ & 3x_3^2 x_1 \ln \nu_{31} + 3x_3^2 x_2 \ln \nu_{32} + 6x_1 x_2 x_3 \ln \nu_{123} - \ln(x_1 M_1 + \\ & x_2 M_2 + x_3 M_3) + x_1^3 \ln M_1 + x_2^3 \ln M_2 + x_3^3 \ln M_3 + \\ & 3x_1^2 x_2 \ln(2M_1 + M_2)/3 + 3x_1^2 x_3 \ln(2M_1 + M_3)/3 + \\ & 3x_2^2 x_1 \ln(2M_2 + M_1)/3 + 3x_2^2 x_3 \ln(2M_2 + M_3)/3 + \\ & 3x_3^2 x_1 \ln(2M_3 + M_1)/3 + 3x_3^2 x_2 \ln(2M_3 + M_2)/3 + \\ & 6x_1 x_2 x_3 \ln(M_1 + M_2 + M_3)/3 \quad (4) \end{aligned}$$

In eq 4, there are six binary parameters, ν_{12} , ν_{21} , ν_{13} , ν_{31} , ν_{23} , and ν_{32} , and one ternary parameter, ν_{123} . The binary parameters were predicted using the technique proposed by Asfour et al. (1991). According to that, the binary interaction parameters can be predicted as follows:

$$\frac{\nu_{ij}}{(\nu_i^2 \nu_j)^{1/3}} = 1 + 0.044 \frac{(N_j - N_i)^2}{(N_i^2 N_j)^{1/3}} \quad (5)$$

$$\nu_{ji} = \nu_j \left(\frac{\nu_j}{\nu_i} \right)^{1/3} \quad (6)$$

In the above equations, ($i < j$) and N_i and N_j are the effective carbon numbers of pure components of regular mixtures or the carbon numbers in case of n -alkane mixtures. To determine the numerical value of the effective carbon number, the following equation was used (Nhaesi and Asfour 1998):

$$\ln \nu = -1.943 + 0.193N \quad (7)$$

where ν is the kinematic viscosity at 308.15 K in cSt and N is the effective carbon number. The ternary interaction parameter was estimated by means of the following equa-

Table 3. Continued

mole fraction						mole fraction					
x_1	x_2	$\rho/\text{kg L}^{-1}$	$10^6\nu/\text{m}^2 \text{ s}^{-1}$	$10^3\eta/\text{Pa s}$	$10^3\Delta\eta/\text{Pa s}$	x_1	x_2	$\rho/\text{kg L}^{-1}$	$10^6\nu/\text{m}^2 \text{ s}^{-1}$	$10^3\eta/\text{Pa s}$	$10^3\Delta\eta/\text{Pa s}$
$T = 293.15 \text{ K}$						$T = 298.15 \text{ K}$					
Octane (1) + Ethylbenzene (2) + Hexadecane (3)						Octane (1) + Ethylbenzene (2) + Hexadecane (3)					
1.0000	0.0000	0.7026	0.7736	0.5436	0.0000	1.0000	0.0000	0.6986	0.7319	0.5113	0.0000
0.0000	1.0000	0.8672	0.7804	0.6768	0.0000	0.0000	1.0000	0.8628	0.7334	0.6327	0.0000
0.0000	0.0000	0.7735	4.4880	3.4716	0.0000	0.0000	0.0000	0.7700	3.9650	3.0530	0.0000
0.0905	0.7285	0.8178	1.1549	0.9445	-0.2261	0.0905	0.7285	0.8138	1.0818	0.8804	-0.1795
0.1933	0.1919	0.7727	2.5593	1.9775	-0.3917	0.1933	0.1919	0.7691	2.3395	1.7994	-0.2979
0.2941	0.3049	0.7730	1.7767	1.3733	-0.3850	0.2941	0.3049	0.7693	1.6411	1.2625	-0.3050
0.3989	0.4227	0.7738	1.1373	0.8801	-0.2422	0.3989	0.4227	0.7700	1.0664	0.8211	-0.1950
0.5931	0.2098	0.7485	1.1950	0.8944	-0.2542	0.5931	0.2098	0.7447	1.1170	0.8318	-0.2060
0.0891	0.1316	0.7748	3.3021	2.5584	-0.2845	0.0891	0.1316	0.7713	2.9691	2.2901	-0.2180
Octane (1) + Tetradecane (2) + Hexadecane (3)						Octane (1) + Tetradecane (2) + Hexadecane (3)					
1.0000	0.0000	0.7026	0.7736	0.5436	0.0000	1.0000	0.0000	0.6986	0.7319	0.5113	0.0000
0.0000	1.0000	0.7628	3.0690	2.3411	0.0000	0.0000	1.0000	0.7592	2.7530	2.0902	0.0000
0.0000	0.0000	0.7735	4.4880	3.4716	0.0000	0.0000	0.0000	0.7700	3.9650	3.0530	0.0000
0.1034	0.6933	0.7614	2.9634	2.2564	-0.1286	0.1034	0.6933	0.7579	2.6809	2.0319	-0.0908
0.1894	0.1994	0.7632	3.2056	2.4465	-0.2451	0.1894	0.1994	0.7597	2.8811	2.1888	-0.1908
0.3186	0.2948	0.7552	2.5205	1.9036	-0.3018	0.3186	0.2948	0.7518	2.3024	1.7309	-0.2285
0.4191	0.3931	0.7477	2.0389	1.5244	-0.2756	0.4191	0.3931	0.7441	1.8712	1.3924	-0.2169
0.6063	0.2042	0.7376	1.6149	1.1912	-0.2743	0.6063	0.2042	0.7340	1.4938	1.0964	-0.2189
0.1136	0.1012	0.7680	3.7557	2.8844	-0.1402	0.1136	0.1012	0.7645	3.3560	2.5658	-0.1011
Ethylbenzene (1) + Tetradecane (2) + Hexadecane (3)						Ethylbenzene (1) + Tetradecane (2) + Hexadecane (3)					
1.0000	0.0000	0.8672	0.7804	0.6768	0.0000	1.0000	0.0000	0.8628	0.7334	0.6327	0.0000
0.0000	1.0000	0.7628	3.0690	2.3411	0.0000	0.0000	1.0000	0.7592	2.7530	2.0902	0.0000
0.0000	0.0000	0.7735	4.4880	3.4716	0.0000	0.0000	0.0000	0.7700	3.9650	3.0530	0.0000
0.1001	0.7016	0.7697	2.9518	2.2719	-0.1268	0.1001	0.7016	0.7661	2.6782	2.0517	-0.0835
0.2192	0.1904	0.7800	3.1013	2.4189	-0.2248	0.2192	0.1904	0.7764	2.8054	2.1780	-0.1612
0.2974	0.2859	0.7831	2.5975	2.0342	-0.2830	0.2974	0.2859	0.7795	2.3728	1.8496	-0.2084
0.3793	0.4028	0.7864	2.1535	1.6936	-0.2625	0.3793	0.4028	0.7827	1.9773	1.5477	-0.1995
0.6139	0.1865	0.8064	1.5805	1.2745	-0.2705	0.6139	0.1865	0.8026	1.4666	1.1770	-0.2106
0.1090	0.0901	0.7765	3.7425	2.9060	-0.1591	0.1090	0.0901	0.7729	3.3473	2.5872	-0.1152

Table 4. Results of Testing the McAllister Model and Grunberg–Nissan Equation by Using Viscosity Data on Regular Ternary Systems at 293.15 and 298.15 K

system	T/K	McAllister model		Grunberg–Nissan eq	
		AAD	MAX	AAD	MAX
toluene (1) + octane (2) + ethylbenzene (3)	293.15	3.33	-6.13	6.40	8.37
	298.15	3.01	-5.51	6.28	8.14
toluene (1) + octane (2) + tetradecane (3)	293.15	1.78	-4.47	2.69	3.94
	298.15	1.57	-4.28	2.94	4.13
toluene (1) + octane (2) + hexadecane (3)	293.15	1.26	3.31	4.02	8.89
	298.15	1.17	3.29	4.32	8.90
toluene (1) + ethylbenzene (2) + tetradecane (3)	293.15	1.17	-3.42	2.13	3.08
	298.15	0.87	-3.19	2.71	3.77
toluene (1) + ethylbenzene (2) + hexadecane (3)	293.15	1.65	-4.96	3.61	8.67
	298.15	1.66	4.53	4.03	8.28
toluene (1) + tetradecane (2) + hexadecane (3)	293.15	0.82	-2.16	1.69	3.38
	298.15	0.58	-1.95	2.14	3.65
octane (1) + ethylbenzene (2) + tetradecane (3)	293.15	1.73	-3.22	3.17	8.89
	298.15	1.41	-2.64	2.75	8.26
octane (1) + ethylbenzene (2) + hexadecane (3)	293.15	1.19	-3.47	3.22	7.72
	298.15	0.81	-2.54	2.61	7.03
octane (1) + tetradecane (2) + hexadecane (3)	293.15	0.54	-1.23	0.80	1.20
	298.15	0.34	-1.11	0.54	1.37
ethylbenzene (1) + tetradecane (2) + hexadecane (3)	293.15	0.67	-1.57	2.85	4.14
	298.15	0.33	-1.15	3.65	4.96
overall AAD		1.29		3.13	

tion (Nhaesi and Asfour 1999):

$$\frac{\nu_{ijk}}{(\nu_i \nu_j \nu_k)^{1/3}} = 0.9637 + \frac{(N_k - N_j)^2}{N_j} \quad (8)$$

where i , j , and k refer to components 1, 2, and 3, respectively.

Equation 8 was tested using the viscosity data of regular systems generated in our laboratory. First the value of ν_{123} for each system was calculated by means of eq 8, and the binary interaction parameters, for the binary subsystems

of the ternary system under consideration, were predicted by eqs 5, 6, and 7, then the values of the predicted parameters were substituted into the McAllister three-body model for ternary systems, eq 4, to obtain the predicted viscosity. The calculated and experimental viscosities were then compared. The percent average absolute deviation (% AAD) is defined by

$$\% \text{ ADD} = \frac{1}{n} \sum_{i=1}^n \frac{|\nu_i^{\text{exp}} - \nu_i^{\text{cal}}|}{\nu_i^{\text{exp}}} \times 100 \quad (9)$$

The maximum deviation of the predicted data is determined by means of the function "max", which is defined as

$$\% \text{ MAX} = \max \left(\frac{v_i^{\text{exp}} - v_i^{\text{cal}}}{v_i^{\text{exp}}} \right) \times 100 \quad (10)$$

The results of testing the model are reported in Table 4.

Furthermore, the reported absolute viscosity data were used to test the predictive capability of the Grunberg–Nissan equation. The Grunberg–Nissan equation (Grunberg and Nissan 1949) has been recommended by Irving (1977) as being the most effective equation in correlating viscosity data for binary liquid mixtures. This purely empirical equation is given by

$$\ln \eta_m = \sum_{i=1}^n x_i \ln \eta_i + \sum_{i=1}^n \sum_{\substack{j=1 \\ i < j}}^n x_i x_j G_{ij} \quad (11)$$

The model given by eq 11 contains binary adjustable parameters, G_{ij} . The adjustable parameters are determined by fitting experimental viscosity-composition data to eq 11. Isdale et al. (1985) reported a group contribution method to predict the binary adjustable parameter G_{ij} . The number of these parameters depends on the number of components in the system. In the present study, the calculation procedure outlined by Reid et al. (1987) was followed. The calculation results are listed in Table 4.

The results reported in Table 4 clearly show that a comparison of the predictive capabilities of the McAllister model—after the modifications introduced by Nhaesi and Asfour (1998 and 1999) were made—and the Grunberg–Nissan equation (Table 4) for all systems under investigation is in favor of the former method, since the overall % AADs of the McAllister model are lower than those of the Grunberg–Nissan equation.

Conclusions

The kinematic viscosities of 10 regular liquid systems at 293.15 and 298.15 K were measured over the entire composition range with maximum estimated error less than $\pm 3 \times 10^{-10} \text{ m}^2/\text{s}$.

Utilizing the pure component properties, the viscosities of liquid mixtures were predicted by using two different techniques, viz., (i) the McAllister model and (ii) the Grunberg–Nissan equation. The obtained results indicate that McAllister model predicts the data better than the Grunberg–Nissan equation.

Literature Cited

- Abdulghanni, N.; Asfour, Abdul-Fattah A. Prediction of the McAllister Model Parameters from Pure Component Properties of Regular Binary Liquid Mixtures. *Ind. Eng. Chem. Res.* **1998**, *37*, 4893–4897.
- Abdulghanni, N.; Asfour, Abdul-Fattah A. Predictive Models for the Viscosities of Multicomponent Liquid *n*-Alkane and regular Solutions. *Can. J. Chem. Eng.* **2000**, In Press.
- Asfour, Abdul-Fattah A. Mutual and intra-(self-) diffusion coefficients and viscosities of binary liquid solutions at 25.00 °C. Ph.D. Thesis, University of Waterloo, Waterloo, Canada, 1980.
- Asfour, Abdul-Fattah A.; Cooper, E. F.; Wu, J.; Zahran, R. R. Prediction of the McAllister Model Parameters from Pure Components Properties for Liquid Binary *n*-Alkane Systems. *Ind. Eng. Chem. Res.* **1991**, *30*, 1666–1669.
- Chandramouli, V. V. and Laddha, G. S. "Viscosity of Ternary Liquid Mixtures. *Indian J. Technol.* **1963**, *1*, 199–203.
- Grunberg, L.; Nissan, A. H. Mixture Law for Viscosity. *Nature* **1949**, *164*, 799.
- Irving, J. B. The Effectiveness of Mixture Equations. *Natl. Eng. Lab., Rept. 631*, East Kilbride, Glasgow, Scotland, **1977**.
- Isdale, J. D.; MacGillivray, J. C.; Cartwright, G. Prediction of Viscosity of Organic Liquid Mixtures by a Group Contribution Method. *Natl. Eng. Lab., Rept. 631*, East Kilbride, Glasgow, Scotland, **1985**.
- Perry, R. H.; Green, D. Chemical Engineers Handbook, 6th ed.; McGraw-Hill: New York, 1984.
- Reid, R. C.; Praunitz, J. M.; Poling, B. E. The Properties of Gases and Liquids, 4th ed.; McGraw-Hill: New York, 1987.
- Timmermanns, J. Physicochemical constants of pure organic compounds; Wiley-Interscience: New York, 1950; Vol. 1.
- TRC Tables, Thermodynamic Tables-Hydrocarbons, Supplement No. 92; Thermodynamic Research Center: Texas A&M University: College Station, TX, 1988.

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