

Short Articles

Densities and Kinematic Viscosities of Ten Binary 1-Alkanol Liquid Systems at Temperatures of (293.15 and 298.15) K

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The densities and viscosities of ten binary mixtures of 1-propanol, 1-pentanol, 1-heptanol, 1-nonanol, and 1-undecanol have been measured over the entire composition range at temperatures of (293.15 and 298.15) K. The experimental data were employed to test the predictive capabilities of viscosity models including the generalized McAllister three-body interaction model, the GC-UNIMOD model, the generalized corresponding states principle (GCSP) model, and the Allan and Teja correlation. The analysis of the models shows that the generalized McAllister three-body interaction model provided the best predictions for the 1-alcohol mixtures investigated.

Introduction

Viscosity is an important property of liquid mixtures required for the design of flow systems that are widely used in engineering applications, especially in heat exchangers as well as in mass transfer equipment. In addition, it is believed that the knowledge of the dependence of viscosity on temperature and composition may provide better insight into the structure of liquids. This has motivated many researchers to investigate the dependence of viscosity of liquid mixtures on composition. Those efforts have resulted in developing different models. Among the available viscosity models in the literature, four that have been widely used were selected to test the predictive capabilities, and these were the generalized McAllister three-body interaction model (model 1) reported by Nhaesi and Asfour,¹ the GC-UNIMOD model (model 2) reported by Cao et al.,² the generalized corresponding states principle (GCSP) model (model 3) reported by Teja and Rice,³ and the Allan and Teja correlation (model 4) reported by Allan and Teja.⁴ The objective of this work is to obtain and report kinematic viscosities and densities of ten binary systems over the entire composition range at temperatures of (293.15 and 298.15) K.

Experimental Section

Preparation of Solutions. All solutions were gravimetrically prepared with a Mettler balance with a stated precision of $1 \cdot 10^{-7}$ kg. The procedure described earlier by Asfour⁵ was followed. The estimated error in the mole fraction so determined was $\pm 1.5 \cdot 10^{-5}$. Since the 1-alcohols are hygroscopic, they were stored over a 0.4 nm molecular sieve.

Materials. The chemicals used for the calibration of the density meter (octane, toluene, ethylbenzene, undecane, and tridecane) and those used for constituting the liquid systems investigated in this study (1-propanol, 1-pentanol, 1-heptanol, 1-nonanol, and 1-undecanol) were purchased from Sigma-Aldrich and from Fluka. The stated mole fraction purities of those chemicals were 0.99. Gas chromatography (GC) analysis

was employed to verify the purities. A Hewlett-Packard 5890A gas chromatograph with a flame ionization detector (FID) and an HP 1 (cross-linked methyl silicone gum) 30 m (long) \times 0.53 mm (diameter) and 2.65 μ m (film thickness) column was used. The GC analysis confirmed that the purities of the chemicals were better than their stated values. The suppliers' stated purities and the GC analysis results of the chemicals used in the present study are as follows: 1-propanol (Sigma-Aldrich cited a mole fraction of > 0.995 while GC analysis gave a mass fraction of 0.999), 1-pentanol (Sigma-Aldrich cited a mole fraction of > 0.99 while GC analysis returned a mass fraction of 0.998), 1-heptanol (Fluka cited a mole fraction of > 0.99 while GC analysis gave a mass fraction of 0.997), 1-nonanol (Fluka cited a mole fraction of > 0.98 while GC analysis gave a mole fraction of 0.992), 1-undecanol (Sigma-Aldrich cited a mole fraction of > 0.99 while GC analysis gave a mass fraction of 0.996), octane (Sigma-Aldrich cited a mole fraction of > 0.99 while GC analysis gave a mass fraction of 0.995), toluene (cited a mole fraction of > 0.998 while GC analysis gave a mass fraction of 0.999), ethylbenzene (Sigma-Aldrich cited a mole fraction of > 0.998 while GC analysis gave a mass fraction of 0.998), undecane (Sigma-Aldrich cited a mole fraction of > 0.99 while GC analysis gave a mass fraction of 0.999), and tridecane (Sigma-Aldrich cited a mole fraction of > 0.99 while GC analysis gave a mass fraction of 0.995).

Density Measurements. Density was measured with an Anton-Paar DMA 60 processing unit and a DMA 602 measuring cell with a stated uncertainty of $\pm 3 \cdot 10^{-6}$ kg \cdot L $^{-1}$. Our experimental work indicated an uncertainty of $\pm 1.2 \cdot 10^{-4}$ kg \cdot L $^{-1}$. The temperature of the measuring cell was maintained within ± 0.01 K of the desired level by a Haake N4 circulator. The circulator water temperature is monitored by an Omega electronic thermometer fitted with a calibrated platinum temperature sensor (ITS-90) with an uncertainty of ± 0.01 K. The measuring cell and the processing unit were kept inside a wooden chamber. The temperature inside the chamber is controlled by an arrangement described in details earlier by Asfour⁵ and is kept within ± 0.5 K of the desired temperature.

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To calculate the density of the injected samples, the oscillation period reading is substituted into an equation suggested by the instrument supplier. The density meter equation has the following form:

$$\rho = \frac{At^2}{1 - Bt^2} - C \quad (1)$$

where ρ is the density of the sample. A , B , and C are the calibration constants, and t is the oscillation period in seconds. The values of the calibration constants were determined by using the density values of some compounds with accurately known density values, which were fitted to eq 1. The following compounds, with their densities available from the literature, Thermodynamic Research Center (TRC) tables⁶ in $\text{kg}\cdot\text{L}^{-1}$, were employed to determine the values of the constants A , B , and C : at $T = 293.15$ K, octane $\rho = 0.70267$ $\text{kg}\cdot\text{L}^{-1}$, toluene $\rho = 0.8669$ $\text{kg}\cdot\text{L}^{-1}$, ethylbenzene $\rho = 0.8671$ $\text{kg}\cdot\text{L}^{-1}$, tridecane $\rho = 0.7561$ $\text{kg}\cdot\text{L}^{-1}$, and undecane $\rho = 0.7402$ $\text{kg}\cdot\text{L}^{-1}$; at $T = 298.15$ K, octane $\rho = 0.69862$ $\text{kg}\cdot\text{L}^{-1}$, toluene $\rho = 0.8623$ $\text{kg}\cdot\text{L}^{-1}$, ethylbenzene $\rho = 0.8628$ $\text{kg}\cdot\text{L}^{-1}$, tridecane $\rho = 0.75271$ $\text{kg}\cdot\text{L}^{-1}$, and undecane $\rho = 0.7365$ $\text{kg}\cdot\text{L}^{-1}$. At 293.15 K, the values of the parameters were determined to be the following: $A = 3.143115$ $\text{kg}\cdot\text{s}^{-2}\cdot\text{L}^{-1}$, $B = 0.1603187$ s^{-2} , and $C = 0.9829897$ $\text{kg}\cdot\text{L}^{-1}$, and the standard deviation is $8.7\cdot 10^{-5}$ $\text{kg}\cdot\text{L}^{-1}$. At $T = 298.15$ K, the values were found to be as follows: $A = 3.459062$ $\text{kg}\cdot\text{s}^{-2}\cdot\text{L}^{-1}$, $B = 0.07160815$ s^{-2} , and $C = 1.066801$ $\text{kg}\cdot\text{L}^{-1}$, and the standard deviation is $1.56\cdot 10^{-4}$ $\text{kg}\cdot\text{L}^{-1}$.

Viscosity Measurements

Cannon–Ubbelohde glass viscometers were employed for measuring the kinematic viscosities of the systems under investigation. Two sizes of the viscometers were used in the present study: 100 and 150. Those viscometers were used to measure the kinematic viscosities that range between (3 to 15 and 7 to 35) 10^{-6} $\text{m}^2\cdot\text{s}^{-1}$, respectively. The viscometer was placed in a Cannon CT-1000, constant temperature bath where temperature can be controlled to within ± 0.01 K. To calculate the viscosities of the samples to be studied, the efflux time was measured three times, and the average value was substituted into the equation suggested by the viscometer manufacturer. The values of the efflux times were reproducible to within ± 0.1 %. The uncertainty in the kinematic viscosity measurements was estimated to be $\pm 2\cdot 10^{-9}$ $\text{m}^2\cdot\text{s}^{-1}$. The uncertainty in case of the absolute viscosities was determined to be $\pm 1.6\cdot 10^{-6}$ Pa·s.

The viscometer equation for the Cannon–Ubbelohde viscometer is given by:

$$v = Ct - \frac{E}{t^2} \quad (2)$$

where v is the kinematic viscosity of the sample. The C and E are the calibration constants, and t is the efflux time in seconds. The accuracy of the stop watch that was used for measuring efflux times is within ± 0.01 s. The values of the calibration constants at each temperature level were determined by using calibration fluids of known viscosities supplied by Cannon Instrument Company, namely, S3 with (2.9 to 4.6) 10^{-6} $\text{m}^2\cdot\text{s}^{-1}$, S6 with (5.7 to 11) 10^{-6} $\text{m}^2\cdot\text{s}^{-1}$, and N10 with (10 to 21) 10^{-6} $\text{m}^2\cdot\text{s}^{-1}$. The viscosities of the calibration fluids and their corresponding efflux times were fitted using the least-squares technique to eq 2 to estimate the values of the calibration constants C and E .

Table 1. Pure Components Properties and Their Comparison with Their Corresponding Literature Values at Different Temperatures for Density ρ , Kinematic ν , and Dynamic Viscosity μ

compound	ρ		$10^6 \nu$	μ	
	exptl	literature	$\text{m}^2\cdot\text{s}^{-1}$	exptl	literature
$T = 293.15$ K					
1-propanol	0.8035	0.80375 ⁶	2.828	2.272	2.196 ⁶
1-pentanol	0.8146	0.8151 ⁶	4.946	4.029	4.0608 ⁶
1-heptanol	0.8222	0.8225 ⁶	8.640	7.104	7.058 ⁷
1-nonanol	0.8278	0.828 ⁶	14.110	11.683	11.635 ⁸
1-undecanol	0.8324	0.8335 ⁶	20.640	17.182	17.284 ⁸
$T = 298.15$ K					
1-propanol	0.7996	0.79975 ⁶	2.459	1.966	1.943 ⁶
1-pentanol	0.8110	0.8115 ⁶	4.308	3.494	3.5128 ⁶
1-heptanol	0.8187	0.8186 ⁶	7.320	5.993	5.898 ⁶
1-nonanol	0.8244	0.8247 ⁶	11.730	9.671	9.6921 ⁹
1-undecanol	0.8290	0.8297 ⁶	16.920	14.025	14 ⁶

Results and Discussion

The measured experimental values of density, kinematic viscosity, and the calculated absolute viscosity, μ , of the pure components employed in this study at temperatures of (293.15 and 298.15) K and the corresponding literature values are listed in Table 1. The comparison provided by Table 1 shows that the reported experimental values for density and absolute viscosity are in agreement with those reported in the literature. The experimental values of the densities, kinematic viscosities, and the calculated absolute viscosities of the investigated binary systems are reported in Table 2. The measured kinematic viscosity values reported in Table 2 were used to test the predictive capabilities of the previously mentioned models.

Rauf et al.¹⁰ reported data on the systems: 1-propanol + 1-heptanol and 1-propanol + 1-nonanol at $T = 298.15$ K. The data reported by Rauf et al.¹⁰ are not reliable for the following reasons: (i) their temperature stability when measuring viscosity was reported as ± 0.1 K (a factor of 10 less than achieved in this work); viscosity is a property which is a strong function of temperature, (ii) those authors employed water, which has relatively much lower viscosities than 1-alkanols for calibrating their viscometers, and (iii) 1-alkanols are known to be hygroscopic. No mention was made by Rauf et al.¹⁰ to indicate that they kept their 1-alkanols over molecular sieve. All such factors can result in significant errors. In addition, data on (1-nonanol + 1-undecanol) at temperatures of (293.15 and 298.15) K were reported by Faria et al.⁸ The main objection the present authors have about the work of those authors is that they reported the calibration of their density meter by using tridistilled water and air. The density range here is very wide relative to the density values they measured. This obviously increases the errors in measurement. The present authors employed compounds for calibration with densities that are in the same range as those measured to minimize the experimental errors. If one plots our reported densities (1-nonanol + 1-undecanol) at the two temperatures, one can easily see that the changes of density with composition in our case are much smoother than the densities reported by Faria et al.⁸ In addition, density is a function of temperature. Those authors did not indicate the kind of temperature measuring device they employed, whether it was calibrated or not, and if calibrated if it was on the basis of ITS-90 or IPTS-68. This is critical information that is needed to be supplied by those authors.

Table 3. Results of Testing Different Models

system	T	model 1		model 2		model 3		model 4	
	K	% AAD	% MAX	% AAD	% MAX	% AAD	% MAX	% AAD	% MAX
1-propanol + 1-pentanol	293.15	1.08	-2.23	1.28	-2.04	1.65	-2.51	94.36	94.55
	298.15	0.5	-0.96	0.61	-0.99	0.81	-1.28	93.75	93.92
1-propanol + 1-heptanol	293.15	1.54	-3.82	2.13	-3.81	7.39	-11.15	94.49	94.64
	298.15	0.77	-2.29	0.69	-2	5.76	-9.09	93.87	94.08
1-propanol + 1-nonanol	293.15	1.39	-3.92	2.48	-4.37	84.88	94.96	94.64	95.02
	298.15	1.47	-3.71	1.11	-1.96	84.38	94.61	94	94.43
1-propanol + 1-undecanol	293.15	2.52	-4.66	6.9	-11.13	49.20	60.89	94.62	95.23
	298.15	2.97	5.53	5.2	8.46	48.74	60.46	93.95	94.66
1-pentanol + 1-heptanol	293.15	0.38	1.02	0.66	-1.47	3.71	5.16	94.2	94.27
	298.15	0.28	0.7	0.57	-1.19	3.57	4.74	93.53	93.61
1-pentanol + 1-nonanol	293.15	0.7	-1.91	1.77	-2.94	4.45	6.56	94.19	94.37
	298.15	0.77	-2.25	1.83	-2.97	4.10	5.66	93.49	93.69
1-pentanol + 1-undecanol	293.15	1.09	3.52	2.42	-4.63	9.73	13.13	94.05	94.31
	298.15	1.45	-3.24	2.57	-5.36	9.03	12.51	93.3	93.61
1-heptanol + 1-nonanol	293.15	0.8	-2.34	1.59	-3.03	0.67	1.39	94	94.12
	298.15	0.92	-2.3	1.73	-2.94	0.61	-1.33	93.23	93.39
1-heptanol + 1-undecanol	293.15	1.3	3.65	1.17	2.51	4.66	6.64	93.86	94.16
	298.15	1.14	3.22	1.12	2.1	4.32	6.36	93.06	93.39
1-nonanol + 1-undecanol	293.15	1.49	3.91	1.21	3.12	2.57	4.96	93.62	93.87
	298.15	1.4	3.6	1.2	2.8	2.42	4.67	92.78	93.08
overall % AAD		1.20		1.92		16.63		93.85	

calculated from the densities and kinematic viscosities. Had they reported their measured viscosities we may have been able to draw many more conclusions about the quality of their data.

The generalized McAllister three-body interaction model for multicomponent n -alkane and for regular solutions was developed and reported by Nhaesi and Asfour.¹ They suggested the following equation for calculating the kinematic viscosity of any multicomponent liquid system:

$$\ln \nu_m = \sum_{i=1}^n x_i^3 \ln(\nu_i M_i) + 3 \sum_{i=1}^n \sum_{\substack{j=1 \\ i \neq j}}^n x_i^2 x_j \ln(\nu_{ij} M_{ij}) + 6 \sum_{i=1}^n \sum_{\substack{j=1 \\ i < j}}^n \sum_{\substack{k=1 \\ i < j < k}}^n x_i^2 x_j x_k \ln(\nu_{ijk} M_{ijk}) - \ln(M_{\text{avg}}) \quad (3)$$

For n -alkane mixtures, the binary interaction parameters in the previous equation are calculated using the following equation:

$$\frac{\nu_{ij}}{(\nu_i^2 \nu_j)^{1/3}} = 1 + 0.044 \frac{(N_j - N_i)^2}{(N_i^2 N_j)^{1/3}} \quad (4)$$

As suggested earlier by Shan,¹¹ the generalized version of the predictive model for multicomponent n -alkane mixtures was used for the prediction of the viscosities of the 1-alkanol binary mixtures. The GC-UNIMOD model was reported by Cao et al.² The viscosity equation in that model is given by,

$$\ln(\nu) = \sum_{i=1}^n \left[\phi_i \ln\left(\nu_i \frac{M_i}{M}\right) + 2\phi_i \ln\left(\frac{x_i}{\phi_i}\right) + \sum_{\text{all groups } k} \nu_k^{(i)} [\theta_{ki} - \theta_{ki}^{(i)}] \right] \quad (5)$$

where ϕ_i is the average segment fraction of component i , $\theta_{ki}^{(i)}$ is the residual viscosity of group k for component i in a mixture-of-group of pure liquid i in component i and $\nu_k^{(i)}$ is the number of groups k per molecule of component i .

The GCSP model was reported by Teja and Rice.³ The model requires knowledge of the critical properties. These data were taken from Reid et al.¹² The model is given by the following equation:

$$\ln(\mu\xi) = \ln(\mu\xi)^{r1} + \frac{\omega - \omega^{r1}}{\omega^{r2} - \omega^{r1}} [\ln(\mu\xi)^{r2} - \ln(\mu\xi)^{r1}] \quad (6)$$

where $r1$ and $r2$ refer to the two reference fluids, μ is the absolute viscosity, ω is the acentric factor of the nonspherical fluid, and ξ is a constant obtained from the critical properties of the fluid and is given by the following equation:

$$\xi = P_c^{-2/3} T_c^{1/6} M^{-1/2} \quad (7)$$

where P_c and T_c are the critical pressure and temperature, respectively. To apply the GCSP equation for liquid mixtures the mixing rules described in details earlier by Wong et al.¹³ are used.

Allan and Teja⁴ proposed the following correlative Antoine-type equation for the estimation of the absolute viscosity:

$$\ln \mu = A \left[-\frac{1}{B} + \frac{1}{T + C} \right] \quad (8)$$

where A , B , and C are constants that are correlated to the carbon numbers in the hydrocarbons composing the mixture. For n -alkanes, N is the number of carbon atoms per molecule of the component. For non n -alkane hydrocarbons, viscosity data measured experimentally are needed for the estimation of the effective carbon number. Allan and Teja⁴ described their own method, in the same paper, for calculating the effective carbon numbers.

The kinematic viscosity values calculated by these models were compared with the experimental values. The predictive capabilities of the viscosity models were tested in terms of percentage of average absolute deviation (% AAD) and the maximum percentage deviation of the model from experimental data (% MAX). The % AAD is calculated with the help of the following equation:

$$\% \text{AAD} = \frac{1}{n} \left[\sum \frac{|\nu_i^{\text{exp}} - \nu_i^{\text{cal}}|}{\nu_i^{\text{exp}}} \cdot 100 \right] \quad (9)$$

The % MAX is given by the following equation:

$$\% \text{ MAX} = \text{MAX} \left(\frac{\nu_i^{\text{measured}} - \nu_i^{\text{predicted}}}{\nu_i^{\text{measured}}} \right) \cdot 100 \quad (10)$$

where n is the number of the experimental points and ν is the kinematic viscosity.

It should be noted here that the acentric factors, critical data, molecular weights, and so forth that are needed for the calculations involved in all models were obtained from Reid et al.¹² The results of testing the different models are shown in Table 3. The four models that were tested in the present study showed a variation in their predictive capabilities. The data reported in Table 3 show that the generalized McAllister model gave the best overall predictive capability of all of the tested models. The overall percentage of the AAD values was 1.20 %. It should be noted here that the % AAD obtained in the case of all models are larger than the uncertainties observed in experimentally measuring the values of the viscosities.

Conclusions

The kinematic viscosities and densities of ten binary mixtures of 1-propanol, 1-pentanol, 1-heptanol, 1-nonanol, and 1-undecanol were measured at temperatures of (293.15 and 298.15) K over the entire composition range. The measured kinematic viscosity values reported in this work were used to test the predictive capabilities of a selected group of widely accepted and used viscosity models. The predictive capability of each of the viscosity models was determined by calculating the percent average absolute deviation (% AAD). The generalized McAllister model showed the best overall predictive capability of all models.

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