

Viscometric and Volumetric Properties of 10 Regular Binary Systems at 308.15 K and 313.15 K

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Abstract The densities and kinematic viscosities of 10 binary subsystems of the regular quinary system, benzene (1) + toluene (2) + ethylbenzene (3) + heptane (4) + cyclooctane (5), were measured at 308.15 K and 313.15 K over the entire composition range. The viscosity-composition data reported herein were utilized to examine the predictive capability of some viscosity models, namely, the predictive version of the McAllister model, a group contribution method (GC-UNIMOD), a generalized corresponding states principle (GCSP), and the Allan and Teja correlation. The results of testing showed that the McAllister model outperformed all other models except for systems containing cyclooctane. The results also showed an overall average absolute deviation (%AAD) of 1.25 % for systems that did not contain cyclooctane.

Keywords Binary mixtures · Density · Regular solutions · Viscosity · Viscosity models

1 Introduction

Reliable engineering design of most mass and heat transfer equipment requires accurate viscosity and density data. Moreover, an understanding of the behavior of liquid mixtures and their relation with temperature is extremely important for many chemical process applications.

In addition, a knowledge of the dependence of viscosities of liquid mixtures on composition, which is scarce in the literature, may lead to a clearer picture of the

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interactions between the different molecules involved in such mixtures. This in turn may help in developing new predictive models for the dependence of viscosity on composition.

The present work aims at reporting viscosity and density data for 10 binary liquid solutions at 308.15 K and 313.15 K over the entire composition range. The reported experimental densities and kinematic viscosities-composition data were employed in calculating the corresponding values of the absolute viscosities and excess volumes of mixing for all examined systems. In addition, kinematic viscosity-composition data were used to test the predictive capability of some literature viscosity models. According to Asfour's [1] earlier classification of solutions of liquid mixtures, the components of the quinary system under investigation were chosen from the regular type and with differences in their structures and shapes.

It should be pointed out that the experimental results reported in the present study represent additions to our database that is continuing to expand in order to provide reliable viscosity-composition data for multicomponent liquid systems at different temperatures. The reported data should help in both testing and developing future predictive models.

All the pure components employed in the present study are miscible when mixed over the temperature range of interest and over the entire composition range. This was found to be true for all the binary, ternary, quaternary, and quinary systems investigated in the study.

2 Experimental

2.1 Materials

Pure components constituting the systems investigated and the chemicals used in the density meter calibration were purchased from Aldrich Chemical Company and Fluka Chemika. The stated purities according to the manufactures were claimed to be 99+ mol %. Further analysis for all chemicals using gas chromatography analysis in our laboratory led to values of purities that exceeded the stated ones (cf. Table 1). Therefore, these chemicals were used as purchased without further purification. An HP 5890 gas chromatograph equipped with an FID and a 5 m × 0.53 mm methyl silicon capillary column has been used for that purpose.

2.2 Preparation of Solutions

The same technique proposed earlier by Asfour [1] was employed in this study for preparing the 10 binary mixtures. A Mettler HK 160 balance with a stated precision of $\pm 2 \times 10^{-7}$ kg was used in weighing the different samples that were placed in vials fitted with Teflon disks and aluminum seals in order to minimize evaporation losses. The vials, Teflon disks, and aluminum seals were purchased from Chromatographic Specialties Ltd.

Table 1 Specifications of the chemicals used in the present study

Supplier	Compound	Specification (mol %)	GC analysis (mass %)
Aldrich Chemical Company	Benzene	99+	99.95
	Toluene	99+	99.04
	Ethylbenzene	99+	99.43
	Heptane	99+	99.53
	Cyclooctane	99+	99.64
	<i>p</i> -Xylene ^a	99+	99.24
	Undecane ^a	99+	99.94
Fluka-Chemika	1-Hexanol ^a	≥ 99	99.12
	1-Heptanol ^a	≥ 99	99.82

^a Compounds used for the density meter calibration

2.3 Density Measurements

In the present study, the densities were measured using an Anton Paar DMA 60/602 density meter which has a stated precision of $3 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$. The density meter is connected to a Haake N4-B circulator fitted with a calibrated platinum temperature sensor (IPTS-68). The density meter is enclosed in a controlled temperature wooden box where temperature fluctuations were kept to within $\pm 0.1 \text{ K}$ as suggested earlier by Asfour [1].

A DP95 digital RTD thermometer (ITS-90), supplied by Omega, was employed for measuring the bath temperature. The thermometer has a temperature uncertainty of 0.005 K . The temperature fluctuations within the density meter cell were maintained to within $\pm 0.01 \text{ K}$.

The densities of the different components were calculated from the following equation proposed by the supplier of the density meter.

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

where ρ is the density in $\text{g} \cdot \text{cm}^{-3}$, τ is the oscillation period in s, and (A , B , and C) are equation parameters that were determined at 308.15 K and 313.15 K using compounds with accurately known densities at the temperatures of interest. The calibration fluids were selected so that their densities cover the range of densities of the compounds constituting the liquid mixture systems. The following fluids, the densities of which are known from the literature in $\text{g} \cdot \text{cm}^{-3}$, were employed in calibrating the density meter at 308.15 K : *p*-xylene ($\rho = 0.8478 \text{ g} \cdot \text{cm}^{-3}$) [2], double-distilled water ($\rho = 0.994061 \text{ g} \cdot \text{cm}^{-3}$) [3], undecane ($\rho = 0.7291 \text{ g} \cdot \text{cm}^{-3}$) [4], 1-hexanol ($\rho = 0.8080 \text{ g} \cdot \text{cm}^{-3}$) [4], 1-heptanol ($\rho = 0.8117 \text{ g} \cdot \text{cm}^{-3}$) [4], and N0.8 ($\rho = 0.8538 \text{ g} \cdot \text{cm}^{-3}$) and at 313.15 K : *p*-xylene ($\rho = 0.8436 \text{ g} \cdot \text{cm}^{-3}$) [2], double-distilled water ($\rho = 0.9922497 \text{ g} \cdot \text{cm}^{-3}$) [3], undecane ($\rho = 0.7255 \text{ g} \cdot \text{cm}^{-3}$)

[4], 1-hexanol ($\rho = 0.8054 \text{ g} \cdot \text{cm}^{-3}$) [4], 1-heptanol ($\rho = 0.8077 \text{ g} \cdot \text{cm}^{-3}$) [4], and N0.8 ($\rho = 0.8494 \text{ g} \cdot \text{cm}^{-3}$). The N0.8 fluid is a viscosity standard purchased from Cannon Instrument Company for viscometer calibration. The densities and viscosities of that fluid were accurately determined by the supplier at the temperatures of interest. The calibration fluids had not been used as components of any of the investigated systems. Error analysis calculations indicated an uncertainty of $3.5 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$ in the density measurements.

2.4 Viscosity Measurements

The kinematic viscosities of all compounds in the present study were measured using a set of eight Cannon-Ubbelohde capillary viscometers with a stated precision of $\pm 0.1\%$. Half of the viscometers used were of the size 25B whereas the other half were of the size 50B. These particular sizes of viscometers were chosen so that they cover the range of kinematic viscosities of the fluids, and their mixtures, under investigation.

The following equation was suggested by the supplier for the calculation of kinematic viscosities of the different compounds:

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

where ν is the kinematic viscosity in $\text{m}^2 \cdot \text{s}^{-1}$, t is the efflux time of the sample measured in seconds by using an electronic stopwatch with an uncertainty of 0.01 s. C and E are equation parameters to be determined by calibration standards with accurately known kinematic viscosity values at the temperatures of interest. The calibration standard fluids employed in calibrating the viscometers used in the present study were purchased from Cannon Instrument Company. The standard fluids have the following nominal viscosity ranges over the temperatures of interest: N0.4 (0.4 to 0.47) $10^{-6} \text{m}^2 \cdot \text{s}^{-1}$, N0.8 (0.6 to 0.74) $10^{-6} \text{m}^2 \cdot \text{s}^{-1}$, and N1.0 (0.97 to 1.3) $10^{-6} \text{m}^2 \cdot \text{s}^{-1}$. In order to minimize human error, three readings of the efflux time were taken that should always agree within ± 0.1 s and the substituted value is the average of these three measurements. The uncertainty in the kinematic viscosity measurements was found to be within $2 \times 10^{-9} \text{m}^2 \cdot \text{s}^{-1}$.

3 Results and Discussion

Table 2 reports the experimental values of the densities and kinematic viscosities of the pure components involved in the present study along with their corresponding literature values. One can observe from Table 2 that there is excellent agreement between the experimental values and their corresponding literature values.

The experimental values of the densities and kinematic viscosities were utilized to calculate the corresponding absolute viscosities. The densities were used in calculating the excess volumes of mixing for all systems over the entire composition range. Table 3 reports the data for such properties.

Table 2 Physical properties of pure components and comparisons with literature values at 308.15 K and 313.15 K

Compound	ρ (g · cm ⁻³)		$\nu \times 10^6$ (m ² · s ⁻¹)	
	Experimental value	Literature value	Experimental value	Literature value
<i>T</i> = 308.15 K				
Benzene	0.8629	0.8629 [18]	0.6110	0.6066 [4]
Toluene	0.8528	0.8527 [19]	0.5792	0.5741 [4]
Ethylbenzene	0.8537	0.8548 [20]	0.6621	0.6614 [4]
Heptane	0.6714	0.6705 [21]	0.5209	0.5336 [4]
Cyclooctane	0.8236	0.8238 [22]	2.1887	–
<i>T</i> = 313.15 K				
Benzene	0.8577	0.8575 [4]	0.5762	0.5722 [4]
Toluene	0.8483	0.8482 [4]	0.5512	0.5465 [4]
Ethylbenzene	0.8495	0.8494 [4]	0.6231	0.6286 [4]
Heptane	0.6671	0.6665 [4]	0.4990	0.5122 [4]
Cyclooctane	0.8197	0.81950 [23]	1.9958	2.0195 [23]

The excess volume of mixing, V^E , can be calculated from the following equation for any binary mixture:

$$V^E = \frac{\sum_i x_i M_i}{\rho} - \sum_i \frac{x_i M_i}{\rho_i} \quad (3)$$

where M is the molar mass, ρ is the density, and i denotes a pure component property.

Plots of the total apparent molar volumes, V^E/x_1x_2 , [5] versus composition at 308.15 K and 313.15 K are shown in Figs. 1 and 2.

Models that were tested using our viscosity-composition data were the predictive version of the McAllister three-body model proposed by Asfour et al. [6] and Nhaesi and Asfour [7,8], a generalized corresponding states principle (GCSP) reported by Teja and Rice [9], a group contribution method (GC-UNIMOD) reported by Cao et al. [10], and the Allan and Teja Correlation [11].

McAllister [12] successfully developed his cubic equation for correlating the kinematic viscosities of binary liquid mixtures. This equation was regarded by many investigators as one of the best available correlating technique for binary liquid mixtures. The reported McAllister three-body interaction model is as follows:

$$\begin{aligned} \ln v_m = & x_1^3 \ln v_1 + 3x_1^2 x_2 \ln v_{12} + 3x_1 x_2^2 \ln v_{21} \\ & + x_2^3 \ln v_2 - \ln[x_1 + x_2 M_2/M_1] + 3x_1^2 x_2 \ln[(2 + M_2/M_1)/3] \\ & + 3x_1 x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln[M_2/M_1] \end{aligned} \quad (4)$$

Table 3 Density and viscosity for the 10 binary regular systems at 308.15 K and 313.15 K

x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (m Pa · s)
Benzene (1)–Toluene (2)									
$T = 308.15$ K									
1.0000	0.8629	0.0000	0.6110	0.5272	1.0000	0.8577	0.0000	0.5762	0.4942
0.0000	0.8528	0.0000	0.5792	0.4940	0.0000	0.8483	0.0000	0.5512	0.4676
0.0403	0.8531	0.0151	0.5794	0.4943	0.0403	0.8486	0.0089	0.5515	0.4680
0.1393	0.8537	0.0458	0.5854	0.4998	0.1393	0.8491	0.0410	0.5512	0.4681
0.2551	0.8545	0.0673	0.5814	0.4968	0.2551	0.8499	0.0599	0.5522	0.4693
0.3116	0.8550	0.0786	0.5811	0.4968	0.3116	0.8503	0.0754	0.5516	0.4690
0.3863	0.8557	0.0778	0.5817	0.4977	0.3863	0.8509	0.0738	0.5529	0.4705
0.5033	0.8566	0.0948	0.5872	0.5030	0.5033	0.8518	0.0916	0.5573	0.4747
0.6139	0.8578	0.0909	0.5920	0.5078	0.6139	0.8529	0.0874	0.5610	0.4785
0.7301	0.8591	0.0777	0.6013	0.5166	0.7301	0.8541	0.0756	0.5635	0.4813
0.8551	0.8608	0.0487	0.6072	0.5227	0.8551	0.8557	0.0443	0.5691	0.4870
Toluene (1)–Ethylbenzene (2)									
$T = 308.15$ K									
1.0000	0.8528	0.0000	0.5792	0.4940	1.0000	0.8483	0.0000	0.5512	0.4755
0.0000	0.8537	0.0000	0.6621	0.5652	0.0000	0.8495	0.0000	0.6231	0.5294
0.0424	0.8537	0.0027	0.6544	0.5587	0.0424	0.8495	-0.0036	0.6246	0.5306
0.1280	0.8537	-0.0065	0.6545	0.5587	0.1280	0.8494	-0.0105	0.6181	0.5250
0.2164	0.8536	-0.0085	0.6409	0.5471	0.2164	0.8493	-0.0121	0.6105	0.5185
0.2928	0.8536	-0.0116	0.6336	0.5408	0.2928	0.8493	-0.0161	0.6033	0.5124
0.3930	0.8535	-0.0101	0.6302	0.5379	0.3930	0.8492	-0.0153	0.5990	0.5186
0.4922	0.8534	-0.0156	0.6268	0.5349	0.4922	0.8491	-0.0186	0.5914	0.5022
$T = 313.15$, K									

Table 3 continued

x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)
0.5716	0.8534	-0.0141	0.6144	0.5243	0.5716	0.8490	-0.0218	0.5852	0.4968		
0.7107	0.8532	-0.0136	0.6006	0.5125	0.7107	0.8488	-0.0173	0.5712	0.4853		
0.8425	0.8530	-0.0056	0.5988	0.5108	0.8425	0.8486	-0.0103	0.5634	0.4781		
Heptane (1)–Toluene (2)											
$T = 308.15$ K											
1.0000	0.6713	0.0000	0.5209	0.3497	1.0000	0.6671	0.0000	0.4990	0.3329		
0.0000	0.8528	0.0000	0.5792	0.4940	0.0000	0.8483	0.0000	0.5512	0.4676		
0.0901	0.8309	0.0080	0.5573	0.4631	0.0901	0.8265	-0.0009	0.5313	0.4392		
0.1949	0.8070	0.0517	0.5460	0.4406	0.1949	0.8026	0.0442	0.5145	0.4129		
0.2903	0.7866	0.1014	0.5275	0.4150	0.2903	0.7822	0.0964	0.5042	0.3944		
0.3959	0.7659	0.1019	0.5179	0.3967	0.3959	0.7616	0.0946	0.4950	0.3770		
0.4836	0.7496	0.1308	0.5151	0.3861	0.4836	0.7454	0.1231	0.4922	0.3668		
0.5809	0.7328	0.1309	0.5201	0.3811	0.5809	0.7286	0.1213	0.4888	0.3562		
0.6809	0.7166	0.1121	0.5116	0.3666	0.6809	0.7125	0.1023	0.4896	0.3488		
0.7920	0.6998	0.0971	0.5108	0.3575	0.7920	0.6956	0.0921	0.4903	0.3410		
0.8884	0.6861	0.0573	0.5254	0.3605	0.8884	0.6820	0.0537	0.4937	0.3367		
Heptane (1)–Ethylbenzene (2)											
$T = 308.15$ K											
1.0000	0.6713	0.0000	0.5209	0.3497	1.0000	0.6671	0.0000	0.4990	0.3329		
0.0000	0.8537	0.0000	0.6621	0.5652	0.0000	0.8495	0.0000	0.6231	0.5294		
0.1034	0.8315	0.0012	0.6274	0.5217	0.1034	0.8274	-0.0143	0.5977	0.4945		
0.2048	0.8106	0.0002	0.6075	0.4925	0.2048	0.8065	-0.0111	0.5742	0.4631		
0.2931	0.7930	0.0139	0.5832	0.4625	0.2931	0.7888	0.0092	0.5569	0.4393		

Table 3 continued

x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)
0.3754	0.7772	0.0140	0.5662	0.4400	0.3754	0.7730	0.0037	0.5420	0.4190	0.5420	0.4190
0.4880	0.7563	0.0150	0.5547	0.4195	0.4880	0.7522	-0.0056	0.5299	0.3986	0.5299	0.3986
0.5929	0.7377	-0.0070	0.5504	0.4061	0.5929	0.7336	-0.0224	0.5189	0.3807	0.5189	0.3807
0.6899	0.7209	0.0184	0.5353	0.3859	0.6899	0.7167	0.0073	0.5119	0.3669	0.5119	0.3669
0.8051	0.7018	0.0115	0.5257	0.3690	0.8051	0.6977	0.0020	0.5039	0.3516	0.5039	0.3516
0.8979	0.6871	-0.0083	0.5326	0.3659	0.8979	0.6830	-0.0151	0.5015	0.3425	0.5015	0.3425
Benzene (1)–Ethylbenzene (2)											
$T = 308.15$ K											
1.0000	0.8629	0.0000	0.6110	0.5272	1.0000	0.8577	0.0000	0.5762	0.4942	0.5762	0.4942
0.0000	0.8537	0.0000	0.6621	0.5652	0.0000	0.8495	0.0000	0.6231	0.5294	0.6231	0.5294
0.0877	0.8541	0.0347	0.6538	0.5584	0.0877	0.8498	0.0282	0.6215	0.5282	0.6215	0.5282
0.1855	0.8546	0.0634	0.6509	0.5563	0.1855	0.8502	0.0578	0.6156	0.5234	0.6156	0.5234
0.2950	0.8552	0.0896	0.6399	0.5472	0.2950	0.8508	0.0822	0.6079	0.5172	0.6079	0.5172
0.4137	0.8560	0.1102	0.6299	0.5392	0.4137	0.8515	0.1050	0.5985	0.5096	0.5985	0.5096
0.4980	0.8566	0.1187	0.6282	0.5382	0.4980	0.8521	0.1098	0.5962	0.5080	0.5962	0.5080
0.5965	0.8575	0.1183	0.6276	0.5382	0.5965	0.8528	0.1138	0.5909	0.5039	0.5909	0.5039
0.7108	0.8587	0.1028	0.6181	0.5308	0.7108	0.8539	0.0969	0.5850	0.4996	0.5850	0.4996
0.7904	0.8597	0.0841	0.6122	0.5263	0.7904	0.8548	0.0765	0.5796	0.4954	0.5796	0.4954
0.8983	0.8612	0.0472	0.6165	0.5309	0.8983	0.8562	0.0448	0.5781	0.4949	0.5781	0.4949
Benzene (1)–Heptane (2)											
$T = 308.15$ K											
1.0000	0.8629	0.0000	0.6110	0.5272	1.0000	0.8577	0.0000	0.5762	0.4942	0.5762	0.4942
0.0000	0.6713	0.0000	0.5209	0.3497	0.0000	0.6671	0.0000	0.4990	0.3329	0.4990	0.3329

Table 3 continued

x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)
0.1099	0.6836	0.2162	0.5147	0.3518	0.1099	0.6794	0.2181	0.4919	0.3342	0.4919	0.3342
0.2052	0.6953	0.3813	0.5167	0.3593	0.2052	0.6911	0.3765	0.4856	0.3356	0.4856	0.3356
0.2896	0.7066	0.4870	0.5041	0.3562	0.2896	0.7024	0.4815	0.4822	0.3387	0.4822	0.3387
0.4212	0.7265	0.5912	0.4999	0.3632	0.4212	0.7221	0.5908	0.4777	0.3450	0.4777	0.3450
0.5078	0.7409	0.6685	0.5026	0.3724	0.5078	0.7364	0.6646	0.4798	0.3534	0.4798	0.3534
0.6087	0.7600	0.6383	0.5165	0.3925	0.6087	0.7554	0.6347	0.4854	0.3667	0.4854	0.3667
0.7263	0.7855	0.5371	0.5213	0.4094	0.7263	0.7808	0.5326	0.4968	0.3879	0.4968	0.3879
0.7936	0.8019	0.4395	0.5315	0.4262	0.7936	0.7971	0.4357	0.5057	0.4031	0.5057	0.4031
0.8987	0.8306	0.2576	0.5699	0.4734	0.8987	0.8256	0.2571	0.5339	0.4408	0.5339	0.4408
Benzene (1)–Cyclooctane (2)											
$T = 308.15$ K											
1.0000	0.8629	0.0000	0.6110	0.5272	1.0000	0.8577	0.0000	0.5762	0.4942	0.5762	0.4942
0.0000	0.8236	0.0000	2.1887	1.8026	0.0000	0.8197	0.0000	1.9958	1.6360	1.9958	1.6360
0.1004	0.8249	0.2174	1.8105	1.4936	0.1004	0.8210	0.2104	1.6660	1.3678	1.6660	1.3678
0.1826	0.8264	0.3505	1.5663	1.2944	0.1826	0.8224	0.3450	1.4511	1.1934	1.4511	1.1934
0.3035	0.8290	0.5001	1.2935	1.0723	0.3035	0.8249	0.4951	1.2038	0.9930	1.2038	0.9930
0.4080	0.8319	0.5755	1.1086	0.9222	0.4080	0.8276	0.5706	1.0379	0.8590	1.0379	0.8590
0.5122	0.8352	0.6071	0.9680	0.8085	0.5122	0.8309	0.6005	0.9083	0.7548	0.9083	0.7548
0.5243	0.8357	0.6037	0.9528	0.7963	0.5243	0.8314	0.5977	0.8946	0.7437	0.8946	0.7437
0.6891	0.8427	0.5389	0.7912	0.6667	0.6891	0.8381	0.5315	0.7486	0.6274	0.7486	0.6274
0.7904	0.8481	0.4248	0.7125	0.6042	0.7904	0.8433	0.4214	0.6732	0.5677	0.6732	0.5677
0.9001	0.8551	0.2412	0.6609	0.5651	0.9001	0.8501	0.2405	0.6191	0.5263	0.6191	0.5263

Table 3 continued

x_1	ρ ($\text{g} \cdot \text{cm}^{-3}$)	V^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	ν ($10^{-6} \text{m}^2 \cdot \text{s}^{-1}$)	η ($\text{mPa} \cdot \text{s}$)	x_1	ρ ($\text{g} \cdot \text{cm}^{-3}$)	V^E ($\text{cm}^3 \cdot \text{mol}^{-1}$)	ν ($10^{-6} \text{m}^2 \cdot \text{s}^{-1}$)	η ($\text{mPa} \cdot \text{s}$)
Toluene (1)–Cyclooctane (2)									
$T = 308.15 \text{ K}$									
1.0000	0.8528	0.0000	0.5792	0.4940	1.0000	0.8483	0.0000	0.5512	0.4676
0.0000	0.8236	0.0000	2.1887	1.8026	0.0000	0.8197	0.0000	1.9958	1.6360
0.0997	0.8246	0.2194	1.7496	1.4427	0.0997	0.8207	0.2168	1.6152	1.3256
0.1951	0.8260	0.3620	1.4501	1.1978	0.1951	0.8221	0.3582	1.3531	1.1124
0.3032	0.8281	0.4683	1.2108	1.0026	0.3032	0.8241	0.4643	1.1325	0.9333
0.3904	0.8300	0.5180	1.0539	0.8748	0.3904	0.8260	0.5129	0.9931	0.8203
0.4868	0.8325	0.5311	0.9409	0.7834	0.4868	0.8285	0.5239	0.8461	0.7010
0.5898	0.8356	0.5184	0.8354	0.6981	0.5898	0.8314	0.5077	0.7913	0.6579
0.6919	0.8392	0.4396	0.7467	0.6266	0.6919	0.8349	0.4358	0.7080	0.5912
0.8003	0.8434	0.3265	0.6726	0.5673	0.8003	0.8391	0.3244	0.6392	0.5364
0.8880	0.8473	0.2070	0.6328	0.5361	0.8880	0.8429	0.2006	0.5971	0.5033
Ethylbenzene (1)–Cyclooctane (2)									
$T = 308.15 \text{ K}$									
1.0000	0.8537	0.0007	0.6621	0.5652	1.0000	0.8495	0.0000	0.6231	0.5294
0.0000	0.8236	0.0000	2.1887	1.8026	0.0000	0.8197	0.0000	1.9958	1.6360
0.0907	0.8248	0.2082	1.8032	1.4874	0.0907	0.8209	0.2066	1.6513	1.3556
0.2033	0.8271	0.3520	1.4581	1.2061	0.2033	0.8232	0.3488	1.3490	1.1104
0.3072	0.8295	0.4400	1.2315	1.0215	0.3072	0.8256	0.4374	1.1601	0.9578
0.3701	0.8312	0.4581	1.1348	0.9433	0.3701	0.8272	0.4618	1.0596	0.8765
0.4761	0.8342	0.4764	1.0032	0.8369	0.4761	0.8302	0.4718	0.9437	0.7835
0.5798	0.8375	0.4460	0.9036	0.7568	0.5798	0.8334	0.4464	0.8506	0.7089

Table 3 continued

x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	x_1	ρ (g · cm ⁻³)	V^E (cm ³ · mol ⁻¹)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)	ν (10 ⁻⁶ m ² · s ⁻¹)	η (mPa · s)
0.7008	0.8417	0.3685	0.8003	0.6736	0.7008	0.8376	0.3667	0.7645	0.6403		
0.7922	0.8451	0.2898	0.7515	0.6351	0.7922	0.8409	0.2885	0.7110	0.5979		
0.8908	0.8490	0.1699	0.7017	0.5958	0.8908	0.8448	0.1756	0.6664	0.5629		
Heptane (1)–Cyclooctane (2)											
$T = 308.15$ K											
1.0000	0.6713	0.0000	0.5209	0.3497	1.0000	0.6671	0.0000	0.4990	0.3329		
0.0000	0.8236	0.0000	2.1887	1.8026	0.0000	0.8197	0.0000	1.9958	1.6360		
0.0938	0.8077	0.0707	1.7396	1.4050	0.0938	0.8038	0.0634	1.6025	1.2880		
0.1897	0.7930	-0.0923	1.4187	1.1251	0.1897	0.7891	-0.1011	1.3229	1.0439		
0.2896	0.7775	-0.1610	1.1893	0.9246	0.2896	0.7736	-0.1861	1.1124	0.8605		
0.3979	0.7608	-0.2134	1.0007	0.7613	0.3979	0.7568	-0.2369	0.9417	0.7127		
0.4949	0.7461	-0.2706	0.8857	0.6608	0.4949	0.7422	-0.3008	0.8363	0.6207		
0.5964	0.7309	-0.2881	0.7832	0.5725	0.5964	0.7269	-0.3149	0.7414	0.5389		
0.6919	0.7167	-0.2932	0.7015	0.5028	0.6919	0.7127	-0.3092	0.6670	0.4754		
0.7795	0.7036	-0.2354	6377	0.4487	0.7795	0.6997	-0.2610	0.6083	0.4256		
0.8934	0.6869	-0.1455	0.5826	0.4002	0.8934	0.6828	-0.1477	0.5499	0.3754		

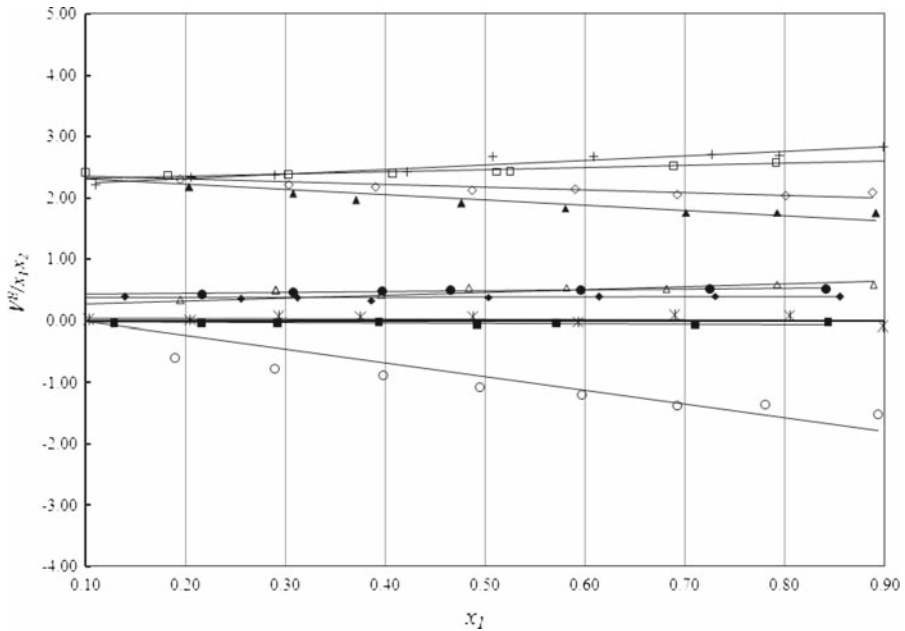


Fig. 1 Total apparent molar volume versus composition at 308.15 K. \blacklozenge Benzene (1)–Toluene (2), \blacksquare Toluene (1)–Ethylbenzene (2), * Heptane (1)–Ethylbenzene (2), \triangle Heptane (1)–Toluene (2), \diamond Benzene (1)–Ethylbenzene (2), \circ Benzene (1)–Heptane (2), $+$ Benzene (1)–Cyclooctane (2), \blacktriangle Toluene (1)–Cyclooctane (2), \boxtimes Ethylbenzene (1)–Cyclooctane (2), \square Heptane (1)–Cyclooctane (2)

where M_1 and M_2 are the molar masses of pure components 1 and 2, respectively, and v_{12} and v_{21} are binary interaction parameters. The determination of these interaction parameters requires the availability of costly and time consuming experimental data which is considered as the main drawback of the McAllister model [12].

Asfour et al. [6] and Nhaesi and Asfour [7, 8] successfully converted the McAllister model from a correlative technique into a predictive one. This was achieved by developing a new technique for the calculation of the McAllister interaction parameters numerically by only employing the viscosities of the pure components constituting a mixture, the number of carbon numbers of the components for the case of n -alkane systems, or the number of effective carbons for the case of regular solutions. They reported the following equations for both n -alkanes and regular solution binary mixtures:

$$\frac{v_{12}}{(v_1^2 v_2)^{1/3}} = 1 + 0.044 \frac{(N_2 - N_1)^2}{(N_1^2 N_2)^{1/3}} \tag{5}$$

$$\frac{v_{12}}{(v_1^2 v_2)^{1/3}} = 0.8735 + 0.0715 \frac{(N_2 - N_1)^2}{(N_1^2 N_2)^{1/3}} \tag{6}$$

$$v_{21} = v_{12} \left(\frac{v_2}{v_1} \right)^{1/3} \tag{7}$$

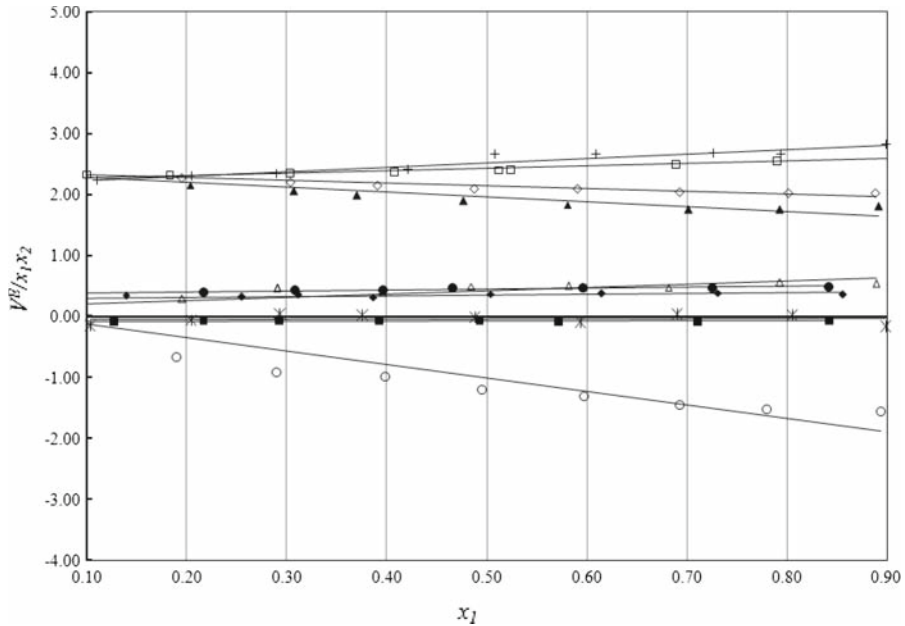


Fig. 2 Total apparent molar volume versus composition at 313.15 K. ♦ Benzene (1)–Toluene (2), ■ Toluene (1)–Ethylbenzene (2), * Heptane (1)–Ethylbenzene (2), Δ Heptane (1)–Toluene (2), ◇ Benzene (1)–Ethylbenzene (2), * Benzene (1)–Heptane (2), + Benzene (1)–Cyclooctane (2), ▲ Toluene (1)–Cyclooctane (2), ⌘ Ethylbenzene (1)–Cyclooctane (2), □ Heptane (1)–Cyclooctane (2)

where N_1 and N_2 are the number of carbons (or effective carbons; as indicated earlier) for components 1 and 2, respectively. Nhaesi and Asfour [7] reported the following equation to calculate the effective carbon number for any component by substituting its kinematic viscosity value at 308.15 K:

$$\ell_{nv} = -1.943 + 0.193N \tag{8}$$

The values of N_1 and N_2 calculated from the above equation can then be substituted back into Eq. 6 along with their corresponding kinematic viscosity values; ν_1 and ν_2 are used to determine the value of the first interaction parameter ν_{12} . The value of the second parameter ν_{21} can be obtained by using Eq. 7.

This procedure was performed for all pure components involved in the 10 binary liquid mixtures investigated in the present study. All the results for pure components were substituted into the McAllister Eq. 4 to estimate the corresponding predicted values of kinematic viscosities of each mixture, ν_m .

The experimental and predicted values of kinematic viscosities of all mixtures were then compared using the percent absolute average deviation concept (%AAD) as follows:

$$\%AAD = \frac{1}{n} \sum_{i=1}^n \frac{|v_i^{\text{measured}} - v_i^{\text{predicted}}|}{v_i^{\text{measured}}} \times 100 \tag{9}$$

The maximum deviation of the predicted results may be determined from the following function:

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

Table 3 reports the results of the above mentioned comparisons as well as the results of testing the different models.

It should be pointed out here that, applying Eq. 6 for some of the investigated systems, namely, benzene–toluene, benzene–ethylbenzene, and toluene–ethylbenzene, led to higher errors than were expected. This confirmed earlier findings that were reported by Al-Gherwi et al. [13]. It was found that applying Eq. 5 which was proposed for *n*-alkanes for those particular systems gave much better results and dramatically reduced the error. These authors' explanation for such phenomena was that the effects of the benzene rings contained in the compounds constituting those mixtures tend to off-set each other and that interactions would mainly be due to the side chain, viz., CH₃ and CH₂–CH₃ *n*-alkane groups (Table 4).

Al Gherwi et al. [13], El-Hadad [14], and Cai [15] also observed in their studies of the viscosities of liquid mixtures containing cyclohexane that Eq. 8 tended to over-predict the value of the effective carbon number of cyclohexane. Much lower errors that resulted from testing the McAllister model were obtained when applying 75 % of the value that was calculated from Eq. 8.

In the present study, for the case of cyclooctane, an effective carbon number value calculated from Eq. 8 was 14.126. That value as well as 75 % of that value, which is 10.595, were both employed for testing the McAllister model. The second value gave better results as shown in Table 5 which confirmed the findings of the former studies referred previously.

The present authors noticed that unexpected error values resulted when testing the McAllister three-body interaction model given by Eq. 4 for systems containing cyclooctane. We believe that such a result requires the development of the four-body interaction model to be tested instead. This is simply due to the relatively large difference between the molecular diameter of cyclooctane and the second component constituting the binary system that led to those high deviations. Similar results were reported by McAllister [16] while studying the acetone–water system.

Figures 3 and 4 summarize the results of testing the predictive capability of the different investigated models including and excluding cyclooctane-containing systems, respectively, and the effect of that on the calculated %AAD.

It should be pointed out here that, applying the GC-UNIMOD method, required data on the UNIFAC group specifications and sample group assignments which were taken from Poling et al. [17].

4 Conclusions

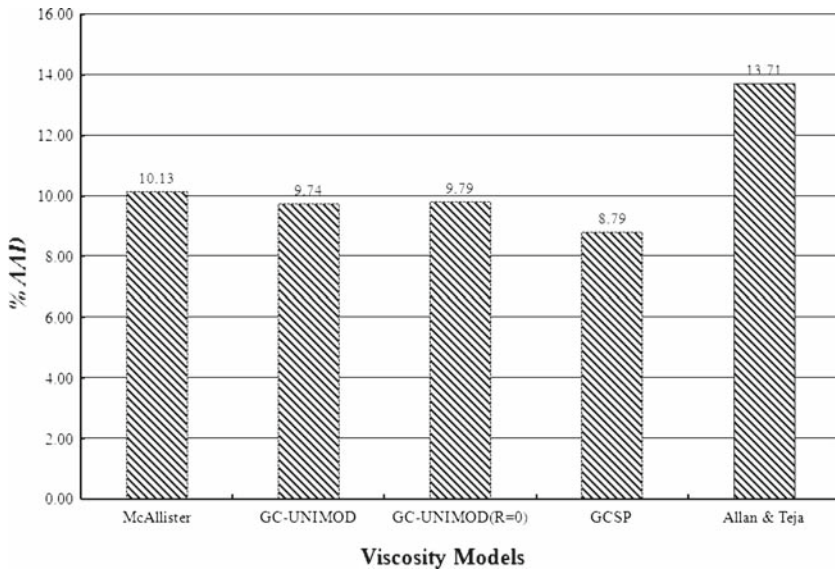
Densities and kinematic viscosities of 10 binary regular mixtures were measured over the entire composition range at 308.15 K and 313.15 K. The measured values of the

Table 4 Results of testing the predictive capability of the different investigated models using experimental viscosity data

System	T (K)	McAllister model		GC-UNIMOD (R=0)		GC-UNIMOD		GCSP		Allan and Teja correlation	
		%AAD	%MAX	%AAD	%MAX	%AAD	%MAX	%AAD	%MAX	%AAD	%MAX
Benzene (1)–Toluene (2)	308.15	0.62	1.57	0.51	0.87	0.88	1.81	0.84	1.71	23.29	24.07
	313.15	0.70	1.34	0.35	0.68	0.77	1.51	0.98	1.50	22.49	23.52
Toluene (1)–Ethylbenzene (2)	308.15	0.44	1.15	0.54	1.10	1.13	1.90	0.53	1.10	22.25	24.35
	313.15	0.41	0.75	0.48	0.73	0.58	1.14	0.48	0.72	21.80	23.52
Heptane (1)–Toluene (2)	308.15	2.38	5.14	3.09	4.98	2.31	3.57	4.94	7.64	8.22	23.91
	313.15	2.07	3.67	3.43	4.85	2.48	3.44	5.34	7.47	7.92	23.52
Heptane (1)–Ethylbenzene (2)	308.15	2.22	4.79	3.39	5.58	2.31	3.96	4.28	6.76	7.10	20.81
	313.15	2.41	4.04	3.13	4.55	1.91	2.94	4.04	5.74	6.97	19.87
Benzene (1)–Ethylbenzene (2)	308.15	0.57	1.38	0.44	0.78	0.52	1.32	1.27	2.18	21.57	23.64
	313.15	0.33	0.81	0.37	0.74	0.83	1.26	0.86	1.45	20.88	22.61
Benzene (1)–Heptane (2)	308.15	1.48	4.01	4.46	6.77	4.40	6.68	9.60	13.49	6.39	22.64
	313.15	1.33	3.43	4.72	6.39	4.65	6.30	9.76	13.39	6.19	22.49
Benzene (1)–Cyclooctane (2)	308.15	20.96	35.50	24.36	33.81	24.62	34.17	15.10	20.68	9.03	23.64
	313.15	20.01	33.95	22.82	31.69	23.07	32.04	14.00	19.21	8.65	22.61
Toluene (1)–Cyclooctane (2)	308.15	25.24	43.41	24.56	34.37	25.37	35.39	20.01	28.46	11.37	23.91
	313.15	24.76	47.38	23.69	37.53	24.47	38.67	19.36	31.22	11.30	23.52
Ethylbenzene (1)–Cyclooctane (2)	308.15	23.53	39.55	21.29	28.90	21.84	29.65	18.37	25.13	11.63	20.61
	313.15	22.07	37.32	19.51	27.21	20.04	27.88	16.74	23.62	11.16	19.67
Heptane (1)–Cyclooctane (2)	308.15	25.92	45.18	17.28	25.22	17.28	25.22	15.11	22.25	18.16	31.10
	313.15	25.10	43.46	16.36	23.68	16.36	23.68	14.26	20.84	17.75	30.16
Overall %AAD		10.13		9.74		9.79		8.79		13.71	

Table 5 Effect of cyclooctane effective carbon number (N) change on the predictive capability of McAllister model

System	T (K)	Cyclooctane ($N = 14.126$)		Cyclooctane ($N = 10.595$)	
		%AAD	%MAX	%AAD	%MAX
Benzene (1)–Cyclooctane (2)	308.15	20.96	35.50	12.82	21.48
	313.15	20.01	33.95	11.96	20.07
Toluene (1)–Cyclooctane (2)	308.15	25.24	43.41	16.53	28.82
	313.15	24.76	47.38	16.08	31.68
Ethylbenzene (1)–Cyclooctane (2)	308.15	23.53	39.55	16.22	27.05
	313.15	22.07	37.32	14.88	25.53
Heptane (1)–Cyclooctane (2)	308.15	25.92	45.18	16.80	29.70
	313.15	25.10	43.46	16.06	28.17
Overall %AAD		23.45		15.17	

**Fig. 3** Comparison of the predictive capabilities of the tested viscosity models including cyclooctane containing systems

densities and kinematic viscosities were employed in calculating the corresponding absolute viscosities and excess volumes of mixtures at 308.15 K and 313.15 K for the 10 investigated systems.

Kinematic viscosity-composition data were utilized to examine the predictive capabilities of some viscosity models, namely, the McAllister three-body model, the GC-UNIMOD method, the GCSP method, and the Allan and Teja correlation. The reported results showed lower %AADs for the McAllister model compared to the other three for all binary systems except for those containing cyclooctane.

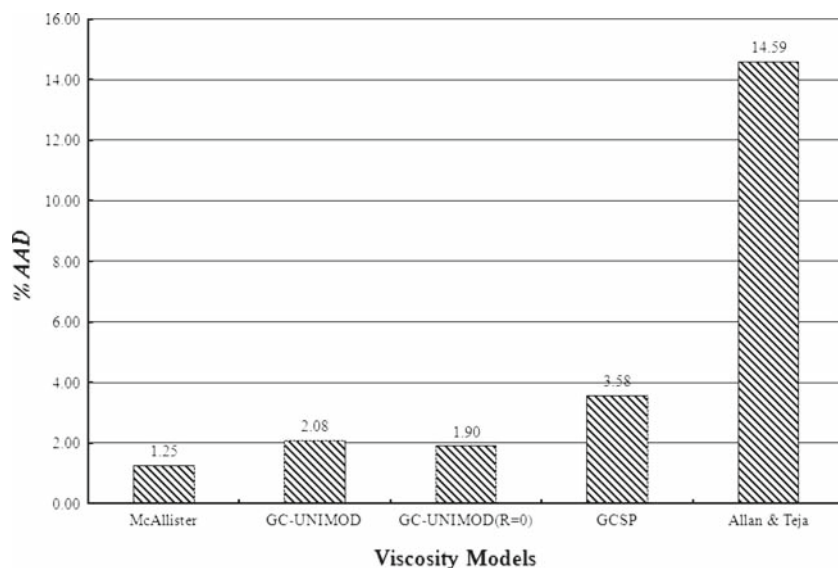


Fig. 4 Comparison of the predictive capabilities of the tested viscosity models excluding cyclooctane containing systems

It is our view that the deviations from expected values for such systems are due to the relatively high ratio between the molecular diameters of cyclooctane and the second component in the system. The present authors are currently attempting to develop a four-body interaction model and to extend the techniques reported earlier by Asfour et al. [6] and Nhaesi and Asfour [7, 8] to cyclooctane-containing systems. This is needed in order to improve the predictive capability of the McAllister model for these systems.

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