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Estimation of excess molar volumes and theoretical viscosities of binary mixtures of benzene + *n*-alkanes at 298.15 K

Omer El-Amin Ahmed Adam^{1,3} · Akl M. Awwad²

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Abstract Excess molar volumes, (V_m^E), have been derived from the literature viscosity data for the binary mixtures of benzene with *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane as a function of composition at 298.15 K and atmospheric pressure conditions. The V_m^E values were found to be positive over the entire composition range for all mixtures. Concentration dependence of V_m^E were fitted with Redlich–Kister polynomial equation to estimate the binary coefficients and standard errors. From density data, the partial molar volumes (V_m), partial molar volumes at infinite dilution ($\bar{V}_m^0$), excess partial molar volumes at infinite dilution ($\bar{V}_m^{0,E}$), and apparent molar volumes (V_ϕ), were calculated over the whole composition range as were the limiting apparent molar volumes at infinite dilution ($\bar{V}_\phi^0$) and excess apparent molar volumes at infinite dilution ($\bar{V}_\phi^{0,E}$). Viscosity of the binary mixtures of benzene with *n*-alkanes were estimated using Kendall–Monroe, Frenkel, Hind et al., Katti–Chaudhri, Grunberg–Nissan, Wilke and Herráez et al. equations. The agreement between experimental and predicted values for all systems was found to be quite reasonable as evidenced from

computed standard deviation and average percentage deviation (APD). Wilke relation gives maximum deviations for all the systems in comparison to other methods employed. Other relations give comparatively good results.

Keywords Density · Viscosity · Binary mixture · Excess molar volume · Molecular interactions · Viscosity deviation

Introduction

Excess thermodynamic properties and deviations of non-thermodynamic ones from ideal behavior of binary liquid mixtures are fundamental for the design of industrial equipment and for the interpretation of the liquid state, particularly when polar components are involved [1]. These quantities have the advantage of illustrating the sign and magnitude of the nonideality [2].

Volumetric properties of binary mixtures are complex properties because they depend not only on solute–solvent, solvent–solvent and solute–solvent interactions, but also on the structural effects arising from interstitial accommodation due to the difference in molar volume and free volume between components present in the solution [3].

Partial molar properties are useful in providing information about solute–solvent interactions. This is because at infinite dilution, solute–solute interactions disappear. Of course this information is of great interest because it is composition independent.

Alkanes are important series of homologous, nonpolar, and organic solvents. They have often been used in the study of solute dynamics because their physicochemical properties as a function of chain length are well-known [4]. They are also employed in a large range of chemical processes [5].

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✉ Omer El-Amin Ahmed Adam
omaramin1967@gmail.com

¹ Chemistry Department, University of Kassala,
P.O. Box 266, Kassala 31111, Sudan

² Royal Scientific Society, P.O. Box 1438, Al-Jubaiha,
Amman 11941, Jordan

³ Present Address: Chemistry Department, Faculty of Science
and Arts in Baljurashi, Al baha University,
P.O. Box 1988, Baljurashi 65635, Saudi Arabia

Properties such as viscosity or surface tension are required in many empirical equations for different operations such as mass and heat transfer processes. Determination of equations that modelize the mass transfer process requires knowledge of the density, viscosity, and surface tension of the liquid phase [6].

The measurement of viscosity reveals information about the molecular packing, molecular motion, and various types of intermolecular interactions as related to size, shape, and chemical nature of the component molecules [7].

In recent years, there has been considerable interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures [8, 9].

Generally, V_m^E can be considered as a result of three types of interactions between component molecules of liquid mixtures [10, 11].

(1) Physical interactions consisting mainly of dispersion forces or weak dipole–dipole interaction making a positive contribution, (2) chemical or specific interactions, which include charge transfer, H-bonding and other complex formation interactions, resulting in a negative contribution, and (3) structural contribution due to differences in size and shape of the component molecules of the mixtures, due to fitting of component molecules into each other's structure, hereby reducing the volume and compressibility of the mixtures, resulting in a negative contribution.

In a previous work by Akl et al. [12], results of density and viscosity measurement were determined for binary mixtures of benzene + *n*-alkanes at 298.15 K and atmospheric pressure. Excess molar volumes (V_m^E), excess molar viscosities ($\Delta \ln \eta$), and excess molar activation energies, (ΔG^{*E}) were calculated. The effect of orientational order of *n*-alkane on solution molar volumes and viscosities is investigated as well as the adequacy of the absolute rate and free volume theories to predict solution viscosities. For longer *n*-alkane ΔG^{*E} and $\Delta \ln \eta$ are positive and associated with the orientational order.

In the present work, the data of density and viscosity reported in the literature [12] have been used to evaluate the excess molar volume (V_m^E) along with other derived parameters, such as partial molar volumes at infinite dilution ($\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$), excess partial molar volumes at infinite dilution ($\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$), apparent molar volumes ($V_{\phi,1}$ and $V_{\phi,2}$), limiting apparent molar volumes at infinite dilution ($\bar{V}_{\phi,1}^0$ and $\bar{V}_{\phi,2}^0$) and excess apparent molar volumes at infinite dilution ($\bar{V}_{\phi,1}^{0,E}$ and $\bar{V}_{\phi,2}^{0,E}$).

These parameters have been interpreted in terms of molecular interactions and structural effects. The work provides a test of various empirical equations to correlate viscosity data of binary mixtures in terms of pure component viscosities.

Theoretical analysis

Excess molar volume

Excess molar volumes (V_m^E), were calculated for the binary mixtures of benzene with *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane using viscosity data by a correlation proposed by Singh [13]. According to the relation, the deviations in viscosity, $\Delta \eta$, and excess molar volumes, V_m^E , are related to each other as:

$$\Delta \eta = K \times V_m^E \quad (1)$$

where, K is a fitting parameter. The values of K for the investigated mixtures were evaluated using the experimentally reported $\Delta \eta$ and V_m^E data [12] (Table 1).

From the experimental $\Delta \eta$ data, V_m^E values at the whole mole fraction range were calculated at 298.15 K and results were presented in Table 2.

Figures 1, 2, 3 show that V_m^E values calculated from viscosity data are positive over the entire composition range for all investigated mixtures and follow the sequence: *n*-hexane < *n*-octane < *n*-decane < *n*-dodecane < *n*-tetradecane < *n*-hexadecane. V_m^E values increase systematically (0.43031, 0.74732, 0.89911, 1.01524, 1.06634 and 1.19575 cm³ mol^{−1}) at benzene mole fraction (x_1) range (0.39880–0.43415) as chain length increases, indicating volume expansion upon mixing of higher *n*-alkanes with benzene. With increasing size of *n*-alkanes, volume expansion will be larger, indicating dispersion type of interactions between the component liquids [14].

The volumetric behavior of this class of mixtures could be explained by random mixing model [15], and the interaction between benzene and *n*-alkane depends strongly on the size of the *n*-alkane. For each system studied it was observed that the excess molar volume is slightly skewed towards the benzene-rich region of the mole fraction. Calculated values of V_m^E compare well with those reported by Peña and Delgado [16] for all mixtures, Calvar et al. [17] for benzene + *n*-hexane, +*n*-octane, and Letcher and Perkins [18] for benzene + *n*-dodecane, +*n*-hexadecane.

The excess molar volumes (V_m^E) were fitted by the Redlich–Kister [19] polynomial equation:

$$V_m^E = x_2(1 - x_2) \sum_{i=0}^{i=n} A_i(1 - 2x_2)^i \quad (2)$$

where x_2 is the mole fraction of *n*-alkane.

The appropriate degree (n) of Eq. (2) was determined by standard deviation (σ) being calculated as:

$$\sigma = \left[\sum (V_{\text{exp}}^E - V_{\text{cal}}^E)^2 / (N - (n + 1)) \right]^{1/2} \quad (3)$$

where N is the total number of experimental points; ($n + 1$) is the number of coefficients (A_i) in Eq. (2).

Table 1 Values of fitting parameter (K) of binary mixtures, and molar volumes of pure components (V_m^*) at 298.15

System	$K/\text{m Pa.s.cm}^{-3}.\text{mol}$	$V_m^*/\text{cm}^3.\text{mol}^{-1}$	
Benzene + <i>n</i> -hexane	−0.2145	Benzene	89.458
Benzene + <i>n</i> -octane	−0.1071	<i>n</i> -Hexane	131.540
Benzene + <i>n</i> -decane	−0.0719	<i>n</i> -Octane	163.531
Benzene + <i>n</i> -dodecane	−0.0931	<i>n</i> -Decane	195.913
Benzene + <i>n</i> -tetradecane	−0.1389	<i>n</i> -Dodecane	228.242
Benzene + <i>n</i> -hexadecane	−0.2116	<i>n</i> -Tetradecane	261.287
		<i>n</i> -Hexadecane	294.066

Table 2 Values of excess molar volumes, V_m^E , calculated using Eq. (1) for binary mixtures for (*x*) *n*-alkane + (1−*x*) benzene at 298.15 K

$V_m^E/\text{cm}^3.\text{mol}^{-1}$					
(<i>x</i>) <i>n</i> -Hexane + (1− <i>x</i>) benzene		(<i>x</i>) <i>n</i> -Octane + (1− <i>x</i>) benzene		(<i>x</i>) <i>n</i> -Decane + (1− <i>x</i>) benzene	
0.05393	0.13220	0.04472	0.22234	0.03584	0.25984
0.11224	0.25405	0.09184	0.40061	0.10038	0.48841
0.20795	0.35508	0.17152	0.55951	0.20129	0.77266
0.30955	0.41102	0.29540	0.72549	0.29022	0.89092
0.41965	0.43031	0.40878	0.74732	0.39880	0.89911
0.50041	0.41434	0.49074	0.70538	0.49997	0.83648
0.59341	0.36720	0.58551	0.60583	0.59432	0.71743
0.68570	0.30241	0.73898	0.47019	0.70210	0.55340
0.79132	0.21284	0.92796	0.12684	0.83527	0.32117
0.88344	0.11426			0.91651	0.16049
(<i>x</i>) <i>n</i> -Dodecane + (1− <i>x</i>) Benzene		(<i>x</i>) <i>n</i> -Tetradecane + (1− <i>x</i>) Benzene		(<i>x</i>) <i>n</i> -Hexadecane + (1− <i>x</i>) Benzene	
0.04733	0.22407	0.04444	0.19194	0.05350	0.29540
0.10840	0.48939	0.09068	0.46134	0.09944	0.47192
0.20364	0.79727	0.21254	0.78494	0.21994	0.83828
0.29778	0.94472	0.41693	1.06634	0.32338	1.16970
0.41395	1.01524	0.51212	1.05153	0.43415	1.19575
0.51924	0.96690	0.62706	0.81988	0.51942	1.15131
0.61546	0.86817	0.71387	0.62522	0.64097	1.04078
0.72914	0.67885	0.80062	0.55735	0.69281	1.00728
0.80113	0.55101	0.88223	0.51832	0.83610	0.85819
0.92306	0.22493			0.94161	0.22225

Calculated values of A_i and σ for all systems studied are given in Table 3.

Partial molar volume, $V_{m,1}$ and $V_{m,2}$, of benzene (1) and *n*-alkanes (2), respectively, are given by:

$$V_{m,1} = V_m^E + V_{m,1}^* + (1 - x_1) (\partial V^E / \partial x_1)_{P,T} \quad (4)$$

$$V_{m,2} = V_m^E + V_{m,2}^* - x_1 (\partial V^E / \partial x_1)_{P,T} \quad (5)$$

where $V_{m,1}^*$ and $V_{m,2}^*$ are the molar volumes of the pure liquids (1) and (2), respectively. Combination of Eqs. (2), (4) and (5) leads to Eqs. (6) and (7) for $V_{m,1}$ and $V_{m,2}$:

$$V_{m,1} = V_{m,1}^* + x_2^2 \sum_{i=0}^{i=n} A_i (1 - 2x_1)^i - 2x_1 x_2^2 \sum_{i=1}^{i=n} A_i (1 - 2x_1)^{i-1} \quad (6)$$

$$V_{m,2} = V_{m,2}^* + x_1^2 \sum_{i=0}^{i=n} A_i (1 - 2x_1)^i + 2x_1^2 x_2 \sum_{i=1}^{i=n} A_i (1 - 2x_1)^{i-1} \quad (7)$$

Fig. 1 Excess molar volume V_m^E versus x_2 for benzene(1) with n -hexane(2) and n -octane(2) at 298 K

Fig. 2 Excess molar volume V_m^E versus x_2 for benzene(1) with n -decane(2) and n -dodecane(2) at 298 K

Fig. 3 Excess molar volume V_m^E versus x_2 for benzene(1) with n -tetradecane(2) and n -hexadecane(2) at 298 K

Table 3 Coefficients A_i of Eq. 2 and standard deviation, σ , at 298.15 K

Binary mixture	A_0	A_1	A_2	A_3	A_4	σ
Benzene + n -hexane	0.0051	2.6233	-5.1111	3.4665	-0.9871	0.008
Benzene + n -octane	-0.0123	4.0913	-7.0177	4.2741	-1.3307	0.062
Benzene + n -decane	0.0234	5.9634	-12.8940	9.8982	-2.9941	0.018
Benzene + n -dodecane	-0.0114	5.7372	-10.2400	6.5010	-1.9869	0.011
Benzene + n -tetradecane	-0.0279	6.2820	-12.5210	9.7973	-3.4848	0.080
Benzene + n -hexadecane	-0.0194	6.4531	-12.9770	12.9030	-6.3815	0.080

Values of the partial molar volumes at infinite dilution, $\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$, were obtained by the linear extrapolation of corresponding partial molar volumes using Eqs. (6) and (7). Extrapolation of $V_{m,1}$ to $x_1 \rightarrow 0$ results in $\bar{V}_{m,1}^0$, and consequently, extrapolation of $V_{m,2}$ to $x_2 \rightarrow 0$ results in $\bar{V}_{m,2}^0$. The excess partial molar volumes at infinite dilution, $\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$, were calculated using the following relations [20]:

$$\bar{V}_{m,1}^{0,E} = \bar{V}_{m,1}^0 - V_{m,1}^* \quad (8)$$

$$\bar{V}_{m,2}^{0,E} = \bar{V}_{m,2}^0 - V_{m,2}^* \quad (9)$$

Apparent molar volumes of benzene $V_{\phi,1}$ and apparent molar volume of n -alkanes $V_{\phi,2}$ were calculated from experimental data using the following relations [21]:

$$V_{\phi,1} = \frac{(V_m - x_2 V_2^0)}{x_1} = \frac{(\rho_2 - \rho)x_2 M_2}{x_1 \rho \rho_2} + \frac{M_1}{\rho} \quad (10)$$

$$V_{\phi,2} = \frac{(V_m - x_1 V_1^0)}{x_2} = \frac{(\rho_1 - \rho)x_1 M_1}{x_2 \rho \rho_1} + \frac{M_2}{\rho} \quad (11)$$

Extrapolation of $V_{\phi,1}$ to $x_1 \rightarrow 0$ and $V_{\phi,2}$ to $x_2 \rightarrow 0$ give the values of the limiting apparent molar volumes $\bar{V}_{\phi,1}^0$ and $\bar{V}_{\phi,2}^0$ at infinite dilution, represented earlier as $\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$. The excess apparent molar volumes at infinite dilution, $\bar{V}_{\phi,1}^{0,E}$ and $\bar{V}_{\phi,2}^{0,E}$ were also calculated by equations similar to Eqs. (8) and (9). The values $\bar{V}_{m,1}^0$, $\bar{V}_{\phi,1}^0$, $V_{m,1}^*$, $\bar{V}_{m,1}^{0,E}$, $\bar{V}_{\phi,1}^{0,E}$, $\bar{V}_{m,2}^0$, $\bar{V}_{\phi,2}^0$, $V_{m,2}^*$, $\bar{V}_{m,2}^{0,E}$ and $\bar{V}_{\phi,2}^{0,E}$ for all six binary mixtures at 298.15 K are listed in Table 4. An examination of data in Table 4 reveals that the values of $\bar{V}_{m,1}^0$ and $\bar{V}_{\phi,1}^0$ are nearly of the same magnitude, and the values of $\bar{V}_{\phi,2}^0$ are slightly greater than $\bar{V}_{m,2}^0$ for all binary mixtures. Values of $\bar{V}_{m,1}^{0,E}$, $\bar{V}_{\phi,1}^{0,E}$, $\bar{V}_{m,2}^{0,E}$ and $\bar{V}_{\phi,2}^{0,E}$ are positive over the entire composition range for all systems. This indicates that molar volumes and apparent molar volumes of both components in the mixture are larger than their respective values in the pure state, which indicates the presence of

Table 4 The values $\bar{V}_{m,1}^0$, $\bar{V}_{m,2}^0$, $\bar{V}_{\phi,1}^0$, $\bar{V}_{\phi,2}^0$, $V_{m,1}^*$, $V_{m,2}^*$, $\bar{V}_{m,1}^{0,E}$, $\bar{V}_{m,2}^{0,E}$, $\bar{V}_{\phi,1}^{0,E}$ and $\bar{V}_{\phi,2}^{0,E}$ for all six mixtures at 298.15 K

Benzene (1)+	$\bar{V}_{m,1}^0$	$\bar{V}_{\phi,1}^0$	$V_{m,1}^*$	$\bar{V}_{m,1}^{0,E}$	$\bar{V}_{\phi,1}^{0,E}$	$\bar{V}_{m,2}^0$	$\bar{V}_{\phi,2}^0$	$V_{m,2}^*$	$\bar{V}_{m,2}^{0,E}$	$\bar{V}_{\phi,2}^{0,E}$
<i>n</i> -Hexane(2)	90.111	91.082	89.458	0.653	1.620	131.754	133.143	131.540	0.214	1.603
<i>n</i> -Octane(2)	90.255	92.159	89.458	0.797	2.701	164.070	166.932	163.531	0.539	3.401
<i>n</i> -Decane(2)	91.397	92.423	89.458	1.939	2.965	196.460	200.061	195.913	0.547	4.148
<i>n</i> -Dodecane(2)	91.623	92.630	89.458	2.165	3.172	228.661	233.215	228.242	0.419	4.973
<i>n</i> -Tetradecane(2)	92.181	92.646	89.458	2.723	3.188	261.598	267.354	261.287	0.311	6.067
<i>n</i> -Hexadecane(2)	92.938	92.989	89.458	3.480	3.531	294.715	301.119	294.066	0.649	7.053

All quantities have the unit: $\text{cm}^3 \text{mol}^{-1}$

significant solute–solute and solvent–solvent interactions between like molecules in the mixture [22].

Correlation equations for viscosity

Viscosity data are given in Table 5 as a function of the mole fraction of the *n*-alkane at 298.15 K. The viscosity deviation was calculated according to the following equation:

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (12)$$

where η_1 , η_2 and η are the viscosities of component 1 (benzene), component 2 (*n*-alkane) and the mixture, respectively. All mixtures deviate from ideality with a negative deviation, which indicate that dispersion forces are predominant between benzene and *n*-alkane [23].

Various equations are used in the literature to calculate the viscosity of mixtures in terms of pure component data. To carry out a comparative study, Kendall–Munroe, Frenkel, Hind et al., Katti-Chaudhri, Grunberg–Nissan, Wilke and Herráez et al. equations have been employed to estimate the viscosity of binary liquid mixtures of benzene + *n*-alkanes.

1. Kendall–Monroe [24] derived Eq. (13) for analyzing the viscosity of binary mixtures based on zero adjustable parameter. This equation calculates the mixture viscosity as the cubic-root average of the component viscosities:

$$\eta = (x_1\eta_1^{1/3} + x_2\eta_2^{1/3})^3 \quad (13)$$

2. Frenkel with the help of Eyring's model [25, 26] took into consideration the interaction between molecules and developed the following logarithmic relation for nonideal binary mixtures:

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1x_2 \ln \eta_{12} \quad (14)$$

where, η_{12} is a constant attributed to unlike pair interactions. Its value is obtained from the following equation:

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \quad (15)$$

3. Hind et al. [27] have suggested the following equation for the viscosity of binary liquid mixtures:

$$\ln \eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1x_2 H_{12} \quad (16)$$

where, H_{12} is the Hind interaction parameter and is attributed to unlike pair interactions, and other terms have their usual meaning.

4. Katti–Chaudhri equation is expressed as [28]:

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1x_2 (W/RT) \quad (17)$$

where, W is the interaction energy parameter, V is the volume of the mixture, V_1 and V_2 are the volumes of component 1 and component 2, respectively.

5. Grunberg and Nissan [29] have formulated equation to assess the molecular interactions leading to viscosity changes:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2 G_{12} \quad (18)$$

where, G_{12} is a constant, proportional to interchange energy, η is the dynamic viscosity and the subscripts 1, 2 and 12 stands for the pure components, benzene, *n*-alkanes and mixtures, respectively.

6. Wilke [30] proposed the viscosity equation:

$$\eta = \frac{x_1\eta_1}{x_1 + x_2\phi_{12}} + \frac{x_2\eta_2}{x_2 + \phi_{21}} \quad (19)$$

where, ϕ_{12} and ϕ_{21} are calculated by the following equations:

$$\phi_{12} = \frac{\left[1 + \left(\frac{\eta_1}{\eta_2}\right)^{1/2} (M_2/M_1)^{1/4}\right]}{\{8 + [1 + (M_1/M_2)]\}^{1/2}} \quad (20)$$

$$\phi_{21} = \phi_{12} \frac{\eta_2 M_1}{\eta_1 M_2} \quad (21)$$

where, ϕ and M are the volume fraction and molar mass, and the subscripts 1 and 2 stands for pure components benzene and *n*-alkane, respectively.

Table 5 Viscosity deviation ($\eta_{\text{exp}} - \eta_{\text{calc.}}$) for the binary mixtures at 298.15 K

Viscosity deviation ($\eta_{\text{exp.}} - \eta_{\text{calc.}}$)								
x_2	$\eta_{\text{exp.}}$ (mPa.s)	K. & M.	Frenkel	Hind	Katti	G. & N.	Wilke	Herráez et al.
Benzene + <i>n</i> -hexane								
0.05393	0.5662	−0.0248	0.0186	−0.0100	−0.0039	−0.0284	−0.0366	0.0134
0.11224	0.5225	−0.0476	0.0372	−0.0186	−0.0089	−0.0545	−0.0695	−0.0006
0.20795	0.4720	−0.0648	0.0754	−0.0168	−0.0060	−0.0762	−0.0983	−0.0146
0.30955	0.4294	−0.0735	0.1086	−0.0111	−0.0034	−0.0882	−0.1138	−0.0260
0.41965	0.3921	−0.0757	0.1319	−0.0045	−0.0024	−0.0923	−0.1182	−0.0342
0.50041	0.3712	−0.0720	0.1412	0.0012	−0.0009	−0.0889	−0.1133	−0.0358
0.59341	0.3533	−0.0626	0.1433	0.0082	0.0019	−0.0788	−0.1002	−0.0331
0.68570	0.3394	−0.0505	0.1335	0.0128	0.0039	−0.0649	−0.0823	−0.0280
0.79132	0.3268	−0.0347	0.1063	0.0139	0.0045	−0.0457	−0.0577	−0.0201
0.88344	0.3202	−0.0177	0.0703	0.0126	0.0056	−0.0245	−0.0314	−0.0097
Benzene + <i>n</i> -octane								
0.04472	0.5829	−0.0236	0.0245	−0.0102	−0.0073	−0.0238	−0.0407	0.0194
0.09184	0.5595	−0.0425	0.0514	−0.0162	−0.0115	−0.0429	−0.0748	0.0038
0.17152	0.5352	−0.0592	0.1007	−0.0145	−0.0088	−0.0599	−0.1115	−0.0127
0.29540	0.5061	−0.0767	0.1575	−0.0112	−0.0077	−0.0777	−0.1476	−0.0341
0.40878	0.4934	−0.0788	0.1931	−0.0028	−0.0025	−0.0800	−0.1561	−0.0418
0.49074	0.4904	−0.0743	0.2069	0.0043	0.0025	−0.0755	−0.1508	−0.0418
0.58551	0.4924	−0.0637	0.2094	0.0127	0.0088	−0.0649	−0.1345	−0.0368
0.73898	0.4929	−0.0494	0.1676	0.0113	0.0064	−0.0504	−0.1018	−0.0322
0.92796	0.5124	−0.0133	0.0620	0.0078	0.0058	−0.0136	−0.0300	−0.0084
Benzene + <i>n</i> -decane								
0.03584	0.6003	−0.0179	0.0314	−0.0100	−0.0079	−0.0187	−0.0408	−0.0105
0.10038	0.5986	−0.0330	0.0958	−0.0125	−0.0091	−0.0351	−0.0912	−0.0125
0.20129	0.6012	−0.0517	0.1775	−0.0152	−0.0114	−0.0556	−0.1512	−0.0118
0.29022	0.6130	−0.0591	0.2346	−0.0124	−0.0095	−0.0641	−0.1824	−0.0041
0.39880	0.6372	−0.0589	0.2830	−0.0045	−0.0033	−0.0646	−0.1971	0.0105
0.49997	0.6648	−0.0541	0.3023	0.0025	0.0023	−0.0601	−0.1937	0.0234
0.59432	0.6949	−0.0457	0.2980	0.0089	0.0078	−0.0516	−0.1767	0.0336
0.70210	0.7313	−0.0347	0.2635	0.0126	0.0111	−0.0398	−0.1451	0.0386
0.83527	0.7784	−0.0197	0.1764	0.0114	0.0100	−0.0231	−0.0901	0.0321
0.91651	0.8085	−0.0097	0.0994	0.0076	0.0068	−0.0115	−0.0481	0.0204
Benzene + <i>n</i> -dodecane								
0.04733	0.6259	−0.0121	0.0685	−0.0040	0.0003	−0.0209	−0.0607	0.0023
0.10840	0.6476	−0.0267	0.1459	−0.0095	−0.0036	−0.0456	−0.1297	−0.0020
0.20364	0.6913	−0.0423	0.2471	−0.0137	−0.0066	−0.0742	−0.2121	−0.0098
0.29778	0.7491	−0.0464	0.3264	−0.0099	−0.0041	−0.0880	−0.2622	−0.0119
0.41395	0.8308	−0.0458	0.3862	−0.0040	−0.0007	−0.0945	−0.2926	−0.0134
0.51924	0.9153	−0.0394	0.4046	0.0031	0.0031	−0.0900	−0.2908	−0.0116
0.61546	0.9976	−0.0325	0.3881	0.0075	0.0047	−0.0808	−0.2691	−0.0100
0.72914	1.1016	−0.0224	0.3281	0.0105	0.0054	−0.0632	−0.2190	−0.0071
0.80113	1.1682	−0.0182	0.2644	0.0082	0.0027	−0.0513	−0.1765	−0.0073
0.92306	1.2912	−0.0060	0.1198	0.0056	0.0020	−0.0209	−0.0767	−0.0022
Benzene + <i>n</i> -tetradecane								
0.04444	0.6498	−0.0032	0.0880	−0.0031	0.0060	−0.0267	−0.0719	0.0062
0.09068	0.6807	−0.0182	0.1585	−0.0183	−0.0021	−0.0641	−0.1513	−0.0085
0.21254	0.8158	−0.0143	0.3427	−0.0162	0.0087	−0.1090	−0.2837	−0.0173

Table 5 continued

Viscosity deviation ($\eta_{\text{exp.}} - \eta_{\text{calc.}}$)								
x_2	$\eta_{\text{exp.}}$ (mPa.s)	K. & M.	Frenkel	Hind	Katti	G. & N.	Wilke	Herráez et al.
0.41693	1.0787	−0.0065	0.5080	−0.0132	0.0023	−0.1481	−0.3987	−0.0389
0.51212	1.2214	0.0014	0.5283	−0.0074	−0.0032	−0.1461	−0.4035	−0.0412
0.62706	1.4234	0.0262	0.5173	0.0159	0.0050	−0.1139	−0.3558	−0.0223
0.71387	1.5787	0.0370	0.4645	0.0265	0.0059	−0.0868	−0.2996	−0.0105
0.80062	1.7163	0.0204	0.3534	0.0112	−0.0142	−0.0774	−0.2454	−0.0202
0.88223	1.8423	−0.0076	0.2084	−0.0143	−0.0371	−0.0720	−0.1828	−0.0361
Benzene + <i>n</i> -hexadecane								
0.05350	0.6803	−0.0033	0.1243	−0.0099	0.0082	−0.0625	−0.1211	0.0046
0.09944	0.7563	0.0058	0.2305	−0.0069	0.0223	−0.0999	−0.2034	0.0053
0.21994	0.9761	0.0297	0.4555	0.0007	0.0432	−0.1774	−0.3761	−0.0106
0.32338	1.1612	0.0217	0.5597	−0.0204	0.0161	−0.2475	−0.5023	−0.0564
0.43415	1.4290	0.0553	0.6532	0.0020	0.0155	−0.2530	−0.5420	−0.0568
0.51942	1.6488	0.0744	0.6772	0.0155	0.0024	−0.2436	−0.5407	−0.0554
0.64097	1.9721	0.0792	0.6287	0.0186	−0.0349	−0.2202	−0.5004	−0.0585
0.69281	2.1071	0.0662	0.5720	0.0078	−0.0603	−0.2131	−0.4755	−0.0676
0.83610	2.4922	0.0026	0.3239	−0.0393	−0.1200	−0.1816	−0.3581	−0.0940
0.94161	2.8871	0.0282	0.1558	0.0100	−0.0347	−0.0470	−0.1210	−0.0134

7. Herráez et al. [31] proposed a new correlation equation based on the linear behavior of binary mixtures:

$$\eta = \eta_1 + (\eta_2 - \eta_1) x_2 \quad (22)$$

They introduce an exponential function of the mole fraction, x_2 , in Eq. 22 above, to yield:

$$\eta = \eta_1 + (\eta_2 - \eta_1) x_2^{\left(\sum_{i=0}^n (Bi \cdot x_2^i)\right)} \quad (23)$$

which for $n = 0$ would be:

$$\eta = \eta_1 + (\eta_2 - \eta_1) x_2^{[Bo]} \quad (24)$$

where, B_0 is the universal exponent constant.

The predicted values of viscosities of the binary mixtures, using Eqs. (13), (14), (16), (17), (18), (19) and (24), including standard deviation, at 298.15 K were compared with the experimentally measured values, and results are presented in terms of viscosity deviations ($\Delta\eta$) (Table 5).

Validity of aforementioned relations has been checked by calculating the viscosity deviations. The average percentage deviation (APD) between calculated and experimental viscosity values is calculated by [32]:

$$APD = \left(\frac{100}{N}\right) \sum \left[\frac{(|\eta_{\text{exp}} - \eta_{\text{cal}}|)}{\eta_{\text{exp}}} \right] \quad (25)$$

where N is the number of data points in each set.

The interaction parameters of Eqs. (13), (14), (16), (17), (18), (19) and (24), along with APD and σ values for all binary mixtures are presented in Table 6. A careful perusal

of Table 6 reveals that maximum deviations are obtained using Wilke relation for the prediction of viscosity of binary liquid mixtures under the present study while other relations give comparatively good results. The best results obtained by using Katti–Chaudhri relation. The trend of validity of the presently used relations is as follows: Katti–Chaudhri > Hind et al. > Herráez et al. > Grunberg and Nissan > Kendall–Munroe > Frenkel > Wilke.

The values of interaction parameters η_{12} , H_{12} , W/RT , G_{12} and B_0 are presented in Table 6. η_{12} and H_{12} values are positive for all binary mixtures and increases with increasing alkyl chain length of *n*-alkanes. Correlation parameter, W/RT has negative values for the first two binary mixtures and has positive values for the rest of binary mixtures. The negatives values of W/RT suggest weak interactions, and positive values indicate strong interactions between the unlike molecules [33].

G_{12} values are negative for all binary mixtures except for the two last ones (*n*-tetradecane + benzene and *n*-hexadecane + benzene). The negative values of G_{12} indicates the dominance of dispersion forces [34, 35], while the positive values are attributed to the presence of strong specific interactions between the mixture components [36, 37]. B_0 values are positive for all binaries mixtures, $B_0 > 1$ for mixtures where the sub index 1 represent the component of least viscosity (benzene + *n*-decane, +*n*-dodecane, +*n*-tetradecane, and +*n*-hexadecane), whereas $B_0 < 1$ for mixtures where the sub index 2 represent the component of least viscosity (benzene + *n*-hexane, +*n*-octane).

Table 6 Adjustable parameters of Eqs. (13), (14), (16), (17), (18), (19) and (24), APD values and standard deviations of binary mixture viscosities at 298.15 K

	Benzene + <i>n</i> -hexane	Benzene + <i>n</i> -octane	Benzene + <i>n</i> -decane	Benzene + <i>n</i> -dodecane	Benzene + <i>n</i> -tetradecane	Benzene + <i>n</i> -hexadecane
Kendall and Monroe						
σ	0.056	0.058	0.042	0.032	0.019	0.046
APD	10.98	8.59	4.93	2.96	1.04	1.90
Frenkel						
η_{12}	0.4602	0.5651	0.7245	0.9907	1.3496	1.8445
σ	0.059	0.0581	0.0432	0.040	0.023	0.024
APD	11.60	8.63	5.05	3.69	1.49	0.64
Hind et al.						
H_{12}	0.2800	0.4053	0.5996	0.8041	1.0721	1.3255
σ	0.072	0.062	0.084	0.071	0.106	0.199
APD	13.55	8.73	1.24	0.76	1.02	0.71
Katti and Chaudhri						
W/RT	−0.5332	−0.3768	0.0132	0.3674	0.8304	1.2899
σ	0.005	0.008	0.009	0.005	0.015	0.051
APD	0.84	1.06	0.99	0.32	0.58	1.82
Grunberg and Nissan						
G_{12}	−0.6226	−0.5840	−0.3170	−0.0891	0.2626	0.5781
σ	0.005	0.009	0.014	0.014	0.009	0.023
APD	0.91	1.31	1.52	1.20	0.92	0.66
Wilke						
ϕ_{12}	0.53315	0.56841	0.61068	0.66773	0.72554	0.78865
ϕ_{21}	1.16051	0.97753	0.80972	0.64889	0.53899	0.45366
σ	0.088	0.109	0.143	0.215	0.272	0.407
APD	17.32	16.96	16.65	19.19	18.75	21.98
Herráez et al.						
B_0	0.5643	0.2123	2.8978	1.3382	1.2230	1.2425
σ	0.024	0.029	0.023	0.009	0.026	0.052
APD	4.733	4.161	2.365	0.751	1.516	2.089

Conclusions

Excess molar volume have been calculated from the experimental viscosity data at 298.15 K for benzene + *n*-hexane, or +*n*-octane, or +*n*-decane, or +*n*-dodecane, or +*n*-tetradecane, or +*n*-hexadecane binary mixtures.

The values of V_m^E , $\bar{V}_{m,1}^0$, $\bar{V}_{m,2}^0$, $\bar{V}_{\phi,1}^0$, $\bar{V}_{\phi,2}^0$, $V_{m,1}^*$, $V_{m,2}^*$, $\bar{V}_{m,1}^{0,E}$, $\bar{V}_{m,2}^{0,E}$, $\bar{V}_{\phi,1}^{0,E}$ and $\bar{V}_{\phi,2}^{0,E}$ were calculated for all six mixtures at 298.15 K. The V_m^E values were found to be positive over the whole composition range for all mixtures. Molar volumes and apparent molar volumes of both components in the mixture are larger than their respective values in the pure state. The order of interaction between benzene and *n*-alkanes follows the sequence: *n*-hexane < *n*-octane < *n*-decane < *n*-dodecane < *n*-tetradecane < *n*-hexadecane, i.e., the interaction increase with increasing chain length of the *n*-alkane.

Moreover, an attempt has been made to check the suitability of empirical and semiempirical relations for experimental viscosities data of *n*-alkanes + benzene fits by taking into account a number of empirical adjustment coefficients. The predicted viscosities show good accuracy in comparison with the experimental viscosities. The trend of validity of the presently used relations is as follows: Katti-Chaudhri > Hind et al. > Herráez et al. > Grunberg and Nissan > Kendall-Munroe > Frenkel > Wilke.

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