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Correlation and Prediction of Dense Fluid Transport Coefficients. VIII. Mixtures of Alkyl Benzenes with Other Hydrocarbons

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Abstract The aim of this article is to examine the application of the hard-sphere scheme to the prediction of the viscosity and thermal conductivity of hydrocarbon mixtures, other than *n*-alkane mixtures. According to this scheme, mixture properties are calculated from the pure components properties. Hence these are obtained first. Furthermore, in addition to the temperature, the density is the important parameter rather then the pressure. A Tait-type equation is employed to successfully correlate the density of the pure liquids. Furthermore, in the first part of this article, a modified form of the equation proposed by Sun and Teja is employed in the scheme, to correlate the viscosity and thermal conductivity of pure alkyl benzenes, some alkanes, some cycloalkanes, and one naphthalene. Following this, the article focuses on the successful prediction of the viscosity and thermal conductivity of mixtures of these compounds.

Keywords Hard spheres · Mixtures · Prediction · Thermal conductivity · Viscosity

1 Introduction

During the 1990s, in a series of papers [1–7], a scheme was developed for the simultaneous correlation of viscosity, self-diffusion, and thermal-conductivity coefficient data over a wide range of temperatures and pressures, using a consistent set of values for the close-packed volume V_o. It was thus shown that the scheme provides a satisfactory correlation of dense fluid *n*-alkane transport coefficient data [1,4], and consequently, it can be used with confidence to predict transport coefficients for these

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compounds under other conditions of temperature and pressure. The method has also been applied to simple organic molecular liquids [2] and has been extended to *n*-alkane mixtures [3], aromatic hydrocarbons [5], *n*-alkanols [6], and refrigerants [7]. It has been demonstrated that this scheme can lead to predictions of transport coefficients for these systems, at pressures up to 600 MPa, with an uncertainty of 6 %.

The scheme is based on the assumption that transport coefficients of real dense fluids, expressed in terms of the reduced volume V/V_o (where V is the molar volume), is directly proportional to values given by the exact hard-sphere theory [8]. The proportionality factor, described as the roughness factor R, accounts for molecular roughness and departure from molecular sphericity.

In a recent article [9] in 2009, Sun and Teja pointed out however that the predictive capability of the aforementioned scheme is sometimes limited. For example, they noted that the viscosity correlation for *n*-alkanols [7] (obtained by fitting data for alkanols from methanol to *n*-decanol) cannot be extrapolated to *n*-dodecanol, because negative values of the coupling parameter are obtained in this case. This limits the use of the method to only cases where transport property data are available. Hence, based on previous study [10,11], Sun and Teja proposed a modification of the original rough-hard sphere method that although not applied to the self-diffusion coefficient, is simpler to use, and yields comparable results. They further reported generalizations of their method for dense fluids containing aromatic hydrocarbons, refrigerants, and four homologous series of *n*-alkanes, *n*-alkanols, halogenated methanes, alkanediols, and some polar liquids. At the same time they investigated the predictive capabilities of the method by calculating transport properties of compounds not used in the correlations.

The aim of this article is to examine the application of the aforementioned hard-sphere scheme to the prediction of the viscosity and thermal conductivity of mixtures. As mentioned, so far this scheme has only been applied successfully to *n*-alkane mixtures [3]. Hence, the article extends the scheme's application to other non-alkane mixtures.

According to this scheme, mixture properties are calculated from the pure components properties. Hence, these will be obtained first. Furthermore, in addition to the temperature, the density is the important parameter rather then the pressure. A Tait-type equation is employed to successfully correlate the density of the pure liquids.

Therefore, in the first part of this article the modified form of the equation proposed by Sun and Teja [9] is employed in the scheme, to correlate the viscosity and thermal conductivity of pure alkyl benzenes, some alkanes, some cycloalkanes, and a single naphthalene. Following this, the article focuses on the prediction of the viscosity and thermal conductivity of mixtures of these compounds.

2 Density

The Tait equation is usually expressed in the form [12]:

$$\frac{\rho - \rho_o}{\rho} = C \log_{10}\left[\frac{B + P}{B + P_o}\right], \tag{1}$$

where ρ $(\mathrm{kg \cdot m^{-3}})$ and ρ_o $(\mathrm{kg \cdot m^{-3}})$ are the liquid densities at the corresponding pressures, and P (MPa), P_o (MPa), B (MPa), and C (−) are parameters. In most cases, P_o is taken to be equal to the atmospheric pressure (0.101 MPa) and ρ_o is the corresponding atmospheric-pressure density. Parameter C has generally been found to be a constant (in most cases equal to about 0.20), while parameter B definitely varies with temperature. Following our previous study [12], the liquid density at atmospheric pressure was correlated as:

$$\rho_o = \rho_c \left\{ 1 + \sum_{i=1}^{5} a_i \, (1 - T_r)^{i/3} \right\}, \tag{2}$$

where T_r is the reduced temperature (=T/T_c), T (K) is the absolute temperature, and T_c and ρ_c are the critical temperature and density, respectively. Similarly, the parameter B (MPa), following our previous discussion [12], was correlated as a polynomial function of the reduced temperature, T_r (−), as:

$$B = \sum_{i=0}^{3} b_i T_r^i. \tag{3}$$

In the predictive scheme for the calculation of the viscosity and thermal conductivity of liquid mixtures that will follow, the density is required (a) for correlating pure liquid data where no density values are given and (b) for predicting the viscosity and thermal conductivity of mixtures. Hence, a large number of density data was considered.

In Table 1, the experimental measurements [12–15], T. Makita, Personal communication (1985), [16–31] used to compute the aforementioned equations for the parameters a_i, b_i, and C and the experimental temperature ranges and maximum pressures considered are shown. It should be noted that the maximum pressure shown in the table refers to the point above which deviations started to increase considerably, i.e., the correlation is valid up to the maximum pressure quoted in the table. In most cases, this coincides with the maximum experimental pressure. In Table 1, the average absolute percentage deviation, as well as the maximum absolute percentage deviation for every data set for each liquid, is also shown. In total, 2,648 data points were considered, with a total average absolute deviation of 0.08 %. It should finally be noted that in the specific case of *n*-alkanes, we employed unaltered data calculated by Assael et al. [12]. The coefficients a_i, b_i, and C, obtained following the optimization of the above data, are shown in Tables 2 and 3 together with the critical temperature and critical density employed.

3 Viscosity and Thermal Conductivity

According to the proposed scheme [1–7], it was found that the reduced coefficients for viscosity, η^*, and thermal conductivity, λ^*, (and equivalently for self-diffusion), are defined as

Table 1 Comparison of calculated pure liquid density values with experiment

Liquid	Year of publication and first author	References	Temperature range (K)	Maximum pressure (MPa)	No. of data	Aver. dev. (%)	Max. dev. (%)
Alkyl benzenes							
Benzene	81 Dymond	[13]	298–353	0.1	4	0.02	0.03
	82 Dymond	[14]	298–373	263	26	0.12	0.48
	76 Mamedov	[15]	298–375	51	8	0.07	0.17
	85 Makita	[Personal communication]	298–348	112	65	0.01	0.03
Toluene	85 Dymond	[16]	288–353	0.1	5	0.04	0.08
	82 Kashiwagi	[17]	273–373	250	94	0.05	0.59
	69 Mopsik	[18]	223–298	203	43	0.05	0.11
	76 Mamedov	[15]	298–473	50	12	0.12	0.06
	02 Masui	[19]	298–423	30	65	0.06	0.18
o-Xylene	76 Mamedov	[15]	298–375	50	8	0.08	0.15
	85 Makita	[Personal communication]	298–348	112	69	0.06	0.12
	93 Garg	[20]	318–373	10	72	0.05	0.15
m-Xylene	76 Mamedov	[15]	298–473	50	12	0.21	0.48
	85 Makita	[Personal communication]	298–348	111	71	0.16	0.15
	93 Garg	[20]	318–373	10	72	0.10	0.21
	09 Caudwell	[21]	298–473	200	81	0.04	0.13
p-Xylene	76 Mamedov	[15]	373	41	4	0.06	0.10
	85 Makita	[Personal communication]	298 –348	109	57	0.04	0.09
	93 Garg	[20]	318–373	10	72	0.07	0.18
Ethylbenzene	76 Mamedov	[15]	298–375	50	8	0.05	0.12
	85 Makita	[Personal communication]	298–348	112	73	0.05	0.14
	93 Garg	[20]	318–373	10	71	0.08	0.19
Mesitylene	85 Dymond	[16]	298–353	0.1	4	0.02	0.05
	87 Easteal	[22]	298–313	281	15	0.05	0.12
Alkanes							
n-Hexane	94 Assael	[12]	298–333	300	141	0.14	0.30
n-Heptane	94 Assael	[12]	278–393	200	152	0.05	0.22
n-Octane	94 Assael	[12]	258 –393	320	225	0.09	0.23
n-Decane	94 Assael	[12]	229–348	500	220	0.16	0.32
n-Dodecane	94 Assael	[12]	298–393	200	225	0.13	0.35
n-Tetradecane	94 Assael	[12]	298–375	370	119	0.06	0.15
n-Hexadecane	94 Assael	[12]	298–373	300	157	0.12	0.28
Heptamethylnonane	01 Canet	[23]	293–353	60	91	0.03	0.09
2,2,4-Trimethylpentane	90 Malhorta	[24]	278–338	240	52	0.04	0.15

Table 1 continued

Liquid	Year of publication and first author	References	Temperature range (K)	Maximum pressure (MPa)	No. of data	Aver. dev. (%)	Max. dev. (%)
2,6,10,14-Tetramethyl pentadecane	95 Et-Tahir	[25]	298–363	40	15	0.02	0.04
Cycloalkanes							
Cyclopentane	69 Brazier	[26]	303	50	2	0.10	0.18
	70 Kush	[27]	298–353	78	10	0.14	0.29
	04 Assael	[28]	223–298	25	24	0.03	0.08
Cyclohexane	70 Kush	[27]	298–353	118	10	0.09	0.21
	07 Amorim	[29]	318–413	62	54	0.06	0.19
	69 Mopsik	[18]	298–348	105	35	0.05	0.13
Methylcyclohexane	69 Brazier	[26]	303	50	2	0.06	0.08
	05 Mikkelsen	[30]	283–353	45	80	0.01	0.03
	97 Baylaucq	[31]	303–343	40	9	0.07	0.15
Naphthalene							
1-Methylnaphthalene	09 Caudwell	[21]	298–473	190	14	0.04	0.13

$$\eta^* = 6.035 \times 10^8 \sqrt{\frac{1}{MRT}}\eta V^{2/3} \tag{4}$$

$$\lambda^* = 1.936 \times 10^7 \sqrt{\frac{M}{RT}}\lambda V^{2/3} \tag{5}$$

are functions of the reduced molar volume $V_r = V/V_o$, where V ($m^3 \cdot mol^{-1}$) is the molar volume, and V_o is a characteristic molar volume of the liquid, weakly dependent on temperature (originally thought of as a close-packed volume). In the above equations, M represents the molecular mass and R is the universal gas constant. According to this scheme [1–7], the aforementioned functions were found to be universal for all liquids and equal to

$$\log_{10}\left[\frac{\eta^*}{R_\eta}\right] = \sum_{i=0}^{7} a_{\eta i} V_r^{-i} \tag{6}$$

$$\log_{10}\left[\frac{\lambda^*}{R_\lambda}\right] = \sum_{i=0}^{4} a_{\lambda i} V_r^{-i} \tag{7}$$

Table 2 Critical constants and coefficients a_i of Eq. 2

Liquid	Critical temp. (K)	Critical density ($\mathrm{kg \cdot m^{-3}}$)	a_1 (−)	a_2 (−)	a_3 (−)	a_4 (−)	a_5 (−)
Alkyl benzenes							
Benzene	562.06	306	2.36136	−1.40482	1.84911	0	0
Toluene	591.75	292	1.89936	1.20834	−2.10808	1.88366	0
*o*Xylene	630.30	287	3.75071	−4.42558	3.62757	0	0
m-Xylene	617.00	283	5.51454	−14.1085	19.75340	−8.45633	0
p-Xylene	616.20	281	0.91600	2.95582	−1.14546	0	0
Ethylbenzene	617.16	284	1.09396	2.30069	−0.62411	0	0
Mesitylene	637.30	275	2.61176	−1.28634	1.61215	0	0
Alkanes							
n-Hexane	507.9	234	1.59756	1.84266	−1.72631	0.49431	0.64631
n-Heptane	540.15	236	1.33159	3.30092	−4.50961	2.76549	0
n-Octane	568.95	237	1.96977	−1.10062	6.36417	−8.69347	4.42005
n-Decane	617.65	239	0.32914	7.36434	−9.98509	5.28361	0
n-Dodecane	658.65	240	−0.03049	8.32535	−10.82684	5.55178	0
n-Tetradecane	693	241	3.50991	−4.09768	3.61064	0	0
n-Hexadecane	722	241	2.61306	−1.99964	2.40011	0	0
Heptamethylnonane	1045.8	221.8	1.1051	−1.5113	3.8342	0	0
2,2,4-Trimethylpentane	543.9	244.5	2.3940	−1.2319	1.5527	0	0
2,6,10,14-Tetramethyl pentadecane	720	230	7.1447	−12.318	8.5802	0	0
Cycloalkanes							
Cyclopentane	511.7	269.8	2.3624	−1.1306	1.46384	0	0
Cyclohexane	553.5	273.2	2.4069	−1.4572	1.8269	0	0
Methylcyclohexane	572.2	273.2	2.5004	−1.6089	1.8682	0	0
Naphthalene							
1-Methylnaphthalene	768	307.8	3.6875	−3.9243	3.2869	0	0

where parameters R_η and R_λ account for deviations from the behavior of smooth hard spheres [1]. The coefficients $a_{\eta i}$ and $a_{\lambda i}$ are shown in Table 4. Characteristic molar volumes as well as the parameters R_η and R_λ were obtained by employing accurate experimental data. As the viscosity is more sensitive to the characteristic molar volume, this quantity is obtained first, together with R_η, from accurate viscosity data. Following this, R_λ is obtained from thermal-conductivity data as a weak function of temperature.

The viscosity and the thermal conductivity of the mixtures will be obtained from the pure components, as a function of the density and the employment of mixing rules on the characteristic molar volume V_o and the roughness parameters R_η and R_λ. Hence, these parameters must first be calculated for the pure components.

Table 3 Coefficients b_i of Eq. 3 and constant C of Eq. 1

Liquid	b_0 (MPa)	b_1 (MPa)	b_2 (MPA)	b_3 (MPa)	C (−)
Alkyl benzenes					
Benzene	430.834	−921.473	518.287	0	0.2000
Toluene	548.309	−1467.483	1415.369	−506.483	0.2160
o-Xylene	428.834	−921.473	518.287	0	0.2000
m-Xylene	428.700	−889.152	472.054	0	0.2127
p-Xylene	420.834	−921.473	518.287	0	0.2000
Ethylbenzene	420.834	−921.473	518.287	0	0.2000
Mesitylene	420.834	−921.473	518.287	0	0.2000
Alkanes					
n-Hexane	331.208	−713.86	401.61	0	0.2000
n-Heptane	331.208	−713.86	401.61	0	0.2000
n-Octane	330.408	−713.86	401.61	0	0.2000
n-Decane	328.808	−713.86	401.61	0	0.2000
n-Dodecane	327.208	−713.86	401.61	0	0.2000
n-Tetradecane	325.608	−713.86	401.61	0	0.2000
n-Hexadecane	331.208	−713.86	401.61	0	0.2000
Heptamethylnonane	201.717	−267.457	−383.3	0	0.2000
2,2,4-Trimethylpentane	329.69	−742.858	424.587	0	0.2050
2,6,10,14-Tetramethyl pentadecane	326.517	−724.229	424.587	0	0.2000
Cycloalkanes					
Cyclopentane	1356.62	−5988.606	9584.81	−5326.36	0.2000
Cyclohexane	418.669	−906.789	508.409	0	0.2000
Methylcyclohexane	366.725	−786.471	439.064	0	0.2000
Naphthalene					
1-Methylnaphthalene	541.82	−1273.86	802.75	0	0.2008

Table 4 Coefficients of Eqs. 6 and 7

i	$a_{\eta i}$	$a_{\lambda i}$
0	1.0945	1.0655
1	−9.26324	−3.538
2	71.0385	12.121
3	−301.9012	−12.469
4	797.6900	4.562
5	−1221.9770	–
6	987.5574	–
7	−314.4636	–

3.1 Pure Liquid Viscosity

The experimental data [1,5,25,32–34] employed for the calculation of V_o and R_η are shown in Table 5, together with the experimental temperature ranges and maximum pressures considered. As in the case of the density data, it should be noted that the maximum pressure shown in the table refers to the point above which deviations started to increase considerably, i.e., the correlation is valid up to the maximum pressure quoted in the table. In most cases, this coincides with the maximum experimental pressure. Only in the case of 6,10,14-tetramethylpentadecane, viscosities for pressures over 10 MPa could not be fitted. This could be attributed to the very high viscosity of this compound. All data considered were fitted to the following two equations proposed by Sun and Teja [9]:

$$R_\eta = \text{constant} \tag{8}$$

$$V_o = D_0 + D_1/T^{0.3} \tag{9}$$

In the original scheme of Assael and Dymond [1–7], the temperature dependence of the characteristic molar volume followed no such simple but restricted rule, but it was rather left to a polynomial form. Hence, it is also of interest to examine the application of this rule here. In the specific cases of the alkyl benzenes and the *n*-alkanes, the viscosity data employed originally by Assael et al. [1,5] were employed here unaltered, as they already covered quite a wide range of temperatures and pressures. New viscosity data were employed for hexamethylnonane, 2,2,4-trimethylpentane, 2,6,10,14-tetramethylpentadecane, the three cycloalkanes, and naphthalene.

In Table 5, the average and maximum absolute percentage deviations, as well as the number of points that deviate by more than 5 % from the scheme, for every data set for each liquid, is also shown. Experimental uncertainties quoted are less than 5 %. In total, 2,076 data points were considered, with a total average absolute deviation of 1.4 % (only 2 % of the data points deviated by more than 5 % from the values calculated by the above equations). The coefficients R_η, D_0, and D_1, obtained following the optimization of the above data, are shown in Table 6. The following points can be noted:

(1) In relation to the restricted form of Eq. 9, certainly no deterioration of the fit was noticed when compared with the original fits [1,5].
(2) Employing Eq. 9 made the fitting procedures much easier—only two constants now represent the characteristic molar volume.
(3) The roughness factor R_η was equal to 1 mostly in the case of alkyl benzenes, which could be attributed to the presence of the benzene ring, while it seems to increase according to the complexity of the molecule.

So, in conclusion, so far it seems that employing the form of Eq. 9 was a good suggestion.

Table 5 Comparison of calculated pure liquid viscosity values with experiment

Liquid	Year of publication and first author	References	Temperature range (K)	Maximum pressure (MPa)	No. of data	Aver. Dev. (%)	Max. dev. (%)	dev. $>5\,\%$
Alkyl benzenes								
Benzene	92 Assael	[5]	283–433	403	226	1.2	6.7	6
Toluene	92 Assael	[5]	218–426	230	272	1.3	9.4	11
o-Xylene	92 Assael	[5]	298–348	112	69	0.5	1.4	–
m-Xylene	92 Assael	[5]	298–348	112	94	0.6	1.6	–
p-Xylene	92 Assael	[5]	298–393	110	63	0.8	2.3	–
Ethylbenzene	92 Assael	[5]	298–348	112	73	1.7	5.0	–
Mesitylene	92 Assael	[5]	298–393	53	33	0.3	1.2	–
Alkanes								
n-Hexane	92 Assael	[1]	289–373	200	117	2.0	6.2	4
n-Heptane	92 Assael	[1]	292–348	112	292	1.4	6.4	3
n-Octane	92 Assael	[1]	294–373	200	141	1.7	8.1	5
n-Decane	92 Assael	[1]	283–423	255	220	2.1	6.3	7
n-Dodecane	92 Assael	[1]	294–374	265	101	1.1	5.0	–
n-Tetradecane	92 Assael	[1]	293–424	0.1	9	1.3	2.3	–
n-Hexadecane	92 Assael	[1]	298–323	30	7	0.8	1.5	–
Heptamethylnonane	95 Et-Tahir	[25]	298–363	40	15	3.3	7.4	5
2,2,4-Trimethylpentane	96 Padua	[35]	198–348	100	74	1.5	4.5	–
	06 Gmez-Daz	[36]	293–323	0.1	5	2.3	3.4	–
2,6,10,14-Tetramethyl pentadecane	95 Et-Tahir	[25]	295–365	0.1	5	1.0	2.1	–
Cycloalkanes								
Cyclopentane	04 Harris	[32]	258–298	280	158	1.6	5.3	1
	00 Assael	[33]	219–309	23	67	1.5	3.5	–
Cyclohexane	05 Yang	[34]	298–333	0.1	5	0.2	0.3	–
Methylcyclohexane	95 Et-Tahir	[25]	298–363	40	15	1.4	3.2	–
Naphthalene								
1-Methylnaphthalene	95 Et-Tahir	[25]	298–363	40	15	2.37	4.9	–

3.2 Pure Liquid Thermal Conductivity

Having obtained the characteristic molar volume, V_{o}, the roughness factor R_{λ} is considered to follow a linear temperature dependence, as

$$R_{\lambda} = L_0 + L_1 T \tag{10}$$

The experimental data [1,5,37–40] employed for the calculation of L_{o} and L_1 are shown in Table 7, together with the experimental temperature ranges and maximum pressures

Table 6 Roughness factor R_η, coefficients D_i of Eq. 9 and coefficients L_i of Eq. 10

Liquid	R_η (–)	$10^6 D_0$ ($m^3 \cdot mol^{-1}$)	$10^5 D_1$ ($m^3 \cdot K^{0.3} \cdot mol^{-1}$)	L_0 (–)	$10^3 L_1$ (K^{-1})
Benzene	1.00	26.733	18.443	1.269	0.804
Toluene	1.00	36.627	19.155	1.620	0.385
o-Xylene	1.00	43.813	22.098	1.738	0.478
m-Xylene	1.00	40.340	23.584	1.973	0.135
p-Xylene	1.00	40.423	24.023	1.851	0.318
Ethylbenzene	1.00	48.027	19.504	2.183	−0.592
Mesitylene	1.00	51.547	24.329	–	–
n-Hexane	1.289	37.457	23.132	2.682	0.426
n-Heptane	1.336	39.517	29.274	1.986	1.422
n-Octane	1.383	41.835	35.639	2.454	0.652
n-Decane	1.477	48.073	47.849	2.339	2.388
n-Dodecane	1.572	61.797	55.970	2.813	2.194
n-Tetradecane	1.666	53.426	76.606	3.444	1.997
n-Hexadecane	1.761	86.022	74.538	2.387	6.970
Heptamethylnonane	1.70	84.078	75.186		
2,2,4 Trimethylpentane	1.153	66.829	23.589	1.980	0.089
2,6,10,14 Tetramethyl pentadecane	1.70	115.015	86.937		
Cyclopentane	1.385	30.078	15.793	1.608	−0.078
Cyclohexane	1.30	17.928	31.490	0.971	1.489
Methylcyclohexane	1.00	70.897	9.798	1.547	−0.055
1- Methylnaphthalene	0.900	56.402	28.401		

considered. As in the case of the viscosity, in the specific cases of the alkyl benzenes and the *n*-alkanes, the thermal-conductivity data employed originally by Assael et al. [1,5] were employed here unaltered, as they already covered quite a wide range of temperatures and pressures. New thermal-conductivity data were employed for 2,2,4-trimethylpentane, cyclopentane, cyclohexane, and methylcyclohexane. Unfortunately, no thermal-conductivity data were found for mesitylene, hexamethylnonane, 2,6,10,14-tetramethylpentadecane, and naphthalene over wide range of temperatures and pressures.

In Table 7, the average and maximum absolute percentage deviations, as well as the number of points that deviate by more than 5 % from the scheme, for every data set for each liquid, are also shown. The experimental uncertainties quoted are less than 5 %. In total, 1,149 data points were considered, with a total average absolute deviation of 0.67 %, while no experimental point deviated by more than 4.8 %. Hence, Eqs. 8–10 seem to perform very well, in addition to being rather simple compared to the original expressions.

Table 7 Comparison of calculated pure liquid thermal-conductivity values with experiment

Liquid	Year of publication and first author	References	Temperature range (K)	Maximum pressure (MPa)	No. of data	Aver. dev. (%)	Max. dev. (%)	dev. >5 %
Alkyl benzenes								
Benzene	92 Assael	[5]	299–361	335	81	0.36	1.1	–
Toluene	92 Assael	[5]	253–373	590	214	0.4	1.7	–
o-Xylene	92 Assael	[5]	295–360	45	28	0.7	1.3	–
m-Xylene	92 Assael	[5]	295–360	42	27	0.4	0.9	–
p-Xylene	92 Assael	[5]	296–360	42	28	0.2	0.6	–
Ethylbenzene	92 Assael	[5]	305–357	50	28	0.3	1.0	–
Mesitylene	–							
Alkanes								
n-Hexane	92 Assael	[1]	297–373	645	120	2.1	4.8	–
n-Heptane	92 Assael	[1]	275–373	500	95	0.6	2.7	–
n-Octane	92 Assael	[1]	282–362	600	112	0.9	4.2	–
n-Decane	92 Assael	[1]	298–373	200	40	0.7	2.0	–
n-Dodecane	92 Assael	[1]	298–373	200	42	0.7	2.9	–
n-Tetradecane	92 Assael	[1]	301–367	0.1	21	0.1	0.3	–
n-Hexadecane	92 Assael	[1]	297–338	0.1	10	0.1	0.3	–
Heptamethylnonane	–							
2,2,4-Trimethylpentane	04 Mensah-Brown	[39]	313–344	255	36	1.2	2.7	–
2,6,10,14-Tetramethyl pentadecane	–							
Cycloalkanes								
Cyclopentane	01 Assael	[37]	235–308	18	41	0.3	0.9	–
	04 Watanabe	[38]	257–317	0.1	15	0.2	0.3	–
Cyclohexane	04 Watanabe	[38]	281–319	0.1	12	0.1	0.2	–
Methylcyclohexane	08 Perkins	[40]	301–403	42	199	0.4	1.0	–
Naphthalene								
1-Methylnaphthalene	–							–

3.3 Liquid Mixture Viscosity and Thermal Conductivity

According to the idea proposed by Assael et al. [3] to predict the viscosity and the thermal conductivity of multicomponent mixtures, it was assumed that the mixture behaves as a single-component liquid, with molecular parameters given by the mole fraction average of the values for the individual components. Thus,

$$V_{\mathrm{o,m}} = \sum_i x_i V_{\mathrm{o},i} \tag{11}$$

$$R_{\eta,\mathrm{m}} = \sum_i x_i R_{\eta,i} \tag{12}$$

$$R_{\lambda,\mathrm{m}} = \sum_i x_i R_{\lambda,i}, \tag{13}$$

while the mixture density, ρ_m $(\mathrm{kg \cdot m^{-3}})$, was calculated from the pure component density, assuming that no volume change takes place during mixing, as

$$\rho_\mathrm{m} = \frac{\sum_i m_i}{\sum_i V_i} = \left(\sum_i \frac{w_i}{\rho_i} \right)^{-1}. \tag{14}$$

In the above equations, x_i, m_i, and w_i, represent the mole fraction, the mass, and the mass fraction of component i.

Finally, the molecular mass, M, of the new single-component liquid was taken as a mole fraction average of the two components. Although other mixing rules were also considered [48], this one was found to be the best.

In the case of the viscosity of mixtures of *n*-alkanes [3], the above scheme was tested on 1,234 data sets covering 32 different binary mixtures. Only 7 % of all data were found to deviate by more than 5 %. It was thus considered that the scheme could successfully predict the viscosity of *n*-alkane mixtures. It is thus of great interest if this idea could be extended to mixtures other than *n*-alkanes only.

In Table 8, the mixtures considered in this study are shown. These are mixtures of alkyl benzenes with other alkyl benzenes, alkanes, cycloalkanes, and a naphthalene. The aforementioned scheme described by Eqs. 11, 12, and 14 could not be used to predict the viscosity of these mixtures. Deviations were very large and by far exceeded the experimental uncertainties. Thus, the first conclusion that can be drawn is that the mixing rules described for the prediction of the transport properties of *n*-alkanes cannot be extended to other kinds of mixtures.

Although the above conclusion is quite discouraging, it was thought to investigate the possibility that a similar kind of mixing rule might apply. Following a series of unsuccessful attempts, the best probable mixing rule is obtained if one substitutes Eq. 12 by the following equation:

$$R_{\eta,\mathrm{m}} = x_1 R_{\eta,1} + x_2 R_{\eta,2} + G x_1 x_2 R_{\eta,1} R_{\eta,2}. \tag{15}$$

In this equation, G is a dimensionless constant taking the value of -0.3 in the presence of a benzene ring in any of the two components, otherwise it is equal to zero. Table 8 shows the deviations of the mixture viscosity values predicted by the aforementioned scheme and Eq. 15. In total, 518 data points were considered, covering 19 mixtures. The temperature and pressure ranges in some cases were restricted according to the pure component density and viscosity data described in the previous tables. Furthermore, in the specific case of the toluene + heptamethylnonane and toluene + 2,6,10,14-tetramethylpentadecane mixtures, the experimental mixture density values were employed, as the values calculated by Eq. 14 showed large deviations. From the 518 data points considered, only 7 % showed absolute deviations larger than 7 %, and only 1 % showed absolute deviations larger than 10 %, from the experimental data. Hence, Eq. 15 can be employed for the prediction of hydrocarbon mixtures.

Table 8 Comparison of predicted liquid mixture viscosity values with experiment

2nd Component	Year of publication and first author	References	Temperature range (K)	Maximum pressure (MPa)	No. of data	Dev. >7 %	Dev. >10 %
Benzene mixtures							
n-Hexane	81 Dymond	[13]	283–375	0.1	7	–	–
	67 Herric	[41]	298	0.1	10	–	–
n-Octane	81 Dymond	[13]	283–395	0.1	32	–	–
n-Decane	81 Dymond	[13]	283–395	0.1	8	–	–
n-Dodecane	81 Dymond	[13]	298–395	0.1	18	–	–
n-Tetradecane	07 Hernandez	[42]	298–395	0.7	20	7	3
n-Hexadecane	81 Dymond	[13]	298–315	0.1	8	–	–
	67 Herric	[41]	298	0.1	9	–	–
Methylcyclohexane	06 Baragi	[43]	298–310	0.1	27	2	–
Toluene mixtures							
n-Hexane	91 Dymond	[44]	298–375	0.1	12	1	–
Cyclopentane	00 Assael	[45]	220–325	0.1	20	1	–
Methylcyclohexane	06 Baragi	[43]	298–310	0.1	27	–	–
Heptamethylnonane	95 Et-Tahir	[25]	298–335	0.1	9	2	1
2,6,10,14-Tetramethyl pentadecane	95 Et-Tahir	[25]	298–365	0.1	14	2	2
Mesitylene	92 Assael	[46]	298–325	52	54	–	–
1-Methylnaphthalene	95 Et-Tahir	[25]	313–355	40	27	5	–
p-Xylene mixtures							
n-Heptane	04 Yang	[34]	298–345	0.1	54	14	–
n-Octane	04 Yang	[34]	298–355	0.1	63	2	–
Cyclohexane	04 Yang	[34]	298–335	0.1	45	1	–
Methylcyclohexane	06 Baragi	[43]	298–310	0.1	27	–	–
Mesitylene mixture							
Methylcyclohexane	06 Baragi	[43]	298–310	0.1	27	–	–

In the case of the thermal conductivity of mixtures, Eqs. 11, 13, and 14 were employed unaltered. Few measurements of the thermal conductivity of alkyl benzene mixtures exist. These are shown in Table 9. From the 159 data points employed, none of the predicted values deviated by more than 5 % from the experimental ones.

4 Conclusions

In relation to the pure liquid viscosity and thermal-conductivity correlation, the following points can be made:

(a) No deterioration of the fit was noticed when comparing the restricted form of the equation proposed by Sun and Teja [9], Eq. 9, with the original fits [1,5]. More-

Table 9 Comparison of predicted liquid mixture thermal-conductivity values with experiment

2nd Component	Year of publication and first author	References	Temperature range (K)	Maximum Pressure (MPa)	No. of data	Dev. <7 %	Dev. >7 %
Benzene mixtures							
2,6,10,14-Tetramethyl pentadecane	80 Mensah-Brown	[39]	313–345	350	115	–	–
Toluene mixtures							
n-Heptane	97 Qun-Fang	[47]	253–295	0.1	15	–	–
Cyclopentane	01 Assael	[39]	253–310	20	29	–	–

over, employing Eq. 9 made fitting procedures much easier—only two constants now represent the characteristic molar volume.

(b) The roughness factor R_η was equal to 1 mostly in the case of alkyl benzenes, which could be attributed to the presence of the benzene ring, while seems to increase according to the complexity or linearity of the molecule.

So, in conclusion, it seems that employing the form of Eq. 9 was a good suggestion.

In relation to the prediction of the viscosity of the mixtures, it seems that the simple mole fraction average mixing rule employed for the *n*-alkanes has to be slightly altered to accommodate alkyl benzene mixtures. The new mixing rule seems to be able to predict the viscosity of these mixtures satisfactorily. In the case of the prediction of the thermal conductivity of mixtures, the mixing rule employed originally for the *n*-alkanes is still employed satisfactorily.

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