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High-Pressure (up to 140 MPa) Dynamic Viscosity of the Methane and Toluene System: Measurements and Comparative Study of Some Representative Models[1]

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The dynamic viscosity of toluene and methane mixtures containing 25.03, 37.19, 49.95, 64.11, and 95.00 mol% methane has been measured using a falling-body viscometer. The measurements (280 data points) have been performed in the temperature range 293.15 to 373.15 K and at pressures up to 140 MPa. The data have been discussed in the framework of recent representative models (hard-sphere scheme, friction theory, and free-volume model) as well as with simple mixing laws and empirical models (particularly the LBC model and the self-referencing model) used in the literature. This comparative study shows that the average absolute deviation of the models is between 4.9 and 26.8%, and the maximum deviation is between 11.6 and 49.5%.

KEY WORDS: density; high pressure; methane; mixtures; models; toluene; viscosity.

1. INTRODUCTION

In recent years a large number of studies have been dedicated to the variation of the dynamic viscosity η with temperature, chemical species, and composition for mixtures, but many experimental studies are carried out only at atmospheric pressure. Experimental studies as a function of pressure are less frequent; however, their number is increasing. An interesting aspect concerns hydrocarbon mixtures. From an industrial perspective the application is obvious (for example, the oil industry) and from a

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fundamental viewpoint, the models proposed in the literature can be tested against data for systems that are sometimes very complex. There are few studies on binary systems containing methane, which are generally composed of another light hydrocarbon or gas such as hydrogen or carbon dioxide. A three-year research program, supported by the European Commission, had the aim of filling this gap in data.

Recently, in the framework of this program, the systems methane + methylcyclohexane [1], methane + *cis*-decalin [2], and methane + *n*-decane [3] have been studied up to 140 MPa. These mixtures are supposed to be representative of high pressure/high temperature petroleum reservoir fluids. In the present work, we have chosen to study the viscosity of the methane + toluene system versus pressure, temperature, and composition since it represents three interests. The first interest is to obtain reliable new data, the second is fundamental in nature as the data can be used to test models for a binary system that is quite asymmetric (methane and toluene have very different molecular weights and structures), and the third is related to engineering areas which deal with gas mixtures involving methane. These areas include the oil industry, but these results are also of crucial interest in many chemical and engineering processes. To the knowledge of the authors, no viscosity and density data are available for the methane + toluene system for comparison with results obtained in this work.

2. EXPERIMENTAL TECHNIQUES

2.1. Apparatus

The dynamic viscosity η was determined with the aid of a specially designed isobaric transfer falling-body viscometer, details of which are provided in Ref. 4. In this apparatus, a stainless-steel cylinder falls through a fluid of unknown viscosity under given conditions of temperature and pressure. The viscosity is a function of the falling time, of the density of both the cylinder and the fluid, and involves constants determined by calibrating the viscometer with substances of known viscosity and density (toluene, propane, *n*-hexane, and *n*-decane). Moreover, methane has been used as a calibration substance for the sample containing 95 mol% of methane. We used in that case the Younglove and Ely values [5]. Each measurement of the falling time was repeated six times at thermal and mechanical equilibrium, and they are reproducible within 1%. The final value is an average of these measurements.

Values of the density ρ for pressures up to 60 MPa were measured with an Anton Paar DMA60 resonance densimeter combined with an additional 512P high pressure cell. Details of the calibration of this type of apparatus, with vacuum and water as reference fluids, are described in Ref. 6. The density measurements were extrapolated up to 140 MPa according to the procedure described in Ref. 7, using a Tait-like relationship for the variation of the density with pressure. The validity of this method is discussed in Refs. 7 and 8, which has been tested with values provided by Dymond [9] for pure alkanes and binary mixtures up to 500 MPa. For example, for *n*-octane at $T = 348.15$ K, using two parameters adjusted with density values below 40 MPa, a small difference of $-0.4\ \mathrm{kg \cdot m^{-3}}$ (i.e., −0.06%) between experimental and calculated values at 105.2 MPa is obtained, and the error is only −0.08% at 202.5 MPa which is larger than our upper pressure limit of viscosity measurements. The maximum error [8] is −0.13% at 79.8 MPa. Also, as shown in the next section (experimental results) the extrapolated values are in good agreement with the values estimated with an equation of state, at the same temperature and pressure conditions.

For the viscosity measurements, the uncertainty in the temperature was estimated to be ±0.5 K and for the density measurements, the uncertainty in the temperature was estimated to be ±0.05 K. The uncertainty in the pressure was estimated to be ±0.05 MPa for the density measurements and ±0.1 MPa for the viscosity measurements. The overall uncertainty in the reported density values is less than $1\ \mathrm{kg \cdot m^{-3}}$, while the uncertainty in the viscosity according to Ref. 4 is approximately 3% except at very low viscosity. For viscosities less than 0.07 mPa · s the absolute uncertainty is of the order of 0.002 mPa · s independent of the value of the viscosity. That concerns only the mixture with the highest concentration of methane ($x = 0.95$) for which the accuracy is also linked to the accuracy of the methane data used for the calibration.

2.2. Characteristics of the Samples

The substances used are commercially available chemicals with the following purity levels: methane (CH_4: AGA Scientifique 5.5, purity > 99.9995%, molar mass $M = 16.04\ \mathrm{g \cdot mol^{-1}}$), toluene ($C_7H_8$: Sigma-Aldrich, purity > 99.9%, molar mass $M = 92.14\ \mathrm{g \cdot mol^{-1}}$). The mixtures were prepared by weighing (with a Mettler balance with a precision of 0.001 g) in a high pressure reservoir cell, following the procedure described in Ref. 8, to obtain the methane mole fractions $x = 0.2503$, 0.3719, 0.4995, 0.6411, and 0.9500. An error of 0.01 g on the weighing of any of the two components leads to an error lower than 0.0001 on the mole fraction of the mixture. The samples containing 25.03, 49.95, and 95.00 mol%

of methane were provided by TotalFinaElf and prepared using a mercury cell in liquid nitrogen. The phase diagram of the methane + toluene system has been reported [10–13], and the study of the mixtures has been performed in the single-phase dense state, at least, 10 MPa above the saturation curve according to this diagram. Transfers of the sample from the preparation cell to the measuring cells have been carried out at pressures around 50 MPa.

Measurements of the viscosity and density were carried out from 293.15 to 373.15 K in steps of 20 K. Measurements of viscosity were made up to 140 MPa in steps of 20 MPa, starting at the lowest pressure (consistent with the phase diagram): 20 MPa for $x = 0.2503$, 30 MPa for $x = 0.3719$, 40 MPa for $x = 0.4995$, and 50 MPa for $x = 0.6411$ and 0.9500. Measurements of density were carried out in steps of 5 MPa, up to 60 MPa from 20 MPa for $x = 0.2503$, 30 MPa for $x = 0.3719$, 35 MPa for $x = 0.4995$, and 45 MPa for $x = 0.6411$ and 0.9500. A total of 280 experimental points was measured for viscosity, and 150 experimental points for density. Finally, 200 density values were obtained by extrapolation above 60 MPa and up to 140 MPa.

3. EXPERIMENTAL RESULTS

The viscosity and density measurements for mixtures of methane and toluene are reported in Tables I to V. Figure 1 shows the surface $\eta(P, T)$ at $x = 0.4995$ of methane. The variations of viscosity and density versus pressure and temperature are smooth for each composition, and these quantities increase with pressure and decrease with temperature. Figure 2 shows the variation of density with composition at 293.15 K for several pressures, and Fig. 3 shows the variation of viscosity at the same conditions. It should be noted here that for methane we used viscosity and density values from Younglove and Ely [5] (they indicated 2% uncertainty in our pressure and temperature range), and for toluene viscosity and density values provided by Vieira dos Santos and Nieto de Castro [14] (0.5% uncertainty), for the calibration of the experimental device.

The experimental density values have been compared with those generated by the Lee and Kesler [15] equation of state, using the mixing laws proposed by Plöcker et al. [16]. The average absolute deviation between our values (including the extrapolated values with the Tait-like equation) and the calculated values with the equation of state is around 1.1%, with a maximum deviation of 6%. The influence on the dynamic viscosity (calculating the viscosity with the experimental falling times and the calculated densities) is less than 1%.

Table I. Dynamic Viscosities and Densities of Methane (25.03 mol%) + Toluene (74.97 mol%)[a]

	T (K)									
	293.15		313.15		333.15		353.15		373.15	
P (MPa)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)
20	0.8102	0.435	0.7914	0.346	0.7725	0.282	0.7533	0.248	0.7336	0.214
25	0.8143		0.7961		0.7776		0.7591		0.7404	
30	0.8183	0.472	0.8005	0.375	0.7826	0.305	0.7648	0.268	0.7466	0.230
35	0.8220		0.8047		0.7873		0.7701		0.7524	
40	0.8256	0.510	0.8087	0.404	0.7916	0.328	0.7749	0.289	0.7579	0.246
45	0.8290		0.8125		0.7958		0.7796		0.7630	
50	0.8323	0.549	0.8161	0.434	0.7998	0.352	0.7840	0.309	0.7679	0.263
55	0.8356		0.8197		0.8037		0.7881		0.7725	
60	0.8386	0.589	0.8230	0.465	0.8073	0.376	0.7922	0.330	0.7769	0.280
70	0.8444	0.631	0.8295	0.497	0.8143	0.402	0.7997	0.350	0.7850	0.297
80	0.8499	0.674	0.8355	0.530	0.8207	0.427	0.8066	0.370	0.7926	0.314
90	0.8550	0.717	0.8411	0.563	0.8268	0.454	0.8130	0.391	0.7996	0.332
100	0.8599	0.762	0.8465	0.598	0.8325	0.481	0.8191	0.411	0.8061	0.350
110	0.8646	0.808	0.8515	0.633	0.8379	0.509	0.8247	0.432	0.8122	0.369
120	0.8690	0.855	0.8563	0.669	0.8430	0.538	0.8301	0.452	0.8180	0.388
130	0.8732	0.903	0.8609	0.707	0.8478	0.568	0.8352	0.473	0.8235	0.407
140	0.8772	0.952	0.8653	0.745	0.8525	0.598	0.8400	0.494	0.8287	0.426

[a] For $P > 60$ MPa density values have been obtained by extrapolation with Tait-like equation.

Table II. Dynamic Viscosities and Densities of Methane (37.19 mol%) + Toluene (62.81 mol%)[a]

	T (K)									
	293.15		313.15		333.15		353.15		373.15	
P (MPa)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)	ρ ($g \cdot cm^{-3}$)	η (mPa·s)
30	0.7794	0.347	0.7610	0.275	0.7423	0.231	0.7236	0.207	0.7046	0.178
35	0.7836		0.7658		0.7476		0.7296		0.7115	
40	0.7879	0.375	0.7703	0.299	0.7527	0.250	0.7351	0.223	0.7176	0.192
45	0.7919		0.7746		0.7576		0.7403		0.7235	
50	0.7955	0.404	0.7787	0.322	0.7619	0.269	0.7452	0.238	0.7289	0.207
55	0.7992		0.7825		0.7663		0.7498		0.7340	
60	0.8025	0.433	0.7862	0.346	0.7703	0.288	0.7542	0.254	0.7389	0.221
70	0.8090	0.464	0.7932	0.370	0.7779	0.307	0.7624	0.269	0.7479	0.235
80	0.8150	0.495	0.7996	0.394	0.7849	0.326	0.7700	0.285	0.7562	0.249
90	0.8206	0.527	0.8056	0.419	0.7915	0.345	0.7770	0.301	0.7638	0.264
100	0.8259	0.560	0.8112	0.443	0.7976	0.365	0.7835	0.317	0.7709	0.278
110	0.8309	0.593	0.8164	0.468	0.8034	0.384	0.7883	0.333	0.7776	0.292
120	0.8356	0.628	0.8214	0.493	0.8080	0.403	0.7951	0.349	0.7839	0.307
130	0.8401	0.663	0.8268	0.518	0.8139	0.422	0.8012	0.365	0.7898	0.321
140	0.8448	0.700	0.8322	0.544	0.8194	0.441	0.8069	0.381	0.7954	0.335

[a] For $P > 60$ MPa density values have been obtained by extrapolation with Tait-like equation.

Table III. Dynamic Viscosities and Densities of Methane (49.95 mol%) + Toluene (50.05 mol%)[a]

	T (K)									
	293.15		313.15		333.15		353.15		373.15	
P (MPa)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
35	0.7125		0.6926		0.6725		0.6525		0.6319	
40	0.7177	0.260	0.6986	0.213	0.6793	0.183	0.6601	0.164	0.6406	0.153
45	0.7225		0.7041		0.6855		0.6671		0.6484	
50	0.7271	0.279	0.7092	0.228	0.6912	0.195	0.6734	0.176	0.6556	0.164
55	0.7315		0.7141		0.6966		0.6793		0.6622	
60	0.7356	0.299	0.7185	0.244	0.7016	0.207	0.6849	0.188	0.6683	0.174
70	0.7432	0.320	0.7268	0.259	0.7108	0.220	0.6949	0.200	0.6794	0.185
80	0.7502	0.341	0.7342	0.275	0.7192	0.233	0.7038	0.212	0.6893	0.196
90	0.7567	0.363	0.7411	0.292	0.7268	0.246	0.7120	0.225	0.6983	0.207
100	0.7627	0.386	0.7474	0.308	0.7338	0.260	0.7195	0.237	0.7065	0.218
110	0.7683	0.409	0.7532	0.325	0.7404	0.273	0.7264	0.250	0.7141	0.229
120	0.7736	0.433	0.7587	0.342	0.7465	0.287	0.7328	0.263	0.7212	0.240
130	0.7786	0.457	0.7638	0.360	0.7522	0.301	0.7388	0.276	0.7278	0.252
140	0.7833	0.482	0.7687	0.377	0.7577	0.315	0.7445	0.289	0.7341	0.263

[a] For $P > 60$ MPa density values have been obtained by extrapolation with Tait-like equation.

Table IV. Dynamic Viscosities and Densities of Methane (64.10 mol%) + Toluene (35.90 mol%)[a]

	T (K)									
	293.15		313.15		333.15		353.15		373.15	
P (MPa)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
45	0.6349		0.6149		0.5949		0.5752		0.5554	
50	0.6411	0.172	0.6219	0.147	0.6028	0.129	0.5839	0.114	0.5652	0.102
55	0.6468		0.6283		0.6099		0.5917		0.5739	
60	0.6521	0.184	0.6342	0.158	0.6163	0.139	0.5987	0.124	0.5817	0.112
70	0.6615	0.197	0.6448	0.169	0.6278	0.149	0.6110	0.134	0.5954	0.122
80	0.6699	0.209	0.6541	0.180	0.6378	0.159	0.6216	0.144	0.6071	0.132
90	0.6774	0.222	0.6625	0.191	0.6466	0.169	0.6310	0.154	0.6174	0.141
100	0.6843	0.235	0.6702	0.202	0.6547	0.178	0.6395	0.164	0.6266	0.150
110	0.6906	0.248	0.6773	0.213	0.6620	0.187	0.6472	0.173	0.6350	0.159
120	0.6964	0.261	0.6838	0.224	0.6688	0.197	0.6543	0.182	0.6428	0.168
130	0.7019	0.274	0.6899	0.235	0.6751	0.206	0.6609	0.191	0.6500	0.177
140	0.7070	0.288	0.6956	0.246	0.6810	0.219	0.6670	0.201	0.6567	0.186

[a] For $P > 60$ MPa density values have been obtained by extrapolation with Tait-like equation.

Table V. Dynamic Viscosities and Densities of Methane (95.00 mol%) + Toluene (5.00 mol%)[a]

	T (K)									
	293.15		313.15		333.15		353.15		373.15	
P (MPa)	ρ $(g \cdot cm^{-3})$	η $(mPa \cdot s)$	ρ $(g \cdot cm^{-3})$	η $(mPa \cdot s)$	ρ $(g \cdot cm^{-3})$	η $(mPa \cdot s)$	ρ $(g \cdot cm^{-3})$	η $(mPa \cdot s)$	ρ $(g \cdot cm^{-3})$	η $(mPa \cdot s)$
45	0.3168		0.2975		0.2800		0.2668		0.2528	
50	0.3289	0.042	0.3099	0.038	0.2927	0.036	0.2797	0.033	0.2659	0.032
55	0.3396		0.3210		0.3041		0.2914		0.2778	
60	0.3495	0.046	0.3310	0.042	0.3147	0.040	0.3020	0.037	0.2885	0.036
70	0.3672	0.050	0.3492	0.046	0.3337	0.043	0.3213	0.041	0.3083	0.039
80	0.3831	0.054	0.3655	0.050	0.3509	0.047	0.3386	0.044	0.3263	0.042
90	0.3975	0.058	0.3803	0.054	0.3667	0.051	0.3546	0.048	0.3430	0.045
100	0.4109	0.062	0.3941	0.057	0.3815	0.054	0.3696	0.051	0.3588	0.049
110	0.4235	0.066	0.4070	0.061	0.3955	0.057	0.3838	0.054	0.3738	0.051
120	0.4355	0.070	0.4193	0.064	0.4089	0.060	0.3974	0.057	0.3883	0.054
130	0.4468	0.073	0.4311	0.067	0.4218	0.063	0.4105	0.060	0.4024	0.057
140	0.4577	0.076	0.4424	0.070	0.4342	0.066	0.4232	0.063	0.4161	0.060

[a] For $P > 60$ MPa density values have been obtained by extrapolation with Tait-like equation.

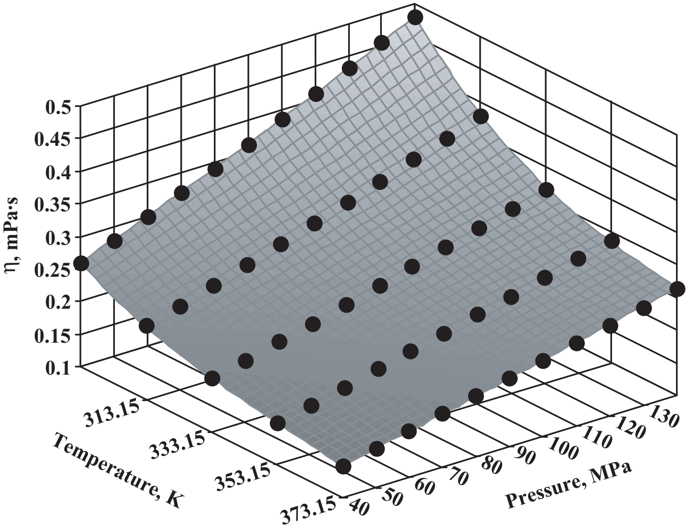

Fig. 1. Surface $\eta(P, T)$ at $x_{\text{Methane}} = 0.4995$.

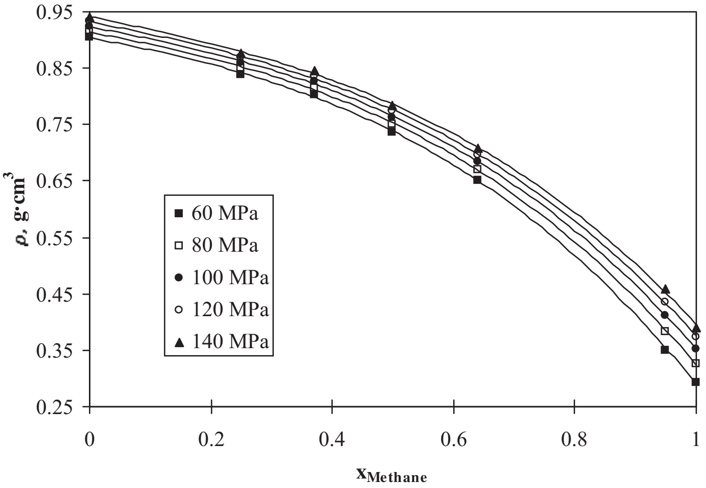

Fig. 2. Variations of density with composition at 293.15 K for several pressures. Pure methane data are taken from Ref. 5 and pure toluene data from Ref. 14.

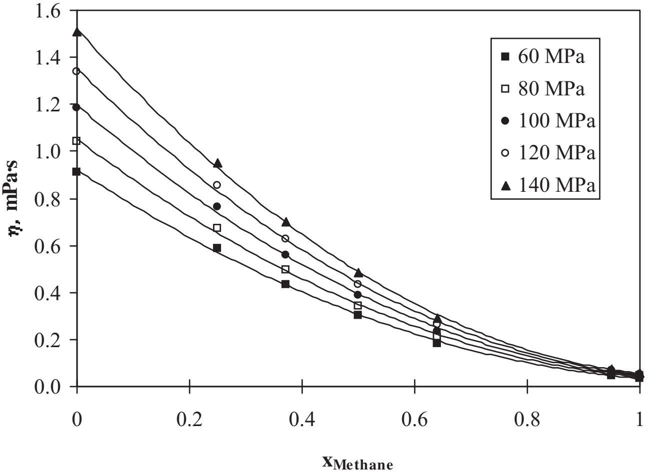

Fig. 3. Variations of viscosity with composition at 293.15 K for several pressures. Pure methane data are taken from Ref. 5 and pure toluene data from Ref. 14.

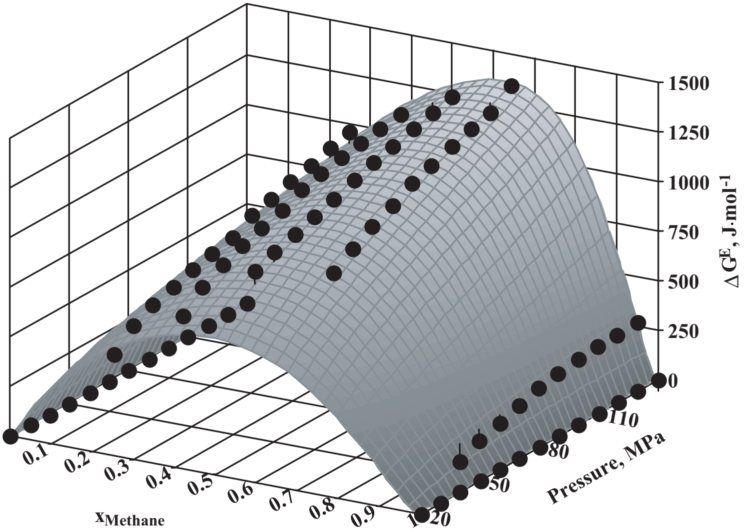

Fig. 4. Variations of ΔG^E with composition and pressure at 333.15 K.

Finally, from the experimental values of viscosity it is possible to evaluate the excess activation energy of viscous flow ΔG^E defined as

$$\ln(\eta V) = x \ln(\eta_{\mathrm{C1}} V_{\mathrm{C1}}) + (1-x) \ln(\eta_{\mathrm{Tol}} V_{\mathrm{Tol}}) + \Delta G^E/(RT) \tag{1}$$

where R is the gas constant, η_{C1} is the methane dynamic viscosity, η_{Tol} is the toluene dynamic viscosity, V_{C1} is the methane molar volume, V_{Tol} is the toluene molar volume, and V is the mixture molar volume. This well known relationship is theoretically justified by Eyring's representation of the dynamic viscosity of a fluid. Figure 4 presents ΔG^E at 333.15 K for several pressures and compositions. The maximum values of ΔG^E are high, and the positive values correspond to attractive interactions. The interested reader can find examples of the variations ΔG^E with pressure, temperature, and composition for the very associative systems water + diacetone alcohol and water + 2-propanol in Refs. 17 and 18. For the water + diacetone alcohol system ΔG^E can reach $5000\ \mathrm{J \cdot mol^{-1}}$, and for the water + 2-propanol system ΔG^E can reach $3000\ \mathrm{J \cdot mol^{-1}}$. For the case of the methane + *n*-decane mixture in previous work [3], it has been shown that the maximum ΔG^E values are of the order of $3000\ \mathrm{J \cdot mol^{-1}}$.

4. VISCOSITY MODELS

Taking into account the fact that ΔG^E indicates attractive interactions, this system is consequently nonideal and, therefore, this system appears to be a good test system to evaluate the predictive performance of various viscosity models. In the following, three models with various semi-empirical basis (mixing laws, residual viscosity method, and self-referencing method) and three recently developed models with a theoretical basis (hard-sphere scheme, friction theory, and free-volume model) will be considered. In order to evaluate the performances of a model it is necessary to define characteristic quantities for which the results will be expressed. In the equations, hereafter η_{exp} refers to the experimental value of viscosity and η_{cal} the value calculated using the considered model. We define the following quantities:

$$\text{Deviation} = 100(1-\eta_{\mathrm{cal}}/\eta_{\mathrm{exp}})(\%)$$

$$\text{Absolute deviation} = |\text{Deviation}|.$$

These quantities are expressed as percentages. For the entire set of data we define the following three characteristic quantities (N_b is the number of experimental points):

$$\text{Average Absolute Deviation} = \text{AAD} = \frac{1}{N_b}\sum_{i=1}^{N_b} \text{Absolute deviation(i)}$$

$$\text{Maximum deviation} = D_{\mathrm{M}} = \text{MAX(Absolute deviation(i))}$$

$$\text{Bias} = B = \frac{1}{N_b}\sum_{i=1}^{N_b} \text{Deviation(i)}$$

4.1. Mixing Laws

In a comparative study of predictive models for mixtures it is necessary to mention first the mixing laws. There are many kind of mixing laws, and it is not the purpose of this study to do an extensive survey of them. We will focus on only two of them, which are very well known and used without any adjustable parameter so that they can be considered as predictive. The first one has been proposed by Grunberg and Nissan (GN) [19]:

$$\ln(\eta) = x\ln(\eta_{\mathrm{C1}}) + (1-x)\ln(\eta_{\mathrm{Tol}}) \tag{2}$$

We obtained for the mixture $\text{AAD} = 26.8\%$, $B = 26.8\%$, and $D_{\mathrm{M}} = 40.5\%$ (at $x = 0.4995$). The second mixing law has been proposed by Katti and Chaudhri (KC) [20]:

$$\ln(\eta V) = x\ln(\eta_{\mathrm{C1}}V_{\mathrm{C1}}) + (1-x)\ln(\eta_{\mathrm{Tol}}V_{\mathrm{Tol}}) \tag{3}$$

This equation corresponds to the case $\Delta G^E = 0$, and it is considered in a certain sense to be representative of the viscosity of "ideal" mixtures. We obtained for our system with this equation AAD = 21.0%, $B = 21.0\%$, and $D_M = 43.6\%$ (at $x = 0.4995$).

These results are not satisfactory because this system is nonideal and the GN and KC mixing laws do not take into account the interactions in this system. In many cases adjustable parameters are introduced, but the mixing laws will then lose their predictive capability.

4.2. Residual Viscosity Method

As methane is one of the components involved in our system, it is interesting to verify the performance of a commonly used model in petroleum engineering, proposed by Lohrenz et al. [21] (LBC model) based on the empirical correlation of Jossi et al. [22]:

$$[(\eta - \eta_0)\,\xi + 10^{-4}]^{1/4} = a_1 + a_2\rho_r + a_3\rho_r^2 + a_4\rho_r^3 + a_5\rho_r^4 \tag{4}$$

where η_0 is the dilute gas viscosity (estimated following the procedure described in Ref. 22), $\rho_r = \rho/\rho_c$ is the reduced density (ρ_c is the critical density), and $\xi = T_c^{1/6} M^{-1/2} P_c^{-2/3}$ (P_c and T_c are the critical pressure and critical temperature taken from Ref. 24). For the mixture the rules proposed by Jossi et al. [22] have been used. The a_i parameters have been evaluated by Jossi et al. [22] using a database containing eleven various compounds. Applying this method to our experimental data, we obtained AAD = 13.2%, $B = -12.7\%$, and $D_M = 49.5\%$ (at $x = 0.9500$). In comparison with the mixing laws, the value of AAD is better, but the maximum deviation is still large.

4.3. Self-Referencing Method

The self-referencing model [25] has been developed in order to model the viscous behavior of petroleum cuts for which the complex composition is difficult to characterize. For this kind of fluids, it is difficult to use equations based on physical properties such as molecular weight, critical parameters, or acentric factor since they have to be known for each of the components. The formulation has the advantage of only requiring one experimental determination at a reference pressure P_0 and a selected temperature T_0. This is the reason why this method can be referred to as a self-referencing model. This method does not involve either the molecular weight, or any other physical properties, or critical parameters. It can be applied without restriction to pure substances, to synthetic mixtures, or to chemically very rich systems such as petroleum cuts for which the method was originally developed. The method involves nine coefficients originally determined by numerical analysis on a database containing linear alkanes and alkylbenzenes. On the basis of knowledge of the values of these coefficients, the method can be used directly without further adjustment, and for this reason, it may be considered as being general and predictive. The formulation of this method is as follows:

$$\ln\left(\frac{\eta(P,T)}{\eta(P_0,T_0)}\right)=(ay^2+by+c)\ln\left(1+\frac{(P-P_0)}{dy^2+ey+f}\right)+(gy_0^2+hy_0+i)\left(\frac{1}{T}-\frac{1}{T_0}\right) \tag{5}$$

where $y=y_0+(gy_0^2+hy_0+i)(1/T-1/T_0)$ and $y_0=\ln[\eta(P_0,T_0)]$. This equation is used with P in MPa, T_0 and T in K, and $\eta(P_0,T_0)$ in mPa·s. In this work, the reference point has been chosen, for each composition, to be the lowest pressure at 293.15 K. For the calculation there are 275 points, when the 5 reference points are excluded.

First, we applied the model using the coefficients adjusted by Kanti et al. [25]. The overall results for the 275 data are $\text{AAD}=46.3\%$, $B=-46.3\%$, and $D_M=254\%$ (at $x=0.9500$), which are poor results. This is due to the fact that the 9 parameters have been adjusted on alkanes and alkylbenzenes with a carbon number greater or equal to seven so that they are very different from methane.

Second, we modified this self-referencing method. In the pressure-temperature range considered, the nine parameters $a, b,\ldots, i$ have been fitted for each pure compound. For toluene $\text{AAD}=0.97\%$, $B=0.38\%$, and $D_M=3.42\%$, and for methane $\text{AAD}=0.38\%$, $B=0.34\%$, and $D_M=4.38\%$. Then, for each composition we used $\alpha_m=x\alpha_{C1}+(1-x)\,\alpha_{Tol}$ ($\alpha=a, b,\ldots, i$). For the mixture we have obtained $\text{AAD}=5.47\%$, $B=-5.08\%$, and $D_M=11.6\%$ (at $x=0.4995$), which is a very satisfactory result for such a predictive method. This clearly shows, as suggested in the original article, that the use of the reference measurement point is important because this measurement contains and provides useful information on the system studied.

4.4. Hard-Sphere Scheme

Recently [26, 27] a scheme has been developed for the simultaneous correlation of self-diffusion, viscosity, and thermal conductivity of dense fluids. The transport coefficients of real dense fluids expressed in terms of

$V_r = V/V_0$ with V_0 the close-packed volume and V the molar volume, are assumed to be directly proportional to values given by the exact hard-sphere theory. The proportionality factor, described as a roughness factor R_x (for the property x), accounts for molecular roughness and departure from molecular sphericity. Universal curves for the viscosity were developed and are expressed as

$$\ln\left(\frac{\eta^*_{\text{exp}}}{R_\eta}\right) = \sum_{i=0}^{7} a_{\eta i}(1/V_r)_i \qquad \text{with } \eta^*_{\text{exp}} = \frac{16\sqrt{\pi}}{5}(2N_A)^{1/3}\frac{\eta_{\text{exp}}V^{2/3}}{\sqrt{MRT}} \tag{6}$$

In Eq. (5), N_A is Avogadro's number. It seems [28] that the coefficients $a_{\eta i}$ are universal, independent of the chemical nature of the compound. For alkanes [27] and aromatics [29], the authors give correlation formulas relative to V_0 and R_η. The latter is independent of pressure and temperature, but the former is temperature dependent and is generally decreasing with increasing temperature.

The hard-sphere model has been applied keeping constant the universal coefficients $a_{\eta i}$ of Assael et al. [27, 29] and calculating the coefficients R_η for each compound and V_0 for each compound at each temperature. So, in our case there are six parameters for each pure compound. For methane $\text{AAD} = 2.39\%$, $B = 0.29\%$, and $D_M = 6.17\%$, and for toluene $\text{AAD} = 0.94\%$, $B = -0.22\%$, and $D_M = 2.83\%$. Then, for each composition we used the following mixing rules [30, 31] $R_{\eta m} = xR_{\eta C1} + (1-x)\,R_{\eta Tol}$ and $V_{0m} = xV_{0C1} + (1-x)\,V_{0Tol}$. For the mixture we have obtained $\text{AAD} = 5.98\%$, $B = 4.52\%$, and $D_M = 20.3\%$ (at $x = 0.4995$), which is a very interesting result. Assael et al. [30] have already noted that for the methane + *n*-decane system using the data of Knapstad et al. [32] limited to 42 MPa, this method gives good results.

In order to be entirely predictive we used the density values generated by the Lee and Kesler [15] equation of state using the mixing rules proposed by Plöcker et al. [16]. We found $\text{AAD} = 7.98\%$, $B = 6.89\%$, and $D_M = 23.6\%$ (at $x = 0.2503$). In fact we noticed that this method is very sensitive to the choice of the mixing rules used with the equation of state [8].

4.5. Friction Theory

Recently, the friction theory (*f-theory*) for viscosity modeling has been introduced [33, 34]. According to the *f-theory*, the total viscosity η can be separated into a dilute gas term η_0 and a friction term η_f as follows:

$$\eta = \eta_0 + \eta_f \tag{7}$$

The dilute viscosity is defined as the viscosity at zero density and can be obtained from the model proposed by Chung et al. [35]. The friction term has been linked to the van der Waals repulsive pressure term p_r and attractive pressure term p_a by three temperature dependent friction coefficients κ_r, κ_a, and κ_{rr} as follows:

$$\eta_f = \kappa_r p_r + \kappa_a p_a + \kappa_{rr} p_r^2 \tag{8}$$

The repulsive and attractive pressure terms can be obtained by cubic equations of state (EOS), such as the Peng and Robinson EOS modified by Stryjek and Vera (PRSV) [36].

In the first version of this theory [33] the viscosity of the pure compounds is modeled using the PRSV EOS together with the following expressions for the friction coefficients [33]:

$$\begin{aligned}
\kappa_r &= a_0 + a_1(\exp[\Gamma - 1] - 1) + a_2(\exp[2(\Gamma - 1)] - 1) \\
\kappa_a &= b_0 + b_1(\exp[\Gamma - 1] - 1) + b_2(\exp[2(\Gamma - 1)] - 1) \\
\kappa_{rr} &= c_2(\exp[2\Gamma] - 1)
\end{aligned} \tag{9}$$

with $\Gamma = \frac{T_c}{T}$, where T_c is the critical temperature. The necessary critical parameters and constants (the acentric factor appears in the calculation of η_0 [35]) are those indicated in Ref. 24. There are seven adjustable parameters for each compound. For methane AAD = 0.94%, $B = 0.41\%$, and $D_M = 10.9\%$, and for toluene, AAD = 1.01%, $B = 0.09\%$, and $D_M = 2.91\%$. For the mixtures the mixing rules proposed in Ref. 33 have been used, resulting in AAD = 7.16%, $B = 1.94\%$, and $D_M = 25.8\%$ (at $x = 0.4995$).

In the second version of this theory [34], the authors use sixteen universal parameters and one parameter (named "characteristic critical viscosity") characteristic of the compound. The values of the universal parameters and the mixing rules used for the mixtures are reported in Ref. 34. The authors advised us (personal communication, 2001) to adjust the critical viscosity of methane over the experimental pressure and temperature ranges. We found for methane AAD = 5.96%, $B = -1.92\%$, $D_M = 16.0\%$, and for toluene AAD = 2.00%, $B = 0.09\%$, and $D_M = 6.66\%$. Finally, for the mixture, we obtained AAD = 5.36%, $B = 1.94\%$, and $D_M = 17.1\%$ (at $x = 0.9500$). These results are interesting (AAD around 5%) because all of the parameters involved are universal except the characteristic critical viscosity.

4.6. Free-Volume Theory

Another approach, based on the free-volume concept, has been very recently proposed [37, 38] for modeling of the viscosity of Newtonian fluids in both gaseous and dense states. Like the *f-theory* the total viscosity η can be separated into a dilute gas term η_0 and an additional $\Delta\eta$ term, such as

$$\eta = \eta_0 + \Delta\eta \tag{10}$$

The term $\Delta\eta$ characterizes the passage into a dense state. The model has been successfully applied to methane (885 data points for which $0.01 \leqslant P \leqslant 200$ MPa and $90 \leqslant T \leqslant 600$ K), and gives AAD = 2.59% and $D_M = 14.8\%$. It has also been applied with very good results to various hydrocarbons [37].

This approach connects the term $\Delta\eta$ to molecular structure via a representation of the free volume fraction. The viscosity, in this theory, appears as the product of the fluid modulus $\rho RT/M$ and the mean relaxation time of the molecule defined by $N_A L^2 \zeta/(RT)$, and the viscosity can be expressed as

$$\Delta\eta = \frac{\rho N_A \zeta L^2}{M} \tag{11}$$

where N_A is Avogadro's number, ζ is the friction coefficient of a molecule, and L^2 is an average characteristic molecular quadratic length. The friction coefficient ζ is related to the mobility of the molecule and to the diffusion process (diffusion of the momentum for viscosity). Moreover, the free volume fraction $f_v = v_f/v$ ($v_f = v - v_0$, v is the specific molecular volume, and v_0 is the molecular volume of reference or hard core volume) is, at a temperature T, defined by $f_v = (\frac{RT}{E})^{\frac{3}{2}}$ assuming that the molecule is in a state such that the molecular potential energy of interaction with its neighbors is E/N_A. It has been assumed [38] that $E = \alpha\rho + PM/\rho$ (P = pressure) where the term $PM/\rho = PV$ is connected to the energy necessary to form the vacant vacuums available for the diffusion of the molecules and where $E_0 = \alpha\rho$ is connected to the energy barrier that the molecule must exceed in order to diffuse. The use of the empirical relation of Doolittle [39], $\Delta\eta = A \exp(B/f_v)$, where B is the characteristic of the free volume overlap, has led to expressing ζ in the form $\zeta = \zeta_0 \exp(B/f_v)$. By inserting this expression in Eq. (11) gives

$$\Delta\eta = \frac{\rho N_A L^2 \zeta_0 \exp(B/f_v)}{M} \tag{12}$$

Further, it has been demonstrated [40] that

$$\zeta_0 = \frac{E}{N_A b_f} \sqrt{\frac{M}{3RT}} \tag{13}$$

where b_f is the dissipation length of the energy E. Finally,

$$\eta = \eta_0 + \frac{\rho \ell (\alpha\rho + \frac{PM}{\rho})}{\sqrt{3RTM}} \exp\left(B \left(\frac{\alpha\rho + \frac{PM}{\rho}}{RT} \right)^{\frac{3}{2}} \right) \tag{14}$$

or alternatively

$$\eta = \eta_0 + \rho\ell \sqrt{\frac{RT}{3M}} f_v^{-2/3} \exp\left(\frac{B}{f_v} \right) \tag{15}$$

where $\ell = L^2/b_f$ is a length parameter. This equation involves three physical parameters ℓ, α, and B which are characteristic of the molecule.

For methane, in the considered (P, T) range, using [38] $\ell = 0.590803$ Å, $\alpha = 37.8049\ \mathrm{J \cdot m^3 \cdot mol^{-1} \cdot kg^{-1}}$, and $B = 0.009002163$, we obtained AAD = 4.53%, $B = -0.07\%$, and $D_M = 12.8\%$. For toluene, using $\ell = 0.727323$ Å, $\alpha = 75.68358\ \mathrm{J \cdot mol^{-1} \cdot m^3 \cdot kg^{-1}}$, and $B = 0.00925373$ we obtained AAD = 1.15%, $B = -0.47\%$, and $D_M = 7.60\%$. Then, for the mixtures we used [8] the following mixing rules $1/B_m = x/B_{C1} + (1-x)/B_{Tol}$, $\ell_m = x\ell_{C1} + (1-x)\,\ell_{Tol}$, and $1/f_{vm} = x/f_{vC1} + (1-x)/f_{vTol}$ (calculating for each pure compound $f_v = (\frac{RT}{E})^{\frac{3}{2}}$ with $E = \alpha\rho + PM/\rho$). We obtained AAD = 4.92%, $B = 0.25\%$, and $D_M = 15.0\%$ (at $x = 0.9500$) which is an excellent result. In order to use a fully predictive model, we generated the density values with the Lee–Kesler equation of state using the Plöcker et al. mixing rules (which represent density with a maximum deviation of 6.0%). We obtained for viscosity AAD = 5.25%, $B = 0.60\%$, and $D_M = 13.4\%$ (at $x = 0.9500$).

5. CONCLUSION

The methane + toluene system is interesting because the molecules of the two pure compounds are very different from each other and the system is asymmetrical. This study provides viscosity and density data in an extended (P, T) range for various compositions. The measured data for this system are very useful in order to evaluate the capability of various models to predict the dynamic viscosity. Table VI summarizes all the results, and it is interesting to notice that the recent models with theoretical backgrounds give absolute average deviations of less than 10% with

Table VI. Comparison of Results Obtained with Different Viscosity Models

Model	AAD (%)	D_M (%)	B (%)
Grunberg and Nissan	26.8	40.5	26.8
Katti and Chaudhri	21.0	43.6	21.0
Residual viscosity method	13.2	49.5	−12.7
Self-referencing method	5.47	11.6	−5.08
Hard sphere scheme	5.98	20.3	4.52
Friction theory	5.36	17.1	1.94
Free volume model	4.92	15.0	0.25

maximum deviations of less than 20%. This is promising and encouraging for further studies in order to improve the predictive character of such models and also in an understanding of the dynamic viscosity of mixtures as well as pure compounds.

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