International Journal of Thermophysics, Vol. 23, No. 6, November 2002 (© 2002)

High-Pressure (up to 140 MPa) Dynamic Viscosity of the Methane+Decane System

X. Canet,[1] A. Baylaucq,[1] and C. Boned[1, 2]

Received February 12, 2002

The dynamic viscosity of *n*-decane and methane mixtures containing 31.24, 48.67, 60.00, 75.66 and 95.75% (mol%) of methane has been measured using a falling-body viscometer. The measurements (295 data points) have been performed in the temperature range 293.15 to 373.15 K and at pressures up to 140 MPa for viscosity. The data have been used to calculate the excess activation energy of viscous flow using a mixing law. Moreover, a self-referencing model, previously developed in the laboratory, gives an average absolute deviation of the viscosity of about 3% with a maximum deviation of 16%.

KEY WORDS: decane; density; high pressure; methane; viscosity.

1. INTRODUCTION

It is well known that the dynamic viscosity η of fluids is of great interest in various research areas both applied and fundamental. A large number of results are dedicated to the variation of η versus temperature, chemical species, and composition for mixtures, but many of them are carried out only at atmospheric pressure. Experimental studies as a function of pressure are less frequent, although their number is increasing. Moreover, recently, some models with a more or less physical basis have been proposed. It is necessary to provide reliable input data for the development of general valid models for the quantitative prediction of viscosity and also to enhance an understanding from the point of view of physical interpretation. An interesting aspect concerns hydrocarbon mixtures. From an industrial perspective, the application is obvious (for example, the oil

---

[1] Laboratoire des Fluides Complexes, Faculté des Sciences, Université de Pau, Avenue de l'Université, BP 1155, 64013 Pau Cedex, France.

[2] To whom correspondence should be addressed. E-mail: christian.boned@univ-pau.fr

industry) and from a fundamental viewpoint, the data can be used in order to test models for complex systems.

A review of the literature shows that there are few studies on binary systems containing methane, which is generally combined with another light hydrocarbon or gas such as hydrogen or carbon dioxide. Besides, most of the measurements have been made at pressures lower than 50 MPa (see Refs. 1–8, for example). However, the methane+propane system has been studied up to 55 MPa [9]. Results can also be found on the methane+decane binary, but comparisons of the results of Knapstad et al. [10] and Lee et al. [11] show differences of about 40%.

A three-year research program, supported by the European Commission, had the aim of filling this gap of data. Recently, in the framework of this program, the methane+methylcyclohexane system has been studied up to 140 MPa [12] but in a narrow composition range, near pure methane. In this work, we have chosen to study the methane+decane system, as a function of pressure, temperature, and composition for several reasons. The first is to have reliable data on this particular system, the second is fundamental in nature as the data can be used to test models for systems that are quite asymmetric (because methane and decane have two very different molecule conformations), and the last concerns mixtures containing a gas like methane, such as found in the petroleum industry.

2. EXPERIMENTAL TECHNIQUES

2.1. Apparatus

The dynamic viscosity η has been determined with the aid of a specially designed isobaric transfer falling-body viscometer, details of which are provided in Ref. 13. In this apparatus, a stainless-steel cylinder falls through a fluid of unknown viscosity under selected 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 (decane, toluene, propane, and hexane). Moreover methane has been used as calibration substance for the sample containing 95.75% (mole) of methane. We used in that case the Younglove and Ely database [14]. Each measurement of the falling time was repeated six times at thermal and mechanical equilibrium, and they are reproducible to better than 1%. The final value is an average of these measurements. Values of the density ρ for pressures between 0.1 and 65 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, have been described in Ref. 15.

The density measurements were extrapolated up to 140 MPa according to the procedure described in Ref. 16, using a Tait-like relationship for the variation of the density with pressure. The validity of this method is discussed in Refs. 16 and 17, which has been tested with values provided by Dymond [18] for pure alkanes and binary mixtures up to 500 MPa. For example, for isooctane at $T = 348.15$ K, using two parameters adjusted only with density values for pressures lower than or equal to 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 higher than our upper pressure limit of viscosity measurements. The maximum error [17] is -0.13% at 79.8 MPa. Also, in Section 3 the extrapolated values are compared with corresponding values estimated with an equation of state and the comparison shows good agreement between the values.

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 (HBM manometer) and ± 0.1 MPa for the viscosity measurements (HBM P3M manometer). The overall uncertainty in the reported density values is less than $1\ \mathrm{kg \cdot m^{-3}}$, while the uncertainty in the viscosity [13] is approximately 3% except at very low viscosities. For a viscosity of less than $0.07\ \mathrm{mPa \cdot s}$ one can consider that the absolute uncertainty is approximately $0.002\ \mathrm{mPa \cdot s}$ independent of the magnitude of the viscosity. Besides, for the composition close to pure methane (mole fraction of methane $x = 0.9575$) the accuracy is linked to the accuracy of the pure methane data used for the calibration.

2.2. Preparation of Samples and Experimental Procedures

The substances used are commercially available chemicals with the following purity levels: methane (CH_4: AGA Scientifique 5.5, Purity > 99.9995%, molar mass $M = 16.04\ \mathrm{g \cdot mol^{-1}}$) and *n*-decane ($C_{10}H_{22}$: Sigma-Aldrich, purity > 99.9%, molar mass $M = 142.28\ \mathrm{g \cdot mol^{-1}}$). The mixtures were prepared by very careful weighing (with a Mettler balance) in a high pressure reservoir cell, following the procedure described in Ref. 17, to obtain methane mole fractions $x = 0.3124$, 0.4867, 0.6000, 0.7566, and 0.9575. The samples containing 75.66, 60.00, and 31.24 mol% of methane were provided by TotalFinaElf and prepared very precisely using a mercury cell in liquid nitrogen in order to do some comparisons with literature data. The phase diagram of the methane+decane system has been given in Ref. 19, and we carried out the measurements in a monophasic dense state according to this diagram, at least 10 MPa above the saturation pressure.

The transfer of the sample from the preparation cell to the viscometer has been carried out at high pressure (40 MPa). Measurements of viscosity η and density ρ 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, from the following lowest pressure (compatible with the phase diagram): 20 MPa for $x = 0.3124$, 30 MPa for $x = 0.4867$ and 0.6000, and 40 MPa for $x = 0.7566$ and 0.9575. Measurements of density were carried out in steps of 5 MPa, up to 60 MPa from 20 MPa for $x = 0.3124$, 25 MPa for $x = 0.4867$ and 0.6000, 35 MPa for $x = 0.7566$, and 40 MPa for $x = 0.9575$. A total of 295 experimental points was measured for viscosity, and 175 experimental points for density. Finally, 200 density values were extrapolated to pressures above 60 MPa, up to 140 MPa.

3. EXPERIMENTAL RESULTS

The results are presented in Tables I to V. Figure 1 shows the surface $\eta(P, T)$ at $x = 0.7566$ of methane. The variations of η and ρ with pressure and temperature are smooth. For each composition both the viscosity and density increase with pressure and decrease with temperature. Figure 2 shows the variations of density with composition at $T = 333.15$ K for several pressures, and Fig. 3 shows the variation of viscosity at the same conditions. Since we have used the methane values of Younglove and Ely [14] (2% uncertainty in our pressure and temperature ranges), and the decane values of Oliveira and Wakeham [20] (0.5% uncertainty), for calibration of the experimental device, we show these values on Figs. 2 and 3.

Figure 4 shows comparisons at 293.15 K and 30 MPa between our values and those of Knapstad et al. [10] as a function of composition. Other comparisons can be seen in Ref. 17. The comparison has always been satisfactory in the small pressure range ($P \leqslant 40$ MPa) corresponding to Ref. 10. Moreover, at the beginning of the European project a cross-check has been made for $x = 0.6$ between our data ($T = 373.15$ K) and those measured by the Department of Petroleum Engineering at Heriot Watt University (Edinburgh/Scotland) [21] ($T = 377.55$ K), and the Institut Français du Petrole laboratory (France) [22, 23] ($T = 377.15$ K). As our temperature is 4 K lower than the other laboratories, our viscosity values should be a little higher. Consequently, we extrapolated our values up to 377.15 K, and Fig. 5 shows the comparison up to 140 MPa. The comparison is still satisfactory. It is important to mention here that for Ref. 10 the

Table I. Dynamic Viscosities and Densities of Methane (31.24 mol%) + Decane (68.76 mol%)

	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)
20	0.7004	0.638	0.6853	0.496	0.6701	0.410	0.6551	0.355	0.6427	0.298
25	0.7042		0.6896		0.6748		0.6604		0.6487	
30	0.7078	0.700	0.6936	0.544	0.6793	0.440	0.6653	0.379	0.6542	0.317
35	0.7113		0.6975		0.6835		0.6702		0.6593	
40	0.7145	0.765	0.7010	0.594	0.6874	0.475	0.6746	0.406	0.6640	0.339
45	0.7176		0.7046		0.6912		0.6787		0.6687	
50	0.7207	0.834	0.7077	0.647	0.6948	0.514	0.6825	0.436	0.6729	0.364
55	0.7236		0.7108		0.6983		0.6861		0.6769	
60	0.7265	0.907	0.7138	0.703	0.7016	0.557	0.6896	0.470	0.6807	0.392
70	0.7318	0.984	0.7194	0.762	0.7078	0.603	0.6961	0.505	0.6879	0.421
80	0.7368	1.065	0.7247	0.824	0.7136	0.652	0.7020	0.544	0.6945	0.452
90	0.7415	1.151	0.7295	0.891	0.7191	0.704	0.7075	0.584	0.7006	0.485
100	0.7459	1.241	0.7341	0.961	0.7242	0.758	0.7126	0.626	0.7062	0.519
110	0.7502	1.337	0.7384	1.035	0.7290	0.815	0.7174	0.671	0.7116	0.555
120	0.7542	1.438	0.7425	1.113	0.7336	0.873	0.7219	0.717	0.7166	0.592
130	0.7580	1.544	0.7464	1.196	0.7380	0.934	0.7262	0.764	0.7214	0.631
140	0.7617	1.657	0.7501	1.283	0.7421	0.997	0.7302	0.814	0.7259	0.670

Table II. Dynamic Viscosities and Densities of Methane (48.67 mol%) + Decane (mol 51.33%)

	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 ($mPa \cdot s$)
25	0.6648		0.6488		0.6326		0.6163		0.5992	
30	0.6691	0.470	0.6537	0.377	0.6381	0.310	0.6227	0.267	0.6065	0.232
35	0.6731		0.6582		0.6433		0.6284		0.6129	
40	0.6770	0.512	0.6625	0.412	0.6482	0.338	0.6338	0.290	0.6189	0.251
45	0.6807		0.6665		0.6527		0.6387		0.6245	
50	0.6842	0.557	0.6704	0.449	0.6569	0.367	0.6433	0.314	0.6295	0.271
55	0.6875		0.6740		0.6609		0.6477		0.6345	
60	0.6908	0.603	0.6776	0.487	0.6648	0.397	0.6518	0.338	0.6391	0.291
70	0.6969	0.653	0.6841	0.526	0.6719	0.428	0.6594	0.363	0.6475	0.311
80	0.7027	0.704	0.6903	0.566	0.6784	0.460	0.6663	0.388	0.6552	0.332
90	0.7081	0.758	0.6959	0.608	0.6845	0.492	0.6726	0.413	0.6623	0.352
100	0.7132	0.815	0.7013	0.651	0.6901	0.526	0.6785	0.439	0.6688	0.373
110	0.7180	0.874	0.7063	0.695	0.6954	0.561	0.6840	0.465	0.6749	0.394
120	0.7226	0.937	0.7111	0.740	0.7003	0.597	0.6891	0.492	0.6806	0.415
130	0.7270	1.003	0.7156	0.788	0.7050	0.634	0.6940	0.519	0.6860	0.442
140	0.7312	1.072	0.7199	0.836	0.7095	0.673	0.6985	0.547	0.6911	0.478

Table III. Dynamic Viscosities and Densities of Methane (60.00 mol%) + Decane (40.00 mol%)

	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)
30	0.6294	0.328	0.6123	0.264	0.5955	0.216	0.5784	0.194	0.5640	0.175
35	0.6343		0.6180		0.6019		0.5860		0.5723	
40	0.6389	0.357	0.6231	0.290	0.6077	0.239	0.5925	0.216	0.5796	0.194
45	0.6431		0.6280		0.6129		0.5984		0.5863	
50	0.6472	0.387	0.6325	0.317	0.6179	0.263	0.6039	0.237	0.5924	0.212
55	0.6511		0.6367		0.6226		0.6090		0.5980	
60	0.6547	0.417	0.6407	0.343	0.6271	0.286	0.6138	0.257	0.6033	0.230
70	0.6616	0.449	0.6481	0.371	0.6352	0.310	0.6223	0.277	0.6128	0.248
80	0.6679	0.481	0.6549	0.399	0.6426	0.333	0.6299	0.296	0.6213	0.265
90	0.6737	0.514	0.6610	0.427	0.6494	0.357	0.6368	0.315	0.6290	0.282
100	0.6792	0.549	0.6668	0.456	0.6557	0.381	0.6431	0.333	0.6360	0.300
110	0.6843	0.584	0.6721	0.485	0.6615	0.404	0.6490	0.352	0.6425	0.317
120	0.6891	0.621	0.6771	0.515	0.6670	0.428	0.6544	0.371	0.6486	0.334
130	0.6937	0.658	0.6819	0.545	0.6722	0.452	0.6595	0.390	0.6543	0.351
140	0.6980	0.697	0.6863	0.576	0.6771	0.476	0.6643	0.410	0.6597	0.368

Table IV. Dynamic Viscosities and Densities of Methane (75.66 mol%) + Decane (24.33 mol%)

	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	0.5640		0.5446		0.5253		0.5067		0.4905	
40	0.5705	0.201	0.5524	0.167	0.5342	0.143	0.5167	0.128	0.5014	0.107
45	0.5762		0.5594		0.5420		0.5254		0.5111	
50	0.5815	0.227	0.5655	0.187	0.5489	0.160	0.5330	0.144	0.5195	0.121
55	0.5863		0.5712		0.5552		0.5398		0.5269	
60	0.5909	0.252	0.5764	0.207	0.5611	0.177	0.5461	0.159	0.5334	0.135
70	0.5987	0.276	0.5858	0.226	0.5714	0.193	0.5571	0.174	0.5455	0.149
80	0.6057	0.300	0.5940	0.246	0.5805	0.209	0.5667	0.189	0.5559	0.163
90	0.6120	0.323	0.6014	0.265	0.5886	0.224	0.5753	0.203	0.5651	0.177
100	0.6177	0.346	0.6082	0.284	0.5959	0.240	0.5830	0.218	0.5734	0.191
110	0.6230	0.369	0.6143	0.302	0.6027	0.256	0.5901	0.232	0.5809	0.205
120	0.6278	0.391	0.6200	0.321	0.6089	0.271	0.5966	0.247	0.5879	0.219
130	0.6324	0.413	0.6254	0.339	0.6147	0.287	0.6027	0.261	0.5945	0.233
140	0.6366	0.435	0.6304	0.368	0.6201	0.302	0.6083	0.275	0.6006	0.248

Table V. Dynamic Viscosities and Densities of Methane (95.75 mol%) + Decane (4.25 mol%)

	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)
40	0.3273	0.041	0.3078	0.037	0.2894	0.035	0.2738	0.032	0.2590	0.030
45	0.3401		0.3210		0.3033		0.2884		0.2739	
50	0.3515	0.046	0.3327	0.042	0.3155	0.040	0.3012	0.038	0.2870	0.035
55	0.3617		0.3433		0.3266		0.3127		0.2986	
60	0.3710	0.051	0.3529	0.047	0.3377	0.045	0.3230	0.042	0.3092	0.040
70	0.3878	0.056	0.3702	0.052	0.3545	0.049	0.3418	0.047	0.3283	0.045
80	0.4028	0.060	0.3854	0.056	0.3704	0.054	0.3586	0.051	0.3454	0.049
90	0.4164	0.065	0.3993	0.061	0.3849	0.058	0.3739	0.055	0.3612	0.053
100	0.4289	0.069	0.4122	0.065	0.3983	0.062	0.3882	0.059	0.3758	0.057
110	0.4406	0.074	0.4242	0.069	0.4109	0.066	0.4016	0.063	0.3897	0.060
120	0.4516	0.078	0.4355	0.073	0.4228	0.070	0.4144	0.067	0.4029	0.064
130	0.4621	0.082	0.4463	0.077	0.4342	0.074	0.4266	0.070	0.4156	0.067
140	0.4721	0.087	0.4566	0.081	0.4451	0.078	0.4384	0.074	0.4279	0.071

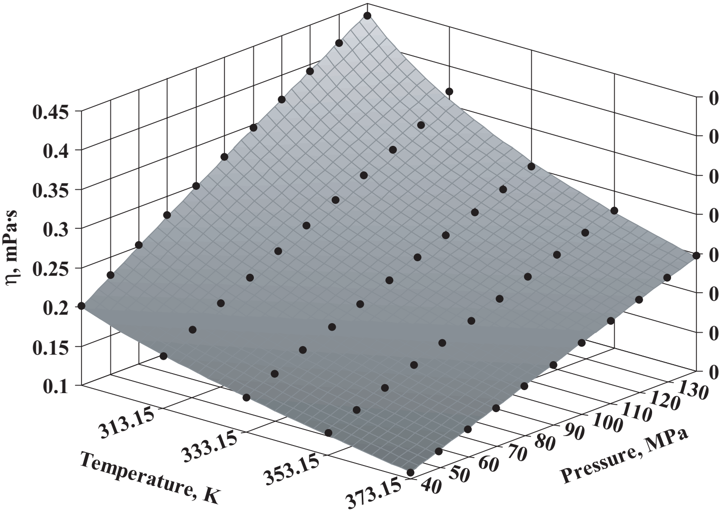


Fig. 1. Surface $\eta(P, T)$ at $x_{\text{Methane}} = 0.7566$.

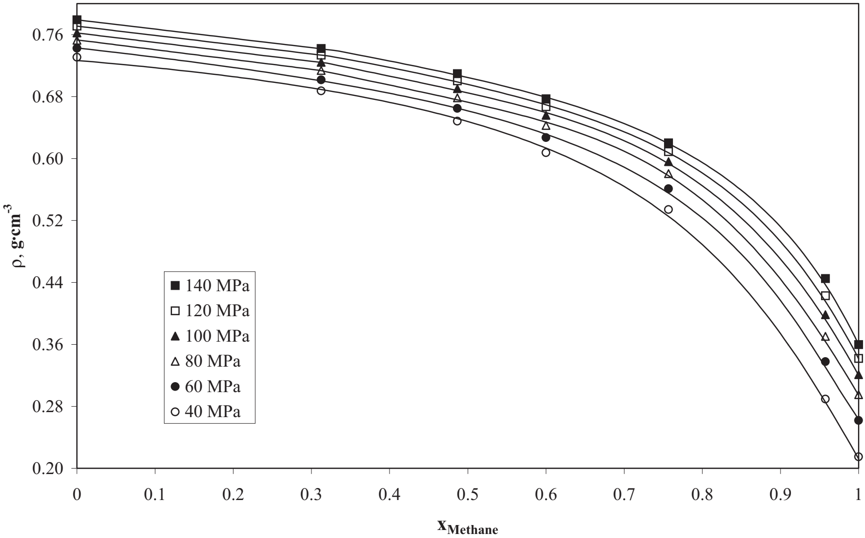


Fig. 2. Variations of density with composition at $T = 333.15$ K for several pressures. Pure methane data are taken from Ref. 14 and pure decane data from Ref. 20, possibly interpolated.

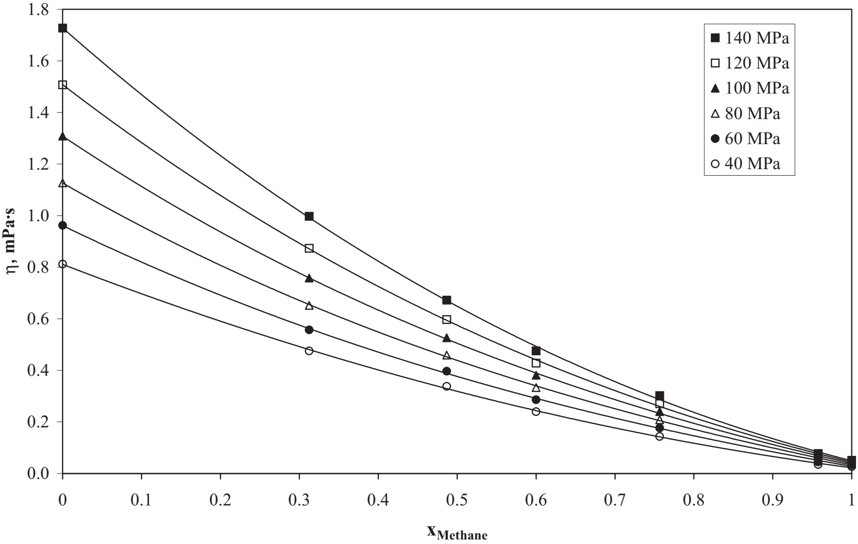


Fig. 3. Variations of viscosity with composition at $T = 333.15$ K for several pressures. Pure methane data are taken from Ref. 14 and pure decane data from Ref. 20, possibly interpolated.

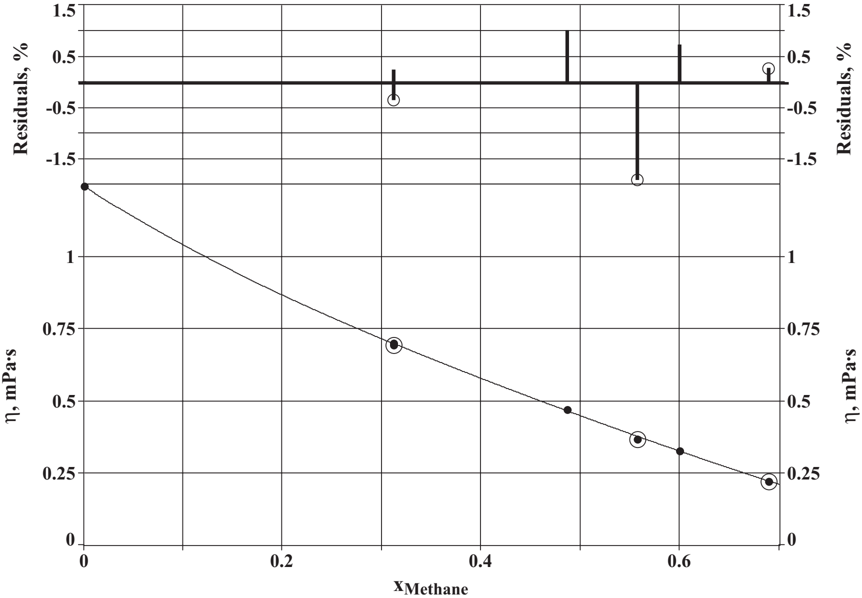


Fig. 4. Variations of viscosity with composition at $T = 293.15$ K and $P = 30$ MPa. Comparison between our values (●) and those of Knapstad et al. [10] (⊙).

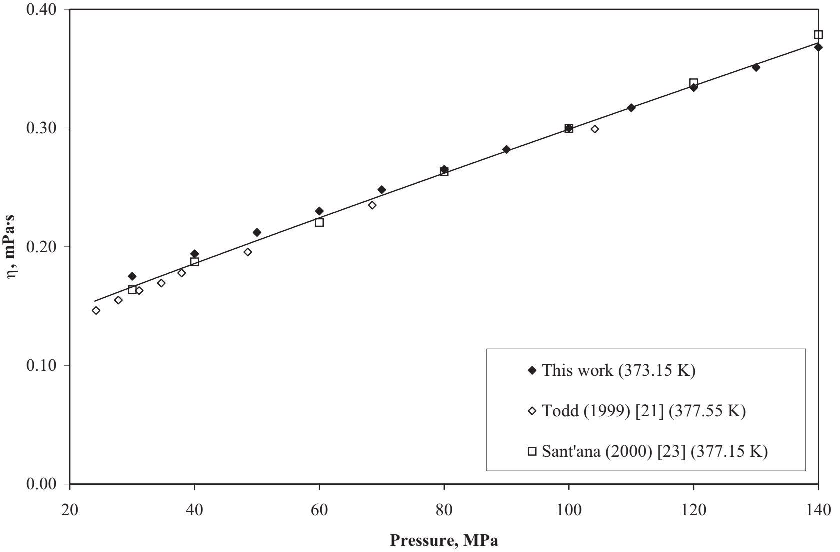


Fig. 5. Variations of viscosity with pressure for $x_{\text{Methane}} = 0.6$ near $T = 373.15$ K. Comparison between our values, Heriot Watt University values [21], and those of Institut Français du Petrole [22, 23].

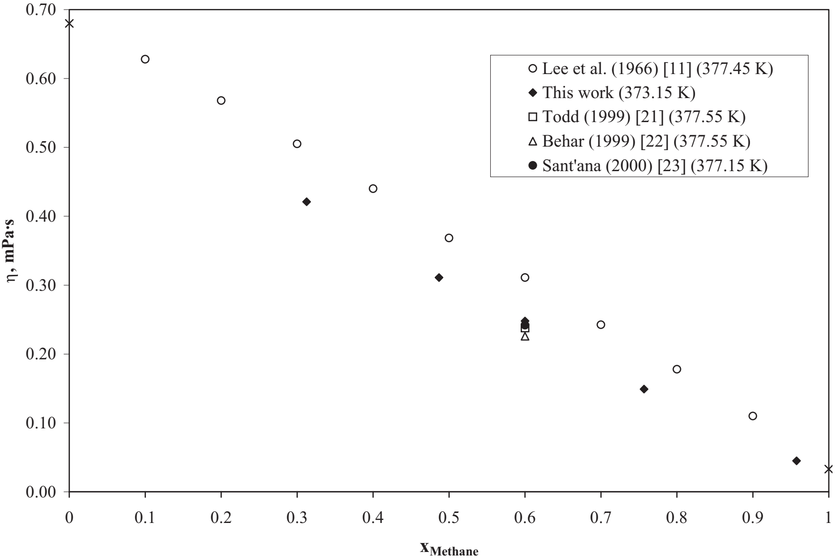
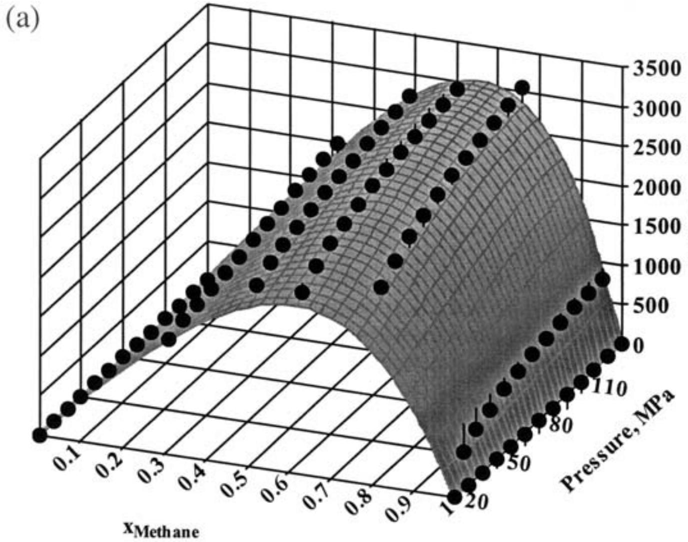


Fig. 6. Variations of viscosity with composition x_{Methane} near $T = 373.15$ K at $P = 70$ MPa. Comparison between our values and the Lee et al. values [11]. Pure methane data are taken from Ref. 14 and pure decane data from Ref. 20, possibly interpolated.



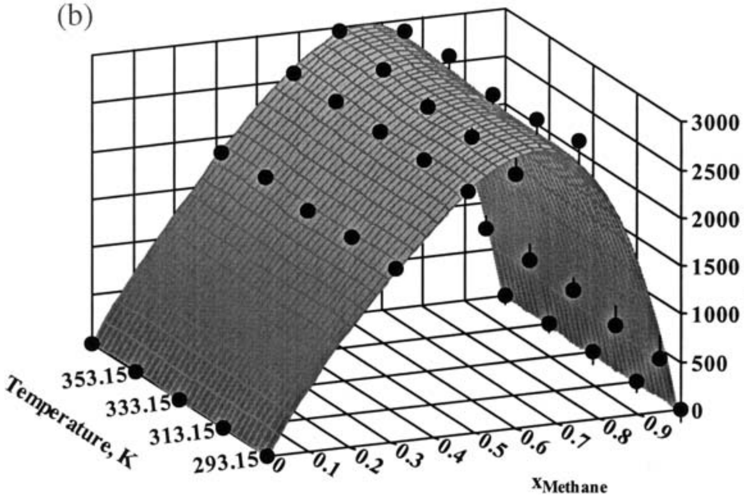


Fig. 7. (a) Variations of ΔG^E with composition and pressure at $T = 333.15$ K. (b) Variations of ΔG^E with composition and temperature at $P = 100$ MPa.

authors used an oscillation vessel viscometer (1% uncertainty at 293.15 K for pure decane to 4% uncertainty at 423.15 K for the mixture with the maximum content of methane $x=0.847$). For Refs. 21 to 23 they used a capillary viscometer (2% uncertainty). Finally, Fig. 6 shows, at 70 MPa and $T \approx 377$ K, comparisons between the new results and Lee et al. values [11]. Data for $x=0$ and $x=1$ can be found in Refs. 14 and 20. It seems that there has been an overestimation of the viscosity of this binary as has already been noted by Knapstad et al. [10] at lower pressures.

The experimental density values have been compared with those generated by the Lee and Kesler [24] equation of state using the coefficients recommended by Muñoz and Ricardo [25], and using the mixing rules proposed by either Spencer and Danner [26] or by Joffe [27] for the mixtures. The average absolute deviation between our results (including the extrapolated values with the Tait-like equation) and the calculated values from the equation of state is for both cases very close, about 3.3%, with a maximum deviation of 19.5% using the first mixing rule (in some sense, this result invalidates this mixing rule, at least, for this binary system) and 7.3% with the second one (both at $x=0.9575$). The influence on the dynamic viscosity (calculating the viscosity with the experimental falling times and the calculated densities) is less than 1%.

Finally, from the experimental values of viscosity it is possible to evaluate simply the excess activation energy of viscous flow ΔG^E defined as $\ln(\eta V) = x\ \ln(\eta_{C1} V_{C1}) + (1-x)\ln(\eta_{C10} V_{C10}) + \Delta G^E/(RT)$ where R is the universal gas constant, x is the mole fraction of methane, and $V = M/\rho$ is the molar volume (for the mixture the molar mass is $M = xM_{C1} + (1-x)\,M_{C10}$). This well known relationship is theoretically justified by Eyring's representation of the dynamic viscosity of a fluid. Figure 7(a) shows variations of ΔG^E with mole fraction x and pressure P at $T=333.15$ K, and Fig. 7(b) shows ΔG^E at $P=100$ MPa versus x and temperature. The values of ΔG^E at the maxima are important, and their positive values correspond to attractive interactions. The interested reader can find examples of variations of ΔG^E with pressure, temperature, and composition for the very associative systems water + diacetone alcohol and water + 2-propanol in Refs. 28 and 29. 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 $\mathrm{J \cdot mol^{-1}}$, like in the case of the methane + decane mixture.

4. VISCOSITY MODELING

Taking into account the behavior of ΔG^E which seems to indicate attractive interactions, this system is consequently nonideal. Therefore, this system appears to be a good test system to evaluate the predictive performances of various representative models. In the following, two models with different semiempirical basis (mixing rules, self-referencing method) will be considered. In the equations below, η_{exp} is the experimental value of viscosity and η_{cal} is the value calculated using the considered model. For the entire set of data considered, we define the following quantities:

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

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

These quantities are expressed as percentages. For all the points considered we define the three following characteristic quantities:

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

$$\text{Maximum deviation} = \text{MxD} = \text{MAX(Absolute deviation(i))}$$

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

Finally MxD characterizes the maximum deviation produced by the model.

4.1. Mixing Rules

In a study of predictive models for mixtures it is essential to consider the use of various mixing rules. There are many such rules, and it is not the purpose of this study to do an extensive survey of them. We will focus only on two very well known and widely used without any adjustable parameters so that they can be considered as predictive. For pure methane and decane we have used in the following equations the methane values of Younglove and Ely [14] (2% uncertainty for viscosity in our pressure and temperature ranges), and the decane values of Oliveira and Wakeham [20] (0.5% uncertainty for viscosity), possibly interpolated. The first mixing rule has been proposed by Grunberg and Nissan (GN) [30]:

$$\ln(\eta) = x \ln(\eta_{C1}) + (1 - x) \ln(\eta_{C10}) \tag{1}$$

We obtained for the mixture AAD = 45.6% , Bias = 45.6%, and MxD = 64.9% (at $x = 0.7566$). The second mixing rule has been proposed by Katti and Chaudhri (KC) [31]:

$$\ln(\eta V) = x \ln(\eta_{C1} V_{C1}) + (1 - x) \ln(\eta_{C10} V_{C10}) \tag{2}$$

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 = 49.8%, Bias = 49.8%, and MxD = 71.9% (at $x = 0.7566$).

These results are not acceptable because this system is not an ideal one and the GN and KC rules do not take into account the interactions in the system. In many cases adjustable parameters are then introduced but the mixing rules lose their predictive feature.

4.2. The Self-Referencing Method

The self-referencing model [32] has been developed in our laboratory in order to model the viscous behavior of petroleum cuts where their complex composition is difficult to handle. For this kind of fluids, it is difficult to use equations based on physical properties such as molar mass, critical parameters or acentric factor since, for a mixture, they have to be known for each of the components. The formulation has the advantage of only requiring one experimental determination at one pressure P_0 and one temperature T_0. This is the reason why this method is referred to as a self-referencing model. The method involves neither molar mass nor any other physical properties (including critical parameters). It can similarly be applied without restriction to pure substances, synthetic mixtures and even chemically very rich systems such as petroleum cuts for which the method was originally developed. The method involves nine coefficients ($a, b, \ldots, i$) 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 that it is general and predictive. The formulation of this method is as follows:

$$\ln\left(\frac{\eta(P,T)}{\eta(P_0,T_0)}\right) = (ay^2+by+c)\ln\left(1+\frac{(P-P_0)}{dy^2+ey+f}\right) + (gy_0^2+hy_0+i)\left(\frac{1}{T}-\frac{1}{T_0}\right) \tag{3}$$

where $y = y_0 + (gy_0^2+hy_0+i)(1/T - 1/T_0)$ and $y_0 = \ln[\eta(P_0, T_0)]$. In this equation P is in MPa, T_0 and T in K, and $\eta(P_0, T_0)$ in mPa·s. We have 295 experimental data for viscosity, from which we take one reference point for each composition, i.e., the viscosity value at the lower pressure and at the reference temperature $T_0 = 293.15$ K. Therefore, we have 290 points in total for viscosity calculation.

First, we applied the model using the coefficients adjusted by Kanti et al. [32] on linear alkanes and alkylbenzenes. The overall results on all the 290 data (the five reference points are excluded for the calculation of AAD), are AAD = 35.2%, Bias = −35.2%, and MxD = 235% (at $x = 0.9575$), which are unacceptable results. This is probably due to the fact that in the database of Kanti et al. [32] the alkanes have carbon numbers greater or equal to seven which are consequently very different from methane.

Second, we modified this self-referencing method. In the pressure-temperature range considered, we have fitted [17] the nine parameters $a, b,..., i$ for each pure compound separately. For pure methane AAD = 0.38%, Bias = 0.34%, and MxD = 4.38%, and for pure decane, AAD = 0.23%, Bias = −0.02%, and MxD = 1.08%. Then, for each composition we used $\alpha_m = x\alpha_{C1} + (1-x)\,\alpha_{C10}$ ($\alpha = a,b,..., i$). For the mixture we have obtained AAD = 3.77%, Bias = −2.80%, and MxD = 15.4% (at $x = 0.7566$), which is a satisfactory result for such a predictive method. This clearly shows, as suggested in the original article, the use of a reference measurement point is important as this measurement contains and provides useful information on the system studied.

5. CONCLUSION

The methane+decane system is interesting because the molecules of the two pure compounds are very different and the system is asymmetrical. This study provides data in an extended (P, T) range for various mole fractions. The measured data for this system may prove very useful to improve the predictive nature of more sophisticated models than the ones considered here and also in an understanding of such a complicated property as the dynamic viscosity of mixtures (and pure compounds).

ACKNOWLEDGMENTS

This work has been accomplished within the European project EVIDENT under the JOULE Program, Contract No. JOF3-CT97-0034. The research Center of TotalFinaElf Company in Pau is thanked for its technical assistance during the careful preparation of some of the samples.

REFERENCES

1. S. Y. Chuang, P. S. Chappelear, and R. Kobayashi, *J. Chem. Eng. Data* **21**:403 (1976).
2. J. Kestin, S. T. Ro, and W. A. Wakeham, *Phys. A* **119**:615 (1983).
3. D. E. Diller, *Int. J. Thermophys.* **3**:237 (1982).
4. D. E. Diller, *J. Chem. Eng. Data* **29**:215 (1984).

5. J. P. Dolan, R. T. Ellington, and A. L. Lee, *J. Chem. Eng. Data* **9**:484 (1964).
6. L. T. Carmichael, V. M. Berry, and B. H. Sage, *J. Chem. Eng. Data* **12**:44 (1967).
7. J. Kestin and J. Yata, *J. Chem. Phys.* **49**:4780 (1968).
8. E. T. S. Huang, F. W. Swift, and F. Kurata, *AIChE J.* **13**:846 (1966).
9. J. G. Giddings, J. T. F. Kao, and R. Kobayashi, *J. Chem. Phys.* **45**:578 (1966).
10. B. Knapstad, P. A. Skjolsvik, and H. A. Oye, *Ber. Bunseng. Phys. Chem.* **94**:1156 (1990).
11. M. J. Lee, M. H. Gonzalez, and B. E. Eakin, *J. Chem. Eng. Data* **11**:281 (1966).
12. B. Tohidi, R. W. Burgass, A. Danesh, and A. C. Todd, *J. Chem. Eng. Data* **46**:385 (2001).
13. P. Daugé, A. Baylaucq, L. Marlin, and C. Boned, *J. Chem. Eng. Data* **46**:823 (2001).
14. B. A. Younglove and J. F. Ely, *J. Phys. Chem. Ref. Data* **16**:577 (1987).
15. B. Lagourette, C. Boned, H. Saint-Guirons, P. Xans, and H. Zhou, *Measure. Sci. Technol.* **3**:699 (1992).
16. A. Et-Tahir, C. Boned, B. Lagourette, and P. Xans, *Int. J. Thermophys.* **6**:1309 (1995).
17. X. Canet, *Thése de Doctorat* (Université de Pau, France, 2001).
18. J. H. Dymond, J. Robertson, and J. D. Isdale, *J. Chem. Thermodyn.* **14**:51 (1982).
19. B. H Sage and V. M. Berry, in *Phase Equilibria in Hydrocarbon Systems Behavior of the Methane-Propane-n-Decane System*, Monograph on API Research Project 37, edited by American Petroleum Institute (1971).
20. C. M. B. P. Oliveira and W. A. Wakeham, *Int. J. Thermophys.* **13**:773 (1992).
21. A. Todd, private communication (Department of Petroleum Engineering at Heriot Watt University, Edinburgh, Scotland, 1999), European project, Contract N° JOF3-CT97-0034, Internal report.
22. E. Behar, private communication (Institut Français du Pétrole, Rueil-Malmaison, France, 1999), European project, Contract N° JOF3-CT97-0034, Internal report.
23. H. B. de Sant'ana, *Thése de Doctorat* (Université de Clermont-Ferrand et Institut Français du Petrole, France, 2000).
24. B. I. Lee and M.G. Kesler, *AIChE J.* **21**:510 (1975).
25. F. Muñoz and R. Ricardo, *Fluid Phase Equil.* **13**:171 (1983).
26. C. F. Spencer and R. P. Danner, *J. Chem. Eng. Data* **17**:236 (1972).
27. J. Joffe, *Ind. Eng. Chem.* **39**:837 (1947).
28. C. Boned, M. Moha-Ouchane, A. Allal, and M. Benseddik, *Int. J. Thermophys.* **19**:1325 (1998).
29. M. Moha-Ouchane, C. Boned, A. Allal, and M. Benseddik, *Int. J. Thermophys.* **19**:161 (1998).
30. L. Grunberg and A. H. Nissan, *Nature* **164**:799 (1949).
31. P. K. Katti and M. M. Chaudhri, *J. Chem. Eng. Data* **9**:442 (1964).
32. M. Kanti, H. Zhou, S. Ye, C. Boned, B. Lagourette, H. Saint-Guirons, P. Xans, and F. Montel, *J. Phys. Chem.* **93**:3860 (1989).