International Journal of Thermophysics, Vol. 22, No. 6, November 2001 (© 2001)

Density and Viscosity of the 1-Methylnaphthalene + 2,2,4,4,6,8,8-Heptamethylnonane System from 293.15 to 353.15 K at Pressures up to 100 MPa

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Received November 15, 2000

The dynamic viscosity η of the binary mixture 1-methylnaphthalene + 2,2,4,4,6,8,8-heptamethylnonane was measured in the temperature range 293.15 to 353.15 K (in progressive 10 K steps) at pressures of 0.1, 20, 40, 60, 80, and 100 MPa. The composition of the system is described by nine molar fractions (0 to 1 in 0.125 progressive steps). The density ρ was measured at pressures from 0.1 to 60 MPa in progressive 5 MPa steps. The measurements of η are used to determine the excess viscosity η^{E} and the excess activation energy of flow ΔG^{E} as a function of pressure, temperature, and composition. Some models have been used to represent the viscosity of this binary mixture.

KEY WORDS: 1-methylnaphtalene; 2,2,4,4,6,8,8-heptamethylnonane; binary mixture; density; excess activation energy of flow; excess viscosity; high pressure; viscosity.

1. INTRODUCTION

In relation to the petroleum industry (TotalFinaElf), our laboratory decided, some years ago, to study the dynamic viscosity and density of synthetic mixtures to simulate a heavy distillation fraction. For this purpose, the laboratory decided to carried out a comprehensive study concerning several such binaries with various chemical compounds for which the boiling temperature

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at atmospheric pressure is close to 510 K. The binary systems tridecane+1-methylnaphthalene [1] and tridecane+2,2,4,4,6,8,8-heptamethylnonane [2] (boiling temperature at atmospheric pressure: 507.1 K for tridecane, 514.7 K for 1-methylnaphthalene, and 513.1 K for 2,2,4,4,6,8,8-heptamethylnonane) have already been studied. To complete the measurements, the binary system 1-methylnaphthalene+2,2,4,4,6,8,8-heptamethylnonane has been studied. We conducted experimental determinations on these two pure substances and on the associated binary mixtures with the aim of providing data that can be used to develop (with similar data obtained on other systems) representative models for the viscosity of petroleum distillation fractions.

A quantity that is often required to determine, as well as to model, the dynamic viscosity is the density. We, therefore, also present the values of density measured for the binary system.

2. EXPERIMENTAL

The viscosity is determined between 0.1 and 100 MPa with the aid of a falling body viscometer, technical details of which are provided in Ref. 3. Values of density have been measured between 0.1 and 60 MPa with an Anton–Paar DMA 60 vibrating tube densimeter with an additional 512-P high-pressure cell. The values are extrapolated up to 100 MPa with a Tait-like equation according to the procedure described in Ref. 3. The uncertainty in temperature T is estimated as ± 0.5 K for the measurement of η and ± 0.05 K for the measurements of ρ. The uncertainty in pressure P is estimated to be ± 0.1 MPa for the measurements of η and ± 0.05 MPa for the measurements of ρ (except at $P = 0.1$ MPa). The uncertainty in ρ is less than $1\ \mathrm{kg \cdot m^{-3}}$. The relative uncertainty in η is of the order of 2%. As discussed in previous papers [3, 4], this error is comparable to that estimated by other authors for similar experimental systems. At atmospheric pressure the kinematic viscosity η/ρ has been determined with a classical capillary viscometer. For this purpose, several KPG tubes, connected to an automatic Schott Geräte analyzer, were used. In this case, during the measurement, the uncertainty of the temperature is ± 0.01 K. After multiplying by ρ, the dynamic viscosity η is obtained with an uncertainty of less than 1%.

The two substances used are commercially available chemicals with the following purity levels: 1-methylnaphthalene ($C_{11}H_{10}$; Aldrich; purity, 98%; molar mass $M = 142.201\ \mathrm{g \cdot mol^{-1}}$) and 2,2,4,4,6,8,8-heptamethylnonane ($C_{16}H_{34}$; Aldrich; purity, >98%; molar mass $M = 226.44\ \mathrm{g \cdot mol^{-1}}$). The mixtures were prepared by weighing at atmospheric pressure and room temperature so as to obtain the molar fractions $x_i = 0.125, 0.250, 0.375, 0.500, 0.625, 0.750$, and 0.875. The samples were studied immediately after being prepared to prevent water absorption from the ambient air. The pure fluids were stored in hermetically sealed bottles. The samples were in the liquid state over the range of the experimental temperatures and pressures.

3. RESULTS

Measurements of η and ρ were carried out from 293.15 to 353.15 K in steps of 10 K. Measurements of viscosity η were made at 0.1, 20, 40, 60, 80, and 100 MPa. A total of 378 experimental points was obtained for η, 84 for the two pure substances and 294 for the binary mixtures ($x_i \neq 0$ and 1). Measurements of density ρ were carried out at pressures from 0.1 up to 60 MPa in 5 MPa steps. There are 819 experimental values for ρ, 182 for the two pure substances and 637 for the binary mixtures ($x_i \neq 0$ and 1). Moreover, values of ρ at 80 and 100 MPa have been evaluated by extrapolation with the aid of the well-known Tait-type equation [3]. Table I presents the values obtained as a function of P and T, with the composition expressed as a mole fraction.

Figure 1 shows the variations of the viscosity $\eta(P, T)$ of 1-methylnaphthalene and Fig. 2 shows the variations of the viscosity $\eta(P, T)$ of 2,2,4,4,6,8,8-heptamethylnonane. Figure 3 shows a comparison between our data and previous measurements [3,5] found in the literature, at $T = 353.15\ K$, using the equation $\eta(P) = (a + bP + cP^2 + dP^3)^{-1}$ for 2,2,4,4,6,8,8-heptamethylnonane. It is important to point out that several functions give similar results. Figures 4 and 5 show results for the binary system and present the variations of $\eta(T, x)$ at $P = 20$ MPa and the variations of $\eta(P, x)$ at $T = 323.15$ K. Similar curves can be obtained for other pressures and temperatures. An examination of the curves reveals a nonmonotonic behavior with respect to the composition, which might be the effect of repulsive interactions. Very few studies can be found in the literature about the influence of pressure on such behavior (with minima or maxima) of the viscosity except for an observation made by Zhang et al. [6] on the binary system benzene+cyclohexane. Figure 6 presents the variations of $\rho(P)$ for the equimolar binary mixture at the temperatures 293.15, 313.15, 333.15, and 353.15 K. The shape is consistent with the logarithmic relation proposed by Tait to model the influence of pressure on $1/\rho$; this logarithmic form is the one used for the extrapolation [3]. Finally, it should be noted that the variations of ρ with T are practically linear.

4. DISCUSSION

The excess viscosity η^{E} is often introduced, but several definitions of this quantity can be found. We chose a very simple one: $\eta^{\mathrm{E}} = \eta - x_1\eta_1 - x_2\eta_2$,

Table I. Viscosity and Density of the Binary System 1-Methylnaphthalene (Mole Fraction x_M) + 2,2,4,4,6,8,8-Heptamethylnonane (Uncertainty in Density, $< 1\ \mathrm{kg \cdot m^{-3}}$; Relative Uncertainty in viscosity, $\Delta\eta/\eta = 2\%$)

T (K)	P (MPa)	ρ ($\mathrm{g \cdot cm^{-3}}$)	η ($\mathrm{mPa \cdot s}$)	ρ ($\mathrm{g \cdot cm^{-3}}$)	η ($\mathrm{mPa \cdot s}$)	ρ ($\mathrm{g \cdot cm^{-3}}$)	η ($\mathrm{mPa \cdot s}$)
		$x_M = 0$		$x_M = 0.125$		$x_M = 0.250$	
293.15	0.1	0.784	3.64	0.799	3.46	0.817	3.24
293.15	5	0.788		0.803		0.820	
293.15	10	0.791		0.806		0.823	
293.15	15	0.794		0.809		0.826	
293.15	20	0.797	5.36	0.812	4.96	0.829	4.54
293.15	25	0.800		0.815		0.832	
293.15	30	0.803		0.818		0.835	
293.15	35	0.806		0.820		0.837	
293.15	40	0.808	7.62	0.823	7.02	0.840	6.23
293.15	45	0.811		0.825		0.842	
293.15	50	0.813		0.828		0.845	
293.15	55	0.816		0.830		0.847	
293.15	60	0.818	10.83	0.832	9.67	0.849	8.48
293.15	80	0.826[a]	15.61	0.841[a]	13.48	0.858[a]	11.43
293.15	100	0.834[a]	22.63	0.848[a]	18.99	0.865[a]	15.90
303.15	0.1	0.778	2.92	0.793	2.75	0.810	2.61
303.15	5	0.781		0.796		0.813	
303.15	10	0.785		0.800		0.817	
303.15	15	0.788		0.803		0.820	
303.15	20	0.791	4.20	0.806	3.97	0.823	3.63
303.15	25	0.794		0.809		0.826	
303.15	30	0.797		0.812		0.829	
303.15	35	0.800		0.815		0.831	
303.15	40	0.803	5.90	0.817	5.50	0.834	4.97
303.15	45	0.805		0.820		0.837	
303.15	50	0.808		0.822		0.839	
303.15	55	0.810		0.825		0.841	
303.15	60	0.813	8.10	0.827	7.58	0.844	6.77
303.15	80	0.821[a]	11.16	0.836[a]	10.37	0.852[a]	9.14
303.15	100	0.829[a]	15.42	0.844[a]	13.89	0.860[a]	12.05
313.15	0.1	0.771	2.43	0.786	2.29	0.803	2.14
313.15	5	0.775		0.790		0.807	
313.15	10	0.778		0.793		0.810	
313.15	15	0.782		0.797		0.813	
313.15	20	0.785	3.47	0.800	3.24	0.817	2.97
313.15	25	0.788		0.803		0.820	
313.15	30	0.791		0.806		0.823	
313.15	35	0.794		0.809		0.825	
313.15	40	0.797	4.71	0.812	4.39	0.828	3.98
313.15	45	0.800		0.814		0.831	
313.15	50	0.802		0.817		0.833	
313.15	55	0.805		0.819		0.836	
313.15	60	0.807	6.42	0.822	5.86	0.838	5.23

Table I. *(Continued)*

T (K)	P (MPa)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
313.15	80	0.816[a]	8.67	0.831[a]	7.70	0.847[a]	6.73
313.15	100	0.824[a]	11.59	0.839[a]	10.00	0.856[a]	8.54
323.15	0.1	0.764	2.01	0.779	1.86	0.796	1.76
323.15	5	0.768		0.783		0.800	
323.15	10	0.772		0.787		0.804	
323.15	15	0.775		0.790		0.807	
323.15	20	0.779	2.89	0.794	2.62	0.810	2.40
323.15	25	0.782		0.797		0.814	
323.15	30	0.785		0.800		0.817	
323.15	35	0.788		0.803		0.820	
323.15	40	0.791	3.86	0.806	3.53	0.823	3.18
323.15	45	0.794		0.809		0.825	
323.15	50	0.797		0.811		0.828	
323.15	55	0.799		0.814		0.830	
323.15	60	0.802[a]	5.15	0.816[a]	4.69	0.833[a]	4.15
323.15	80	0.811[a]	6.85	0.825[a]	6.15	0.842[a]	5.34
323.15	100	0.819	9.12	0.834	7.97	0.850	6.78
333.15	0.1	0.757	1.69	0.772	1.57	0.789	1.48
333.15	5	0.761		0.776		0.793	
333.15	10	0.765		0.780		0.797	
333.15	15	0.769		0.784		0.801	
333.15	20	0.773	2.37	0.788	2.18	0.804	2.04
333.15	25	0.776		0.791		0.808	
333.15	30	0.780		0.794		0.811	
333.15	35	0.783		0.797		0.814	
333.15	40	0.786	3.18	0.800	2.89	0.817	2.66
333.15	45	0.789		0.803		0.820	
333.15	50	0.791		0.806		0.822	
333.15	55	0.794		0.809		0.825	
333.15	60	0.797	4.19	0.811	3.78	0.828	3.45
333.15	80	0.806[a]	5.46	0.821[a]	4.89	0.837[a]	4.45
333.15	100	0.815[a]	7.19	0.829[a]	6.29	0.845[a]	5.70
343.15	0.1	0.751	1.44	0.766	1.34	0.783	1.30
343.15	5	0.755		0.770		0.787	
343.15	10	0.759		0.774		0.791	
343.15	15	0.763		0.778		0.795	
343.15	20	0.767	2.00	0.782	1.88	0.798	1.78
343.15	25	0.771		0.785		0.802	
343.15	30	0.774		0.789		0.805	
343.15	35	0.777		0.792		0.808	
343.15	40	0.781	2.67	0.795	2.47	0.811	2.31
343.15	45	0.784		0.798		0.814	
343.15	50	0.786		0.801		0.817	
343.15	55	0.789		0.803		0.820	
343.15	60	0.792	3.50	0.806	3.21	0.822	2.95
343.15	80	0.802[a]	4.50	0.816[a]	4.13	0.832[a]	3.73
343.15	100	0.810[a]	5.77	0.825[a]	5.25	0.841[a]	4.66

Table I. *(Continued)*

T (K)	P (MPa)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
353.15	0.1	0.744	1.24	0.759	1.17	0.776	1.10
353.15	5	0.749		0.763		0.780	
353.15	10	0.753		0.768		0.784	
353.15	15	0.757		0.772		0.788	
353.15	20	0.761	1.72	0.776	1.58	0.792	1.50
353.15	25	0.765		0.779		0.796	
353.15	30	0.768		0.783		0.799	
353.15	35	0.772		0.786		0.803	
353.15	40	0.775	4.50	0.790	2.06	0.806	1.93
353.15	45	0.778		0.793		0.809	
353.15	50	0.781		0.796		0.812	
353.15	55	0.784		0.798		0.814	
353.15	60	0.787	5.77	0.801	2.64	0.817	2.46
353.15	80	0.797[a]	3.79	0.811[a]	3.40	0.827[a]	3.06
353.15	100	0.806[a]	4.87	0.820[a]	4.21	0.836[a]	3.75
		$x_M = 0.375$		$x_M = 0.500$		$x_M = 0.625$	
293.15	0.1	0.837	3.09	0.860	2.97	0.888	2.88
293.15	5	0.840		0.863		0.891	
293.15	10	0.843		0.866		0.894	
293.15	15	0.846		0.869		0.897	
293.15	20	0.849	4.22	0.872	4.04	0.900	3.91
293.15	25	0.851		0.875		0.902	
293.15	30	0.854		0.877		0.905	
293.15	35	0.857		0.880		0.907	
293.15	40	0.859	5.68	0.882	5.39	0.910	5.14
293.15	45	0.862		0.885		0.912	
293.15	50	0.864		0.887		0.914	
293.15	55	0.866		0.889		0.917	
293.15	60	0.869	7.64	0.891	7.06	0.919	6.57
293.15	80	0.877[a]	10.24	0.900[a]	9.33	0.927[a]	8.46
293.15	100	0.885[a]	13.64	0.907[a]	12.09	0.935[a]	10.75
303.15	0.1	0.830	2.47	0.853	2.38	0.881	2.32
303.15	5	0.833		0.856		0.884	
303.15	10	0.836		0.860		0.887	
303.15	15	0.839		0.863		0.890	
303.15	20	0.842	3.37	0.865	3.23	0.893	3.03
303.15	25	0.845		0.868		0.896	
303.15	30	0.848		0.871		0.899	
303.15	35	0.851		0.874		0.901	
303.15	40	0.853	4.51	0.876	4.24	0.904	3.92
303.15	45	0.856		0.879		0.906	
303.15	50	0.858		0.881		0.908	
303.15	55	0.861		0.884		0.911	
303.15	60	0.863	6.00	0.886	5.53	0.913	5.03
303.15	80	0.872[a]	7.89	0.894[a]	7.13	0.922[a]	6.30
303.15	100	0.880[a]	10.31	0.902[a]	9.10	0.929[a]	8.11

Table I. *(Continued)*

T (K)	P (MPa)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
313.15	0.1	0.823	2.02	0.846	1.95	0.874	1.90
313.15	5	0.826		0.850		0.877	
313.15	10	0.830		0.853		0.881	
313.15	15	0.833		0.856		0.884	
313.15	20	0.836	2.81	0.859	2.62	0.887	2.54
313.15	25	0.839		0.862		0.890	
313.15	30	0.842		0.865		0.892	
313.15	35	0.845		0.868		0.895	
313.15	40	0.848	3.70	0.870	3.39	0.898	3.20
313.15	45	0.850		0.873		0.900	
313.15	50	0.853		0.876		0.903	
313.15	55	0.855		0.878		0.905	
313.15	60	0.858	4.78	0.880	4.32	0.907	4.01
313.15	80	0.867[a]	6.09	0.889[a]	5.44	0.916[a]	5.00
313.15	100	0.875[a]	7.64	0.898[a]	6.78	0.924[a]	6.17
323.15	0.1	0.816	1.70	0.839	1.64	0.867	1.60
323.15	5	0.820		0.843		0.871	
323.15	10	0.823		0.846		0.874	
323.15	15	0.827		0.850		0.877	
323.15	20	0.830	2.26	0.853	2.16	0.880	2.13
323.15	25	0.833		0.856		0.883	
323.15	30	0.836		0.859		0.886	
323.15	35	0.839		0.862		0.889	
323.15	40	0.842	2.93	0.865	2.74	0.892	2.67
323.15	45	0.844		0.867		0.894	
323.15	50	0.847		0.870		0.897	
323.15	55	0.850		0.872		0.899	
323.15	60	0.852	3.76	0.875	3.47	0.902	3.31
323.15	80	0.861[a]	4.78	0.884[a]	4.37	0.911[a]	4.06
323.15	100	0.870[a]	6.01	0.892[a]	5.46	0.919[a]	4.92
333.15	0.1	0.809	1.44	0.832	1.40	0.860	1.38
333.15	5	0.813		0.836		0.864	
333.15	10	0.817		0.840		0.867	
333.15	15	0.820		0.843		0.871	
333.15	20	0.824	1.94	0.847	1.86	0.874	1.80
333.15	25	0.827		0.850		0.877	
333.15	30	0.830		0.853		0.880	
333.15	35	0.833		0.856		0.883	
333.15	40	0.836	2.49	0.859	2.35	0.886	2.26
333.15	45	0.839		0.861		0.888	
333.15	50	0.841		0.864		0.891	
333.15	55	0.844		0.867		0.893	
333.15	60	0.847	3.18	0.869	2.94	0.896	2.78
333.15	80	0.856[a]	4.03	0.879[a]	3.66	0.905[a]	3.40
333.15	100	0.865[a]	5.08	0.887[a]	4.51	0.914[a]	4.09
343.15	0.1	0.802	1.25	0.826	1.21	0.853	1.19

Table I. *(Continued)*

T (K)	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 ($mPa \cdot s$)
343.15	5	0.806		0.829		0.857	
343.15	10	0.810		0.833		0.860	
343.15	15	0.814		0.837		0.864	
343.15	20	0.818	1.67	0.840	1.61	0.867	1.54
343.15	25	0.821		0.844		0.871	
343.15	30	0.824		0.847		0.874	
343.15	35	0.827		0.850		0.877	
343.15	40	0.830	2.13	0.853	2.02	0.880	1.92
343.15	45	0.833		0.856		0.882	
343.15	50	0.836		0.859		0.885	
343.15	55	0.839		0.861		0.888	
343.15	60	0.841	2.69	0.864	2.51	0.890	2.38
343.15	80	0.851[a]	3.36	0.873[a]	3.09	0.900[a]	2.90
343.15	100	0.860[a]	4.15	0.882[a]	3.77	0.908[a]	3.47
353.15	0.1	0.795	1.09	0.818	1.07	0.846	1.06
353.15	5	0.800		0.823		0.850	
353.15	10	0.804		0.827		0.854	
353.15	15	0.808		0.830		0.857	
353.15	20	0.812	1.42	0.834	1.37	0.861	1.33
353.15	25	0.815		0.837		0.864	
353.15	30	0.818		0.841		0.868	
353.15	35	0.822		0.844		0.871	
353.15	40	0.825	1.78	0.847	1.70	0.874	1.64
353.15	45	0.828		0.850		0.877	
353.15	50	0.831		0.853		0.879	
353.15	55	0.834		0.856		0.882	
353.15	60	0.836	2.23	0.858	2.09	0.885	1.97
353.15	80	0.846[a]	2.77	0.868[a]	2.55	0.895[a]	2.38
353.15	100	0.855[a]	3.42	0.877[a]	3.08	0.903[a]	2.83
		$x_M = 0.750$		$x_M = 0.875$		$x_M = 1$	
293.15	0.1	0.922	2.90	0.964	3.02	1.016	3.26
293.15	5	0.925		0.967		1.019	
293.15	10	0.928		0.969		1.022	
293.15	15	0.931		0.972		1.024	
293.15	20	0.933	3.76	0.974	3.75	1.026	3.92
293.15	25	0.936		0.977		1.029	
293.15	30	0.938		0.979		1.031	
293.15	35	0.941		0.982		1.033	
293.15	40	0.943	4.82	0.984	4.68	1.035	4.75
293.15	45	0.945		0.986		1.038	
293.15	50	0.948		0.988		1.040	
293.15	55	0.950		0.991		1.042	
293.15	60	0.952	6.15	0.993	5.87	1.044	5.86
293.15	80	0.960[a]	7.81	1.001[a]	7.34	1.052[a]	7.36
293.15	100	0.968[a]	9.86	1.008[a]	9.46	1.059[a]	9.52

Table I. *(Continued)*

T (K)	P (MPa)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
303.15	0.1	0.915	2.33	0.957	2.40	1.009	2.58
303.15	5	0.918		0.959		1.012	
303.15	10	0.921		0.962		1.014	
303.15	15	0.924		0.965		1.017	
303.15	20	0.926	3.02	0.968	2.98	1.019	3.23
303.15	25	0.929		0.970		1.022	
303.15	30	0.932		0.973		1.024	
303.15	35	0.934		0.975		1.026	
303.15	40	0.937	3.83	0.978	3.69	1.029	3.94
303.15	45	0.939		0.980		1.031	
303.15	50	0.941		0.982		1.033	
303.15	55	0.944		0.984		1.035	
303.15	60	0.946	4.83	0.987	4.58	1.037	4.73
303.15	80	0.954[a]	6.06	0.995[a]	5.65	1.045[a]	5.60
303.15	100	0.962[a]	7.36	1.002[a]	6.95	1.053[a]	6.56
313.15	0.1	0.908	1.91	0.949	1.97	1.002	2.09
313.15	5	0.911		0.952		1.004	
313.15	10	0.914		0.955		1.007	
313.15	15	0.917		0.958		1.010	
313.15	20	0.920	2.51	0.961	2.47	1.012	2.59
313.15	25	0.923		0.964		1.015	
313.15	30	0.925		0.966		1.017	
313.15	35	0.928		0.969		1.020	
313.15	40	0.931	3.12	0.971	3.02	1.022	3.14
313.15	45	0.933		0.974		1.024	
313.15	50	0.935		0.976		1.027	
313.15	55	0.938		0.978		1.029	
313.15	60	0.940	3.84	0.980	3.67	1.031	3.73
313.15	80	0.949[a]	4.68	0.989[a]	4.40	1.039[a]	4.37
313.15	100	0.957[a]	5.65	0.997[a]	5.21	1.047[a]	5.06
323.15	0.1	0.901	1.61	0.942	1.64	0.994	1.75
323.15	5	0.904		0.945		0.997	
323.15	10	0.907		0.948		1.000	
323.15	15	0.910		0.951		1.003	
323.15	20	0.913	2.03	0.954	1.99	1.005	2.17
323.15	25	0.916		0.957		1.008	
323.15	30	0.919		0.959		1.010	
323.15	35	0.922		0.962		1.013	
323.15	40	0.924	2.49	0.965	2.40	1.015	2.60
323.15	45	0.927		0.967		1.018	
323.15	50	0.929		0.970		1.020	
323.15	55	0.932		0.972		1.022	
323.15	60	0.934	3.05	0.974	2.89	1.025	3.06
323.15	80	0.943[a]	3.72	0.983[a]	3.45	1.033[a]	3.54
323.15	100	0.951[a]	4.50	0.991[a]	4.14	1.041[a]	4.14
333.15	0.1	0.894	1.37	0.935	1.41	0.987	1.47

Table I. *(Continued)*

T (K)	P (MPa)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)	ρ (g·cm^{-3})	η (mPa·s)
333.15	5	0.897		0.938		0.990	
333.15	10	0.900		0.941		0.992	
333.15	15	0.904		0.944		0.995	
333.15	20	0.907	1.76	0.947	1.73	0.998	1.82
333.15	25	0.910		0.950		1.001	
333.15	30	0.913		0.953		1.004	
333.15	35	0.915		0.956		1.006	
333.15	40	0.918	2.14	0.958	2.05	1.009	2.17
333.15	45	0.921		0.961		1.011	
333.15	50	0.923		0.963		1.014	
333.15	55	0.926		0.966		1.016	
333.15	60	0.928	2.60	0.968	2.46	1.018	2.55
333.15	80	0.937[a]	3.15	0.977[a]	2.94	1.027[a]	2.94
333.15	100	0.946[a]	3.79	0.985[a]	3.52	1.035[a]	3.40
343.15	0.1	0.886	1.19	0.928	1.20	0.979	1.27
343.15	5	0.890		0.931		0.982	
343.15	10	0.894		0.934		0.985	
343.15	15	0.897		0.937		0.988	
343.15	20	0.900	1.52	0.941	1.50	0.991	1.55
343.15	25	0.903		0.944		0.994	
343.15	30	0.906		0.947		0.997	
343.15	35	0.909		0.949		1.000	
343.15	40	0.912	1.85	0.952	1.78	1.002	1.93
343.15	45	0.915		0.955		1.005	
343.15	50	0.917		0.957		1.007	
343.15	55	0.920		0.960		1.010	
343.15	60	0.922	2.23	0.962	2.11	1.012	2.24
343.15	80	0.932[a]	2.67	0.971[a]	2.50	1.021[a]	2.55
343.15	100	0.940[a]	3.16	0.980[a]	2.93	1.030[a]	2.88
353.15	0.1	0.879	1.04	0.920	1.05	0.972	1.10
353.15	5	0.883		0.924		0.975	
353.15	10	0.887		0.927		0.978	
353.15	15	0.890		0.931		0.981	
353.15	20	0.894	1.31	0.934	1.28	0.984	1.43
353.15	25	0.897		0.937		0.987	
353.15	30	0.900		0.940		0.990	
353.15	35	0.903		0.943		0.993	
353.15	40	0.906	1.58	0.946	1.51	0.996	1.67
353.15	45	0.909		0.949		0.999	
353.15	50	0.912		0.951		1.001	
353.15	55	0.914		0.954		1.004	
353.15	60	0.917	1.89	0.956	1.78	1.006	1.92
353.15	80	0.926[a]	2.24	0.966[a]	2.10	1.015[a]	2.19
353.15	100	0.935[a]	2.64	0.975[a]	2.53	1.024[a]	2.51

[a] Density calculated from the Tait equation.

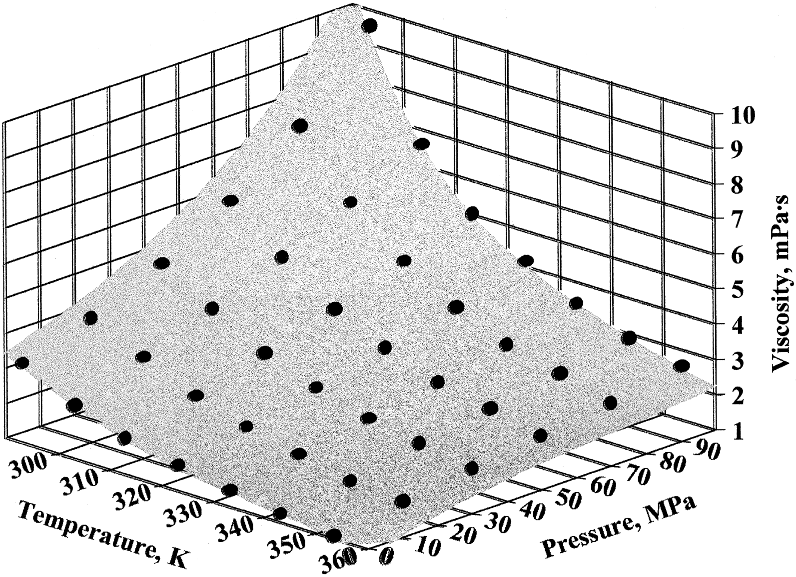

Fig. 1. Viscosity η as a function of pressure and temperature for 1-methylnaphthalene.

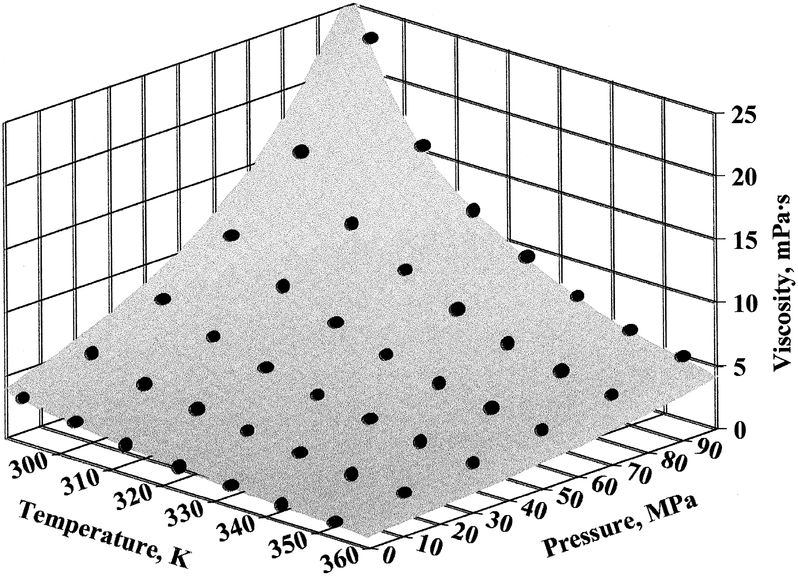

Fig. 2. Viscosity η as a function of pressure and temperature for 2,2,4,4,6,8,8-heptamethylnonane.

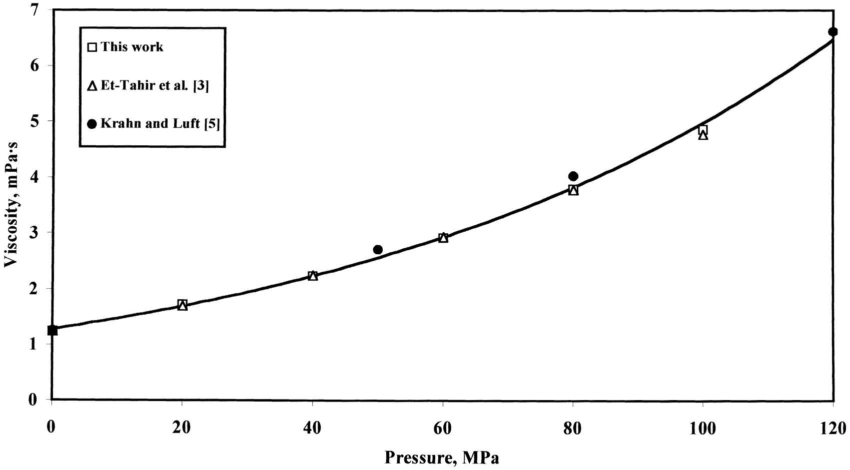

Fig. 3. Comparisons of the viscosity of 2,2,4,4,6,8,8-heptamethylnonane as a function of pressure at $T = 353.15$ K.

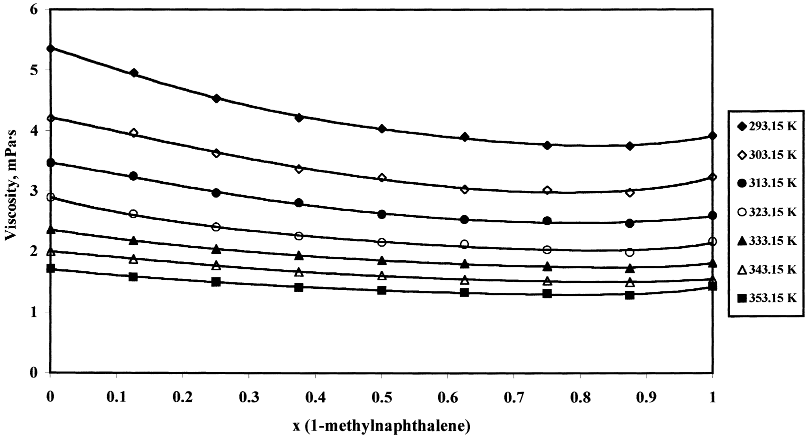

Fig. 4. Viscosity η isotherms as a function of composition at $P = 20$ MPa.

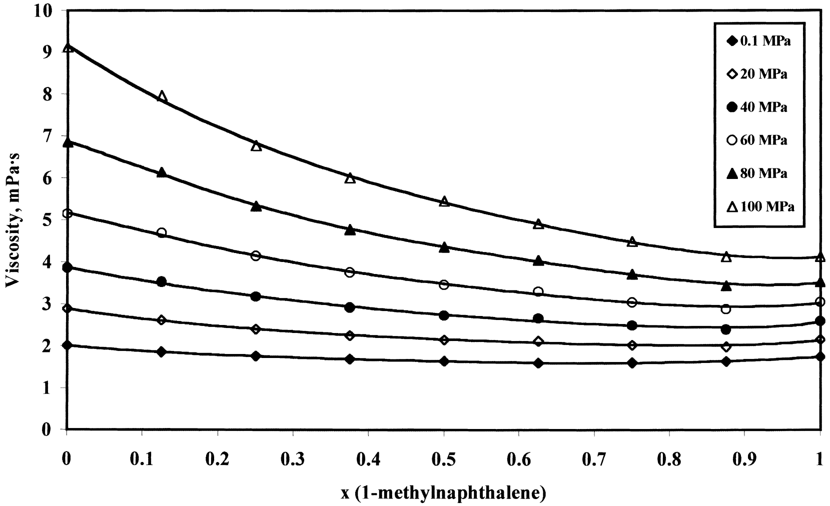

Fig. 5. Viscosity η isobars as a function of composition at $T = 323.15$ K.

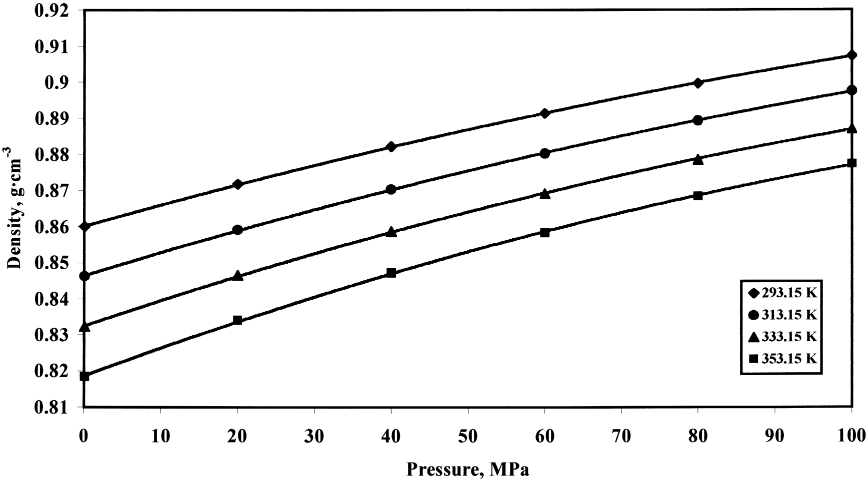

Fig. 6. Density ρ as a function of pressure at $T = 293.15$, 313.15, 333.15, and 353.15 K for the equimolar binary mixture.

where η_1 and η_2 are the viscosities of the pure components, and x_1 and $x_2 = 1 - x_1$ are the mole fractions of the components (see, e.g., Refs. 7 and 8). Figures 7 and 8 display the variations of $\eta^{\mathrm{E}}(P, x)$ at $T = 323.15$ K and the variations of $\eta^{\mathrm{E}}(P, T)$ for the equimolar binary mixture. We remark that η^{E} is always negative, and we also note that $|\eta^{\mathrm{E}}|$ increases with pressure and decreases with temperature.

The data obtained on the binary system in the course of this investigation represent a total of 378 experimental points for the viscosity, which can be used to test a variety of models incorporating the effects of temperature, pressure, and composition. To assess and compare the performance of various models, we define the following quantities:

$$\mathrm{Dev}(i) = 100(1 - \eta_{\mathrm{cal}}/\eta_{\mathrm{exp}}), \qquad \mathrm{Dev\ abs}(i) = |\mathrm{Dev}(i)| \geqslant 0,$$

$$\mathrm{DM} = \mathrm{Max}(\mathrm{Dev\ abs}(i))$$

$$\mathrm{AAD} = \frac{1}{N} \sum_{i=1}^{N} \mathrm{Dev\ abs}(i), \qquad \mathrm{bias} = \frac{1}{N} \sum_{i=1}^{N} \mathrm{Dev}(i)$$

where N is the number of experimental points, η_{exp} is the measured viscosity, and η_{cal} is the value calculated using a given model.

4.1. Mixing Laws

4.1.1. Grunberg–Nissan and Katti–Chaudhri Mixing Laws

A study has been carried out, in the case of the mixture, with Grunberg and Nissan's (GN) [9] and Katty and Chaudhri's (KC) [10] relationships:

$$\ln(\eta) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2), \qquad \text{GN ideal-type}$$

$$(\mathrm{AAD} = 10.1\%, \mathrm{DM} = 22.5\%, \mathrm{bias} = -10.1\%)$$

$$\ln(\eta) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + x_1 x_2 d, \qquad \text{GN with one adjustable parameter}$$

$$(\mathrm{AAD} = 2.2\%, \mathrm{DM} = 9.7\%, \mathrm{bias} = -0.3\%)$$

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2), \qquad \text{KC ideal type}$$

$$(\mathrm{AAD} = 4.7\%, \mathrm{DM} = 14.7\%, \mathrm{bias} = -4.6\%)$$

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 w, \qquad \text{KC with one adjustable parameter}$$

$$(\mathrm{AAD} = 2\%, \mathrm{DM} = 8.7\%, \mathrm{bias} = -0.2\%)$$

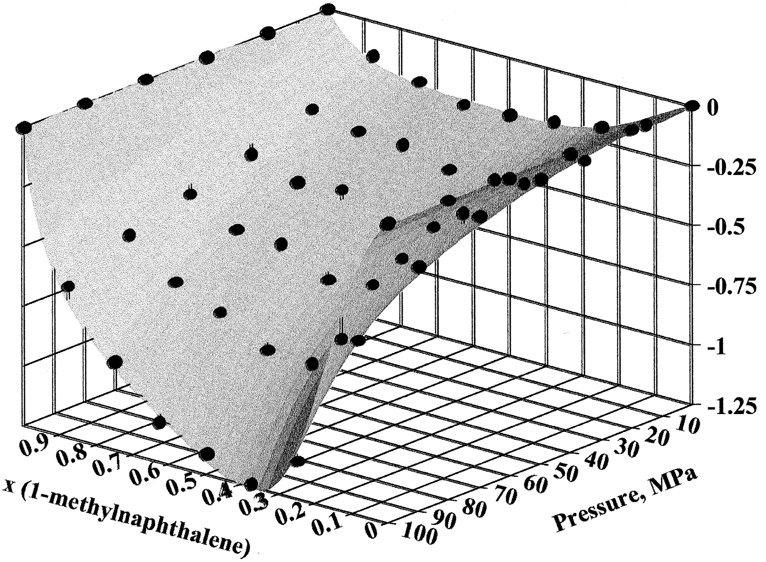

Fig. 7. Excess viscosity η^E as a function of pressure and composition at $T = 323.15$ K.

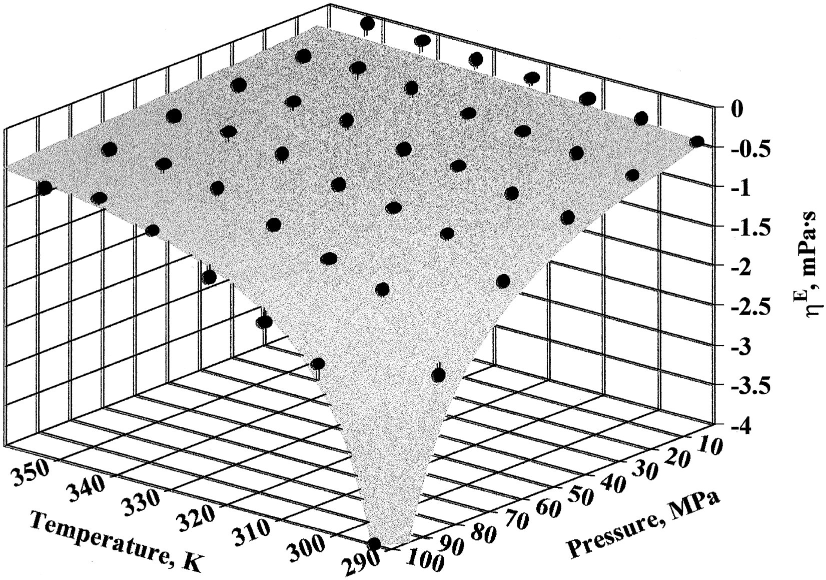

Fig. 8. Excess viscosity η^E as a function of pressure and temperature for the equimolar binary mixture.

where $V_i = M_i/\rho_i$ is the molar volume of component i, M_i is the molecular weight of component i (the molecular weight of the mixture is $\sum x_i M_i$), and ρ_i is the density of component i. The results for the ideal models are remarkable, as they combine simplicity and good performances. The Katti and Chaudhri rule is better than that of Grunberg and Nissan but has a disadvantage; it requires the density ρ. With one adjustable parameter, the AAD is of the same magnitude as the experimental uncertainty (2%).

4.1.2. Excess Energy of Viscous Flow ΔG^E

It is also interesting to calculate the excess activation energy of viscous flow ΔG^E defined such that

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + \Delta G^E/(RT)$$

where R is the universal gas constant. This relation is theoretically justified by Eyring's representation of the dynamic viscosity of a pure fluid [11]. Figure 9 shows the variations of $\Delta G^E(P, x)$ at $T = 293.15$ K. We note that ΔG^E is negative and $|\Delta G^E|$ increases with pressure. For some studies [12, 13], the fact that the excess viscosity is negative (in other words, for the case where $\Delta G^E < 0$) means that the predominant effect in the mixture is the breaking-up of the ordered structures present in the pure liquids. Other authors [14, 15] interpret the negative values of ΔG^E to indicate that the repulsive forces of interaction are the forces which predominate, therefore, corresponding to the breaking of bonds within the ordered structures. For the very associate system water + alcohol, $|\Delta G^E|$ can reach $5000\ \mathrm{J \cdot mol^{-1}}$ [16, 17], whereas in this work, the maximum value of $|\Delta G^E|$ is about $350\ \mathrm{J \cdot mol^{-1}}$, which corresponds to weak interactions and consequently to a weakly interactive system.

4.2. Self-Referencing Model

A completely different model is the self-referencing model [18] developed to model the viscous behavior of petroleum cuts. For these kinds of fluids, it is difficult to use equations based on physical properties such as molar mass, critical pressure, and temperature or acentric factors; as for a mixture, they have to be known for each of the components. The formulation has the advantage that it requires only one experimental determination of viscosity at atmospheric pressure and temperature T_0. The method does not involve molar mass 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

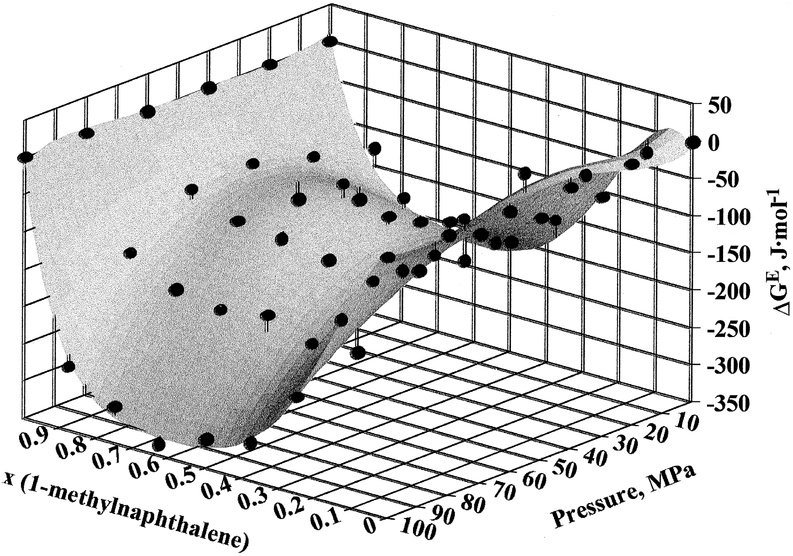

Fig. 9. Excess activation energy of viscous flow ΔG^{E} as a function of pressure and composition at $T = 293.15$ K.

which the method was originally developed. The method involves nine coefficients determined by numerical analysis on an adjustment base consisting of linear alkanes and alkylbenzenes. On the basis of knowledge of the set of these coefficients, the method can be used directly without further adjustment, and for this reason it may be considered general and predictive. The formulation of this method is

$$\ln\left(\frac{\eta(P,T)}{\eta(0.1,T_0)}\right) = (ay^2 + by + c)\ln\left(1 + \frac{(P-0.1)}{dy^2 + ey + f}\right) + (gy_0^2 + hy_0 + i)\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

where $y = y_0 + (gy_0^2 + hy_0 + i)((1/T) - (1/T_0))$ and $y_0 = \ln[\eta(0.1, T_0)]$. Excluding the reference points ($T_0 = 293.15$ K), we obtained AAD = 21.5%, DM = 45.6%, and bias = 21.4% for pure 2,2,4,4,6,8,8-heptamethylnonane (41 points) and 10.9, 24.2, and −10.8% for pure 1-methylnaphthalene (41 points). For the binary system (287 points), we obtained 10.3, 39.4, and 8.1%. The results are less good than in the previous case (mixing rules), but this model has the advantage of not requiring the composition.

4.3. Hard-Sphere Viscosity Model

The transport coefficients of real dense fluids expressed in terms of $V_r = V_0/V$, with V_0 the close-packed volume and V the molar volume, are assumed [19, 20] to be directly proportional to the 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

$$\ln\left(\frac{\eta^*_{\exp}}{R_\eta}\right) = \sum_{i=0}^{7} a_{\eta i}(1/V_r)^i, \qquad \text{with} \quad \eta^*_{\exp} = 6.03510^8\left(\frac{1}{MRT}\right)^{1/2}\eta_{\exp}V^{2/3}$$

It seems [21] that the coefficients $a_{\eta i}$ are universal or independent of the chemical nature of the compound. We have fitted the coefficients V_0 (dependent on T) and R_η (independent on T) for the two pure compounds, and we found AAD = 2.00%, DM = 16.82%, and bias = 0.71% for 1-methylnaphthalene and 3.53, 24.08, and 1.66% for 2,2,4,4,6,8,8-heptamethylnonane (keeping constant the universal coefficients $a_{\eta i}$). The hard-sphere scheme can be adapted to be used on mixtures by using the following relationships [22, 23]:

$$V_{0m} = \sum_{i=1}^{n} x_i V_{0i}, \qquad R_{\eta m} = \sum_{i=1}^{n} x_i R_{\eta i}, \qquad M_m = \sum_{i=1}^{n} x_i M_i$$

Using the characteristic coefficients V_{0i} and R_{η_i} found previously for the pure compounds, we obtained, for 294 points relative to the mixture ($x \neq 0$ and 1), AAD = 6.40%, DM = 22.03% and bias = −5.17%, which is a good result since the method is predictive for the mixtures.

4.4. Free-Volume Viscosity Model

We have used a model based on the concept of free volume [24]. A new expression for the free volume leads to the formulation

$$\eta = \rho\ell\,\frac{(E_0 + (PM/\rho))}{\sqrt{3RTM}}\exp\left[B\left(\frac{E_0 + (PM/\rho)}{2RT}\right)^{3/2}\right]$$

where the energy E_0, the coefficient B, and the length ℓ are three parameters characteristic of the pure compound. Fitting these parameters, we obtained AAD=2.43%, DM=11.22%, and bias=0.37% for 1-methylnaphthalene and AAD=1.84%, DM=11.17%, and bias=0.15% for 2,2,4,4,6,8,8-heptamethylnonane. The model has been adapted [25, 26] for mixtures using

$$M_m = x_1 M_1 + x_2 M_2, \qquad E_{0m} = x_1^2 E_{01} + 2x_1 x_2 (E_{01} E_{02})^{1/2} + x_2^2 E_{02}$$

$$B_m = x_1 B_1 + x_2 B_2, \qquad 1/\ell_m = x_1/\ell_1 + x_2/\ell_2$$

For the 294 points of the binary ($x \neq 0$ and 1), we obtained AAD=10.9%, DM=21.0%, and bias=−10.9%, which is a very satisfactory result for a predictive model (it is necessary to know only the characteristic parameters of each pure compound) for the dynamic viscosity.

4.5. Friction Theory

In the friction theory (*f-theory*) models [27] the viscosity in excess to the dilute gas viscosity is considered as a friction contribution and it is correlated with the van der Waals repulsive and attractive pressure terms, p_r and p_a, of an equation of state such as the Peng and Robinson (PR EOS) [28]. Recently, following these concepts, a general one-parameter *f-theory* model [29] has been proposed based on the viscosity behavior of linear alkanes. The general model consists of a linear correlation on p_a and a second order correlation on p_r, which suffices for an accurate representation of fluids such as linear alkanes. However, to account for the viscosity effects of more complex molecular structures such as 2,2,4,4,6,8,8-heptamethylnonane, a further third-order p_r corrective term may be required [30]. Therefore, the model used in this work can be represented as follows:

$$\eta = \eta^{\mathrm{GM}} + \kappa_{\mathrm{rrr}}\, p_\mathrm{r}^3$$

where η^{GM} corresponds to the PR one-parameter general model given in Ref. 29 and κ_{rrr} is given by

$$\kappa_{\mathrm{rrr}} = d_2(\exp(2/T_\mathrm{r}) - 1)(T_\mathrm{r}^{-1} - 1)^3$$

where T_r is the reduced temperature. With this approach, the modeling of the pure component viscosity requires the fitting of two parameters per compound: the characteristic critical viscosity η_c, to be used in the general model, and the d_2 constant. A least-squares fit to the viscosity of the pure components results in an AAD of 2.19% with a $\eta_\mathrm{c} = 0.0340458\ \mathrm{mPa \cdot s}$ and $d_2 = 1.05763 \times 10^{-19}\ \mathrm{s \cdot MPa^{-2}}$ and a DM of 12.8% at 293.15 K and 100 MPa for 1-methylnaphthalene. For 2,2,4,4,6,8,8-heptamethylnonane an AAD of

2.43% is obtained with a $\eta_c = 0.0580515$ mPa·s and $d_2 = 2.14681 \times 10^{-17}$ s·MPa^{-2} and a DM of 11.6% at 293.15 K and 100 MPa.

In the viscosity prediction of mixtures, the η^{GM} term is treated according to the mixing rules proposed in Ref. 28 and the third-order friction coefficient, κ_{rrr}, with an exponential mixing rule [30] of the form

$$\ln(\kappa_{rrr}) = \sum_{i=1}^{n} x_i \ln(\kappa_{rrr,\,i})$$

where subscript i refers to the pure compounds in the mixture. With this scheme the mixture viscosity is predicted with an AAD of 5.84% and DM of 12.51% at 353.15 K, 0.1 MPa, and at 0.75 mole fraction of 1-methylnaphthalene. Given the kind of viscosity behavior that this binary system develops, these results can be considered to be satisfactory.

It should be stressed that for 1-methylnaphthalene the parameters required in the PR EOS have been taken from Ref. 31. The 2,2,4,4,6,8,8-heptamethylnonane parameters, which are not tabulated in the open literature, have been derived by a least-squares fit of the pvT data presented in this work to the PR EOS. The derived 2,2,4,4,6,8,8-heptamethylnonane parameters are $T_c = 608.904$ K, $p_c = 1.49819$ MPa, and $\omega = 0.580578$.

5. CONCLUSION

For mixtures these models are totally predictive in the sense that only knowledge of the parameters characteristic of the pure compounds along with the composition is sufficient to predict the viscosity. It follows from the discussion that some simple predictive models are able to model the viscosity of such low associative systems as studied here. The experimental data obtained (378 points for dynamic viscosity) could be included in a database and used to carry out further tests of other more sophisticated models, as, for example, models based on molecular dynamics simulation. Of course this study should be considered only as a small part of a more general study concerning various systems (associative and nonassociative mixtures, various binary mixtures with different compounds, ternary systems, and even systems with more than three components).

ACKNOWLEDGMENT

This work has been accomplished within the European project EVIDENT under the JOULE Program, Contract No. JOF3-CT97-0034.

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