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Measurements of the Viscosity and Density of Three Hydrocarbons and the Three Associated Binary Mixtures Versus Pressure and Temperature

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The dynamic viscosity η and density ρ of three pure substances (heptane, methylcyclohexane, 1-methylnaphthalene) and of the three associated binary mixtures (heptane + methylcyclohexane, heptane + 1-methylnaphthalene, methylcyclohexane + 1-methylnaphthalene) were measured as a function of temperature T (303.15, 323.15, and 343.15 K) and pressure P ($\leqslant$100 MPa). For the binary mixtures the mole fraction x of each component was successively 0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, and 1. The total experimental results represent 432 different points: 54 for the pure substances and 378 for the binary mixtures ($x \neq 0$ and 1).

KEY WORDS: density; high pressure; hydrocarbons; mixtures; viscosity.

1. INTRODUCTION

For several years, our laboratory has been working on properties of petroleum fluids as a function of pressure. The investigations reported in this paper concern the dynamic viscosity η and density ρ of three hydrocarbons and the three associated binary mixtures. In petroleum engineering, knowledge of the dynamic viscosity as a function of the reservoir conditions (temperature and pressure, in particular, as well as the composition of the fluid) is of major importance since several models, covering a wide range of aspects, use this coefficient. It so happens that of all thermophysical properties, the viscosity is the most strongly influenced by pressure and temperature. To simulate the behavior of a system with several components,

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the distribution parameters of these components (for example, the mole fraction) must generally be known. The viscosity of the mixture thus depends on these parameters, the temperature T, and the pressure P. While there are abundant data describing variations versus temperature at atmospheric pressure, studies of variations versus pressure are less frequent, particularly for mixtures and more particularly for those likely to be used to model a real petroleum fluid: in other words, a complex fluid.

As part of this work we selected three binaries on the basis of remarks made by Leroy [1] concerning the fraction C_5^+ (hydrocarbons containing five or more atoms of carbon) which a synthetic fluid must contain in order to be representative of a petroleum oil. Leroy's analyses indicate that a mixture with 89% (weight fraction) of saturated hydrocarbons (70% alkanes and 30% cycloalkanes) and 11% aromatics is appropriate for this kind of study. For the alkanes, the binary system pentane + decane appears to be representative of the influence of the family. Leroy [1] has also indicated that to reflect the role of cycloalcanes the system selected should contain at least 70% methylcyclohexane, while for the aromatics study of 1-methylnaphthalene is sufficient. This leads to a synthetic representation with four components and, thus, six associated binary mixtures. To reduce this number, we limited the representation of the alkanes to a single intermediary substance, heptane, which is closer to pentane than decane. There are, in this case only three binaries associated with the components of the synthetic cut.

In accordance with these remarks we conducted a series of experimental determinations on the three pure substances (heptane, methylcyclohexane, and 1-methylnaphthalene) and on the three associated binary mixtures (heptane + methylcyclohexane, heptane + 1-methylnaphthalene, methylcyclohexane + 1-methylnaphthalene) with the goal of providing data which can be used to develop models. Another equally important quantity which is often required to determine (and model) the viscosity η is the density ρ. If the density is known along various isotherms and isobars, the isothermal compressibility coefficient and thermal expansion coefficient of the fluids considered can be determined. We therefore also present the values of density ρ measured as a function of pressure, temperature, and composition for the binary mixtures.

2. EXPERIMENTAL TECHNIQUES

2.1. Apparatus

The dynamic viscosity η and the density ρ of the samples were determined with a falling-body viscometer and an Anton-Paar DMA 45 resonance

densitometer fitted with an additional DMA 512 cell as described by Et-Tahir et al. [2] The values of ρ, determined between 0.1 and 40 MPa, are then extrapolated to 100 MPa with a procedure described in the same paper [2]. It should further be noted that the error in T is estimated as ± 0.5 K for the measurements of η and as ± 0.05 K for those of ρ, the error in P as ± 0.05 MPa (except for $P = 0.1$ MPa), and the error in ρ as ± 0.5 kg $\cdot$ m^{-3}, while the relative uncertainty in η is within 2%. As already discussed by Kanti et al. [3], this uncertainty is comparable to that obtained by other authors with similar experimental apparatus. In Section 3 we provide, as an example a comparison with other data from the literature for heptane and methylcyclohexane.

2.2. Characterization of the Samples

The substances used are commercial chemicals with the following sources and degrees of purity: heptane (Aldrich, purity, >99%; relative molecular mass, $M = 100.205$ g $\cdot$ mol^{-1}), methylcyclohexane (Aldrich; purity, >99%; $M = 98.189$ g $\cdot$ mol^{-1}), 1-methylnaphthalene (Aldrich; purity, >98%, $M = 142.201$ g $\cdot$ mol^{-1}). As we shall see below, there are existing data for the first two substances and our measurements complete the already available data as regards either pressure or temperature. We note that at atmospheric pressure $P = 0.1$ MPa and at $T = 303.15$ K the viscosity of heptane is 370 μPa $\cdot$ s, that of methylcyclohexane 638.7 μPa $\cdot$ s, and that of 1-methylnaphthalene 2617 μPa $\cdot$ s. So the two binary mixtures heptane + 1-methylnaphthalene and methylcyclohexane + 1-methylnaphthalene both involve components with very different viscosities. The mixtures were prepared at ambient pressure and temperature by weighting, so as to obtain the mole fractions $x = 0$, 0.125, 0.25, 0.375, 0.5, 0.675, 0.75, 0.875, and 1 ($x_1 = x$ for component 1 and $x_2 = 1 - x_1 = 1 - x$ for component 2). Finally, all samples are in the liquid state in the experimental pressure and temperature range.

3. RESULTS

The measurements were taken at 303.15, 323.15, and 343.15 K and at 0.1, 20, 40, 60, 80, and 100 MPa for the dynamic viscosity. As has already been indicated, the density values were extrapolated between 40 MPa and 100 MPa. Tables I, II, and III provide for each binary mixture the values obtained for η and ρ versus P, T, and mole fraction x ($x = 0$ and $x = 1$ corresponding to the pure substances). A total of 432 experimental points was obtained (54 for the three pure substances and 378 for the three binary mixtures, $x \neq 0$ and $x \neq 1$). For pure heptane one can refer to previous

Table I. Binary Mixture Heptane + Methylcyclohexane (x, Mole Fraction of Methylcyclohexane)

x	T (K)	P (MPa)	ρ (kg · m^{-3})	η (μPa · s)
0	303.15	0.1	674.8	370
0	303.15	20	692.1	444
0	303.15	40	706.4	533
0	303.15	60	718.5	629
0	303.15	80	729.2	718
0	303.15	100	738.7	820
0	323.15	0.1	657.4	303
0	323.15	20	677.1	368
0	323.15	40	692.6	443
0	323.15	60	705.5	516
0	323.15	80	716.5	587
0	323.15	100	726.2	664
0	343.15	0.1	638.4	252
0	343.15	20	661.6	318
0	343.15	40	678.7	372
0	343.15	60	692.4	437
0	343.15	80	704.0	494
0	343.15	100	713.9	554
0.125	303.15	0.1	683.8	389
0.125	303.15	20	701.4	459
0.125	303.15	40	715.2	558
0.125	303.15	60	726.7	661
0.125	303.15	80	738.3	768
0.125	303.15	100	747.7	867
0.125	323.15	0.1	666.0	317
0.125	323.15	20	686.1	385
0.125	323.15	40	701.4	460
0.125	323.15	60	713.8	536
0.125	323.15	80	725.5	617
0.125	323.15	100	735.1	705
0.125	343.15	0.1	647.3	263
0.125	343.15	20	670.5	327
0.125	343.15	40	687.6	385
0.125	343.15	60	701.3	448
0.125	343.15	80	712.8	511
0.125	343.15	100	722.7	580
0.25	303.15	0.1	693.6	411
0.25	303.15	20	710.8	492
0.25	303.15	40	724.9	590
0.25	303.15	60	737.1	694

Table I. *(Continued)*

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.25	303.15	80	747.8	809
0.25	303.15	100	756.7	920
0.25	323.15	0.1	676.1	335
0.25	323.15	20	695.6	408
0.25	323.15	40	710.9	483
0.25	323.15	60	723.5	567
0.25	323.15	80	734.7	651
0.25	323.15	100	744.3	747
0.25	343.15	0.1	657.5	277
0.25	343.15	20	680.1	343
0.25	343.15	40	697.1	400
0.25	343.15	60	710.6	463
0.25	343.15	80	722.5	530
0.25	343.15	100	732.8	608
0.375	303.15	0.1	703.7	436
0.375	303.15	20	720.8	524
0.375	303.15	40	735.0	627
0.375	303.15	60	747.7	738
0.375	303.15	80	757.5	864
0.375	303.15	100	767.0	983
0.375	323.15	0.1	686.2	354
0.375	323.15	20	705.6	432
0.375	323.15	40	720.9	511
0.375	323.15	60	733.7	600
0.375	323.15	80	744.7	690
0.375	323.15	100	754.4	794
0.375	323.15	0.1	667.7	292
0.375	343.15	20	690.3	360
0.375	343.15	40	706.8	419
0.375	343.15	60	719.8	490
0.375	343.15	80	732.3	567
0.375	343.15	100	740.2	641
0.5	303.15	0.1	714.2	465
0.5	303.15	20	730.9	560
0.5	303.15	40	744.9	683
0.5	303.15	60	756.9	790
0.5	303.15	80	767.5	921
0.5	303.15	100	777.0	1050
0.5	323.15	0.1	696.5	375
0.5	323.15	20	715.6	460

Table I. (*Continued*)

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.5	323.15	40	730.8	546
0.5	323.15	60	743.5	647
0.5	323.15	80	754.4	739
0.5	323.15	100	764.0	839
0.5	343.15	0.1	678.6	309
0.5	343.15	20	700.0	383
0.5	343.15	40	717.2	452
0.5	343.15	60	730.4	526
0.5	343.15	80	742.5	608
0.5	343.15	100	753.0	685
0.625	303.15	0.1	725.1	498
0.625	303.15	20	741.6	617
0.625	303.15	40	755.6	741
0.625	303.15	60	767.6	866
0.625	303.15	80	778.3	995
0.625	303.15	100	788.0	1150
0.625	323.15	0.1	707.7	400
0.625	323.15	20	726.2	488
0.625	323.15	40	741.2	593
0.625	323.15	60	753.9	693
0.625	323.15	80	765.0	804
0.625	323.15	100	774.9	908
0.625	343.15	0.1	689.1	328
0.625	343.15	20	710.5	407
0.625	343.15	40	727.3	485
0.625	343.15	60	741.4	572
0.625	343.15	80	753.4	663
0.625	343.15	100	764.1	748
0.75	303.15	0.1	736.1	538
0.75	303.15	20	752.6	673
0.75	303.15	40	766.9	808
0.75	303.15	60	778.7	953
0.75	303.15	80	788.9	1090
0.75	303.15	100	798.2	1270
0.75	323.15	0.1	718.6	430
0.75	323.15	20	737.0	522
0.75	323.15	40	751.8	654
0.75	323.15	60	764.3	768
0.75	323.15	80	775.2	882
0.75	323.15	100	784.8	990
0.75	343.15	0.1	700.0	350

Table I. *(Continued)*

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.75	343.15	20	721.2	443
0.75	343.15	40	737.9	533
0.75	343.15	60	751.8	623
0.75	343.15	80	763.7	726
0.75	343.15	100	774.2	820
0.875	303.15	0.1	747.8	585
0.875	303.15	20	764.0	737
0.875	303.15	40	777.7	894
0.875	303.15	60	789.4	1060
0.875	303.15	80	799.7	1220
0.875	303.15	100	809.0	1400
0.875	323.15	0.1	729.9	466
0.875	323.15	20	748.3	576
0.875	323.15	40	763.1	724
0.875	323.15	60	775.5	851
0.875	323.15	80	787.0	982
0.875	323.15	100	797.1	1120
0.875	343.15	0.1	711.8	377
0.875	343.15	20	732.6	485
0.875	343.15	40	749.0	590
0.875	343.15	60	762.8	703
0.875	343.15	80	774.6	822
0.875	343.15	100	785.0	930
1	303.15	0.1	760.1	639
1	303.15	20	776.4	809
1	303.15	40	789.9	990
1	303.15	60	801.4	1180
1	303.15	80	811.5	1390
1	303.15	100	820.4	1620
1	323.15	0.1	742.5	501
1	323.15	20	760.5	651
1	323.15	40	775.4	811
1	323.15	60	788.2	957
1	323.15	80	799.4	1110
1	323.15	100	809.4	1280
1	343.15	0.1	724.0	405
1	343.15	20	744.3	534
1	343.15	40	760.8	661
1	343.15	60	774.8	797
1	343.15	80	786.9	932
1	343.15	100	797.6	1070

Table II. Binary Mixture Heptane + 1-Methylnaphthalene (x, Mole Fraction of Heptane)

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0	303.15	0.1	1010.0	2620
0	303.15	20	1021.0	3230
0	303.15	40	1030.0	3880
0	303.15	60	1038.0	4670
0	303.15	80	1044.0	5610
0	303.15	100	1050.0	6690
0	323.15	0.1	994.9	1750
0	323.15	20	1006.0	2140
0	323.15	40	1016.0	2580
0	323.15	60	1025.0	3060
0	323.15	80	1033.0	3580
0	323.15	100	1041.0	4130
0	343.15	0.1	979.4	1270
0	343.15	20	991.5	1580
0	343.15	40	1003.0	1920
0	343.15	60	1013.0	2230
0	343.15	80	1023.0	2560
0	343.15	100	1032.0	2920
0.125	303.15	0.1	969.6	1840
0.125	303.15	20	980.7	2180
0.125	303.15	40	990.7	2580
0.125	303.15	60	999.9	3070
0.125	303.15	80	1008.0	3620
0.125	303.15	100	1016.0	4210
0.125	323.15	0.1	954.0	1300
0.125	323.15	20	966.1	1530
0.125	323.15	40	976.7	1790
0.125	323.15	60	986.1	2070
0.125	323.15	80	995.9	2360
0.125	323.15	100	1004.0	2700
0.125	343.15	0.1	938.4	981
0.125	343.15	20	951.5	1150
0.125	343.15	40	963.2	1330
0.125	343.15	60	973.7	1520
0.125	343.15	80	983.3	1740
0.125	343.15	100	992.2	1960
0.25	303.15	0.1	929.3	1360
0.25	303.15	20	941.3	1600
0.25	303.15	40	951.7	1890
0.25	303.15	60	961.0	2210

Table II. *(Continued)*

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.25	303.15	80	969.4	2540
0.25	303.15	100	977.1	2940
0.25	323.15	0.1	913.2	1000
0.25	323.15	20	926.1	1180
0.25	323.15	40	937.7	1380
0.25	323.15	60	948.1	1560
0.25	323.15	80	957.0	1780
0.25	323.15	100	965.4	2010
0.25	343.15	0.1	897.2	783
0.25	343.15	20	911.3	925
0.25	343.15	40	923.6	1070
0.25	343.15	60	934.6	1210
0.25	343.15	80	944.6	1370
0.25	343.15	100	953.7	1530
0.375	303.15	0.1	886.7	1030
0.375	303.15	20	899.3	1220
0.375	303.15	40	910.4	1440
0.375	303.15	60	920.4	1650
0.375	303.15	80	929.4	1930
0.375	303.15	100	937.7	2210
0.375	323.15	0.1	870.2	781
0.375	323.15	20	884.3	931
0.375	323.15	40	896.3	1090
0.375	323.15	60	906.7	1240
0.375	323.15	80	916.5	1410
0.375	323.15	100	925.0	1570
0.375	323.15	0.1	853.5	621
0.375	343.15	20	869.2	745
0.375	343.15	40	882.3	859
0.375	343.15	60	893.6	974
0.375	343.15	80	903.5	1100
0.375	343.15	100	912.3	1240
0.5	303.15	0.1	845.9	800
0.5	303.15	20	859.3	960
0.5	303.15	40	871.2	1130
0.5	303.15	60	881.9	1300
0.5	303.15	80	891.5	1470
0.5	303.15	100	900.4	1680
0.5	323.15	0.1	829.4	625
0.5	323.15	20	844.2	749

Table II. *(Continued)*

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.5	323.15	40	857.1	875
0.5	323.15	60	868.5	1000
0.5	323.15	80	878.2	1130
0.5	323.15	100	887.2	1270
0.5	343.15	0.1	812.2	503
0.5	343.15	20	829.2	598
0.5	343.15	40	843.0	703
0.5	343.15	60	854.7	808
0.5	343.15	80	864.9	920
0.5	343.15	100	873.9	1030
0.625	303.15	0.1	803.6	644
0.625	303.15	20	817.9	773
0.625	303.15	40	830.5	901
0.625	303.15	60	841.7	1040
0.625	303.15	80	851.9	1190
0.625	303.15	100	861.2	1350
0.625	323.15	0.1	786.3	512
0.625	323.15	20	802.7	605
0.625	323.15	40	816.0	711
0.625	323.15	60	828.4	819
0.625	323.15	80	839.1	925
0.625	323.15	100	848.9	1040
0.625	343.15	0.1	769.5	418
0.625	343.15	20	787.2	497
0.625	343.15	40	802.1	578
0.625	343.15	60	815.0	668
0.625	343.15	80	826.3	763
0.625	343.15	100	836.5	864
0.75	303.15	0.1	760.4	524
0.75	303.15	20	776.0	621
0.75	303.15	40	788.9	729
0.75	303.15	60	800.1	848
0.75	303.15	80	809.8	978
0.75	303.15	100	818.5	1120
0.75	323.15	0.1	743.4	424
0.75	323.15	20	760.6	502
0.75	323.15	40	774.9	592
0.75	323.15	60	787.2	687
0.75	323.15	80	797.6	781
0.75	323.15	100	807.0	881
0.75	343.15	0.1	725.6	350

Table II. *(Continued)*

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.75	343.15	20	745.2	417
0.75	343.15	40	760.9	484
0.75	343.15	60	774.0	560
0.75	343.15	80	785.4	646
0.75	343.15	100	795.4	739
0.875	303.15	0.1	717.7	438
0.875	303.15	20	734.3	521
0.875	303.15	40	747.9	613
0.875	303.15	60	759.4	714
0.875	303.15	80	769.4	822
0.875	303.15	100	778.4	937
0.875	323.15	0.1	700.3	357
0.875	323.15	20	719.0	422
0.875	323.15	40	733.8	494
0.875	323.15	60	746.0	579
0.875	323.15	80	756.6	675
0.875	323.15	100	765.8	780
0.875	343.15	0.1	682.1	295
0.875	343.15	20	703.7	360
0.875	343.15	40	719.9	423
0.875	343.15	60	733.1	491
0.875	343.15	80	744.2	558
0.875	343.15	100	753.8	650
1	303.15	0.1	674.8	370
1	303.15	20	692.1	444
1	303.15	40	706.4	533
1	303.15	60	718.5	629
1	303.15	80	729.2	718
1	303.15	100	738.7	820
1	323.15	0.1	657.4	303
1	323.15	20	677.1	368
1	323.15	40	692.6	443
1	323.15	60	705.5	506
1	323.15	80	716.5	587
1	323.15	100	726.2	664
1	343.15	0.1	638.4	252
1	343.15	20	661.6	318
1	343.15	40	678.7	372
1	343.15	60	692.4	437
1	343.15	80	704.0	494
1	343.15	100	713.9	554

Table III. Binary Mixture 1-Methylnaphthalene + Methylcyclohexane (x, Mole Fraction of 1-Methylnaphthalene)

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0	303.15	0.1	760.1	639
0	303.15	20	776.4	809
0	303.15	40	789.9	990
0	303.15	60	801.4	1180
0	303.15	80	811.5	1390
0	303.15	100	820.4	1620
0	323.15	0.1	742.5	501
0	323.15	20	760.5	651
0	323.15	40	775.4	811
0	323.15	60	788.2	957
0	323.15	80	799.4	1110
0	323.15	100	809.4	1280
0	343.15	0.1	724.0	405
0	343.15	20	744.3	534
0	343.15	40	760.8	661
0	343.15	60	774.8	797
0	343.15	80	786.9	932
0	343.15	100	797.6	1070
0.125	303.15	0.1	793.8	715
0.125	303.15	20	809.3	883
0.125	303.15	40	822.3	1080
0.125	303.15	60	833.6	1260
0.125	303.15	80	843.5	1460
0.125	303.15	100	852.5	1720
0.125	323.15	0.1	776.6	559
0.125	323.15	20	793.7	712
0.125	323.15	40	807.7	855
0.125	323.15	60	819.6	1000
0.125	323.15	80	830.0	1150
0.125	323.15	100	840.5	1340
0.125	343.15	0.1	758.9	450
0.125	343.15	20	778.1	562
0.125	343.15	40	793.7	672
0.125	343.15	60	806.8	805
0.125	343.15	80	818.3	949
0.125	343.15	100	828.4	1100
0.25	303.15	0.1	828.3	829
0.25	303.15	20	842.9	1010
0.25	303.15	40	855.2	1200
0.25	303.15	60	866.0	1390

Table III. *(Continued)*

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.25	303.15	80	875.5	1630
0.25	303.15	100	884.1	1900
0.25	323.15	0.1	811.2	640
0.25	323.15	20	827.3	779
0.25	323.15	40	840.6	918
0.25	323.15	60	852.7	1080
0.25	323.15	80	863.1	1240
0.25	323.15	100	872.4	1420
0.25	343.15	0.1	793.9	513
0.25	343.15	20	811.7	622
0.25	343.15	40	826.6	742
0.25	343.15	60	839.3	885
0.25	343.15	80	850.6	1000
0.25	343.15	100	860.7	1160
0.375	303.15	0.1	861.6	972
0.375	303.15	20	875.1	1160
0.375	303.15	40	887.0	1380
0.375	303.15	60	897.7	1610
0.375	303.15	80	907.4	1880
0.375	303.15	100	916.3	2160
0.375	323.15	0.1	844.9	733
0.375	323.15	20	859.6	884
0.375	323.15	40	872.6	1050
0.375	323.15	60	881.5	1200
0.375	323.15	80	891.7	1400
0.375	323.15	100	901.1	1590
0.375	323.15	0.1	827.7	584
0.375	343.15	20	844.2	712
0.375	343.15	40	858.4	848
0.375	343.15	60	869.1	977
0.375	343.15	80	878.7	1120
0.375	343.15	100	892.0	1260
0.5	303.15	0.1	891.0	1130
0.5	303.15	20	903.2	1370
0.5	303.15	40	915.3	1620
0.5	303.15	60	927.2	1900
0.5	303.15	80	936.4	2210
0.5	303.15	100	945.6	2550
0.5	323.15	0.1	874.1	853
0.5	323.15	20	888.3	1030

Table III. *(Continued)*

x	T (K)	P (MPa)	ρ (kg · m^{-3})	η (μPa · s)
0.5	323.15	40	900.6	1210
0.5	323.15	60	911.4	1400
0.5	323.15	80	921.4	1600
0.5	323.15	100	930.5	1830
0.5	343.15	0.1	857.7	673
0.5	343.15	20	873.2	822
0.5	343.15	40	886.7	960
0.5	343.15	60	898.8	1100
0.5	343.15	80	909.3	1260
0.5	343.15	100	920.7	1430
0.625	303.15	0.1	921.4	1370
0.625	303.15	20	933.4	1600
0.625	303.15	40	944.1	1910
0.625	303.15	60	955.9	2270
0.625	303.15	80	965.1	2640
0.625	303.15	100	973.9	3040
0.625	323.15	0.1	905.4	1010
0.625	323.15	20	918.5	1200
0.625	323.15	40	930.3	1410
0.625	323.15	60	941.0	1640
0.625	323.15	80	950.9	1880
0.625	323.15	100	960.0	2150
0.625	343.15	0.1	889.1	791
0.625	343.15	20	903.7	940
0.625	343.15	40	916.4	1090
0.625	343.15	60	927.7	1260
0.625	343.15	80	937.8	1430
0.625	343.15	100	949.5	1620
0.75	303.15	0.1	951.2	1670
0.75	303.15	20	962.5	1970
0.75	303.15	40	973.0	2340
0.75	303.15	60	982.9	2760
0.75	303.15	80	992.1	3240
0.75	303.15	100	1001.0	3780
0.75	323.15	0.1	935.4	1200
0.75	323.15	20	847.9	1420
0.75	323.15	40	958.8	1660
0.75	323.15	60	969.4	1920
0.75	323.15	80	978.7	2210
0.75	323.15	100	987.3	2530
0.75	343.15	0.1	919.2	929

Table III. *(Continued)*

x	T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
0.75	343.15	20	933.1	1080
0.75	343.15	40	945.0	1250
0.75	343.15	60	956.9	1430
0.75	343.15	80	966.9	1630
0.75	343.15	100	977.5	1870
0.875	303.15	0.1	980.8	2060
0.875	303.15	20	991.5	2470
0.875	303.15	40	1002.0	2970
0.875	303.15	60	1011.0	3530
0.875	303.15	80	1019.0	4180
0.875	303.15	100	1028.0	4900
0.875	323.15	0.1	965.4	1440
0.875	323.15	20	977.0	1700
0.875	323.15	40	987.7	1990
0.875	323.15	60	997.4	2300
0.875	323.15	80	1007.0	2730
0.875	323.15	100	1015.0	3110
0.875	343.15	0.1	949.8	1080
0.875	343.15	20	962.5	1270
0.875	343.15	40	974.1	1500
0.875	343.15	60	984.7	1740
0.875	343.15	80	994.5	1960
0.875	343.15	100	1004.0	2240
1	303.15	0.1	1010.0	2620
1	303.15	20	1021.0	3230
1	303.15	40	1030.0	3880
1	303.15	60	1038.0	4670
1	303.15	80	1044.0	5610
1	303.15	100	1050.0	6690
1	323.15	0.1	994.9	1750
1	323.15	20	1006.0	2140
1	323.15	40	1016.0	2580
1	323.15	60	1025.0	3060
1	323.15	80	1033.0	3580
1	323.15	100	1041.0	4130
1	343.15	0.1	979.4	1270
1	343.15	20	991.5	1580
1	343.15	40	1003.0	1920
1	343.15	60	1013.0	2230
1	343.15	80	1023.0	2560
1	343.15	100	1032.0	2920

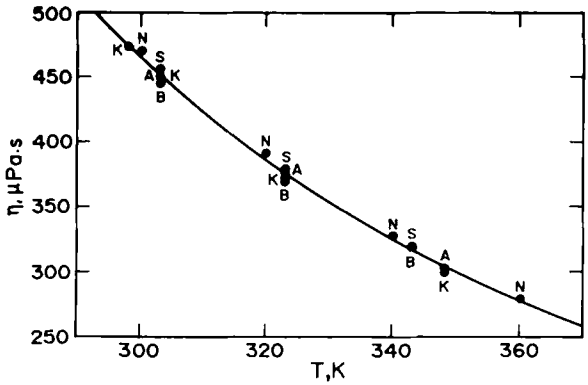

Fig. 1. Variations of dynamic viscosity η of heptane versus temperature at $P = 20$ MPa. (—) $\eta = a + (b/T) + (c/T^2)$. A, Ref. 4; K, Ref. 5; N, Ref. 6; S, Ref. 7; B, present paper.

measurements carried out by Assael et al. [4], Kashiwagi and Makita [5], and Naziev et al. [6] and to the values reported in the compilation [7] of Stephan and Lucas. One can also find in the latter paper a few values for methylcyclohexane, limited to 50 Mpa, and in a previous article [2] we have supplied values at other temperatures. For pure heptane at atmospheric pressure one can refer to the viscosity values recommanded by Dymond and Øye [8]. In all cases, where a comparison is possible (eventually after interpolation), a good agreement was observed with our data

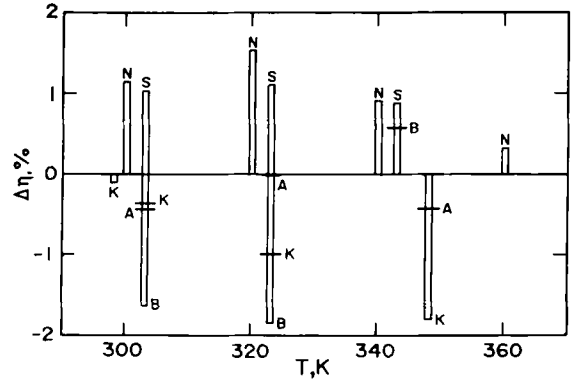

Fig. 2. Deviations $\Delta\eta$ of the literature data for the viscosity of heptane from the correlation of $\eta = a + (b/T) + (c/T^2)$ ($P = 20$ MPa). A, Ref. 4; K, Ref. 5; N, Ref. 6; S, Ref. 7; B, present paper.

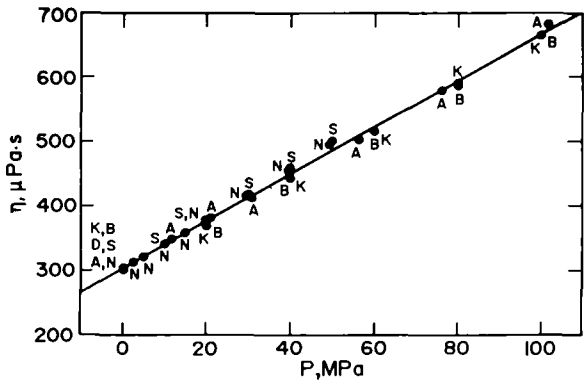

Fig. 3. Variations of dynamic viscosity η of heptane versus pressure at $T = 323.15$ K. (—) $\eta = a + bP + cP^2$. A, Ref. 4; K, Ref. 5; N, Ref. 6; S, Ref. 7; D, Ref. 8; B, present paper.

allowing for experimental errors. Figure 1 shows the variations of the viscosity $\eta(T)$ of the heptane at $P = 20$ MPa. The data are fitted with the equation $\eta(T) = a + (b/T) + (c/T^2)$ (fit standard error, 0.0044; coefficient of determination r^2, 0.9961). It is important to point out that several functions give equivalent results. Figure 2 shows the values of the deviation $\Delta\eta = 100\,(\eta_{expt} - \eta_{calc})/\eta_{expt}$ for the various authors. Figure 3 shows the variations of the viscosity $\eta(P)$ of the heptane at $T = 323.15$ K, and Fig. 4 shows the $\Delta\eta$ values calculated using $\eta(P) = a + bP + cP^2$ (fit standard error, 0.0057;

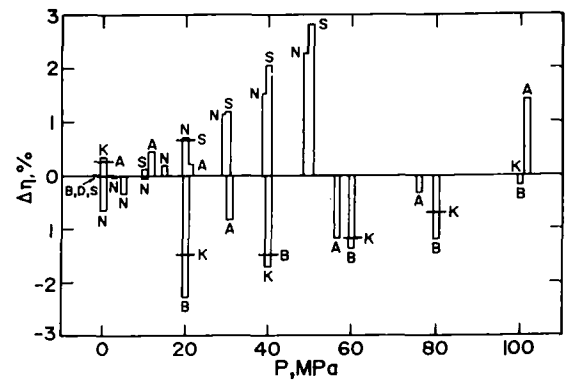

Fig. 4. Deviations $\Delta\eta$ of the literature data for the viscosity of heptane from the correlation of $\eta = a + bP + cP^2$ ($T = 323.15$ K). A, Ref. 4; K, Ref. 5; N, Ref. 6; S, Ref. 7; D, Ref. 8; B, present paper.

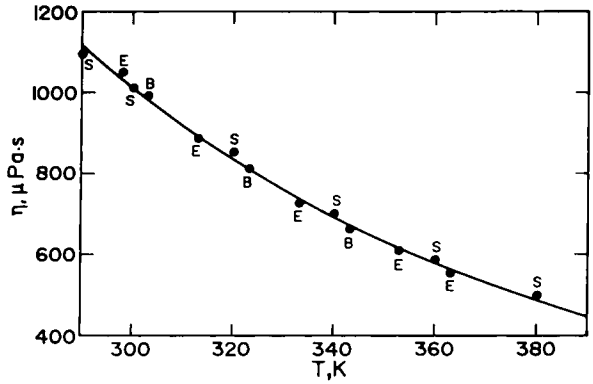

Fig. 5. Variations of dynamic viscosity η of methylcyclohexane versus temperature at $P = 40$ MPa. (—) $\eta = a + (b/T) + (c/T^2)$. E, Ref. 2; S, Ref. 7; B, present paper.

coefficient of determination r^2, 0.9977). Figures 5 and 6 concern methylcylohexane using the same functions for $\eta(T)$ and $\eta(P)$. Figures 7 and 8 show variations of the dynamic viscosity η for the binary mixture heptane + methylnaphthalene as a function of the mole fraction of heptane and the pressure. Figure 9 shows, for each of the two binaries heptane + methylnaphthalene and heptane + methylcyclohexane, variations of the dynamic viscosity η at $P = 40$ MPa and $T = 323.15$ K as a function of the mole fraction of heptane (in Figs. 7 to 9 the solid lines are only guidelines). Similar figures were obtained for the two other binaries. An examination of the

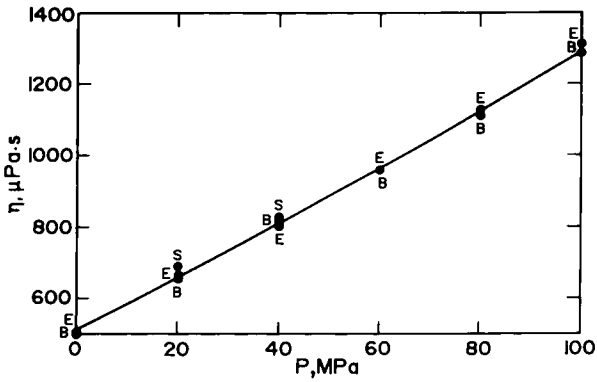

Fig. 6. Variations of dynamic viscosity η of methylcyclohexane versus pressure for various values of temperature. (—) $\eta = a + bP + cP^2$. E, Ref. 2; S, Ref. 7; B, present paper.

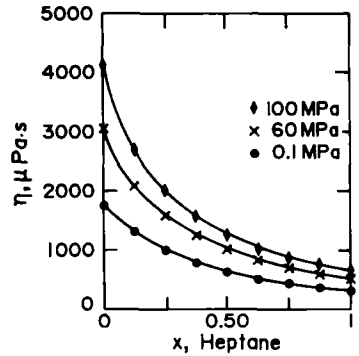

Fig. 7. Binary mixture heptane + methylnaphthalene. Variations of dynamic viscosity η versus mole fraction x of heptane at $T = 323.15$ K for various values of pressure.

figures and tables reveals a general behavior consistent with previous observations made by other authors and by ourselves on different systems. Thus the pressure coefficient of viscosity $(\partial\eta/\partial P)_T$ is greater than zero for all the mixtures and pure substances studied and the shape of variations of viscosity versus pressure is sharply increasing, whereas, on the contrary, the temperature coefficient $(\partial\eta/\partial T)_P$ is always lower than zero. The groups of isotherm and isobar curves are regular. This is also true for density although in the case of isotherm curves a concavity is observed associated

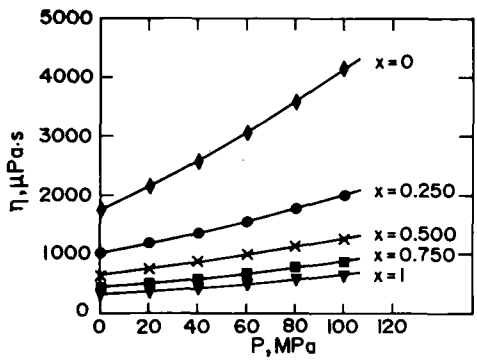

Fig. 8. Binary mixture heptane + methylnaphthalene. Variations of dynamic viscosity η versus pressure at $T = 323.15$ K for various values of mole fraction x of heptane.

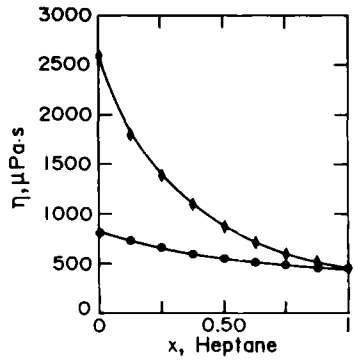

Fig. 9. Variations of dynamic viscosity η versus mole fraction x of heptane at $T = 323.15$ K and $P = 40$ MPa. (◆) Binary mixture heptane + methylnaphthalene. (●) Binary mixture heptane + methylcyclohexane.

with a negative second derivative. The shape is compatible with the logarithmic shape proposed by Tait to model the influence of pressure on $1/\rho$; the latter logarithmic shape is the one used for the extrapolation (see, e.g., Ref. 2). Finally, it should be noted that variations of ρ with T are practically linear, although it should be remembered that in the present research the temperature variation is relatively small, the principal focus being concentrated on pressure variations and on sampling in mole fractions.

All the experimental data obtained in these investigations will be used to test various representative models in which the effects of temperature, pressure and composition are taken into account. A preliminary study seems to indicate that a few methods provide results characterized by an absolute average deviation (AAD) below 10% with a deviation maximum (DM) lower than 25%. In the case of the mixtures, the Grunberg and Nissan ideal-type relationship [9] deserves special mention as it combines simplicity and good performance (AAD = 13.8% and DM = 39.1%), although it has the disadvantage of requiring knowledge of the viscosity of the pure substances for each P, T set. For the nonideal model of Grunberg and Nissan, with one adjustable parameter, AAD = 3.8% and DM = 16.7%, which is a remarkable result. More remarkable is the performance that can be obtained with the self-referencing model (Kanti et al. [10] and Et-Tahir et al. [11]) which can be applied to both pure substances and mixtures and which requires only knowledge of viscosity at 0.1 MPa at a reference temperature T_0. For binary mixtures this model gives AAD = 7.4% and DM = 18%. It appears that these models can be

applied satisfactorily (see also Ref. 11 and Ref. 12), at least in the case where the components are weakly associative and are acceptable in simulating certain industrial projects. Finally, it should also be stressed that the data supplied here could subsequently be included in databases and serve to conduct further tests of conceptual viscosity models much more sophisticated than those discussed in this paper.

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