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Determination of the Viscosity of Various Hydrocarbons and Mixtures of Hydrocarbons Versus Temperature and Pressure

A. Et-Tahir,[1] C. Boned,[1,2] B. Lagourette,[1] and P. Xans[1]

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The dynamic viscosity η and density ρ of 10 pure substances and three binary systems were measured as a function of temperature T (298.15, 313.15, 333.15, 353.15, and 363.15 K) and pressure P ($\leqslant 100$ MPa). The pure substances were toluene, *p*-xylene, *m*-xylene, *o*-xylene, methylcyclohexane, methylnaphthalene, decahydronaphthalene, phenyldodecane, heptamethylnonane, and tetramethylpentadecane (pristane). The three binaries were toluene + tetramethylpentadecane, toluene + methylnaphthalene, and toluene + heptamethylnonane, for molar fractions x of toluene ranging between 0 and 1. The three binaries are highly "contrasted" systems, i.e., systems in which the viscosities of the pure components are very different for each P, T pair. In all, 547 experimental determinations were carried out (279 experimental data for viscosity of the pure substances and 268 data concerning the mixtures: $x \neq 0$ and 1).

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

1. INTRODUCTION

Dynamic viscosity η is a property of general interest since from a fundamental point of view it enables an approach to the liquid state and from an industrial viewpoint it appears in an increasing number of varied and complex domains. We focused more particularly on hydrocarbons

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[1] Laboratoire Haute Pression, Centre Universitaire de Recherche Scientifique, Avenue de l'Université, 64000 Pau, France.

[2] To whom correspondence should be addressed.

occurring in petroleum fluids, but this is only one area of interest among a great number. Of all the thermophysical data, viscosity is one of the most strongly influenced by temperature and pressure. To simulate the behavior of a system with several components, distribution parameters for these components need to be introduced. The viscosity of the mixture therefore depends on these parameters, on the viscosity of the components, and on temperature T and pressure P. Study of viscosity is of the greatest importance in the attempt to master conditions of transport, but despite the considerable research effort, it remains today an incompletely known property. This situation is in part the result of the following two features: first, the investigations already undertaken have used dissimilar approaches, and there is therefore no general synthetic theory of the viscosity of pure substances, and even less so for the viscosity of mixtures; and second, while there is an abundance in the literature of data describing variations of this property versus temperature at atmospheric pressure, studies of variations of viscosity versus pressure are much rarer, particularly in mixtures.

There is an increasingly pressing need for an effective tool for estimating viscosity as a function of temperature, pressure, and the nature and proportions of the substances which make up the mixture, in particular in the petroleum industries. Although there are a number of models to describe variations of η versus temperature at atmospheric pressure in hydrocarbons and mixtures involving hydrocarbons, there are fewer models describing variations with respect to pressure, and they are often limited to precise P, T intervals and to specific groups of hydrocarbons. Study of the literature on the subject indicates that while certain chemical families have now been subjected to relatively extensive study with respect to pressure (for example linear alkanes), other families have been neglected, and there are even fewer data for binary mixtures.

For several years now, our laboratory has been working on subjects involving petroleum fluids and systematically integrating the pressure parameter, whether experimental studies or connected models. These research themes are linked to the flow properties of fluids (considered through dynamic viscosity) and to certain volumetric properties (density, isothermal compressibility coefficient, isothermal expansion coefficient) and thermodynamic properties (speed of sound and phase equilibrium). The research reported in this paper focuses more particularly on dynamic viscosity η. In the Section 2 we present results concerning substances found in reservoir fluids for which there are few data available in the literature. These are certain branched aromatics, naphthenes, and alkanes which appear in the C_{5+} fraction of crude oil (hydrocarbons containing five or more carbon atoms). We have also studied some of the associated binaries. The experimental results obtained have been used to make a critical analysis of various representative models. Finally, one other equally important property which is usually needed to determine η is the density ρ. Knowledge of this quantity along a sufficient number of isotherms and isobars can be used to determine isothermal compressibility and thermal expansion coefficients of fluids. The principal aim of the research reported in this paper concerns the study of variations of viscosity η with pressure and temperature. However, in Section 2 we also indicate the measured values of density ρ as a function of pressure, temperature, and composition for binary mixtures.

2. EXPERIMENTAL TECHNIQUES

2.1. Measurement of Dynamic Viscosity η

A falling-body viscometer described by Ducoulombier et al. [1] was used to measure the viscosity of the samples. At constant pressure P and at a set temperature T the dynamic viscosity of the liquid studied can be deduced from the relationship

$$\eta = K(\rho_s - \rho_L)\,\Delta t \tag{1}$$

in which Δt is the duration of the fall, K a parameter depending on the falling body, ρ_S the density of the falling body (here $\rho_S = 8700\ \mathrm{kg \cdot m^{-3}}$), and ρ_L the density of the system studied. The method used to assess the constant K within the temperature interval ($298.15 \leqslant T \leqslant 363.15$ K) and pressure interval ($P \leqslant 100$ MPa) is described in the literature [1].

2.2. Measurement of Density ρ

Density of each sample was measured between 298.15 and 363.15 K up to a pressure of 40 MPa. An Anton-Paar DMA 45 densimeter combined with an additional DMA 512 cell was used for this purpose. Details of the calibration of this apparatus have been described by Lagourette et al. [2]. Temperature is regulated by a thermostatically regulated oil bath to within ± 0.05 K. The experimental determinations of ρ were carried out at 5-MPa intervals for different temperatures (298.15, 313.15, 333.15, 353.15, and 363.15 K). The values of ρ for all the pressures between 1 and 40 MPa were interpolated using the modified Tait equation (Hogenboom et al.[3]):

$$\frac{1}{\rho(P, T)} = \frac{1}{\rho(0.1, T)} - A \ln\left(1 + \frac{P - 0.1}{B}\right) \tag{2}$$

where P is in MPa and the constants A and B are numerically adjusted. The Tait equation provides an excellent representation of $\rho(P, T)$, the deviations observed between numerical and measured values being less than $0.2\ \mathrm{kg \cdot m^{-3}}$. Beyond the experimental domain, we deduced values of ρ up to 100 MPa by extrapolation. To verify the validity of the extrapolation we tested it with the values provided by Dymond et al. [4] for the pure alkanes and binaries involving alkanes up to $P = 500$ MPa. For example, for isooctane, the parameters A and B were adjusted only with reference to ρ values for which $P \leqslant 40$ MPa. Extrapolation to 460 MPa (in other words, a pressure 10 times higher than the adjustment limit pressure) gave $\rho_{\mathrm{exp}} - \rho_{\mathrm{cal}} = 7\ \mathrm{kg \cdot m^{-3}}$. For $P = 105.2$ MPa, which corresponds approximately to our upper limit for viscosity measurements, we obtain $\rho_{\mathrm{exp}} - \rho_{\mathrm{cal}} = -0.4\ \mathrm{kg \cdot m^{-3}}$. The same procedure was followed for the other pure substances and mixtures. This clearly demonstrates the excellent representativeness of Eq. (2) chosen for extrapolation of ρ.

2.3. Accuracy of Measurement

It should be emphasized here that an error of $10\ \mathrm{kg \cdot m^{-3}}$ in ρ_{L} generates a relative error of 1/800 for viscosity η. We have just seen that extrapolation to 100 MPa of measurements of ρ_{L} carried out between 0.1 and 40 MPa yielded an error markedly less than $10\ \mathrm{kg \cdot m^{-3}}$. Consequently the principal cause of uncertainty concerning the value of viscosity η is the accuracy of the apparatus and not the value used for ρ_{L}. Repeated tests showed that the duration of fall Δt is reproducible to better than 1%. Temperature inside the viscometer is regulated by oil circulation and the homogeneity of the thermal field is ensured by frequent reversals of the viscometer. The resulting accuracy on knowledge of T is estimated at ± 0.5 K. The pressure is determined with an uncertainty of less than ± 0.05 MPa. It follows from the experimental measurements that the value of $(\Delta\eta/\eta)_P$ caused by a temperature variation of 0.5 K can be estimated as being of the order of 1%. Similarly the value $(\Delta\eta/\eta)_T$ due to pressure variation of 0.05 MPa can be estimated at less than 0.05%. Thus, cumulating the various potential errors it can be allowed that viscosity is measured to within 2% in the interval 0.1–100 MPa. As we had indicated [5], this is comparable to the accuracy indicated by other authors for similar apparatus. At atmospheric pressure the viscosity was measured using a classical capillary viscometer. In this case the measured quantity is kinetic viscosity. Different KPG tubes connected to a semiautomatic Lauda S/1 viscometer were used. During the measurements the temperature of the fluid was maintained constant to within 0.1 K. The results are multiplied by the density to give the viscosity η with a relative error better than 1%.

2.4. Characterization of the Samples

The substances used are commercial substances with the following qualities and degrees of purity: toluene (Fluka; purity > 99.5 %, $M = 92.141\ \mathrm{g \cdot mol^{-1}}$), *p*-xylene (Prolabo; purity > 99 %, $M = 106.168\ \mathrm{g \cdot mol^{-1}}$), *m*-xylene (Prolabo; purity > 99 %, $M = 106.168\ \mathrm{g \cdot mol^{-1}}$), *o*-xylene (Prolabo; purity > 99 %, $M = 106.168\ \mathrm{g \cdot mol^{-1}}$), methylcyclohexane (Fluka; purity > 98 %, $M = 98.189\ \mathrm{g \cdot mol^{-1}}$), 1-methylnaphthalene (Fluka; purity > 97 %, $M = 142.201\ \mathrm{g \cdot mol^{-1}}$), decahydronaphthalene or decaline (Fluka; purity > 98 %, $M = 138.254\ \mathrm{g \cdot mol^{-1}}$), 1-phenyldodecane (Aldrich; purity > 97 %, $M = 178.0\ \mathrm{g \cdot mol^{-1}}$), 2,2,4,4,6,8,8-heptamethylnonane (Sigma; purity > 97 %, $M = 226.0\ \mathrm{g \cdot mol^{-1}}$), and 2,6,10,14-tetramethylpentadecane or pristane (Sigma; quality > 97 %, $M = 269.0\ \mathrm{g \cdot mol^{-1}}$). As we will see subsequently data are already available for the first five substances. In particular, toluene has been subjected to precise studies which we used to cinfirm the correct operation of our apparatus. For the four substances which follow toluene our measurements complement, either in temperature or in pressure, the already available data. Finally, for the five other pure substances our measurements appear to be original. From these pure substances we prepared the three following binaries: toluene + pristane, toluene + methylnaphthalene, toluene + heptamethylnonane. It would have been too long and fastidious to study all the possible binary combinations. The choice of these three systems stems from the fact that, with respect to toluene, each of the three other components has a very different viscosity for each *P*, *T* set as the measurement tables will show. For example, at $P = 0.1$ MPa and $T = 298.15$ K we get $\eta = 551\ \mu\mathrm{Pa \cdot s}$ for toluene and $\eta = 6781$, 2948, and $3299\ \mu\mathrm{Pa \cdot s}$ for the other components. It is in this sense that it can be said that these three binaries are highly "contrasted" systems. The contrast would have been much less marked for the binary toluene + xylene ($\eta = 788\ \mu\mathrm{Pa \cdot s}$ for *o*-xylene and $\eta = 580\ \mu\mathrm{Pa \cdot s}$ for *m*-xylene at $P = 0.1$ MPa and $T = 298.15$ K). The mixtures were prepared at atmospheric pressure and ambient temperature by weightings. Denoting the weight fraction of component *i* as p_i and the molar mass as M_i, the molar fraction is calculated by

$$x_i = \frac{p_i/M_i}{\sum_{j=1}^{j=2} (p_j/M_j)} \tag{3}$$

Finally, all the samples were in the liquid state in the pressure and temperature conditions set during the investigations.

3. RESULTS

The measurements were carried out at 298.15, 313.15, 333.15, 353.15, and 363.15 K and at 0.1, 20, 40, 60, 80, and 100 MPa for dynamic viscosity. As we have indicated the necessary density values were extrapolated between 40 and 100 MPa using Eq. (2). The tables present the experimental values of ρ measured every 5 MPa between 0.1 and 40 MPa. Table I gives the results for pure substances. There are 279 experimental P, T sets. Table II gives the results for the mixtures. The molar fraction values for toluene are 0, 0.4932, 0.7449, 0.8975, and 1 for the binary toluene + pristane; 0, 0.2784, 0.6068, 0.8224, and 1 for the binary toluene + methylnaphthalene; and finally, 0, 0.4498, 0.7104, 0.8804, and 1 for the binary toluene + heptamethylnonane. There are 268 experimental P, T sets for values of x different from 0 and 1 (which correspond to pure substances). Figures 1–3 illustrate the experimental results. Figures 1a and b show that the viscosities of *m*-xylene and *p*-xylene have very similar behavior, while *o*-xylene differs from the previous two isomers. It is interesting to note on the subject of the three isomers of xylene ($M = 106.168\ \mathrm{g \cdot mol^{-1}}$) that *p*-xylene and *m*-xylene have very close critical coordinates ($T_c = 616.2$ and 617.1 K and $P_c = 3.51$ and 3.54 MPa, respectively), while they are very different for *o*-xylene ($T_c = 630.3$ K and $P_c = 3.73$ MPa). It can therefore be thought that the critical coordinates P_c, T_c are influential parameters in the viscous behavior of fluids, at least in the liquid state. It should be stressed that while the tables contain only experimental values of ρ, variations of density on the curves are, however, extended to 100 MPa. Figures 2a–d represent variations of ρ and η for the binary toluene + heptamethylnonane as a function of molar fraction for different conditions of pressure and temperature. Figures 3a–d concern the same binary, but this time the variations of ρ and η are represented versus pressure or temperature for different molar fraction values. The "contrasted" aspect of this binary, which has already been emphasized, will be noted. It is even more marked with the binary toluene + pristane. For example, at $T = 298.15$ K and $P = 80$ MPa, $\eta = 19280\ \mu\mathrm{Pa \cdot s}$ for the pristane and $\eta = 948\ \mathrm{Pa \cdot s}$ for the toluene, in other words, a ratio close to 20. Examination of all the figures and tables reveals well-known general behavior trends 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 higher than zero for all the substances tested and the shape of viscosity variations is exponential, while the temperature coefficient $(\partial\eta/\partial T)_P$ is, on the contrary, always less than zero. The bundles of isotherm and isobar curves are regular. This is also true of density, although in this case the isotherm curves (Figs. 1a and 3a) show a downward-facing concavity (hence associated with a negative second

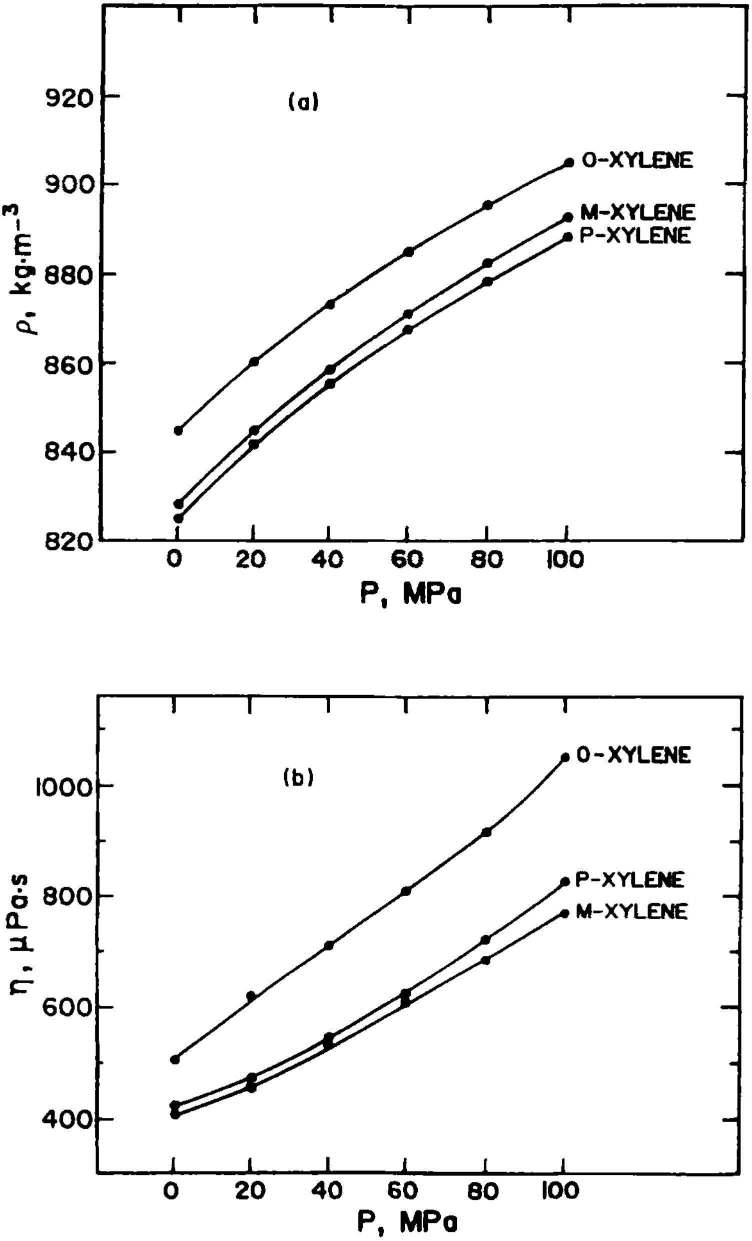


Fig. 1. (a) Variations of density ρ of the three isomers of xylene versus pressure at $T = 333.15$ K. (b) Variations of dynamic viscosity η of the three isomers of xylene versus pressure at $T = 333.15$ K.

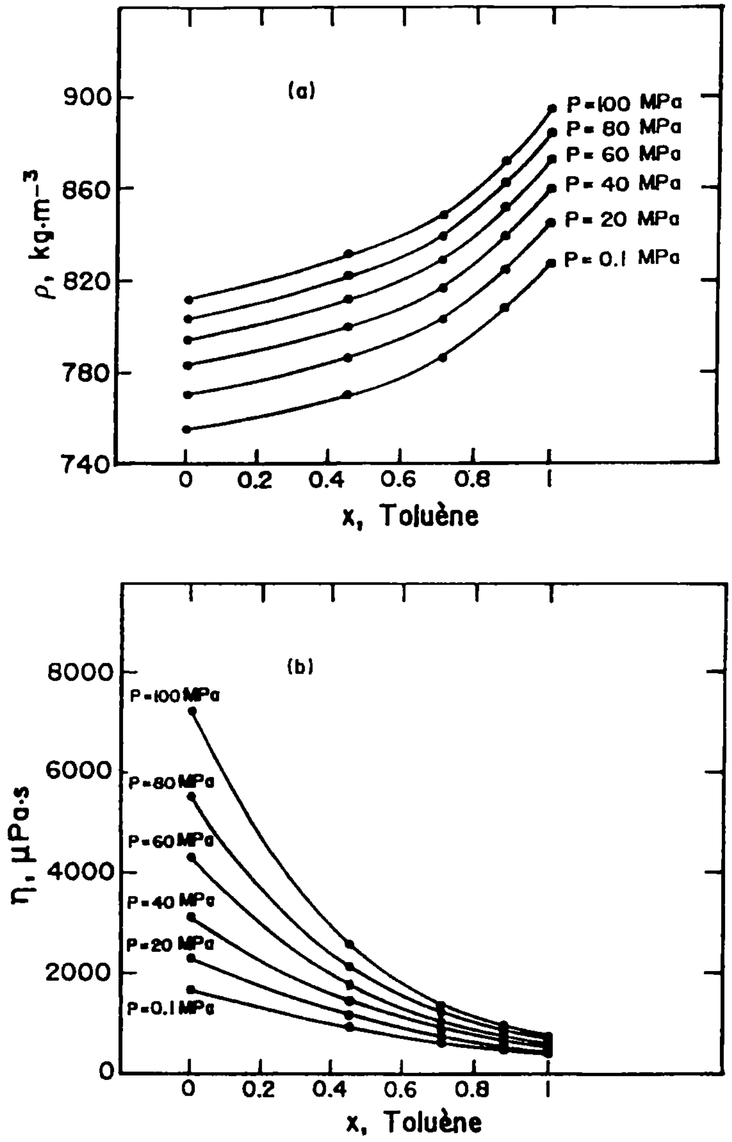


Fig. 2. Binary toluene + heptamethylnonane. (a) Variations of density ρ versus molar fraction x in toluene at $T = 333.15$ K for various values of pressure. (b) Variations of dynamic viscosity η versus molar fraction x in toluene at $T = 333.15$ K for various values of pressure. (c) Variations of density ρ versus molar ratio x in toluene at $P = 40$ MPa for various values of temperature. (d) Variations of dynamic viscosity η versus molar ratio x in toluene at $P = 40$ MPa for various values of temperature.

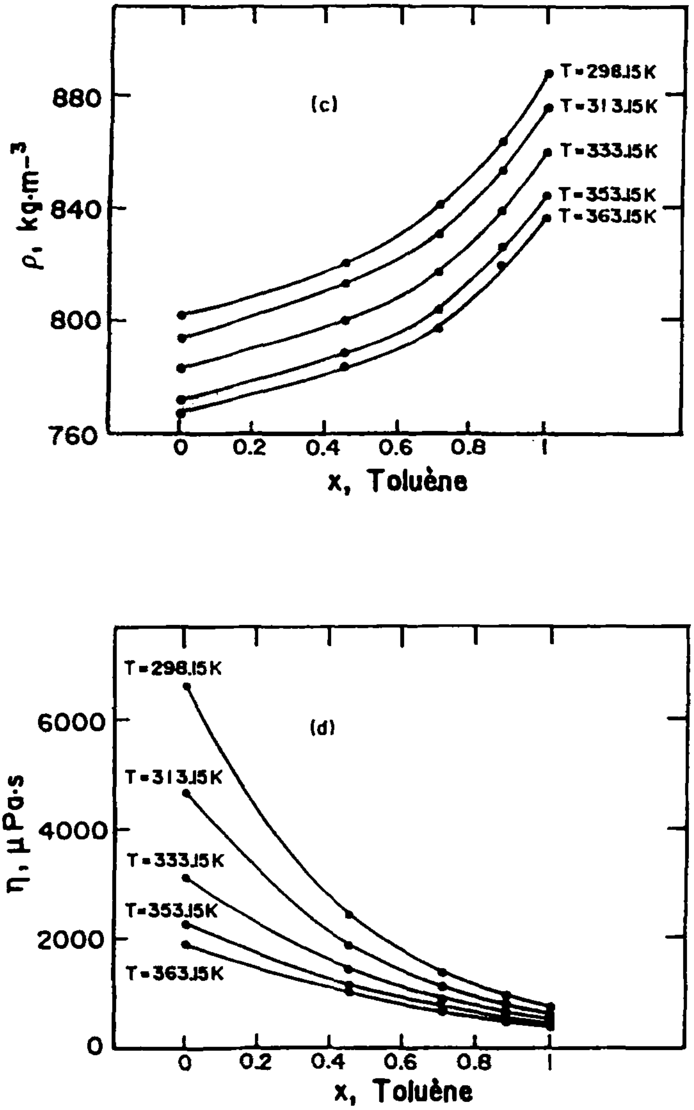
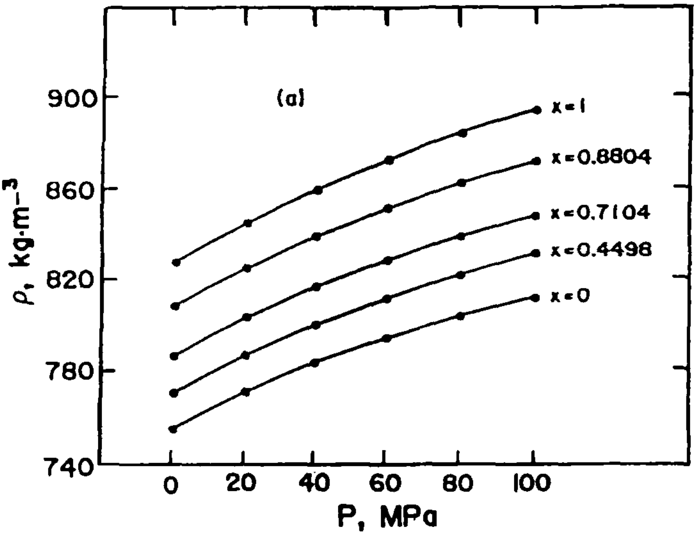


Fig. 2. *(Continued)*

derivative), the shape of wich is compatible with the logarithmic form proposed by Tait to model the influence of pressure on $1/\rho$. It will also be observed that variations of ρ versus T are practically linear, as shown in Fig. 3c.



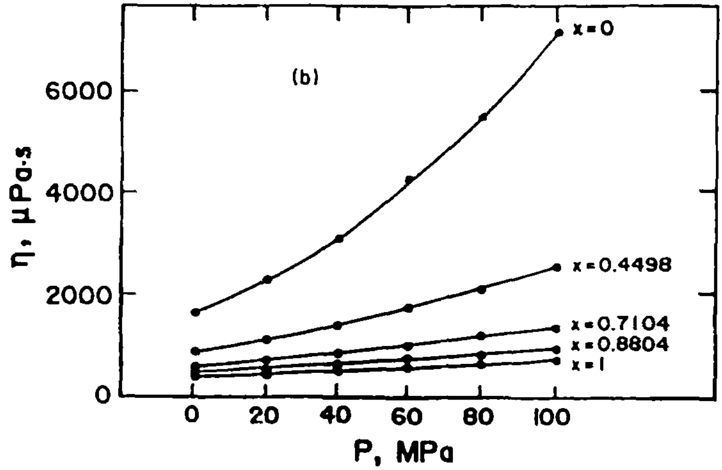


Fig. 3. Binary toluene + heptamethylnonane. (a) Variations of density ρ versus pressure; at $T = 333.15$ K, for various values of the molar fraction in toluene. (b) Variations of dynamic viscosity η versus pressure, at $T = 333.15$ K, for various values of the molar fraction in toluene. (c) Variations of density ρ versus temperature, at $P = 40$ MPa, for various values of the molar fraction in toluene. (d) Variations of dynamic viscosity η versus temperature, at $P = 40$ MPa, for various values of the molar fraction in toluene.

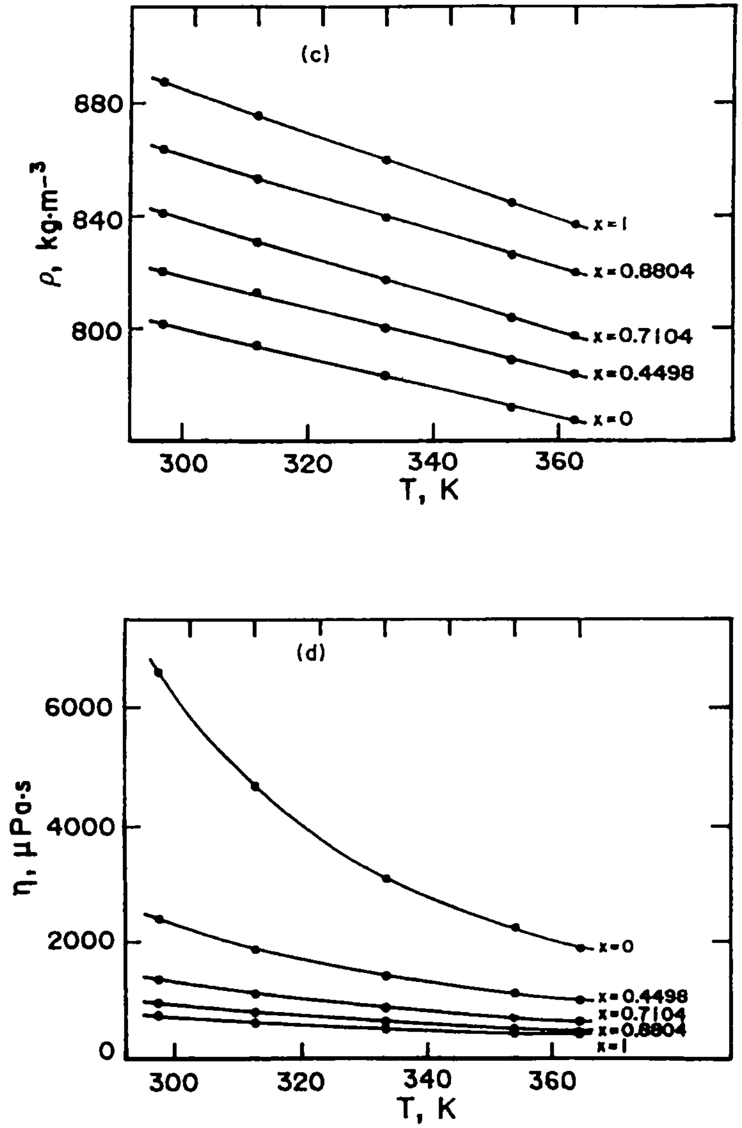


Fig. 3. *(Continued)*

It should be indicated that in certain cases we were able to compare our determinations with those of other authors. For toluene it is possible to refer to the recent data of Krall et al. [6], which appear very accurate but are limited to 30 MPa. It is also possible to refer to the values deter-

Table I. Variations of Dynamic Viscosity η and Density ρ of Pure Substances Versus Pressure and Temperature

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
	Decaline				
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	877.4	847.1	850.8	835.3	825.3
5	880.3	869.0	854.5	839.4	829.4
10	883.4	872.2	858.2	843.5	833.5
15	885.9	875.6	861.3	847.2	837.6
20	888.7	878.6	865.0	850.7	841.4
25	891.5	881.7	867.7	854.4	844.8
30	894.0	884.4	871.0	857.4	848.5
35	896.4	886.7	874.0	860.7	853.2
40	898.4	889.7	876.3	863.7	855.2
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	2374	1764	1314	1003	883
20	3807	2406	1863	1384	1175
40	3797	2978	2200	1696	1507
60	4682	3650	2731	2076	1840
80	5853	4458	3300	2470	2130
100	7132	5332	3908	2916	2590
	Heptamethylnonane				
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	778.3	767.9	754.9	741.9	735.2
5	781.7	772.0	759.2	746.3	739.6
10	785.2	775.4	763.2	750.7	744.4
15	788.3	779.1	766.9	754.7	748.8
20	791.1	782.5	770.9	758.4	753.1
25	794.2	785.5	774.2	762.4	756.8
30	796.9	788.5	777.5	765.8	760.8
35	799.7	791.1	780.8	769.4	764.2
40	802.0	794.1	783.4	772.3	767.5
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	3299	2383	1658	1243	1092
20	4674	3356	2287	1700	1428
40	6595	4665	3102	2249	1894
60	9534	6376	4287	2938	2528
80	12970	8654	5517	3785	3230
100	18110	12080	7218	4781	4274

Table I. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
	Methylcyclohexane				
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	765.0	751.8	734.3	715.7	707.2
5	769.1	756.8	739.3	721.7	713.5
10	773.5	761.1	744.6	727.3	719.9
15	777.0	765.2	748.9	732.7	725.5
20	780.7	769.5	753.5	737.6	731.1
25	784.1	772.8	757.5	742.3	735.8
30	787.2	776.5	761.4	746.5	740.8
35	790.6	779.8	765.3	751.1	745.0
40	793.6	783.1	768.9	754.7	749.0
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	687	568	453	371	339
20	859	734	601	499	459
40	1048	885	725	606	553
60	1257	1064	866	722	659
80	1488	1252	1016	844	769
100	1756	1456	1184	979	899
	Methylnaphthalene				
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	1012.9	1001.4	986.5	971.8	963.7
5	1015.4	1004.2	989.3	975.3	966.9
10	1018.3	1006.7	992.7	978.5	970.4
15	1020.5	1009.5	995.2	981.6	973.9
20	1022.7	1012.3	998.3	984.7	977.1
25	1025.5	1014.7	1001.0	987.8	980.2
30	1027.6	1017.4	1003.7	990.6	983.3
35	1030.1	1019.5	1006.1	993.6	986.4
40	1032.2	1021.9	1008.4	996.0	988.8
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	2948	2130	1488	1113	976
20	3429	2568	1856	1426	1270
40	4149	3035	2135	1684	1471
60	5008	3690	2545	1953	1700
80	6173	4384	2995	2227	1951
100	7382	5128	3465	2568	2255

Table I. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
	1-Phenyldodecane				
Density (kg · m^{-3}) at P (MPa)					
0.1	851.7	841.6	828.1	812.8	806.7
5	854.8	845.0	832.2	816.6	810.5
10	857.7	848.1	835.3	820.0	814.3
15	860.5	850.5	838.7	823.8	817.8
20	863.0	853.6	841.4	827.2	821.5
25	864.6	856.6	844.4	830.2	824.9
30	867.5	859.3	847.1	832.9	828.3
35	869.6	862.0	850.0	835.9	831.3
40	872.0	864.3	852.7	838.9	834.4
Viscosity (μPa · s) at P (MPa)					
0.1	4815	3363	2272	1634	1421
20	6210	4258	2846	2033	1763
40	7936	5369	3476	2477	2116
60	9675	6578	4276	2920	2398
80	11900	8287	5083	3489	2924
100	15410	9654	6075	4198	3404
	2,6,10,14-Tetramethylpentadecane (pristane)				
Density (kg · m^{-3}) at P (MPa)					
0.1	777.6	767.3	753.9	740.6	734.3
5	780.8	771.0	757.6	744.7	738.3
10	784.2	777.4	761.6	748.8	742.5
15	787.0	777.5	765.0	752.8	746.5
20	790.2	780.8	768.3	756.2	750.9
25	793.2	783.5	771.3	759.9	754.6
30	795.6	786.5	774.6	763.2	758.3
35	798.4	789.2	777.9	766.5	761.3
40	800.7	791.8	780.5	769.5	764.3
Viscosity (μPa · s) at P (MPa)					
0.1	6781	4422	2896	1981	1699
20	7751	5048	3786	2153	1807
40	10550	6874	4148	2793	2351
60	14420	9106	5361	3561	2935
80	19280	11570	6868	4408	3676
100		16650	8807	5474	4443

Table I. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
	Toluene				
Density (kg · m^{-3}) at P (MPa)					
0.1	860.8	846.1	827.5	808.3	798.7
5	864.6	850.5	831.8	813.6	804.1
10	868.4	854.6	836.8	818.7	809.8
15	871.9	859.0	840.9	823.4	814.9
20	875.0	862.7	845.2	827.8	819.9
25	878.4	866.0	848.9	832.4	824.6
30	881.5	869.4	852.5	836.4	829.0
35	884.6	872.4	856.5	840.7	833.0
40	887.3	875.7	859.8	844.4	836.6
Viscosity (μPa · s) at P (MPa)					
0.1	551	474	390	326	301
20	635	527	456	374	346
40	746	624	513	434	396
60	857	712	580	495	454
80	948	801	662	543	492
100	1066	902	741	607	565
	m-Xylene				
Density (kg · m^{-3}) at P (MPa)					
0.1	858.8	845.8	828.4	811.2	802.2
5	861.9	849.8	832.5	815.9	807.3
10	865.4	853.3	836.8	820.6	812.4
15	868.6	857.0	840.9	825.0	817.1
20	871.7	860.4	844.9	829.1	822.2
25	875.2	863.8	848.2	833.4	826.2
30	878.2	867.1	851.9	837.1	830.6
35	881.6	870.1	855.5	841.1	834.2
40	884.0	873.1	858.8	844.7	837.9
Viscosity (μPa · s) at P (MPa)					
0.1	580	493	407	342	315
20	678	572	455		
40	783	667	538	463	
60	901	755	608	497	
80	1003	851	684	569	
100	1173	957	768	634	

Table I. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
	o-Xylene				
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	873.8	861.4	844.9	827.6	819.2
5	877.0	865.1	848.6	832.3	823.6
10	880.8	868.6	853.0	836.7	828.4
15	884.0	872.3	856.8	840.8	832.8
20	886.8	875.7	860.5	844.8	837.2
25	889.9	878.8	863.8	848.9	841.3
30	892.7	881.8	867.4	852.6	845.6
35	895.4	884.5	870.8	856.2	849.3
40	897.8	887.4	873.4	859.5	853.0
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	758	627	504	416	381
20	902	768	619	498	453
40	1036	887	709	588	533
60	1224	1014	809	656	614
80	1366	1129	916	739	688
100	1583	1296	1051	834	766
	p-Xylene				
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1		842.2	825.2	808.6	799.7
5		846.6	829.6	813.3	804.4
10		850.7	833.5	818.1	809.5
15		854.7	837.6	822.8	814.2
20		858.4	841.7	827.1	819.0
25		861.2	845.3	831.5	823.3
30		864.5	849.0	835.2	828.0
35		867.2	852.6	839.1	832.0
40		870.2	855.5	842.8	835.6
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1		526	425	351	
20		591	474		
40		694	556	477	
60		801	626	517	
80			721	585	
100			828	665	

Table II. Variations of Dynamic Viscosity η and Density ρ of Binaries Versus Pressure, Temperature, and Composition (p, Toluene Weight Fraction; x, Toluene Molar Fraction)

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
Toluene + 2,6,10,14-tetramethylpentadecane (pristane) ($p = 0.75$, $x = 0.8975$)					
Density (kg·m^{-3}) at P (MPa)					
0.1	832.0	818.8	801.9	784.8	776.3
5	835.8	823.1	806.6	789.5	781.6
10	839.3	827.2	811.0	794.3	786.7
15	842.8	831.0	815.3	799.0	791.5
20	845.9	834.7	819.0	803.3	796.5
25	849.4	838.0	822.7	807.3	800.5
30	852.4	841.0	826.0	811.0	804.9
35	855.2	844.4	829.6	814.7	808.5
40	858.2	847.3	832.9	818.0	811.9
Viscosity (μPa·s) at P (MPa)					
0.1	7820	6430	5160	4280	3970
20	9460	8010	6420	5100	4650
40	11090	9340	7430	6050	5450
60	12740	10700	8620	6990	6380
80	14460	12100	9760	7920	7270
100	16350	13630	11000	8950	8190
Toluene + 2,6,10,14-tetramethylpentadecane (pristane) ($p = 0.50$, $x = 0.7449$)					
Density (kg·m^{-3}) at P (MPa)					
0.1	813.7	800.9	786.1	770.7	763.1
5	817.2	804.9	790.8	775.4	767.9
10	820.4	809.0	794.8	779.8	772.6
15	823.8	812.4	798.8	784.8	777.4
20	827.0	815.8	802.5	788.9	782.1
25	830.1	819.1	806.2	792.5	786.1
30	833.1	822.1	809.1	796.2	790.1
35	835.5	825.1	812.8	800.0	793.8
40	838.2	827.8	815.7	803.1	797.4
Viscosity (μPa·s) at P (MPa)					
0.1	1263	974	755	599	547
20	1494	1182	918	719	647
40	1790	1417	1081	857	763
60	2128	1718	1263	997	901
80	2551	1948	1475	1152	1024
100	2920	2280	1697	1305	1149

Table II. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
Toluene + 2,6,10,14-tetramethylpentadecane (pristane) ($p = 0.25$, $x = 0.4932$)					
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	794.8	783.3	768.6	755.9	749.4
5	798.3	787.4	773.3	760.6	753.8
10	801.4	791.1	777.0	765.0	758.6
15	804.9	794.5	781.0	769.4	763.0
20	807.7	797.9	784.4	773.4	767.4
25	810.8	800.9	787.7	776.8	771.1
30	813.5	803.6	790.7	779.8	774.8
35	815.9	806.6	794.0	783.1	777.8
40	818.6	809.5	796.9	786.1	780.4
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	2255	1658	1202	924	
20	2867	2128	1525	1167	1049
40	3664	2675	1911	1426	1265
60	4425	3294	2338	1736	1540
80	5596	3981	2745	2043	1788
100	6956	4978	3306	2431	2134
Toluene + 1-methylnaphthalene ($p = 0.75$, $x = 0.8224$)					
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	894.8	881.6	864.0	846.3	837.1
5	898.3	885.7	868.1	851.0	842.2
10	901.8	889.1	872.5	855.4	847.0
15	904.9	892.9	876.2	859.8	851.8
20	908.1	896.3	880.2	863.9	856.5
25	911.2	899.3	883.6	867.9	860.6
30	914.0	902.7	887.3	871.6	864.6
35	916.7	905.7	890.6	875.6	868.3
40	919.4	908.7	893.9	878.9	871.9
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	731	608	491	408	372
20	877	725	576	465	428
40	995	827	656	545	492
60	1140	941	755	615	553
80	1294	1064	836	693	627
100	1440	1188	947	766	703

Table II. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
Toluene + 1-methylnaphthalene ($p = 0.50$, $x = 0.6068$)					
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	926.6	913.9	897.2	880.1	871.5
5	929.4	917.3	900.6	884.2	875.6
10	933.0	920.5	904.6	888.3	879.8
15	935.3	923.9	908.4	892.1	883.9
20	938.6	927.3	912.1	895.9	888.3
25	941.8	930.0	915.5	899.6	892.4
30	944.2	933.1	918.8	902.9	896.1
35	947.0	935.8	921.8	906.6	899.5
40	949.4	938.8	924.4	909.6	903.1
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	1036	841	657	534	487
20	1223	993	775	613	565
40	1435	1141	889	710	649
60	1639	1310	1004	803	706
80	1915	1475	1133	913	832
100	2115	1693	1274	1032	924
Toluene + 1-methylnaphthalene ($p = 0.20$, $x = 0.2784$)					
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	974.0	966.0	946.3	930.3	922.7
5	976.8	969.1	949.4	934.1	926.2
10	980.0	971.9	952.9	937.5	930.0
15	982.5	975.0	956.0	941.0	933.5
20	985.0	978.1	959.0	944.1	937.3
25	988.2	980.5	961.8	947.5	940.8
30	990.6	983.2	964.8	950.6	944.2
35	993.1	985.6	967.5	954.0	947.3
40	995.2	988.6	970.1	957.0	950.3
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	1646	1285	967	771	690
20	2070	1730	1322	1042	939
40	2412	2026	1551	1207	1071
60	2771	2406	1797	1381	1243
80	3240	2708	2065	1584	1408
100	3789	3168	2352	1787	1592

Table II. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
Toluene + 2,2,4,4,6,8,8-heptamethylnonane ($p = 0.75$, $x = 0.8804$)					
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	837.0	824.7	808.1	790.9	782.7
5	841.0	829.0	812.4	796.0	787.8
10	844.8	832.8	817.1	801.0	792.9
15	848.3	836.8	821.1	805.7	797.9
20	851.4	840.5	825.2	810.1	803.0
25	854.9	843.9	828.8	814.4	807.3
30	858.0	847.2	832.5	818.4	811.7
35	861.0	850.2	836.1	822.4	815.6
40	863.7	853.5	839.3	826.0	819.6
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	684	580	469	389	357
20	830	678	547	440	397
40	956	800	645	519	465
60	1105	913	757	607	548
80	1273	1038	846	696	633
100	1431	1188	957	783	699
Toluene + 2,2,4,4,6,8,8-heptamethylnonane ($p = 0.50$, $x = 0.7104$)					
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	815.7	802.9	786.4	770.1	762.3
5	819.2	807.0	790.8	775.1	767.4
10	823.0	810.7	795.2	779.8	772.4
15	826.5	814.8	799.2	784.2	777.2
20	829.6	818.1	803.5	788.6	781.9
25	832.7	821.5	807.1	792.9	786.2
30	835.4	824.8	810.8	796.6	790.5
35	838.5	827.5	814.1	800.5	794.2
40	841.2	830.8	817.0	803.8	797.3
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	946	780	610	499	458
20	1144	933	731	591	483
40	1368	1113	877	710	646
60	1670	1335	1031	841	758
80	1943	1541	1209	969	863
100	2272	1818	1364	1114	1000

Table II. *(Continued)*

	Temperature (K)				
	298.15	313.15	333.15	353.15	363.15
Toluene + 2,2,4,4,6,8,8,-heptamethylnonane ($p = 0.25$, $x = 0.4498$)					
Density ($kg \cdot m^{-3}$) at P (MPa)					
0.1	796.2	786.4	770.6	757.3	750.2
5	799.6	790.4	774.7	762.0	754.9
10	803.1	793.8	779.0	766.4	760.0
15	806.2	797.6	783.0	770.8	764.7
20	809.4	801.3	786.7	774.8	769.1
25	812.4	804.3	790.4	778.8	773.1
30	815.2	807.6	794.0	782.4	777.4
35	817.9	810.3	797.3	786.1	780.8
40	820.6	813.2	800.2	789.0	784.1
Viscosity ($\mu Pa \cdot s$) at P (MPa)					
0.1	1499	1196	916	722	650
20	1908	1505	1146	914	822
40	2424	1881	1430	1127	1008
60	2987	2366	1759	1369	1233
80	3739	2862	2119	1649	1477
100	4666	3545	2562	2053	1740

mined by Kashiwagi and Makita [7], Dymond et al. [8], and Santos and Nieto de Castro [9]. For the xylene isomers, there are the values determined by Kashiwagi and Makita [7], which go up to 110 MPa and are limited to 348.15 K, and the values of Mamedov et al. [10], which are limited to 40 MPa. Finally, in the compilation published by Stephan and Lucas [11] there are also a few values for methylcyclohexane, limited to 50 MPa. In all these cases, where comparison was possible, there was agreement between our own determinations to within the margin of experimental error. As examples Figs. 4a and b refer to toluene and Figs. 5a and b to *m*-xylene.

Finally, it is well-known that on an isobar the behavior of viscosity as a function of temperature is generally correctly described using laws obtained by modification of Andrade's exponential representation [12].

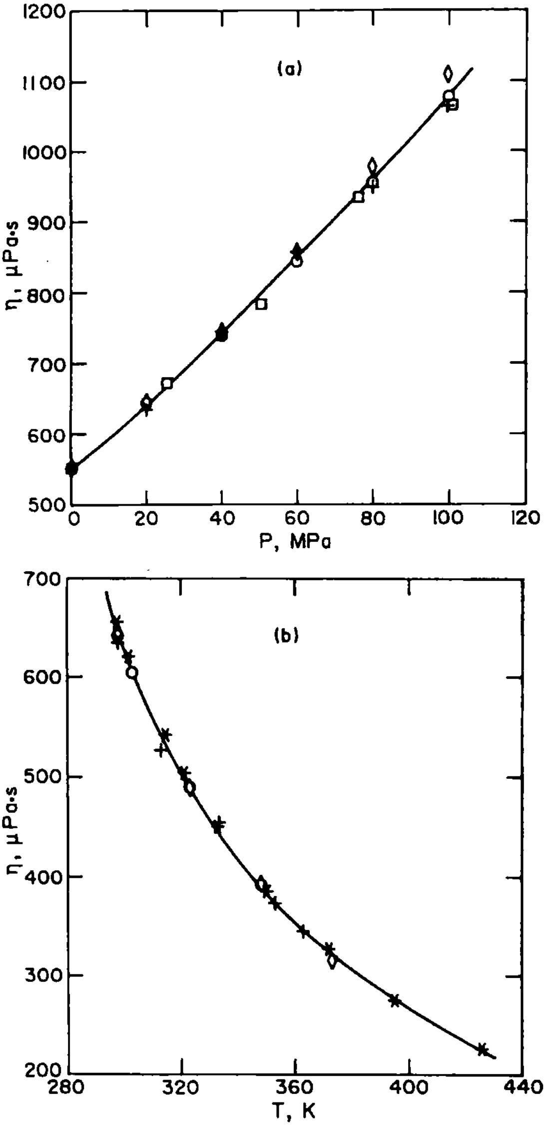


Fig. 4. Viscosity of toluene. Comparison with other determinations. (a) Variations of dynamic viscosity η versus pressure, at $T = 298.15$ K. (+) This work; (□) Dymond et al. [8]; (◇) Santos and Nieto de Castro [9]; (○) Kashiwagi and Makita [7]. (b) Variations of dynamic viscosity η versus pressure, at $P = 20$ MPa. (+) This work; (∗) Krall et al. [6]; (◇) Santos and Nieto de Castro [9]; (○) Kashiwagi and Makita [7].

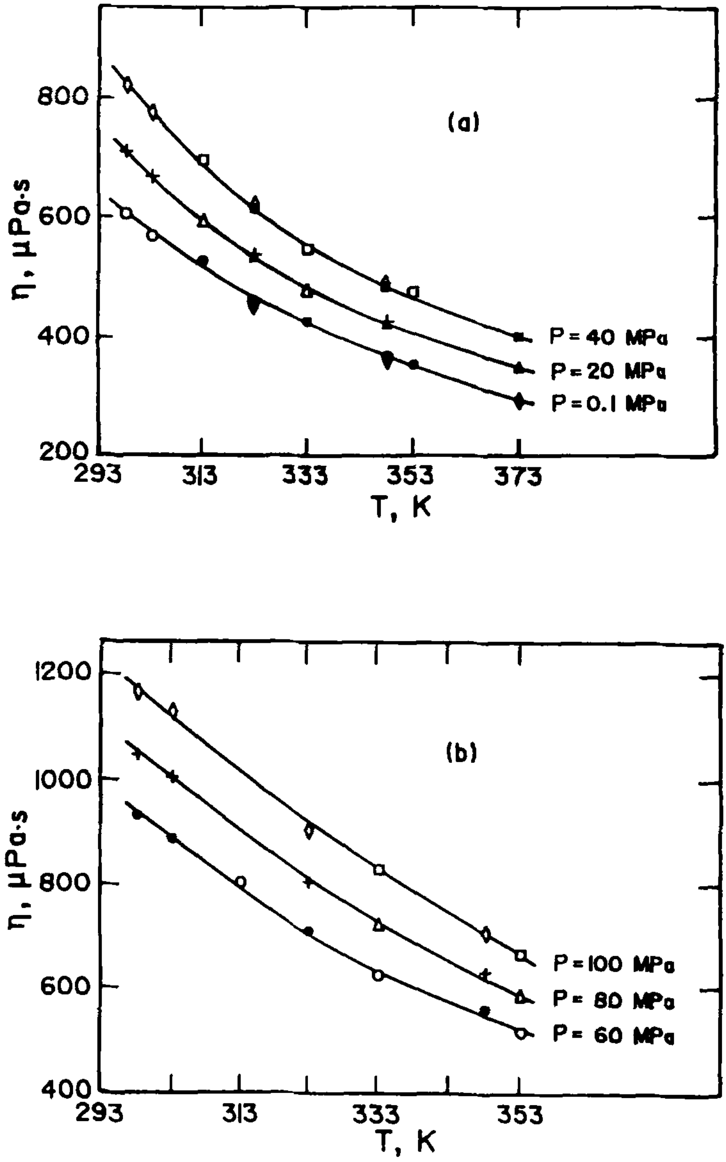


Fig. 5. Viscosity of *m*-xylene. Comparison with other determinations. (a) Variations of dynamic viscosity η versus temperature between 0.1 and 40 MPa. (□, △, ○) This work; (◇, +, ●) Kashiwagi and Makita [7]; (◆, ▲, ■) Mamedov et al. [10]. (b) Variations of dynamic viscosity η versus temperature between 60 MPa and 100 MPa. (□, △, ○) This work; (◇, +, ●) Kashiwagi and Makita [7].

This is the case, for example, of the formulation

$$\eta = \exp\left[A + \frac{B}{C-T}\right] \tag{4}$$

On the basis of the experimental data we determined for each isobar and for each of the samples the constants A, B, and C. For example, the accuracy obtained on all 279 experimental P, T sets for the pure substances was less than the experimental uncertainty, i.e., 2%. The most unfavorable case is that of heptamethylnonane, which presents an isobar on which can be found the maximum deviation for all the P, T sets, that is, 1.9% at $P = 100$ MPa. By comparison the maximum deviation for methylcyclohexane is 0.3%, obtained this time at $P = 40$ MPa. The representation is therefore highly effective but its major drawback lies in the fact that a set of constants A, B, C has to be calculated for each isobar of each substance or binary. There do not appear to be, for a given substance or binary, any regular variations of A, B, C with pressure and molar fraction and, a fortiori, when moving from one sample to another. This considerably reduces the interest of the representation which is useful above all for interpolation between two temperatures. But no character of generality can be drawn from it in any satisfactory way.

4. ANALYSIS OF THE RESULTS

This article reports experimental results concerning density ρ and dynamic viscosity η of certain pure substances and some mixtures involving these substances—these mixtures generally being sharply "contrasted"—as a function of temperature (298.15 to 363.15 K), pressure (up to 100 MPa), and molar fraction. The viscous behavior of the systems was analyzed, considering various possible forms of representation of varying degrees of difficulty in their implementation and theoretical justification. The reader will find all the details of our analysis given by Et-Tahir [13]. One initial consequence of the study was to show that the introduction of the pressure parameter did not alter the performance of the methods tested, this remark resulting from observations made for each model taken separately. This remark receives some confirmation in a recent paper by Chhabra [14]. He compared the values generated by his model with 2125 experimental points concerning only atmospheric pressure and the temperature interval 278.15 to 333.15 K. The average deviation observed on the entire base is 7%, with more satisfactory descriptions for some binaries than for others; for example, 2% for the binary *n*-octane + *n*-decane (very small asymmetry) and 28.5% for the binary *n*-hexane + *n*-hexadecane (more asymmetric but much less contrasted than our binaries). Although these comparisons were performed with reference to viscosity values measured only at $P = 0.1$ MPa, it can be seen that although they are considered satisfactory by their authors, they do not exhibit any manifest superiority with respect to those relevant to our analysis in which the effects of temperature, pressure, and composition are simultaneously dealt with. Another important point is that several of the methods considered provide results characterized by absolute average deviations of less than 10% and maximum deviations less than 25%. On this subject, while the data in the literature generally include the average absolute deviation, quite surprisingly the maximum deviation is rarely specified, and yet it also gives important information on the predicting ability of the method considered. In the case of mixtures the ideal-type relationship of Grunberg and Nissan [15] deserves special mention, as it combines simplicity and good performance, though it does have the disadvantage of requiring knowledge of viscosity of the pure substances for each P, T set. The average absolute deviation was 7.7% and the maximum deviation was 24.7%. Even more remarkable is the performance of the self-referencing model [16], which can be applied equally well to pure substances as to mixtures and which requires only knowledge of the viscosity at 0.1 MPa for one reference temperature, T_0 (for the binaries the average absolute deviation was 6.9% and the maximum deviation was 22.8%). Moreover, it lends itself well to combination with mixing rules, in which case it is enough to know the two viscosities at 0.1 MPa, at temperature T_0, of the two pure components. For all the binaries an average absolute deviation of 9.5% was observed with a maximum deviation of 41.8%. As regards the corresponding-states model [17], one notes the major influence of the choice of reference (which is certainly true for the different versions of the model which are found in the literature) for results which are not very satisfactory compared to those of other methods (the maximum deviation can reach 70%). Finally the Bloomfield–Dewan–Flory excess viscosity model (see, e.g., Ref. 5) and the group contribution model (e.g., Ref. 18), appear to provide any improvement with respect to ideality only in the case of highly contrasted binaries. For the excess viscosity model we obtained an average absolute deviation of 8.0% (maximum deviation, 39.1%) and for the group contribution method we obtained 8.3% (and 27.5%).

From a practical point of view, the usefulness of developing excessively sophisticated models, which are therefore complex and difficult to implement, and which one encounters with increasing frequency, is not immediately apparent. They do not generally lead to an easier description of the phenomenon, often because of the introduction of numerous adjustable parameters. We could quote, for example, the model of Wang et al. [19], which is based on free volume, but needs four adjustable parameters per pure substance and two extra interaction parameters for each binary. In another area, let us mention the recent developments concerning the use of an equation of state to describe the viscosity and thermal conductivity of pure substances [20] which requires five adjustable parameters per substance. The interest of these investigations is considerable in the sense that they can lead to conceptual progress, but in the present state of affairs they are relatively uncompetitive from a practical point of view.

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