670 J. Chem. Eng. Data **1994**, *39*, 670–672

Viscosity of Several Liquid Hydrocarbons in the Temperature Range 298–453 K at Pressures up to 200 MPa

Ulrich G. Krahn and Gerhard Luft*

Institut für Chemische Technologie, Technische Hochschule Darmstadt,
Petersenstrasse 20, 64287 Darmstadt, Germany

The viscosity of liquid 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, 2,2,4,4,6,8,8-heptamethylnonane, squalane, polyisobutylene ($M = 500$ g/mol), ethylbenzene, and 1,2-diphenylethane at elevated pressures was determined with a rolling ball viscometer. The viscosity measurements were performed at 298, 353, and 453 K and pressures up to 200 MPa with an accuracy of ±2%. The results were described by an empirical equation as a function of pressure and temperature.

Introduction

The viscosity of hydrocarbons under high pressure is of great importance for industrial processes involving polymerization or oil production. Measurements on branched-chain compounds provide additional information on the influence of molecular shape on the viscosity of nonassociating compounds.

This paper reports part of a program on viscosity measurements of ethene (*1*), pure hydrocarbons, and their mixtures (*2*). The aim of the study is to evaluate models or empirical equations which are able to describe the dependence of the viscosity on pressure, temperature, concentration, and molar mass of the hydrocarbon component (*2*).

Experimental Section

Materials. The manufacturer and the purity of the hydrocarbons used are given in Table 1. The hydrocarbons were filtered and degassed prior to use.

Viscosity Measurements. The viscosity was measured with a rolling ball viscometer, constructed by Stanislawski and Luft (*1, 2*). This viscometer allows measurements over a wide range of viscosities.

It consists of a Schott KPG-tube installed in a steel frame, which also holds two pairs of coils and an electromagnet fastened on the open end of the glass tube. These two pairs of coils define the positions of the start and stop of the measurement. After a magnetic steel ball has been put into the tube, the steel frame is placed in a high-pressure autoclave and the autoclave is completely filled with the sample.

The rolling time is detected inductively. Both measuring coils consist of a high-frequency oscillating part and a sensing part. Since they are connected in series opposition, the effect of the sensing coils cancels out in the absence of the ball.

To start the experiment, the viscometer is tilted in the measuring position and the electromagnet is released. After a constant velocity is reached, the ball passes the first pair of coils and the inductive signal starts the timer. At the end of the measuring distance the timer is stopped by the signal from the second pair of coils.

At the beginning of a series of measurements the viscometer was calibrated with decane in the total range of temperature and pressure, using the viscosity values of decane published by Ducoulombier (*3*) and by Naake (*4*). Naake measured the viscosity of decane and of mixtures of decane and methane with an oscillating disk viscometer. The viscosities used are given in Table 2.

The temperature in the autoclave was measured radially and axially by two NiCr/Ni thermocouples with an accuracy of ±0.2 K. The pressure could be determined by a calibrated strain gauge pressure sensor with an accuracy of ±0.3%.

Each measuring point was determined ca. 10 times. The standard deviation of the rolling times is ±0.3%.

The rolling times were evaluated by a method of Hubbard and Brown (*5*). By their analysis of the dimensions of all parameters influencing the rolling times in a rolling ball viscometer, a resistance factor (f) was defined, which is dependent on the diameters of the ball and tube, the measuring distance, the rolling time, the angle of inclination, the density of the ball, and the density and viscosity of the measured substance. For Reynolds numbers (Re) smaller than 50, the dependence of $\log(f)$ on the incline of the viscometer was found to be a linear function of $\log(Re)$ having a slope of -1. For this reason the calibration curves only depended on the temperature and the pressure.

The scattering of the measurements was less than 1%. The total uncertainty of the viscosity values obtained was estimated to be 2% (*1, 2*), taking into account the accurcy of the literature values used in the calibration.

Results and Discussion

Table 3 shows the measured viscosity of 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, 2,2,4,4,6,8,8-heptam-

Table 1

hydrocarbon	manufacturer	purity/%
2,3,4-trimethylpentane	Aldrich-Chemie GmbH & Co. KG	99
2,2,4-trimethylpentane	Aldrich-Chemie GmbH & Co. KG	>99
2,2,4,4,6,8,8-heptamethylnonane	Aldrich-Chemie GmbH & Co. KG	98
squalane	Aldrich-Chemie GmbH & Co. KG	99
polyisobutylene ($M = 500$ g/mol)	Polysciences Limited	
ethylbenzene	Aldrich-Chemie GmbH & Co. KG	>99
1,2-diphenylethane	Aldrich-Chemie GmbH & Co. KG	99

0021-9568/94/1739-0670$04.50/0

Table 2. Viscosity η of Decane from Naake (*4*)

T/K	P/MPa	η/(mPa·s)	T/K	P/MPa	η/(mPa·s)
298.15	0.1	0.866	393.15	0.1	0.317
298.15	20.0	1.070	393.15	20.0	0.406
298.15	40.0	1.319	393.15	40.0	0.490
323.15	0.1	0.615	393.15	60.0	0.575
323.15	20.0	0.770	393.15	80.0	0.668
323.15	40.0	0.933	393.15	100.0	0.760
323.15	60.0	1.108	393.15	120.0	0.866
323.15	80.0	1.300	393.15	140.0	0.971
323.15	100.0	1.503	393.15	160.0	1.085
353.15	0.1	0.450	393.15	180.0	1.203
353.15	20.0	0.565	393.15	200.0	1.340
353.15	40.0	0.680	423.15	0.1	0.250
353.15	60.0	0.810	423.15	20.0	0.326
353.15	80.0	0.938	423.15	40.0	0.397
353.15	100.0	1.077	423.15	60.0	0.465
353.15	120.0	1.233	423.15	80.0	0.543
353.15	140.0	1.391	423.15	100.0	0.617
353.15	160.0	1.573	423.15	120.0	0.694
353.15	180.0	1.755	423.15	140.0	0.773
373.15	0.1	0.375	423.15	160.0	0.863
373.15	20.0	0.475	423.15	180.0	0.950
373.15	40.0	0.573	423.15	200.0	1.046
373.15	60.0	0.673	473.15	20.0	0.228
373.15	80.0	0.778	473.15	40.0	0.290
373.15	100.0	0.895	473.15	60.0	0.345
373.15	120.0	1.018	473.15	80.0	0.400
373.15	140.0	1.146	473.15	100.0	0.453
373.15	160.0	1.284	473.15	120.0	0.511
373.15	180.0	1.437	473.15	140.0	0.567
373.15	200.0	1.602	473.15	160.0	0.626
			473.15	180.0	0.686
			473.15	200.0	0.755

ethylnonane, squalane, polyisobutylene (M = 500 g/mol), ethylbenzene, and 1,2-diphenylethane. The measurements were performed at 298, 353, and 453 K and pressures up to 200 MPa with an estimated accuracy of ±2%.

The viscosity isobars of the hydrocarbons can be described by a modified Arrhenius equation:

$$\ln\{\eta/(\mathrm{mPa{\cdot}s})\} = a + b/(T/\mathrm{K} - c) \tag{1}$$

The pressure dependence of the viscosity of hydrocarbons is smaller than exponential and can be described by the equation

$$\ln\{\eta/(\mathrm{mPa{\cdot}s})\} = a + b(P/\mathrm{MPa}) - c(P/\mathrm{MPa})^2 \tag{2}$$

In the measured pressure and temperature ranges eqs 1 and 2 can be combined to an empirical equation:

$$\ln\{\eta/(\mathrm{mPa{\cdot}s})\} = a + b(T/\mathrm{K} - c) + \{d + e/(T/\mathrm{K} - c)\}(P/\mathrm{MPa}) - f(P/\mathrm{MPa})^2 \tag{3}$$

The average deviation of the results was minimized by the simplex method of Nelder and Mead (*6*). The resulting values of the adjustable parameters of eq 3 are listed in table 4. while the deviations between the measured values and literature data are given in Table 5.

Data of the viscosity of 2,2,4-trimethylpentane in the temperature range 298−373 K at pressures up to 500 MPa published by Dymond et al. (*7*) fit our results in the measured pressure range (0.1−200 MPa) within 2%. The results of ethylbenzene at temperatures from 298 to 348 K at pressures up to 110 MPa reported by Kashiwagi and Makita (*8*) agree with an average deviation of 0.6% with the viscosities calculated by means of eq 3. The results for squalane at 298 and 313 K at pressures up to 100 MPa measured by Kuss et al. (*9*) and for ethylbenzene in the temperature range 298−473 K at pressures up to 40 MPa recommended by Stephan and Lucas (*10*) deviate systematically from our correlated results by 5.7% and 7.3%, respectively, as can be seen from Table 5.

Table 3. Viscosity η as a Function of Temperature and Pressure

T/K	P/MPa	η/(mPa·s)	T/K	P/MPa	η/(mPa·s)
2,3,4-Trimethylpentane					
298.15	0.1	0.576	353.15	120.0	0.925
298.15	50.0	0.926	353.15	160.0	1.203
298.15	80.0	1.242	353.15	195.0	1.489
298.15	120.0	1.602	453.15	50.0	0.277
298.15	160.0	2.123	453.15	80.0	0.354
298.15	195.0	2.642	453.15	120.0	0.452
353.15	50.0	0.548	453.15	160.0	0.542
353.15	80.0	0.696	453.15	195.0	0.653
2,2,4-Trimethylpentane					
298.15	0.1	0.484	353.15	120.0	0.858
298.15	50.0	0.836	353.15	160.0	1.134
298.15	80.0	1.084	353.15	195.0	1.436
298.15	120.0	1.471	453.15	50.0	0.271
298.15	160.0	1.869	453.15	80.0	0.347
298.15	195.0	2.286	453.15	120.0	0.457
353.15	50.0	0.500	453.15	160.0	0.569
353.15	80.0	0.636	453.15	195.0	0.678
2,2,4,4,6,8,8-Heptamethylnonane					
298.15	0.1	3.354	353.15	120.0	6.621
298.15	50.0	8.425	353.15	160.0	10.809
298.15	80.0	14.394	353.15	195.0	16.199
298.15	120.0	28.292	453.15	0.1	0.421
298.15	160.0	55.791	453.15	50.0	0.890
298.15	195.0	98.501	453.15	80.0	1.225
353.15	0.1	1.253	453.15	120.0	1.795
353.15	50.0	2.708	453.15	160.0	2.512
353.15	80.0	4.033	453.15	195.0	3.363
Squalane					
298.15	0.1	29.118	353.15	120.0	28.503
298.15	50.0	84.616	353.15	160.0	45.851
298.15	80.0	148.378	353.15	195.0	68.476
298.15	120.0	293.733	453.15	0.1	1.090
298.15	160.0	594.802	453.15	50.0	2.174
298.15	195.0	954.157	453.15	80.0	2.973
353.15	0.1	5.059	453.15	120.0	4.128
353.15	50.0	11.264	453.15	160.0	5.580
353.15	80.0	17.006	453.15	195.0	7.294
Polyisobutylene (M = 500 g/mol)					
298.15	0.1	554.895	453.15	0.1	2.823
353.15	0.1	27.751	453.15	50.0	6.915
353.15	50.0	110.408	453.15	80.0	10.828
353.15	80.0	225.302	453.15	120.0	18.882
353.15	120.0	565.497	453.15	160.0	31.764
353.15	160.0	1264.453	453.15	195.0	46.695
Ethylbenzene					
298.15	50.0	0.897	353.15	120.0	0.747
298.15	80.0	1.070	353.15	160.0	0.905
298.15	120.0	1.334	353.15	195.0	1.107
298.15	160.0	1.621	453.15	50.0	0.275
298.15	195.0	1.895	453.15	80.0	0.332
353.15	0.1	0.364	453.15	120.0	0.410
353.15	50.0	0.511	453.15	160.0	0.499
353.15	80.0	0.601	453.15	195.0	0.571
1,2-Diphenylethane					
353.15	0.1	1.537	453.15	80.0	0.987
353.15	50.0	2.331	453.15	120.0	1.254
353.15	80.0	2.947	453.15	160.0	1.553
453.15	50.0	0.807	453.15	195.0	1.856

Viscosities calculated by means of eq 3, using the empirical parameters from Table 4, are shown in Figures 1−3, together with literature values and the results from Table 3. In the ranges of temperature and pressure measured, the viscosity increases monotonically with increasing pressure and with decreasing temperature (Figure 1). At a fixed temperature and pressure the viscosity increases with increasing molar mass of the hydrocarbons (Figure 3), while the slope of the isotherms is nearly independent of the chain length of the homologous alkanes like n-alkanes or oligomeric isobutenes (2,2,4-trimethylpentane, 2,2,4,4,6,8,8-heptamethylnonane, polyisobutylene). For this reason the curves of homologous alkanes in Figure 3 are almost parallel. In the case of isomeric hydrocarbons the slope of the isotherms increases with the branching frequency of the molecules. Therefore, among isomeric alkanes the viscosity of the n-alkane is always the lowest at high pressure, while at atmospheric pressure the

Table 4. Parameters in Eq 3 of the Viscosity of Hydrocarbon Liquids

compound	*a*	*b*	*c*	$d \times 10^3$	*e*	$f \times 10^6$
2,3,4-trimethylpentane	−4.723	1750	−121.1	4.77	2.183	11.10
2,2,4-trimethylpentane	−3.604	697	53.8	10.25	0.367	18.27
2,2,4,4,6,8,8-heptamethylnonane	−2.819	641	138.5	5.91	2.226	14.19
squalane	−2.628	785	167.7	6.16	2.023	19.25
polyisobutylene (*M* = 500 g/mol)	−2.964	1086	181.1	3.91	4.077	23.42
ethylbenzene	−3.406	699	61.3	6.84	0.094	8.30
1,2-diphenylethane	−4.089	1595		3.07	1.993	7.18

Table 5. Comparison with Data from the Literature

compound	average deviation/%		ref
	exptl. value	lit. value	
2,3,4-trimethylpentane	1.2		
2,2,4-trimethylpentane	2.7	2.0	7
2,2,4,4,6,8,8-heptamethylnonane	3.1		
squalane	2.2	5.7	9
polyisobutylene (*M* = 500 g/mol)	1.6		
ethylbenzene	0.9	0.6, 7.3	8, 10
1,2-diphenylethane	0.2		

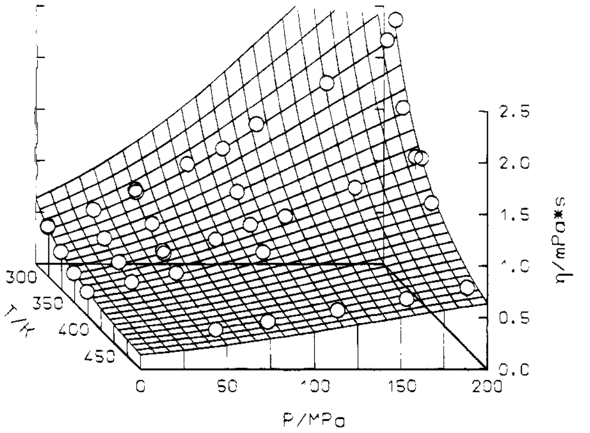

Figure 1. Viscosity of 2,2,4-trimethylpentane as a function of pressure and temperature. Curves were calculated from eq 3, using the parameters of Table 4.

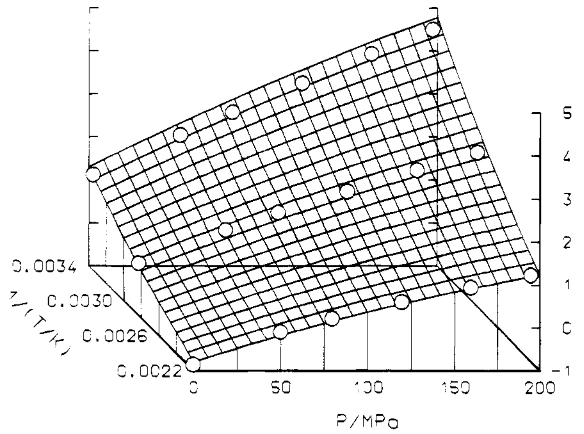

Figure 2. Logarithm of the viscosity of 2,2,4,4,6,8,8-heptamethylnonane as a function of pressure and reciprocal temperature. Curves were calculated from eq 3, using the parameters of Table 4.

viscosity of branched-chain alkanes is often lower. The effects of chain length and branching on the pressure dependence of the viscosity agree well with the results of isomeric hexanes and heptanes measured by Kuss (*11*).

Glossary

η	viscosity, mPa·s
T	temperature, K
P	pressure, MPa
$a-f$	adjustable parameters

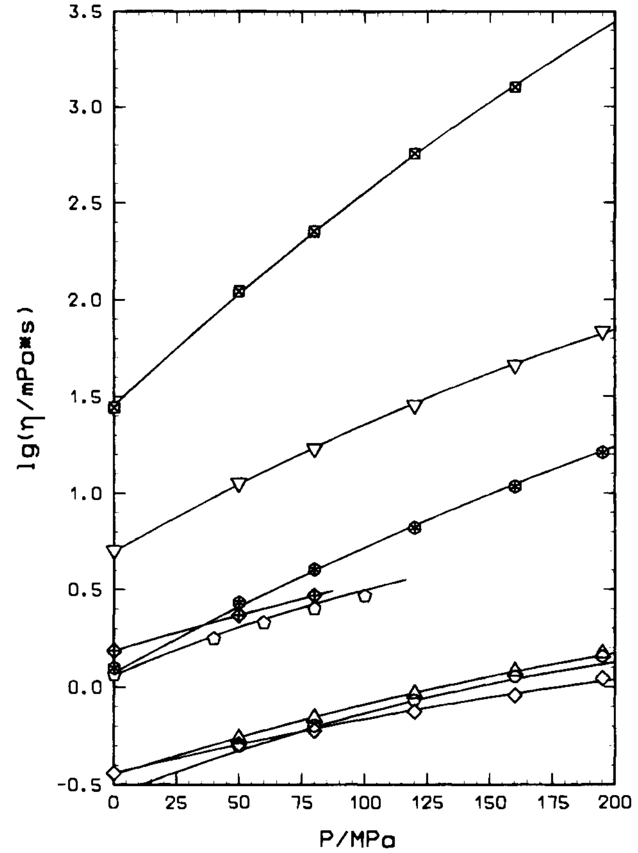

Figure 3. Dependence of the viscosity of hydrocarbons at 353.15 K on pressure. Curves were calculated from eq 3, using the parameters of Table 4. Key: (○) 2,2,4-trimethylpentane; (△) 2,3,4-trimethylpentane; (◇) ethylbenzene; (⊖) 1,2-diphenylethane; (⬠) hexadecane (*3*); (⊕) 2,2,4,4,6,8,8-heptamethylnonane; (▽) squalene; (⊠) polyisobutylene (*M* = 500 g/mol).

Literature Cited

(1) Stanislawski, U.; Luft, G. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 756.
(2) Krahn, U. G. Dissertation, TH Darmstadt, Darmstadt, Germany, 1993.
(3) Ducoulombier, D.; Zhou, H.; Boned, C.; Peyrelasse, J.; Saint-Guirons, H.; Xans, P. *J. Phys. Chem.* **1986**, *90*, 1692. S
(4) Naake, L. D. Dissertation, University of Karlsruhe, Karlsruhe, Germany, 1984.
(5) Hubbard, R. M.; Brown, G. G. *Ind. Eng. Chem.* **1943**, *15*, 212.
(6) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308.
(7) Dymond, J. H.; Glen, N. F.; Isdale, J. D. *Int. J. Thermophys.* **1985**, *6*, 233.
(8) Kashiwagi, H.; Makita, T. *Int. J. Thermophys.* **1982**, *3*, 289.
(9) Kuss, E.; Golly, H. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 131.
(10) Stephan, K.; Lucas, K. *Viscosity of Dense Fluids*; Plenum Press: New York and London, 1979.
(11) Kuss, E.; Pollmann, P. *Z. Phys. Chem. (Neue Folge)* **1969**, *68*, 205.

Received for review September 13, 1993. Revised May 13, 1994. Accepted June 13, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.