Table II. Thermodynamic Protonation Constants of Glycine, L-Leucine, L-Serine, L-Threonine, L-Lysine, and L-Glutamic Acid, Together with Parameters A and B of Eq 1

amino acid	p:q[a]	log K_0	A	B
glycine	1:1	9.85 ± 0.02	0.73	0.85
	1:2	2.54 ± 0.02	0.83	1.41
L-leucine	1:1	9.95 ± 0.03	0.26	0.31
	1:2	2.44 ± 0.03	1.31	1.84
L-serine	1:1	9.28 ± 0.01	0.17	0.17
	1:2	2.18 ± 0.03	1.74	2.49
L-threonine	1:1	9.23 ± 0.02	0.65	0.74
	1:2	2.28 ± 0.03	0.61	0.82
L-lysine	1:1	11.10 ± 0.04	2.30	3.47
	1:2	9.47 ± 0.02	0.48	0.63
	1:3	2.27 ± 0.03	0.88	1.92
L-glutamic acid	1:1	9.69 ± 0.04	1.13	2.19
	1:2	4.18 ± 0.04	0.71	1.34
	1:3	2.32 ± 0.03	0.97	1.40

[a] p:q refers to L_pH_q systems; L = amino acid, H = H^+.

base behavior of amino acids. Comparison of the constants of glycine and leucine with those of serine and threonine shows that the presence of the electrophilic OH group close to the α-carbon of the amino acid reduces the basicity for the amino group and increases the acidity of the carboxyl group. A similar effect is produced in glutamic acid by the presence of a second acid group, and in L-lysine by a second amine group, although in both these cases the effect is softened by the length of the interposed carbon chain.

Registry No. L-Leucine, 61-90-5; L-serine, 56-45-1; L-threonine, 72-19-5; L-lysine, 56-87-1; L-glutamic acid, 56-86-0.

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Viscosity of Pure Hydrocarbons

Børge Knapstad,† **Per A. Skjølsvik, and Harald A. Øye***

Institute of Inorganic Chemistry, The Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Accurate viscosity measurements have been performed on eight pure hydrocarbons at atmospheric pressure in the temperature range 20–150 °C, or up to approximately 20 °C below the boiling point of the hydrocarbon, by use of an absolute oscillating viscometer. The hydrocarbons are cyclohexane and benzene and the *n*-alkanes of hexane, heptane, octane, decane, dodecane, and tetradecane. The viscosities are described with a modified Arrhenius equation, and the deviation in fit is 0.12% or less. The accuracy is estimated to be 0.33–0.56%. The lowest viscosities are assumed to have the highest deviation. Literature data reported by Dymond and Young normally fit our viscosities within our estimated accuracy. Other literature viscosities tend to be higher than our results, especially for the *n*-alkanes.

1. Introduction

A high-precision viscometer for studies of low-viscous liquids up to 1100 °C has been developed at the Institute of Inorganic Chemistry. The viscometer is absolute and no calibration is needed. Our determination of the viscosity of molten NaCl has been recommended as a standard to the U.S. National Bureau of Standards by Janz (*1*). The viscosity measurements of pure hydrocarbons at atmospheric pressure are part of a program on viscosity measurements of oil-related fluids pressurized up to 400 bar. The aim of the present study is to produce accurate data over a wide temperature range for computer modelling of viscosity and to check or eventually establish new reference values.

2. Experimental Section

2.1. Apparatus. A thorough description of the oscillation viscometer is given by Tørklep and Øye (*2*). The viscometer measures the damping of a right circular cylinder oscillating in contact with the liquid under consideration. The cylinder may be a solid cylinder immersed in the liquid, or it may be a cylindrical hollow cup containing the liquid. Absolute viscosities are calculated from the damping by using the working equations of the solid cylinder, Tørklep and Øye (*2*), or the hollow cup, Brockner, Tørklep, and Øye (*3*).

A completely filled hollow cup is used in this study (Figure 1). To maintain a filled cup, a capillary tube, F, fixed to the bottom lid of the cup, is inserted into a sample reservoir, G, situated at room temperature. The sample reservoir is open at the top, and the capillary tube fixed to the cup can oscillate freely during the measurements. This system allows us to change the temperature set point, both up and down, and still maintain a completely filled cup. Figure 1 also shows a syringe, I, with a 50-cm-long needle. The needle is inserted through a bottom septum of the reservoir, G, and can go through the capillary

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† Present address: Norsk Hydro a.s, Oil and Gas Group, N-1321 Stabekk, Norway.

* To whom correspondence should be addressed.

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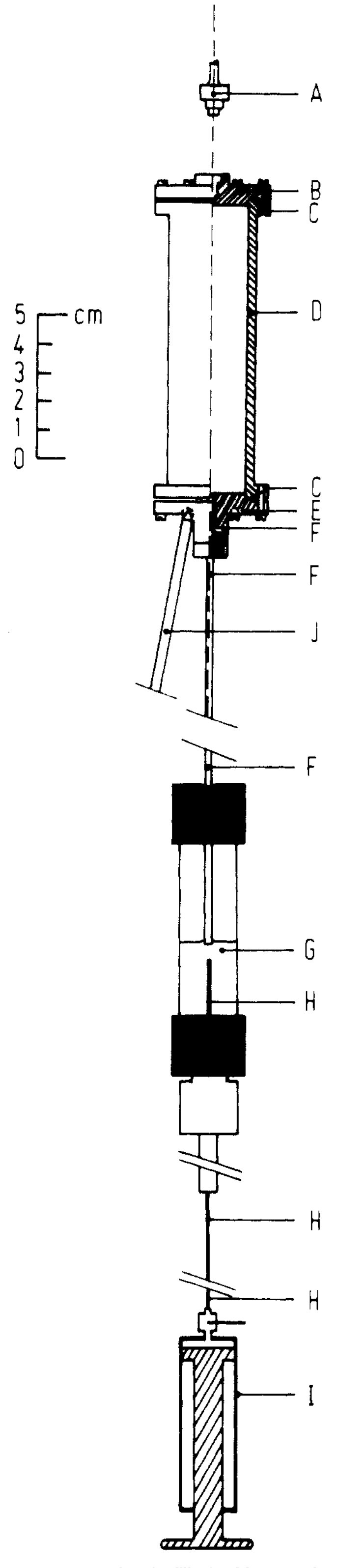


Figure 1. Hollow cup completely filled with sample. A, lower part of the torsion pendulum; B, lid; C, gold ring seals; D, main cylindrical segment; E, lid; F, capillary tube, 30 cm long; G, liquid reservoir at room temperature; H, syringe needle, 50 cm long; I, syringe; J, thermocouple.

tube, F, and up to the inside top of the hollow cup. The syringe is used to withdraw eventually dissolved gas which is evolved at the highest temperatures for some of the samples in this study.

The liquid reservoir can be pushed up and down in relation to the capillary tube, F. In this manner the end of the capillary tube is situated 1 mm below the surface during measurements and deeper in the liquid reservoir while waiting for the next stable temperature.

Table I. Purity of Hydrocarbons Used in This Study

hydrocarbon	manufacturer	manufacture purity, %	GC anal., this work, wt % before distilln	 after distilln
n-hexane	E. Merck, FRG	>99	99.30[a]	99.40[a]
benzene	E. Merck, FRG	>99.5	100.00	
cyclohexane	Fluka AG, Switzerland	>99.5	99.98	
n-heptane	Fluka AG, Switzerland	>99.5	99.78	
n-octane	Fluka AG, Switzerland	>99.5		
n-decane	Fluka AG, Switzerland	>99	100.00	
n-dodecane	Fluka AG, Switzerland	>98	99.66	100.00
n-tetradecane	Fluka AG, Switzerland	>99		

[a] The impurity content of *n*-hexane is seen as a shoulder of the main *n*-hexane peak on the gas chromatogram. The shoulder is probably caused by an isomer of *n*-hexane, which may give a viscosity change of +0.09% to −0.04% at 20 °C (*5*).

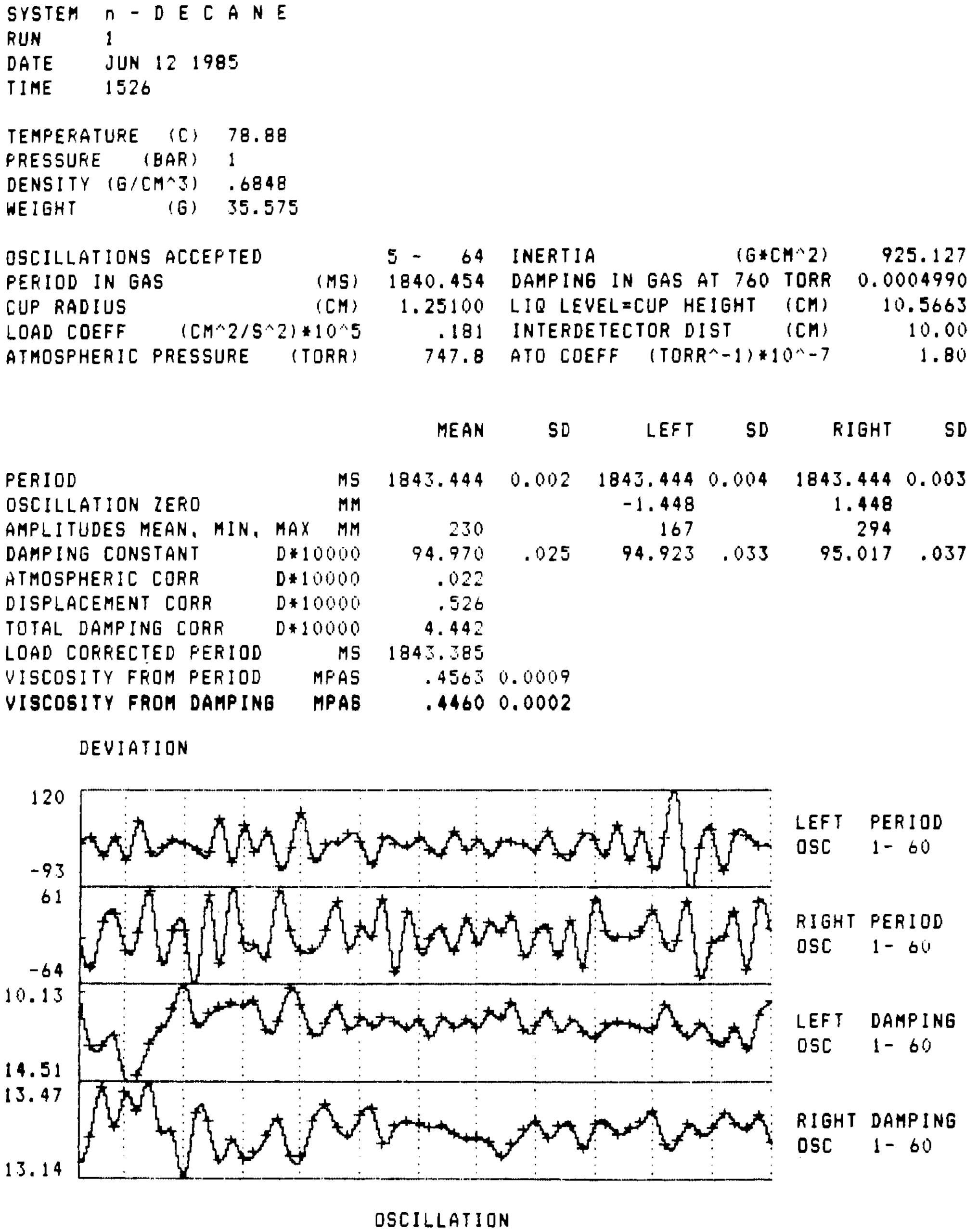
2.2. Chemicals. The chemicals used are given in Table I. Gas chromatography analysis of the original pure hydrocarbons from the manufacturer showed that *n*-dodecane and *n*-hexane had to be purified by distillation. The distillation column filled with stainless steel Dixon rings has approximately 80 theoretical stages. The product was analyzed by a Hewlett-Packard Model 5308 gas chromatograph equipped with a microprocessing unit Model 18850 A terminal. The stainless steel column was packed with 120/140 mesh Carbosieve B. The GC printouts gave the result in area percent. These results were transformed to weight percent by using relative sensitivity values for flame ionization detectors described by Dietz (*4*).

2.3. Control and Measurement of Temperature. The hollow cup was thermostated inside a triple-walled column connected to a water bath circulator (Heto 10 TE 623, Denmark) with a temperature stability better than ±0.05 °C for *n*-hexane, cyclohexane, and benzene. A double-walled Pyrex column connected to an oil bath circulator (Julabo SC 12, Seebach, West Germany) with an accuracy of ±0.01 °C was used to thermostat the cup for the other *n*-alkanes. The circulator oil was silicone oil (SF 96 Fluid 50 CS, General Electric, NY).

A calibrated Ni–NiCr thermocouple was used to measure the temperature. The reference point was an ice–water mixture. Calibration was performed against another Ni–NiCr thermocouple. This thermocouple was calibrated against the melting point of Sn, a mercury in glass precision thermometer at 22, 25, and 27 °C, and against a Pt100 resistance thermometer from 40 to 175 °C in intervals of 20 °C. The calibration procedure was done with the same electrical cables, connections, and voltmeter as used in the experiments, but the thermocouple was not calibrated in situ. The overall accuracy of the temperature readings with the thermocouple in situ is estimated to be

$$S(^\circ\mathrm{C}) = \pm(|(t - 25) \times 10^{-3}| + 0.10) \qquad (1)$$

2.4. Electronics and Operational System. The electronic system that operates the viscometer encompasses three units named viscometer controllers (Elkem A/S R&D Centre, Kristiansand, Norway). They are situated between the viscometer and an Apple IIe microcomputer. The viscometer is fully op-



```
SYSTEM  n - D E C A N E
RUN     1
DATE    JUN 12 1985
TIME    1526

TEMPERATURE  (C)  78.88
PRESSURE   (BAR)  1
DENSITY (G/CM^3)  .6848
WEIGHT       (G)  35.575

OSCILLATIONS ACCEPTED          5 -   64  INERTIA            (G*CM^2)    925.127
PERIOD IN GAS             (MS) 1840.454  DAMPING IN GAS AT 760 TORR  0.0004990
CUP RADIUS                (CM)  1.25100  LIQ LEVEL=CUP HEIGHT  (CM)    10.5663
LOAD COEFF    (CM^2/S^2)*10^5      .181  INTERDETECTOR DIST    (CM)      10.00
ATMOSPHERIC PRESSURE    (TORR)    747.8  ATO COEFF  (TORR^-1)*10^-7       1.80


                                   MEAN     SD       LEFT    SD      RIGHT    SD

PERIOD                      MS 1843.444  0.002  1843.444 0.004  1843.444 0.003
OSCILLATION ZERO            MM                    -1.448           1.448
AMPLITUDES MEAN, MIN, MAX   MM      230              167              294
DAMPING CONSTANT       D*10000   94.970   .025    94.923  .033    95.017  .037
ATMOSPHERIC CORR       D*10000     .022
DISPLACEMENT CORR      D*10000     .526
TOTAL DAMPING CORR     D*10000    4.442
LOAD CORRECTED PERIOD       MS 1843.385
VISCOSITY FROM PERIOD     MPAS    .4563 0.0009
VISCOSITY FROM DAMPING    MPAS    .4460 0.0002
```

Figure 2. Printout example of a typical run, *n*-decane at 78.88 °C.

erated from the keyboard of the Apple IIe by a menu-driven Applesoft Basic program package developed by K. Tørklep, Kristiansand, Norway. The program package enables the operator to select correct parameters of the run and computes the measured viscosity. The principle and arrangement to detect the oscillations are described by Tørklep and Øye (*2*), Rytter and Tørklep (*6*), and Otha et al. (*7*).

2.5. Procedures. The cup was taken out of the viscometer, heated up to 150 °C for the minimum of 1 hour, evacuated, and filled with nitrogen gas. Then it was cooled down to 0–5 °C together with the sample bottle. The cup was then turned upside down, and the pure hydrocarbons were poured into the cup. The cup was closed, turned to normal position, and connected to the torsion pendulum in the viscometer. This start-up procedure was arranged so the cup temperature steadily increased to the first temperature set point. Eventual gas bubbles in the capillary tube were washed out with the sample flow from the cup.

Temperature stability within 0.05 °C was reached after 2–3 h, and viscosity measurements also showed stable viscosity values. At the highest temperature the set point of temperature was raised to approximately 5 °C higher than desired. After about 2 h, gas bubbles inside the cup were sucked out by means of the syringe described earlier. The temperature was reduced by 5 °C, and a measurement series of four parallel runs was done as soon as the temperature was stable. Some of the samples evolved gas after the temperature reduction, so the measurement series was done after another removal of gas bubbles and temperature reduction. The measurements were performed in steps of 15, 20, or 25 °C. When the temperature series was complete, some temperatures were remeasured as a control of stability. The temperature was measured both before and immediately after a measurement series with the thermocouple in contact with the bottom of the cup.

A printout example is given in Figure 2 of *n*-decane at 78.88 °C. The information to be stressed is the two last printout lines, viscosity from period and viscosity from damping. The viscosity from the damping is the accurate one, while the viscosity calculated from the very small change of period in gas to the period in liquid only is used as an indication of malfunction (*8*).

Table II. Experimental Viscosities: Average Values of Four Parallel Runs Given in Order Performed

hydrocarbon	temp, °C	mean viscosity, mPa·s	SD, %
benzene	49.32	0.4402	0.16
	35.51	0.5220	0.19
	59.72	0.3922	0.05
	25.41	0.5984	0.08
	39.57	0.4948	0.02
	15.40	0.6942	0.07
cyclohexane	25.22	0.8899	0.06
	25.26	0.8894	0.08
	60.68	0.5277	0.13
	60.70	0.5278	0.07
	50.60	0.6033	0.05
	35.92	0.7493	0.09
	35.84	0.7494	0.03
	15.54	1.0568	0.05
	25.08	0.8938	0.15
	25.34	0.8903	0.04
	25.32	0.8889	0.03
	15.55	1.0536	0.04
	15.57	1.0540	0.04
n-hexane	44.15	0.2465	0.08
	15.47	0.3243	0.06
	25.63	0.2929	0.10
	35.34	0.2671	0.07
	36.97	0.2629	0.08
	53.42	0.2267	0.09
	53.39	0.2268	0.13
n-heptane	73.35	0.2458	0.12
	60.25	0.2760	0.18
	40.65	0.3321	0.09
	40.53	0.3322	0.06
	20.10	0.4101	0.05
	30.77	0.3665	0.11
	24.21	0.3924	0.10
	24.13	0.3928	0.08
	18.86	0.4157	0.14
n-octane	20.58	0.5373	0.13
	96.77	0.2526	0.16
	79.16	0.2944	0.14
	60.07	0.3509	0.14
	40.11	0.4300	0.05
n-decane	20.32	0.9111	0.02
	150.00	0.2394	0.07
	149.15	0.2411	0.08
	123.30	0.2973	0.17
	101.07	0.3608	0.14
	101.07	0.3606	0.06
	78.88	0.4460	0.07
	60.13	0.5440	0.07
	38.99	0.7005	0.03
	39.02	0.7003	0.03
	19.90	0.9168	0.04
n-dodecane	152.33	0.3193	0.06
	152.33	0.3194	0.13
	124.13	0.4067	0.07
	100.37	0.5099	0.08
	80.13	0.6311	0.16
	79.75	0.6337	0.03
	59.99	0.8041	0.05
	59.99	0.8048	0.12
	40.28	1.0573	0.04
	40.33	1.0566	0.01
	20.67	1.4684	0.01
n-tetradecane	19.79	2.3184	0.04
	19.83	2.3178	0.05
	40.55	1.5522	0.04
	150.83	0.4145	0.07
	124.35	0.5306	0.06
	99.41	0.6885	0.09
	80.34	0.8630	0.12
	60.13	1.1370	0.09
	41.16	1.5335	0.03
	19.85	2.3200	0.01

Table III. Parameters in Eq 3

hydrocarbon	*a*	*b*, K	$c \times 10^3$, K^2	$d \times 10^6$, K^3	SD, %
benzene	−3.374 75	442.965	122.8	0	0.11
cyclohexane	−4.159 91	911.472	88.07	0	0.12
n-hexane	−5.336 44	1585.81	−107.0	0	0.09
n-heptane	−5.193 95	1599.43	−99.03	0	0.10
n-octane	−8.196 95	4751.80	−1141.46	117.3	0.12
n-decane	−8.014 41	4969.45	−1257.66	141.3	0.09
n-dodecane	−7.741 70	5019.23	−1314.39	159.0	0.09
n-tetradecane	−7.370 53	4808.83	−1248.41	159.5	0.10

The latter value should not deviate more than 1–2% from the damping viscosity value. Larger deviations are due to bubble formations, the presence of particles in the sample, temperature disequilibrium, or erroneous input values.

3. Results

Eight pure hydrocarbons, benzene, cyclohexane, and the *n*-alkanes of hexane, heptane, octane, decane, dodecane, and tetradecane, were investigated. The temperature range was from 15 to 20 °C up to 150 °C or 20 °C below the boiling point. More than 300 single runs were performed, and Table II summarizes results by listing the average value of four parallel runs at each temperature in the order they were performed.

The experimental data have been used to fit the parameters in the model equation

$$\eta = A \exp(B(1/T - 1/T_m) + C((1000/T - 1000/T_u)^2 - (1000/T_m - 1000/T_u)^2) + D((1000/T - 1000/T_l)^3 - (1000/T_m - 1000/T_l)^3)) \qquad (2)$$

where η is the viscosity (mPa·s) and T is the temperature (K). T_u, T_m, and T_l are the upper, mean, and lower temperatures in a measurement series introduced to improve orthogonality in the fitted parameters A, B, C, and D. The data were fitted by use of the simplex method of Nelder and Mead as applied by Hertzberg (*9*). The relative least square sum in the viscosity was used as the minimizing criterion. The entire experimental data material, and not the average values in Table II, were used to determine the parameters A, B, C, and D. The standard deviations in fit were 0.09–0.12%. The standard deviations of four parallel runs was normally below 0.15%.

A simpler equation is obtained by direct transformation of eq 2:

$$\ln \eta/\text{mPa·s} = a + b/T + c/T^2 + d/T^3 \qquad (3)$$

The transformed parameters are given in Table III.

The viscosity is plotted against temperature in an Arrhenius plot in Figure 3. Dotted circles give the extrapolated viscosity at the boiling point at 1 atm.

The density values used in the computation of the viscosities were taken from the TRC Tables (*10*). The tabulated densities were fitted to a second-order function with standard deviations in the range 10^{-5}–10^{-4} g/cm^3, or the relative standard deviation is approximately 0.002–0.02%.

4. Discussion

4.1. Error Analysis. Estimated standard deviations of relevant viscometer parameters and their influence on damping viscosity are given in Table IV for a typical measurement. A detailed error analysis was given earlier for both the solid cylinder and the hollow cup by Tørklep and Øye (*2*) and Brockner, Tørklep, and Øye (*3*). In these measurements a completely filled hollow cup was used, and errors in liquid height, vapor pressure above the liquid, and meniscus correction that occur in a partly filled cup were avoided. The estimated error in the net damping constant is lower than earlier due to a new electronic operational system.

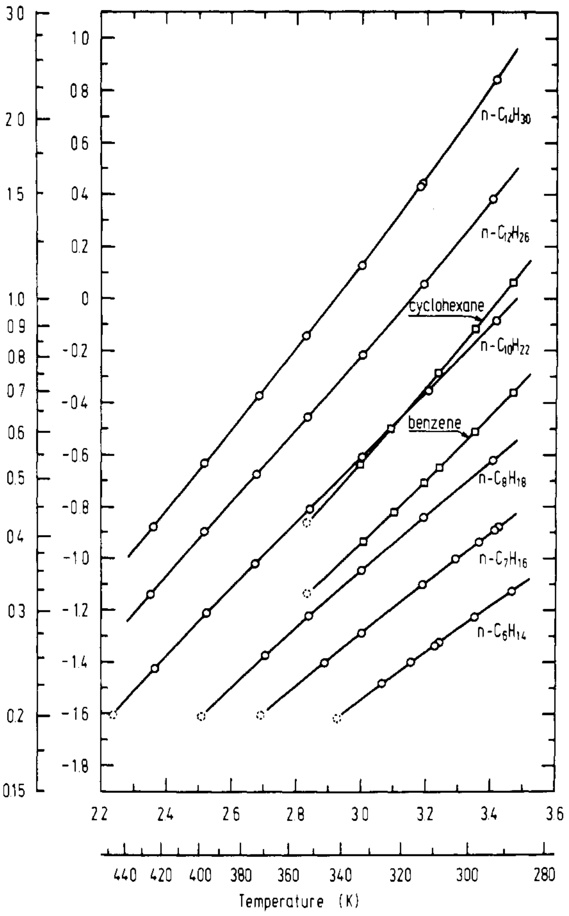


Figure 3. Arrhenius plot (ln η versus 1000/K) of the viscosities of the pure hydrocarbons. Dotted circles give the boiling point at atmospheric pressure.

Table IV. Error Table (All Changes Positive) Showing Computer-Calculated Effects on Damping Viscosity of n-Decane at 78.88 °C

experimental parameters	estd abs error	estd SD, %	rel viscosity change, %
net decrement	7×10^{-6}	0.07	0.17
inertia of osc system	10^{-7} kg m^2	0.11	0.22
cup radius	2 μm	0.02	-0.11
cup height	20 μm	0.02	-0.04
density	0.0003 g/cm^3	0.04	0.04
temperature (indirect)	0.15 °C		0.02
period in gas	40 μs	0.002	0
period in liquid	40 μs	0.002	0
RMS - $\sum((\Delta\eta)^2)^{1/2}$			0.30

An estimated error in the damping decrement of 7×10^{-6} is obtained from a standard deviation of 5×10^{-6} or better for each single run and a standard deviation of 5×10^{-6} in the mean value of four parallel runs.

The estimated error in density of 0.0003 g/cm^3 is the difference in density measured by TRC (*10*) and Dymond and Young (*11*, *12*). The total standard deviation in the error table vary within 0.25-0.41%, corresponding to different viscosities. The damping of the liquid in the capillary tube, F (Figure 1), is negligible. The total damping correction in the printout example (Figure 2) will not change if the damping of the tube is taken into consideration. This very small damping effect is obtained by a capillary radius which gives a corresponding low damping contribution (eq 5 and 6; Brockner, Tørklep, and Øye (*3*)). An overall accuracy of the thermocouple will give a deviation of ±0.2% in the viscosity calculated from eq 2.

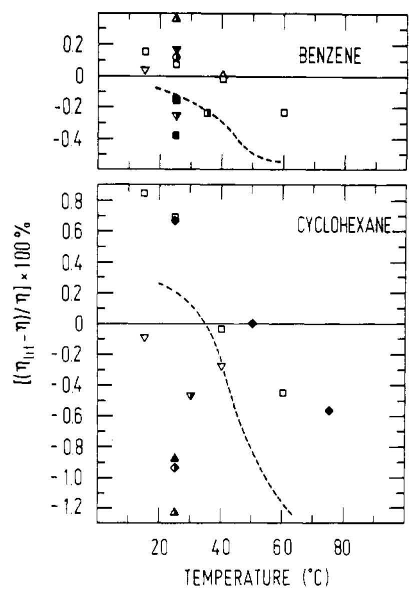


Figure 4. Deviation plot of the literature data compared to our correlated viscosities calculated from eq 2. Dotted line, evaluated viscosities by TRC (*10*); □, Dymond and Young (*12*); ▽, Mato and Hernandez (*13*); ▼, Mussche and Verhoeye (*14*); △, Irving and Simpson (*15*); ▲, Grunberg (*16*); △, Aminabhavi, Manjeshwar, and Balungi (*17*); ◑, Asfour and Dullien (*18*); ●, Manjeshwar and Aminabhavi (*19*); ◨, Teja and Rice (*20*); ▽, Oswal and Rathnam (*21*); ■, Celda, Gavara, Tejero, and Figueruelo (*22*); ●, Isdale, Dymond and Brawn (*23*); ◈, Katti, Chaudhri, and Prakash (*24*).

Table V. Experimental Viscosities of Water: Average Values of Four Parallel Runs at Each Temperature Given in Order Performed

temp, °C	viscosity, mPa·s	temp, °C	viscosity, mPa·s
20.09	0.9993	74.48	0.3816
44.66	0.5997	50.76	0.5408
60.24	0.4652	19.75	1.0076

4.2. Evaluation of Accuracy. When serious errors are eliminated by filling the cup completely (*3*), the accuracy of the hollow cup system is close to that of the solid cylinder system. Solid cylinder measurements of molten salts are estimated to an accuracy of 0.2% SD (Tørklep and Øye (*2*)). To obtain such an accuracy, the period and damping in gas must be measured immediately before the viscosity measurement.

In this experimental series the period and damping in gas were measured as a function of temperature and used in all the liquid runs. Check runs were done of the period and damping in gas, and the deviation from the temperature function was within the estimated error in Table IV.

The relative viscosity change is dependent on the net damping constant. Hence the standard deviation from the error table varies from ±0.25% to ±0.41% with decreasing viscosity. The estimated standard deviation in Table IV, combined with the ±0.2% standard deviation of the thermocouple and the ±0.1% standard deviation in fit gives an overall accuracy of ±0.33% to ±0.56%. The lowest viscosities are assumed to have the highest uncertainty. The estimated uncertainties can be recognized to be at the 68% confidence level.

4.3. Comparison with Other Results. Viscosity measurements by Dymond and Young (*11*, *12*) of benzene, cyclohexane, and the normal alkanes of hexane, octane, decane, and dodecane fit our results within +0.74 to -0.45% and usually better than ±0.4%. Other literature viscosities tend to be higher than our results for the *n*-alkanes but are more scattered for benzene and cyclohexane. Deviation plots of literature data from the correlated viscosities from eq 2 are given in Figures 4-7.

4.4. Verification against Water. The viscosity of water has been extensively studied and literature data are in good agreement with each other. To verify the obtained results of

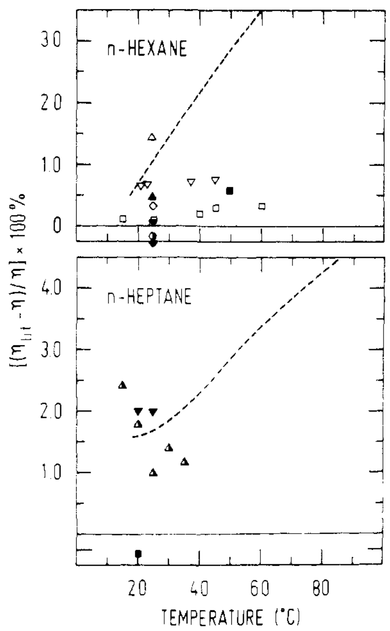


Figure 5. Deviation plot of the literature data compared to our correlated viscosities calculated from eq 2. ▽, Eicher and Zwolinski (*5*); dotted line, evaluated viscosities by TRC (*10*); □, Dymond and Young (*11*); ▼, Mussche and Verhoeye (*14*); ◐, Asfour and Dullien (*18*); ◧, Teja and Rice (*20*); ■, Celda, Gavara, Tejero, and Figueruelo (*22*); ●, Isdale, Dymond, and Brawn (*23*); △, Singh, Sinha, and Singh (*25*); ▲, Heric and Brewer (*26*); ◇, Ghai and Dullien (*27*); △, Öz and Gäumann (*28*).

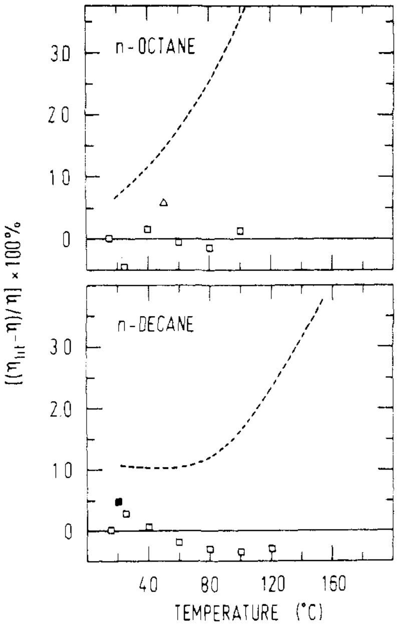


Figure 6. Deviation plot of the literature data compared to our correlated viscosities calculated from eq 2. Dotted line, evaluated viscosities by TRC (*10*); □, Dymond and Young (*11*, *12*); ■, Celda, Gavara, Tejero, and Figueruelo (*22*); △, Islam and Waris (*29*).

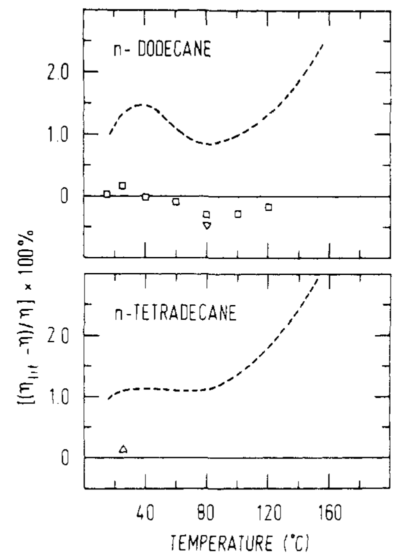


Figure 7. Deviation plot of the literature data compared to our correlated viscosities calculated from eq 2. Dotted line, evaluated viscosities by TRC (*10*); □, Dymond and Young (*11*); △, Aminabhavi, Manjeshwar, and Balungi (*17*); ▽, Hogenboom, Webb, and Dixon (*30*).

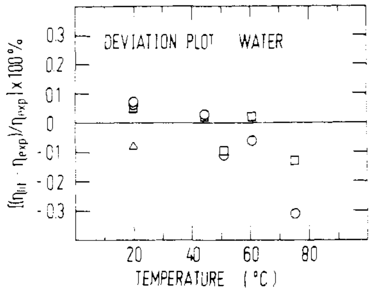


Figure 8. Deviation plot of literature data of water compared to our experimental measurements. O, Watson, Basu, and Sengers (*31*); □, Kestin et al. (*32*); △, accurate measurements obtained at this institute (*33*).

pure hydrocarbons, a test measurement of water was done following the same procedure as for the hydrocarbons. Table V gives the mean experimental viscosity of four parallel runs at each temperature in the order performed. In Figure 8 correlations reported by Watson, Basu, and Sengers (*31*) and Kestin et al. (*32*) and accurate viscosities in the range 19.5–25.5 °C recently obtained at this institute (*33*) are compared to the measured viscosity of water in this study. At 20 °C the viscosity value Watson, Basu, and Sengers is 0.07% higher, and that of Kestin et al. is 0.05% higher than our results. The recently obtained accurate viscosity at this institute at 20 °C is 0.08% lower. With increasing temperature the literature data decrease to −0.13% and −0.31% compared to our measured viscosity of water at 75 °C. This verification of water is in good agreement with the estimated total accuracy of ±0.33 to ±0.56% corresponding to reported viscosities.

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Glossary

S	accuracy of temperature readings, °C
t	temperature, °C
η	viscosity, mPa·s
A, B, C, D	model parameters in eq 2
T_u, T_m, T_l	upper, mean, and lower temperature in a measurement series, K
T	temperature, K
a, b, c, d	model parameters in eq 3

Registry No. Benzene, 71-43-2; cyclohexane, 110-82-7; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-decane, 124-18-5;

n-dodecane, 112-40-3; *n*-tetradecane, 629-59-4.

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Equilibrium Diagrams at 19 °C of Water–Malic Acid–2-Methyl-1-propanol, Water–Malic Acid–1-Pentanol, and Water–Malic Acid–3-Methyl-1-butanol Ternary Systems

Marcia M. L. Duarte,[†] **Jean Lozar, Guy Malmary, and Jacques Molinier***

Laboratoire de Genie Chimique, Ecole Nationale Supérieure de Chimie de Toulouse, 118, Route de Narbonne, 31077 Toulouse Cedex, France

The purpose of this work is to study the malic acid recovering possibilities from wine distillery wastewater through a liquid–liquid extracting process. 2-Methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol may be suitable as extracting solvents. Water–malic acid–alcohol ternary system solubility diagrams and tie lines were established at the temperature of 19 °C. Partition coefficients are comprised between 0.18 and 0.75. 3-Methyl-1-butanol is the most selective solvent with regard to malic acid.

Introduction

Malic acid is a costly product that is extracted from natural substances. It is an organic acid used as an acidulant in the food processing and pharmaceutical industries (*1*). In order to recover malic acid from wine distillery wastewater, which is present with a concentration rate of about 3.4 g/L (*2*), we considered the possibility of using the liquid–liquid extracting process.

Previous works about malic acid extraction by different solvents (methyl isobutyl ketone, methylisobutylcarbinol, *n*-octyl alcohol, oleoyl alcohol, 2-methyl-1-propanol and ether) show fairly weak values for the partition coefficient, located between 0.018 and 0.12 (*3*–*5*).

The solvation character of oxygen atoms tied to the carbon chain lends especially to alcohols' extracting properties with regard to acids. Thus we have selected 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol.

Experimental Section

Chemicals. Solvents, with a minimum purity of 98%, have been obtained from Prolabo. Malic acid (Prolabo) had a purity of 99%.

Experimental Procedures. Solubility isotherms and tie-line data were determined with an experimental device maintained at the constant temperature of 19 ± 0.1 °C in a thermostated vessel. Several malic acid solutions at different concentrations were prepared to determine the tie lines. The solutions were mixed in glass-stoppered separatory funnels and then added to the solvent and shaken for 30 min. That the times allowed for the acid solute distribution equilibrium point and the amount of shaking were sufficient to establish equilibrium was proved by showing that increasing each did not alter the results. After decantation waiting for another 30 min, malic acid, present in the phases in equilibrium, was neutralized with standard sodium hydroxide (0.1 or 1.0 N) and phenolphthalein used as indicator. The error induced when titrating and weighing is less than 1%.

The cloud-point method was used to determine liquid–liquid solubility isotherms. Solubility points were obtained with a relative accuracy of 1%. Solid–liquid saturation curves were determined from saturated solutions, malic acid being titrated with standard sodium hydroxide (1.0 N).

Results and Discussion

Figures 1–3 were set at 19 °C from the data of Tables I–III. These figures represent solubility isotherms and tie-line curves of water–malic acid ternary systems with successive solvents:

[†] Departamento de Engenharia Quimica Universidade Federal do Rio Grande do Norte, 59000 Natal RN, Brazil.

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