J. Chem. Eng. Data **1986**, *31*, 143-145 143

(18) Steinberg, M.; Powell, J. R. *Nuclear Technol.*, in press.

Received for review July 9, 1982. Revised manuscript received May 8, 1985. Accepted October 30, 1985. Research sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

Supplementary Material Available: The distribution data shown in Figures 1-19 in tabular form (20 pages). Ordering information is given on any current masthead page.

Viscosity of Some *n*-Alkane/1-Chloroalkane Binary Liquid Mixtures

Antonio Aucejo,* Eduvigis Part, Pascual Medina, and Margarita Sancho-Tello

Departamento de Química Técnica, Facultad de Químicas, Universidad de Valencia, Burjassot, Spain

In the present work, we have measured the viscosities, densities, and refractive indexes of nine *n*-alkane/1-chloroalkane binary liquid mixtures, at 25 °C. At the same time, the experimental data of all the studied systems have been correlated by using three models given in the literature. These are the equations proposed by Grunberg, McAllister, and Heric to correlate viscosities of binary liquid mixtures.

Introduction

The viscosities of liquid mixtures are required for many practical problems concerning heat and mass transport and fluid flow. A summary of the equations proposed for the calculation of liquid mixture viscosities can be seen in the work of Irving (*1*). But as this author points out, the number of systems for which we dispose of some experimental data is relatively small.

In the present work, viscosities of nine binary liquid mixtures, *n*-alkane/1-chloroalkane, at 25.0 °C, have been measured by means of a capillary viscometer. Densities and refractive indexes have also been measured.

Experimental Section

All the chemicals used were supplied by Merck. They were distilled in a distillation column equivalent to 100 theoretical plates.

Refractive indexes were measured with a RL-PZO (Warszawa) refractometer, and densities were measured with a previously calibrated Anton Paar, Model DMA 35, digital densimeter. All solutions were prepared by weighing the individual compounds. A Mettler balance with an accuracy of ±0.0001 g was used.

The viscosities of the pure compounds and mixtures were measured with eight Ubbelohde modified viscometers, previously calibrated with pure substances for which viscosities and densities were known from the literature. These values are given in Table I.

The viscosity measurements were made in a thermostat controlled to ±0.1 °C.

The following equation was used to calculate the viscosities (*7, 8*)

$$\eta/\rho = At - B/t \qquad (1)$$

Table I. Viscosities and Densities of Pure Compounds Used in the Calibrations at 25.0 °C

compd	η, cP	ref	ρ, g cm^{-3}	ref
n-pentane	0.2250	(*2*)	0.6214	(*2*)
acetone	0.3029	(*3*)	0.7844	(*3*)
ethyl acetate	0.4244	(*4*)	0.8945	(*4*)
toluene	0.5526	(*5*)	0.8621	(*5*)
chlorobenzene	0.7580	(*4*)	1.1010	(*4*)
n-dodecane	1.363	(*1*)	0.7451	(*1*)
butyl alcohol	2.524	(*6*)	0.8056	(*6*)
aniline	3.770	(*2*)	1.0175	(*2*)
hexyl alcohol	4.592	(*2*)	0.8159	(*2*)
octyl alcohol	7.363	(*6*)	0.8211	(*6*)

where η is the viscosity, ρ is the liquid density, t is its flow time in the viscometer, and A and B are viscometer constants, determined by the calibration fluids.

Flow time was taken as an average of 10 measurements.

Results and Discussion

The measured properties of pure compounds used in this work as well as the experimental values found in the literature appear in Table II.

Experimental results for the nine systems studied are shown in Tables III-XI. All measurements were made at 25.0 ± 0.1 °C.

A very large number of equations has been proposed in the literature for predicting mixture viscosities from pure compounds. The majority of these are purely empirical.

In this paper, a few of the predictive equations of mixture viscosities have been tested.

The Grunberg and Nissan (*9*) equation has been recommended by Irving (*1*) to represent viscosity data for binary mixtures; this empirical expression may be written as

$$\ln \nu_m = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 x_2 G \qquad (2)$$

where G is a characteristic constant of the system.

McAllister (*10*) derived a semitheoretical equation based upon Eyring's absolute reaction rate theory, assuming 3-body or 4-body interactions, depending upon the relative size of the components molecules.

For 3-body interaction the equation derived by him is

$$\ln \nu_m = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \times \ln \nu_2 - \ln (x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln [(2 + M_2/M_1)/3] + 3x_1 x_2^2 \ln [(1 + 2M_2/M_1)/3] + x_2^3 \ln (M_2/M_1) \qquad (3)$$

0021-9568/86/1731-0143$01.50/0

Table II. Physical Properties of Compounds in the Present Work and in the Literature at 25.0 °C

	η, cP		ρ, g cm^{-3}		n_D	
compd	exptl	lit.	exptl	lit.	exptl	lit.
n-pentane	0.2238	0.2166–0.2296 (*4*)	0.621	0.6213–0.6214 (*2,4*)	1.3547	1.3547–1.3549 (*2,4*)
n-decane	0.8582	0.8511–0.8614 (*2*, *4*, *12*)	0.726	0.7259–0.7264 (*2*, *4*, *12*, *14*)	1.4097	1.4096–1.4099 (*2*, *4*)
n-dodecane	1.364	1.353–1.378 (*2*, *4*, *13*)	0.745	0.7449–0.7455 (*2*, *4*, *13*, *14*)	1.4196	1.4195–1.4196 (*2*, *4*, *13*)
1-chlorobutane	0.4262	0.4261–0.427 (*15*, *16*)	0.880	0.8797–0.8811 (*15*, *16*)	1.3997	1.3995–1.4001 (*2*, *15*)
1-chlorooctane	1.131	1.128–1.150 (*15*, *16*, *17*)	0.869	0.8692–0.8695 (*15*, *16*)	1.4285	1.4285–1.4286 (*15*, *18*)
1-chlorooctadecane	7.335	7.385 (*15*)	0.859	0.8597–0.8605 (*15*, *18*)	1.4505	1.4506–1.4513 (*15*, *18*)

Table III. *n*-Pentane (1)/1-Chlorobutane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1016	0.4004	0.850	1.3945
0.2097	0.3720	0.826	1.3895
0.2358	0.3641	0.820	1.3885
0.4030	0.3274	0.785	1.3802
0.5062	0.3054	0.753	1.3757
0.6042	0.2870	0.721	1.3717
0.7007	0.2701	0.700	1.3681
0.7975	0.2558	0.674	1.3635
0.8963	0.2391	0.648	1.3592

Table IV. *n*-Decane (1)/1-Chlorobutane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1032	0.4681	0.853	1.4010
0.2020	0.5006	0.829	1.4019
0.3087	0.5437	0.808	1.4030
0.3992	0.5768	0.793	1.4041
0.5065	0.6297	0.778	1.4050
0.5992	0.6636	0.765	1.4060
0.6974	0.7109	0.755	1.4071
0.7967	0.7607	0.744	1.4080
0.8968	0.8110	0.735	1.4090

Table V. *n*-Dodecane (1)/1-Chlorobutane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1032	0.5072	0.851	1.4030
0.2020	0.5794	0.827	1.4057
0.2999	0.6598	0.813	1.4076
0.3986	0.7447	0.798	1.4104
0.4981	0.8232	0.786	1.4123
0.6017	0.9282	0.774	1.4140
0.7015	1.034	0.765	1.4154
0.7981	1.130	0.758	1.4168
0.8948	1.220	0.751	1.4180

Table VI. *n*-Pentane (1)/1-Chlorooctane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1047	0.9664	0.852	1.4238
0.2064	0.8559	0.836	1.4192
0.3057	0.7414	0.817	1.4143
0.4042	0.6389	0.798	1.4080
0.5005	0.5441	0.776	1.4020
0.6018	0.4631	0.754	1.3951
0.7019	0.3926	0.725	1.3869
0.8048	0.3240	0.695	1.3776
0.8982	0.2747	0.661	1.3670

Table VII. *n*-Decane (1)/1-Chlorooctane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1115	1.067	0.850	1.4260
0.2067	1.026	0.836	1.4240
0.3061	0.9966	0.821	1.4220
0.4041	0.9690	0.806	1.4198
0.5050	0.9433	0.792	1.4182
0.6124	0.9242	0.775	1.4159
0.7070	0.8969	0.764	1.4144
0.7970	0.8862	0.752	1.4131
0.8983	0.8740	0.740	1.4114

The selection of the cubic equation is justified since in all the systems the ratio of the radius is smaller then 1.5.

Table VIII. *n*-Dodecane (1)/1-Chlorooctane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1064	1.143	0.852	1.4267
0.2068	1.151	0.835	1.4255
0.3080	1.177	0.823	1.4243
0.4061	1.185	0.810	1.4232
0.5066	1.218	0.797	1.4223
0.6038	1.232	0.786	1.4214
0.6927	1.262	0.775	1.4208
0.7984	1.288	0.766	1.4203
0.8945	1.317	0.755	1.4198

Table IX. *n*-Pentane (1)/1-Chlorooctodecane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1054	6.009	0.850	1.4470
0.2014	4.945	0.845	1.4450
0.3067	3.902	0.834	1.4406
0.4166	2.952	0.822	1.4354
0.4993	2.325	0.810	1.4317
0.6122	1.613	0.789	1.4226
0.7054	1.157	0.765	1.4136
0.8048	0.7477	0.735	1.4009
0.9029	0.4310	0.687	1.3821

Table X. *n*-Decane (1)/1-Chlorooctadecane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1067	6.162	0.849	1.4480
0.2123	5.192	0.843	1.4457
0.3131	4.379	0.834	1.4431
0.3996	3.651	0.825	1.4401
0.5080	2.885	0.811	1.4360
0.6105	2.385	0.798	1.4321
0.7027	1.919	0.785	1.4280
0.8012	1.487	0.769	1.4230
0.8979	1.145	0.750	1.4174

Table XI. *n*-Dodecane (1)/1-Chlorooctadecane (2) System

x_1	η, cP	ρ, g cm^{-3}	n_D
0.1097	6.289	0.851	1.4486
0.2096	5.429	0.843	1.4465
0.3134	4.684	0.834	1.4441
0.4067	4.000	0.825	1.4412
0.5044	3.481	0.814	1.4387
0.6047	2.887	0.802	1.4350
0.6853	2.488	0.791	1.4327
0.8050	2.012	0.777	1.4282
0.8971	1.662	0.762	1.4246

The equation involves only two undetermined constants, to be calculated from experimental data: ν_{12} and ν_{21}.

The following relation was proposed by Heric (*11*) to correlate viscosities of binary mixtures

$$\log \nu_m = x_1 \log \nu_1 + x_2 \log \nu_2 + x_1 \log M_1 + x_2 \log M_2 - \log (x_1M_1 + x_2M_2) + \delta_{12} \quad (4)$$

where δ_{12} is a deviation function

$$\delta_{12} = x_1x_2[\alpha_{12} + \alpha'_{12}(x_1 - x_2)] \quad (5)$$

The coefficients α_{12} and α'_{12} may be determined from a least-squares method. The parameters corresponding to eq 2, 3, and 5 are listed in Table XII.

Table XII. Numerical Values of the Constants[a] Involved in Eq 2, 3, and 5 Used for Predicting Viscosity of Binary Mixtures

system	G (eq 2)	ν_{12} (eq 3)	ν_{21} (eq 3)	α_{12} (eq 5)	α'_{12} (eq 5)
n-pentane/1-chlorobutane	−0.091	0.38795	0.42644	−0.0192	−0.0086
n-decane/1-chlorobutane	0.228	0.93982	0.72387	0.1452	−0.0283
n-dodecane/1-chlorobutane	0.483	1.30072	0.98060	0.2924	−0.1319
n-pentane/1-chlorooctane	0.111	0.59277	0.90248	0.1561	0.0337
n-decane/1-chlorooctane	−0.166	1.1821	1.1647	−0.0749	0.0340
n-dodecane/1-chlorooctane	−0.073	1.5859	1.4341	−0.0303	−0.0135
n-pentane/1-chlorooctadecane	2.04	3.3203	4.4211	1.312	0.5437
n-decane/1-chlorooctadecane	0.592	2.9822	5.3084	0.3624	0.0545
n-dodecane/1-chlorooctadecane	0.281	3.4361	5.6590	0.1763	0.0045

[a] These constants, substituted in eq 2, 3, and 5, will yield the kinematic viscosities of the liquid mixtures in centistoke units.

Table XIII. Average Percentage Deviation of Experimental and Calculated Viscosities

system	% error eq 2	% error eq 3	% error eq 4
n-pentane/1-chlorobutane	0.47	0.47	0.54
n-decane/1-chlorobutane	0.48	0.40	0.47
n-dodecane/1-chlorobutane	1.59	0.60	0.75
n-pentane/1-chlorooctane	0.64	0.59	0.69
n-decane/1-chlorooctane	0.52	0.34	0.37
n-dodecane/1-chlorooctane	0.37	0.35	0.33
n-pentane/1-chlorooctadecane	5.65	1.85	2.03
n-decane/1-chlorooctadecane	0.95	0.79	0.78
n-dodecane/1-chlorooctadecane	0.56	0.55	0.58

The fittings of eq 2, 3, and 4 are compared in Table XIII. The average percentage deviation is taken as the criterion for the fitting of each equation.

$$\%\ \text{av error} = \frac{1}{n}\sum_{i=1}^{n}\frac{|\text{calcd} - \text{exptl}|}{\text{exptl}} \times 100 \qquad (6)$$

where n is the number of experimental measurements.

Conclusions

From the analysis of the present data, it could be said that eq 3 and 4 produced the same degree of accuracy and both were better than eq 2 in all the systems.

The three equations give greater errors as the system becomes more nonideal (*n*-dodecane/1-chlorobutane and *n*-pentane/1-chlorooctadecane).

The overall mean deviation for McAllister's model, Heric's model, and Grunberg's model was found to be 0.66%, 0.73%, and 1.25%, respectively.

Glossary

A	calibration constant
B	calibration constant
G	parameter of the Grunberg's equation
M	molecular weight
n_D	refractive index
t	flow time
x	mole fraction
α_{12}, α'_{12}	binary parameter of the Heric's equation
δ_{12}	deviation function of the Heric's equation
η	absolute viscosity
ν_{12}, ν_{21}	binary parameter of the McAllister's equation
ν	kinematic viscosity
ρ	density

Subscripts

1	first-named compound in a binary system
2	second-named compound in a binary system
m	mixture

Registry No. *n*-Pentane, 109-66-0; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; 1-chlorobutane, 109-69-3; 1-chlorooctane, 111-85-3; 1-chlorooctadecane, 3386-33-2.

Literature Cited

(1) Irving, J. B. "Viscosities of Binary Liquid Mixtures: The Effectiveness of Mixture Equations"; National Engineering Laboratory: East Kilbride, Glasgow, U.K., 1977; NEL Report No. 630.
(2) Riddic, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed; Wiley-Interscience: New York, 1970; Vol. II.
(3) Hafez, M.; Hartland, S. *J. Chem. Eng. Data* **1976**, *21*, 179–182.
(4) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Interscience: New York, 1950.
(5) Asfour, A.; Dullien, F. A. L. *J. Chem. Eng. Data* **1981**, *26*, 312–316.
(6) Rauf, M. A.; Stewart, G. H. *J. Chem. Eng. Data* **1983**, *28*, 324–328.
(7) Wright, F. J. *J. Chem. Eng. Data* **1961**, *6*, 454–456.
(8) Mulcahy, D. E. *J. Phys. D: Appl. Phys.* **1984**, *17*, 219–223.
(9) Grunberg, L.; Nissan, A. H. *Nature* **1949**, *164*, 799–800.
(10) McAllister, R. A. *AIChE J.* **1960**, *6*, 427–431.
(11) Heric, E. L. *J. Chem. Eng. Data* **1966**, *11*, 66–68.
(12) Dymond, J. H.; Young, K. J. *Int. J. Thermophys.* **1981**, *2*, 237–247.
(13) Dymond, J. H.; Young, K. J. *Int. J. Thermophys.* **1980**, *1*, 331–344.
(14) Jambon, C.; Delmas, G. *Can. J. Chem.* **1977**, *55*, 1360–1366.
(15) Coursey, B. M.; Heric, E. L. *J. Chem. Eng. Data* **1969**, *14*, 426–430.
(16) Mumford, S. A.; Phillips, J. W. C. *J. Chem. Soc.* **1950**, 75–84.
(17) Heston, W. M.; Hennelly, E. J.; Smyth, C. P. *J. Am. Chem. Soc.* **1950**, *72*, 2071–2075.
(18) Dreisbach, R. R. *Adv. Chem. Ser.* **1961**, *29*, 74–88.

Received for review May 31, 1984. Revised manuscript received June 10, 1985. Accepted September 11, 1985.