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Viscosity of Some Binary Liquid Mixtures of Oleic Acid and Triolein with Selected Solvents

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Viscosity data are presented for ten binary oleic acid + solvent and triolein + solvent systems at 45 °C. Experimental viscosities have been fitted to the multibody equations of McAllister, based on the absolute rate theory, and the second-order Auslander equation. The latter permits a more accurate representation of the experimental data.

Introduction

The correlation of mixture viscosities has attracted considerable attention in recent years. A number of empirical and semiempirical equations have been proposed, for instance those of Bingham (*2*), Cronauer, Rothfus, and Kermore (*3*), Katti and Chaudhri (*6*), Kendall and Monroe (*7*), and McAllister (*8*). In this paper we concentrate on the equations of McAllister, based on Eyring's model for viscosity. The binary systems under study are oleic acid with methanol, ethanol, 2-propanol, acetone, hexane, and benzene and triolein with 2-propanol, acetone, hexane, and benzene. Viscosity data have been obtained at 45 °C. The systems chosen have a wide range of molecular size ratios and are therefore particularly suitable for testing McAllister's multibody interaction models. The data have also been fitted to the generalized equation of Auslander (*1*).

Experimental Section

Absolute ethanol was of 99% purity. The remaining solvents were of BDH "AnalaR" grade and were used without further purification. The 99% oleic acid was supplied by Unilever Research, and triolein was supplied by BDH Chemicals. The refractive index and density of the chemicals were determined and compared with values published in the literature. Refractive indices were only measured for the solvents. The experimental and published values are compared in Table I.

Four Cannon-Fenske viscometers of different capillary diameters were used to cover the viscosity range. The viscometers were calibrated by Poulton, Selfe and Lee Limited at 15.56, 54.44, and 98.89 °C. Viscometer constants at 45 °C were obtained by interpolation. The viscometers were suspended in a water bath maintained at 45 ± 0.05 °C. Due to the viscous nature of the mixtures the viscometers were not filled via the measuring limb as recommended by the Institute of Petroleum Standards (*5*). Instead, the volume of liquid required to fill the inverted limb to the etch mark was determined, and this quantity of the mixture carefully introduced by a syringe into the upright viscometer. About 30 min was allowed for temperature equilibration before readings were taken. Times were measured with a stopwatch accurate to 0.1 s, the minimum flow time being 200 s. Flow times were measured till three consecutive readings differed from each other by no more than 0.2%, and the mean was recorded. The precision in viscosity was 0.2%.

Theory

The Eyring viscosity equation is (*4*)

$$\nu = hN/M \exp(G^*/RT) \qquad (1)$$

where G^* is the free energy of activation for viscous flow. Since the excess free energy of activation, G^{*E}, is given by the difference between the free energy of activation of the mixture and the free energy of activation of an ideal mixture, eq 1 gives (*4*)

$$G^{*E} = RT(\ln \nu\bar{M} - x_1 \ln \nu_1 M_1 - x_2 \ln \nu_2 M_2) \qquad (2)$$

where $\bar{M}$ is the average molecular weight.

McAllister (*8*) considered the interactions between like and unlike molecules and from eq 1 developed a correlation for three-body interactions, arbitrarily restricted to a molecular size ratio of 1.5.

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln\left(x_1 + x_2\frac{M_2}{M_1}\right) + 3x_1^2x_2 \ln\left[\left(2 + \frac{M_2}{M_1}\right)\Big/3\right] + 3x_1x_2^2 \ln\left[\left(1 + \frac{2M_2}{M_1}\right)\Big/3\right] + x_2^3 \ln (M_2/M_1) \qquad (3)$$

When the size of one component molecule differed appreciably from the size of the second component molecule, the three-body model, eq 3, was considered inadequate, and four- and five-body interaction models were derived to better represent the viscosity data. The four-body model is

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln\left(x_1 + x_2\frac{M_2}{M_1}\right) + 4x_1^3x_2 \ln\left[\left(3 + \frac{M_2}{M_1}\right)\Big/4\right] + 6x_1^2x_2^2 \ln\left[\left(2 + \frac{2M_2}{M_1}\right)\Big/4\right] + 4x_1x_2^3 \ln\left[\left(1 + \frac{3M_2}{M_1}\right)\Big/4\right] + x_2^4 \ln (M_2/M_1) \qquad (4)$$

and the five-body model is

$$\ln \nu = x_1^5 \ln \nu_1 + 5x_1^4x_2 \ln \nu_{11112} + 10x_1^3x_2^2 \ln \nu_{11122} + 10x_1^2x_2^3 \ln \nu_{11222} + 5x_1x_2^4 \ln \nu_{12222} + x_2^5 \ln \nu_2 - \ln\left(x_1 + x_2\frac{M_2}{M_1}\right) + 5x_1^4x_2 \ln\left[\left(4 + \frac{M_2}{M_1}\right)\Big/5\right] + 10x_1^3x_2^2 \ln\left[\left(3 + \frac{2M_2}{M_1}\right)\Big/5\right] + 10x_1^2x_2^3 \ln\left[\left(2 + \frac{3M_2}{M_1}\right)\Big/5\right] + 5x_1x_2^4 \ln\left[\left(1 + \frac{4M_2}{M_1}\right)\Big/5\right] + x_2^5 \ln (M_2/M_1) \qquad (5)$$

Constants ν_{12} and ν_{21} in eq 3, ν_{1112}, ν_{1122}, and ν_{2221} in eq 4 and ν_{11112}, ν_{11122}, ν_{11222}, and ν_{12222} in eq 5 represent interactions

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Table I. Pure Component Properties at 25 °C

component	d/g cm^{-3} exptl	d/g cm^{-3} lit.[a]	refractive index exptl	refractive index lit.[a]
methanol	0.7864	0.7865	1.3264	1.3265
ethanol	0.7850	0.7852	1.3592	1.3592
2-propanol	0.7807	0.7809	1.3753	1.3752
acetone	0.7852	0.7852	1.3567	1.3567
hexane	0.6552	0.6549	1.3721	1.3723
benzene	0.8735	0.8737	1.4979	1.4979
oleic acid	0.8940[b]	0.8940[b]		
triolein	0.8952[b]	0.8948[b]		

[a] Reference 9. [b] Determined at 45 °C.

between unlike molecules. These are left as adjustable parameters whose values are determined by fitting experimental data to the respective equations. Since there is no mechanism whereby these constants can be predicted from pure component data, the merit of McAllister's equations as opposed to a purely empirical fit is open to question.

Another equation that has been successfully used in correlating a variety of mixture intensive properties is that of Auslander (*1*). The equation is

$$x_1(x_1 + B_{12}x_2)(\nu - \nu_1) + A_{21}x_2(B_{21}x_1 + x_2)(\nu - \nu_2) = 0 \tag{6}$$

A_{21}, B_{12}, and B_{21} are constants representing binary interactions and are determined from a least-squares fit of the experimental data.

The viscosity data were also fitted to an empirical equation in the form

$$\nu = x_1\nu_1 + x_2\nu_2 + x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots] \tag{7}$$

Table II. Kinematic Viscosity and Excess Free Energy of Activation for Oleic Acid and Triolein Solvent Mixtures at 45 °C

x_1	ν, cSt	G^{*E}, cal/mol	x_1	ν, cSt	G^{*E}, cal/mol	x_1	ν, cSt	G^{*E}, cal/mol
Methanol (1)–Oleic Acid (2)								
0.0000	16.159	0.0	0.3134	11.939	703.2	0.7651	4.142	1106.5
0.0807	15.417	206.7	0.3940	10.859	858.9	0.8739	2.267	882.3
0.1199	14.665	288.2	0.5098	8.816	1024.9	0.9437	1.421	628.0
0.2091	13.509	490.6	0.6116	7.033	1126.9	1.0000	0.554	0.0
Ethanol (1)–Oleic Acid (2)								
0.0000	16.159	0.0	0.3248	11.186	515.4	0.6903	5.369	774.1
0.0774	15.227	145.6	0.4270	9.593	636.2	0.8139	3.451	675.6
0.1092	14.496	189.3	0.5156	8.157	714.9	0.9017	2.189	478.9
0.1975	13.113	330.5	0.5907	7.018	765.8	1.0000	0.981	0.0
2-Propanol (1)–Oleic Acid (2)								
0.0000	16.159	0.0	0.3381	11.110	404.7	0.8044	3.967	470.2
0.0548	15.410	78.6	0.5196	8.247	528.5	0.8998	2.686	314.5
0.1196	14.489	164.5	0.6093	6.805	548.8	0.9447	2.168	209.7
0.2106	13.101	273.7	0.7149	5.198	529.9	1.0000	1.511	0.0
Acetone (1)–Oleic Acid (2)								
0.0000	16.159	0.0	0.4208	7.005	668.3	0.8133	1.517	665.6
0.0406	15.231	81.5	0.5125	5.417	748.3	0.9028	0.780	404.8
0.2055	11.326	372.7	0.5867	4.222	781.8	1.0000	0.333	0.0
0.3084	9.234	534.3	0.7140	2.496	755.6			
Hexane (1)–Oleic Acid (2)								
0.0000	16.159	0.0	0.3156	7.500	340.7	0.7052	2.035	458.6
0.0647	14.085	85.9	0.4167	5.680	419.3	0.8048	1.275	381.5
0.1036	13.019	138.3	0.5044	4.273	455.7	0.8994	0.770	254.8
0.2232	9.715	266.4	0.6201	2.858	477.5	1.0000	0.386	0.0
Benzene (1)–Oleic Acid (2)								
0.0000	16.159	0.0	0.4084	7.219	478.9	0.7838	2.079	497.8
0.0452	13.789	69.9	0.5017	5.726	546.0	0.8564	1.472	412.0
0.1752	12.053	247.5	0.6107	4.106	575.1	0.9305	0.930	246.1
0.3115	9.189	404.8	0.6960	3.043	564.9	1.0000	0.538	0.0
2-Propanol (1)–Triolein (2)								
0.0000	32.753	0.0	0.3919	26.619	1010.4	0.7993	12.426	1437.0
0.1372	31.532	390.2	0.4763	24.396	1179.3	0.8958	7.835	1154.5
0.2007	30.441	554.7	0.6106	20.548	1399.1	0.9444	4.811	818.3
0.3127	28.474	834.2	0.6974	17.091	1467.6	1.0000	1.511	0.0
Acetone (1)–Triolein (2)								
0.0000	32.753	0.0	0.2942	26.110	1013.3	0.7564	9.793	1958.2
0.0254	32.150	90.3	0.4346	21.745	1420.9	0.8083	7.891	1948.0
0.0966	30.844	349.4	0.5088	19.309	1479.2	0.9016	3.961	1560.8
0.1972	28.377	693.0	0.6992	11.835	1918.9	1.0000	0.333	0.0
Hexane (1)–Triolein (2)								
0.0000	32.753	0.0	0.4176	19.219	1153.1	0.8095	4.734	1412.2
0.1058	29.564	324.7	0.5053	15.734	1314.7	0.9025	2.118	1065.7
0.2135	26.003	633.3	0.6104	11.959	1470.5	1.0000	0.333	0.0
0.3206	22.660	923.1	0.7037	8.457	1518.5			
Benzene (1)–Triolein (2)								
0.0000	32.753	0.0	0.5486	18.050	1451.6	0.8604	4.898	1384.6
0.1096	31.194	355.2	0.6129	15.455	1540.4	0.9315	2.340	984.2
0.3038	26.235	909.9	0.6957	11.980	1602.8	1.0000	0.538	0.0
0.4248	22.387	1205.5	0.7821	8.312	1575.3			

Table III. Constants of Equations 3-5

component 1	eq 3		eq 4			eq 5			
	$\ln \nu_{12}$	$\ln \nu_{21}$	$\ln \nu_{1112}$	$\ln \nu_{1122}$	$\ln \nu_{2221}$	$\ln \nu_{11112}$	$\ln \nu_{11122}$	$\ln \nu_{11222}$	$\ln \nu_{12222}$
Component 2 is Oleic Acid									
methanol	4.009	1.918	3.677	1.271	2.996	3.297	0.721	3.376	2.431
ethanol	3.055	2.176	2.651	1.849	2.709	3.229	1.754	2.559	2.588
2-propanol	2.639	2.363	2.311	1.955	2.729	1.994	1.823	2.530	2.634
acetone	2.342	2.037	1.668	1.712	2.499	1.121	1.573	2.127	2.502
benzene	2.128	2.053	1.559	1.777	2.413	1.300	1.159	2.568	2.252
hexane	1.522	1.994	1.028	1.476	2.329	0.644	1.221	1.871	2.395
Component 2 is Triolein									
2-propanol	6.179	2.219	6.293	0.830	4.421	6.069	0.011	5.385	2.895
acetone	6.926	1.739	6.554	0.642	4.196	6.345	−0.609	5.404	2.819
benzene	6.008	1.945	5.653	1.052	4.226	5.082	0.752	4.611	3.086
hexane	5.437	2.135	5.045	1.257	3.904	4.558	0.644	4.416	2.952

Table IV. Constants of Equations 6 and 7

component 1	eq 6			eq 7				
	A_{21}	B_{12}	B_{21}	A	B	C	D	E
Component 2 is Oleic Acid								
methanol	0.5427	0.2297	1.7183	2.8301	−3.4987	−7.9795	−1.0639	9.7285
ethanol	0.1586	0.0991	5.5006	−0.4619	−0.9942	−4.1318	−2.4841	5.3999
2-propanol	0.1133	0.0362	7.2304	−1.2358	−2.1797	−0.4335	−2.4375	3.8709
acetone	1.1494	1.7518	0.1937	−10.4980	−2.0658	−0.9391	−0.0721	1.6445
benzene	−0.0404	−0.1879	−10.3267	−11.0225	−4.4947	14.3546	14.9023	−34.1889
hexane	0.3841	0.7820	0.5439	−15.7148	3.2317	0.2046	−1.7815	1.3307
Component 2 is Triolein								
2-propanol	−0.1897	−0.2139	−11.4997	27.2227	8.6265	−7.5480	−18.8168	29.4031
acetone	1.4795	0.7997	0.7482	11.9840	−3.934	−0.1316	−5.5371	−12.7842
benzene	1.5760	0.6609	0.5681	12.6232	−7.7781	−6.2150	−11.7000	−0.6839
hexane	2.5044	2.1803	0.1858	−1.8113	−10.1938	−7.3049	−1.1531	−0.8317

Table V. Average and Maximum Percentage Deviations of Experimental Viscosities from Equations 3-7

component 1	$(V_2/V_1)^{1/3}$	eq 3		eq 4		eq 5		eq 6		eq 7	
		av	max	av	max	av	max	av	max	av	max
Component 2 is Oleic Acid											
methanol	1.97	3.4	7.8	3.2	10.7	2.7	13.3	1.3	2.2	0.17	0.26
ethanol	1.74	3.4	7.8	1.2	2.0	0.6	1.6	1.2	5.4	0.16	0.21
2-propanol	1.60	3.3	8.2	1.2	4.2	1.0	1.8	0.9	2.6	0.10	0.18
acetone	1.62	2.8	6.5	0.8	2.6	0.7	2.5	0.7	1.8	0.13	0.28
benzene	1.52	2.8	6.1	1.8	8.9	1.3	5.2	3.84	10.4	0.24	0.31
hexane	1.34	1.6	4.3	0.4	0.9	0.4	0.9	1.3	2.5	0.14	0.25
Component 2 is Triolein											
2-propanol	2.32	19.8	43.7	6.6	10.0	5.1	12.5	2.7	6.3	0.21	0.32
acetone	2.35	20.6	50.3	6.8	13.6	4.4	7.8	0.8	3.3	0.18	0.26
benzene	2.21	17.1	39.0	6.7	12.0	3.2	7.9	1.6	5.9	0.14	0.22
hexane	1.94	14.6	39.8	6.1	9.8	3.5	10.5	1.4	3.3	0.18	0.30

Results

Experimental viscosities and excess Gibbs free energy of activation for viscous flow are listed in Table II. Equations 3–7 were fitted to the viscosity data by the least-squares technique. Constants of the equations are reported in Tables III and IV, while average and maximum percentage deviations of experimental viscosities from calculated values are shown in Table V. The standard deviation in G^{*E} is 0.7 cal/mol.

Discussion

The relationship between size ratio, $(V_1/V_2)^{1/3}$, and the error in McAllister's three-, four-, and five-body equations is shown in Table V. In keeping with McAllister's analysis, there is a general downward trend in errors with decrease in molecular size ratio for the three equations, but the decrease is not consistent. Errors for the triolein systems are higher than for the oleic acid systems, showing some dependence on molar volume ratio as well as molecular size ratio. The five-body model, eq 5, represents a substantial improvement on the three- and four-body models, but this is to be expected as eq 5 incorporates more adjustable parameters.

The three-parameter Auslander equation gives the best results and is to be preferred to the McAllister equations since it is mathematically less complex. The derivation of the Auslander equation follows much the same reasoning as McAllister's with respect to molecular interactions, and higher order equations, analogous to eq 4 and 5, may be derived. A three-body Auslander equation may be more suitable than the two-body eq 7 since its cubic form would permit the representation of both maxima and minima.

Conclusions

The trend in McAllister's equations of increasing fitting error with increasing molecular size ratio is observed in this study, but the inconsistency of the numerical values of the errors precludes the formulation of any general rules of application. The less complex, three-parameter Auslander equation fits the data more accurately, and the use of the second and higher order Auslander equations is recommended for representing the physical properties of mixtures.

Glossary

A_{21}, B_{12}, B_{21}	constants in eq 6
A-E	constants in eq 7
G^*	molar Gibbs free energy of activation for viscous flow
h	Plank constant
M	molecular weight
N	Avogadro number
R	gas constant
T	absolute temperature
x	mole fraction
ν	kinematic viscosity
ν_{12}, ν_{21}, etc.	fitting constants in eq 3-5

Subscripts

1,2	components 1 and 2

Superscripts

E	excess property

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Gas–Liquid Equilibrium in Hydrogen + *n*-Hexadecane and Methane + *n*-Hexadecane at Elevated Temperatures and Pressures

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Experimental results are presented for gas-liquid phase equilibria in binary mixtures of *n*-hexadecane with hydrogen at four temperatures from 190 to 391 °C and with methane from 190 to 430 °C. At each temperature, measurements were made at pressures from 20 to 250 atm or to near the critical pressure of the mixtures.

Introduction

This work is part of a continuing study of phase equilibrium in mixtures of light gases and heavy hydrocarbon liquids at elevated temperatures and pressures. In the past, attention was specifically aimed at polynuclear aromatic and naphthenic hydrocarbons such as tetralin (*3*), methylnaphthalene (*6*), diphenylmethane (*4*), and bicyclohexyl (*2*).

In this work we study mixtures of a long chain paraffin with hydrogen and with methane. Measurements were made at temperatures from 190 to 390 °C and pressures from 20 to 250 atm for hydrogen + *n*-hexadecane. No literature data are available for these mixtures at conditions comparable to this study. For the methane + *n*-hexadecane system, the temperatures studied were in the range 190–430 °C and pressures were from 20 atm to approaching the critical pressure of the mixtures. Sultanov and co-workers (*5*) reported experimental results for this system at temperatures from 100 to 350 °C up to the critical pressures of the mixtures. Low-pressure solubility data of methane in *n*-hexadecane were determined by Chappelow and Prausnitz (*1*) in the temperature range 25–200 °C.

Experimental Section

The same apparatus and procedures described by Simnick et al. (*3*) were used in this work.

Hydrogen gas was supplied by Airco with a minimum purity of 99.95%. Methane was obtained from Matheson and *n*-hexadecane from Matheson Coleman and Bell Co.; the purities of both chemicals are claimed to be 99+%. The thermal stability of *n*-hexadecane was checked by gas chromatography during all of the experiments. No more than 1% of impurities was detected in the *n*-hexadecane from the cell effluents at any conditions studied.

Fluctuations in the temperature of the equilibrium cell during the course of all the measurements on an isotherm were within 0.1 °C.

The attainment of equilibrium in the flow apparatus used was verified by varying the liquid feed flow rate. Tests were made at 100 atm and 390.9 °C with mixtures of hydrogen + *n*-hexadecane and at several pressures at 189.3 °C with mixtures of methane + *n*-hexadecane. No appreciable variations of the phase compositions were observed as the flow rate was varied.

Results and Discussion

Figure 1 shows the solubility of hydrogen in *n*-hexadecane at four temperatures from 188.5 to 390.9 °C as a function of pressure, while Figure 2 shows the saturated equilibrium compositions of the vapor phase for the same mixtures. At each condition of temperature and pressure, at least two samples of both the overhead and bottom cell effluents were taken, and the agreement among replicate samples was within 1% in mole fraction of hydrogen. The individual data points are shown in the figures when they can be differentiated. The average values of the replicate samples are given in Table I. The vapor compositions at 188.5 °C are practically all hydrogen, and equilibrium ratios of *n*-hexadecane at this isotherm are extremely sensitive to the last few digits in the value of y_H. The values of y_H are, therefore, reported in the table to five digits.

The experimental results for methane + *n*-hexadecane are shown in Figures 3 and 4. At 189.3 °C, the pressures were measured up to 250 atm. For the three higher isotherms,

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