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Binary Liquid Viscosities and Their Estimation from Classical Solution Thermodynamics

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A model is presented for the viscosity of liquid mixtures that is based upon familiar principles of solution thermodynamics and Eyring's concept of fluid viscosity. The free energy of activation for viscous flow is divided into ideal and excess parts, and the excess function gives a measure of the deviation from ideal behavior for each species at each concentration. The model does not dictate how the deviation should be predicted; however, three equations used in predicting VLE data were successful in predicting mixture viscosities. The model can describe highly nonideal systems but reduces, simply, to fit ideal systems and limiting viscosity behavior as $x_i \rightarrow 1$. Liquid viscosities and densities of six organic binary mixtures were measured at 24.7 °C. These and five published sets of viscosity data are used to compare this new method with four established ones.

Introduction

That there is no universally accepted method for predicting the viscosity of liquid mixtures is the result of two unsolved problems: first, there is no comprehensive theory that adequately describes the molecular interactions that influence this transport property; second, nonidealities have not been concisely described in terms of familiar thermodynamic liquid solution principles. The first problem is unlikely to be solved in the very near future, although there has been considerable effort at developing interaction information. Wei and Rowley (*1*, *2*) extracted interaction information from binary VLE data as excess free energy parameters and applied these to their local composition model for shear viscosity. Their approach is based upon the nonrandom two-liquid (NRTL) model and involves intermolecular interaction terms and a nonrandomness parameter. Krishnan and Laddha (*3*) also calculated excess free energies from VLE data and used them to predict binary viscosities. Their work clearly showed that the fraction of the excess free energy of mixing (VLE) that affects the viscosity is most likely both system and composition dependent. In addition to providing a summary of the various equations for estimating mixture viscosities, Diab and Maddox (*4*) provide a group contribution technique similar to that used by Ratcliff and Khan (*5*) to predict mixture viscosities. This method defines the viscosity of an ideal mixture as a mole fraction average of the logarithmic pure component viscosities and lodges all nonideality in the structural and group contribution terms. This suggests that functional groups rather than molecules are responsible for interaction and nonideality. Lobe (*6*) developed a volume-fraction, exponential equation for mixture viscosity. His use of volume fractions rather than mole fractions is supported by the "hole" and "free volume" theories associated with molecular volumes. Much earlier, McAllister (*7*) suggested a three-body viscosity equation to account for molecular interaction in binary solutions, and later Heric (*8*) and Heric and Brewer (*9*) accounted for molecular interaction by dividing the free energy of activation into two parts. One part accounts for the residual (excess) free energy of activation, while the other accounts for the ideal free energy of activation. Their discussion of the effect of molecular size on excess functions gives insight into solution nonideality and molecular interaction.

In this paper, we give a method for calculating the nonideality associated with liquid mixture viscosity that is similar to that used for VLE data. The effort leads to an equation containing mole fractions, pure component shear viscosities, and activity coefficients that can be used to predict mixture shear viscosities. The equation is applied to some binary systems showing monotonically increasing or decreasing viscosity, maxima, and minima, or a combination of both. Viscosities of binary solutions containing aromatics, alcohols, paraffins, and water are examined, and several sets of new binary viscosity data are reported. The aforementioned methods are compared to the one proposed here.

Theoretical Section

The absolute temperature functionality for shear viscosity was first proposed as

$$\log_e \mu = A + B/T \qquad (1)$$

by Arrhenius (*10*) and later Andrade (*11*). Physical significance was later attached to A and B when Eyring (*12*) explained his "hole in the liquid" hypothesis. According to it, a shear stress forces a molecule into a hole while traversing an activation energy barrier. A free energy of activation, similar to that proposed in the reaction rate principle, was then introduced into eq 1, giving it the familiar form

$$\log_e \mu = \log_e \frac{hN_0}{V} + \frac{\Delta G^\circ}{RT} \qquad (2)$$

Equation 2 was modified by Glasstone et al. (*13*) and Powell et al. (*14*) to

$$\log_e \mu_m = \log_e \frac{hN_0}{V_m} + \frac{x_1 \Delta G_1^\circ}{RT} + \frac{x_2 \Delta G_2^\circ}{RT} - \frac{\Delta G_m^E}{\beta RT} \qquad (3)$$

to accommodate binary mixtures. An equation somewhat similar to this with dimensionless viscosity defined as

$$\hat{\mu} \equiv \mu V / hN_0 \qquad (4)$$

is the basis for our examination of the nonideality problem:

$$\log_e \hat{\mu}_m = \sum_i x_i \log_e \hat{\mu}_i^\circ + \sum_i x_i \log_e \gamma_i^v \qquad (5)$$

In this, $\hat{\mu}_m$ and $\hat{\mu}_i^\circ$ are the mixture and pure component dimensionless viscosities, respectively. The γ_i^v are the mole fraction viscosity activity coefficients; to be clearly distinguished from their counterpart, they are the VLE activity coefficients. Two limiting situations can be expected in regard to eq 5: First, as $x_i \rightarrow 1$, $\mu_m \rightarrow \mu_i^\circ$ because $\gamma_i^v \rightarrow 1$. Second, when this occurs, it is likely that other γ_i^v will not equal unity; however, their corresponding x_i's $\rightarrow 0$. This might be viewed as an extension of the Lewis and Randall rule to component viscosity in solution. Just as the thermodynamic concept of fugacity is a measure of the ability of a molecule to escape from its liquid environment into the vapor state by overcoming a free energy

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Table I. Densities, Viscosities, Refractive Indices, and Boiling Points of Pure Liquids Used

	ρ, g/mL		η, cP		n_D		bp, °C	
	this work, 24.7 °C	ref *15*, 25 °C	this work, 24.7 °C	ref *15*, 25 °C	this work, 24.7 °C	ref *15*, 25 °C	this work	ref *15*
MEK	0.7990	0.7997	0.3774	0.3805	1.3761	1.3764	79.2	79.6
HEX	0.6611	0.6548	0.3044	0.2985	1.3749	1.3723	69.1	68.7
HEP	0.6795	0.6795	0.3899	0.3967	1.3856	1.3851	98.2	98.4
BZ	0.8730	0.8737	0.6053	0.6028	1.4975	1.4979	80.0	80.1

barrier, so might one envision that according to Eyring's theory a molecule moving under a shear stress in a liquid environment with other molecules, whether similar or dissimilar, can escape into a vacant site only be overcoming a free energy barrier. For this reason, we state that

$$\Delta G_m/RT = \log_e \hat{\mu}_m = \sum_i x_i \log_e \hat{\mu}_i \qquad (6)$$

where

$$\log_e \hat{\mu}_i \equiv (\partial \log_e \hat{\mu}_m/\partial n_i)_{T,P,n_j} \qquad (7)$$

This should display the same characteristics as any partial molal quantity. It should be noted that

$$\log_e \hat{\mu}_i = \log_e (\gamma_i^{\mathrm{v}} \hat{\mu}_i^\circ) \qquad (8)$$

and as $\gamma_i^{\mathrm{v}} \rightarrow 1$, $\hat{\mu}_i \rightarrow \hat{\mu}_i^\circ$.

Returning to eq 5, we note that the free energy of activation for viscous flow should be

$$\Delta G_m = \Delta G^{\mathrm{id}} + \Delta G^{\mathrm{E}} \qquad (9)$$

where

$$\Delta G^{\mathrm{id}}/RT \equiv \sum x_i \log_e \mu_i^\circ \qquad (10)$$

and

$$\Delta G^{\mathrm{E}}/RT \equiv \sum x_i \log_e \gamma_i^{\mathrm{v}} \qquad (11)$$

Equation 10 is our choice for defining the viscosity of hypothetical, ideal solutions. It is supported by basic thermodynamic solution principles and Eyring's concept of fluid viscosity. Equation 11 assigns the total nonideality of the mixture in mole fraction proportion to the respective components. It gives deviation from ideal behavior at each composition and yet in no way dictates how the coefficients might be predicted or what type of solutions they might apply to.

Although Newtonian liquid viscosity is a dynamic property expressible on a macro scale and is independent of the rate of fluid shear, it is, nevertheless, a function of the state of the fluid and, therefore, thermodynamic properties such as temperature, pressure, and in the case of solutions, composition.

If we accept the hypothesis that the free energy of activation for viscous flow is a thermodynamic property, then the classical laws of thermodynamics should apply to the functional relationships governing this property. Accordingly, for a binary viscosity solution, the equation

$$\left(\frac{\partial \log_e \hat{\mu}_m}{\partial T}\right)_{p,x_i} dT + \left(\frac{\partial \log_e \hat{\mu}_m}{\partial P}\right)_{T,x_i} dP - [x_1\, d \log_e(\gamma_1^{\mathrm{v}} \hat{\mu}_1^\circ) + x_2\, d \log_e (\gamma_2^{\mathrm{v}} \hat{\mu}_2^\circ)] = 0 \qquad (12)$$

should apply. It follows, that for this single phase system at constant T and P

$$x_1 \frac{d \log_e \gamma_1^{\mathrm{v}}}{dx_1} + x_2 \frac{d \log_e \gamma_2^{\mathrm{v}}}{dx_1} = 0 \qquad (13)$$

That is, the viscosity activity coefficients in a binary solution should obey the Duhem relation, i.e., eq 13.

Experimental Details

Spectrophotometry grade benzene, ACS certified 2-butanone, and HPLC grade *n*-heptane and *n*-hexane were used to prepare six binary solutions for viscosity and density measurements. Large volumes were prepared and stoppered, and all measurements were made from these stocks. Weight measurements always in excess of 25 g each were made with a digital electronic balance with a precision display of 0.01 g. The accuracy of this was verified with standardized weights of 50, 100, and 500 g. Solutions were prepared to an accuracy of 0.0004 g/g.

Viscosity measurements were carried out with a factory-calibrated Ubbelohde, ASTM size 0 viscometer and a Cannon-Fenske, ASTM size 25 viscometer. Double-distilled water was used to calibrate the latter with the former. The viscometers were vertically aligned by clamps in a water-filled bath equipped with a Brinkmann MGW Lauda RC3 controlled heater. The bath temperature was measured with a thermometer that had gradations of 0.1 °C and which had been standardized against a certified thermometer with gradations of 0.05 °C. Solutions were temperature stabilized, and fluctuations of no more than ±0.1 °C were observed. Four measurements of viscosity with deviations of no more than 0.2% in efflux time were taken and averaged for each solution.

Density measurements were made in 25-mL glass pycnometers calibrated with deaerated double-distilled water at an absolute density of 0.997 15 at 24.7 °C. Three trials were made for each solution. The densities, viscosities, refractive indices, and normal boiling points that we measured for the pure components are presented in Table I alongside values taken from the literature (*15*). The greatest discrepancies occur for the hexane properties.

For the mixture results presented in Table II there is an uncertainty in the fourth decimal place that is related to experimental errors in temperature, compositions, efflux times, and the viscometer constants. Several sets of our mixture data are presented in Figure 1 for comparison with sets taken from the literature (*16*–*18*). The *n*-hexane–benzene system shows the greatest discrepancy, principally in the high hexane concentration region of the data sets. The slight temperature difference would not account for the differences.

Results and Discussion

Solutions were selected for study that display diverse viscometric behavior. For example, the viscosity of the selected acetone–water system (*19*) shows a wide range of viscosity varying from η = 0.30 cP to η = 1.37 cP, at which point a maximum exists. Such trends are common to aqueous solutions. The *n*-hexane–benzene system shows monotonically increasing behavior, while *n*-heptane–*n*-hexane displays a very slight decreasing slope, and 2-butanone–*n*-hexane has a very shallow minimum at x_1 = 0.11. Toluene–methanol exemplifies a maximum/minimum behavior. We conclude from these that simple additive equations have limited value for estimating the viscosity of binary solutions except for the very few systems that may be almost ideal.

In the present work, viscosity and molar density data were first smoothed and values recomputed at 0.1 fraction intervals over the full composition range. This was done to analyze and

Table II. Shear Viscosities and Densities of Binary Solutions at 24.7 °C

x_1	η, cP	ρ, g mL^{-1}	x_1	η, cP	ρ, g mL^{-1}
n-Heptane (1)–2-Butanone (2)					
0.000	0.3774	0.7990	0.5955	0.3649	0.7104
0.1271	0.3686	0.7731	0.7044	0.3677	0.6998
0.2092	0.3655	0.7582	0.8014	0.3721	0.6924
0.3055	0.3637	0.7437	0.9011	0.3789	0.6850
0.4593	0.3646	0.7249	1.000	0.3899	0.6795
Benzene (1)–2-Butanone (2)					
0.000	0.3774	0.7990	0.5597	0.4674	0.8417
0.1513	0.3919	0.8107	0.6057	0.4775	0.8440
0.2663	0.4141	0.8197	0.7302	0.5097	0.8534
0.2941	0.4175	0.8221	0.8777	0.5571	0.8640
0.4321	0.4408	0.8319	1.000	0.6053	0.8730
n-Heptane (1)–*n*-Hexane (2)					
0.000	0.3044	0.6611	0.6023	0.3554	0.6724
0.1005	0.3132	0.6626	0.7154	0.3649	0.6744
0.1957	0.3202	0.6650	0.8009	0.3727	0.6763
0.3837	0.3365	0.6689	0.8944	0.3801	0.6775
0.5080	0.3471	0.6712	1.000	0.3899	0.6795
2-Butanone (1)–*n*-Hexane (2)					
0.000	0.3044	0.6611	0.6043	0.3277	0.7277
0.0550	0.3018	0.6638	0.6943	0.3371	0.7429
0.2337	0.3032	0.6814	0.8004	0.3496	0.7607
0.2985	0.3054	0.6881	0.9053	0.3647	0.7802
0.4168	0.3122	0.7026	1.000	0.3774	0.7990
0.5063	0.3211	0.7143			
Benzene (1)–*n*-Hexane (2)					
0.000	0.3044	0.6611	0.5967	0.3871	0.7657
0.1026	0.3104	0.6752	0.7149	0.4256	0.7927
0.2013	0.3191	0.6904	0.7940	0.4600	0.8131
0.2817	0.3276	0.7042	0.8993	0.5212	0.8413
0.4385	0.3516	0.7332	1.000	0.6053	0.8730
Benzene (1)–*n*-Heptane (2)					
0.000	0.3976	0.6795	0.5204	0.4382	0.7524
0.1007	0.3923	0.6916	0.6729	0.4487	0.7829
0.1109	0.3913	0.6920	0.6893	0.5006	0.7872
0.1922	0.4003	0.7022	0.6967	0.4544	0.7894
0.2760	0.4019	0.7136	0.8532	0.5208	0.8272
0.2915	0.4023	0.7163	0.9152	0.5442	0.8457
0.3953	0.4142	0.7312	1.000	0.6119	0.8730
0.4839	0.4157	0.7453			

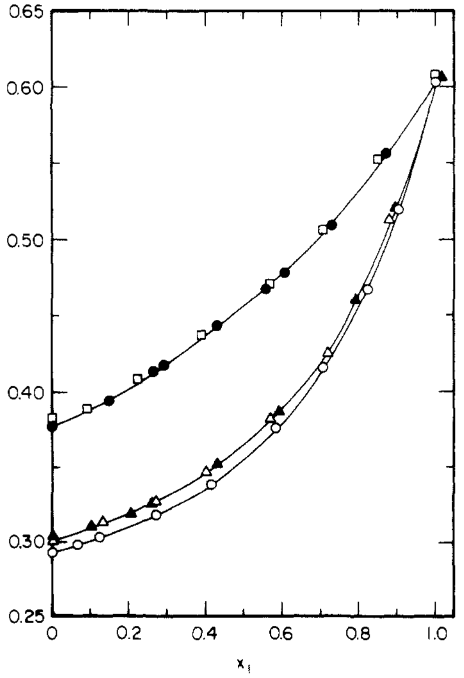

Figure 1. Comparison of some published viscosity data at 25 °C with our data obtained at 24.7 °C: ▲, benzene (1)–*n*-hexane (2); △, ref *16*; ○, ref *17*; ●, benzene (1)-2-butanone (2); □, ref *18*.

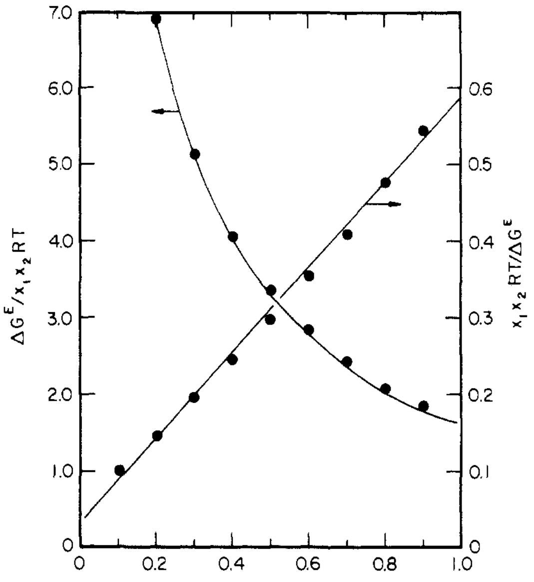

Figure 2. Excess free energy of activation for viscous flow functions for the viscosity of the 1-propanol (1)–water (2) system at 25.0 °C.

compare the method we propose to the four, established methods presented here.

Wei and Rowley's NRTL local composition model (*2*)

$$\log_e (\mu V)_m = \sum_i \phi_i \xi_i^\circ + \sum_i \phi_i \left[\sum_j \phi_j G_{ji}(\xi_{ji} - \xi_i^\circ)/\sum_l \phi_l G_{li}\right] - \sigma H^E/RT \quad (A)$$

Lobe's volume-fraction exponential model (*6*)

$$\nu_m = \nu_1 \phi_1 \exp\left[\frac{\alpha_2 \phi_2}{RT}\right] + \nu_2 \phi_2 \exp\left[\frac{\alpha_1 \phi_1}{RT}\right] \quad (B)$$

McAllister's three-body model (*7*)

$$\log_e (\mu V)_m = x_1^3 \log_e (\mu_1 V_1) + 3x_1^2 x_2 \log_e (\mu V)_{12} + 3x_1 x_2^2 \log_e (\mu V)_{21} + x_2^3 \log_e (\mu_2 V_2) \quad (C)$$

Heric and Brewer's free energy of activation model (*9*)

$$\log_e \hat{\mu}_m = \sum x_i \log_e \hat{\mu}_i^\circ + x_1 x_2 [A' + B'(x_1 - x_2) + C'(x_1 - x_2)^2 + ...] \quad (D)$$

Equation A was only tested for data close to 25 °C, since the non-variable activation parameter was reported for that temperature only. It is not used for aqueous solutions because it is reported to be unsuitable for these (*1*, *2*). The constants α_1 and α_2 in eq B were computed by using a Marquardt, nonlinear regression with an a priori estimate of the constants. The two parameters in eq C, $(\mu V)_{12}$ and $(\mu V)_{21}$, were computed by the method of least squares. For eq D the first two Redlich–Kister type parameters were derived from a least-squares fit of the smoothed data. Every point was given equal weight; however, this may be undesirable since the product $x_1 x_2$ may cause a spread in the results as either x_1 or $x_2 \rightarrow 1.0$.

Our method for predicting the viscosities of solutions depends directly upon the viscosity activity coefficients as defined in eq 5. These coefficients, whether determined experimentally or indirectly from predictive equations such as the van Laar, Margules, Wilson, etc., are related to $\Delta G^E/RT$ as shown in eq 11. With a set of binary viscosity data, eq 5 and 11 were used to compute a set of $\Delta G^E/RT$ values as a function of x_1. Regular solution behavior, indicated by the linearity of the $x_1 x_2 RT/\Delta G^E$ versus x_1 plot as depicted in Figure 2, was ap-

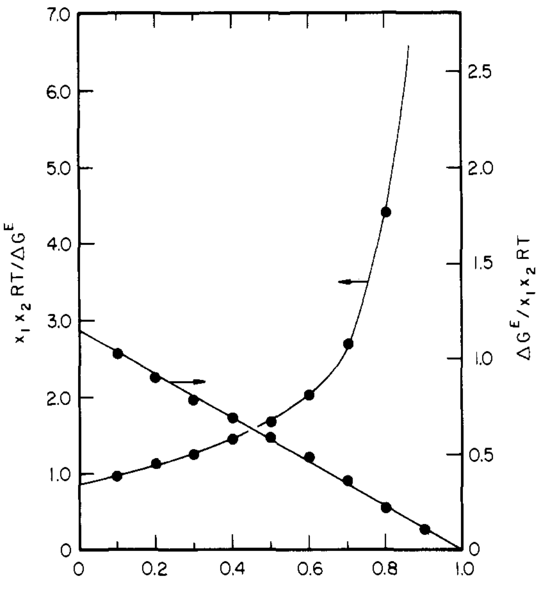

Figure 3. Excess free energy of activation for viscous flow functions for the viscosity of the toluene (1)–methanol (2) system at 25.0 °C.

parent for the majority of the systems. For these the van Laar equations gave the best fit and were selected for use. For the dimethyl sulfoxide–water and methanol–toluene systems the plots of $\Delta G^E/x_1x_2RT$ versus x_1 were linear, as illustrated in Figure 3. For these the Margules equations were selected for use.

Best values for the van Laar parameters were computed by numerical regression on a least-squares fit of the data applied to

$$\frac{x_1x_2RT}{\Delta G^E} = \frac{x_1}{A_{21}} + \frac{x_2}{A_{12}} \qquad (14)$$

In similar fashion the Margules parameters were obtained from the equation

$$\frac{\Delta G^E}{x_1x_2RT} = x_1(B_{21} - B_{12}) + B_{12} \qquad (15)$$

The Wilson equations, which are not linear with respect to their parameters, were also examined for their ability to represent the viscosity activity coefficients. A nonlinear least-squares method was used to calculate the set of Wilson parameters that minimized the function

$$\sum_{i=2}^{8} x_i \log_e \gamma_i^{v} + x_i \log_e (x_i + \Lambda_{12}(1 - x_i)) + (1 - x_i) \log_e ((1 - x_i) + \Lambda_{21}x_i) \qquad (16)$$

thereby giving the best fit to the activity coefficient data.

With these parameters for each mixture, the viscosity activity coefficients and the mixture viscosity were calculated by using the pure component viscosities. This elaborate procedure was used for the purpose of comparing the various methods.

It is also possible to obtain the experimental excess free energy and viscosity activity coefficients by the method of tangent intercepts. This is illustrated in Figure 4, where a line is constructed tangent to the free energy of activation curve at $x_1 = 0.5$. The vertical distance separating the ideal and total free energies at this point gives the excess free energy. At the terminal concentrations, the line intercepts give $\log_e (\gamma_1^{v}\mu_1^{o})$ and $\log_e (\gamma_2^{v}\mu_2^{o})$. From these, the activity coefficients can be evaluated corresponding to $x_1 = 0.5$. In this manner, activity coefficients can be determined over the whole range of composition.

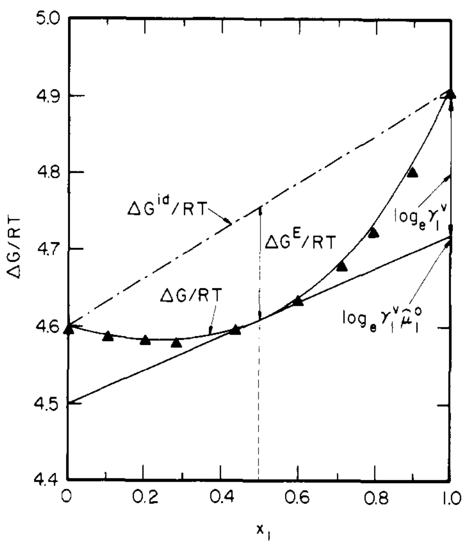

Figure 4. Tangent intercept rule applied to the benzene (1)–*n*-heptane (2) viscosity data at 24.7 °C passed through a spline and smoothed.

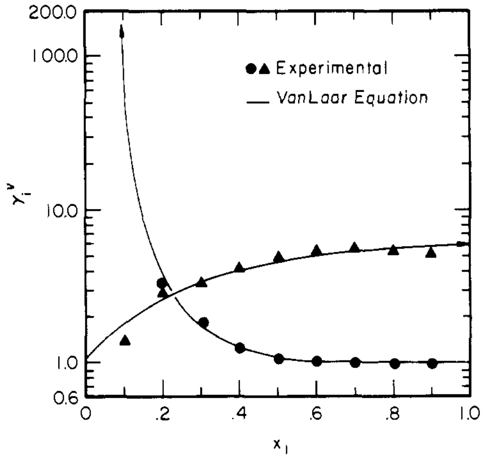

Figure 5. Experimentally determined activity coefficients compared to the van Laar predictions for the 1-propanol (1)–water (2) system at 25 °C.

The results presented in Table III show how the five methods compare on an average absolute deviation (AAD) basis. The AAD's are given by

$$\text{AAD} = \frac{100\%}{n}\sum_{i}^{n}\left|\frac{\mu_i^{\text{exptl}} - \mu_i^{\text{calcd}}}{\mu_i^{\text{exptl}}}\right| \qquad (17)$$

Except for the NRTL method, the parameters for the methods are also given in Table III. All five of the methods give small AAD's for most solutions. Exceptions include aqueous solutions. For eq 5 the constants presented are for the predictive equation (van Laar, Margules, or Wilson) that gives the smallest AAD for that mixture at the specified temperature. It is noteworthy that these give the smallest AAD's for the majority of the mixtures.

Figures 5, 6, and 7 depict the ability of the van Laar, Margules, and Wilson equations to fit the experimental data of three solutions in terms of their viscosity activity coefficients. The data and the predictions in these figures obey the Duhem relation, eq 13, very well. In Figure 8 viscosities estimated by each of the five methods are compared with viscosity data. We have included the NRTL method for comparative purposes here, although its use on aqueous systems is not recommended. For this system, the Lobe (*6*) method and the one developed here are clearly superior.

Van Laar and other predictive equation parameters can be determined by another method using pure component viscosity

Table III. Comparisons of Viscosity Models of Liquid Mixtures

mixture	eq A % AAD	eq B α_1/RT α_2/RT % AAD	eq C $\log_e (\mu V)_{12}$ $\log_e (\mu V)_{21}$ % AAD	eq D A' B' % AAD	eq 5 A_{12} A_{21} % AAD
n-heptane (1)–2-butanone (2) at 24.7 °C		0.751	−16.8883	−0.0481	−0.0434
		−1.304	−17.0329	−0.0909	−0.2258
	0.552	0.256	0.175	0.228	0.083
2-butanone (1)–*n*-hexane (2) at 24.7 °C		−1.347	−17.1628	0.0961	−0.3113
		0.689	−17.1724	−0.1552	−0.0947
	1.973	0.168	0.112	0.155	0.079
benzene (1)–*n*-hexane (2) at 24.7 °C		0.147	−17.0919	−0.1798	−0.4540
		−0.608	−17.0792	−0.6053	−0.8323
	0.511	0.150	0.172	0.242	0.088
benzene (1)–2-butanone (2) at 24.7 °C		0.529	−16.9664	−0.0191	−0.1944
		−0.776	−17.1045	−0.2170	−0.2432
	5.887	0.145	0.122	0.139	0.117
benzene (1)–*n*-heptane (2) at 24.7 °C		−1.554	−16.7991	0.1075	3.6736[a]
		0.551	−16.8302	−0.36200	0.0445
	1.782	0.358	0.467	0.607	0.390
n-heptane (1)–*n*-hexane (2) at 24.7 °C		−0.465	−16.7799	0.02027	0.0200
		0.280	−16.9162	0.0230	0.0417
	1.892	0.030	0.042	0.071	0.063
toluene (1)–methanol (2)[b] at 20 °C		1.150	−16.8940	−0.5640	1.1416[c]
		−2.573	−16.8653	0.5774	0.1302
		0.852	0.166	0.199	0.100
1-propanol (1)–water (2)[d] at 25 °C		1.492	−16.3386	−4.5353	21.5699
		0.835	−14.8241	4.3116	1.8224
		1.420	7.499	12.477	0.959
at 30 °C		1.457	−16.4589	−4.1764	19.9430
		0.684	−15.0386	4.1150	1.7521
		1.381	6.990	11.278	0.968
at 35 °C		1.408	−16.5413	−3.9668	18.8669
		0.606	−15.2377	3.9815	1.6927
		1.082	6.724	10.770	0.717
at 40 °C		1.201	−16.6741	−3.8388	17.5753
		0.587	−15.3919	3.7719	1.6330
		1.693	6.315	9.565	1.249
DMSO (1)–water (2)[e] at 25 °C		2.585	−16.3113	−3.9741	7.7378[c]
		0.440	−14.1939	4.8767	0.9895
		7.137	3.520	4.224	3.483
water (1)–acetone (2)[f] at 25 °C		2.567	−16.1115	3.6072	1.0466
		0.776	−17.9445	2.6234	25.4587
		5.275	5.779	8.499	4.325
at 30 °C		2.304	−16.2515	3.3637	0.9299
		0.806	−17.9882	2.5034	21.6413
		5.218	5.011	7.348	4.469
at 37.8 °C		0.747	−16.5161	2.9267	0.8116
		2.053	−18.0238	2.2836	16.9126
		4.068	4.648	6.690	4.017

[a] These are the Wilson parameters: $\Lambda_{12} = A_{12}$; $\Lambda_{21} = A_{21}$. [b] Reference *20*. [c] These are the Margules parameters: $B_{12} = A_{12}$; $B_{21} = A_{21}$. [d] Reference *21*. [e] Reference *22*. [f] Reference *19*.

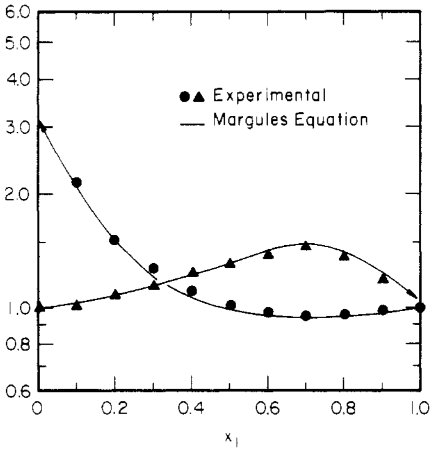

Figure 6. Experimentally determined activity coefficients compared to the Margules predictions for the toluene (1)–methanol (2) system at 20 °C.

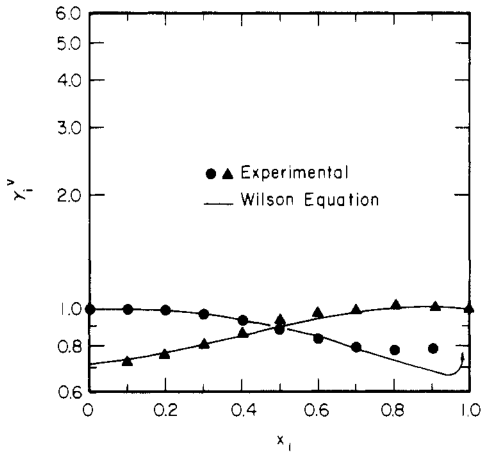

Figure 7. Experimentally determined activity coefficients compared to the Wilson predictions for the benzene (1)–*n*-heptane (1) system at 25 °C.

data and binary data at two random concentrations, preferably removed from the pure component concentrations. This requires the calculation of A_{12} and A_{21} in eq 14 or parameters in other predictive equations using two values of $\Delta G^E/RT$ ob-

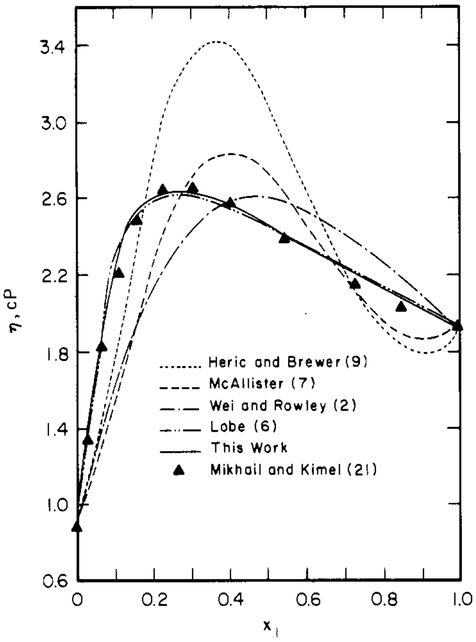

Figure 8. Comparison of five methods for estimating the viscosity of 1-propanol (1) and water (2) at 25 °C.

Table IV. Comparison of Constants and AAD's Using Data Points at x_1 = 0.4 and 0.6 with Constants from the Best Fit Data

mixture		at x_1 = 0.4, 0.6	best fit data
benzene (1)–*n*-heptane (2)	Λ_{12}	3.4131	3.6737
at 24.7 °C	Λ_{21}	0.1134	0.0445
	% AAD	0.788	0.390
toluene (1)–methanol (2)	B_{12}	1.0853	1.1416
at 20 °C	B_{21}	0.0918	0.1302
	% AAD	0.281	0.100
1-propanol (1)–water (2)	A_{12}	38.0060	21.5699
at 25 °C	A_{21}	1.7510	1.8224
	% AAD	3.332	0.959

tained from eq 9 by way of eq 6 and 10. This gives slightly larger AAD's as shown in Table IV. The 1-propanol–water system is very nonideal, and as expected, the two, random-point procedure leads to a greater AAD than the best fit data procedure. With only two binary viscosity data points, the method proposed here is better than the methods of McAllister (*7*) and Heric and Brewer (*9*) and as good as or better than the Lobe (*6*) procedure.

If components in a solution have similar force fields and do not differ significantly in molecular size and symmetry, then their excess free energy of activation will be very small. Such mixtures will display ideal behavior. Normal hexane and heptane differ molecularly by a single carbon unit, and one component will recognize the other, in terms of molecular interaction, as being very similar to itself. At a heptane mole fraction of 0.5080, $\Delta G_m/RT = -0.5379$ but $\Delta G^E/RT = 0.0112$. This binary system is thus nearly ideal, and when eq 9, taking the $\gamma_i^v = 1.0$, was used to calculate the ideal viscosity, the result compared favorably with the data.

Glossary

A, B	constants in eq 1
A', B', C'	constants in eq D
A_{ij}	constants in van Laar equation
B_{ij}	constants in Margules equation
G_{ij}	NRTL nonrandomness parameters
ΔG	free energy of activation for viscous flow
H	enthalpy
h	Planck's constant
N_0	Avogadro's number
n	number of moles
P	pressure
R	gas constant
T	absolute temperature
V	molar volume
x_i	mole fractions

Greek Letters

α_i	constants in eq B
β	constant in eq 3
γ_i^v	viscosity activity coefficients
η	shear viscosity, cP
Λ_{ij}	constants in Wilson equation
μ	shear viscosity
ν	kinematic viscosity
ξ_{ij}	intermolar force terms
ρ	density
σ	mixing parameter
ϕ_i	volume fractions

Superscripts

^	dimensionless quantity
o	pure component
E	excess
id	ideal
calcd	calculated
exptl	experimental

Subscripts

i, j, l	component
m	mixture

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