Viscosities of Nonelectrolyte Liquid Mixtures. I. n-Hexadecane + n-Octane

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Viscosities and densities of the n-alkanes, hexane, heptane, octane, nonane, decane, dodecane, tetradecane, hexadecane, and tetracosane, were measured for temperatures from 303 to 338 K. Viscosities were measured using a standard Utube Ostwald viscometer; a pycnometer was used to measure both pure alkane and mixture densities. Results for the binary system *n*-hexadecane + *n*-octane at 318.16, 328.16, and 338.16 K are presented here, and comparisons with selected correlating equations are made.

KEY WORDS: alkane; congruence; corresponding states; density; mixtures; viscosity.

1. INTRODUCTION

Many industrial liquid mixtures contain alkanes as major components; hence, it is important to understand and to be able to predict the viscosities of binary and multicomponent mixtures. Presently, there are still few experimental data on mixture transport properties, particularly viscosity, as a function of temperature, pressure, and composition. To make meaningful comparisons with theory or to test correlation equations, sufficient accurate experimental data must be available over reasonable reduced pressure, temperature, and composition ranges.

There is currently no equation or series of relations which predicts accurately the viscosity of nonelectrolyte liquid mixtures with temperature and composition. Of the empirical equations proposed to date, the majority falls into categories of mathematical averages with an additional

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parameter, the "interaction viscosity," included to correct for the deviation of the results from the averages.

Some previous studies have provided new experimental data on binary, ternary, and quaternary mixtures of industrially important *n*-alkanes. Measurements on *n*-hexadecane + *n*-hexane were made by Dymond and Young from 283 to 378 K [1]. The collective work of Coursey, Heric, and Brewer included measurements on systems of *n*-hexane $+$ n-hexadecane, n-hexane + n-octane, n-hexane + n-tetradecane, n-octane + n-tetradecane, n-octane + n-hexadecane, n-tetradecane + n-hexadecane, nhexane + n-octane + n-tetradecane, and n-hexane + n-tetradecane + nhexadecane [2, 3]. The principle of congruence, involving the excess Gibbs energy of activation, was shown in these studies to be useful for predicting binary mixture viscosities. Additionally, Marsh and Organ [4] found that the principle of congruence held for excess molar volumes and enthalpies for some multicomponent mixtures of alkanes which simulated the compositions of mixtures equivalent to the *n*-hexane and *n*-hexadecane composition.

A study by Wakefield [5] identified the most commonly used equations for predicting mixture viscosities. The majority of the viscosity equations developed for mixtures was found to be useful for binary mixtures; some of the generalized equations used for binary systems have been extended to ternary systems with mixed results. For multicomponent systems, there are essentially no useful relations available, nor are the binary equations readily extendable to mixtures with more than two components. Empirical correlation terms are generally incorporated in the expressions to improve the usefulness of the approximations.

To make meaningful comparison with theory or to test existing correlation equations, measurements are required over a range of pressures, reduced temperatures, and compositions. In this study the results for the pure liquids *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*dodecane, *n*-tetradecane, *n*-hexadecane, and *n*-tetracosane and the mixture n -octane + n -hexadecane at 318.16, 328.16, and 338.16 K are reported.

2. EXPERIMENTAL

2.1. Source and Purity of Samples

Samples of the following n -alkanes were obtained from Alfa Chemical Company, Danvers, Mass., for use in this work: n-octane, n-decane, ndodecane, n-tetradecane, n-hexadecane, and n-tetracosane. Also, n-hexane, n -nonane, and additional samples of n -octane and n -hexadecane were

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obtained from Sigma Chemical Company, St. Louis, Mo. The stated label purities for these *n*-alkanes ranged from 99 to 99.9 + mol% Gas-liquid chromatography, using a flame ionization detector with a capillary column, indicated purities considerably better than the label values, and hence they were used without further purification.

Viscosities of the pure liquids were measured and compared with accepted literature values as a check on the technique. All liquids were filtered through a fine-grade filter (0.7-cm thickness, 90-F porosity) prior to use. Mixtures of *n*-hexadecane $(1) + n$ -octane (2) were prepared by weight to have a mole fraction of approximately $x₁ = 0.15, 0.35, 0.50, 0.65,$ and 0.80.

2.2. Viscosity Measurement

A standard U-tube Ostwald viscometer was used for all measurements. A constant temperature was maintained in a 40-liter double-walled, insulated, glass Lauda temperature bath. A Sargent temperature controller, Model ST, was used to control the bath temperature. The bath water was stirred continuously by means of a submerged pump to prevent significant temperature gradients.

Temperatures were determined to within ± 0.002 K, on IPTS-68, using a Rosemont 25- Ω transfer standard platinum resistance thermometer, the resistance being measured with a Cropico Smith Difference Bridge No. 3 connected to a Leeds and Northrup Model 9868 null detector, The temperature was monitored to ± 0.005 K with a Hewlett-Packard digital quartz thermometer. Bath temperatures remained constant to within $+0.005$ K.

Efflux times were measured using either a Precision Scientific Co. timer or a Heuer digital stopwatch. Time measurements were considered to be accurate to within ± 0.01 s. Generally, between four and six consistent efflux time readings were taken at each temperature for each solution to assure consistency.

2.3. Viscosity Calibration

Water and several *n*-alkanes ranging from *n*-pentane to *n*-hexadecane were used to calibrate the Ostwald viscometer. Viscosity values for these liquids were taken from the literature [6] as they are well established over the experimental temperature range. Table I lists the literature viscosities and densities and experimentally measured efflux times for the calibration liquids from 318 to 338 K.

The Poiseuille equation corrected for capillary flow was used to

		Shear viscosity $\eta_M(10^{-3} \text{ Pa} \cdot \text{s})$			$\rho_M(g \cdot cm^{-3})$	
n -Alkane	Molecular weight	Experimental	Literature	Experimental	Literature	
		$T = 318.16 \text{ K}$				
n -Hexane	86.178		0.2504		0.6362	
n -Heptane	100.206		0.3262		0.6621	
n-Octane	114.233	0.4138	0.4136	0.6828	0.6822	
n -Nonane	128.260	0.5232	0.5236		0.6978	
n-Decane	142.287	0.6573	0.6561		0.7112	
n -Dodecane	170.341	0.9982	0.998		0.7308	
n -Tetradecane	198.395	1.4322	1.455		0.7458	
n-Hexadecane	226.449	2.0392	2.038	0.7563	0.7562	
n-Tetracosane	338.666	5.729 ^a		0.782^{a}		
		$T = 328.16$ K				
n -Hexane			0.2307		0.6268	
n -Heptane			0.2984		0.6533	
n -Octane		0.3706	0.3749	0.6745	0.6739	
n-Nonane		0.4665	0.4696		0.6897	
n -Decane		0.5823	0.5822		0.7035	
n-Dodecane		0.8679	0.8677		0.7236	
n -Tetradecane		1.2223	1.240		0.7390	
n -Hexadecane		1.7032	1.705	0.7493	0.7495	
n-Tetracosane		4.7875		0.776^{a}		
		$T = 338.16$ K				
n -Hexane			0.2128		0.6172	
n-Heptane			0.2739		0.6443	
n -Octane			0.3415	0.6661	0.6655	
n -Nonane		0.4188	0.4238		0.6815	
n-Decane		0.5220	0.5206		0.6957	
n-Dodecane		0.7637	0.7621		0.7162	
n -Tetradecane		1.0600	1.071		0.7322	
n-Hexadecane		1.4500	1.448	0.7423	0.7427	
n-Tetracosane		3.849		0.770^{a}		

Table I. Comparison of Experimental and Literature [5] Pure n-Alkane Viscosities and Densities

^a Denotes estimated value. All literature densities are interpolated [5].

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calibrate the viscometer using measured flow times for liquids of known viscosity:

$$
\frac{\eta}{\rho t} = A - (B/t^2) \tag{1}
$$

where A and B are constants, ρ is the corrected density, η is the viscosity, and t is the average efflux time. A calibration plot of $(\eta/\rho t)$ against $(1/t^2)$ was constructed. When possible, experimental densities were used to calculate the kinematic viscosity for ordinate values. Use of the calibration curve plot is justified, as the volume of the viscometer is sufficiently large and surface tension effects can be neglected. Marsh [7] has discussed the experimental conditions required for an accuracy of $+0.1\%$ in viscosity measurements.

2.4. Density Measurement

Results of the density determinations made on the pure compounds were found to compare favorably with literature values. Density measurements on the mixtures were required to calculate absolute viscosities. A Pyrex flask-type pycnometer containing a precision 1-mmbore entrance tube, approximately 18 cm^{-3} capacity, was calibrated with respect to a reference mark at 318.16, 328.16, and 338.16K. Degassed, filtered, distilled water was used as the calibration fluid.

The height of the fluid in the capillary was measured with respect to a reference mark to 0.02 mm with a cathetometer. In most cases for both the pure liquids and the mixtures, duplicate measurements were made and the results averaged. Densities are estimated to be accurate to within $+ 0.0001 \text{ g} \cdot \text{cm}^{-3}$.

3. RESULTS

Table I contains experimental and literature viscosities and densities for selected pure *n*-alkanes ranging from *n*-hexane to *n*-tetracosane at 318.16, 328.16, and 338.16 K. Literature viscosities were taken from the TRC Thermodynamic Tables---Hydrocarbons [6] and were seen to support the experimental values. Literature densities were reported at 313.16, 323.16, 333.16, and 343.16K; densities reported as literature values at 318.16, 328.16, and 338.16 K were interpolated from the densities at the intermediate temperatures. Literature values for n-tetracosane were not available over the experimental temperature range and *n*-tetracosane was a solid at 318.16 K. Thus, the viscosity of *n*-tetracosane at 318.16 K was

Mole fraction		Mixture shear viscosity					
n -Hexadecane, X_{16}	<i>n</i> -Octane, X_8		Mixture density $\rho_M(g\cdot cm^{-3})$				
$T = 318.16$ K							
0.00000	1.00000	0.4138	0.68277				
0.15004	0.84996	0.5758	0.70095				
0.34994	0.65006	0.8378	0.71970				
0.50011	0.49989	1.0728	0.73083				
0.63982	0.36018	1.3173	0.74035				
0.79956	0.20044	1.6266	0.74940				
1.00000	0.00000	2.0392	0.75629				
$T = 328.16 \text{ K}$							
0.00000	1.00000	0.3706	0.67448				
0.15004	0.84996	0.5128	0.69296				
0.34994	0.65006	0.7386	0.71214				
0.50011	0.49989	0.9314	0.72352				
0.63982	0.36018	1.1325	0.73293				
0.79956	0.20044	1.3808	0.74226				
1.00000	0.00000	1.7032	0.74925				
$T = 338.16$ K							
0.00000	1.00000	0.3415	0.66607				
0.15004	0.84996	0.4601	0.68501				
0.34994	0.65006	0.6550	0.70450				
0.50011	0.49989	0.8178	0.71609				
0.63982	0.36018	0.9858	0.72572				
0.79956	0.20044	1.1872	0.73495				
1.00000	0.00000	1.4500	0.74226				

Table II. Mixture Viscosity Data for the Binary System *n*-Hexadecane $+ n$ -Octane

estimated, as were the densities of pure n-tetracosane at all experimental temperatures. Discrepancies noted in n -octane viscosities indicate that the TRC tables could be in error.

Experimental viscosities and densities for pure n-hexadecane, pure noctane, and the mixtures of *n*-hexadecane $+ n$ -octane at 318.16, 328.16, and 338.16 K are reported in Table II. These values are estimated to have an accuracy of ± 0.5 and $\pm 0.1\%$, respectively.

4. DISCUSSION

4.1. Arithmetic Average of Viscosities

To test the agreement of experimental values with those predicted by a straight arithmetic average, the following deviation term, $\Delta \eta$, was defined as

$$
A\eta = \eta_M - \sum_{i=1}^{2} x_i \eta_i \tag{2}
$$

where η_M is the mixture viscosity, x_i is the mole fraction, and η_i is the viscosity of component *i*. Table III lists the deviations of the system, $\Delta \eta_i$, for *n*-hexadecane + *n*-octane at 318.16, 328.16, and 338.16 K.

The deviation from the arithmetic means, plotted as $-A\eta$, against the average carbon chain length, \bar{n} , is seen in Fig. 1. The greatest deviation from predictive values is seen at 318.16 K, while less extreme deviation is seen at 328.16 and 338.16 K. The average carbon chain length is defined as

$$
\bar{n} = \sum_{i=1}^{2} n_i x_i \tag{3}
$$

where n_i is the number of carbon atoms in the individual alkane, i, and x, is the mole fraction of component i. The composition dependence appears to be consistent for all temperatures, while the temperature dependence is stronger at 318.16 than at 328.16 or 338.16 K.

4.2. Grunberg and Nissan Equation

Dymond and Young [1] found the Grunberg and Nissan equation to be useful for the system *n*-hexane + *n*-hexadecane over the temperature range 298.19 to 378.29 K. The expression for multicomponent mixtures is

$$
G = \left[\ln n_M - \sum_{i=1}^{k} x_i \ln n_i \right] / (x_1 x_2)
$$
 (4)

where G is the Grunberg and Nissan parameter and k is the total number of components in the mixture. In the Dymond and Young study, the parameter G was seen to be approximately independent of temperature but had a strong composition dependence, which was linear with the mole fraction,

Values of the Grunberg and Nissan parameters for *n*-hexadecane $+ n$ octane at 318.16, 328.16, and 338.16 K are given in Table III. Variation of

Table III. Viscosity Results for the Binary System n -Hexadecane $(1) + n$ -Octane (2) **Table III.** Viscosity Results for the Binary System n-Hexadecane $(1) + n$ -Octane (2)

% difference % difference 0.000 -0.13637 -3.8424 -3.8424 -0.13637 304.093 -2.5182 -2.5182 -2.768 493.045 0.8496 -1.4085 0.7366 -2.3482 326.021 0.5280 --2.9641 0.7008 1.1314 0.000 1.8066 --6.0709 0.7726 --3.1164 1.0457 -2.5261 -2.5820 454.478 $+0.148$ $+0.1898$ 0.7624 -2.9783 303.718 1.6431 -1.0144 0.7728 -3.1225 0.0000 2.1453 -5.2030 0.7828 -3.5053 0.000 0.3873 -4.5062 0.6746 -0.0178 530.381 0.7507 --1.6382 0.7272 -2.1148 541.947 0.951.69 + 1.6642 + 1.669 + 1.669 + 1.669 + 1.669 + 1.669 + 1.669 + 1.669 + 1.67 + 1.689 + 1.689 + 1.6 478.161 1.1389 -0.5651 0.7527 -2.6974 18.389 -1.4062 -1.8395 0.7628 -2.7672 0.000 0.3506 -2.6647 0.6655 $+0.0856$ 292.885 0.4788 --4.0643 0.6916 0.9620 1.093.983.983.983.99

1.090.1 0.717.0 1.798.1 0.999.00 0.899.00 532.205 0,8086 $+1.1250$ 0.7308 -2.0542 473.249 -2.3945 -2.3945 -2.3945 -2.3945 310.938 -2.4259 -2.4259 1.5399 -6.2000 -6.7625 -2.7268 $+0.0856$ density -0.1362 -1.2768 -2.3482 -2.5820 -2.9783 -3.1225 -3.5053 -0.0178 -1.1314 -2.1148 -2.3192 -2.6974 -2.7672 -3.1164 -0.9620 -2.0542 -2.3949 -2.4559 -2.7268 -1.9021 density ρ of activation r/ r_1 viscosity density ρ Trapp Excess Gibbs energy viscosity %difference Trapp 0.6916 0.7179 0.6837 0.7099 0.7366 0.7497 0.7624 0.7728 0.7828 0.6746 0.7008 0.7272 0.7403 0.7527 0.7628 0.7726 0.6655 0.7308 0.7431 0.7530 0.7625 % difference viscosity -1.8395 2.6647 -4.5062 $+1.6642$ -4.0643 -1.9847 -1.0043 -3.8424 -2.5182 -1.4085 $+0.1898$ -1.0144 -5.2030 -1.6382 -0.5651 -6.0709 $+1.1250$ -2.4259 -6.2000 $+2.5261$ -2.9641 *A⁺G^E* (*J* · mol⁻¹), Trapp shear Trapp shear viscosity 0.3873 1.4062 1,4788 .2160 1.0457 3148 2.1453 0.5280 0.7507 0.9159 1.1389 1.8066 0.3506 0.6680 0.8086 1,9957 5399 0.4297 0.5903 0.8496 1.6431 \overline{r} Excess Gibbs energy $A^{\dagger}G^{E}$ (J · mol⁻¹), ofactivation 318.389 292.885 173.249 0.000 804.093 193.045 517.253 154.478 803.718 0.000 0.000 530.381 141.947 178.161 0.000 0.000 193.983 32.205 810.938 0.000 126.021 Grunberg & $p(g \cdot \text{cm}^{-3})$ \bar{n} \bar{q} $\eta(10^{-3} \text{ Pa} \cdot \text{s})$ parameter, G Average carbon Deviation from Grunberg& parameter, G 0.500101 0.9314 0.932 12.000101 0.9314 0.9314 0.9530 Nissan Density chain length, arithmetic avg. Nissan 0.00500 0.172200-1 0.69001 0.68900 10.6900 0.62001 0.63628 0.398290 1742010— 2.5662101 0.970210 0.95910 1466471 0.56074 0.79956 1.1872 0.73495 14.39648 --0.04061 0.56074 0.15004 0.5758 0.70095 9,20032 --0.08188 0.71419 0.34994 0.8378 0,71970 10.79952 --0.14479 0.64736 0.6001 1.0001 1.0001 1.0001 12,00001 12,000 12,000 12,000 12,000 12,000 12,000 12,000 12,000 12,000 1 0.63982 1.3173 0.74035 13.11856 --0.13646 0.59659 0.58416 0,79956 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.6266 1.62 10.5223 0.5223 0.522 0.5223 0.5223 0.5223 0.75223 0.75223 449990.0 0.389010-0.22 0.996210 10.712121210 0.99720 10.7995210 0,63982 1.1325 0.73293 13.11856 --0.09072 0.61291 0.79956 1.3808 1.3808 1.3808 1.3808 1.3808 1.3908 1.3908 1.3908 1.3908 1.3908 1.3908 1.3908 1.3908 1.3908 1.39 0.500910 11082010-1 0.0000000 0.09212.00 0.0782001210 0.09212.00 0.617800 0.1780 0.63982 0,9858 0,72572 13,1t856 --0.06494 0.58558 0.71419 0.64736 0.62001 0.59659 0.75223 0.68544 0.63530 0.61291 0.59808 0.63628 0.63866 0.60049 0.58558 Deviation from $4\eta(10^{-3} Pa \cdot s)$ arithmetic avg. -0.08188 -0.15388 -0.05774 -0.09833 -0.10565 -0.09072 -0.05529 -0.04772 -0.07807 -0.06494 -0.14479 -0.13646 -0.08680 -0.07441 -0.04061 $\ddot{}$ \circ \circ $\ddot{\circ}$ 0.000000 0.4138 0.68277 0.68277 0.00000 0.0000 0.0000 0.0000 0.0000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0 0.000000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.0 1.00000 1.7032 0,74925 16.0000 0,1000 0,1000 0,1000 0,1000 0,1000 0,1000 0,1000 0,1000 0,1000 0,100 0.000000 0.00000 0.00000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.000 0.000 0.0 \circ t.000 2.0392 0,75629 16.000 0,0000 0 Average carbon chain length, 4.39648 1.00000001 4.39648 9,20032 3.11856 9,20032 3.11856 4.39648 9.20032 2.00088 3.11856 6.00000 8.00000 2.00088 6.00000 8.00000 0.79952 2.00088 6.00000 8.00000 0.79952 0.79952 \vec{z} $\eta(10^{-3} \text{ Pa} \cdot s)$ $\rho(g \cdot \text{cm}^{-3})$ 0.75629 0.71214 0.72352 0.73293 0.74226 0.74925 0.71609 0.73495 Density 1,70095 0.71970 0.73083 1.74035 0.74940 0.67488 0.69296 1.66607 1.68501 0.70450 1.72572 0.68277 $r(10^{-3}$ Pa $\cdot s)$ viscosity 0.4138 0.5128 1.9314 3808 0.3415 1,6550 1.8178 Shear 1.5758 0.8378 .0728 3173 6266 2.0392 0.3706 0.7386 1.1325 .7032 1,9858 1872 0.4601 n-hexadecane, Mole fraction n-hexadecane, Mole fraction 0.00000 0.15004 0.50011 0.79956 .0000 0.00000 1.15004 0.34994 0.50011 0.63982 0.79956 .00000 0.00000 1.15004 0.34994 0.50011 1,63982 1.79956 .00000 0.34994 1,63982 \tilde{x}_1 338.16 318.16 328.16 T(K)

Fig. 1. Arithmetic deviation: n -hexadecane + n -octane.

the Grunberg and Nissan parameter, G, with composition, represented by the average carbon chain length, \bar{n} , is seen in Fig. 2. At higher carbon numbers where the system is primarily hexadecane, there seems to be agreement with the expected linear dependence of G with the mole fraction.

A strong temperature dependence is indicated, however, by the line for 318.16 K falling between that of 328.16 and that of 338.16 K. While some deviation from expected G values at 328.16 and 338.16 K can possibly be attributed to the slight deviation in experimental viscosities compared to literature values [6] and the subsequent sensitivity of the Grunberg and Nissan equation to these differences, there is still a dependence of G on both temperature and mole fraction for the system *n*-hexadecane + *n*octane. Also, at higher *n*-octane mole fractions, the parameter G shows a stronger than expected temperature and mole fraction dependence.

It should be noted that the largest deviation from arithmetic averages of pure component viscosities was at 318.16 K, and this temperature was again shown to be the most sensitive for this empirical equation, with most differences being smaller than 5%.

Dymond and Young [1] found no temperature dependence for parameters for *n*-hexane + *n*-hexadecane. The Grunberg and Nissan parameters found for n -octane + n -hexadecane show a small temperature

Fig. 2. Grunberg and Nissan equation: *n*-hexadecane + *n*-octane.

dependence. It should be noted that Dymond has had success in using the hard-sphere model for transport properties [8] and, in particular, for predicting viscosities of liquid hydrocarbons.

4.3. Principle of Congruence

Developed to predict thermodynamic properties of homologous mixtures, the principle of congruence has been used to predict viscosities of mixtures of n-alkanes and substituted alkanes by Heric, Coursey, and Brewer [2, 3, 9] and by Dymond, Young, and Robertson [1, 10]. While satisfactory agreement was seen for many binary and some ternary *n*alkane mixtures over selected temperature ranges, there is still some question as to whether the congruence principle, originally proposed by Bronsted and Koefoed for thermodynamic variables [11], should be applied to nonequilibrium transport properties. Coursey and Heric contend that the viscosities of binary, and some ternary, nonelectrolyte liquid mixtures could be determined accurately by using the congruence principle to find, initially, the excess molal Gibbs energy of activation for flow, $\Delta G^{\dagger E}$. Eyring's equation for pure liquid viscosity is related to the Gibbs "energy of activation for flow" by

$$
\eta = \frac{hN_A}{V_m} \exp(AG^{\dagger E/RT})
$$
\n(5)

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where η is the pure liquid viscosity, V_m is the liquid molar volume, $AG^{\dagger E}$ is the molar Gibbs energy of activation for viscous flow, R is the gas constant, h is Planck's constant, N_A is Avogadro's number, and T is the absolute temperature.

The Gibbs energy of activation for an ideal mixture is defined as

$$
\Delta G^{\dagger \text{ideal}} = \sum_{i=1}^{k} x_i \Delta G_i^{\dagger} \tag{6}
$$

From the definition of excess properties, the following relation is given:

$$
\Delta G^{\dagger E} = \Delta G^{\dagger} - \Delta G^{\dagger \text{ideal}} \tag{7}
$$

where AG^{+E} is the "excess" molar Gibbs energy of activation for flow, AG^{\dagger} is the actual activation for flow, and AG^{tideal} is defined by Eq. (6). From Eqs. (5), (6), and (7), Coursey and Heric derived Eq. (8), which forms the basis for the application of the principle of congruence to simple mixtures of n-alkanes.

$$
\Delta G^{\dagger E} = RT \left[\ln(\eta_M V_M) - \sum_{i=1}^k x_i \ln(\eta_i V_i) \right]
$$
 (8)

Table III lists the values of $AG^{\dagger E}$ calculated for the system *n*hexadecane + n -octane at 318.16, 328.16, and 338.16 K. Figure 3 is a plot of $\Delta G^{\dagger E}$ against \vec{n} , the average mixture carbon chain length for the experimental temperatures. In previous studies, a steady increase in ΔG^{+E} with increasing temperatures was observed for similar mixtures [2, 3, 9].

In Fig. 3, however, some unusual trends are noted. First, the values at 328.16 K exhibit the highest values of AG^{+E} : for all compositions of noctane + *n*-hexadecane. Also, at a lower average carbon chain length, \bar{n} , the 338.16 K value at the lowest *n*-hexadecane composition $[x_{16}=0.15004]$ falls below the 318.16 K point, is the same for the next lowest n -hexadecane composition $[x_{16} = 0.34994]$ at 318.16 K, and is higher than 318.16 K but lower than the 338.16K value at the equimolar composition $[x_{16}=0.50011]$. Then, at the predominantly *n*-hexadecane compositions $[x_{16}=0.63982$ and $x_{16}=0.79956$], the $AG^{\dagger E}$ values are higher for 338.16 than 3t8.16 K but lower than the 328.16 K values. The system mixture viscosity is considered to be accurate to within $\pm 0.5\%$, and despite the nature of the variations of the binary mixture *n*-hexadecane $+ n$ -octane at these temperatures, it is concluded that the congruence principle holds to some extent for this mixture but should not be expected to be as accurate as a predictive technique for other compositions and temperatures.

Fig. 3. Congruence principle: n -hexadecane + n -octane.

4.4. Method of Corresponding States

In 1981 Ely and Hanley $\lceil 12 \rceil$ reported a procedure for predicting the viscosity of mixtures based solely on the critical properties and acentric factors of the pure components. It was assumed that the configurational properties of the mixture can be equated to those of a hypothetical pure fluid, the properties of such a pure fluid being determined using a suitable reference fluid and the principle of corresponding states.

Ely and Hanley introduced an extended corresponding states formalism:

$$
\eta_M(\rho, T) = \eta_X(\rho, T) \tag{9}
$$

where the viscosity, η_M , of a mixture at density, ρ , and temperature, T, and set of composition variables, $\{X\}$, is set equal to the viscosity of a hypothetical pure fluid. Then, by corresponding states,

$$
\eta_X(\rho, T) = \eta_0(\rho_0, T_0) F_{\eta}
$$
\n(10)

and

$$
F_{\eta} = \left(\frac{M_X^{\eta}}{M_0}\right)^{1/2} f_{X,0}^{1/2} h_{X,0}^{-2/3} \tag{11}
$$

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In these expressions, X refers to the fluid of interest, 0 refers to the reference fluid, *M* is the molecular weight, and T_0 , $[T_0 = T/f_{X0}]$, ρ_0 , $[\rho_0 = \rho h_{X,0}]$, $f_{X,0}$, and $h_{X,0}$ are functions of the critical parameters and acentric factor. In the present version, methane is used as the reference fluid.

One weakness in using the method of corresponding states with methane as the reference fluid is that the lowest reduced temperature of methane is not sufficiently low to have corresponding states with many higher *n*-alkanes at normal fluid conditions. It is expected that this disadvantage will be rectified by the use of propane as the reference fluid. Another possible difficulty is that the one-fluid concept is not particularly suitable for transport properties as it does not always account accurately for mixing effects.

A computer program (TRAPP) developed at the National Bureau of Standards by Ely and Hanley was made available by Monica Baltatu of Fluor Engineering, Irvine, California. Using as input data the mixture viscosity and density data for the binary system n -hexadecane + n -octane at 318.16, 328.16, and 338.16 K, values for the system viscosities and densities were calculated using Program TRAPP and are presented in Table III. Errors in determining the mixture viscosities and densities using the corresponding-states principle were determined as

$$
percentage error = \frac{experimental - calculated}{experimental} \times 100\% \tag{12}
$$

At all temperatures the predicted viscosities were seen to deviate in random fashion from the experimental values, with most differences being smaller than 5%. Viscosities differed more with increasing temperatures, although only to a small extent. The predicted densities, however, showed progressively better agreement with experimental values with increasing temperatures. The predicted values were generally higher than the experimental values. Although the method of corresponding states does not predict the viscosities of the mixtures within experimental error, it does show promise as a predictive technique.

5. CONCLUSIONS

Viscosities and densities were measured for the binary system nhexadecane + n-octane at 318.16, 328.16, and 338.16 K. The empirical Grunberg and Nissan equation gave a good agreement at all temperatures for mixtures with high mole fractions of n -hexadecane. The principle of congruence developed to predict thermodynamic properties of mixtures is **not conclusively supported for this system. Significant temperature and composition effects were noted for the mixtures to the extent that congruence is noted. Ely and Hanley's method of corresponding states gave good predictions considering that no viscosity data for the pure components were required as the input parameters. The density predictions were not as satisfactory.**

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