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Viscosities of Nonelectrolyte Liquid Mixtures. III. Selected Binary and Quaternary Mixtures

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This paper is the final in a series of three viscosity and density studies of pure *n*-alkanes and selected binary and quaternary mixtures. A standard U-tube viscometer was used for viscosity measurements, and a Pyrex flask-type pycnometer was used for density determinations. Results are given here for pure alkane and selected binary mixtures of *n*-tetradecane + *n*-octane, for selected quaternary mixtures of *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane, and for pure and selected quaternary mixtures of *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane at 303.16 and 308.16 K. The principle of congruence was tested, as was the Grunberg and Nissan equation, as they have been shown to be useful as prediction techniques for other *n*-alkane binary mixtures. Comparisons were made between the two groups of quaternary alkane mixtures and the binary *n*-tetradecane + *n*-octane mixtures of the same "pseudo" composition to understand better the dependence of mixture viscosities on the composition parameter.

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

1. INTRODUCTION

The first two phases of this study concentrated on the nature of *n*-hexadecane + *n*-octane mixtures in binary and quaternary mixtures designed to simulate binary behavior. Experimental temperatures included the reduced range from 318.16 to 338.16 K to maintain the *n*-tetracosane in the liquid state and, further, to prevent significant evaporation losses of the lighter *n*-alkanes, octane and hexane.

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In an analysis of more than 45 equations proposed over the last 100 years, of the empirical equations proposed, the majority can be classified as categories of mathematical averages: arithmetic, geometric, reciprocal, or logarithmic (power) averages [1]. Since these equations are simple averages of pure component properties and concentration weighting factors, they are not to be considered as justified by transport property theory.

The majority of the mixture viscosity equations found in the literature is useful primarily for binary systems; some of the generalized correlations used for binary mixtures have been extended to ternary mixtures with reasonable success. For diverse, multicomponent systems, however, there are no consistently useful relations for predicting mixture viscosities. Further, it has been seen that the binary system predictive relations are not readily extendable to higher systems. However, empirical correction terms, sometimes known as "interaction viscosities," are added to the binary equations and give somewhat reasonable results for selected quaternary systems over limited temperature ranges.

Of the various mixture viscosity parameters, temperature is perhaps the variable to which viscosity is most sensitive. Temperature, however, is not included in the mixture relations as a dependent variable. Also, the true effects of composition on mixture values are not accurately represented in the use of weighting factors, i.e., mole, weight, or volume fractions.

In this phase of the study, systems of *n*-tetradecane + *n*-octane were selected to determine the effects on mixture viscosity and density by temperature and composition parameters. Again, it was determined that the midrange of the *n*-alkanes represented by this series of mixtures would provide a clearer understanding of the general behavior of *n*-alkane mixture viscosities.

The two temperatures 303.16 and 308.16 K were selected for the remaining series of mixtures in these studies. As most reported studies have been for alkane mixtures at 298.16 K, viscosities at temperatures above the standard value are favorable in terms of better understanding the temperature dependence on mixture shear viscosity.

The results for the pure *n*-alkanes and binary mixtures of *n*-tetradecane + *n*-octane at 303.16 and 308.16 K are presented here. Pure component viscosities were compared with literature values [2] as a check on agreement of values. Predictive relations such as the principle of congruence and the Grunberg and Nissan equation were tested using the new experimental data to determine further the dependence of mixture viscosity on temperature and composition variables.

2. EXPERIMENTAL

Samples of *n*-hexadecane, *n*-tetradecane, *n*-dodecane, *n*-decane, *n*-heptane, and *n*-octane were obtained from the Alfa Chemical Company, Danvers, Mass.; additional samples of *n*-octane and *n*-nonane, as well as *n*-hexane and *n*-hexadecane were obtained from the Sigma Chemical Company, St. Louis, Mo. As a verification of the stated label purity (99 mol % or better), a gas chromatography analysis utilizing a flame ionization detector was conducted. Results of the analysis confirmed stated label purities and the liquids were used without further purification by distillation.

The methods and techniques used to determine viscosities and densities have been described in detail previously in this series [3, 4].

3. RESULTS

Table I lists the experimental shear viscosities and densities for pure *n*-tetradecane + *n*-octane. Experimental viscosities and densities for pure *n*-hexadecane, *n*-dodecane, *n*-decane, *n*-hexane, and the quaternary mixtures of *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane are found in Table II. Viscosities and densities of the pure fluids and quaternary mixtures of *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane at 303.16 and 308.16 K are presented in Table III. Viscosities and densities for this reduced temperature range are estimated as accurate to within 0.5% and $\pm 0.0001\ \mathrm{g \cdot cm^{-3}}$, respectively.

3.1. Arithmetic Average of Viscosities

As discussed previously [3], the strict arithmetic average for predicting mixture viscosities using only pure-component viscosities and individual mole fractions has long been a frequently used empirical equation for simple binary mixtures. Deviations from the arithmetic average are generally described by

$$\Delta\eta = \eta_{\mathrm{M}} - \sum_{i=1}^{k} x_i \eta_i \tag{1}$$

where $\Delta\eta$ is the arithmetic average viscosity deviation, η_{M} is the viscosity of the mixture, x_i is the mole fraction of component i, η_i is the viscosity of component i, and k is the number of mixture components.

It is now understood that viscosity does not depend strictly on pure-component viscosities and component mole fraction. However, in the absence of other more rigorous relations by which to predict mixture

Table I. Mixture Viscosity Data for the Binary System *n*-Tetradecane + *n*-Octane

	Mole fraction		Shear viscosity	Mixture density	Average carbon-	Deviation from arithmetic average	Grunberg & Nissan	Gibbs energy of activation
T	*n*-Tetradecane, x_{14}	*n*-Octane, x_8	η_M (10^{-3} Pa·s)	ρ_M (g·cm^{-3})	chain length $\bar{n}$	$\Delta\eta$ (10^{-3} Pa·s)	parameter	$\Delta G^{\dagger E}$(J·mol^{-1})
303.16 K	0.00000	1.00000	0.48433	0.69459	8.00000	0		
	0.15042	0.84958	0.63029	0.70844	13.08500	−0.07286	0.33799	142.6313
	0.35041	0.64959	0.85889	0.72353	11.89124	−0.12720	0.35908	264.0279
	0.49994	0.50006	1.0560	0.73293	10.99964	−0.13658	0.38350	307.9293
	0.64854	0.35146	1.2759	0.74099	10.10246	−0.12186	0.41180	299.5854
	0.84750	0.15250	1.6121	0.74965	8.90252	−0.06714	0.45177	183.5311
	1.00000	0.00000	1.9010	0.75608	14.00000	0		
308.16 K	0.00000	1.00000	0.45677	0.69059	8.00000	0		
	0.15042	0.84958	0.59254	0.70458	13.08500	−0.05905	0.34596	146.7459
	0.35041	0.64959	0.80257	0.71975	11.89124	−0.10590	0.36109	269.7120
	0.49994	0.50006	0.97886	0.72912	10.99964	−0.11375	0.38738	315.3685
	0.64854	0.35146	1.1757	0.73717	10.10246	−0.09986	0.42739	313.1646
	0.84750	0.15250	1.4756	0.74624	8.90252	−0.05554	0.46987	192.0800
	1.00000	0.00000	1.7286	0.75250	14.00000	0		

viscosities, several variations of this arithmetic average have been proposed substituting kinematic viscosities in place of absolute viscosities, thereby introducing the pure-component and mixture densities into the dependence. Also, logarithmic variations of the arithmetic average formula have been used in addition to variations which treat the pure-component viscosities as weighted or power averages. As a final treatment, researchers have introduced deviation terms known as "interaction viscosities." These empirical terms are determined using a least-squares fit on experimental data and are generally added to the equation in the form of

$$\eta_M = \sum_{i=1}^{k} x_i \eta_i + \delta_{12} \tag{2}$$

where δ_{12} is the interaction viscosity, for a binary system is this case, and all other terms have been defined previously. Generally, this modified form of the arithmetic average cannot be extended to multicomponent mixtures of similar components, nor do the values hold at higher temperatures.

Table I lists the calculated deviations from the arithmetic averages for the binary system *n*-tetradecane + *n*-octane at 303.16 and 308.16 K. The negative arithmetic deviations at both temperatures are plotted versus $\bar{n}$, the average mixture carbon-chain length, in Fig. 1.

$$\bar{n} = \sum_{i=0}^{k} x_i n_i \tag{3}$$

where x_i is the component mole fraction, n_i is the number of carbon atoms in component *i*, and *k* is the number of mixture components.

As seen in Fig. 1, the deviations at both temperatures show smooth parabolic curves. Maximum deviation at both temperatures occurs at equimolar mixture composition. Also, greater numerical deviations are noted at 303.16 than 308.16 K. There also seems to be a continuity in the values throughout the composition range, which would support the hypothesis that mixture viscosities could be predicted from only pure-component viscosities, at least over this limited temperature range.

Values of the arithmetic deviations calculated for the quaternary system *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane at 303.16 and 308.16 K using Eq. (2) ($k = 4$) are given in Table II. In Fig. 2, the negative arithmetic deviations are plotted against the average carbon-chain length of the mixture, $\bar{n}$. At both experimental temperatures, a smooth parabolic fit was observed throughout the composition range.

Table III lists the values of the deviations from the arithmetic averages calculated for the $C_{16} + C_{12} + C_{10} + C_6$ system at 303.16 and 308.16 K.

Table II. Mixture Viscosity Data for the Quatern

T	Mole fraction				Shear viscosity η_M (10^{-3} Pa·s)	Mixture densi ρ_M (g·cm^{-3}
	n-Heptane, x_7	n-Nonane, x_9	n-Dodecane, x_{12}	n-Hexadecane, x_{16}		
303.16 K	1.0000	0.0000	0.0000	0.0000	0.36646	0.67652
	0.0000	1.0000	0.0000	0.0000	0.62634	0.70998
	0.0000	0.0000	1.0000	0.0000	1.2572	0.74179
	0.0000	0.0000	0.0000	1.0000	2.7534	0.76672
	0.07483	0.07466	0.42552	0.42499	1.6364	0.74986
	0.17416	0.17445	0.32635	0.32504	1.2993	0.74110
	0.25004	0.24921	0.25028	0.25047	1.0711	0.73327
	0.32462	0.32501	0.17506	0.17531	0.87037	0.72380
	0.42475	0.42538	0.07493	0.07494	0.63766	0.70890
308.16 K	1.0000	0.0000	0.0000	0.0000	0.34556	0.67255
	0.0000	1.0000	0.0000	0.0000	0.58908	0.70610
	0.0000	0.0000	1.0000	0.0000	1.1577	0.73809
	0.0000	0.0000	0.0000	1.0000	2.4778	0.76345
	0.07483	0.07466	0.42552	0.42499	1.49606	0.74628
	0.17416	0.17445	0.32635	0.32504	1.19796	0.73742
	0.25004	0.24921	0.25028	0.25047	0.99293	0.72942
	0.32462	0.32501	0.17506	0.17531	0.81081	0.72011
	0.42475	0.42538	0.07493	0.07494	0.59860	0.70485

Table III. Mixture Viscosity Data for the Quatern

T	Mole fraction				Shear viscosity η_M (10^{-3} Pa·s)	Mixture densi ρ_M (g·cm^{-3}
	n-Heptane, x_6	n-Decane, x_{10}	n-Dodecane, x_{12}	n-Hexadecane, x_{16}		
303.16 K	1.0000	0.0000	0.0000	0.0000	0.2845[a]	0.64613
	0.0000	1.0000	0.0000	0.0000	0.79603	0.72229
	0.0000	0.0000	1.0000	0.0000	1.2572	0.74179
	0.0000	0.0000	0.0000	1.0000	2.7534	0.76672
	0.08312	0.07472	0.42175	0.42041	1.6266	0.74951
	0.17435	0.17551	0.32506	0.32508	1.3125	0.74099
	0.24928	0.24931	0.25090	0.25051	1.0902	0.73311
	0.32880	0.32389	0.17333	0.17398	0.88458	0.72371
	0.42524	0.42483	0.07514	0.07479	0.65466	0.70869
308.16 K	1.0000	0.0000	0.0000	0.0000	0.2724[a]	0.64613
	0.0000	1.0000	0.0000	0.0000	0.74309	0.71864
	0.0000	0.0000	1.0000	0.0000	1.1577	0.73809
	0.0000	0.0000	0.0000	1.0000	2.4778	0.76345
	0.08312	0.07472	0.42175	0.42041	1.4878	0.74593
	0.17435	0.17551	0.32506	0.32508	1.2120	0.73732
	0.24928	0.24931	0.25090	0.25051	1.0128	0.72945
	0.32880	0.32389	0.17333	0.17398	0.82273	0.71946
	0.42524	0.42483	0.07514	0.07479	0.61531	0.70469

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[a] Denotes estimated or interpolated value.

System *n*-Hexadecane + *n*-Dodecane + *n*-Nonane + *n*-Heptane

Average carbon-chain length $\bar{n}$	Deviation from arithmetic average $\Delta\eta$ (10^{-3} Pa · s)	"Simulated" Grunberg & Nissan parameter (G^{SIM})	Actual Grunberg & Nissan parameter (G^{ACT})	Gibs energy of activation $\Delta G^{\dagger E}$ (J · mol^{-1})
7.0000				
9.0000				
12.0000				
16.0000				
13.1018	−0.14292	0.42886	73.9435	238.1964
11.9060	−0.17904	0.42330	35.4866	362.8099
11.0041	−0.18092	0.43586	32.0816	397.4479
10.1031	−0.15494	0.47039	37.5144	384.0407
8.8999	−0.08497	0.55028	81.2256	258.2009
7.0000				
9.0000				
12.0000				
16.0000				
13.1018	−0.11944	0.42847	73.1676	240.0959
11.9060	−0.14819	0.42834	35.7688	371.0620
11.0041	−0.15064	0.44015	32.3985	407.4442
10.1031	−0.12987	0.47252	37.8339	392.4995
8.8999	−0.07119	0.55690	83.1001	267.8535

System *n*-Hexadecane + *n*-Dodecane + *n*-Decane + *n*-Heptane

Average carbon-chain length $\bar{n}$	Deviation from arithmetic average $\Delta\eta$ (10^{-3} Pa · s)	"Simulated" Grunberg & Nissan parameter (G^{SIM})	Actual Grunberg & Nissan parameter (G^{ACT})	Gibs energy of activation $\Delta G^{\dagger E}$ (J · mol^{-1})
6.000				
10.0000				
12.0000				
16.0000				
13.03348	−0.14431	0.45901	77.8061	273.2510
11.90320	−0.18055	0.47455	39.4236	407.3759
11.00774	−0.18436	0.50295	37.2308	464.6758
10.07534	−0.16374	0.56221	46.2922	472.9738
8.89806	−0.10489	0.75590	113.1368	367.8557
6.0000				
10.0000				
12.0000				
16.0000				
13.03348	−0.12032	0.45178	76.6020	274.1273
11.90320	−0.14772	0.48617	39.7578	416.3856
11.00774	−0.15154	0.51590	37.6037	475.1306
10.07534	−0.13927	0.55680	45.2757	473.1433
8.89806	−0.08852	0.77211	112.9513	372.8502

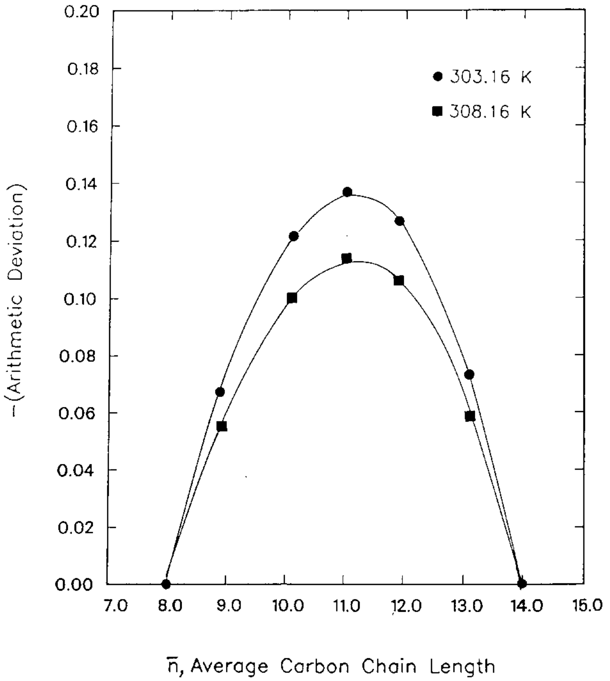

Fig. 1. Arithmetic deviation: *n*-tetradecane + *n*-octane.

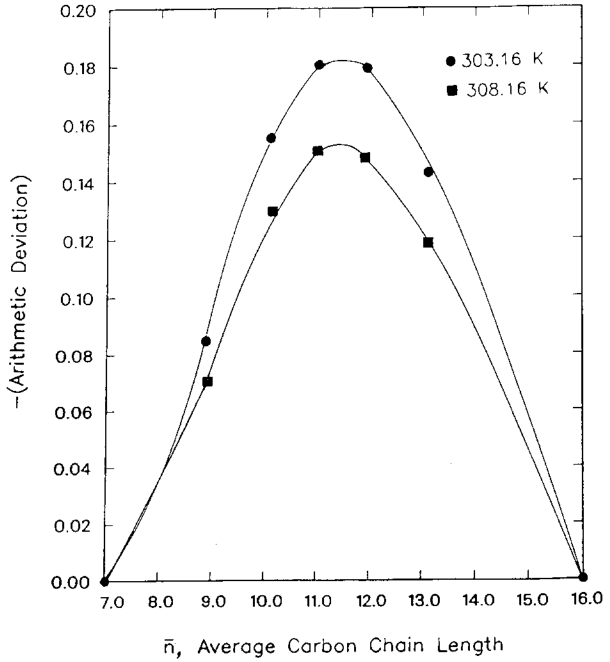

Fig. 2. Arithmetic deviation: *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane.

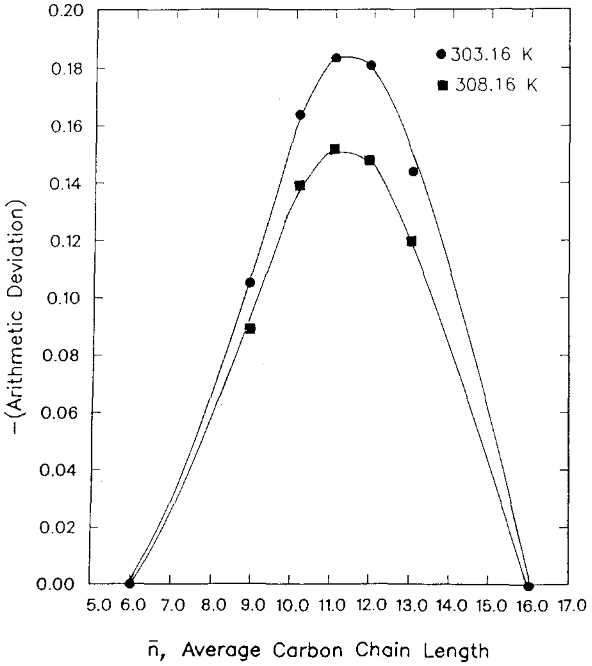

Fig. 3. Arithmetic deviation: *n*-hexadecane + *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane.

Figure 3 is a plot of the arithmetic deviation against $\bar{n}$. Here a slightly concave curve fits the data points at both temperatures, and there is a regular, but not smooth, fit of the deviations over the composition range.

The arithmetic average previously was seen to be useful for *n*-tetradecane + *n*-octane at 303.16 and 308.16 K. It is reasonable to expect that a more complex multicomponent system will, however, show a greater deviation from a smooth fit than a more simple binary system.

Compared to the concave fit exhibited for the similar quaternary mixture $C_{16}+C_{12}+C_{10}+C_6$, it is observed that the average deviations were within 1 % of each other with the exception of the lowest $\bar{n}$ values, i.e., the smallest composition of *n*-hexane. As no concave trends were observed for the $C_{16}+C_{12}+C_9+C_7$ systems, it is possible that some evaporation of *n*-hexane occurred, although precautions were taken to prevent such losses. Also, mixtures including *n*-heptane and *n*-nonane exhibited a behavior more similar to that of the binary *n*-tetradecane + *n*-octane mixtures than to that of the systems which included *n*-heptane and *n*-nonane.

3.2. Grunberg and Nissan Equation

As discussed previously [4], the Grunberg and Nissan equation has been found to be useful for viscosities of binary mixtures. The expression is

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

for binary systems where G is the Grunberg and Nissan parameter, η_M is the mixture viscosity, η_i is the viscosity of the pure component i, k is the total number of components in the mixture, and x_1 and x_2 are the mole fractions of mixture components 1 and 2, respectively.

Table I contains the values of G calculated for binary systems of *n*-tetradecane + *n*-octane at 303.16 and 308.16 K. The G values are plotted vs $\bar{n}$, the mixture average carbon-chain length, in Fig. 4.

Values of the Grunberg and Nissan parameter are generally seen to give a straight-line fit when plotted against a composition parameter such as mole fraction or average carbon-chain length. As seen in Fig. 4, the Grunberg and Nissan equation is not seen to fit the data conclusively, but

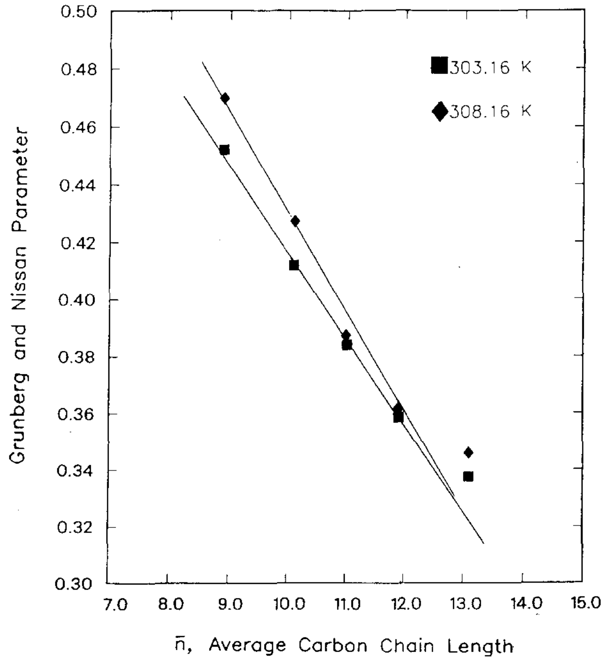

Fig. 4. Grunberg and Nissan equation: *n*-tetradecane + *n*-octane.

sufficient straight-line behavior is observed to consider the technique useful. However, it should be noted that the agreement is not sufficient to warrant the use of the equation for any accurate prediction of unknown mixture viscosities for *n*-tetradecane + *n*-octane at 303.16 and 308.16 K.

Two approaches were taken in analyzing the Grunberg and Nissan equation for the quaternary mixture *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane. The first involved expanding the general form of Eq. (4), setting $k = 4$. Values of G determined using this equation are listed as G^{ACT}. These values range from 37 to 113 (dimensionless) for the quaternary mixtures containing hexane, whereas most binary-system G values range between 0 and 1. Thus, these values, when plotted against the average carbon-chain length, $\bar{n}$, showed a slightly hyperbolic curve rather than the expected straight line. The quaternary mixture $C_{16} + C_{12} + C_{10} + C_6$ did not obey the Grunberg and Nissan empirical equation.

As the quaternary systems were prepared to simulate "pseudobinary" $C_{14} + C_8$ mixtures, it was thought that the use of the original binary form of the Grunberg and Nissan equation could be tested by using equimolar mixtures of $x_{10} + x_6$ and one could simulate x_8. Then, by using the actual pure-component viscosities for x_8 and x_{14}, "simulated G" values were determined and are listed as G^{SIM}.

When the simulated G values were plotted against $\bar{n}$, the average carbon-chain length, a straight line fit the majority of the data with the distinct exception of the mixture with the lowest mole fraction of *n*-hexane. It is unclear as to what to attribute the failure of this single data point at both 303.16 and 308.16 K. In comparison to the "true" binary $C_{14} + C_8$ mixture behavior in which a straight-line fit was not followed, especially for the higher average carbon-chain length, the simulated quaternary-system values, G^{SIM}, did not agree well (some were 50% higher) with the actual binary-system G values, G^{ACT}. Thus, as the simulated G values did not agree with the actual G values, the prediction method was deemed to be unsuccessful.

Values of G calculated for the quaternary mixtures of *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane at 303.16 and 308.16 K are found in Table II. As with the similar quaternary mixtures composed of *n*-decane and *n*-hexane found in Table III, the actual G values exhibited a hyperbolic type curve, although the G values for the quaternary system with *n*-hexane and *n*-decane were much higher than for the *n*-heptane + *n*-nonane system for the mixtures containing the smallest amounts of *n*-dodecane and *n*-hexadecane.

Compared to the binary *n*-tetradecane + *n*-octane system, though, the quaternary pseudobinary behavior was not at all similar. As with the quaternary mixtures containing *n*-decane and *n*-hexane, an attempt to calculate simulated G values was made using the combined $C_{16}+C_{12}$ mole fractions as x_{14} and the combined C_9+C_7 mole fractions as x_8. Then the actual (x_8+x_{14}) pure-component viscosities were used to determine the "simulated G" values also listed in Table II. It may be concluded that the Grunberg and Nissan equation is not readily extendable to higher component systems, even at lower temperatures.

3.3. Principle of Congruence

Proposed originally by Bronsted and Koefoed [5], the principle of congruence was developed to predict the excess Gibbs energy of mixing, a thermodynamic variable, for homologous series of mixtures.

Coursey and Heric [6, 7] showed that the viscosities of binary and some ternary nonelectrolyte liquid mixtures could be determined accurately using the congruence principle to find the excess molal Gibbs free energy of activation, $\Delta G^{\dagger E}$. Using Eyring's equation for pure liquid viscosity,

$$\eta=\frac{hN_A}{V_m}\exp(\Delta G^{\dagger E}/RT) \tag{5}$$

the excess molal Gibbs energy for flow was then applied to yield the mixture viscosity. In Eq. (5), η is the pure-liquid viscosity, h is Planck's constant, N_A is Avogadro's number, V_m is the pure-liquid molar volume, R is the gas constant, and T is the absolute temperature.

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

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

where $\Delta G^{\dagger \text{ideal}}$ represents the arithmetic sum of pure component Gibbs energies of activation for flow, $\Delta G_i^{\dagger}$, times the mole fraction of the ith component, x_i. The total number of components in the system is given by k.

In order to describe an excess Gibbs energy of activation, which is an exact relation for thermodynamic systems, for a viscous mixture, one must make the assumption that the viscous mixtures for which values of $\Delta G^{\dagger E}$ are calculated are specifically ideal viscous mixtures. Such ideal mixtures are hypothetical viscous mixtures and assume ideal initial, final, and activated states for viscous flow. Although the symbols used in describing $\Delta G^{\dagger E}$ for the viscous mixtures in these studies are the same as those used in true ideal thermodynamic mixtures, the distinction should be noted as described above.

We define

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

where $\Delta G^{\dagger E}$ is the "excess" molar Gibbs energy of activation for flow, $\Delta G^{\dagger}$ is the actual activation energy for flow, and $\Delta G^{\dagger\text{ideal}}$ is defined by Eq. (7). Heric and Coursey assumed Eyring's equation for viscosity as it is related to Gibbs energy of flow and developed the following equation for the viscosty of mixtures based on the application of the principle of congruence to simple mixtures of *n*-alkanes:

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

Table I contains the values of $\Delta G^{\dagger E}$ calculated for the binary mixtures of *n*-tetradecane + *n*-octane at 303.16 and 308.16 K. It is convenient to express differences in Gibbs energies of activation for flow, $\Delta G^{\dagger E}$, with respect to a standard composition variable such as average carbon-chain length, $\bar{n}$.

Figure 5 shows the variation of $\Delta G^{\dagger E}$ with $\bar{n}$, the average carbon-chain length of the *n*-tetradecane + *n*-octane mixtures at 303.16 and 308.16 K. The smooth parabolic curves which are separated uniformly with respect to temperature support the congruence principle for this binary system over

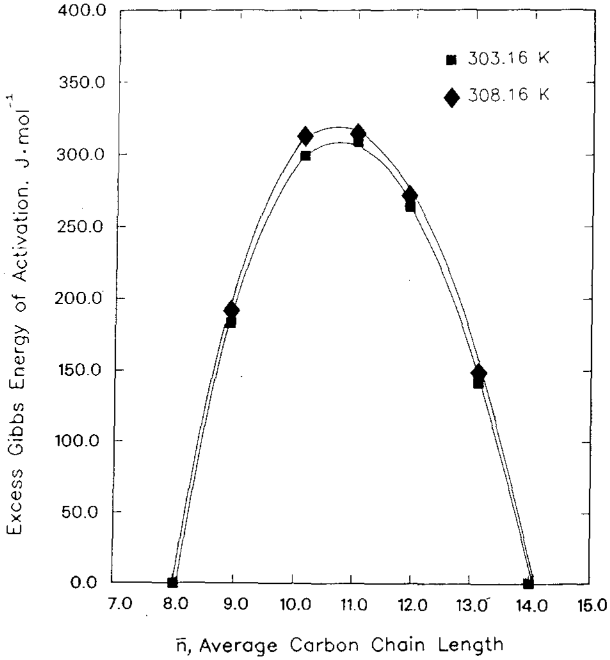

Fig. 5. Congruence principle: *n*-tetradecane + *n*-octane.

these limited temperatures. It would be expected, given this agreement with the congruence principle, that mixture viscosities for unmeasured systems of $C_{14}+C_8$ composition at these temperatures could be predicted with a reasonable degree of accuracy.

Further, for the quaternary mixtures of $C_{16}+C_{12}+C_9+C_7$ the values of $\Delta G^{\dagger E}$ calculated are listed in Table II. Figure 6 shows the behavior of $\Delta G^{\dagger E}$ with $\bar{n}$; over the midrange of mixture compositions, the principle of congruence is supported.

As the average carbon-chain length increases to the value of $\bar{n}=13.10$, the values are almost identical. For other $\bar{n}$ values the temperature difference of 5 K resulted in a difference of 9–10 $J \cdot mol^{-1}$ from the other $\Delta G^{\dagger E}$ values. Thus, with this singular exception, it is assumed that the congruence principle is an effective technique for this quaternary system at 303.16 and 308.16 K.

For the quaternary mixtures of *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane at 303.16 and 308.16 K, Table III contains the values of $\Delta G^{\dagger E}$ calculated at the two temperatures. The behavior of $\Delta G^{\dagger E}$ with $\bar{n}$ is seen in Fig. 7. Although slightly concave, the systems show a reasonably parabolic fit, which supports the congruence principle for the $C_{16}+C_{12}+$

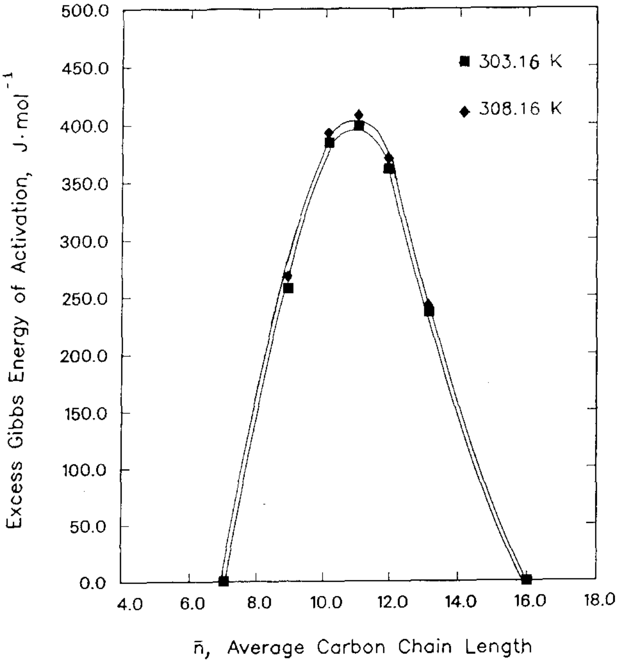

Fig. 6. Congruence principle: *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane.

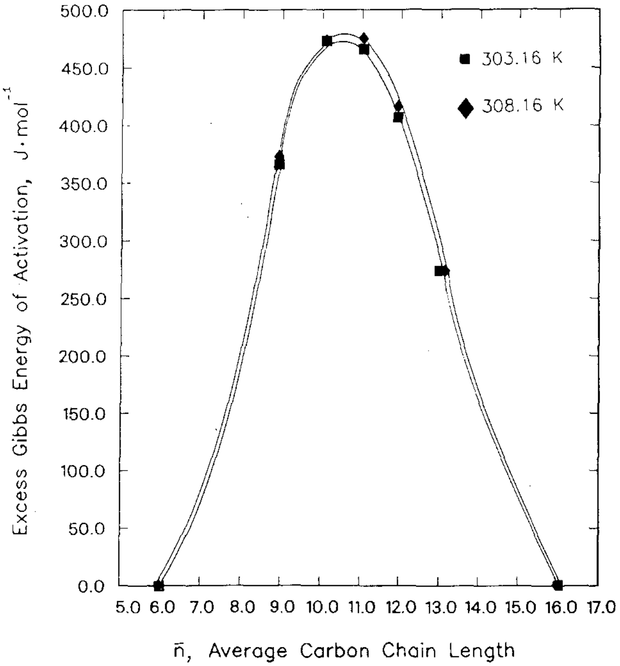

Fig. 7. Congruence principle: *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane.

$C_{10} + C_6$ system at 303.16 and 308.16 K. Recalling the definite parabolic fit of the binary $C_{14} + C_8$ system, it is observed that the quaternary system [16 + 12 + 10 + 6] shows close pseudobinary behavior in terms of mixture viscosities.

For the almost-identical *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane mixtures, however, $\Delta G^{\dagger E}$ values for these mixtures were greater by approximately 35–100 J·mol^{-1}. Also, the binary mixtures of *n*-tetradecane + *n*-octane showed the lowest $\Delta G^{\dagger E}$ values by approximately 80–90 J·mol^{-1}.

While it is expected that both quaternary mixtures would not simulate identically the behavior of the binary mixtures, it is interesting to note the major differences between the two quaternary mixtures which could account for part of the differences in the $\Delta G^{\dagger E}$ values. It is expected, though, that the better congruence agreement found in the heptane/nonane-containing systems was due to the closer simulation of *n*-octane behavior than the hexane/decane systems. Thus, the composition effects on viscosity by the lightest hydrocarbons are emphasized at these low temperatures.

4. CONCLUSIONS

Viscosities and densities were measured for selcted binary systems of *n*-tetradecane + *n*-octane and for selected quaternary systems of *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane as well as *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane at 303.16 and 308.16 K.

The arithmetic average, used frequently to predict viscosities for simple binary mixtures, gave a reasonable agreement for the $C_{14} + C_8$ system. The plot of $-\Delta\eta$ vs $\bar{n}$, the average carbon-chain length, showed smaller deviations at 308.16 than 303.16 K, but the curves were so smooth that it is expected that this nonrigorous empirical method could be used with a certain degree of success to predict mixture viscosities for unmeasured $\mathrm{C}_{14} + \mathrm{C}_8$ compositions over this 5 K temperature range.

Data from the *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane systems showed reasonably parabolic curves at the maximum and minimum of the composition range. As these systems are quaternary, it can be concluded that the "pseudobinary" behavior compared closely but did not match exactly the actual binary-system measurements. Values for the decane/hexane systems gave arithmetic deviations slightly higher than those for the nonane/heptane systems at higher $\bar{n}$, presumably due to evaporation of *n*-hexane and the ability of nonane and heptane to simulate more closely octane behavior in the mixture.

The Grunberg and Nissan equation did not show the anticipated straight-line fit of G vs $\bar{n}$ at either temperature in the binary systems of *n*-tetradecane + *n*-octane. With increasing mixture composition of *n*-tetradecane, the G values showed a slight tendency to deviate from straight-line behavior in the binary systems of *n*-tetradecane + *n*-octane. The quaternary mixtures of *n*-hexadecane + *n*-dodecane + *n*-decane + *n*-hexane did not follow the Grunberg and Nissan equation. G values calculated for these systems showed hyperbolic, rather than linear, behavior. Also, when the $\mathrm{C}_{16} + \mathrm{C}_{12}$ mole fractions and $\mathrm{C}_{10} + \mathrm{C}_6$ mole fractions were added and "pseudo-G" values were calculated, curvature was seen in the plot of G against $\bar{n}$, although at higher $\bar{n}$ values reasonably linear behavior was seen.

Further, for the systems of *n*-hexadecane + *n*-dodecane + *n*-nonane + *n*-heptane, the G values were lower than for the systems containing decane and hexane by approximately 40% at the lowest values of $\bar{n}$. "Simulated G values" determined by summing the $\mathrm{C}_{16} + \mathrm{C}_{12}$ and $\mathrm{C}_9 + \mathrm{C}_7$ mole fractions and using the actual C_{14} and C_8 viscosities in as the pure-component values showed an almost-linear relationship at the lower values of $\bar{n}$. However, at higher values of $\bar{n}$, the systems showed significant deviation from linear behavior. Thus, this empirical technique is not useful for this quaternary system over the 5 K temperature range.

Another empirical predictive technique, the principle of congruence, was seen to give satisfactory results at both temperatures. It is believed that this method would yield reliable mixture values for unmeasured $C_{14}+C_8$ mixture at these limited temperatures, 303.16 and 308.16 K.

The principle of congruence was supported to a limited extent by the quaternary systems containing decane/hexane. While a smoother parabolic fit was seen in $\Delta G^{\dagger E}$ against $\bar{n}$ for the binary systems of *n*-tetradecane + *n*-octane, the semismooth parabolic fit of the quaternary system indicates that the empirical predictive technique has limited usefulness over the 5 K temperature range. Values of $\Delta G^{\dagger E}$ calculated for the decane/hexane systems were greater by 35–109 $J \cdot mol^{-1}$ then those determined for the systems containing nonane/hexane. While both quaternary systems of mixtures did not resemble precisely the behavior of the true binary $C_{14}+C_8$ systems at 303.16 and 308.16 K, the distinctions between the abilities of $C_{10}+C_6$ and C_9+C_7 to reflect *n*-octane behavior were noted. Thus, even over this limited temperature range, the strong composition dependence was noted.

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