Viscosity of Some Binary Systems of Hexadecane and Normal Chloroalkanes

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Viscosities at 25° C. are presented for nine binary liquid systems of *n*-hexadecane with 1-chloroalkanes from 1-chlorobutane through 1-chlorooctadecane. Dependence of the excess Gibbs free energy of activation for flow and the limiting values of the corresponding partial molal properties on chain length of the 1-chloroalkane is discussed. Experimental viscosities are compared with values calculated with several different equations.

THE QUALITATIVE correlation of liquid viscosity with molecular structure has long been recognized, and viscosities of liquid mixtures have also been a useful guide in correlation of the properties of mixtures. However, with the exception of recent exploratory work (*6, 14*) with *n*-alkanes, little systematic work has been done with a series of related mixtures in which the properties could be correlated with molecular structure. The initial part of such a systematic study is presented here.

EXPERIMENTAL

Equipment. The equipment and techniques parallel that of earlier work (*14, 16*). A water bath thermostatically controlled to ±0.01° C. was used. Bath temperature was monitored with a Beckman thermometer which had been set with a calibrated thermometer. The calibration of the latter was against an NBS certified standard. Times were measured with an electric stop clock which had been calibrated against an electronic time standard. The cathetometer used in pycnometric density determinations on the pure components indicated distance to ±0.05 mm. All weighings were made with a Mettler 300-gram-capacity precision balance with certified balance weights.

Viscosities were determined with Cannon-Fenske ASTM viscometers with different capillary diameters because of the 20-fold increase in viscosity in the 1-chloroalkane series. Three NBS oils of certified viscosity were employed as primary calibration standards for ASTM 50 and 100 viscometers. Kinetic energy corrections compared favorably with those predicted for the given capillary diameters (*30*).

Densities of the pure components were determined with a 4.5-ml. Lipkin pycnometer with precision capillary arms of 1-mm. I.D. The pycnometer was calibrated with distilled water, with heights of the liquid in the capillary arms measured relative to a single etched mark on each arm. The calibration was rechecked periodically.

The viscometers and pycnometer were maintained in the bath until constant flow time or liquid volume, respectively, was obtained. As room temperature was only slightly lower than 25° C., temperature equilibrium was established rapidly. Evaporation losses were negligible, both from pycnometer and viscometers.

Liquids were mixed in a 50-ml. modified glass syringe sealed by glass at the needle end. Again, evaporation rates were negligible. Transfer to the viscometers and pycnometer was by overpressure through capillary tubing installed within the syringe plunger. The glass equipment was provided with ball and socket joints to minimize evaporation on transfer. Joints were treated with hexane to remove traces of nonvolatile components.

Materials. *n*-HEXADECANE. Humphrey Chemical Co. petroleum-derived product was washed twice with H_2SO_4 and once with aqueous $NaHCO_3$ at room temperature, given a crude drying with anhydrous Na_2SO_4, and twice distilled at about 5 Torr from P_2O_5. Nitrogen, dried by passage through concentrated H_2SO_4 and pelleted NaOH, was used for an inert atmosphere during distillation. Only the middle half of each of three distillations was recovered.

As all of 1-chloroalkanes were liquids, it would seem desirable to use the same purification procedure for each one. However, due to a wide range in boiling points, two methods were employed: routine fractional distillation in 30- and 48-inch Vigreux columns, or purification by preparative chromatography in a Hewlett-Packard FM 775 Prepmaster, equipped with a 10-foot 10% silicone rubber column, with helium as the carrier gas. The measurement of component purity was through analytical vapor phase chromatography. The elution profile of the starting material was used to establish the presence of impurities, and another profile was taken for comparison after purification. For the latter, using maximum instrument sensitivity, the areas of the elution region of the major component and of impurities were compared and the ratio taken as the measure of the mole % impurity. No identification of the nature of the impurity was attempted. Both Perkin-Elmer 820 and Varian Aerograph AP-93 VPC instruments were used, with columns of varying polarity.

1-CHLOROBUTANE, 1-CHLOROPENTANE, 1-CHLORODODECANE. Eastman Grade materials were initially treated as *n*-hexadecane was, then twice distilled over P_2O_5, 1-chlorobutane and 1-chloropentane at atmospheric pressure, and 1-chlorododecane at about 5 Torr. Only the middle third of each distillation was recovered. No impurity peaks were present in the final materials.

1-CHLOROHEXANE. Eastman Grade had an appreciable impurity (3 to 4%), which could not be resolved from the major component by chromatography with the silicone rubber column. The material was therefore treated as the 1-chlorobutane, at a very low recovery rate. Analytical chromatographs indicated the purity of the final material was 99 mole %.

1-CHLOROOCTANE. Eastman grade was used without purification after several analytical chromatographs revealed no impurity peaks.

1 - CHLORODECANE, 1 - CHLOROOCTADECANE. Eastman Grade materials were purified chromatographically. No impurity peaks were found in the final materials.

1-CHLOROTETRADECANE. Eastman Technical grade was purified by chromatography. A 2.5% low-boiling impurity was reduced to 0.1%.

1-CHLOROHEXADECANE. Eastman Practical grade was purified by chromatography. A 1% low-boiling impurity was reduced to 0.1%.

Comparison of some of the experimentally determined properties of the components used in this work with literature values is given in Table I. Present experimental values represent the mean of at least three determinations. Stated

Table I. Properties of Purified Components at 25° C.

	Mol. Wt.	Molar Volume, Ml. (Exptl.)	Density, G. per Ml.			Kinematic Viscosity, Cs.		
			Exptl. ± 10^5 std. error	Literature		Exptl. ± 10^3 std. error	Literature	
n-Hexadecane	226.449	293.75	0.77090 ± 3	0.7698-0.7712	(*1, 12, 24, 26, 28*)	3.970 ± 1	3.937-4.020	(*1, 24, 25, 26*)
1-Chlorobutane	92.569	105.08	0.88095 ± 3	0.8797-0.8812	(*5, 9, 10, 21, 24*)	0.4837 ± 0.3	0.476-0.494	(*5, 21, 24, 29*)
1-Chloropentane	106.596	121.55	0.87700 ± 3	0.8769-0.8795	(*5, 9, 24*)	0.6227 ± 0.6	0.622	(*5, 24*)
1-Chlorohexane	120.624	138.11	0.87338 ± 2	0.8733-0.8745	(*5, 9, 24*)	0.7952 ± 0.1	0.783-0.796	(*5, 24*)
1-Chlorooctane	148.678	171.05	0.86922 ± 3	0.8695-0.8706	(*9, 13, 24*)	1.298 ± 1	1.305-1.32	(*13, 24*)
1-Chlorodecane	176.732	204.11	0.86586 ± 4	0.8666	(*9*)	2.046 ± 0		
1-Chlorododecane	204.786	237.12	0.86363 ± 5	0.8634-0.8644	(*9, 13*)	3.089 ± 1	3.07	(*13*)
1-Chlorotetradecane	232.840	270.15	0.86190 ± 3	0.8628	(*9*)	4.496 ± 0		
1-Chlorohexadecane	260.894	303.14	0.86065 ± 1	0.8615-0.8616	(*9, 24*)	6.299 ± 2	6.40	(*24*)
1-Chlorooctadecane[a]	288.949	336.11	0.85968 ± 5	0.8605	(*9*)	8.590 ± 0		

	Dynamic Viscosity, Cp.			Refractive Index		
	Exptl.	Literature		Exptl.	Literature	
n-Hexadecane	3.060	3.031-3.10	(*1, 17, 24, 25, 26, 28*)	1.43286	1.4319 -1.43250	(*1, 26*)
1-Chlorobutane	0.4261	0.419-0.435	(*5, 21, 24, 29*)	1.39996	1.39953-1.4001	(*9, 10, 29*)
1-Chloropentane	0.5461	0.545-0.547	(*5, 24*)	1.41000	1.4100 -1.41026	(*9, 27, 28*)
1-Chlorohexane	0.6945	0.684-0.696	(*5, 24*)	1.41762	1.4177	(*9*)
1-Chlorooctane	1.128	1.135-1.150	(*13, 24*)	1.42850	1.4286	(*9*)
1-Chlorodecane	1.772			1.43603	1.4360	(*9*)
1-Chlorododecane	2.668	2.650	(*13*)	1.44151	1.4414	(*9*)
1-Chlorotetradecane	3.875			1.44479	1.4455	(*9*)
1-Chlorohexadecane	5.421	5.51	(*24*)	1.44815	1.4487	(*9*)
1-Chlorooctadecane[a]	7.385			1.45062	1.4513	(*9*)

[a] Supercooled liquid.

uncertainties are in terms of standard deviations. For refractive indices, the agreement between readings is not poorer than ±0.00003 units, which is within the manufacturer's stated accuracy of the instrument, the Bausch and Lomb Precision refractometer.

RESULTS AND DISCUSSION

Table I lists the viscosities, densities, and refractive indices of the purified components. For some of the halides, the disagreement between present and literature values is considerable. This is true even for the viscosities, which, of the three properties listed, is generally least significantly affected by small amounts of impurities, because it can be measured by conventional techniques to only ±0.1%. For viscosity, the greatest disagreement with the literature is found for 1-chlorobutane. The value of Chernyavskaya (*5*) is 3.1% higher than the present value, while that of Kuss (*21*) is 1.7% lower.

The limited number of literature values for some of these compounds makes it difficult to conclude whether the previous values are more dependable than present values. However, differences in viscosity are less significant in terms of excess properties than in the absolute sense (*14*). The systematic behavior described below indicates that the present work is of acceptable quality.

Experimental kinematic viscosities and excess Gibbs free energies of activation for flow (Δ^*G^E) for the mixtures are listed in Table II. The excess molar Gibbs free energy of activation for flow is defined through the Eyring viscosity equation (*11*).

$$\nu = \left(\frac{\lambda}{a}\right)^2 \frac{hN}{M} \exp\left(\Delta^*G/RT\right) \tag{1}$$

By definition, $\Delta^*G^E = \Delta^*G - \Delta^*G^i$, while for an ideal binary mixture, $\Delta^*G^i = x_1\Delta^*G_1 + x_2\Delta^*G_2$. If it is assumed that for a mixture $\ln(\lambda/a) = x_1 \ln(\lambda_1/a_1) + x_2 \ln(\lambda_2/a_2)$, then Δ^*G^E is related to viscosities by

$$\Delta^*G^E = RT[\ln(\nu M) - x_1 \ln(\nu_1 M_1) - x_2 \ln(\nu_2 M_2)] \tag{2}$$

and if $\Delta^*G^E > 0$, the viscosity is greater than that of an ideal mixture. In Figure 1, Δ^*G^E is plotted *vs.* mole fraction of *n*-hexadecane for the nine systems. The behavior throughout these systems is qualitatively similar. That is, Δ^*G^E for each system is broadly parabolic. The similarity is more evident as a reduced function, $(\Delta^*G^E/\Delta^*G^E_{\max})/x_1x_2$—that is, as the ratio of Δ^*G^E in each system to the extreme value of Δ^*G^E in that same system. The equation

$$(\Delta^*G^E/\Delta^*G^E_{\max})/x_1x_2 = 4.01 - 1.39\ (x_1 - x_2) \tag{3}$$

fits all of the systems to a standard error of ±0.05 in the ordinate. The asymmetry in Δ^*G^E is not removed if one shifts from mole to volume fraction; the effect for smaller systems is to shift $\Delta^*G^E_{\max}$ from $x_1 < 0.5$ to $\phi_1 > 0.5$.

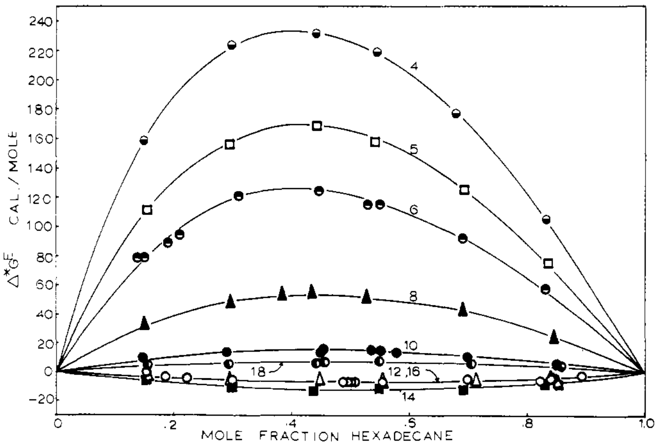

Figure 1. Excess molar Gibbs free energy of activation for flow—number indicates carbon number in *R*Cl

Table II. Properties of Binary Mixtures at 25° C.

n-Hexadecane Mole fraction	*n*-Hexadecane Volume fraction	Kinematic Viscosity, Cs.	$\Delta^* G^E$, Cal./Mole
n-Hexadecane–1-chlorobutane			
0.1495	0.3294	0.8134	158.3
0.2967	0.5412	1.202	223.6
0.4418	0.6887	1.640	231.1
0.5454	0.7703	2.010	219.3
0.6777	0.8546	2.514	176.9
0.8309	0.9322	3.172	105.1
n-Hexadecane–1-chloropentane			
0.1532	0.3042	0.9542	110.5
0.2897	0.4964	1.301	156.2
0.4420	0.6569	1.746	167.6
0.5367	0.7368	2.055	158.4
0.6903	0.8434	2.615	124.9
0.8323	0.9231	3.200	76.2
n-Hexadecane–1-chlorohexane			
0.1413	0.2593	1.108	78.5
0.1478	0.2695	1.120	79.3
0.1944	0.3392	1.220	89.4
0.2058	0.3554	1.249	92.8
0.3072	0.4854	1.529	121.5
0.4454	0.6308	1.909	123.6
0.5320	0.7074	2.166	115.4
0.5438	0.7171	2.213	116.5
0.6893	0.8251	2.709	92.7
0.8311	0.9128	3.252	57.1
n-Hexadecane–1-chlorooctane			
0.1502	0.2329	1.599	31.6
0.2936	0.4165	1.916	47.8
0.2943	0.4173	1.918	48.0
0.3835	0.5165	2.132	53.0
0.4348	0.5692	2.260	53.7
0.5265	0.6563	2.497	51.8
0.6890	0.7918	2.957	42.2
0.8444	0.9031	3.442	24.8
0.8454	0.9038	3.446	24.8
n-Hexadecane–1-chlorodecane			
0.1457	0.1971	2.280	9.2
0.2910	0.3713	2.521	13.3
0.4463	0.5370	2.793	13.6
0.4487	0.5394	2.804	15.1
0.5414	0.6295	2.978	14.3
0.5466	0.6343	2.988	14.2
0.5758	0.6614	3.040	12.9
0.6979	0.7688	3.277	8.6
0.8464	0.8880	3.618	7.6
n-Hexadecane–1-chlorododecane			
0.1515	0.1812	3.200	−1.2
0.1862	0.2208	3.207	−5.0
0.2216	0.2607	3.234	−5.1
0.3003	0.3471	3.294	−5.9
0.4930	0.5464	3.449	−7.3
0.4970	0.5504	3.455	−6.8
0.5030	0.5563	3.457	−7.4
0.5038	0.5570	3.459	−7.1
0.5553	0.6073	3.502	−7.5
0.6988	0.7418	3.650	−4.4
0.8222	0.8514	3.757	−5.8
0.8423	0.8687	3.787	−4.1
0.8458	0.8717	3.791	−3.9
0.8918	0.9108	3.841	−3.2
n-Hexadecane–1-chlorotetradecane			
0.1514	0.1625	4.366	−6.1
0.3014	0.3193	4.251	−10.9
0.4365	0.4572	4.168	−12.7
0.5484	0.5690	4.115	−12.0
0.6928	0.7103	4.044	−11.6
0.8300	0.8415	4.002	−7.7
0.8527	0.8629	3.994	−7.2
n-Hexadecane–1-chlorohexadecane			
0.1550	0.1509	5.817	−4.0
0.2969	0.2903	5.429	−5.7
0.4487	0.4409	5.056	−6.0
0.5536	0.5458	4.812	−6.7
0.7085	0.7020	4.477	−7.2
0.8447	0.8405	4.237	−3.1
0.8532	0.8492	4.209	−4.7
n-Hexadecane–1-chlorooctadecane			
0.1535	0.1368	7.647	3.4
0.2941	0.2669	6.874	6.0
0.4461	0.4131	6.113	6.7
0.4551	0.4219	6.070	6.7
0.5450	0.5114	5.659	6.3
0.6982	0.6691	5.019	4.7
0.8554	0.8379	4.439	2.4

In each system, $\Delta^* G^E$ has been related to composition through a dependence frequently used in expressing excess quantities.

$$\Delta^* G^E = x_1 x_2 \left[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \cdots\right] \qquad (4)$$

The fitted constants of Equation 4 and the standard maximum errors in cal. per mole are shown in Table III. The estimated experimental uncertainty is ±0.7 cal. per mole. All orders of Equation 4 through the sixth were examined with the aid of a digital computer. The data were weighted according to the uncertainty in mole fraction (*15*). That order was selected for a system beyond which additional terms did not significantly improve the fit.

Figure 2 shows $\overline{\Delta^* G^E}_{\max}$ in each system plotted *vs.* the chain length of the 1-chloroalkane. In addition, $\overline{\Delta^* G^E}$ has been resolved into the corresponding partial molal quantities, $\overline{\Delta^* G_i^E}$.

$$\overline{\Delta^* G^E} = x_1 \overline{\Delta^* G_1^E} + x_2 \overline{\Delta^* G_2^E} \qquad (5)$$

$\overline{\Delta^* G_i^E}$ were obtained by differentiation of Equation 4, $\overline{\Delta^* G_i^E} = \Delta^* G^E - x_i \, (d\overline{\Delta^* G^E}/dx_i)$. $\overline{\Delta^* G_i^E}$ are shown in Figure 3 for four representative systems and the limiting values at infinite dilution, $(\Delta^* G_i^E)_{x_i = 0}$, are listed in Table III. The latter are also plotted in Figure 2.

$\Delta^* G^E_{\max}$ and $(\overline{\Delta^* G_i^E})_{x_i = 0}$ are clearly related to the difference in chain length between *n*-hexadecane and the chloroalkane. They pass from the largest positive value for C_4H_9Cl through negative values and again to positive values at highest chain lengths of the chlorides. The minimum in $\Delta^* G^E_{\max}$, about −13.2 cal. per mole, is at about $n_2 = 13.9$, and the parameter is positive for $17.5 < n_2 < 11.5$. For $n_2 \geqq 12$, $\overline{\Delta^* G_i^E}$ for both components in a system are symmetric, as shown in a single constant for $\Delta^* G^E$ in those systems (Table III). It is probable, however, that for n_2 significantly greater than the $C_{18}H_{37}Cl$ used as the upper limit of this work, $\Delta^* G^E$ again becomes asymmetric, just as for $n_2 < 12$. In the asymmetric systems, the departure from ideal viscosity is due more to *n*-hexadecane behavior

Table III. Derived Properties of Mixtures Related to the Gibbs Free Energy of Activation for Flow

Component 1 is *n*-Hexadecane

Chain Length of Chloride	Constants in Series Expansion of Δ^*G^E, Equation 4			Error[a] in Δ^*G^E, Cal./Mole		Limiting Values at Infinite Dilution of Partial Molal Excess Quantity, Cal./Mole	
	A	B	C	Std.	Max.	$(\Delta^*\overline{G}_1^E)_{x_1=0}$	$(\Delta^*\overline{G}_2^E)_{x_2=0}$
4	904.8	–340.6	181.8	1.8	2.4	1430	750
5	652.6	–218.7	92.9	0.3	0.4	960	530
6	481.5	–154.5	56.1	2.8	4.6	690	380
8	213.4	–41.8		0.5	0.8	255	170
10	56.8	–19.1		1.1	2.0	76	38
12	–28.4			1.0	2.4	–28.4	–28.4
14	–51.5			0.6	0.8	–51.5	–51.5
16	–28.1			0.9	1.4	–28.1	–28.1
18	26.0			0.5	0.8	26.0	26.0

[a] The error has been calculated as

$$\left\{\sum (\text{exptl.} - \text{calcd.})^2/\text{number of observations}\right\}^{1/2}$$

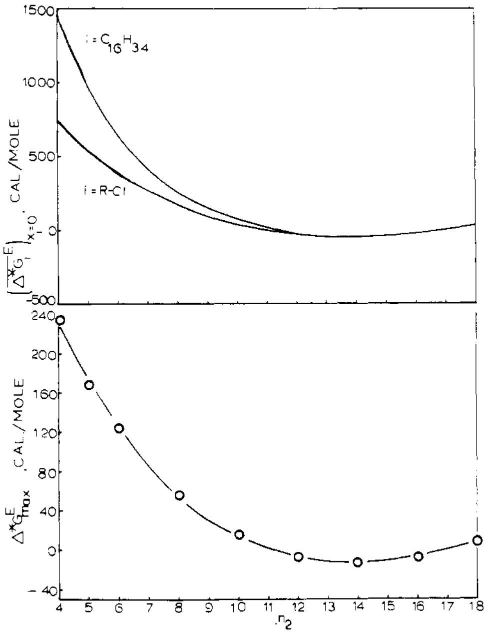

Figure 2. Extreme values of the excess Gibbs free energy of activation for flow and limiting values of the partial molal excess as a function of the 1-chloroalkane chain length

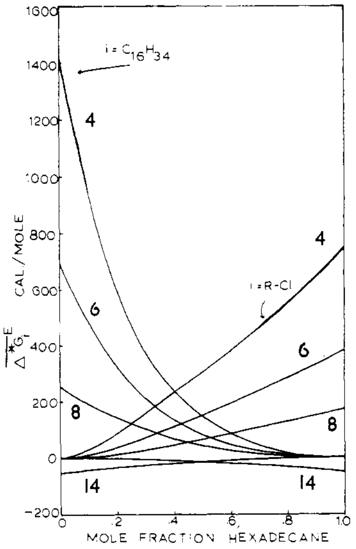

Figure 3. Partial molal excess Gibbs free energies of activation for flow for four representative systems—number indicates carbon number in *R*Cl

than that of the chloride. Thus, in the C_4H_9Cl system at infinite dilution, the partial molal quantity of *n*-hexadecane is about 700 cal. per mole greater than that of the chloride.

Effects of both polarity and chain length may be seen in the behavior of Δ^*G^E and $\Delta^*\overline{G}_i^E$ in these systems. For *n*-hexadecane–*n*-hexane and *n*-hexadecane–1-chlorohexane, the chain lengths are the same, and differences must be due to the polar effects. The excess flow properties of the former system (*14*) are greater than those in the latter. This probably results from two factors that occur upon mixing: an increase in the fluidity of the halide in the mixture *vs.* that in the pure state due to the breaking of dipole-dipole forces, and differences between the changes in free volume in the two systems. Regarding free volumes, in the former system the maximum ΔV is –0.6 ml. per mole (*14*), while in the latter ΔV is about +0.4 ml. per mole in an equimolal solution (*7*).

The influence of chain length may be described in terms of previously suggested flow models. Moore *et al.* (*23*) postulated that, because of increasing molecular disorder with increasing chain length, there is an accompanying trend toward segmental cooperative translational movement of adjacent molecules in viscous flow. This is in contrast with the gross movement of the entire molecule in the flow of spherical molecules. Another aspect of flow has been described by Hennelley *et al.* (*13*), who established the existence of rotational flow behavior for the 1-bromoalkanes. There is a transition from gross molecular rotation to rotation of the dipolar segment only in the region around 12 carbons in chain length.

As over the range of chain lengths of chlorides considered here there is a broad transition in rotational behavior from C_4H_9Cl to $C_{18}H_{37}Cl$, the trend in Δ^*G^E values can be related to the difference between the flow mechanism of *n*-hexadecane and that of the chloride in each system.

The plot of $\Delta^*G^E_{max}$ in Figure 2 indicates that this property may exhibit congruent behavior (*3*). That is, the parameter $\Delta^*G^E_{max}$ of each system may be characterized by the chain length of the chloroalkane component in the system. Prior examples of such congruent behavior have been reported by Koefoed (*20*) and Brown *et al.* (*4*). This suggests the possibility that in a multicomponent system of a normal alkane with a number of 1-chloroalkanes, the viscosity may be predicted by considering the system to be pseudobinary—that is, the normal alkane as one component and the chloride mixture as an average species with viscometric properties determined by the average chain length of the halides. This approach will be investigated in our laboratory.

The systematic nature of the present systems provides an unusual opportunity for evaluating the effectiveness of several viscosity equations for correlation or prediction in mixtures. Each is related to an assumption regarding the behavior of Δ^*G^E, Equation 2.

For correlation, Katti and Chaudhri (*18*) assumed that Δ^*G^E could be treated in terms of a two-body interaction model (*14*). This approach relates Δ^*G^E to a single empirically determined interaction parameter. McAllister (*22*) used a three-body interaction model to relate mixture viscosity to two empirically determined parameters. If it is assumed, however, that these three-body parameters are linearly related to the interactions between each pair in the trio, the relation reduces to a representation of Δ^*G^E itself in terms of two interaction parameters.

Results obtained with the equations of Katti and Chaudhri and McAllister have not been tabulated in this work because a clear indication of the effectiveness of each is available from the number of constants for Δ^*G^E for each system in Table III. There is no advantage in using either over the fitting of Δ^*G^E directly, as in Equation 4.

The equation for Δ^*G^E also serves as a point of reference for equations which have been used to predict viscosities of mixtures. For example, if $\Delta^*G^E = 0$ is assumed, the viscosity is ideal, and

$$\ln (\nu M) = \sum_i x_i \ln (\nu_i M_i)$$

For systems with M_i quite similar, this reduces to the equation used by Cronauer *et al.* (*8*).

$$\ln \nu = \sum_i x_i \ln \nu_i$$

Both of these equations serve as a useful approximation for the higher chained systems, where the simplifications of the equations are not greatly in error. Thus, for the five longest chlorides, results by these equations show a standard deviation of only 1 to 2%. The error is correlated with increasing chain length, however, and becomes about 30% for the 1-chlorobutane-*n*-hexadecane system. Other equations, such as those of Bingham (*2*) or Kendall and Monroe (*19*), show similar trends in error.

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NOMENCLATURE

A, B, C = constants for fitting of data, Equation 4
Δ^*G = molar Gibbs free energy of activation for flow, cal. per mole
$\overline{\Delta^*G_i^E}$ = partial molal excess Gibbs free energy of activation for flow, cal. per mole
$(\overline{\Delta^*G_i^E})_{x_i=0}$ = limiting value of the partial molal excess property at infinite dilution, cal. per mole
M = molecular weight, grams
N = Avogadro number
R = gas constant, cal. per deg. mole
T = absolute temperature, deg. Kelvin
V = molar volume, ml. per mole
ΔV = excess volume of mixing, ml. per mole
a = distance through which shearing force acts, cm.
h = Planck constant, erg. sec.
n = carbon number in a species (average if a mixture)
x = mole fraction
λ = distance between adjacent moving layers of molecules, cm.
η = kinematic viscosity; i.e., dynamic viscosity per density, cs.
ϕ = volume fraction

Subscripts

1 = component 1 [*n*-hexadecane (HD)]
2 = component 2 [1-chloroalkane (*R*Cl)]
i, j = generalized components
max = extreme value of indicated function

Superscripts

E = excess
i = ideal

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