tion, including some based on estimated heats of vaporization. Data for seven amines are now available, and a revision of Skinner's equation is possible.

The following equation [in the notation of McCullough and Good (*12*)] was derived for enthalpies of formation of alkyl amines:

$$\Delta Hf_{298.15} = -3.15 - 2.35a - 2.58X - 3.98X' + 0.65T + 0.70T' \quad (3)$$

Calculated and observed enthalpies of formation are compared in Table IV.

NOMENCLATURE

∂ = differential operator
T = temperature
m = mass, grams
n = number of moles
P = pressure, atm.
$\mathcal{E}$(calor.) = heat equivalent of calorimeter, cal. deg.$^{-1}$
$\mathcal{E}$(cont.) = heat equivalent of contents, cal. deg.$^{-1}$
$\Delta E_{\text{dec.}}$ = energy of decomposition, cal.
$\Delta E_{\text{ign.}}$ = electrical ignition energy, cal.
$\Delta E_{\text{cor. to std. states}}$ = energy for reduction to standard states, cal.
$\Delta Ec^\circ/M$ = standard energy of idealized combustion reaction, cal. gram^{-1}
ΔEc° = standard energy of idealized combustion reaction, kcal. mole^{-1}
ΔHc° = standard enthalpy of combustion, kcal. mole^{-1}
ΔHv = enthalpy of vaporization to real gas
ΔHf° (l) = standard enthalpy of formation of liquid, kcal. mole^{-1}
ΔHf° (g) = standard enthalpy of formation of gas, kcal. mole^{-1}
i = superscript indicating initial state
f = superscript indicating final state

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Viscosity of Some Binary Liquid Nonelectrolyte Mixtures

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Viscosities and densities are presented for mixtures of 14 binary nonelectrolyte systems at 25° C. Experimental viscosities are compared with values calculated with several different equations. The excess Gibbs free energy of activation of flow and the excess volume in each system are compared. Some dependence of behavior on molecular size is described.

VISCOSITIES of liquid mixtures provide information for the elucidation of the fundamental behavior of liquid mixtures, aid in the correlation of mixture viscosities with those of the pure components, and provide a basis for the selection of physicochemical methods of analysis.

In the present work, both viscometric and volumetric behavior are described for 14 binary mixtures of nonelectrolyte liquids. The viscometric information includes viscosity as a function of composition on the bases of weight, volume, and mole fraction, comparison of experimental viscosities with those calculated with several different equations, and excess Gibbs free energy of activation of flow. The volumetric information includes density as a function of composition on the bases of weight, volume, and mole fraction, and excess volumes of mixing.

The object of the present study is a comparison among several binary systems of hexadecane with smaller molecules and hexane with the same molecules. Some systems containing tetradecane have also been included.

EXPERIMENTAL

Equipment. A thermostatically controlled bath constant to ±0.01° C. was used. Bath temperature was set and monitored with a Beckman thermometer which had been standardized against a certified thermometer. Times were measured with an electric stopclock calibrated against an electronic time standard. Weighings were made with a precision balance and certified balance weights. Density determination involved use of a cathetometer which indicated length to the nearest ±0.05 mm.

Three Cannon-Fenske viscometers of different capillary diameters were used because of the tenfold range of viscosities of the components. The viscometers were calibrated with National Bureau of Standards oils, and experimental results by the different viscometers were in agreement. Kinetic energy corrections were applied to viscosity data. Errors due to alignment and loading of viscometers were minimized by reproducible precautionary procedures.

Densities were determined with Lipkin pycnometers (*25*) constructed with precision glass capillary tubing of 1-mm. I.D. Total pycnometer volume was 3 ml. Pycnometers were calibrated with distilled water, with heights of liquid in the capillary arms measured then, as in determining unknown densities later, relative to a single etched mark on each arm.

In making determinations, both pycnometers and viscometers were maintained in the bath until at least two consecutive measurements of the liquid height in the capillaries or the flow time indicated that the sample had reached the temperature of the bath. As the ambient temperature was not far below bath temperature, time required for the mixtures to reach bath temperature was short, and evaporation of mixtures from either pycnometers or viscometers was experimentally negligible for even the most volatile mixtures.

Liquids were mixed in a modified glass syringe sealed by glass at the needle end. Again evaporation rates were negligible. Transfer of mixtures to viscometers and pycnometers was by overpressure through capillary tubing. The mixing syringe, transfer tubing, viscometers, and pycnometers were all provided with ball-and-socket joints to minimize evaporation effects accompanying transfer. Joints on viscometers and pycnometers were treated with low boiling solvent after sample transfer to remove traces of high boiling components on those surfaces.

Materials. As all components were liquid, routine fractional distillation techniques in a 48-inch Vigreux column were used for purification. For all liquids except 2-bromobutane (very faint yellow), the purified material was colorless.

n-HEXANE. Matheson, Coleman and Bell chromatoquality grade was used without further purification, after it was determined that distillation did not improve agreement between experimental and literature values of the physical properties.

BENZENE. Baker analyzed grade was distilled twice from CaH_2. Only the middle half of each distillation was recovered.

CARBON TETRACHLORIDE. Fisher certified reagent grade was distilled twice from P_2O_5. Only the middle half of each distillation was recovered.

2-BROMOBUTANE AND 4-METHYLCYCLOHEXANONE. DPI Eastman grade was purified in the same manner as carbon tetrachloride.

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

n-HEXADECANE. Humphrey Chemical Co. petroleum-derived product was treated in the same manner as *n*-tetradecane, but only the middle half of each of three distillations was recovered.

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

	Molecular Weight	Molar Volume, Ml. (Exptl.)	Density, G. per Ml.			Kinematic Viscosity, Cs.		
			Exptl. $\pm 10^5$ std. error	Literature		Exptl. $\pm 10^4$ std. error	Literature	
Benzene	78.1147	89.422	0.87355 ± 7	0.87351-0.87370	(*12, 13, 29, 30, 33, 34*)	0.6917 ± 2	0.6863	(*16*)
Carbon tetrachloride	153.8232	97.107	1.58406 ± 7	1.5842 -1.5846	(*3, 12, 28, 30, 33, 34*)	0.5684 ± 2	0.5692	(*16*)
2-Bromobutane	137.0253	109.278	1.25391 ± 1	1.2510	(*12*)	0.4490 ± 2		
4-Methylcyclohexanone	112.1731	123.002	0.91196 ± 2	0.912 (24.4°)	(*1*)	1.7710 ± 1	1.776[a]	(*19*)
n-Hexane	86.1785	131.534	0.65518 ± 4	0.65482-0.6550	(*3, 13, 15, 29*)	0.4520 ± 2		
n-Tetradecane	198.3952	260.936	0.76032 ± 5	0.75917-0.7593	(*7, 12*)	2.7418 ± 4	2.740	(*13*)
n-Hexadecane	226.4494	293.789	0.77079 ± 6	0.7698 -0.7712	(*3, 6, 15, 28*)	3.9726 ± 7	4.008	(*13*)

	Molecular Weight	Molar Volume, Ml. (Exptl.)	Dynamic Viscosity, Cp.			Refractive Index		
			Exptl.	Literature		Exptl.	Literature	
Benzene	78.1147	89.422	0.6042	0.5996-0.608	(*8, 16, 24*)	1.49772	1.4979	(*13, 29, 33*)
Carbon tetrachloride	153.8232	97.107	0.9004	0.8963-0.902	(*3, 16, 28*)	1.45714	1.45704-1.45759	(*12, 33, 36, 37*)
2-Bromobutane	137.0253	109.278	0.5630	0.557 -0.591	(*8, 20*)	1.43427	1.4342	(*12, 20*)
4-Methylcyclohexanone	112.1731	123.002	1.6151			1.44323	1.44322 (24.4°)	(*1*)
n-Hexane	86.1785	131.534	0.2961	0.2923-0.308	(*3, 13, 22*)	1.37219	1.37226	(*13, 29*)
n-Tetradecane	198.3952	260.936	2.0839	2.035 -2.081	(*13, 22*)	1.42731	1.4268	(*12*)
n-Hexadecane	226.4494	293.789	3.0620	3.0306-3.10	(*3, 13, 28*)	1.43273	1.43250	(*6, 13*)

[a] Interpolated from plot of fluidity *vs.* temperature.

Some experimentally determined properties of the components used in this work are listed in Table I with literature values. Experimental values of the present properties represent the mean of at least three determinations and generally more. Stated uncertainties are in terms of standard deviations. For refractive indices the agreement between readings is not poorer than ±0.00003 unit, which is within the manufacturer's stated accuracy of the instrument, the Bausch and Lomb Precision refractometer.

RESULTS

The experimental viscosities and densities of the various mixtures are listed in Table II, as well as the excess molar volumes (ΔV^E) and the excess molar Gibbs free energies of activation of flow (Δ^*G^E). The excess molar volume is defined as $\Delta V^E = V - (x_1V_1 + x_2V_2)$. The excess molar Gibbs free energy of activation of flow is defined through the Eyring viscosity equation (*14*)

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

By definition, $\Delta^*G^E = \Delta^*G - \Delta^*G^i$, while for an ideal mixture (*32*) $\Delta^*G^i = x_1\Delta^*G_1 + x_2\Delta^*G_2$. If it is assumed (*23*) 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 and molar volumes by

$$\Delta^*G^E = RT[\ln \eta\, V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2] \tag{2}$$

and if $\Delta^*G^E > 0$, the viscosity is greater than that of an ideal mixture.

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

Concentration of First-named Component						
Weight fraction	Volume fraction	Mole fraction	Kinematic Viscosity, Cs.	Density, G./Ml.	Δ^*G^E, Cal./Mole	ΔV^E, Ml./Mole
			n-Hexadecane–*n*-hexane			
0.8959	0.8797	0.7660	2.7691	0.75793	128.7	−0.35
0.8876	0.8704	0.7504	2.6937	0.75675	134.6	−0.32
0.8830	0.8651	0.7417	2.6545	0.75629	138.3	−0.36
0.8667	0.8468	0.7121	2.5327	0.75413	152.4	−0.35
0.8262	0.8017	0.6441	2.2412	0.74939	175.4	−0.48
0.8182	0.7928	0.6314	2.1768	0.74826	175.7	−0.45
0.8161	0.7905	0.6281	2.1695	0.74816	178.2	−0.50
0.8124	0.7864	0.6224	2.1344	0.74779	176.4	−0.53
0.7440	0.7118	0.5251	1.7793	0.73931	201.1	−0.54
0.7434	0.7112	0.5244	1.7782	0.73934	201.7	−0.57
0.7372	0.7045	0.5163	1.7490	0.73857	202.7	−0.57
0.6556	0.6181	0.4201	1.4299	0.72889	209.6	−0.62
0.6527	0.6150	0.4170	1.4266	0.72835	212.2	−0.57
0.6364	0.5980	0.3998	1.3746	0.72652	212.3	−0.60
0.5749	0.5348	0.3398	1.1996	0.71905	207.0	−0.53
0.4852	0.4448	0.2640	0.9958	0.70882	188.7	−0.55
0.4128	0.3741	0.2111	0.8665	0.70059	167.9	−0.51
0.3275	0.2928	0.1564	0.7438	0.69097	138.6	−0.44
0.2338	0.2060	0.1040	0.6364	0.68033	101.9	−0.29
0.1334	0.1157	0.0553	0.5452	0.66941	59.2	−0.18
			n-Hexadecane–2-bromobutane			
0.8027	0.8688	0.7112	2.6167	0.83283	139.9	0.39
0.6964	0.7886	0.5812	2.1052	0.87081	182.2	0.52
0.5969	0.7067	0.4726	1.7108	0.91016	200.7	0.50
0.5082	0.6270	0.3847	1.4338	0.94807	209.2	0.56
0.4097	0.5303	0.2957	1.1605	0.99465	197.2	0.51
0.3448	0.4613	0.2415	1.0075	1.02784	181.7	0.48
0.2521	0.3541	0.1694	0.8186	1.07978	148.7	0.40
0.1643	0.2423	0.1063	0.6687	1.13444	106.8	0.27
0.1091	0.1662	0.0690	0.5818	1.17169	69.9	0.20
0.0608	0.0953	0.0377	0.5210	1.20671	42.6	0.11
			n-Hexadecane–carbon tetrachloride			
0.7897	0.8853	0.7183	2.9093	0.86278	148.4	0.37
0.6518	0.7937	0.5598	2.3221	0.93592	199.7	0.58
0.5217	0.6915	0.4256	1.8410	1.01790	217.0	0.67
0.4328	0.6106	0.3414	1.5521	1.08298	212.2	0.68
0.3410	0.5154	0.2601	1.2903	1.16010	195.2	0.62
0.2782	0.4420	0.2075	1.1321	1.21965	177.0	0.56
0.2142	0.3591	0.1563	0.9793	1.28619	148.7	0.58
0.1618	0.2840	0.1159	0.8655	1.34842	120.6	0.42
0.1011	0.1877	0.0710	0.7438	1.42772	80.9	0.29
0.0496	0.0968	0.0342	0.6508	1.50305	42.4	0.16
			n-Hexadecane–benzene			
0.9045	0.9148	0.7656	2.9875	0.77773	123.0	0.57
0.7945	0.8142	0.5715	2.2539	0.78629	183.0	0.94
0.7087	0.7338	0.4563	1.8615	0.79331	196.0	1.11
0.5662	0.5967	0.3105	1.4260	0.80608	185.9	1.17
0.5208	0.5519	0.2727	1.3202	0.81071	175.8	1.10
0.3271	0.3553	0.1436	0.9915	0.83128	116.9	0.82
0.2619	0.2868	0.1091	0.9115	0.83872	93.3	0.71
0.1696	0.1880	0.0658	0.8181	0.85010	59.5	0.50
0.0866	0.0970	0.0317	0.7491	0.86094	29.1	0.29

(*Continued*)

Table II. Properties of Binary Mixtures at 25° C. (*Continued*)

Concentration of First-named Component						
Weight fraction	Volume fraction	Mole fraction	Kinematic Viscosity, Cs.	Density, G./Ml.	Δ^*G^E, Cal./Mole	ΔV^E, Ml./Mole
4-Methylcyclohexanone–*n*-hexadecane						
0.9241	0.9114	0.9609	1.8362	0.89862	9.6	0.12
0.8325	0.8077	0.9094	1.9435	0.88292	26.3	0.30
0.7556	0.7232	0.8619	2.0442	0.87046	39.4	0.41
0.6695	0.6313	0.8035	2.1698	0.85713	52.6	0.51
0.5837	0.5423	0.7389	2.3053	0.84430	62.3	0.60
0.4031	0.3634	0.5768	2.6402	0.81912	70.3	0.71
0.3149	0.2798	0.4813	2.8313	0.80761	65.2	0.70
0.1970	0.1718	0.3313	3.1360	0.79296	47.9	0.62
0.1262	0.1087	0.2257	3.3585	0.78469	30.8	0.47
n-Tetradecane–*n*-hexane						
0.8991	0.8847	0.7946	2.0744	0.74933	82.4	−0.35
0.8171	0.7938	0.6600	1.6736	0.74023	112.1	−0.46
0.7292	0.6988	0.5391	1.4014	0.73058	143.4	−0.53
0.6468	0.6121	0.4430	1.1851	0.72153	148.9	−0.52
0.5675	0.5307	0.3631	1.0186	0.71307	143.6	−0.52
0.4877	0.4506	0.2925	0.8914	0.70463	136.6	−0.50
0.3925	0.3577	0.2192	0.7643	0.69479	117.6	−0.46
0.3122	0.2812	0.1647	0.6770	0.68653	97.2	−0.40
0.2186	0.1943	0.1084	0.5939	0.67705	70.7	−0.31
0.1171	0.1026	0.0545	0.5196	0.66677	38.1	−0.17
n-Tetradecane–2-bromobutane						
0.8161	0.8798	0.7540	2.0197	0.81842	89.7	0.34
0.7114	0.8026	0.6300	1.6925	0.85607	120.0	0.41
0.6037	0.7153	0.5127	1.4141	0.89843	140.2	0.51
0.4976	0.6203	0.4062	1.1757	0.94509	144.8	0.48
0.4070	0.5310	0.3216	0.9997	0.98906	138.7	0.44
0.2601	0.3670	0.1954	0.7596	1.06991	108.9	0.37
0.2004	0.2925	0.1476	0.6769	1.10707	90.6	0.29
0.1284	0.1955	0.0924	0.5862	1.15536	62.7	0.22
0.0808	0.1266	0.0572	0.5317	1.18976	41.2	0.16
4-Methylcyclohexane–*n*-tetradecane						
0.9167	0.9018	0.9512	1.8029	0.89619	3.3	0.13
0.8423	0.8166	0.9043	1.8329	0.88260	5.3	0.24
0.7581	0.7232	0.8471	1.8778	0.86791	9.3	0.34
0.6719	0.6306	0.7836	1.9298	0.85359	12.9	0.42
0.5911	0.5466	0.7189	1.9846	0.84077	15.6	0.47
0.4966	0.4513	0.6357	2.0656	0.82628	20.0	0.52
0.3220	0.2836	0.4565	2.2272	0.80098	18.3	0.58
0.2241	0.1941	0.3381	2.3386	0.78790	13.4	0.50
0.1080	0.0917	0.1764	2.5071	0.77302	5.0	0.37
2-Bromobutane–*n*-hexane						
0.9280	0.8708	0.8902	0.4373	1.17637	−10.6	0.02
0.8724	0.7813	0.8114	0.4311	1.12263	−16.0	0.04
0.8243	0.7102	0.7468	0.4267	1.07962	−20.1	0.08
0.7613	0.6250	0.6674	0.4226	1.02869	−23.9	0.08
0.6824	0.5289	0.5747	0.4207	0.97102	−25.2	0.10
0.5996	0.4389	0.4850	0.4201	0.91701	−25.6	0.13
0.4384	0.2897	0.3292	0.4232	0.82767	−23.0	0.14
0.3105	0.1905	0.2207	0.4292	0.76853	−17.9	0.11
0.1604	0.0908	0.1073	0.4380	0.70877	−11.3	0.14
Carbon tetrachloride–*n*-hexane						
0.9335	0.8531	0.8872	0.5096	1.44654	−40.8	0.08
0.9002	0.7887	0.8349	0.4908	1.38662	−52.5	0.09
0.8581	0.7144	0.7721	0.4731	1.31764	−62.1	0.09
0.7355	0.5350	0.6091	0.4418	1.15055	−73.8	0.15
0.6725	0.4593	0.5350	0.4338	1.08050	−72.9	0.14
0.5859	0.3691	0.4421	0.4279	0.99690	−67.8	0.14
0.3986	0.2152	0.2708	0.4273	0.85400	−48.8	0.15
0.2320	0.1110	0.1447	0.4344	0.75750	−29.1	0.14
Benzene–*n*-hexane						
0.9182	0.8939	0.9253	0.6296	0.84906	−36.7	0.14
0.8411	0.7989	0.8538	0.5862	0.82761	−60.8	0.23
0.7605	0.7043	0.7779	0.5525	0.80647	−76.7	0.31
0.6966	0.6327	0.7170	0.5300	0.79070	−85.8	0.34
0.6162	0.5464	0.6392	0.5069	0.77157	−92.6	0.40
0.5333	0.4615	0.5577	0.4912	0.75285	−90.6	0.45
0.4486	0.3790	0.4730	0.4773	0.73490	−86.3	0.46
0.3495	0.2873	0.3722	0.4656	0.71551	−75.6	0.39
0.2366	0.1886	0.2548	0.4561	0.69452	−58.3	0.32
0.1654	0.1294	0.1795	0.4534	0.68208	−43.0	0.25

(*Continued on page 578*)

Table II. Properties of Binary Mixtures at 25° C. (*Continued*)

Concentration of First-named Component						
Weight fraction	Volume fraction	Mole fraction	Kinematic Viscosity, Cs.	Density, G./Ml.	Δ^*G^E, Cal./Mole	ΔV^E, Ml./Mole
		4-Methylcyclohexanone–*n*-hexane				
0.9030	0.8699	0.8773	1.3900	0.88012	–42.2	–0.22
0.8414	0.7921	0.8029	1.2176	0.86071	–59.4	–0.31
0.7676	0.7035	0.7173	1.0592	0.83821	–71.8	–0.36
0.6938	0.6194	0.6351	0.9323	0.81677	–80.3	–0.39
0.6196	0.5392	0.5558	0.8328	0.79606	–82.6	–0.39
0.5246	0.4422	0.4588	0.7297	0.77111	–82.2	–0.39
0.4411	0.3619	0.3775	0.6594	0.75023	–76.8	–0.36
0.3405	0.2705	0.2840	0.5907	0.72621	–66.9	–0.28
0.2426	0.1870	0.1974	0.5385	0.70412	–52.6	–0.17
0.1340	0.1000	0.1062	0.4921	0.68139	–33.5	–0.10
		Carbon tetrachloride–benzene				
0.9402	0.8966	0.8887	0.5719	1.51002	2.0	0.03
0.8705	0.7875	0.7734	0.5782	1.43234	4.7	0.05
0.8172	0.7114	0.6941	0.5832	1.37904	5.8	0.00
0.7429	0.6144	0.5947	0.5904	1.30940	6.3	0.05
0.6103	0.4634	0.4430	0.6058	1.20224	6.8	0.04
0.5140	0.3683	0.3494	0.6185	1.13452	6.9	0.06
0.4059	0.2736	0.2576	0.6322	1.06728	5.3	0.06
0.2836	0.1792	0.1674	0.6475	1.00081	2.2	0.01
0.1675	0.0999	0.0927	0.6650	0.94399	1.2	0.05
		n-Hexadecane–*n*-tetradecane				
0.9762	0.9759	0.9730	3.8796	0.77024	–8.0	0.11
0.9467	0.9460	0.9396	3.8362	0.76997	–7.2	0.10
0.9041	0.9030	0.8920	3.7765	0.76947	–5.8	0.11
0.8186	0.8166	0.7981	3.6600	0.76848	–3.4	0.14
0.7192	0.7165	0.6918	3.5299	0.76747	–1.2	0.13
0.6299	0.6268	0.5986	3.4170	0.76661	0.2	0.10
0.5475	0.5441	0.5145	. . .	0.76591	. . .	0.04
0.4972	0.4938	0.4642	3.2581	0.76529	1.5	0.07
0.3732	0.3701	0.3429	3.1200	0.76416	2.4	0.01
0.2880	0.2852	0.2617	. . .	0.76341	. . .	–0.04
0.2768	0.2741	0.2511	3.0157	0.76309	2.2	0.04
0.2027	0.2005	0.1822	. . .	0.76264	. . .	–0.08
0.1840	0.1820	0.1650	2.9219	0.76232	2.2	–0.03
0.0971	0.0959	0.0861	2.8351	0.76155	1.3	–0.08
0.0856	0.0845	0.0758	. . .	0.76131	. . .	–0.04

ΔV^E are plotted in Figure 1 and Δ^*G^E in Figure 2. Excess volume plots of the systems carbon tetrachloride-benzene, hexane-carbon tetrachloride, and hexane-2-bromobutane have been omitted from Figure 1 to avoid overcrowding. The maxima in ΔV^E for these systems are, respectively, +0.05, +0.14, and +0.12 ml. per mole.

A number of equations have been proposed for the prediction of mixture viscosities. Thus for an ideal mixture Δ^*G^E is zero, so by Equation 2 the ideal viscosity equation is

$$\ln \eta V = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 \tag{3}$$

Other equations for the prediction of viscosity in mixtures include those employed by Bingham (*4*)

$$\phi = x_1\phi_1 + x_2\phi_2 \tag{4}$$

Kendall and Monroe (*24*),

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 \tag{5}$$

and Cronauer, Rothfus, and Kermore (*9*),

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 \tag{6}$$

The effectiveness of these equations as applied to the present systems is shown in Table III.

For correlation of mixture viscosities, two equations combining an interaction model with fitting of empirically evaluated interaction parameters have recently been proposed. The equation of Katti and Chaudhri (*23*), based upon the regular solution model (*17*, *21*), may be put into the form (*18*)

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln (x_1M_1 + x_2M_2) + x_1x_2\alpha_{12} \tag{7}$$

A somewhat more involved equation by McAllister, based upon a three-body interaction model (*26*), is

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + x_1^3 \ln M_1 + x_2^3 \ln M_2 - \ln (x_1M_1 + x_2M_2) + 3x_1^2x_2 \ln \left(\frac{2M_1 + M_2}{3}\right) + 3x_1x_2^2 \ln \left(\frac{M_1 + 2M_2}{3}\right) + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} \tag{8}$$

Both of these last two equations treat viscosity by the Eyring model, Equation 1. The constants of Equations 7 and 8 are listed in Table IV, with the errors in applying these equations to the present systems.

The viscosity data have also been fitted on a strictly empirical basis in the form

$$p = f_1p_1 + f_2p_2 + f_1f_2[A + B(f_1 - f_2) + C(f_1 - f_1)^2 + D(f_1 - f_2)^3 + \ldots\ldots] \tag{9}$$

where f_i is a concentration variable (weight, volume, or mole fraction) and p and p_i are, respectively, the physical property of mixture and pure component i. Constants of Equation 9 are listed in Table V for the case where f_i is mole fraction.

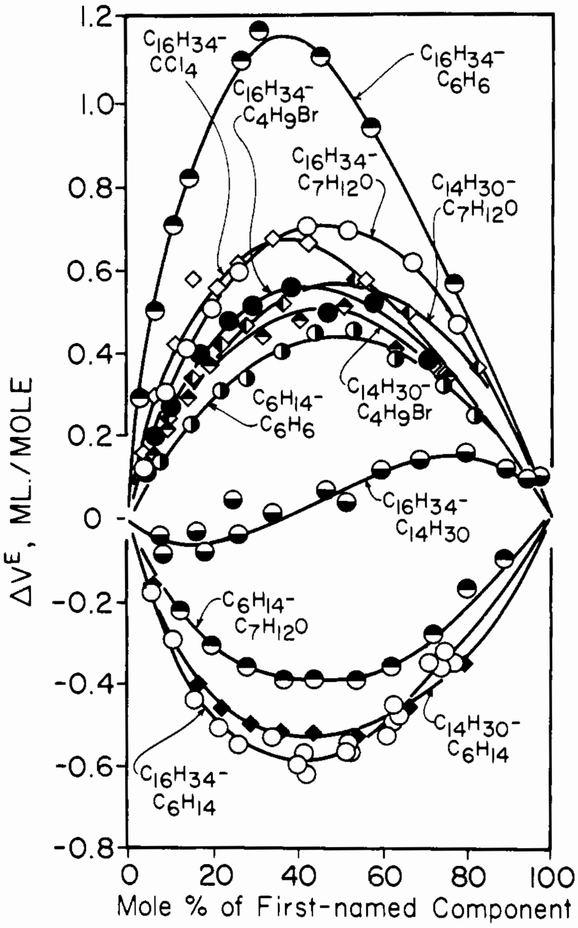

Figure 1. Excess molar volumes

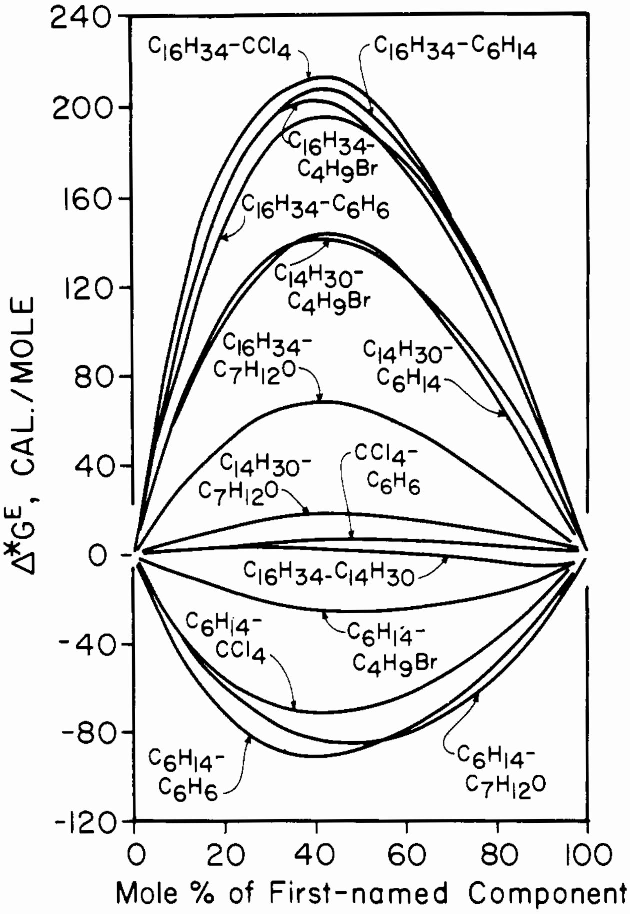

Figure 2. Excess molar Gibbs free energy of activation of flow

A power series expansion in mole fraction of the form in Equation 9 has also been fitted to the departure from the ideal viscosity, as it is possible that such a function might be fitted more simply than Equation 9. The result is an equation extending Equation 7, replacing α_{12} by the power series (*18*):

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln (x_1M_1 + x_2M_2) + x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \ldots.] \quad (10)$$

Results by Equation 10 and the appropriate constants are also given in Table V. The constants of Equations 7 to 10 were evaluated on the basis of weighted data (*18*).

In selecting the number of constants for each system relative to Equations 9 and 10, all orders of power expansion through the sixth were examined with the aid of a digital computer. That order was selected for a system beyond which additional terms did not significantly improve the fit. Thus the order of the fitting equations varies between systems.

DISCUSSION

For a given component in Table I the different physical properties are generally not from the same literature source. Therefore, it is not feasible to state the purity of the present components on the basis of these properties. With benzene, for example, both density and dynamic viscosity values fall within the range of literature values quoted in Table I, while both kinematic viscosity and refractive index are in good agreement. The present kinematic viscosity is about 1% high and the refractive index is about 0.0002 unit low.

The components showing poorest agreement of density with literature values are 2-bromobutane, tetradecane, and hexadecane. For the first the difference is 0.0029 gram per ml.; however, only one literature value is available for comparison. The errors for the other two components appear to be more clearly established. Both compounds also show the greatest disagreement between present and literature refractive indices, although dynamic viscosities agree well with literature values. For these two hydrocarbons, the starting material contained less than 1% impurity by the manufacturer's specifications.

Apparently, the impurities remaining in the purified components are insufficient to detract from the significance of the present work. This may be illustrated by comparing present results with literature values for systems containing either tetradecane or hexadecane, where the impurity is probably the greatest among the components used in the study. Thus for hexane-hexadecane Desmyter and van der Waals (*11*) found a maximum ΔV^E of −0.62 ml. per mole at about 0.4 mole fraction of hexadecane, while Gomez-Ibáñez and Liu (*15*) obtained −0.59 ml. per mole. By the present work the value is −0.58 ± 0.03 ml. per mole. The agreement is satisfactory.

Another useful comparison is between present kinematic viscosities and those reported by Holmes, Olander, and Wilke (*22*) for tetradecane-hexane mixtures. In terms of a deviation function, D (compare with Equation 9)

$$D = p - (f_1p_1 + f_2p_2)$$

the greatest disagreement is about 0.5% (or 0.01 cs.) at equimolal composition. Yet in the present work the viscosity of tetradecane is 2½% greater and that of hexane is 4% less than that reported in the previous work (*22*).

Table III. Errors in Several Equations Used in Prediction of Mixture Viscosities[a]

	$\phi = \Sigma x_i\phi_i$ Equation 4	$\ln \eta = \Sigma x_i \ln\eta_i$ Equation 5	$\ln \nu = \Sigma x_i \ln\nu_i$ Equation 6	$\ln \eta V = \Sigma x_i \ln\eta_i V_i$ Equation 3	Ratio[b]
2-Bromobutane–*n*-hexane	±	−	−	−	
	0.6	5.0	7.2	4.4	
	0.4	3.9	5.6	3.4	1.0
Carbon tetrachloride–*n*-hexane	+	−	−	−	
	1.5	14.7	17.7	13.3	
	1.1	11.4	13.8	10.3	1.2
n-Hexadecane–*n*-Tetradecane	±	±	±	±	
	1.9	1.4	1.4	1.4	
	1.3	0.7	0.7	0.7	1.4
Carbon tetrachloride–benzene	+	+	−	+	
	2.9	1.0	4.7	1.2	
	2.2	0.7	3.6	0.8	1.2
4-Methylcyclohexanone–*n*-tetradecane	−	−	−	+	
	3.3	4.0	1.2	3.3	
	2.7	3.3	0.9	2.1	1.5
4-Methylcyclohexanone–*n*-hexadecane	+	±	+	+	
	6.7	2.1	5.6	11.2	
	4.4	1.3	3.7	7.8	2.2
Benzene–*n*-hexane	−	−	−	−	
	12.3	19.4	17.0	16.9	
	9.6	15.3	13.3	13.2	1.5
4-Methylcyclohexanone–*n*-hexane	+	−	−	−	
	19.5	14.7	16.0	15.0	
	14.9	11.8	12.8	12.0	3.9
n-Tetradecane–2-bromobutane	+	+	+	+	
	29.2	13.8	20.4	21.7	
	22.2	10.5	15.7	16.7	6.1
n-Hexadecane–carbon tetrachloride	+	+	+	+	
	31.5	19.1	29.4	30.7	
	23.7	14.6	22.8	23.8	7.0
n-Hexadecane–benzene	+	+	+	+	
	37.0	14.2	17.5	28.2	
	25.6	10.0	12.7	20.8	5.8
n-Hexadecane–2-bromobutane	+	+	+	+	
	41.6	20.5	27.6	29.8	
	31.7	15.6	21.3	23.0	8.8
n-Tetradecane–*n*-hexane	+	+	+	+	
	46.2	17.8	15.2	22.2	
	35.8	13.9	11.8	17.4	6.0
n-Hexadecane–*n*-hexane	+	+	+	+	
	57.8	24.6	21.6	30.1	
	51.1	20.3	17.8	25.1	8.6

[a] Positive sign indicates that the calculated viscosity is less than the experimental viscosity. The first number is the maximum error and the second is the standard error,

$$\left\{\Sigma\left[\frac{100(\text{viscosity}_{\text{exptl.}} - \text{viscosity}_{\text{calcd.}})}{\text{viscosity}_{\text{exptl.}}}\right]^2 \Big/ \text{number of observations}\right\}^{1/2}$$

both as per cent. In the third column of data errors are given as kinematic viscosity; otherwise, as dynamic viscosity. [b] Ratio of kinematic viscosities of binary components.

As the properties of the purified components themselves vary between results of different workers, comparison on an absolute basis of present mixture properties with the few literature values available is not truly representative. The data have, therefore, been compared on a relative basis, with large-scale plots of the deviations. Concordant plots of D *vs.* composition for data from different sources were taken as establishing agreement between the sets of data. The comparisons indicate that the present results are of acceptable quality.

Uncertainties in a given property listed in Table II are similar in the various systems, approximating the following representative values: kinematic viscosity, ±0.10%; density, ±0.009%; excess volume, ±0.02 ml. per mole; excess Gibbs free energy of flow, ±0.7 cal. per mole. These are somewhat larger than those predicted on the basis of the replication of measurements on the pure components. Mixing or transfer errors in this work were apparently not reduced to insignificant levels.

All but four of the present systems exhibit positive ΔV^E at all compositions (Figure 1). Three systems show continually negative ΔV^E: hexane–4-methylcyclohexanone, hexane-tetradecane, and hexane-hexadecane. One system, tetradecane-hexadecane, shows a sign inversion in ΔV^E.

Prigogine (*31*) has treated the role of various factors, such as difference in molecular sizes, the nature of intermolecular interactions, and *r*-meric relationships, in determining the excess volume of mixing. Deshpande and Pandya

Table IV. Errors by Viscosity Equations of McAllister (26)[a] and Katti and Chaudhri (23)[b]

Component 1 is first-named component of pair

			Error, %, as η			Error, %, as ν	
System	ν_{12}	ν_{21}	Std.[c]	Max.	α_{12}	Std.[c]	Max.
n-Hexadecane–*n*-hexane	2.4183	1.5482	0.55	0.81	1.3867	3.10	5.11
n-Hexadecane–2-bromobutane	2.4204	1.7263	0.47	0.84	1.4327	3.76	5.98
n-Hexadecane–carbon tetrachloride	2.7211	2.1000	0.72	1.03	1.5360	3.87	6.22
n-Hexadecane–benzene	2.7365	1.8974	0.28	0.52	1.3634	2.37	3.80
4-Methylcyclohexanone–*n*-hexadecane	2.7138	3.1186	0.41	0.76	0.4520	1.50	2.73
n-Tetradecane–*n*-hexane	1.7577	1.1655	0.43	0.91	1.0120	2.15	3.86
n-Tetradecane–2-bromobutane	1.8234	1.2421	0.23	0.45	0.9843	2.28	3.17
4-Methylcyclohexanone–*n*-tetradecane	2.0775	2.3525	0.30	0.50	0.1209	0.40	0.92
2-Bromobutane–*n*-hexane	0.4147	0.4149	0.09	0.23	−0.1766	0.09	0.22
Carbon tetrachloride–*n*-hexane	0.4059	0.4236	0.32	0.53	−0.5014	1.40	1.97
Benzene–*n*-hexane	0.4523	0.4590	0.38	0.59	−0.6229	1.77	2.53
4-Methylcyclohexanone–*n*-hexane	0.9046	0.5950	0.34	0.63	−0.5729	0.53	0.97
Carbon tetrachloride–benzene	0.5882	0.6227	0.12	0.16	0.0450	0.12	0.25
n-Hexadecane–*n*-tetradecane	3.4358	3.1602	0.51	1.21	0.0013	0.69	1.35

[a] Equation 8 of text. [b] Equation 7 of text. [c] Defined in Table III.

Table V. Errors in Fitting Mixture Viscosities by Equations 9 and 10

Constants are based on component ν value of present work, Table I. Component 1 is first-named of pair.

						Errors, % as ν	
	A	*B*	*C*	*D*	*E*	Std.[a]	Max.
	Equation 9, Mole Fraction Constants						
n-Hexadecane–*n*-hexane	−2.0791	−0.2170	0.1340	0.2822		0.22	0.50
n-Hexadecane–2-bromobutane	−1.6035	−0.1041	−0.0571	0.1916		0.23	0.43
n-Hexadecane–carbon tetrachloride	−0.6685	0.3665				0.11	0.22
n-Hexadecane–benzene	−1.3004	0.0898	0.0718	0.1888		0.09	0.16
4-Methylcyclohexanone–*n*-hexadecane	−0.3029	0.4033	−0.4788			0.17	0.45
n-Tetradecane–*n*-hexane	−1.1675	−0.1419	−0.0580			0.42	0.96
n-Tetradecane–2-bromobutane	−0.8472	0.0031	−0.0585			0.07	0.16
4-Methylcyclohexanone–*n*-tetradecane	−0.2760	0.0972	−0.2420			0.08	0.14
2-Bromobutane–*n*-hexane	−0.1221	0.0073	−0.0139			0.07	0.12
Carbon tetrachloride–*n*-hexane	−0.3155	−0.1044	−0.0804			0.13	0.24
Benzene–*n*-hexane	−0.3616	−0.1895	−0.1221			0.18	0.31
4-Methylcyclohexanone–*n*-hexane	−1.3597	−0.5693	−0.3192	−0.1383		0.10	0.23
Carbon tetrachloride–benzene	−0.1203	0.0432	−0.0304			0.09	0.14
n-Hexadecane–*n*-tetradecane	−0.2421	−0.0358	0.2277	−0.5359	−0.9991	0.23	0.64
	Equation 10, Mole Fraction Constants						
n-Hexadecane–*n*-hexane	1.3864	−0.4399	0.1972			0.22	0.55
n-Hexadecane–2-bromobutane	1.3451	−0.5433	0.1703			0.27	0.66
n-Hexadecane–carbon tetrachloride	1.4135	−0.5079	0.2864			0.16	0.26
n-Hexadecane–benzene	1.3113	−0.3486	0.0830			0.20	0.34
4-Methylcyclohexanone–*n*-hexadecane	0.4545	0.2287	−0.1159			0.21	0.52
n-Tetradecane–*n*-hexane	0.9763	−0.2983	0.0448			0.41	0.95
n-Tetradecane–2-bromobutane	0.9512	−0.3147	0.0798			0.07	0.14
4-Methylcyclohexanone–*n*-tetradecane	0.1314	0.0546	−0.1013			0.08	0.17
2-Bromobutane–*n*-hexane	−0.1765	−0.0010				0.09	0.23
Carbon tetrachloride–*n*-hexane	−0.4810	−0.1780	−0.0891			0.08	0.16
Benzene–*n*-hexane	−0.5961	−0.2270	−0.1198			0.12	0.20
4-Methylcyclohexanone–*n*-hexane	−0.5593	−0.0542	−0.1066			0.07	0.12
Carbon tetrachloride–benzene	0.0450	0.0016				0.12	0.24
n-Hexadecane–*n*-tetradecane	0.0136	−0.0067	−0.0838	−0.1588		0.29	0.82

[a] Defined in Table III.

(*10*) have shown that this approach, while qualitatively useful, will not necessarily lead to agreement with actual values. While this question is not pursued here, it is readily possible to discern from present results some systematic behavior in these systems.

Consider the mixtures of benzene, carbon tetrachloride, 2-bromobutane, and 4-methylcyclohexanone with each of the normal alkanes, hexane and hexadecane. With the longer (larger) of these latter two components ΔV^E is continually more positive than with the shorter (smaller). The effect is most pronounced with 4-methylcyclohexanone, where it is sufficient to give a positive ΔV^E with hexadecane (and also with tetradecane), whereas with hexane ΔV^E is negative. This difference in sign must reflect the superposition of the size effect upon another which causes contraction. The contraction may arise from disruption by the mixing process of an expanded dipole-dipole structure in pure 4-methylcyclohexanone.

In the *r*-meric systems hexane-hexadecane and hexane-tetradecane the negative ΔV^E agrees with the usual behavior of normal alkane mixtures as noted by Desmyter and van der Waals (*11*) in their investigation of the congruence principle of Brønsted and Koefoed (*5*).

On that basis the system tetradecane-hexadecane should also show continually negative ΔV^E values, but, instead, exhibits negative values only in tetradecane-rich mixtures, and in hexadecane-rich mixtures becomes positive. The maximum ΔV^E values in this system are not large, about 0.15 ml. per mole, but the effect appears to be clearly established. Thus, both viscosities and refractive indices show an inversion of sign when considered relative to the ideal values of these properties. Extra determinations of density were made (Table II) to confirm this alternation in sign of ΔV^E, as the negative ΔV^E appear to be only slightly greater than the uncertainty in the measurements. Apparently this inversion can not be accounted for on the basis of minor impurities which may be present. Gas chromatograms of these two purified components showed but a single elution curve in each instance, without any discernable formation of shoulders owing to overlapping of impurity peaks.

The behavior in this system may be related to that in ethanol-acetonitrile mixtures (*35*), where a similar inversion in the sign of the excess volumes occurred. There the behavior, with a maximum excess volume of about 0.05 ml. per mole, was ascribed to configurational effects in the mixtures of the two polar species. While the present system is nonpolar, the temperature is near the melting points of the components. For long linear molecules a tendency for some order ("stacked logs") is a common assumption. The result of mixing the two different hydrocarbons may then be compared with that of the ethanol-acetonitrile system. In the former the maximum excess volume is three times that of the latter, and this relationship is approximately the same as the ratio of molar volumes of mixtures in the two systems. The relative excess volumes are thus about the same in these two systems.

Nine of the present systems show positive Δ^*G^E at all compositions (Figure 2); that is, a viscosity greater than the ideal value. Eight of these systems are composed of either tetradecane or hexadecane with a second component that is a relatively smaller molecule, and the last is carbon tetrachloride–benzene. Δ^*G^E is smaller in this last system than in the other eight. Four systems show a consistently negative Δ^*G^E; they are of hexane plus a second molecule of comparable size. The remaining system is tetradecane-hexadecane, with a sign inversion in Δ^*G^E.

For systems of hexadecane with 2-bromobutane, carbon tetrachloride, benzene, and hexane there is considerable similarity in the curves of Δ^*G^E *vs.* mole fraction. The maxima for all four of these binary systems fall between 0.4 and 0.45 mole fraction hexadecane, with a narrow range of Δ^*G^E values between 195 and 210 cal. per mole. For the hexadecane–4-methylcyclohexanone system, however, Δ^*G^E is about 130 cal. per mole less. This may be explained as the resultant of two competing effects, with the first dominant: mixing of the components causes positive Δ^*G^E; breaking of the more ordered structure of the 4-methylcyclohexanone causes negative Δ^*G^E. In contrast, in the hexane–4-methylcyclohexanone system the second effect must be dominant to account for the over-all negative sign of Δ^*G^E. This occurs even with the negative ΔV^E resulting from the collapse of order in the mixtures. That is, the increased disorder in breaking of the ordered structure is more important than the loss in free volume in the effect on viscosity.

Correlation between free volume and viscosity has frequently been noted in the literature—for example, Batschinsky (*2*). By that correlation, positive ΔV^E should decrease viscosity below the ideal value and negative ΔV^E should have the opposite effect. On this basis only five of the present systems could be classified as showing "normal" behavior: hexane–2-bromobutane, hexane–carbon tetrachloride, hexane-benzene, hexane-tetradecane, and hexane-hexadecane. The tetradecane-hexadecane system is marginal in that, although grossly ΔV^E and Δ^*G^E are properly related in sign on the basis of the free volume model, the functions do not appear to have sign inversions at the same mixture composition. The most striking contrast is among those four systems containing hexadecane with the Δ^*G^E near 200 cal. per mole. In these systems the maximum ΔV^E varies from more than a positive 1 ml. per mole for hexadecane-benzene to more than a negative 0.5 ml. per mole for hexadecane-hexane. Clearly the viscosity behavior in these systems cannot be explained solely on the basis of free volume effects. Reed and Taylor (*32*) have considered the major additional factor to be the excess molar entropy of activation of flow, Δ^*S^E.

The behavior of Δ^*G^E in systems of tetradecane with hexane, 2-bromobutane, and 4-methylcyclohexanone is clearly similar to the behavior of hexadecane with these same components. The effect of size reduction in passing from hexadecane to tetradecane in the present systems is seen to be about 50 to 60 cal. per mole at the Δ^*G^E maxima.

The absence of a pronounced difference in molecular size in the mixtures of hexane with carbon tetrachloride, benzene, and 2-bromobutane results in less difference between Δ^*G^E for these systems and for hexane–4-methylcyclohexanone than when hexadecane is mixed with these same second components. Moreover, in these four systems with hexane Δ^*G^E is negative in all instances.

Of the equations considered in Table III, that of Bingham (Equation 4) has been most considered in the literature. Apparently, however, Table III shows that the Bingham equation is not well suited to the present systems. It generally predicts viscosity lower than the experimental value, especially for mixtures of components of dissimilar kinematic viscosities. The ratio of kinematic viscosities of each component pair is given in the last column of Table III. With little irregularity there appears to be a well-defined correlation between the efficacy of the Bingham equation and these viscosity ratios. The correlation is poorer in terms of the ratios of molar volumes of the components and poorer still in terms of presence or absence of polarity in the components, magnitude or sign of ΔV^E, or sign of ΔV^E relative to sign of Δ^*G^E. Treatment of the fluidities as additive in volume fraction, as proposed by Bingham (*4*), rather than mole fraction, decreases the error but not enough to render the equation very useful. For example, the error in the hexadecane-hexane system is decreased from 50 to about 25%.

The other three equations in Table III are comparable in efficacy to the Bingham equation. The ideal viscosity equation, Equation 3, is naturally best correlated with Δ^*G^E behavior. It is not surprising that the error in using the Bingham equation is also well correlated with Δ^*G^E.

The regular viscosity equation of Katti and Chaudhri (*23*), Equation 7, is seen from Table IV to reduce the error significantly below that of the ideal equation of Table III. For the former, the standard errors in the various systems range from 0.1 to 3.9%, compared with 0.7 to 25.1% for the latter. Only in the tetradecane-hexadecane system, where it is obviously not possible to fit both the positive and negative Δ^*G^E values effectively with a single interaction parameter, does the regular solution equation fail to improve the fit of the data over the results of the ideal equation.

In most of the systems, Equation 8, the two-constant three-body equation of McAllister (*26*) gives results notably better than those by Equation 7. With the former, the standard errors range from 0.1 to 0.7%. McAllister suggested that the effectiveness of the three-body model is related to the relative molecular sizes of the two mixture components. He noted that beyond a $(V_1/V_2)^{1/3}$ value of about 1.5, interaction involving more than three bodies might be more appropriate. He applied a four-body equation to the system water-acetone (*26*) and found that it reduced the error of the three-body model of that system by about two-thirds.

It has not been considered worthwhile to test McAllister's four-body equation here because of the inconsistent relationship between the molecular size ratios and the errors in applying the three-body equation. This inconsistency may arise from several factors which are of equal or greater significance than size difference, such as molecular shape, the modes of molecular energy, and the mechanism of flow. Moore, Gibbs, and Eyring (*27*) have shown, in fact, that these last three are interrelated.

The relationships between the size ratio and the error in the three-body model in the present work may be illustrated by the following few representative examples:

System	$(V_1/V_2)^{1/3}$	Standard Error in Kinematic Viscosity, %
Tetradecane-hexadecane	1.04	0.51
Hexane–4-methylcyclohexanone	1.02	0.34
Tetradecane–2-bromobutane	1.34	0.23
Hexadecane-benzene	1.49	0.28

Thus there is no apparent correlation between the error and the ratio of volumes of the components.

Except for the systems tetradecane-hexane, 2-bromobutane–hexane, carbon tetrachloride–benzene, in which the error is similar by either approach, the range of standard errors by Equation 10 is less than that by the three-body model. As Equation 10 allows more constants than the three-body model, the improvement is not unexpected. Adoption of Equation 10, however, involves the use of empirical correction terms beyond α_{12} of Equation 7 that are essentially without theoretical meaning. The approach of Equation 10, in fact, does not represent a great improvement in fitting the kinematic viscosities over the mathematically less complex Equation 9. Evidently, Table V shows that the number of terms required by the latter is only slightly more than those for Equation 10 in fitting the data to a like standard error.

In using Equation 9, the data are somewhat better represented when mole fraction is the concentration variable than when either weight or volume fraction is used, although the difference is not great. Accordingly, only the mole fraction form has been included in Table V.

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NOMENCLATURE

A,B,C,D,E = constants for fitting of data, Equations 9 and 10
Δ^*G = molar Gibbs free energy of activation of flow
M = molecular weight
N = Avogadro number
R = gas constant
Δ^*S = molar entropy of activation of flow
T = absolute temperature
V = molar volume
ΔV = molar volume of mixing
a = distance through which shearing force acts
f = concentration variable
h = Planck constant
p = physical property
x = mole fraction
α_{12} = constant, Equation 7
η = dynamic viscosity
λ = distance between adjacent moving layers of molecules
ν = kinematic viscosity—i.e., dynamic viscosity/density
ν_{12}, ν_{21} = constants, Equation 8
ϕ = fluidity

Subscripts

1 = component 1
2 = component 2

Superscripts

E = excess
i = ideal

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