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Kinematic Viscosity–Composition Data for Eight Binary Systems Containing Toluene or Ethylbenzene and C_8–C_{16} *n*-Alkanes at 308.15 and 313.15 K

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Kinematic viscosity–composition data for eight binary mixtures, viz., toluene–*n*-octane, toluene–*n*-decane, toluene–*n*-dodecane, toluene–*n*-tetradecane, toluene–*n*-hexadecane, ethylbenzene–*n*-octane, ethylbenzene–*n*-tetradecane, and ethylbenzene–*n*-hexadecane, have been determined at 308.15 and 313.15 K over the entire composition range and fitted with polynomial expressions, as well as with the McAllister three-body mode (*1*). In addition, pure component and mixture activation energies for viscous flow were correlated to the number of carbon atoms and composition, respectively.

Introduction

Present knowledge of liquid mixture behavior is not sufficiently developed to generally allow calculation of mixture viscometric properties from the pure component properties alone. Consequently, experimental data are needed to determine such properties and provide information about the structure and behavior of such systems.

In an earlier communication (*2*), the kinematic viscosities of the same systems studied in this work were reported at 293.15 and 298.15 K. The present work is part of a continuing program (*2–4*) aiming at providing such data for systems of nonassociating components with significant differences in shape and structure, i.e. toluene and ethylbenzene versus *n*-alkanes. To the best of our knowledge, similar data for the systems considered in this study have not been reported before.

Experimental Section

Materials. All reagents used were purchased from Aldrich Chemical Co. A chromatographic test of reagent purity, using a 5 m × 0.53 mm methyl silicone capillary column and a flame ionization detector (FID), produced the results shown in Table I.

Equipment. The main instruments used in this study were (i) a Mettler Model HK 160 electronic balance with a stated precision of 2×10^{-7} kg and (ii) a set of five Cannon-Ubbelohde viscometers with a stated precision of ±0.2%, comprising two viscometers of size 25 (range 0.5–2.0 cSt), two of size 50 (range 0.8–4.0 cSt), and one of size 75 (range 1.6–8.0 cSt). The viscometers were placed in a Model M1-18M constant-temperature bath supplied by Cannon Instruments Co. The bath temperature was controlled within ±0.01 K, with water as the bath medium, and measured by a calibrated thermometer (IPTS-68). An electronic stopwatch accurate within ±0.01 s was used for measuring efflux times.

Procedure. Solution compositions were determined gravimetrically. Special care was taken during solution preparation to avoid evaporation losses (*5*, *6*). Kinematic viscosities were obtained from the measured efflux time, *t*, and the equation

$$\nu = Ct - E/t^n \tag{1}$$

where *C* and *E* are calibration constants and $n = 2$ for the type of viscometers used in this work. The calibration constants *C* and *E* were determined by using calibration standards N.4 (0.4227 cSt at 308.15 K and 0.4062 cSt at 313.15 K), N.8 (0.6669 cSt at 308.15 K and 0.634 cSt at 313.15 K), N1.0 (1.079 cSt at 308.15 K and 1.013 cSt at 313.15 K), and S3 (3.038 cSt at 308.15 K and 2.719 cSt at 313.15 K).

Table I. Chromatographic Verification of Reagent Purity

compound	specification	GC analysis, mass %
n-octane	99+	99.7
n-decane	99+	99.8
n-dodecane	99+	99.9
n-tetradecane	99	99.8
n-hexadecane	99+	99.2
toluene	99+	99.9
ethylbenzene	99+	99.8

Results and Discussion

The pure component kinematic viscosities are shown in Table II. Available TRC Table (*7*) values are also shown for comparison. It follows from this table that experimental and literature values are in close agreement.

Table III shows the mixture experimental kinematic viscosities measured in this study. For each viscosity value, the corresponding efflux time was the average of three measurements with a reproducibility better than 0.1%. The maximum expected error is 2.73×10^{-10} m²/s. The experimental ν_m values were correlated by the polynomial expression

$$\nu_m = \sum_{i=0}^{n} A_i X_A^{\,i} \text{ (cSt)} \tag{2}$$

The degree of the correlating polynomial was chosen so as to minimize the standard deviation of the fit. The computed values of the adjustable parameters A_i and the corresponding standard deviations are given in Table IV. It follows from the standard deviations listed in this table that the correlating equation (2) fits the experimental data very well.

The McAllister three-body model (*1*), which is given by the following equation

$$\ln \nu_m = X_A^3 \ln \nu_A + 3X_A^2X_B \ln \nu_{AB} + 3X_AX_B^2 \ln \nu_{BA} + X_B^3 \ln \nu_B - \ln\left(X_A + X_B\frac{M_B}{M_A}\right) + 3X_A^2X_B \ln\left[\left(2 + \frac{M_B}{M_A}\right)\Big/3\right] + 3X_AX_B^2 \ln\left[\left(1 + 2\frac{M_B}{M_A}\right)\Big/3\right] + X_B^3 \ln\left(\frac{M_B}{M_A}\right) \tag{3}$$

was used to fit the experimental kinematic viscosity–compo-

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Table II. Comparison of Pure Component Experimental and Reported Kinematic Viscosities

	308.15 K		313.15 K	
compound	exptl value × 10^6, m^2/s	lit. value (7) × 10^6, m^2/s	exptl value × 10^6, m^2/s	lit. value (7) × 10^6, m^2/s
n-octane	0.6580	0.6649	0.6261	0.6353
n-decane	1.0293	1.039	0.9652	0.9770
n-dodecane	1.5556	1.575	1.4462	1.4650
n-tetradecane	2.2732	2.305	2.0900	2.1180
n-hexadecane	3.2199	3.252	2.9292	2.9530
toluene	0.5783	0.5741	0.5508	0.5463
ethylbenzene	0.6565	0.6614	0.6242	0.6286

Table III. Experimental Kinematic Viscosities for Binary Mixtures of Toluene and Ethylbenzene with *n*-Alkanes at 308.15 and 313.15 K

308.15 K			313.15 K			308.15 K			313.15 K		
ω_A	X_A	$\nu_m \times 10^6$, m^2/s	ω_A	X_A	$\nu_m \times 10^6$, m^2/s	ω_A	X_A	$\nu_m \times 10^6$, m^2/s	ω_A	X_A	$\nu_m \times 10^6$, m^2/s
Toluene–*n*-Octane											
0.0000	0.0000	0.6580	0.0000	0.0000	0.6261	0.4421	0.4956	0.5849	0.4407	0.4942	0.5581
0.0358	0.0440	0.6503	0.0421	0.0517	0.6178	0.5478	0.6003	0.5759	0.5413	0.5939	0.5495
0.0849	0.1032	0.6389	0.0854	0.1038	0.6093	0.6502	0.6974	0.5699	0.6473	0.6947	0.5439
0.1685	0.2008	0.6229	0.1666	0.1986	0.5949	0.7655	0.8019	0.5673	0.7637	0.8003	0.5409
0.2515	0.2940	0.6082	0.2559	0.2989	0.5805	0.8764	0.8979	0.5697	0.8760	0.8976	0.5427
0.3481	0.3983	0.5952	0.3519	0.4023	0.5681	1.0000	1.0000	0.5783	1.0000	1.0000	0.5508
Toluene–*n*-Decane											
0.0000	0.0000	1.0293	0.0000	0.0000	0.9652	0.3894	0.4962	0.7637	0.3880	0.4947	0.7258
0.0326	0.0495	1.0009	0.0284	0.0432	0.9434	0.4890	0.5965	0.7188	0.4856	0.5931	0.6834
0.0647	0.0966	0.9758	0.0677	0.1008	0.9127	0.5996	0.6981	0.6766	0.5971	0.6959	0.6434
0.1366	0.1964	0.9189	0.1409	0.2021	0.8609	0.7199	0.7988	0.6386	0.7226	0.8009	0.6065
0.2155	0.2979	0.8652	0.2167	0.2993	0.8150	0.8506	0.8979	0.6055	0.8483	0.8962	0.5750
0.2954	0.3929	0.8182	0.2959	0.3936	0.7706	1.0000	1.0000	0.5783	1.0000	1.0000	0.5508
Toluene–*n*-Dodecane											
0.0000	0.0000	1.5556	0.0000	0.0000	1.4462	0.3497	0.4986	0.9949	0.3606	0.5104	0.9239
0.0292	0.0527	1.4889	0.0282	0.0508	1.3892	0.4422	0.5944	0.9031	0.4467	0.5988	0.8489
0.0564	0.0996	1.4313	0.0522	0.0924	1.3435	0.5544	0.6969	0.8094	0.5597	0.7015	0.7633
0.1224	0.2049	1.3063	0.1213	0.2033	1.2239	0.6811	0.7979	0.7243	0.6838	0.7999	0.6876
0.1819	0.2913	1.2098	0.1884	0.3003	1.1242	0.8266	0.8981	0.6478	0.8279	0.8989	0.6151
0.2667	0.4021	1.0916	0.2702	0.4063	1.0207	1.0000	1.0000	0.5783	1.0000	1.0000	0.5508
Toluene–*n*-Tetradecane											
0.0000	0.0000	2.2732	0.0000	0.0000	2.0900	0.3150	0.4975	1.2890	0.3132	0.4954	1.2094
0.0245	0.0513	2.1604	0.0240	0.0503	1.9874	0.4079	0.5973	1.1241	0.4008	0.5902	1.0651
0.0486	0.0991	2.0573	0.0479	0.0977	1.8893	0.5180	0.6983	0.9703	0.5092	0.6908	0.9233
0.1027	0.1977	1.8496	0.0957	0.1856	1.7329	0.6448	0.7963	0.8387	0.6566	0.8046	0.7746
0.1638	0.2967	1.6531	0.1627	0.2960	1.5413	0.8052	0.8989	0.6967	0.8029	0.8977	0.6628
0.2266	0.3868	1.4842	0.2284	0.3892	1.3798	1.0000	1.0000	0.5783	1.0000	1.0000	0.5508
Toluene–*n*-Hexadecane											
0.0000	0.0000	3.2199	0.0000	0.0000	2.9292	0.2918	0.5031	1.6401	0.2879	0.4984	1.5361
0.0151	0.0363	3.0920	0.0224	0.0533	2.7556	0.3754	0.5963	1.4038	0.3786	0.5995	1.3125
0.0427	0.0987	2.8747	0.0415	0.0961	2.6168	0.4904	0.7028	1.1529	0.4865	0.6995	1.0903
0.0984	0.2114	2.4990	0.0986	0.2119	2.3072	0.6149	0.7969	0.9524	0.6116	0.7946	0.9037
0.1532	0.3078	2.1988	0.1455	0.2950	2.0638	0.7813	0.8978	0.7543	0.7856	0.9000	0.7117
0.2128	0.3992	1.9281	0.2103	0.3956	1.7957	1.0000	1.0000	0.5783	1.0000	1.0000	0.5508
Ethylbenzene–*n*-Octane											
0.0000	0.0000	0.6580	0.0000	0.0000	0.6261	0.4718	0.4900	0.6229	0.4719	0.4902	0.5942
0.0480	0.0515	0.6519	0.0449	0.0482	0.6215	0.5742	0.5919	0.6219	0.5788	0.5966	0.5942
0.0908	0.0971	0.6471	0.0913	0.0976	0.6157	0.6861	0.7016	0.6248	0.6798	0.6955	0.5959
0.1757	0.1865	0.6384	0.1858	0.1971	0.6071	0.7859	0.7980	0.6308	0.7846	0.7967	0.6012
0.2819	0.2969	0.6304	0.2799	0.2949	0.6013	0.8918	0.8987	0.6412	0.8895	0.8965	0.6101
0.3809	0.3983	0.6252	0.3800	0.3974	0.5959	1.0000	1.0000	0.6565	1.0000	1.0000	0.6242
Ethylbenzene–*n*-Tetradecane											
0.0000	0.0000	2.2732	0.0000	0.0000	2.0900	0.3463	0.4975	1.3163	0.3451	0.4961	1.2363
0.0290	0.0529	2.1682	0.0279	0.0509	1.9865	0.4264	0.5814	1.1882	0.4369	0.5918	1.1061
0.0567	0.1010	2.0534	0.0516	0.0923	1.9071	0.5527	0.6978	1.0225	0.5558	0.7004	0.9587
0.1178	0.1997	1.8477	0.1174	0.1991	1.7104	0.6827	0.8008	0.8887	0.6782	0.7975	0.8417
0.1829	0.2950	1.6667	0.1889	0.3032	1.5370	0.8240	0.8974	0.7695	0.8276	0.8997	0.7277
0.2573	0.3929	1.4884	0.2633	0.4005	1.3808	1.0000	1.0000	0.6565	1.0000	1.0000	0.6242
Ethylbenzene–*n*-Hexadecane											
0.0000	0.0000	3.2199	0.0000	0.0000	2.9292	0.3188	0.4995	1.6669	0.3176	0.4981	1.5558
0.0243	0.0505	3.0354	0.0242	0.0502	2.7614	0.4097	0.5968	1.4361	0.4115	0.5986	1.3356
0.0449	0.0912	2.8926	0.0488	0.0987	2.6053	0.5217	0.6994	1.2063	0.5218	0.6995	1.1322
0.0998	0.1912	2.5562	0.1039	0.1983	2.3217	0.6509	0.7991	1.0069	0.6558	0.8025	0.9433
0.1671	0.2997	2.2164	0.1695	0.3033	2.0145	0.8061	0.8987	0.8053	0.8059	0.8986	0.7807
0.2401	0.4026	1.9241	0.2333	0.3935	1.8077	1.0000	1.0000	0.6565	1.0000	1.0000	0.6242

Table IV. Least-Squares Constants for Equation 2

system	A_0	A_1	A_2	A_3	A_4	std dev, m^2/s
308.15 K						
toluene–*n*-octane	0.6900	0.1015	0.0136	0.0642	−0.0177	1.29×10^{-4}
toluene–*n*-decane	0.71797	0.0568	0.0720	−0.0448	0.0497	1.31×10^{-4}
toluene–*n*-dodecane	0.7376	0.0512	0.0283	−0.0042	0.0389	7.83×10^{-5}
toluene–*n*-tetradecane	0.7528	0.0301	0.0659	−0.0774	0.0803	9.35×10^{-5}
toluene–*n*-hexadecane	0.7636	0.0258	0.0258	−0.01899	0.0556	1.05×10^{-4}
ethylbenzene–*n*-octane	0.6901	0.1166	0.0379	−0.0004	0.0092	4.97×10^{-5}
ethylbenzene–*n*-tetradecane	0.7528	0.0293	0.0793	−0.0784	0.0702	1.41×10^{-4}
ethylbenzene–*n*-hexadecane	0.7635	0.0143	0.1175	−0.15996	0.1178	2.43×10^{-4}
313.15 K						
toluene–*n*-octane	0.6861	0.0927	0.0790	−0.0549	0.0453	1.69×10^{-4}
toluene–*n*-decane	0.7152	0.0775	−0.0015	0.0569		1.90×10^{-4}
toluene–*n*-dodecane	0.7337	0.0602	−0.0265	0.0801		6.38×10^{-4}
toluene–*n*-tetradecane	0.7491	0.0366	0.0419	−0.0515	0.0719	2.41×10^{-4}
toluene–*n*-hexadecane	0.7610	0.0212	0.0666	−0.0939	0.0932	1.49×10^{-4}
ethylbenzene–*n*-octane	0.6863	0.11296	0.0561	−0.0346	0.0286	1.33×10^{-4}
ethylbenzene–*n*-tetradecane	0.7483	0.0542	−0.0241	0.0704		5.56×10^{-4}
ethylbenzene–*n*-hexadecane	0.76097	0.0201	0.0892	−0.1187	0.09795	1.25×10^{-4}

Table V. Values of the McAllister Three-Body Model Parameters

system	$\nu_{AB} \times 10^6$, m^2/s	$\nu_{BA} \times 10^6$, m^2/s	std dev, m^2/s
308.15 K			
toluene (A)–*n*-octane (B)	0.5477	0.6019	7.51×10^{-10}
toluene (A)–*n*-decane (B)	0.6789	0.8683	1.21×10^{-9}
toluene (A)–*n*-dodecane (B)	0.8789	1.2011	1.26×10^{-9}
toluene (A)–*n*-tetradecane (B)	1.1309	1.6471	3.12×10^{-9}
toluene (A)–*n*-hexadecane (B)	1.5158	2.2366	5.61×10^{-9}
ethylbenzene (A)–*n*-octane (B)	0.6016	0.6205	3.29×10^{-10}
ethylbenzene (A)–*n*-tetradecane (B)	1.1470	1.6497	4.82×10^{-9}
ethylbenzene (A)–*n*-hexadecane (B)	1.4699	2.2120	5.75×10^{-9}
313.15 K			
toluene (A)–*n*-octane (B)	0.5215	0.5773	5.48×10^{-10}
toluene (A)–*n*-decane (B)	0.64705	0.8168	1.39×10^{-9}
toluene (A)–*n*-dodecane (B)	0.8314	1.1272	8.44×10^{-9}
toluene (A)–*n*-tetradecane (B)	1.0860	1.5314	2.49×10^{-9}
toluene (A)–*n*-hexadecane (B)	1.4426	2.0420	4.91×10^{-9}
ethylbenzene (A)–*n*-octane (B)	0.5758	0.5913	4.99×10^{-10}
ethylbenzene (A)–*n*-tetradecane (B)	1.0915	1.5258	1.49×10^{-9}
ethylbenzene (A)–*n*-hexadecane (B)	1.3964	2.0247	3.61×10^{-9}

sition data. The values of the adjustable parameters ν_{AB} and ν_{BA}, included in eq 3, were determined by the least-squares method for the systems investigated here at each temperature level. The values of ν_{AB} and ν_{BA} are reported in Table V. The standard deviation of the fit indicates that the model given by eq 3 fits the experimental data very well.

Figures 1 and 2 show the experimental viscosity data for 313.15 K plotted versus mixture composition. It follows from these figures that the mixture kinematic viscosities vary monotonically with composition. For the systems toluene–*n*-octane (Figure 1) and ethylbenzene–*n*-octane (Figure 2), the viscosity–composition relationship is virtually linear. However, as the chain length of the *n*-alkane component increases, the corresponding viscosity–composition curves display progressively larger curvatures. The same qualitative viscosity–composition behavior was also observed at 308.15 K, as well as at 293.15 and 298.15 K, as reported earlier (*2*). Thus at all four temperatures studied, the systems containing *n*-octane displayed a nearly linear viscosity–composition relationship, whereas the remaining systems displayed deviations from linearity that increased with increasing chain length of the *n*-alkane component. At all four temperatures studied, temperature had no appreciable effect on the curvature of the individual viscosity–composition curves.

The viscosity–composition data of this study, as well as those reported earlier (*2*), were also used to calculate the activation energy for viscous flow for pure components, as well as for mixtures from Arrhenius-type plots. The pure *n*-alkane activation energies obtained in this manner are shown plotted versus the number of carbon atoms in Figure 3. As it can be seen from this figure, a nearly perfect straight-line relationship exists. The calculated mixture activation energies for the systems toluene–*n*-decane, toluene–*n*-dodecane, and toluene–*n*-tetradecane are shown plotted versus composition in Figure 4. The remaining systems exhibited behavior similar to those shown in Figure 4; however, they were not shown to avoid cluttering the diagram. It follows from this figure that the mixture activation energies do not vary linearly with composition.

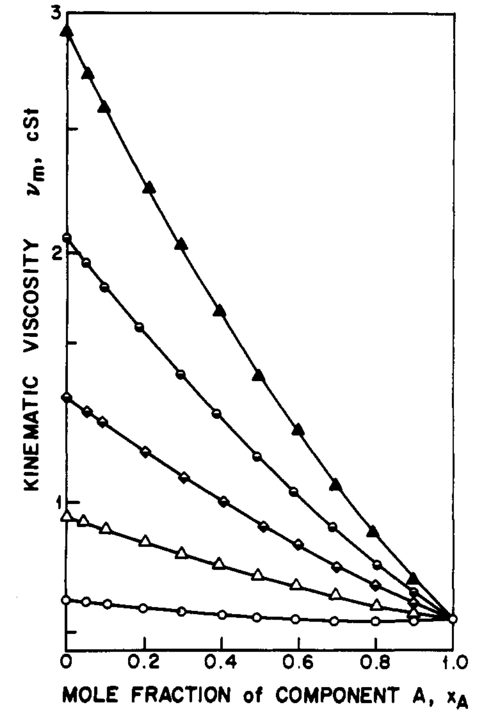

Figure 1. Variation of kinematic viscosity with composition for systems containing toluene at 313.15 K. Key: ○, toluene–*n*-octane; △, toluene–*n*-decane; ◆, toluene–*n*-dodecane; ⊖, toluene–*n*-tetradecane; ▲, toluene–*n*-hexadecane.

Conclusions

Kinematic viscosities for eight binary systems were determined at 308.15 and 313.15 K with a maximum estimated error of 2.73×10^{-10} m^2/s.

The experimental values were correlated by polynomial expressions that fitted the data well. Viscosity changed mono-

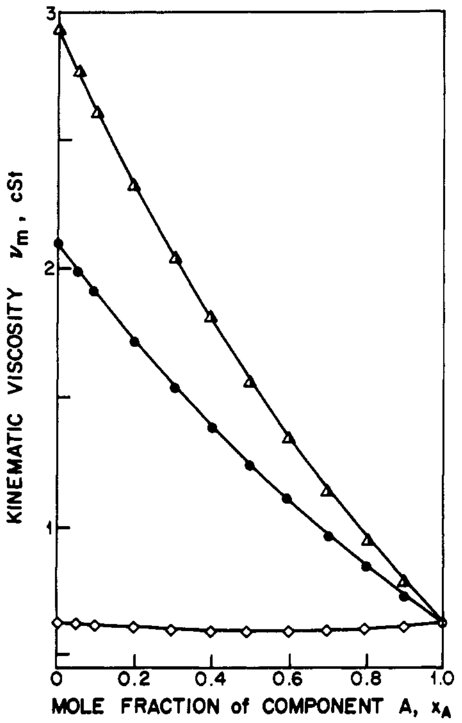

Figure 2. Variation of kinematic viscosity with composition for systems containing ethylbenzene at 313.15 K. Key: ◇, ethylbenzene-*n*-octane; ●, ethylbenzene-*n*-tetradecane; Δ, ethylbenzene-*n*-hexadecane.

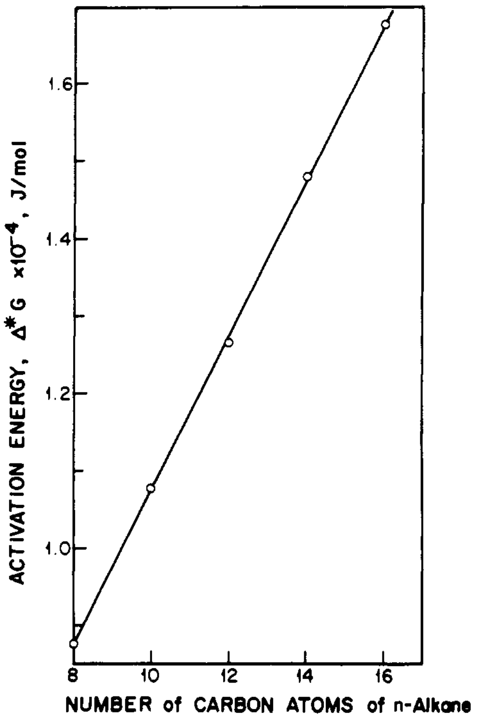

Figure 3. Variation of activation energy of viscous flow of *n*-alkanes with number of carbon atoms.

tonically with composition for all systems studied. Individual viscosity-composition curves were nearly linear for the systems containing *n*-octane and displayed mild, but progressively larger, curvatures as the chain length of the *n*-alkane component increased. The McAllister three-body model also fitted the data very well.

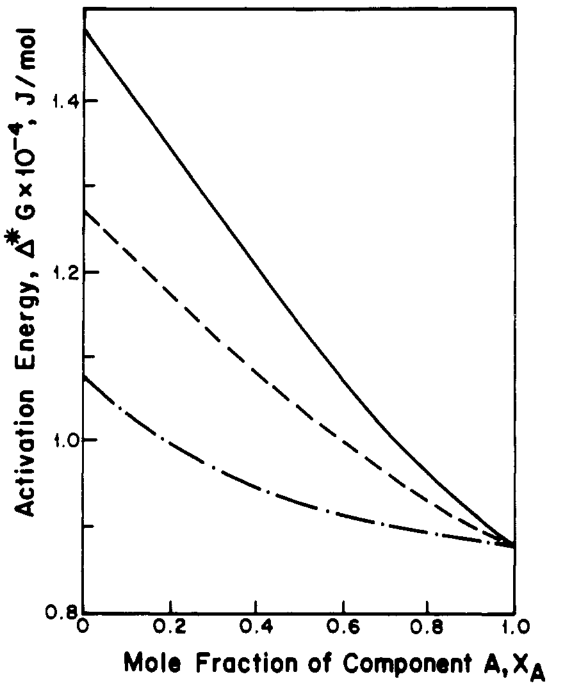

Figure 4. Variation of activation energy of viscous flow of some of the mixtures employed in this study with composition. Key: —•—, toluene-*n*-decane; - -, toluene-*n*-dodecane, —, toluene-*n*-tetradecane.

Calculated pure *n*-alkane activation energies for viscous flow displayed a linear dependence on the number of carbon atoms in the chain. Mixture activation energies displayed a nonlinear dependence on composition.

Nomenclature

A	adjustable paramter
C	calibration constant
E	calibration constant
X	mole fraction
Δ^*G	activation energy for viscous flow
ν	kinematic viscosity
ω	mass fraction

Subscripts

A	first-named component in a binary mixture
m	mixture

Registry No. *n*-Octane, 111-65-9; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3; toluene, 108-88-3; ethylbenzene, 100-41-4.

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