Viscosities of Eight Binary Liquid *n*-Alkane Systems at 293.15 K and 298.15 K

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The kinematic viscosities of the following eight *n*-alkane binary liquid systems were measured over the entire composition range at 293.15 K and 298.15 K and at atmospheric pressure: octane + undecane, octane + tridecane, octane + pentadecane, decane + pentadecane, undecane + pentadecane, tridecane + pentadecane, decane + tridecane, and undecane + tridecane. The data have been correlated by Heric's model (1967), as well as with the McAllister three-body interaction model (1960).

Introduction

Experimental data of *n*-alkane binary liquid systems are relatively scarce in the literature. Data on such systems are needed for their own value as well as for the testing of the various models which are used to predict the viscometric properties of such systems.

The present work is part of an on-going program in our laboratory aimed at providing reliable viscometric data. To the best of our knowledge, the data reported in this study have not been published before.

Experimental Section

Materials. All five reagents used in this study were purchased from Aldrich Chemical Company. These were octane, decane, undecane, tridecane, and pentadecane. Their stated purity was 99+ mol %, except for undecane, which was 99 mol % pure. 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 1.

Equipment. The instruments used in this study were as follows: (i) an electronic Mettler HK 160 balance with a reproducibility of $\pm 2 \times 10^{-7}$ kg and (ii) a set of five Cannon-Ubbelohde viscometers with a stated precision of ±0.2%, comprising two viscometers of size 25 A (range 0.5−2.0 cSt), two of size 50 B (range 0.8−4 cSt), and one of size 75 J (range 1.6−8.0 cSt).

Procedure. Solutions were prepared gravimetically. To prevent evaporation losses, the solutions were prepared according to the procedure described by Asfour (1980), which can be summarized as follows: The solutions were composed in glass vials fitted with Teflon disks and sealed with aluminum seals. Because of the chemical resistance of Teflon, the disks were used with the Teflon side facing the solution. The other side of the disks is made of sealing silicon rubber, which ensures that punctures made by the glass syringes, which were used to withdraw samples from the vials, were properly sealed.

Kinematic viscosities were obtained from the measured efflux time t and the following equation where C and E are calibration constants and $n = 2$ for the type of viscometers used in this study:

$$\nu = Ct - E/t^n \qquad (1)$$

The calibration constants C and E were determined by using calibration standards purchased from Cannon Instrument Company. The range of the standards covers the viscosity range of interest. The temperature control of the viscosity measurement was achieved with a model M1-18M constant temperature bath also purchased from Cannon Instrument Company. The bath temperature was controlled within ±0.01 K by using water as a bath medium. The bath temperature was measured by a calibrated mercury-in-glass thermometer graduated to 0.01 °C. An electronic stopwatch accurate within ±0.01 s was used for measuring efflux times.

Table 1. Chromatographic Verification of Reagent Purity

compound	specification	GC analysis, mass %
octane	99+	99.7
decane	99+	99.8
undecane	99	99.9
tridecane	99+	99.5
pentadecane	99+	99.9

Table 2. Comparison of Pure Component Experimental and Reported Kinematic Viscosities at 293.15 and 298.15 K

	$10^6\nu$, m^2 s^{-1}			
	T = 293.15 K		T = 298.15 K	
compound	exptl	lit.[a]	exptl	lit.[a]
octane	0.7734	0.7758	0.7309	0.7352
decane	1.258	1.268	1.172	1.182
undecane	1.587	1.601	1.468	1.483
tridecane	2.464	2.486	2.243	2.266
pentadecane	3.668	3.726	3.314	3.347

[a] *TRC Tables*, 1988.

Results and Discussion

The kinematic viscosity data for the pure components employed in this study were compared with corresponding

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Table 3. Experimental Viscosity−Composition Data for Binary Mixtures of *n*-Alkanes at 293.15 and 298.15 K

T = 293.15 K			T = 298.15 K			T = 293.15 K			T = 298.15 K		
x_1	$10^6\nu$, m^2 s^{-1}	$10^3\eta$, Pa·s	x_1	$10^6\nu$, m^2 s^{-1}	$10^3\eta$, Pa·s	x_1	$10^6\nu$, m^2 s^{-1}	$10^3\eta$, Pa·s	x_1	$10^6\nu$, m^2 s^{-1}	$10^3\eta$, Pa·s
Octane (1) + Undecane (2)											
0.0000	1.587	1.174	0.0000	1.468	1.081	0.5964	1.055	0.7599	0.5959	0.9901	0.7093
0.1007	1.491	1.099	0.0992	1.380	1.012	0.6995	0.9777	0.7001	0.7154	0.9098	0.6474
0.2018	1.390	1.020	0.2059	1.289	0.9412	0.7954	0.9090	0.6472	0.8041	0.8511	0.6023
0.2995	1.304	0.953	0.2978	1.214	0.8829	0.8978	0.8387	0.5933	0.9011	0.7905	0.5559
0.4108	1.207	0.8779	0.3916	1.140	0.8255	1.0000	0.7737	0.5433	1.0000	0.7309	0.5105
0.5076	1.126	0.8145	0.5019	1.062	0.7644						
Octane (1) + Tridecane (2)											
0.0000	2.464	1.863	0.0000	2.243	1.688	0.6002	1.301	0.950	0.5956	1.219	0.8850
0.1023	2.228	1.637	0.1246	1.995	1.492	0.6949	1.16	0.8400	0.6970	1.085	0.7811
0.1966	2.028	1.519	0.1988	1.856	1.383	0.7976	1.018	0.7304	0.7898	0.9689	0.6921
0.3011	1.819	1.354	0.3028	1.673	1.239	0.9047	0.8829	0.6269	0.8988	0.8392	0.5929
0.3813	1.669	1.237	0.3936	1.523	1.122	1.0000	0.7734	0.5433	1.0000	0.7309	0.5105
0.4993	1.494	1.076	0.4971	1.362	0.9963						
Octane (1) + Pentadecane (2)											
0.0000	3.698	2.841	0.0000	3.314	2.534	0.6008	1.609	1.187	0.5978	1.497	1.1
0.1032	3.255	2.488	0.1114	2.907	2.211	0.7150	1.32	0.9631	0.7035	1.264	0.9185
0.2005	2.874	2.185	0.1978	2.613	1.978	0.7994	1.146	0.8279	0.8008	1.069	0.7686
0.2833	2.575	1.948	0.2962	2.304	1.732	0.8985	0.9507	0.6782	0.9026	0.8872	0.6291
0.3826	2.241	1.683	0.3951	2.016	1.506	1.0000	0.7734	0.5433	1.0000	0.7309	0.5104
0.5038	1.861	1.385	0.4927	1.754	1.300						
Decane (1) + Pentadecane (2)											
0.0000	3.698	2.841	0.0000	3.314	2.534	0.5780	2.091	1.567	0.6025	1.866	1.39
0.0958	3.387	2.593	0.0973	3.047	2.322	0.6958	1.823	1.357	0.7033	1.672	1.239
0.1989	3.079	2.348	0.1999	2.776	2.108	0.7980	1.622	1.201	0.8079	1.483	1.092
0.2947	2.806	2.131	0.2983	2.534	1.916	0.9126	1.407	1.033	0.9014	1.326	0.9696
0.3865	2.557	1.934	0.3925	2.315	1.743	1.0000	1.258	0.9183	1.0000	1.172	0.8505
0.4839	2.312	1.741	0.4933	2.091	1.567						
Undecane (1) + Pentadecane (2)											
0.0000	3.698	2.841	0.0000	3.314	2.534	0.6010	2.298	1.731	0.5973	2.105	1.578
0.1013	3.428	2.626	0.1026	3.083	2.351	0.7004	2.104	1.579	0.7022	1.936	1.445
0.2015	3.179	2.428	0.2004	2.871	2.183	0.8000	1.921	1.435	0.7975	1.775	1.320
0.3004	2.945	2.242	0.2994	2.667	2.021	0.8974	1.754	1.304	0.9019	1.61	1.192
0.4036	2.715	2.06	0.3983	2.47	1.866	1.0000	1.587	1.174	1.0000	1.468	1.081
0.5046	2.508	1.896	0.5079	2.266	1.705						
Tridecane (1) + Pentadecane (2)											
0.0000	3.698	2.841	0.0000	3.314	2.534	0.5972	2.920	2.223	0.5985	2.643	2.003
0.1030	3.556	2.728	0.1000	3.194	2.439	0.7003	2.804	2.131	0.7037	2.533	1.917
0.2020	3.418	2.618	0.2001	3.079	2.349	0.8019	2.685	2.038	0.8004	2.436	1.840
0.3023	3.291	2.517	0.2975	2.968	2.260	0.9018	2.572	1.948	0.8983	2.345	1.768
0.3967	3.166	2.418	0.3984	2.856	2.172	1.0000	2.464	1.863	1.0000	2.243	1.688
0.5078	3.030	2.310	0.5000	2.746	2.085						
Decane (1) + Tridecane (2)											
0.0000	2.464	1.863	0.0000	2.243	1.688	0.5974	1.681	1.247	0.5995	1.550	1.144
0.0987	2.321	1.75	0.0939	2.124	1.594	0.7015	1.563	1.155	0.7013	1.451	1.067
0.1990	2.182	1.64	0.1985	1.995	1.493	0.7973	1.46	1.075	0.8001	1.352	0.9901
0.2995	2.045	1.532	0.2931	1.884	1.405	0.9014	1.354	0.992	0.9011	1.259	0.9179
0.3997	1.918	1.433	0.3988	1.764	1.311	1.0000	1.258	0.918	1.0000	1.172	0.8505
0.4986	1.797	1.338	0.5031	1.65	1.222						
Undecane (1) + Tridecane (2)											
0.0000	2.464	1.863	0.0000	2.243	1.688	0.5897	1.918	1.433	0.5976	1.754	1.304
0.1389	2.326	1.754	0.1023	2.155	1.619	0.7108	1.818	1.355	0.7028	1.677	1.244
0.2035	2.264	1.705	0.2031	2.067	1.549	0.8027	1.740	1.294	0.8000	1.607	1.189
0.3044	2.170	1.632	0.2991	1.988	1.487	0.8980	1.666	1.236	0.9004	1.536	1.134
0.4076	2.076	1.558	0.3981	1.906	1.423	1.0000	1.587	1.174	1.0000	1.468	1.081
0.4924	2.001	1.498	0.4981	1.828	1.362						

values from the TRC data tables (1988). The experimental and literature data are reported in Table 2. It can easily be seen from this table that, our data are in close agreement with the literature data.

Table 3 reports the mixtures' experimental kinematic and absolute viscosities gathered in this study at 293.15 and 298.15 K and over the entire composition range. The density data were reported earlier by Wu and Asfour (1994). 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 less than $\pm 2.6 \times 10^{-9}$ m^2/s. The experimental ν_m values were correlated with Heric's model (1967)

$$\ln \nu_m = \sum_{i=1}^{n} x_i \ln \nu_i + \sum_{i=1}^{n} x_i \ln M_i - \ln \sum_{i=1}^{n} x_i M_i + \delta_{i...n} \quad (2)$$

where x_i is the mole fraction of component i in a binary mixture of components i and j, M is the molecular weight, and $\delta_{i...n}$ is defined by

$$\delta_{i...n} = \sum_{\substack{i=1 \\ i<j}}^{n} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \quad (3)$$

A, B, and C are adjustable parameters which can be determined from experimental data.

Table 4. Least-Squares Constants for Eq 3

system	A_{12}	$10^{-2}B_{12}$	$10^{-1}C_{12}$	% AAD	$10^{9}\sigma$, $m^2\ s^{-1}$
		$T = 293.15$ K			
octane (1) + undecane (2)	0.1360	0.1651	−0.8688	0.06	1.097
octane (1) + tridecane (2)	0.3717	5.149	0.5053	0.28	6.724
octane (1) + pentadecane (2)	0.6083	11.370		0.15	3.255
decane (1) + pentadecane (2)	0.2868	2.987	−0.3616	0.04	1.358
undecane (1) + pentadecane (2)	0.1883	1.971		0.04	1.729
tridecane (1) + pentadecane (2)	0.0386	0.9392		0.02	0.7080
decane (1) + tridecane (2)	0.1095	0.6974		0.02	0.4589
undecane (1) + tridecane (2)	0.0489	0.8272		0.02	0.4733
		$T = 298.15$ K			
octane (1) + undecane (2)	0.1416	1.979	0.2241	0.07	1.212
octane (1) + tridecane (2)	0.3484	6.766	0.3240	0.06	0.9927
octane (1) + pentadecane (2)	0.6256	12.980	0.1423	0.02	0.3296
decane (1) + pentadecane (2)	0.2290	4.128		0.01	0.3558
undecane (1) + pentadecane (2)	0.1816	0.3382		0.05	1.655
tridecane (1) + pentadecane (2)	0.0403	0.5603		0.02	0.8154
decane (1) + tridecane (2)	0.1146	1.471		0.03	0.8357
undecane (1) + tridecane (2)	0.0433	0.6200		0.02	0.6756

In selecting the number of constants for each system relative to eq 3, all orders of power expansion through the sixth were carefully examined . The order was selected for a system beyond which additional terms did not significantly improve the fit. Thus, the order of the fitting equations varies from one liquid mixture to another. The computed values of the adjustable parameters and the corresponding standard deviations are reported in Table 3. Furthermore, the calculated and the experimental kinematic viscosities were compared. The percent average absolute deviation (AAD) is defined by

$$\mathrm{AAD} = \frac{1}{n}\left[\sum_{i=1}^{n}\left|\frac{\nu_i^{\mathrm{calcd}} - \nu_i^{\mathrm{exptl}}}{\nu_i^{\mathrm{exptl}}}\right| \times 100\right] \qquad (4)$$

where n is the number of the experimental points. The values of AAD are also listed in Table 4. Examination of both the standard deviation σ and the AAD of the fit indicates that the model fits the experimental data very well.

The experimental kinematic viscosity−composition data were fitted to the McAllister three-body interaction model given by the following equation:

$$\ln \nu_m = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln\left(x_1 + x_2\frac{M_2}{M_1}\right) + 3x_1^2 x_2 \ln\left[\left(2 + \frac{M_2}{M_1}\right)/3\right] + 3x_1 x_2^2 \ln\left[\left(1 + 2\frac{M_2}{M_1}\right)/3\right] + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \qquad (5)$$

where ν_{12} and ν_{21} are adjustable parameters that can be evaluated from experimental data. Table 5 lists the values of the parameters ν_{12} and ν_{21} for the investigated systems.

The standard deviation of the fit indicates that the data are well represented by the model.

According to Tables 4 and 5, Heric's model is not superior to the three-body interaction McAllister model. The major shortcoming of Heric's model is that it requires a variable number of adjustable parameters whereas the McAllister three-body interaction model has only two adjustable parameters for binary liquid mixtures.

Plots of the experimental kinematic viscosity−composition data obtained at 298.15 K are shown in Figure 1. It is clear from the figure that binary mixture kinematic viscosities vary monotonically with composition. Furthermore, it is clear that the data for the systems undecane + tridecane and tridecane + pentadecane approach nearly ideal behavior. This was earlier confirmed by a plot of the

Table 5. Values of the McAllister Three-Body Model Parameters

system	$10^{6}\nu_{12}$, $m^2\ s^{-1}$	$10^{6}\nu_{21}$, $m^2\ s^{-1}$	% AAD	$10^{9}\sigma$, $m^2\ s^{-1}$
	$T = 293.15$ K			
octane (1) + undecane (2)	1.018	1.293	0.06	1.097
octane (1) + tridecane (2)	1.271	1.811	0.30	6.939
octane (1) + pentadecane (2)	1.588	2.495	0.18	3.510
decane (1) + pentadecane (2)	1.966	2.765	0.04	1.358
undecane (1) + pentadecane (2)	2.227	2.916	0.06	2.060
tridecane (1) + pentadecane (2)	2.86	3.254	0.02	0.7080
decane (1) + tridecane (2)	1.624	2.023	0.02	0.4589
undecane (1) + tridecane (2)	1.867	2.150	0.02	0.4733
	$T = 298.15$ K			
octane (1) + undecane (2)	0.9623	1.199	0.07	1.212
octane (1) + tridecane (2)	1.189	1.657	0.07	1.217
octane (1) + pentadecane (2)	1.45	2.274	0.06	1.203
decane (1) + pentadecane (2)	1.818	2.505	0.01	0.3559
undecane (1) + pentadecane (2)	2.048	2.629	0.06	1.614
tridecane (1) + pentadecane (2)	2.588	2.937	0.02	0.8154
decane (1) + tridecane (2)	1.507	1.854	0.03	0.8357
undecane (1) + tridecane (2)	1.714	1.966	0.02	0.6755

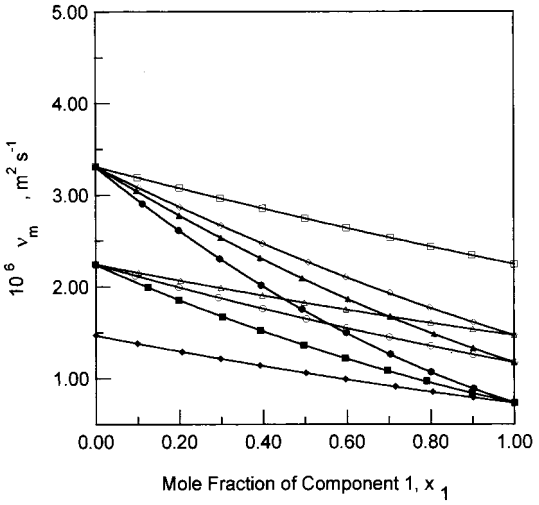

Figure 1. Change of the kinematic viscosity with concentration at 298.15 K: (◆) octane + undecane; (■) octane + tridecane; (●) octane + pentadecane; (▲) decane + pentadecane; (◇) undecane + pentadecane; (□) tridecane + pentadecane; (○) decane + tridecane; (△) undecane + tridecane.

excess volume composition diagram reported by Wu and Asfour (1994).

Conclusions

Kinematic viscosities for eight binary systems were determined at 293.15 and 298.15 K with a maximum estimated error less than $\pm 2.6 \times 10^{-9}$ m^2/s.

The experimental data were correlated by using Heric's model, which fitted the data well. The McAllister three-body interaction model was also employed to fit the data. It gave a superior fit to that from Heric's model.

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