Densities and Kinematic Viscosities of Some C_6–C_{16} *n*-Alkane Binary Liquid Systems at 293.15 K

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Densities and kinematic viscosities of 10 binary *n*-alkane liquid systems were determined over the entire composition range at 293.15 K. The systems investigated in this study include *n*-hexane–*n*-heptane, *n*-hexane–*n*-octane, *n*-hexane–*n*-decane, *n*-heptane–*n*-octane, *n*-heptane–*n*-decane, *n*-heptane–*n*-dodecane, *n*-heptane–*n*-tetradecane, *n*-octane–*n*-decane, *n*-octane–*n*-tetradecane, and *n*-tetradecane–*n*-hexadecane. The absolute viscosities were calculated from the density and kinematic viscosity data over the entire composition range for each system.

Introduction

The literature of composition dependence of densities and viscosities of *n*-alkane binary liquid systems is rather limited. Consequently, we initiated an ongoing program in our laboratory that aims at investigating the volumetric and viscometric properties of liquid mixtures with special emphasis on *n*-alkane systems at different temperatures. To the best of our knowledge, the data reported herein have never been published before.

Experimental Section

Procedure. The pure component densities and kinematic viscosities were measured first at the stated temperature. Next, binary mixtures over the entire composition range were prepared according to the procedure described earlier by Asfour (*1*) and their densities and kinematic viscosities were measured.

Preparation of Solutions. Solution compositions were determined gravimetrically. Special care was taken during solution preparation to avoid evaporation losses (*2*). A Mettler HK 160 electronic balance with a stated precision of 2×10^{-7} kg was employed.

Density and Viscosity Measurements. An Anton Paar precision density meter (Model DMA 60 with Model DMA 602 measuring cell) with a stated precision of 1.5×10^{-6} kg/L was used. The density meter is housed in a temperature-controlled chamber where temperature fluctuations were kept within ±0.1 K. Temperature fluctuations in the density meter were kept within ±0.01 K by using a Haake N4-B circulator with a calibrated platinum temperature sensor (IPTS-68). The density was determined by the three-parameter equation

$$\rho = AT^2/(1.0 - BT^2) - C_1 \qquad (1)$$

where ρ is the density and T is the period of oscillation. The best values of the parameters A, B, and C_1 were determined at 293.15 by using the following compounds, the densities (kg/L) of which were obtained from the literature: at 293.15 K, double-distilled and degassed water [ρ = 0.998 2343 (*3*)], carbon tetrachloride [ρ = 1.5940 (*4*)], benzene [ρ = 0.8790 (*5*)], and toluene [ρ = 0.8669 (*5*)].

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Table I. Results of the Chromatographic Test of Reagent Purity

compound	specification, mol %	GC analysis, mass %
n-hexane	99+	99.9
n-heptane	99+	99.5
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

Table II. Pure Component Densities and Viscosities and Their Comparison with Literature Values at 293.15 K

	density, kg/L		kinematic viscosity $\times 10^6$, m^2/s	
compound	exptl values	lit. values (*5*)	exptl values	lit. values (*5*)
n-hexane	0.661 31	0.659 25	0.469 5	0.4727
n-heptane	0.684 34	0.683 75	0.600 13	0.6096
n-octane	0.702 75	0.702 67	0.769 71	0.7758
n-decane	0.729 95	0.730 12	1.254 3	1.268
n-dodecane	0.749 46	0.748 75	1.974 3	2.008
n-tetradecane	0.763 09	0.762 55	3.018 9	3.061
n-hexadecane	0.772 53	0.773 53	4.461 4	4.492

Cannon-Ubbelohde type viscometers were employed for the measurement of the kinematic viscosities, which in turn were obtained from the measured efflux time, t, and the equation

$$\nu = C_2 t - E/t^n \qquad (2)$$

where C_2 and E are calibration constants and $n = 2$ for the type of viscometers used in this study. The calibration constants C_2 and E were determined by using calibration standards N.8 (0.7844 cSt at 293.15 K), N1.0 (1.3280 cSt at 293.15 K), and S3 (4.278 cSt at 293.15 K). These standards were obtained from Cannon Instruments Co. The viscometers placed in a Model M1-18M constant-temperature bath purchased from Cannon. The bath temperature was controlled within ±0.01 K by using water as a bath medium. The bath temperature was measured by a calibrated thermometer (IPTS-68). An electronic stopwatch accurate within ±0.01 s was used for measuring efflux times.

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 an flame ionization detector (FID) produced the results shown in Table I.

Results and Discussion

Table II lists all the pure component densities and kinematic viscosities measured in this study and the corresponding values found in the literature. It can easily be seen from this table that the experimental density and kinematic viscosity values reported here are in close agreement with those reported in the TRC tables (*5*).

The experimental densities and kinematic viscosities studied herein are reported in Table III. The estimated experimental

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Table III. Experimental Density- and Viscosity–Composition Data for Binary Mixtures of *n*-Alkanes at 293.15 K

mass fraction	mole fraction	density kg/L	viscosity: kinematic × 10^6, m^2/s	viscosity: absolute × 10^3, Pa·s	mass fraction	mole fraction	density kg/L	viscosity: kinematic × 10^6, m^2/s	viscosity: absolute × 10^3, Pa·s
				n-Hexane (A)–*n*-Heptane (B)					
0.0000	0.0000	0.6843	0.6001	0.4107	0.5673	0.6038	0.6711	0.5194	0.3486
0.0820	0.0940	0.6824	0.5871	0.4007	0.6710	0.7034	0.6688	0.5067	0.3389
0.1768	0.1998	0.6801	0.5726	0.3895	0.7656	0.7916	0.6666	0.4954	0.3302
0.2648	0.2952	0.6781	0.5601	0.3798	0.8929	0.9065	0.6637	0.4811	0.3193
0.3594	0.3948	0.6759	0.5469	0.3697	1.0000	1.0000	0.6613	0.4695	0.3105
0.4607	0.4983	0.6736	0.5332	0.3592					
				n-Hexane (A)–*n*-Octane (B)					
0.0000	0.0000	0.7027	0.7697	0.5409	0.5283	0.5975	0.6809	0.5814	0.3959
0.0807	0.1042	0.6995	0.7353	0.5144	0.6286	0.6917	0.6767	0.5538	0.3748
0.1550	0.1995	0.6965	0.7049	0.4909	0.7441	0.7940	0.6720	0.5249	0.3527
0.2408	0.2959	0.6929	0.6731	0.4664	0.8661	0.8955	0.6668	0.4973	0.3316
0.3321	0.3973	0.6891	0.6410	0.4417	1.0000	1.0000	0.6613	0.4695	0.3105
0.4250	0.4949	0.6852	0.6114	0.4189					
				n-Hexane (A)–*n*-Decane (B)					
0.0000	0.0000	0.7299	1.2543	0.9156	0.4680	0.5922	0.6977	0.7360	0.5135
0.0669	0.1059	0.7254	1.1487	0.8332	0.5797	0.6949	0.6899	0.6626	0.4571
0.1300	0.1979	0.7210	1.0616	0.7654	0.7035	0.7966	0.6814	0.5938	0.4046
0.2056	0.2994	0.7158	0.9722	0.6959	0.8482	0.9022	0.6716	0.5274	0.3542
0.2945	0.4081	0.7096	0.8812	0.6253	1.0000	1.0000	0.6613	0.4695	0.3105
0.3744	0.4971	0.7041	0.8095	0.5700					
				n-Heptane (A)–*n*-Octane (B)					
0.0000	0.0000	0.7027	0.7697	0.5409	0.5655	0.5974	0.6927	0.6662	0.4615
0.0875	0.0985	0.7013	0.7519	0.5273	0.6701	0.6984	0.6907	0.6492	0.4484
0.1851	0.2056	0.6996	0.7331	0.5129	0.7794	0.8011	0.6886	0.6320	0.4352
0.2762	0.3031	0.6980	0.7164	0.5000	0.8893	0.9016	0.6865	0.6158	0.4227
0.3644	0.3953	0.6964	0.7003	0.4877	1.0000	1.0000	0.6843	0.6001	0.4107
0.4642	0.4969	0.6946	0.6831	0.4744					
				n-Heptane (A)–*n*-Decane (B)					
0.0000	0.0000	0.7299	1.2543	0.9156	0.5147	0.6010	0.7066	0.8260	0.5836
0.0728	0.1003	0.7268	1.1738	0.8532	0.6254	0.7033	0.7015	0.7635	0.5355
0.1492	0.1994	0.7234	1.0992	0.7952	0.7405	0.8021	0.6962	0.7065	0.4918
0.2297	0.2975	0.7197	1.0282	0.7400	0.8549	0.8933	0.6910	0.6562	0.4534
0.3226	0.4034	0.7155	0.9547	0.6831	1.0000	1.0000	0.6843	0.6001	0.4107
0.4140	0.5008	0.7112	0.8903	0.6332					
				n-Heptane (A)–*n*-Dodecane (B)					
0.0000	0.0000	0.7495	1.9743	1.4797	0.4598	0.5913	0.7188	1.0432	0.7499
0.0613	0.0999	0.7454	1.7895	1.3340	0.5802	0.7015	0.7109	0.9087	0.6461
0.1245	0.1947	0.7412	1.6267	1.2058	0.7021	0.8002	0.7031	0.7980	0.5611
0.2030	0.3022	0.7359	1.4493	1.0666	0.8377	0.8977	0.6944	0.6975	0.4843
0.2855	0.4045	0.7304	1.2977	0.9479	1.0000	1.0000	0.6843	0.6001	0.4107
0.3730	0.5028	0.7246	1.1594	0.8401					
				n-Heptane (A)–*n*-Tetradecane (B)					
0.0000	0.0000	0.7631	3.0189	2.3037	0.4256	0.5946	0.7290	1.3026	0.9495
0.0566	0.1063	0.7586	2.6415	2.0038	0.5472	0.7053	0.7193	1.0783	0.7756
0.1122	0.2002	0.7541	2.3413	1.7655	0.6746	0.8041	0.7094	0.8993	0.6379
0.1813	0.3048	0.7485	2.0202	1.5121	0.8210	0.9008	0.6980	0.7425	0.5182
0.2547	0.4035	0.7426	1.7586	1.3060	1.0000	1.0000	0.6843	0.6001	0.4107
0.3371	0.5017	0.7360	1.5110	1.1121					
				n-Octane (A)–*n*-Decane (B)					
0.0000	0.0000	0.7299	1.2543	0.9156	0.5503	0.6038	0.7147	0.9454	0.6757
0.0789	0.0964	0.7278	1.2016	0.8745	0.6447	0.6932	0.7121	0.9032	0.6432
0.1740	0.2078	0.7250	1.1405	0.8269	0.7598	0.7976	0.7090	0.8565	0.6073
0.2539	0.2977	0.7229	1.0952	0.7917	0.8814	0.9025	0.7058	0.8115	0.5728
0.3541	0.4057	0.7201	1.0414	0.7499	1.0000	1.0000	0.7027	0.7697	0.5409
0.4400	0.4946	0.7178	0.9967	0.7154					
				n-Octane (A)–*n*-Tetradecane (B)					
0.0000	0.0000	0.7631	3.0189	2.3037	0.4631	0.5997	0.7347	1.4480	1.0638
0.0610	0.1013	0.7594	2.6992	2.0497	0.5734	0.7001	0.7280	1.2506	0.9105
0.1312	0.2078	0.7551	2.3864	1.8019	0.6947	0.7980	0.7208	1.0805	0.7788
0.2074	0.3125	0.7504	2.1090	1.5826	0.8434	0.9034	0.7119	0.9194	0.6482
0.2735	0.3953	0.7463	1.9012	1.4189	1.0000	1.0000	0.7027	0.7697	0.5409
0.3702	0.5052	0.7404	1.6431	1.2165					
				n-Tetradecane (A)–*n*-Hexadecane (B)					
0.0000	0.0000	0.7725	4.4613	3.4465	0.5624	0.5946	0.7671	3.5555	2.7274
0.0917	0.1033	0.7717	4.2891	3.3100	0.6748	0.7031	0.7660	3.4067	2.6096
0.1776	0.1978	0.7709	4.1440	3.1948	0.7772	0.7993	0.7650	3.2766	2.5067
0.2739	0.3009	0.7700	3.9820	3.0663	0.8911	0.9033	0.7640	3.1442	2.4022
0.3753	0.4068	0.7690	3.8227	2.9396	1.0000	1.0000	0.7631	3.0189	2.3037
0.4628	0.4958	0.7681	3.6922	2.8361					

Table IV. Least-Squares Constants for the Equation $\rho = \sum_{i=0}^{n} A_i X_A^i$, kg/L

system	A_0	A_1	A_2	A_3	A_4	std dev, 10^{-5} kg/L
n-hexane (A)–*n*-heptane (B)	0.6843	−0.0200	−0.000298			3.38
n-hexane (A)–*n*-octane (B)	0.70275	−0.0303	−0.00925	−0.0019		2.69
n-hexane (A)–*n*-decane (B)	0.72999	−0.0428	−0.0114	−0.0145		4.66
n-heptane (A)–*n*-Octane (B)	0.7028	0.0146	−0.0038			2.00
n-heptane (A)–*n*-decane (B)	0.72995	−0.0295	−0.0170	0.0051	−0.0041	1.41
n-heptane (A)–*n*-dodecane (B)	0.7495	−0.03985	−0.0129	−0.0124		4.84
n-heptane (A)–*n*-tetradecane (B)	0.7631	−0.0392	−0.0296	0.0104	−0.0203	2.89
n-octane (A)–*n*-decane (kB)	0.7299	−0.0222	−0.00499			2.96
n-octane (A)–*n*-tetradecane (B)	0.7631	−0.0341	−0.0217	0.0057	−0.0102	1.72
n-tetradecane (A)–*n*-hexadecane (B)	0.7725	−0.0072	−0.0045	0.0023		1.87

Table V. Least-Squares for the Equation $\nu = 10^{-6}\sum_{i=0}^{n} B_i X_A^i$, m²/s

system	B_0	B_1	B_2	B_3	B_4	std dev, m²/s
n-hexane (A)–*n*-heptane (B)	0.6001	−0.1379	0.0073			1.06×10^{-10}
n-hexane (A)–*n*-octane (B)	0.7699	−0.3393	0.0388			2.37×10^{-10}
n-hexane (A)–*n*-decane (B)	1.2531	−1.0028	0.2198			8.77×10^{-10}
n-heptane (A)–*n*-octane (B)	0.7696	−0.1787	0.0091			1.72×10^{-10}
n-heptane (A)–*n*-decane (B)	1.2542	−0.8182	0.2223	−0.1031	0.0452	3.22×10^{-10}
n-heptane (A)–*n*-dodecane (B)	1.9743	−1.90565	0.59898	−0.0676		9.50×10^{-10}
n-heptane (A)–*n*-tetradecane (B)	3.0189	−3.69335	1.4782	−0.2035		2.61×10^{-9}
n-octane (A)–*n*-decane (B)	1.2541	−0.5547	0.0707			6.24×10^{-10}
n-octane (A)–*n*-tetradecane (B)	3.0188	−3.27155	1.1757	−0.15275		2.04×10^{-9}
n-tetradecane (A)–*n*-Hexadecane (B)	4.4596	−.16469	0.2086			2.15×10^{-9}

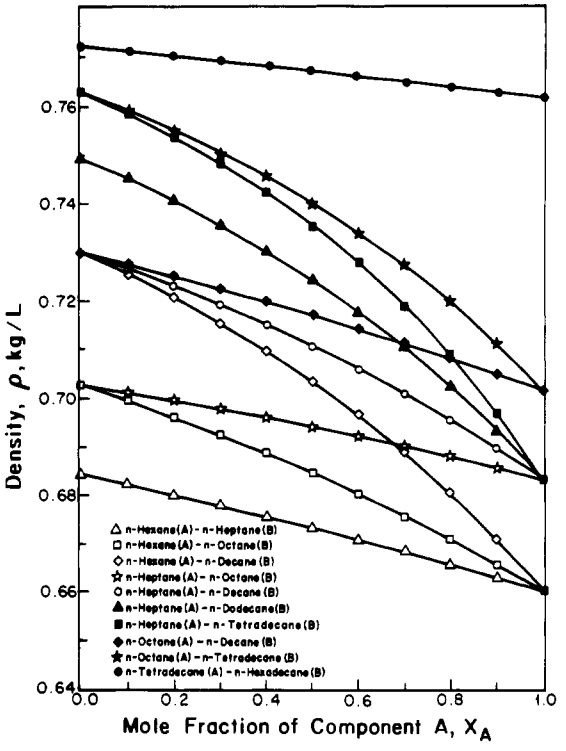

Figure 1. Change of density with composition.

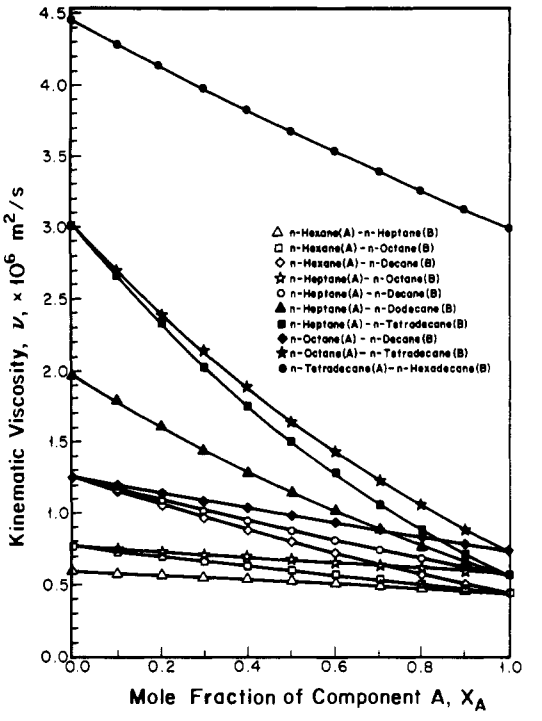

Figure 2. Change of kinematic viscosities with composition.

error in the case of density was determined to be within ±2 × 10^{-5} kg/L. In the case of kinematic viscosities, the error estimate was determined to be better than 6 × 10^{-10} m²/s.

Experimental density–composition and kinematic viscosity–composition data were fitted by polynomial expressions of the forms

$$\rho_m = \sum_{i=1}^{n} A_i X_A^i \tag{3}$$

and

$$\nu_m = \sum_{i=0}^{n} B_i X_A^i \tag{4}$$

The adjustable parameters A_i and B_i were determined by least-squares technique. The degree of the polynomial was varied so as to minimize the standard deviation of the fit. The values of the parameters A_i and B_i and the standard deviation for each system reported herein are given in Tables IV and V. Examination of the standard deviation of the fit indicates that the correlating expressions fit the experimental data very well.

Plots of the experimental density– and kinematic viscosity–composition data obtained at 293.15 K are shown in Figures 1 and 2, respectively. It is clear from these figures that binary mixture densities and kinematic viscosities vary monotonically with composition.

The additive-volume behavior of the majority of the systems reported herein approaches ideality within experimental error. Only the systems *n*-hexane–*n*-decane and *n*-heptane–*n*-tetradecane show a relatively larger departure from ideal solution

Table VI. Values of the Parameters in the McAllister Three-Body Model

system	$\nu_{AB} \times 10^6$, m^2/s	$\nu_{BA} \times 10^6$, m^2/s	std dev, m^2/s
n-hexane (A)–*n*-heptane (B)	0.51	0.56	1.2×10^{-10}
n-hexane (A)–*n*-octane (B)	0.57	0.67	2.7×10^{-10}
n-hexane (A)–*n*-decane (B)	0.72	0.96	5.9×10^{-10}
n-heptane (A)–*n*-octane (B)	0.66	0.71	2.0×10^{-10}
n-heptane (A)–*n*-decane (B)	0.80	1.02	4.4×10^{-10}
n-heptane (A)–*n*-dodecane (B)	1.01	1.44	1.1×10^{-9}
n-heptane (A)–*n*-tetradecane (B)	1.30	2.02	3.6×10^{-9}
n-octane (A)–*n*-decane (B)	0.93	1.08	6.3×10^{-10}
n-octane (A)–*n*-tetradecane (B)	1.42	2.12	2.5×10^{-9}
n-tetradecane (A)–*n*-hexadecane (B)	3.47	3.94	2.0×10^{-9}

behavior than the rest of the systems reported in this study.

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

$$\ln \nu_m = X_A^3 \ln \nu_A + 3X_A^2X_B \ln \nu_{AB} + 3X_AX_B^2 \ln \nu_{BA} + X_B^3 \ln \nu_B - \ln\left[X_A + X_B\frac{M_B}{M_A}\right] + 3X_A^2X_B \times \ln\left[\left[2 + \frac{M_B}{M_A}\right]/3\right] + 3X_AX_B^2 \ln\left[\left[1 + 2\frac{M_B}{M_A}\right]/3\right] + X_B^3 \ln\left[\frac{M_B}{M_A}\right] \quad (5)$$

where ν_{AB} and ν_{BA} are adjustable parameters that can be obtained from experimental data. Table VI lists the values of the parameters ν_{AB} and ν_{BA} for the systems investigated in this study. The standard deviation of the fit indicates that the model given by eq 5 fits the experimental data very well.

Conclusions

The densities and kinematic viscosities of 10 *n*-alkane binary mixtures have been determined at 293.15 K. The reproducibility of determining the density and kinematic viscosity data is 2×10^{-5} kg/L and 6×10^{-10} m^2/s, respectively.

If the additivity of volumes on mixing is employed as a criterion of ideal solution behavior, then all the systems reported herein, with the exception of the systems *n*-hexane–*n*-decane and *n*-heptane–*n*-tetradecane, approach ideal behavior.

The experimental data were correlated by using polynomial expressions that fitted the data well. Also, the McAllister three-body model gave an excellent fit to the experimental kinematic viscosity–composition data.

Nomenclature

A	adjustable parameter
B	adjustable parameter
C_1	calibration constant
C_2	calibration constant
E	calibration constant
X	mole fraction
ν	kinematic viscosity
ρ	density
ω	mass fraction

Subscripts

A	first-named component in a binary mixture
m	mixture

Registry No. *n*-Hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-decane, 124-18-5; *n*-dodecane, 112-40-5; *n*-tetradecane, 629-59-4; *n*-hexadecane, 544-76-3.

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Excess Enthalpy of Binary Systems of Halothane + Cyclic Ethers

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The excess molar enthalpies H^E of binary liquid systems of halothane + cyclic ethers (1,4-dioxane, oxane, or oxolane) were determined at atmospheric pressure and 298.15 K by using an isothermal flow microcalorimeter. The experimental data were correlated by means of the Redlich–Kister equation. The systems are highly exothermic, $H^E < 0$, with asymmetric H^E vs composition curves.

Introduction

This work pursues our systematic studies on the excess molar enthalpies H^E of binary systems containing halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) with cyclic ethers with the aim of investigating the influence of the oxygen atoms on the properties of ether + halothane mixtures. In a previous paper (*1*), the binary system halothane + 1,3-dioxolane has

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