Densities and Viscosities of Binary Mixtures of JP-10 with *n*-Octane or *n*-Decane at Several Temperatures

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The densities and viscosities of the binary mixtures of JP-10 + *n*-octane and JP-10 + *n*-decane were determined from $T = 293.15$ K to $T = 313.15$ K at atmospheric pressure, over the entire composition range. Excess volume V_m^E of the binary mixtures was calculated. The experimental data indicate that the addition of *n*-alkane has a distinct effect on the density and viscosity of JP-10, and V_m^E values of the binary systems are negative. Experimental data were fitted to the Redlich−Kister equation, and the adjustable parameters and the standard deviations between experimental and calculated values were estimated. Conclusions were qualitatively discussed in terms of molecular interactions. The viscosity data have been correlated with several semiempirical equations, and the Grunberg−Nissan equation gives satisfactory results.

Introduction

The fuels for small missiles must meet several general technical requirements, such as large volumetric energy content or heating value, low viscosity, and acceptable flash point.[1] JP-10 ($C_{10}H_{16}$, tricycle [5.2.1.0$^{2.6}$] decane), also called exotetrahydrodicyclopentadiene, is one of a variety of cyclic, high-energy-density fuels being considered for defense applications. The structure can be see in Figure 1. These single-component fuels take advantage of increasing energy storage available through strained cyclic geometries.[2] So JP-10 is presently a kind of standard missile fuel used by the Navy and the Air Force. Fuels used for the Air Force should experienced low operating temperatures, which need low viscosity and freezing point for flow and ignition of the fuel in the severe operating conditions. Many conventional hydrocarbon fuels such as JP-5 and JP-10 show a decrease in capabilities of combustion as the density of the fuel increases. Presently, many industrial liquid mixtures contain *n*-alkanes as major components,[3] so there is an increasing interest in adding *n*-alkanes into fuel to improve the fuel's performance. The densities and viscosities of the binary mixtures of JP-10 + *n*-octane and JP-10 + *n*-decane are measured as important fundamental data for the chemical design and the optimization of chemical processes. Besides, the excess molar volume (V_m^E) of the binary mixtures can provide important information concerning a deeper understanding of the liquid molecular structure and intermolecular interactions.

Experimental Section

Materials and Characterization. The *n*-alkanes (*n*-octane and *n*-decane) with purity better than 99 % as claimed is supplied by J&K Chemical Reagent Company, particularly degassed by ultrasound prior to their experimental use. The sample of JP-10 fuel is provided by Liming Research Institute of Chemical Industry with purity better than 98 % analyzed by a Hewlett-Packard 6890/5973 GC/MS. The physical parameters are listed in Table 1, where ρ is the density in g·cm^{-3} and η is the viscosity in mPa·s.

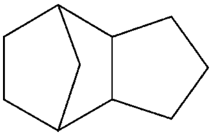

Figure 1. Molecular structure of JP-10.

Table 1. Physical Properties of Liquid Samples

	ρ/g·cm^{-3} (298.15 K)		η/mPa·s (298.15 K)	
compound	exptl	lit.	exptl	lit.
JP-10	0.9314	0.9318[a]	2.7398	2.7673[a]
n-octane	0.6985	0.6985[b]	0.5177	0.5184[c]
n-decane	0.7264	0.7264[d]	0.8434	0.8614[e]

[a] Ref 4. [b] Ref 5. [c] Ref 6. [d] Ref 7. [e] Ref 8.

Apparatus and Procedure. The mixtures were prepared by syringing known masses of the pure liquids into stoppered bottles to prevent preferential evaporation and to reduce possible errors in mole fraction calculations, using a Mettler Toledo AL204 balance with a stated precision of ± 1·10^{-4} g.

Densities, ρ, of pure components and their binary mixtures were measured by a vibrating-tube digital densimeter (DMA55 Anton Paar) thermostatted to better than ± 0.01 K (HAAKE C). The densimeter was calibrated with twice distilled water and dried air. The uncertainty of density measurements was ± 5·10^{-5} g·cm^{-3} corresponding to uncertainty of ± 3·10^{-3} cm^3·mol^{-1} in the excess volumes, V_m^E.

The kinematic viscosities, ν, were determined at atmospheric pressure and different temperatures, using several Ubbelohde viscometers. The viscometer was immersed in a well-stirred water bath, providing temperature stabilization with an accuracy of ± 0.1 K. Flow times were always >200 s by selecting an appropriate viscometer, which were measured with an accurate stopwatch to an accuracy of ± 0.01 s. The viscosity η of the liquid was then calculated according to eq 1.

$$\nu = \eta / \rho \tag{1}$$

where ν is the kinematic viscosity; η is the dynamic viscosity; and ρ is the density. Several viscometers with capillary diameters from 0.5 mm up to 0.8 mm were used for kinematic ranges of

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10.1021/je800348s CCC: $40.75

Table 2. Densities ρ and Viscosities η of JP-10 + n-Alkane Mixtures at Several Temperatures

$x_{n\text{-alkane}}$	ρ/g·cm^{-3}	η/mPa·s	$x_{n\text{-alkane}}$	ρ/g·cm^{-3}	η/mPa·s
	JP-10 + n-octane			JP-10 + n-decane	
	T = 293.15 K			T = 293.15 K	
0.0000	0.9352	3.0643	0.0000	0.9352	3.0643
0.1170	0.9061	2.3528	0.0950	0.9127	2.6310
0.2275	0.8791	1.8356	0.1934	0.8900	2.2601
0.3384	0.8524	1.4705	0.2908	0.8683	1.9637
0.4431	0.8277	1.2157	0.3902	0.8468	1.7173
0.5439	0.8042	1.0271	0.4893	0.8260	1.5249
0.6417	0.7818	0.8793	0.6147	0.8007	1.3476
0.7361	0.7604	0.7663	0.6905	0.7860	1.2447
0.8265	0.7403	0.6722	0.7895	0.7674	1.1304
0.9143	0.7211	0.5988	0.8952	0.7482	1.0315
1.0000	0.7025	0.5439	1.0000	0.7300	0.9491
	T = 298.15 K			T = 298.15 K	
0.0000	0.9314	2.7398	0.0000	0.9314	2.7398
0.1170	0.9010	2.1093	0.0950	0.9075	2.3392
0.2275	0.8745	1.6654	0.1934	0.8851	1.9962
0.3384	0.8481	1.3512	0.2908	0.8637	1.7280
0.4431	0.8236	1.1202	0.3902	0.8425	1.5213
0.5439	0.8003	0.9508	0.4893	0.8220	1.3623
0.6417	0.7780	0.8194	0.6147	0.7969	1.1942
0.7361	0.7566	0.7198	0.6905	0.7823	1.1018
0.8265	0.7365	0.6345	0.7895	0.7637	1.0085
0.9143	0.7171	0.5681	0.8952	0.7446	0.9181
1.0000	0.6985	0.5177	1.0000	0.7264	0.8434
	T = 303.15 K			T = 303.15 K	
0.0000	0.9277	2.5136	0.0000	0.9277	2.5136
0.1170	0.8985	1.9445	0.0950	0.9054	2.1905
0.2275	0.8718	1.5529	0.1934	0.8828	1.8894
0.3384	0.8454	1.2725	0.2908	0.8612	1.6384
0.4431	0.8207	1.0561	0.3902	0.8398	1.4413
0.5439	0.7972	0.8917	0.4893	0.8190	1.2871
0.6417	0.7748	0.7691	0.6147	0.7937	1.1431
0.7361	0.7532	0.6752	0.6905	0.7790	1.0585
0.8265	0.7329	0.5929	0.7895	0.7603	0.9726
0.9143	0.7133	0.5302	0.8952	0.7409	0.8852
1.0000	0.6945	0.4795	1.0000	0.7225	0.8172
	T = 313.15 K			T = 313.15 K	
0.0000	0.9222	2.2701	0.0000	0.9222	2.2701
0.1170	0.8935	1.7693	0.0950	0.9002	2.0064
0.2275	0.8666	1.4214	0.1934	0.8778	1.7409
0.3384	0.8398	1.1662	0.2908	0.8563	1.5300
0.4431	0.8149	0.9677	0.3902	0.8348	1.3336
0.5439	0.7910	0.8212	0.4893	0.8140	1.2136
0.6417	0.7683	0.7085	0.6147	0.7884	1.1010
0.7361	0.7464	0.6197	0.6905	0.7733	1.0319
0.8265	0.7256	0.5424	0.7895	0.7542	0.9345
0.9143	0.7056	0.4839	0.8952	0.7343	0.8537
1.0000	0.6863	0.4358	1.0000	0.7154	0.7851

Table 3. Parameters of the Redlich–Kister Equation and Standard Deviations σ of JP-10 + n-Alkane Mixtures

T/K	A_1	A_2	A_3	σ
		JP-10 + n-octane		
293.15	−1.43037	−0.05771	0.04490	0.00330
298.15	−2.07957	−0.06708	0.07291	0.00402
303.15	−2.25591	−0.06708	0.07291	0.00781
313.15	−3.25992	−0.30452	0.02214	0.00718
		JP-10 + n-decane		
293.15	−4.92595	−0.66854	0.02900	0.01118
298.15	−5.31064	−0.82027	−0.0688	0.00913
303.15	−5.52094	−0.96108	−0.10343	0.01206
313.15	−6.91260	−1.48131	−0.05725	0.01550

(0.43 to 3.27) mm^2·s^{-1}. Viscometer calibration was performed by double-distilled water. Viscometers were filled with 15 cm^3 of solution, and the flow times were obtained by averaging over three runs. The uncertainty of the viscosity measurements was within ± 0.5 %.

Results and Discussion

Density and Viscosity Measurement. Experimental values of density and viscosity of all binary mixtures at (293.15, 298.15, 303.15, and 313.15) K are given in Table 2. Excess molar volume $V_m{}^E$ can be obtained from eq 2.

$$V_m^E = \frac{M_1x_1 + M_2x_2}{\rho_m} - \left(\frac{M_1x_1}{\rho_1} + \frac{M_2x_2}{\rho_2}\right) \qquad (2)$$

In the equation, M_i, x_i, and ρ_i (i = 1, 2) are the molar mass, the mole fractions, and the densities of the pure components, respectively. ρ_m is the density of the mixture. In this experiment, the uncertainty of the mole fractions was within $\pm\ 2.2\cdot10^{-4}$.

Excess molar volume $V_m{}^E$ can be represented by the Redlich–Kister eq 3.

$$Y = x_1x_2\sum_{i=1}^{K} A_i(x_1 - x_2)^{i-1} \qquad (3)$$

where Y is $V_m{}^E$ and x_1 and x_2 refer to the mole fractions of n-alkane and JP-10, respectively. A_i are the polynomial coefficients, which were obtained by fitting the equation to the experimental result with a least-squares regression method. The standard deviation, σ, was defined as in eq 4.

$$\sigma = \left[\sum (Y_{\text{exptl}} - Y_{\text{calcd}})^2/(n - k)\right]^{1/2} \qquad (4)$$

where n is the number of measurements and k is the number of estimated parameters. The correlation parameters calculated from eq 3 are listed in Table 3, together with the standard deviations (σ). For all mixtures $\sigma(V_m{}^E) \leq 0.01550\ \text{cm}^3\cdot\text{mol}^{-1}$.

The excess molar volume $V_m{}^E$ varying with the mole fraction of the investigated binary mixtures are shown in Figure 2. It is observed that excess molar volumes for both of the binary systems are negative over the whole composition range, increasing their absolute values as the temperature increased.

These excess values reflect the interactions between unlike molecules. The molecular interactions between the mixing species mainly depend upon the composition, the molecular sizes, shapes of the components, and the experimental temperature. Generally, for mixtures with strong specific interactions between unlike molecules and with negative deviations of Raoult's law, $V_m{}^E$ values are negative at a given temperature.[9−12] It can be summarized that $V_m{}^E$ values may be affected by three factors. The first factor is the specific forces between molecules, such as hydrogen bonds and charge-transfer complexes, breaking of hydrogen bonds and complexes giving positive excess molar volumes, and forming of hydrogen bonds and complexes bringing negative values of $V_m{}^E$. The second factor is the physical intermolecular forces, including electrostatic forces between charged particles and between permanent dipoles and so on, induction forces between a permanent dipole and an induced dipole, and forces of attraction (dispersion forces) and repulsion between nonpolar molecules. Physical intermolecular forces are weak usually, and the sign of $V_m{}^E$ values may be positive or negative. The third factor is the structural characteristics of the component, arising from geometrical fitting of one component into the other's structure, due to the differences in shape and size of components and free volume.[13]

For the systems of JP-10 + n-octane and JP-10 + n-decane, all are nonpolar alkane molecules, so the physical intermolecular force is very weak and the main influencing factor is the structural characteristics of the components, due to the differences in shape and size of components and free volume. JP-10 is a cyclic alkane, but n-octane and n-decane are chain alkanes. Thus, the n-octane and n-decane molecules can easily enter the space of cyclic JP-10. On one hand, this makes the distance between the n-alkane molecule and JP-10 become smaller, and

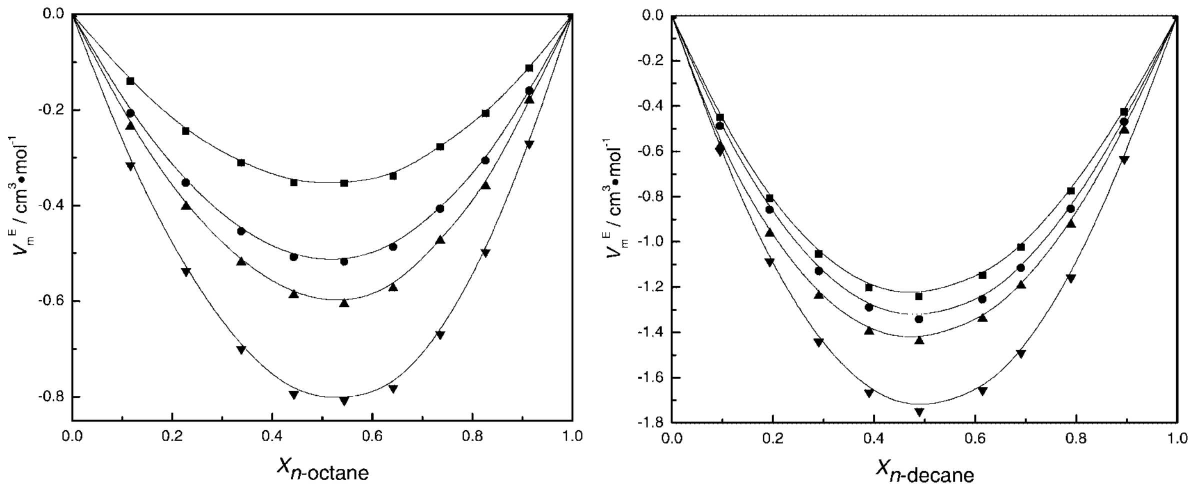

Figure 2. Plot of excess molar volumes against mole fraction for JP-10 + *n*-octane and JP-10 + *n*-decane systems at different temperatures (*T*): ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 313.15 K.

Table 4. Correlation Deviations and Adjustable Parameters of Semiempirical Viscosity Equations for JP-10 + *n*-Alkane Systems at (293.15, 298.15, 303.15, and 313.15) K

		JP-10 + *n*-octane				JP-10 + *n*-decane			
T/K		293.15	298.15	303.15	313.15	293.15	298.15	303.15	313.15
Kendall−Monroe	Dev/%	18.93	17.89	16.53	15.38	11.98	11.79	10.68	8.97
	σ/mPa•s	0.2678	0.2330	0.2019	0.1805	0.2296	0.2012	0.1717	0.1395
	A_{12}	−0.6276	−0.6059	−0.5183	−0.461	−0.5036	−0.5182	−0.5283	−0.4753
Grunberg−Nissan	Dev/%	0.41	0.32	0.44	0.42	0.74	0.77	1.08	1.61
	σ/mPa•s	0.0076	0.0061	0.0095	0.0079	0.0153	0.0318	0.0180	0.0252
	A_{12}	0.4172	0.4365	0.4564	0.4374	1.0743	0.9362	0.8755	0.8574
Hind et al.	Dev/%	6.54	5.85	5.20	4.94	3.24	3.21	2.76	2.84
	σ/mPa•s	0.0891	0.0757	0.0714	0.0575	0.0762	0.0637	0.0435	0.0424
	A_{12}	0.4988	0.8872	0.1625	0.0850	0.4450	0.3029	0.2588	0.2620
	A_{21}	−0.0022	−0.5792	−0.3356	−0.4157	0.6862	0.5933	0.5556	0.4625
McAllister	Dev/%	7.90	8.66	8.56	8.52	0.22	0.64	0.70	0.79
	σ/mPa•s	0.1269	0.1494	0.1124	0.1030	0.0061	0.0020	0.0139	0.0169

on the other hand, this also decreases the total volume of JP-10 and *n*-alkane and results in the negative V_m^E value for the system studied. Therefore, it can be concluded that the differences in shape, size, and free volume of the JP-10 molecule and the *n*-alkane molecule lead to negative values of V_m^E.

Viscosity Data Correlation. Knowledge of the viscosity of pure liquids and respective mixtures and study of the viscosity models are useful for practical and theoretical purposes. Numerous equations for liquid mixture viscosity have been proposed.[14] In this work, four typical semiempirical relations are employed to correlate the experimental viscosity data of the investigated binary systems. The Kendall−Monroe equation,[15] which has no adjustable parameter, is expressed as eq 5.

$$\eta = (x_1\eta_1^{1/3} + x_2\eta_2^{1/3})^3 \tag{5}$$

The single-parameter correlations of Hind[16] and Grunberg−Nissan[17] the and double-parameter McAllister[18] are eqs 6, 7, and 8, respectively.

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2A_{12} \tag{6}$$

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2A_{12} \tag{7}$$

$$\begin{aligned}\ln \eta = x_1^3 \ln \eta_1 + x_2^3 \ln \eta_2 + 3x_1^2x_2 \ln A_{12} + 3x_1x_2^2 \ln A_{21} - \\ \ln[x_1 + x_2M_2/M_1] + 3x_1^2x_2 \ln[2 + (M_2/M_1)/3] + \\ 3x_1x_2^2 \ln[1 + (2M_2/M_1)/3] + x_2^3 \ln[M_2/M_1]\end{aligned} \tag{8}$$

where A_{12} and A_{21} are interaction parameters. The correlation parameters along with the average percentage deviation

$$\mathrm{Dev} = \frac{1}{N}\sum_{i=1}^{N}\frac{|\eta_{\mathrm{calcd}} - \eta_{\mathrm{exptl}}|}{\eta_{\mathrm{exptl}}}\cdot 100\ \% \tag{9}$$

and the standard deviation for binary mixtures of JP-10 + *n*-octane and JP-10 + *n*-decane are listed in Table 4, and the Grunberg−Nissan equation gives satisfactory results.

Conclusions

Densities and viscosities for binary systems of JP-10 + *n*-octane and JP-10 + *n*-decane have been experimentally determined at different temperatures over the entire composition range. Negative values of V_m^E were fitted with Redlich−Kister polynomial equations. Conclusions were qualitatively discussed in terms of molecular interactions. The viscosity data have been correlated with several semiempirical equations (Kendall and Monroe, Grunberg and Nissan, Hind et al., and McAllister equations), and the Grunberg−Nissan equation gives satisfactory results.

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Received for review May 15, 2008. Accepted July 11, 2008. The authors are grateful to the National Natural Science Foundation of China (20703036) and the Natural Science Foundation of Zhejiang Province (Y407093).

JE800348S