Densities of Mixtures Containing *n*-Alkanes with Sunflower Seed Oil at Different Temperatures

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Densities for mixtures containing sunflower seed oil with pentane, hexane, heptane, and octane have been determined at various temperatures between 298.15 K and 313.15 K using a vibrating tube densimeter. The derived excess volumes have been correlated by the Redlich−Kister equation. All the systems showed negative deviations from ideality. The excess volumes increased with an increase in temperature.

Introduction

The knowledge of the densities of *n*-alkane + oil mixtures is useful for the design of the equipment for extraction and refining of edible oils (Mantell Serrano *et al*., 1995). This parameter plays an important role in the size of immersion reactors, desolventizers, and tubes. The temperatures at which extraction processes take place are usually higher than 298.15 K. The most useful solvent in the edible oil extraction industry is hexane, although other solvents are being used in this and other steps in vegetable oil technology (AOCS, 1991). In this work, we report densities of mixtures of sunflower seed oil with pentane, hexane, heptane, and octane at temperatures between 298.15 K and 313.15 K. The densities of pentane + sunflower seed oil mixtures have only been measured at 298.15 K due to the high volatility of pentane. Densities were used to calculate excess molar volumes, and these were fitted to Redlich−Kister polynomials. All measurements were made at atmospheric pressure.

Experimental Section

Materials. Analytical grade pentane, hexane, heptane, and octane were obtained from Fluka with a purity of >99.5 mol %. Sunflower seed oil was supplied by Lincesol and was previously analyzed to calculate its composition in fatty acids. The composition of the sunflower oil was measured by means of a Perkin-Elmer model Sigma 3B gas chromatograph equipped with a flame detector. A fused silica capillary column of 25 m length and 0.25 mm internal diameter containing BP5 packing with a film thickness of 25 mm was used to separate the fatty acids at the following conditions: column temperature = 423.15 K, injector temperature = 523.15 K and head column pressure = 100 kPa. Before the fatty acids were introduced in the column, they were converted into methyl esters by the KOH hydrolysis method (Mehlenbacher, 1977). From this analysis, the resulting composition in mole fraction of the oil was palmitic acid, 0.11; stearic acid, 0.04; oleic acid, 0.27; and linoleic acid, 0.58. From this composition, the average molar mass (M_w) of the oil has been calculated, by the equation

$$M_w = 3(\sum x_i M_i) + 38.05 \qquad (1)$$

where x_i is the mole fraction of the fatty acid, M_i is the molar mass of the fatty acid, and 38.05 is the molar mass of the group CH−C−CH. The calculated molar mass of the oil is 873.58 ± 0.05 g·mol^{-1}. The composition of the sunflower oil is different depending on the sunflower seed (mainly if the seed is coming from an irrigated land or dry farming). The variation in the composition affects mainly the mono- and polyunsaturated fatty acids. It is about 61% ± 7% linoleic acid. This change in composition implies a change in the molar mass of 873.5 ± 0.5 g·mol^{-1}. And this change in the molar mass affects the excess volume by ±0.001cm^3·mol^{-1}.

Table 1. Densities and Refractive Indexes of the Used Oil and Solvents at 298.15 K

component	ρ/g·cm^{-3} (obs)	ρ/g·cm^{-3} (Riddick *et al*., 1986)	n_D (obs)	n_D (Riddick *et al*., 1986)
sunflower oil	0.916 30		1.4728	
pentane	0.621 16	0.621 39	1.3549	1.354 72
hexane	0.654 87	0.654 81	1.3724	1.372 26
heptane	0.679 50	0.679 51	1.3852	1.385 11
octane	0.698 48	0.698 49	1.3951	1.395 05

Table 2. Experimental Densities and Excess Volumes for Pentane (A) + Sunflower Oil (B) at 298.15 K

x_A	ϱ/g·cm^{-3}	V^E/cm^3·mol^{-1}
0.0739	0.913 74	−0.277
0.1607	0.910 39	−0.734
0.1995	0.908 64	−0.896
0.2648	0.905 31	−1.147
0.3498	0.900 28	−1.565
0.4050	0.896 33	−1.805
0.4863	0.889 17	−2.082
0.5988	0.875 66	−2.461
0.7034	0.856 55	−2.732
0.7952	0.829 70	−2.834
0.8861	0.782 22	−2.573
0.9592	0.705 48	−1.688
0.9723	0.683 74	−1.364

Apparatus and Procedure. Solutions were prepared by mass using a Bosch S2000 balance, taking precautions to prevent evaporation. Mole fractions were accurate to ±5 × 10^{-4}. Density measurements were carried out with a Anton Paar DMA 58 vibration tube densimeter, with a resolution of 1 × 10^{-5} g·cm^{-3}. The densimeter was calibrated with water and air, using the corresponding density of the water at each temperature, and air density was calculated by the equation

$$\text{density}_{t,p} = \frac{0.0012930}{1 + 0.00367t}\,\frac{p}{760} \qquad (2)$$

Excess volumes were accurate to ±2 × 10^{-2} cm^{-3}·mol^{-1}. Temperatures were accurate to ±1 × 10^{-2} K. Experimental densities and refractive indexes at 298.15 K of the used

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Table 3. Experimental Densities and Excess Volumes for Hexane (A) + Sunflower Oil (B) at Several Temperatures

	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K	
x_A	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}
0.0319	0.915 12	−0.005	0.911 89	−0.147	0.908 63	−0.117	0.905 32	−0.367
0.0757	0.913 51	−0.130	0.910 24	−0.241	0.907 12	−0.367	0.903 51	−0.324
0.1401	0.910 96	−0.377	0.907 90	−0.699	0.904 57	−0.647	0.901 18	−0.838
0.1980	0.908 34	−0.571	0.905 35	−0.957	0.902 01	−0.924	0.898 74	−1.233
0.2851	0.903 73	−0.852	0.900 84	−1.318	0.897 46	−1.292	0.894 18	−1.603
0.3699	0.898 32	−1.169	0.895 55	−1.715	0.892 19	−1.747	0.889 04	−2.164
0.4352	0.893 39	−1.485	0.890 71	−2.078	0.887 36	−2.148	0.884 06	−2.464
0.4635	0.890 74	−1.473	0.887 94	−1.980	0.884 98	−2.315	0.881 64	−2.609
0.5027	0.886 97	−1.632	0.884 34	−2.202	0.881 24	−2.491	0.878 00	−2.853
0.5858	0.877 23	−1.954	0.874 71	−2.591	0.871 65	−2.887	0.868 23	−3.157
0.7126	0.854 57	−2.126	0.852 26	−2.798	0.849 23	−3.130	0.845 95	−3.486
0.8099	0.825 45	−2.078	0.823 59	−2.844	0.820 80	−3.272	0.816 79	−3.375
0.8719	0.795 89	−1.855	0.794 16	−2.593	0.791 51	−3.055	0.787 15	−3.088
0.9033	0.774 80	−1.563	0.772 10	−1.999	0.769 58	−2.484	0.764 96	−2.466
0.9102	0.770 00	−1.640	0.767 23	−2.056	0.764 94	−2.599	0.760 09	−2.528
0.9500	0.731 87	−1.136	0.729 48	−1.622	0.724 57	−1.514	0.721 21	−1.834

Table 4. Experimental Densities and Excess Volumes for Heptane (A) + Sunflower Oil (B) at Several Temperatures

	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K	
x_A	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}
0.0720	0.913 62	−0.126	0.910 34	−0.223	0.907 03	−0.155	0.903 58	−0.264
0.1043	0.912 35	−0.229	0.909 04	−0.304	0.905 72	−0.238	0.902 33	−0.411
0.1500	0.910 37	−0.332	0.907 10	−0.453	0.903 76	−0.386	0.900 36	−0.555
0.2040	0.907 83	−0.489	0.904 54	−0.603	0.901 14	−0.504	0.897 76	−0.698
0.2419	0.905 87	−0.593	0.902 56	−0.699	0.899 27	−0.710	0.895 81	−0.841
0.3012	0.902 44	−0.743	0.899 14	−0.869	0.895 84	−0.893	0.892 36	−1.020
0.3123	0.901 71	−0.743	0.896 50	−0.942	0.895 19	−0.962	0.891 75	−1.123
0.3932	0.896 09	−0.970	0.892 78	−1.108	0.889 43	−1.128	0.885 98	−1.294
0.5073	0.885 73	−1.204	0.882 41	−1.360	0.879 08	−1.437	0.875 66	−1.641
0.6033	0.873 83	−1.404	0.870 54	−1.596	0.867 16	−1.682	0.863 73	−1.894
0.6977	0.857 32	−1.515	0.853 85	−1.640	0.850 46	−1.757	0.846 99	−1.962
0.8044	0.828 19	−1.453	0.824 81	−1.642	0.821 60	−1.865	0.817 86	−1.983
0.8521	0.808 77	−1.339	0.805 42	−1.546	0.801 89	−1.671	0.798 29	−1.849
0.8983	0.783 39	−1.119	0.779 87	−1.279	0.776 31	−1.412	0.772 75	−1.607
0.9538	0.738 70	−0.679	0.734 87	−0.767	0.731 03	−0.844	0.727 07	−0.934

Table 5. Experimental Densities and Excess Volumes for Octane (A) + Sunflower Oil (B) at Several Temperatures

	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K	
x_A	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}
0.0658	0.913 85	−0.150	0.910 50	−0.174	0.907 12	−0.088	0.903 72	−0.185
0.1008	0.912 39	−0.193	0.909 04	−0.223	0.905 67	−0.157	0.902 27	−0.260
0.1633	0.909 60	−0.324	0.906 23	−0.349	0.902 86	−0.301	0.899 47	−0.425
0.1992	0.907 86	−0.416	0.904 48	−0.440	0.901 09	−0.385	0.897 70	−0.515
0.2624	0.904 45	−0.558	0.901 05	−0.580	0.897 67	−0.552	0.894 24	−0.659
0.3022	0.902 02	−0.622	0.898 63	−0.661	0.895 20	−0.605	0.891 82	−0.760
0.4199	0.893 44	−0.835	0.890 03	−0.887	0.886 66	−0.912	0.883 22	−1.044
0.4980	0.886 17	−0.976	0.882 72	−1.022	0.879 38	−1.087	0.875 91	−1.216
0.5966	0.874 16	−1.072	0.870 63	−1.099	0.867 35	−1.221	0.863 84	−1.348
0.6935	0.857 84	−1.160	0.854 38	−1.251	0.850 93	−1.309	0.847 39	−1.445
0.7998	0.830 61	−1.117	0.826 98	−1.166	0.823 52	−1.25	0.820 00	−1.418
0.8453	0.813 77	−1.000	0.810 23	−1.095	0.806 67	−1.156	0.803 08	1.306
0.8958	0.789 17	−0.825	0.785 58	−0.915	0.781 91	−0.955	0.778 28	−1.102
0.9500	0.751 64	−0.537	0.748 23	−0.685	0.744 86	−0.824	0.740 30	−0.720

solvents with the corresponding literature values (Riddick *et al.*, 1986) are listed in Table 1.

Results and Discussion

The densities of the binary mixtures are reported in Tables 2−5. Derived excess volumes have been fitted to the polynomial Redlich−Kister expression for each set of data:

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_A x_B \sum_{k>0} A_k (x_A - x_B)^k \qquad (3)$$

where x_A denotes the mole fraction of *n*-alkane, x_B is the mole fraction of the oil, and A_k are the adjustable parameters obtained by the least-squares method. The values of these parameters along with the standard deviation σ

$$\sigma = [\sum (x_{obsd} - x_{calcd})^2/(N - M)]^{1/2} \qquad (4)$$

are recorded in Table 6. In eq 4, N is the total number of experimental points and M is the number of parameters. Due to the fit for the system, pentane + oil showed an important standard deviation, 0.1617 cm^3·mol^{-1} for the four-parameter polynomial; the fit was carried out with a five-parameter polynomial. The adjustable parameters for pentane + oil at temperature 298.15 K were $A_0 = -8.7007$; $A_1 = 5.3253$; $A_2 = -1.6060$; $A_3 = 15.1325$; $A_4 = -18.4444$; $\sigma = 0.1028$ cm^3·mol^{-1}.

The coefficients A_k were used to calculate the solid curves in Figure 1. In Figure 1 is graphically represented the evolution of excess molar volume along the mole fraction

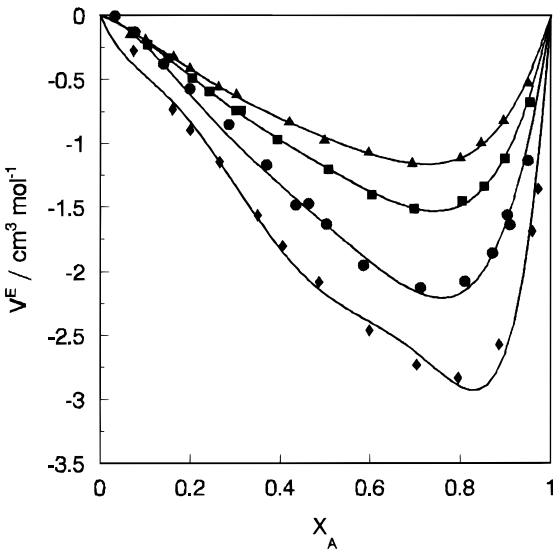

Figure 1. Excess molar volumes for pentane (A) (◆), hexane (A)), heptane (A) (■), and octane (A) (▲) + sunflower oil (B) *versus* mole fraction at 298.15 K

Table 6. Adjustable Parameters for Alkane (A) + Sunflower Oil (B) at Temperature *T*

/K	A_0	A_1	A_2	A_3	σ/cm^3·mol^{-1}
			Hexane + Oil		
298.15	−6.4671	5.9578	5.8864	5.5630	0.0584
303.15	−8.8002	6.8473	−9.0646	8.8803	0.0974
308.15	−9.6196	9.2456	−10.8926	9.2407	0.0948
313.15	−11.0020	8.7183	−10.5679	9.0789	0.1024
			Heptane + Oil		
298.15	−4.7479	4.0559	−3.8923	3.4364	0.0201
303.15	−5.3398	4.1277	−5.0214	4.1393	0.0286
308.15	−5.62935	4.6343	−5.1736	5.6852	0.0325
313.15	−6.30875	5.0316	−6.4896	4.9979	0.0425
			Octane + Oil		
298.15	−3.8233	2.7919	−2.7405	2.3328	0.0119
303.15	−3.9543	2.7423	−3.5134	3.3510	0.0437
308.15	−4.1830	3.2083	−3.1095	4.2110	0.0685
313.15	−4.7126	3.5745	−3.9918	3.3265	0.0295

for the studied solvents at 298.15 K. The excess volume at a specific mole fraction decreases in the order:

pentane + oil > hexane + oil > heptane + oil > octane + oil

Pentane molecules are small enough to introduce into the empty intramolecular spaces of oil molecules, since these are bigger and ramified. As a result, the volume of the mixture is smaller than the addition volume. Obviously, when the volume of the alkane increases, the alkane molecules have problems coming into the empty intramolecular spaces and the excess volume of the mixture is closer to the addition volume (ideality).

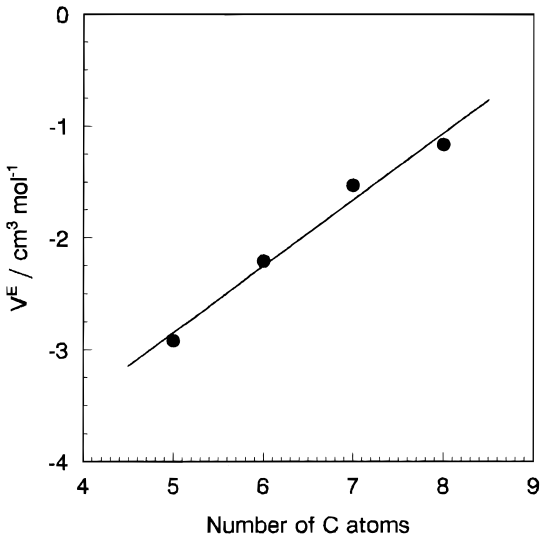

Figure 2. Excess molar volume at the minimum value versus number of carbon atoms of the alkane at 298.15 K.

All the analyzed mixtures at the measured temperatures show negative deviations from ideality (Tables 2−5). It can also be observed that a temperature increase implies an increase in the excess volume.

Figure 2 shows the excess molar volume at the minimum for the alkanes + sunflower oil at 298.15 K, plotted against the number of carbon atoms of the alkane. The mixtures show a linear increase in excess volume as a function of the number of carbons in the alkane. This relationship has been fitted to the equation:

$$V^E_{min}/\text{cm}^3\cdot\text{mol}^{-1} = -5.816 + 0.594n_c \qquad (5)$$

where V^E_{min} is the excess molar volume at the minimum observed value and n_c is the number of carbon atoms in the alkane molecule.

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