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Excess Molar Volumes of Mixtures of Hexane + Natural Oils from 298.15 to 313.15 K

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Excess molar volume data for mixtures containing hexane with three edible oils: olive, corn, and pip of grape have been determined from density measurements at various temperatures between 298.15 and 313.15 K using a vibrating tube densimeter. Results have been correlated by the Redlich−Kister equation. Systems showed negative deviations from ideality in the whole composition range.

Introduction

In the manufacture of the seeds to obtain the corresponding oils, its very important to know the densities and the excess volumes of the miscella formed by the oil and the solvent used to extract the oil. These properties are important for the design of the equipment in extraction and refining plants. Continuing our research about thermodynamic properties of the miscellas (González *et al.*, 1996), we report here the densities and excess molar volumes of mixtures formed by three edible oils with different compositions: olive, corn, and pip of grape with hexane. Hexane is the primary solvent used to extract oils in the industry. The temperatures at which the extraction processes take place are higher than 298.15 K. We have measured densities at temperatures between 298.15 K and 313.15 K and atmospheric pressure. The derived excess molar volumes were fitted to Redlich−Kister polynomials.

Experimental Section

Analytical grade hexane was obtained from Fluka with a purity >99.5 mol %. This purity was checked by GLC. Olive and corn oil were supplied by Koipe and grape pip oil was supplied by Dietisol. These oils were analyzed to calculate its composition in fatty acids. The composition of these was measured by means of a gas chromatograph Perkin-Elmer model Sigma 3B equipped with a flame detector. A fused silica capillary column of 25 m length and 0.25 mm i.d. and packing BP5 with a thickness film 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 of 100 kPa. Before the fatty acids were introduced in the column, they were converted into methyl esters by the KOH hydrolysis method (Mehlenbacher, 1977). The obtained compositions are shown in Table 1. The uncertainity in the % mol data in this table is ±0.1% mol. From this composition, the average molar mass (M) of the oil has been calculated by the equation

$$M/\mathrm{g{\cdot}mol^{-1}} = 3(\sum x_i M_i) + 38.05\ \mathrm{g{\cdot}mol^{-1}} \qquad (1)$$

where x_i is the mole fraction of the fatty acid, M_i is the molar mass of the fatty acid, and 38.05 g·mol^{-1} is the molar mass of the group CHCCH. The calculated molar mass of the oils is shown in Table 1. The composition of the oils is different depending on the seed they come from. The variation in the composition affects mainly the mono- and polyunsaturated fatty acids, as can be observed in Table 1. The change in composition implies a change in the molar mass of (875 ± 1) g·mol^{-1}. And this change in the molar mass affects the excess volume by ±0.002 cm^3·mol^{-1}.

Table 1. Compositions and Average Molar Mass of the Studied Oils

		composition (% mol)				
oil type	supplier	palmitic acid	stearic acid	oleic acid	linoleic acid	M/g·mol^{-1}
olive	Koipe	12.4	2.8	77.8	7.0	875.84
corn	Koipe	10.1	1.9	28.9	59.1	874.18
grape pip	Dietisol	7.4	3.5	21.3	67.8	875.77

Table 2. Densities and Refractive Indexes of the Solvent and the Oils

	ρ/g·cm^{-3} (298.15 K)		n_D^{25}	
compound	exptl	lit.	exptl	lit.
hexane	0.654 85	0.654 84[a]	1.3724	1.372 26[a]
olive oil	0.909 33	0.909−0.915[b]	1.4625[c]	1.4606−1.4633[b,c]
corn oil	0.916 05	0.915−0.920[b]	1.4676[c]	1.465−1.468[b,c]
grape pip oil	0.918 13		1.4739	1.473−1.477

[a] Riddick *et al.*, 1986. [b] Mehelenbacher, 1977. [c] Measured at 338.15 K.

Solutions were prepared by mass using a Salter ER-182A 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 (Riddick *et al.*, 1986), and air density (ρ) was calculated by the equation

$$\rho(t,p) = \frac{0.0012930p}{1 + 0.00367t} \qquad (2)$$

were p is the pressure in atm and t is the temperature in °C.

Excess volumes were accurate to (±2 × 10^{-2}) cm^{-3}·mol^{-1}. Temperatures were accurate to ±1 × 10^{-2} K. Experimental and literature densities and refractive indexes at 298.15 K of the solvent and oils are listed in Table 2.

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Table 3. Experimental Densities and Derived Excess Molar Volumes for Hexane (A) + Oils (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}
			Hexane (A) + Corn Oil (B)					
0.0501	0.914 35	−0.18	0.910 96	−0.20	0.907 56	−0.19	0.904 15	−0.20
0.1183	0.911 78	−0.45	0.908 40	−0.50	0.905 02	−0.53	0.901 62	−0.58
0.1558	0.910 25	−0.62	0.906 85	−0.66	0.903 48	−0.71	0.900 04	−0.74
0.2104	0.907 68	−0.76	0.904 28	−0.82	0.900 89	−0.87	0.897 47	−0.94
0.2504	0.905 63	−0.89	0.902 24	−0.97	0.898 87	−1.06	0.895 47	−1.15
0.2942	0.903 28	−1.12	0.899 86	−1.19	0.896 38	−1.20	0.892 88	−1.23
0.3140	0.902 14	−1.23	0.898 83	−1.40	0.895 44	−1.49	0.891 96	−1.54
0.3720	0.898 14	−1.31	0.894 66	−1.36	0.891 31	−1.50	0.887 91	−1.63
0.4812	0.888 97	−1.59	0.885 54	−1.72	0.882 17	−1.88	0.878 73	−2.02
0.6103	0.873 27	−1.87	0.869 87	−2.05	0.866 43	−2.21	0.862 95	−2.38
0.6829	0.860 61	−1.99	0.857 32	−2.24	0.853 80	−2.40	0.850 41	−2.63
0.7992	0.829 64	−2.20	0.826 25	−2.44	0.821 76	−2.28	0.818 31	−2.53
0.8454	0.810 35	−2.10	0.806 39	−2.17	0.802 84	−2.37	0.799 95	−2.81
0.9051	0.774 02	−1.73	0.770 68	−1.99	0.767 02	−2.18	0.763 35	−2.39
0.9517	0.730 86	−1.36	0.726 95	−1.49	0.722 87	−1.59	0.719 15	−1.80
			Hexane (A) + Olive Oil (B)					
0.0298	0.908 32	−0.05	0.904 83	−0.31	0.901 60	−0.08	0.898 24	−0.09
0.0502	0.907 63	−0.13	0.904 01	−0.25	0.900 87	−0.13	0.897 52	−0.15
0.1720	0.902 90	−0.54	0.899 50	−0.89	0.896 15	−0.63	0.892 79	−0.69
0.2125	0.901 06	−0.68	0.897 64	−1.01	0.894 30	−0.79	0.890 92	−0.85
0.2556	0.898 91	−0.82	0.895 52	−1.17	0.892 20	−1.01	0.888 81	−1.07
0.3227	0.895 29	−1.18	0.891 91	−1.53	0.888 57	−1.39	0.885 16	−1.47
0.4064	0.889 67	−1.49	0.881 97	−1.76	0.882 87	−1.70	0.879 37	−1.74
0.4556	0.885 61	−1.58	0.886 19	−1.75	0.872 64	−1.86	0.875 23	−1.84
0.5129	0.880 23	−1.77	0.876 69	−2.02	0.873 33	−2.00	0.869 83	−2.09
0.5202	0.879 24	−1.65	0.875 91	−2.03	0.878 86	−2.07	0.868 94	−2.04
0.6253	0.866 02	−2.02	0.862 47	−2.26	0.859 09	−2.31	0.855 67	−2.50
0.7365	0.844 39	−2.24	0.840 57	−2.38	0.837 1	−2.47	0.833 54	−2.63
0.7945	0.827 03	−2.07	0.823 34	−2.27	0.819 78	−2.37	0.816 18	−2.55
0.8475	0.805 65	−1.98	0.801 82	−2.14	0.798 25	−2.27	0.794 62	−2.46
0.9039	0.772 23	−1.65	0.768 71	−1.90	0.765 06	−2.05	0.761 18	−2.20
0.9519	0.728 40	−1.14	0.724 71	−1.34	0.720 34	−1.35	0.716 27	−1.47
			Hexane (A) + Pip of Grape Oil (B)					
0.0593	0.916 04	−0.18	0.912 70	−0.21	0.909 35	−0.28	0.905 89	−0.23
0.0993	0.914 52	−0.32	0.911 19	−0.37	0.907 81	−0.42	0.904 39	−0.43
0.1421	0.912 77	−0.48	0.909 43	−0.54	0.906 06	−0.61	0.902 64	−0.63
0.1914	0.910 60	−0.70	0.907 23	−0.74	0.903 82	−0.80	0.900 43	−0.86
0.2500	0.907 56	−0.83	0.904 20	−0.90	0.900 79	−0.98	0.897 39	−1.06
0.2961	0.904 87	−0.93	0.901 51	−1.02	0.898 14	−1.14	0.894 76	−1.25
0.4107	0.896 98	−1.33	0.893 59	−1.44	0.890 21	−1.59	0.886 79	−1.71
0.5032	0.888 45	−1.58	0.885 07	−1.73	0.881 68	−1.90	0.878 26	−2.05
0.5988	0.876 65	−1.83	0.873 26	−2.00	0.869 76	−2.14	0.866 31	−2.31
0.6993	0.858 68	−1.98	0.855 33	−2.20	0.851 71	−2.33	0.848 30	−2.55
0.7944	0.831 89	−1.92	0.829 07	−2.36	0.824 82	−2.29	0.821 37	−2.53
0.8469	0.810 03	−1.87	0.806 98	−2.22	0.802 88	−2.25	0.799 63	−2.57
0.8993	0.778 88	−1.67	0.775 53	−1.93	0.771 73	−2.09	0.767 61	−2.17
0.9500	0.732 14	−1.08	0.728 13	−1.19	0.723 93	−1.26	0.719 93	−1.39

Table 4. Adjustable Parameters for the Mixtures Hexane−Oil at Different Temperatures

T/K	A_0	A_1	A_2	A_3	σ/cm^3·mol^{-1}
			Olive		
298.15	−6.731	5.081	−5.829	7.786	0.06
303.15	−7.704	4.205	−8.183	8.297	0.10
308.15	−7.811	4.961	−6.756	11.168	0.08
313.15	−8.008	5.607	−8.396	11.243	0.08
			Corn		
298.15	−6.263	3.899	−8.809	10.159	0.08
303.15	−6.826	4.538	−9.736	10.710	0.10
308.15	−7.319	4.347	−9.756	12.119	0.14
313.15	−7.818	5.113	−11.635	13.739	0.15
			Pip of Grape		
298.15	−6.120	4.741	−6.738	6.413	0.06
303.15	−6.636	5.815	−8.781	7.303	0.04
308.15	−7.181	5.507	−8.647	7.877	0.08
313.15	−7.827	6.046	−9.341	9.049	0.07

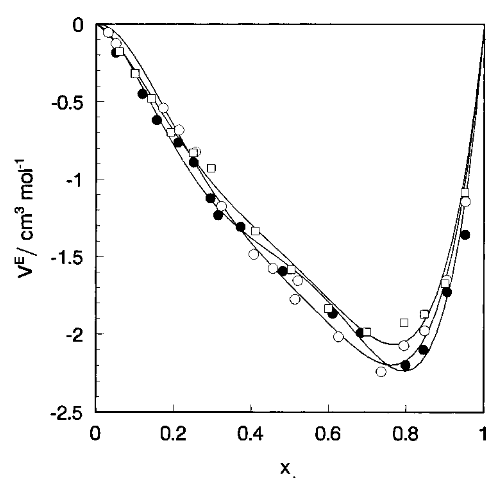

Figure 1. Excess molar volumes for hexane (A) + olive (B) (○), corn (B) (●), and grape pip (B) (□) oils versus mole fraction at 298.15 K.

Results and Discussion

The densities and the excess molar volumes of the binary hexane−oil mixtures are reported in Table 3. Excess volumes have been fitted to the polynomial Redlich−Kister expression for each set of data:

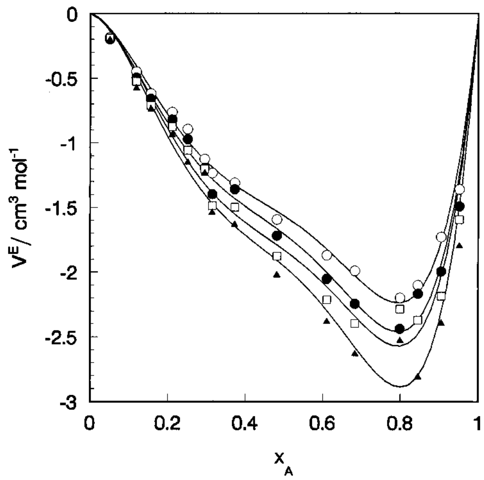

Figure 2. Excess molar volumes for hexane (A) + corn oil (B) at different temperatures: (○) $T = 298$ K, (●) $T = 303$ K, (□) $T = 308$ K, (▲) $T = 313$ K.

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

where x_A denotes the mole fraction of hexane, 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 4. In eq 4, N is the total number of experimental points and M is the number of parameters.

In Figure 1, excess molar volumes of the mixtures hexane + oil versus mole fraction at 298.15 K are plotted. Excess volumes are negative over the composition range. The systems showed large deviations from ideality at all the studied temperatures. Excess molar volumes increase with an increase in temperature, as can be observed in Figure 2. In this figure excess molar volumes of hexane + corn oil versus mole fraction of hexane are plotted at different temperatures. The obtained excess molar volumes showed very slight differences for the different studied oils, as the densities and compositions of the oils were different.

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