Properties of Mixing of Systems that Contain Sunflower Oil with Ketones

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This paper reports densities, ρ, refractive indices, n_D, excess molar volumes, V^E, and variation of refractive indices, Δn_D, of (2-butanone, 3-pentanone, and 4-methyl-2-pentanone) + sunflower oil at temperatures from 283.15 K to 298.15 K. Speeds of sound, u, were measured, and isentropic compressibilities of the same mixtures were calculated at 298.15 K. Redlich−Kister polynomials were fitted to the results of excess volumes, variation of refractive indices, and variation of isentropic compressibilities with the mole fraction of ketone. All the systems showed slight deviations from ideality. The excess volumes increase with the number of carbon atoms of the ketone and increase with an increase of temperature. Experimental properties of the mixtures were compared with predicted values with several mixing rules. In all cases, deviations were found to be less than 4%.

Introduction

Solvent extraction of oils is a common operation in the processing of seeds to obtain edible oils. Oils are mixed with organic solvents in a low-temperature solvent crystallization. The operation, usually named the winterization stage, is necessary in refining to obtain high-quality oils, stable at low temperatures. The need for data on the properties of the oil−solvent mixtures over a wide range of temperature has become apparent, particularly in connection with the designing of processing equipment. Excess volume data for mixtures of alkanes with sunflower oil,[1] alkanes and alcohols with olive oil,[2] and alkyl and vinyl acetates with olive oil[3] have been reported at different temperatures. The refractive indices and speeds of sound of alcohols + olive oil have been presented in another work.[4] In this paper, several physicochemical properties, densities, refractive indices, excess molar volumes, ane variation of refractive indices as a function of concentration are presented for binary systems of three ketones (2-butanone, 3-pentanone, and 4-methyl-2-pentanone) with sunflower oil from 283.15 to 298.15 K. Speeds of sound were measured and isentropic compressibilities of the same mixtures were calculated in the whole concentration range at 298.15 K. Several mixing rules have been used to predict the final property of the mixture, and in all cases, deviations between predicted and experimental data were less than 4%.

Experimental Section

Chemicals. Analytical grade 2-butanone, 3-pentanone, and 4-methyl-2-pentanone were obtained from Fluka with a purity of >99%. Some physical properties of pure solvents along with published values appear in Table 1. Refined sunflower oil was supplied by Koipe. Edible oil was previously analyzed to know its composition in fatty oils and other physicochemical characteristics. Acid value, saponification value, iodine value, peroxide value, and wetness and volatiles were also measured. These were analyzed following standard Spanish procedures.[5] The values obtained are presented in Table 2.

Apparatus and Procedures. The fatty acid composition was analyzed by means of a Shimadzu 4B gas chromatograph equipped with a flame ionization detector. The chromatographic technique and the chemical procedure for the derivatization of fatty acids were described in previous work.[6] Values of the compositions of the sunflower oil in fatty acids are shown in Table 2. The uncertainity in mol % for these results is better than 0.1%. From this composition, the average molar mass of this oil has been computed in accordance with the expression

$$M_{oil} = 3(\sum_{i=1}^{N} x_i M_i) + M_{CH-C-CH} \quad (1)$$

where x_i is the mole fraction and M_i is the molar mass of each fatty acid attending the concentration analysis, N is the number of fatty acids found by analysis, and $M_{CH-C-CH}$ is the molar mass contribution of the triglyceride molecule fraction. The variation in the composition due to different samples of oil affects mainly the mono- and polyunsaturated fatty acids; the change in molar mass is less than ± 1 g·mol^{-1}, and the change in excess molar volume is less than $\pm 2 \times 10^{-9}$ m^3·mol^{-1}.

Mixtures of the required composition were prepared by mass using a Salter ER-182A balance, taking precautions to prevent evaporation; the accuracy of each mass is $\pm 5 \times 10^{-7}$ kg. The densities ρ were measured using an Anton Paar DMA-58 vibrating-tube densitometer with a resolution of $\pm 5 \times 10^{-2}$ kg·m^{-3}. The densitometer was calibrated with water and air, using the corresponding density of the water at each temperature,[7] and air density was calculated by the equation

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

where t is the temperature in degrees Celsius and P is pressure in atmospheres.

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Table 1. Experimental and Literature Values of Pure Liquids at 283.15 K, 288.15 K, 293.15 K, and 298.15 K

	ρ/kg·m^{-3} at the following values of T/K						n_D				u/m·s^{-1}
	283.15 exp	288.15 exp	293.15 exp	298.15 exp	293.15 lit.[a]	298.15 lit.[a]	293.15 exp	298.15 exp	293.15 lit.	298.15 lit.[a]	298.15 exp
3-pentanone	824.3	819.46	814.58	809.75	814.3	809.45	1.39216	1.38972	1.39227	1.39002	1217.4
2-butanone	815.14	810.09	804.75	799.49	804.9	799.7	1.37865	1.37613	1.3788	1.37685	1191.4
4-methyl-2-pentanone	809.84	805.29	800.73	796.15	801.0	796.3	1.39589	1.39344	1.39576	1.39361	1190.0
sunflower oil	926.70	923.23	919.81	915.41	920−925[b]		1.47464	1.47277		1.472−1.476[b]	1453.7

[a] Riddick.[7] [b] Karleskind.[13]

Table 2. Properties of Sunflower Oil

composition (acid, mass %)	palmitic, 8.4; stearic, 3.9; oleic, 28.9; linoleic, 58.3; linolenic, 0.5	composition (acid, mass %)	palmitic, 8.4; stearic, 3.9; oleic, 28.9; linoleic, 58.3; linolenic, 0.5
acid value	0.07	peroxide value	13.4
saponification value	190.3	wetness and volatiles	0.010
iodine value	125.4		

Table 3. Experimental Densities ρ and Excess Volumes V^E for 3-Pentanone (1) + Sunflower Oil (2) Mixtures at Different Temperatures

	T = 283.15 K		T = 288.15 K		T = 293.15 K		T = 298.15 K	
x_1[a]	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}
0.0462	926.16	−0.002	922.68	−0.004	919.26	−0.013	915.86	−0.022
0.0965	925.51	−0.005	922.03	−0.010	918.60	−0.024	915.19	−0.034
0.1518	924.72	−0.006	921.23	−0.015	917.79	−0.031	914.38	−0.048
0.2007	923.94	−0.008	920.45	−0.024	917.00	−0.042	913.58	−0.060
0.2503	923.06	−0.010	919.56	−0.031	916.10	−0.048	912.67	−0.072
0.3063	921.94	−0.012	918.44	−0.041	914.97	−0.063	911.51	−0.081
0.3535	920.88	−0.017	917.36	−0.048	913.88	−0.074	910.41	−0.093
0.4089	919.45	−0.028	915.92	−0.059	912.42	−0.086	908.94	−0.112
0.4481	918.31	−0.038	914.76	−0.069	911.25	−0.100	907.75	−0.124
0.5034	916.45	−0.049	912.89	−0.089	909.35	−0.118	905.83	−0.146
0.5494	914.63	−0.061	911.05	−0.102	907.49	−0.134	903.96	−0.171
0.5976	912.39	−0.075	908.79	−0.120	905.19	−0.148	901.64	−0.190
0.6478	909.57	−0.090	905.95	−0.141	902.31	−0.169	898.74	−0.219
0.6980	906.11	−0.112	902.44	−0.159	898.76	−0.191	895.13	−0.234
0.7493	901.61	−0.132	897.89	−0.180	894.13	−0.206	890.43	−0.244
0.8003	895.73	−0.155	891.91	−0.193	888.05	−0.213	884.26	−0.247
0.8519	887.47	−0.159	883.53	−0.190	879.55	−0.209	875.63	−0.236
0.9009	876.00	−0.146	871.90	−0.172	867.77	−0.192	863.69	−0.215
0.9510	857.44	−0.106	853.08	−0.123	848.66	−0.133	844.37	−0.158

[a] x_1 = mole fraction of ketone.

Table 4. Experimental Refractive Indices n_D and Variation of Refractive Indices Δn_D for 3-Pentanone (1) + Sunflower Oil (2) Mixtures at Different Temperatures

	T = 288.15 K		T = 293.15 K		T = 298.15 K			T = 288.15 K		T = 293.15 K		T = 298.15 K	
x_1[a]	n_D	Δn_D	n_D	Δn_D	n_D	Δn_D	x_1[a]	n_D	Δn_D	n_D	Δn_D	n_D	Δn_D
0.0409	1.476 06	0.0029	1.474 18	0.0029	1.472 35	0.0030	0.5509	1.467 03	0.0356	1.464 98	0.0358	1.463 35	0.0363
0.0987	1.475 45	0.0070	1.473 60	0.0071	1.471 74	0.0072	0.5990	1.465 08	0.0376	1.463 19	0.0380	1.461 19	0.0382
0.1633	1.474 76	0.0116	1.472 85	0.0117	1.471 00	0.0118	0.6513	1.462 79	0.0396	1.460 77	0.0398	1.458 80	0.0401
0.1998	1.474 29	0.0141	1.472 41	0.0142	1.470 50	0.0143	0.6990	1.460 18	0.0409	1.458 06	0.0411	1.456 10	0.0414
0.2513	1.473 57	0.0176	1.471 64	0.0177	1.469 78	0.0179	0.7321	1.457 87	0.0413	1.455 79	0.0415	1.453 76	0.0418
0.2962	1.472 92	0.0207	1.471 05	0.0208	1.469 09	0.0209	0.7984	1.452 07	0.0409	1.450 00	0.0412	1.447 84	0.0414
0.3475	1.472 06	0.0240	1.470 05	0.0241	1.468 23	0.0243	0.8461	1.446 17	0.0389	1.443 92	0.0391	1.441 76	0.0393
0.4014	1.470 97	0.0273	1.469 03	0.0275	1.467 09	0.0277	0.8971	1.436 69	0.0336	1.434 63	0.0340	1.432 35	0.0341
0.4548	1.469 77	0.0305	1.467 79	0.0307	1.465 90	0.0309	0.9500	1.421 38	0.0226	1.419 10	0.0228	1.416 73	0.0229
0.5041	1.468 39	0.0331	1.466 40	0.0333	1.464 36	0.0335							

[a] x_1 = mole fraction of ketone.

Excess volumes were accurate to $\pm 2 \times 10^{-9}$ m^{-3}·mol^{-1}. Temperatures were accurate to $\pm 10^{-2}$ K. Speeds of sound were measured with an Anton Paar DSA-48 sound analyzer with a precision of ± 1 m·s^{-1}. Refractive indices of the samples were measured with an automatic refractometer Mettler Toledo RE 50 with a precision of ±0.000 02. Experimental densities and refractive indices at different temperatures of the used solvents with the corresponding literature values[7] are listed in Table 1.

Results and Discussion

Densities, excess molar volumes, refractive indices, and variation of the refractive indices of the prepared mixtures at different temperatures are listed in Tables 3−8. The experimental densities ρ of the mixtures were used to compute the excess molar volumes V^E from the equation

$$V^E = (x_1M_1 + x_2M_2)/\rho - [(x_1M_1/\rho_1) + (x_2M_2/\rho_2)] \quad (3)$$

where x_1 is the mole fraction of the more volatile compound and x_2 is the mole fraction of the olive oil, M_1 and M_2 are the molar masses of the solvent and oil, respectively, and ρ_1 and ρ_2 are the densities of the pure components.

From experimental speed of sound data, isentropic compressibilities (k_s) were calculated by the Laplace[8]

Table 5. Experimental Densities ρ and Excess Volumes V^E for 2-Butanone (1) + Sunflower Oil (2) Mixtures at Different Temperatures

	$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K	
x_1[a]	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}
0.0444	926.21	0.006	922.75	−0.006	919.32	−0.011	915.91	−0.015
0.1031	925.50	0.009	922.03	−0.010	918.59	−0.016	915.18	−0.025
0.1461	924.93	0.007	921.45	−0.012	918.01	−0.020	914.58	−0.031
0.1975	924.18	0.005	920.69	−0.013	917.23	−0.025	913.80	−0.039
0.2708	922.95	0.001	919.43	−0.014	915.97	−0.036	912.51	−0.052
0.2954	922.48	−0.003	918.96	−0.017	915.49	−0.040	912.02	−0.055
0.3578	921.17	−0.006	917.64	−0.025	914.14	−0.047	910.66	−0.067
0.4226	919.56	−0.015	916.01	−0.037	912.48	−0.062	908.97	−0.083
0.4483	918.83	−0.019	915.27	−0.040	911.73	−0.067	908.22	−0.097
0.5100	916.84	−0.034	913.24	−0.053	909.69	−0.092	906.15	−0.120
0.5516	915.25	−0.045	911.63	−0.066	908.05	−0.103	904.49	−0.138
0.6031	912.91	−0.058	909.26	−0.081	905.64	−0.119	902.05	−0.158
0.6495	910.34	−0.067	906.67	−0.098	903.00	−0.132	899.37	−0.170
0.7002	906.88	−0.083	903.16	−0.114	899.43	−0.148	895.75	−0.188
0.7479	902.70	−0.095	898.94	−0.130	895.14	−0.164	891.37	−0.196
0.7997	896.67	−0.105	892.82	−0.137	888.92	−0.171	885.06	−0.205
0.8491	888.62	−0.112	884.66	−0.142	880.61	−0.171	876.61	−0.203
0.9136	871.70	−0.102	867.48	−0.123	863.15	−0.149	858.82	−0.166
0.9515	854.91	−0.073	850.48	−0.094	845.84	−0.110	841.27	−0.129

[a] x_1 = mole fraction of ketone.

Table 6. Experimental Refractive Indices n_D and Variation of Refractive Indices Δn_D for 2-Butanone (1) + Sunflower Oil (2) Mixtures at Different Temperatures

	$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K			$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K	
x_1[a]	n_D	Δn_D	n_D	Δn_D	n_D	Δn_D	x_1[a]	n_D	Δn_D	n_D	Δn_D	n_D	Δn_D
0.0495	1.475 94	0.0042	1.474 05	0.0042	1.472 30	0.0043	0.5690	1.466 29	0.0440	1.464 33	0.0443	1.462 38	0.0446
0.0890	1.475 60	0.0076	1.473 62	0.0075	1.471 87	0.0077	0.5996	1.465 04	0.0456	1.463 07	0.0460	1.460 76	0.0459
0.1647	1.474 80	0.0140	1.472 82	0.0140	1.471 24	0.0144	0.6466	1.462 89	0.0479	1.460 92	0.0484	1.458 84	0.0486
0.2215	1.474 09	0.0187	1.472 15	0.0188	1.470 56	0.0192	0.6969	1.459 96	0.0498	1.457 97	0.0502	1.455 94	0.0505
0.2512	1.473 63	0.0210	1.471 58	0.0211	1.469 95	0.0215	0.7561	1.455 35	0.0508	1.453 29	0.0512	1.451 28	0.0516
0.3166	1.472 65	0.0263	1.470 64	0.0264	1.468 90	0.0267	0.7925	1.451 76	0.0507	1.449 72	0.0512	1.447 64	0.0515
0.3469	1.472 06	0.0286	1.469 98	0.0286	1.468 25	0.0290	0.8489	1.443 94	0.0482	1.441 91	0.0488	1.439 69	0.0490
0.3952	1.471 11	0.0322	1.469 21	0.0325	1.467 23	0.0327	0.9002	1.433 05	0.0422	1.430 87	0.0426	1.428 66	0.0429
0.4533	1.469 75	0.0364	1.467 64	0.0365	1.465 95	0.0370	0.9493	1.416 18	0.0300	1.413 69	0.0302	1.411 00	0.0300
0.4918	1.468 81	0.0391	1.466 85	0.0394	1.464 99	0.0397							

[a] x_1 = mole fraction of ketone.

Table 7. Experimental Densities ρ and Excess Volumes V^E for 4-Methyl-2-pentanone (1) + Sunflower Oil (2) Mixtures at Different Temperatures

	$T = 283.15$ K		$T = 288.15$ K		$T = 293.15$ K		$T = 298.15$ K	
x_1[a]	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}
0.0518	925.89	−0.015	922.41	−0.020	919.00	−0.039	915.60	−0.050
0.0996	925.06	−0.029	921.58	−0.037	918.17	−0.066	914.76	−0.076
0.1548	924.02	−0.053	920.53	−0.063	917.11	−0.092	913.70	−0.114
0.1994	923.10	−0.080	919.60	−0.090	916.17	−0.119	912.76	−0.146
0.2440	922.08	−0.100	918.58	−0.119	915.13	−0.141	911.71	−0.173
0.2981	920.70	−0.124	917.19	−0.146	913.72	−0.165	910.31	−0.216
0.3500	919.20	−0.148	915.68	−0.174	912.20	−0.197	908.77	−0.241
0.4142	917.05	−0.173	913.51	−0.200	910.02	−0.232	906.56	−0.277
0.4511	915.64	−0.192	912.10	−0.228	908.59	−0.256	905.12	−0.301
0.5052	913.29	−0.225	909.72	−0.256	906.19	−0.287	902.70	−0.334
0.5550	910.74	−0.249	907.16	−0.289	903.60	−0.317	900.08	−0.362
0.6000	908.05	−0.276	904.45	−0.317	900.86	−0.345	897.31	−0.387
0.6710	902.76	−0.311	899.12	−0.355	895.46	−0.376	891.87	−0.424
0.7049	899.63	−0.324	895.95	−0.363	892.28	−0.392	888.65	−0.436
0.7522	894.34	−0.334	890.62	−0.375	886.90	−0.405	883.22	−0.449
0.8004	887.50	−0.345	883.72	−0.384	879.94	−0.416	876.20	−0.461
0.8592	875.94	−0.320	872.06	−0.358	868.17	−0.387	864.33	−0.432
0.9025	863.83	−0.283	859.81	−0.309	855.80	−0.334	851.81	−0.366
0.9490	844.87	−0.205	840.67	−0.223	836.45	−0.237	832.15	−0.237

[a] x_1 = mole fraction of ketone.

equation,

$$k_s = u^{-2}\rho^{-1} \tag{4}$$

where ρ and u denote density and speed of sound of binary mixtures, respectively. The variation of the isentropic compressibility was evaluated from the equation

$$\Delta k_s = k_s - x_1 k_{s1} - x_2 k_{s2} \tag{5}$$

Table 8. Experimental Refractive Indices n_D and Variation of Refractive Indices Δn_D for 4-Methyl-2-pentanone (1) + Sunflower Oil (2) Mixtures at Different Temperatures

	T = 288.15 K		T = 293.15 K		T = 298.15 K			T = 288.15 K		T = 293.15 K		T = 298.15 K	
x_1[a]	n_D	Δn_D	n_D	Δn_D	n_D	Δn_D	x_1[a]	n_D	Δn_D	n_D	Δn_D	n_D	Δn_D
0.0490	1.475 93	0.0033	1.474 08	0.0033	1.472 22	0.0033	0.5591	1.465 57	0.0328	1.463 45	0.0328	1.461 71	0.0333
0.0897	1.475 45	0.0060	1.473 68	0.0061	1.471 78	0.0061	0.5932	1.464 28	0.0342	1.462 20	0.0343	1.460 43	0.0347
0.1253	1.475 04	0.0084	1.473 22	0.0084	1.471 32	0.0085	0.6329	1.462 57	0.0356	1.460 39	0.0356	1.458 60	0.0360
0.2123	1.473 88	0.0140	1.472 02	0.0141	1.470 14	0.0142	0.7003	1.458 79	0.0371	1.456 63	0.0371	1.454 76	0.0375
0.2474	1.473 34	0.0162	1.471 38	0.0162	1.469 62	0.0165	0.7497	1.455 04	0.0372	1.452 78	0.0372	1.451 02	0.0377
0.3070	1.472 35	0.0199	1.470 42	0.0200	1.468 61	0.0202	0.7955	1.450 82	0.0366	1.448 71	0.0367	1.446 86	0.0372
0.3367	1.471 66	0.0215	1.469 61	0.0215	1.468 00	0.0219	0.8537	1.443 52	0.0338	1.441 11	0.0337	1.439 12	0.0341
0.3946	1.470 48	0.0249	1.468 40	0.0248	1.466 68	0.0252	0.9045	1.433 89	0.0282	1.431 97	0.0286	1.429 49	0.0285
0.4481	1.469 28	0.0278	1.467 20	0.0278	1.465 50	0.0283	0.9533	1.420 14	0.0182	1.417 75	0.0182	1.415 57	0.0184
0.5348	1.466 58	0.0319	1.464 66	0.0321	1.462 72	0.0324							

[a] x_1 = mole fraction of ketone.

Table 9. Experimental Speeds of Sound u, Calculated Isentropic Compressibilities k_s, and Variation of Isentropic Compressibilities Δk_s of 2-Butanone (1) + Sunflower Oil (2) Mixtures at 298.15 K

x_1[a]	u/m·s^{-1}	k_s/T·Pa^{-1}	Δk_s/T·Pa^{-1}
0.0453	1452	518	−15.0
0.1117	1450	520	−36.9
0.2345	1444	525	−76.6
0.3417	1440	529	−112
0.3914	1435	534	−125
0.4609	1429	540	−145
0.5219	1423	546	−161
0.5671	1418	551	−172
0.6074	1412	556	−181
0.7051	1395	574	−199
0.8166	1361	612	−202
0.8938	1320	663	−179
0.9742	1237	792	−793

[a] x_1 = mole fraction of ketone.

Table 10. Experimental Speeds of Sound u, Calculated Isentropic Compressibilities k_s, and Variation of Isentropic Compressibilities Δk_s of 3-Pentanone (1) + Sunflower Oil (2) Mixtures at 298.15 K

x_1[a]	u/m·s^{-1}	k_s/T·Pa^{-1}	Δk_s/T·Pa^{-1}
0.0482	1452	518	−13.7
0.0949	1451	520	−26.9
0.1790	1448	522	−51.0
0.3034	1441	529	−84.1
0.3735	1436	533	−102
0.4345	1432	537	−117
0.4998	1426	543	−132
0.5444	1422	547	−142
0.6016	1415	555	−153
0.6910	1400	570	−166
0.8257	1363	611	−167
0.9037	1323	663	−141
0.9532	1281	724	−95.4

[a] x_1 = mole fraction of ketone.

where k_s, k_{s1}, and k_{s2} are the isentropic compressibilities of the mixture and the pure components 1 and 2, respectively. Values of the speed of sound, the derived isentropic compressibilities, and the variation of isentropic compressibility of the binary mixtures ketone−sunflower oil are shown in Tables 9−11.

The excess volume data, variation of refractive index, and variation of isentropic compressibility were correlated as a function of composition using a six or seven constant Redlich−Kister expansion,

$$V^E/\mathrm{m^3\cdot mol^{-1}}\ (\text{or } \Delta n_D \text{ or } \Delta k_s/\mathrm{T\cdot Pa^{-1}}) = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \quad (6)$$

Table 11. Experimental Speeds of Sound u, Calculated Isentropic Compressibilities k_s, and Variation of Isentropic Compressibilities Δk_s of 4-Methyl-2-pentanone (1) + Sunflower Oil (2) Mixtures at 298.15 K

x_1[a]	u/m·s^{-1}	k_s/T·Pa^{-1}	Δk_s/T·Pa^{-1}
0.0429	1452	518	−14.2
0.0807	1451	520	−26.7
0.2235	1442	528	−71.7
0.2985	1438	531	−95.7
0.4127	1429	540	−129
0.4525	1425	544	−140
0.4939	1421	549	−151
0.5566	1413	557	−165
0.6007	1406	564	−175
0.7042	1385	587	−191
0.8040	1354	623	−191
0.9124	1293	705	−149
0.9518	1256	763	−106

[a] x_1 = mole fraction of ketone.

Table 12. Adjustable Parameters and Standard Deviation for Excess Volumes−Mole Fraction Curves for Ketone + Vegetable Oil Systems at Different Temperatures

parameter / m^3·mol^{-1}	T = 298.15 K	T = 293.15 K	T = 288.15 K	T = 283.15 K
2-Butanone + Sunflower Oil				
10^6a_1	−0.4667	−0.3447	−0.2111	−0.1259
10^6a_2	0.7991	0.6261	0.5255	0.4503
10^6a_3	−0.5130	−0.4849	−0.5181	−0.3833
10^6a_4	−0.2455	0.0845	0.1795	0.1070
10^6a_5	−0.8757	−0.7754	−0.6066	−0.4188
10^6a_6	1.0952	0.7446	0.5120	0.6675
$10^9\sigma$	2.64	2.06	1.77	1.14
3-Pentanone + Sunflower Oil				
10^6a_1	−0.5804	−0.4611	−0.3452	−0.1892
10^6a_2	0.9481	0.6876	0.6522	0.4928
10^6a_3	−1.2845	−0.8489	−0.7004	−0.5738
10^6a_4	−0.5195	0.3703	0.3781	0.5845
10^6a_5	1.6313	0.1696	−0.5784	−0.7418
10^6a_6	1.5864	0.6072	0.6246	0.3434
10^6a_7	−2.5512	−0.9970		
$10^9\sigma$	1.82	1.73	1.98	1.83
4-Methyl-2-pentanone + Sunflower Oil				
10^6a_1	−1.3198	−1.1415	−1.0139	−0.8735
10^6a_2	1.1157	1.2105	1.2119	1.1070
10^6a_3	−1.2200	−0.9497	−1.4487	−1.3672
10^6a_4	1.4180	0.5569	0.3299	0.2028
10^6a_5	−0.9831	−1.2978	1.3300	1.2180
10^6a_6		0.8805	1.2842	1.3758
10^6a_7			−2.1969	−1.9966
$10^9\sigma$	3.17	2.94	2.83	2.35

where a_k are the adjustable parameters obtained by the least-squares method. Tables 12−14 summarize the values of the parameters a_k together with the standard deviations

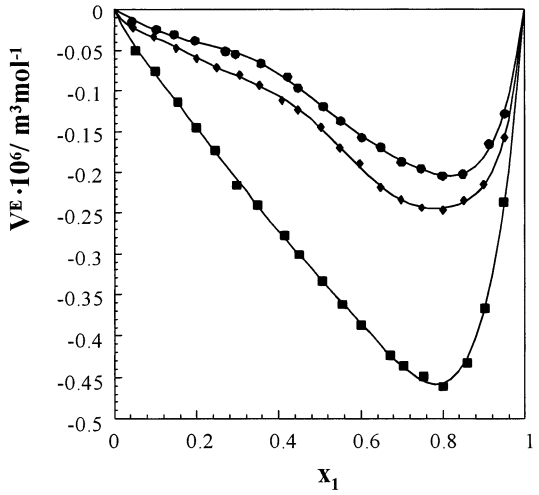

Figure 1. Excess volumes (V^E) for ketones (1) {2-butanone (●); 3-pentanone (◆); 4-methyl-2-pentanone (■)} + sunflower oil (2) at 298.15 K.

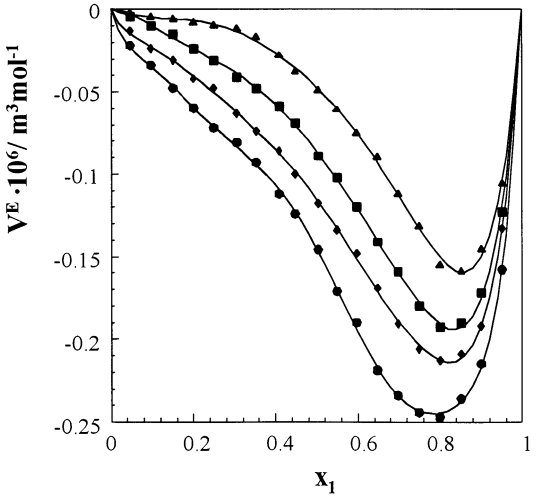

Figure 2. Excess volumes (V^E) for 3-pentanone (1) + sunflower oil (2) at 283.15 K (▲), 288.15 K (■), 293.15 (◆), and 298.15 K (●) versus mole fraction of 3-pentanone.

Table 13. Adjustable Parameters and Standard Deviation for Variation of Refractive Indices−Mole Fraction Curves for Ketone + Vegetable Oil Systems at Different Temperatures

parameter	T = 298.15 K	T = 293.15 K	T = 288.15 K
	2-Butanone + Sunflower Oil		
a_1	0.16043	0.15928	0.15819
a_2	−0.13696	−0.13921	−0.13715
a_3	0.1205	0.12318	0.12335
a_4	−0.044	−0.0331	−0.03278
a_5	0.02392	−0.00645	−0.01565
a_6	−0.1827	−0.19654	−0.19466
a_7	0.15515	0.19182	0.20176
σ	1.69×10^{-4}	1.69×10^{-4}	1.82×10^{-4}
	3-Pentanone + Sunflower Oil		
a_1	0.13369	0.13263	0.13166
a_2	−0.1111	−0.10985	−0.10867
a_3	0.08965	0.0891	0.09233
a_4	−0.03524	−0.03766	−0.04141
a_5	0.0202	0.02384	0.01116
a_6	−0.12562	−0.12458	−0.11773
a_7	0.11085	0.10556	0.11286
σ	1.06×10^{-4}	8.99×10^{-5}	1.06×10^{-4}
	4-Methyl-2-pentanone + Sunflower Oil		
a_1	0.12293	0.12129	0.12105
a_2	−0.0965	−0.09675	−0.09596
a_3	0.07834	0.07638	0.0795
a_4	−0.04252	−0.03379	−0.0399
a_5	0.02173	0.02665	0.01408
a_6	−0.08047	−0.09096	−0.08183
a_7	0.07013	0.06927	0.07777
σ	9.33×10^{-5}	9.84×10^{-5}	7.68×10^{-5}

Table 14. Adjustable Parameters and Standard Deviation for Variation of Isentropic Compressibility−Mole Fraction Curves for Ketone + Vegetable Oil Systems at 298.15 K

parameter	2-butanone	3-pentanone	4-methyl-2-pentanone
a_1	−626.7	−532.2	−611.3
a_2	542.6	459.7	512.7
a_3	−287.7	−256.9	−299.1
a_4	102.4	94.3	187.3
a_5	−891.4	−652.4	−669.3
a_6	964.2	692.3	603.3
σ	2.23	1.01	1.04

$\sigma(V^E)$. These coefficients were used to calculate the solid curves in Figures 1−5. In Figure 1, excess molar volumes of the ketones + olive oil are plotted versus the mole fraction of ketone. Figure 2 shows excess molar volumes of isopropyl ketone + olive oil versus mole fraction of ketone at different temperatures.

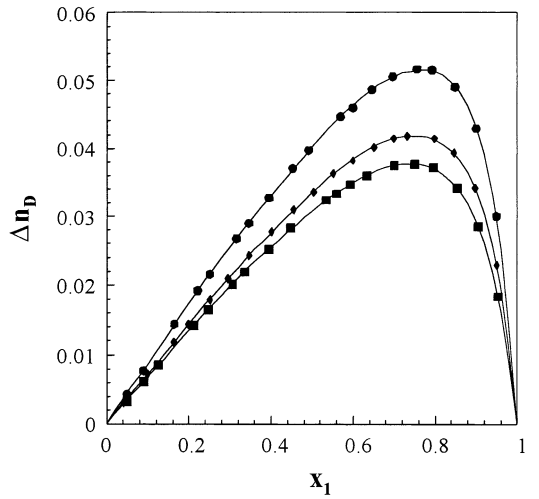

Figure 3. Variation of the refractive index (Δn_D) for ketones (1) {2-butanone (●); 3-pentanone (◆); 4-methyl-2-pentanone (■)} + sunflower oil (2) at 298.15 K.

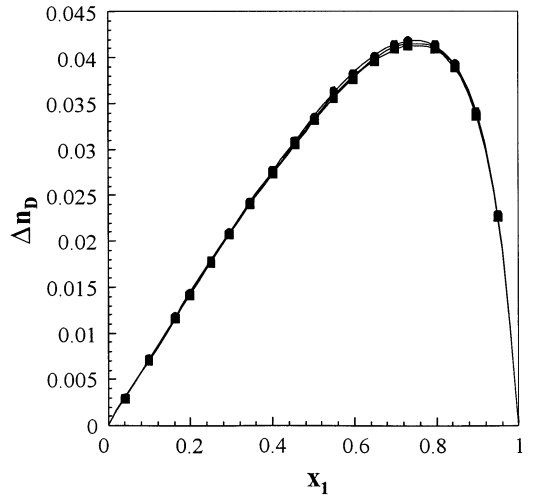

Figure 4. Variation of the refractive index (Δn_D) for 3-pentanone (1) + sunflower oil (2) at 288.15 K (■), 293.15 K (◆), and 298.15 K (●) versus mole fraction of 3-pentanone.

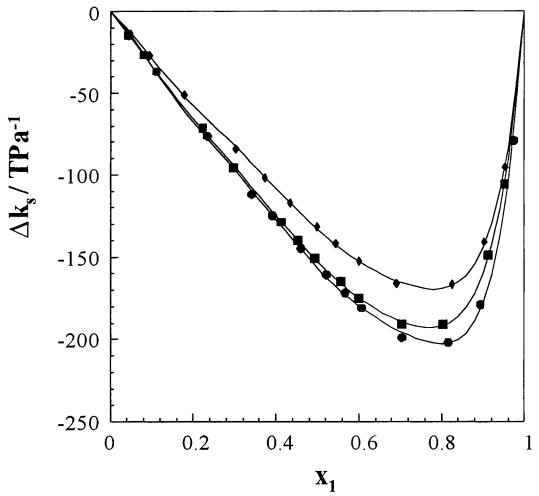

Figure 5. Variation of the isentropic compressibility (Δk_s) for ketones (1) {2-butanone (●); 3-pentanone (◆); 4-methyl-2-pentanone (■)} + sunflower oil (2) at 298.15 K.

Table 15. Average Standard Deviations for Predicted Densities with Respect to Corresponding Data for the Mixtures of Ketones with Sunflower Oil at 298.15 K

	$\delta\rho$/kg·m^{-3}	
	Rackett	Rackett modified
2-butanone	10.80	17.56
3-pentanone	7.42	19.87
4-methyl-2-pentanone	21.63	5.90

The vegetable oil molecules are triglycerides (more than 99%). The difference between the simple esters is that they present two slightly different zones: a central polar axis built up by three ester groups (alcoxycarboxylic) and three long nonpolar chains. The molecule is voluminous but it is not compact, which means that there are hollow spaces between the nonpolar chains where small molecules with low interaction could be introduced. The absence of interactions of ketone molecules with the triglyceride allows the small ketone molecules to occupy some of the empty space in the triglyceride structure and to show a negative excess volume. As the size of the ketone increases, the steric hindrance grows and the excess volume decreases. In all of the studied mixtures, the excess volume increases when the temperature is increased (Figure 2). Figure 3 shows the variation of the refractive index of the mixtures with mole fraction of ketone. Deviations from ideality were found, and this deviation increases as the size of the ketone increases. Figure 4 depicts the variation of the refractive index of the studied mixtures at different temperatures. Very similar results were found at the three tested temperatures.

The variation of the isentropic compressibilities of the mixtures versus mole fraction of ketone at 298.15 K is plotted in Figure 5; Δk_s values are negative over the whole concentration range for all the systems. The negative Δk_s values may be attributed to the existence of dispersion and dipolar interactions between unlike molecules.

The estimated densities of the mixtures were calculated with the Rackett equation[9] and the modified Rackett equation,[10] which is an improved equation for prediction of saturated liquid density,

$$V = (RT_c/P_c)Z_{RA}^{[1+(1-T_r)^{2/7}]} \tag{7}$$

where V is the molar volume, T_r is the reduced temperature, T_c and P_c are the critical properties, and Z_{RA} is an acentric factor dependent parameter that varies according to the molecular structure parameter. Table 15 presents the standard average deviation ($\delta\rho$) for the estimated densities of the mixtures with respect to the experimental data at 298.15 K. On the basis of both evaluations, it can be concluded that the most accurate equation to predict the density of the mixtures is the modified Rackett equation. In these cases, standard deviations were less than 3%. The deviations using the Rackett equation were less than 4%.

The experimental refractive indices were compared with the estimated ones by means of the mixing rules[11] proposed by Lorentz−Lorenz (eq 8), Dale and Gladstone (eq 9), Arago and Biot (eq 10), Eykman (eq 11), Kurtz and Ward (eq 12), and Oster (eq 13):

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2}\right)\right] \tag{8}$$

$$n_D - 1 = \sum_{i=1}^{N}[\phi_i(n_{Di} - 1)] \tag{9}$$

$$n_D = \sum_{i=1}^{N}(\phi_i n_{Di}) \tag{10}$$

$$\frac{n_D^2 - 1}{n_D^2 + 0.4} = \sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 0.4}\right)\right] \tag{11}$$

$$n_D^2 - 1 = \sum_{i=1}^{N}[\phi_i(n_{Di}^2 - 1)] \tag{12}$$

$$\frac{(n_D^2 - 1) - (2n_D^2 + 1)}{n_D^2} = \sum_{i=1}^{N}\left[\phi_i\left(\frac{(n_{Di}^2 - 1) - (2n_{Di}^2 + 1)}{n_{Di}^2}\right)\right] \tag{13}$$

where

$$\phi_i = \frac{\left[\frac{x_i M_i}{\rho_i}\right]}{\sum_{i=1}^{N}\left[\frac{x_i M_i}{\rho_i}\right]} \tag{14}$$

The results of the comparison with the experimental data appear in Table 16, in which the average deviations (δn_D)

Table 16. Average Standard Deviations for Predicted Refractive Indices with Respect to Corresponding Data for the Mixtures of Ketones with Sunflower Oil at 298.15 K

	δn_D					
	Lorentz (eq 8)	Gladstone (eq 9)	Arago (eq 10)	Eykman (eq 11)	Kurtz (eq 12)	Oster (eq 13)
2-butanone	0.000 69	0.000 29	0.000 29	0.000 4	0.000 25	0.000 16
3-pentanone	0.000 64	0.000 32	0.000 32	0.000 41	0.000 1	0.000 15
4-methyl-2-pentanone	0.000 82	0.000 5	0.000 5	0.000 6	0.000 2	0.000 32

Table 17. Average Standard Deviations for Predicted Speeds of Sound with Respect to Corresponding Data for the Mixtures of Ketones with Sunflower Oil at 298.15 K

	δk_s/T·Pa^{-1}	
	Danusso (eq 15)	Nomoto (eq 16)
2-butanone	8.2	6.8
3-pentanone	9.4	3.6
4-methyl-2-pentanone	15.3	2.2

between experimental and estimated data are shown. A good agreement is observed; there were just small differences in all cases. As shown in Table 16 for 298.15 K, the deviations corresponding to the mixture rules proposed by different authors are less than 0.1% for the binary mixtures.

To compare experimental data of the speed of sound of the mixtures (v) with the theoretical data, two equations have been used,[12]

$$v = \frac{1}{\rho}\left[\frac{1}{M}\left(\frac{n_1 M_1}{\rho_1^2 v_1^2} + \frac{n_2 M_2}{\rho_2^2 v_2^2}\right)\right]^{-1/2} \quad (15)$$

$$v = \left(\frac{n_1 R_1 + n_2 R_2}{n_1 v_1 + n_2 v_2}\right)^3 \quad (16)$$

where

$$M = n_1 M_1 + n_2 M_2 \quad (17)$$

$$R = V v^{1/3} \quad (18)$$

$$V = n_1 V_1 + n_2 V_2 \quad (19)$$

where V_1 and V_2 are the molar volumes of the pure components. Table 17 summarizes the results of the standard deviation of the sound velocity computed by these formulas. For both equations, the percentage deviations were less than 2%.

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