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Measurements of Density and Refractive Index of Soybean Oil + Short Aliphatic Alcohols

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Densities and refractive indices of binary mixtures containing soybean oil + (methanol, ethanol, 1-propanol, 2-propanol, or 1-butanol) have been measured from 283.15 to 298.15 K at atmospheric pressure, over the complete homogeneous composition range. Derived properties, such as excess molar volumes, partial excess molar volumes, and excess isobaric compressibilities, have been determined. Values of physical properties were compared with the results obtained by different prediction methods; the results were analyzed according to the non-ideality and large differences of molecular characteristics of the compounds included in this study.

KEY WORDS: aliphatic alcohols; densities; derived magnitudes; excess molar volumes; estimation; refractive indices; soybean oil.

1. INTRODUCTION

In order for chemical engineers to successfully execute conceptual design, plant operations, maintenance and product studies, process modeling and experimental research on thermodynamic properties of mixtures of interest are performed. Food technology is not an exception, and a knowledge of the thermodynamic properties and phase equilibria of fatties and oils is of practical interest in the industrial manufacture of these products. Thus, in the last few years considerable effort has been applied in the field of thermodynamic properties of oils and mixtures with different solvents related to process technology. Such properties are strongly dependent

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on the presence of double bonds, chain lengths, and isomeric structures of fatty acids and molecular characteristics of triglycerides in solvents. Despite these efforts, a considerable lack of accuracy or thermodynamic consistency in some data in the open literature is observed, resulting from the different origins of fatty substances and the complexity of their composition and structure. It is not always possible to obtain reliable values, specially when concerned with mixtures at non-standard conditions. In the scope of investigating the physical properties related to equipment design in the natural oils industry and new environmental friendly procedures of extraction and refining such as modified distillation or wintering, we present as a continuation of previous studies [1–4] the temperature dependence of the density and refractive index of short aliphatic alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol) + natural soybean oil over the range from 283.15 to 298.15 K at atmospheric pressure, as a function of molar fraction. From the experimental values, derived properties were computed, using a temperature-dependent Redlich–Kister type polynomial. Because of the expense of experimental measurements, current process design is strongly computer oriented. Several models have been evaluated in this study; the selection of models was based on ease of use, accuracy, and range of application. The temperature and functional dependence of the partial molar quantities are also analyzed and discussed.

2. EXPERIMENTAL

The substances employed as solvents were supplied by LabScan (methanol, > 99.9 mol%; 1-propanol, > 99.5 mol%, and 2-propanol, > 99.8 mol%), Riedel de Haën (ethanol, > 99.8 mol%), and HiperSolv (1-butanol, > 99.8 mol%). Their mole-fraction purities were better than 0.995 for the chemicals used, as determined by gas–liquid chromatography, in accordance with vendor specifications. Values of the measured properties for pure solvents were consistent with those published in the open literature (Table I). Molecular sieve (3Å) was used to dehydrate the alcohols. The general procedure for handling the chemicals manipulation and the experimental techniques applied in our laboratory are discussed in a previous paper [1]. The soybean oil was supplied by Moyresa and analyzed by means of a gas chromatograph (Shimadzu GC-14B) equipped with a flame detector. Chromatographic techniques and the chemical procedure analysis for fatty acids were described previously [9]. The composition of the fatty acids is given in Table II. From this composition, the average molar mass

Table I. Comparison of Experimental Data with Literature for Pure Components at 298.15 K

Component	ρ (g·cm^{-3})		n_D	
	Expt.	Lit.[a]	Expt.	Lit.
Soybean oil	0.91596	0.921–0.924 [b]	1.47260	1.47476[c]
Methanol	0.78637	0.78637[d]	1.32657	1.32652
Ethanol	0.78513	0.78509	1.35926	1.35941
1-Propanol	0.79952	0.79975	1.38305	1.3837
2-Propanol	0.78095	0.78126[d]	1.37485	1.3752
1-Butanol	0.80614	0.80600	1.39708	1.39741

[a] TRC Thermodynamic tables [5].
[b] Mehlenbacher [6].
[c] Lanz [7].
[d] Riddick et al. [8].

Table II. Characteristics of the Soybean Oil

Composition (mass %)	53.9 Linoleic 23.95 Oleic 10.9 Palmitic 6.5 Linolenic 4.5 Stearic 0.55 Behenic
Acid value	0.105
Saponification value	191.5
Iodine value	129.3
Peroxide value	12.6
Wetness and volatiles	0.018

of this oil has been computed according to the following expression:

$$M_{\text{oil}} = 3\left(\sum_{i=1}^{N} x_i M_i\right) + M_{\text{CH–C–CH}} \tag{1}$$

where x_i is the mole fraction and M_i is the molar mass of each fatty acid, N is the number of fatty acids found by analysis, and $M_{\text{CH–C–CH}}$ is the molar mass contribution of the triglyceride molecule fraction. The computed average molar mass of soybean oil was 873.01 g·mol^{-1}. The variation in the composition due to different samples affects mainly the mono- and poly-unsaturated fatty acids the change in molar mass is less than ± 1 g·mol^{-1}.

The densities of the pure substances and binary mixtures were measured with a digital vibrating tube analyzer (Anton Paar DSA-48) with an uncertainty of $\pm 0.00003\,\mathrm{g\cdot cm^{-3}}$ and the refractive indices by an automatic refractometer (ABBEMAT-HP Dr Kernchen), which measures refractive index at the wavelength of the line D of sodium (589.3 nm), with an uncertainty of ± 0.00001. The mixtures were prepared by mass using a Salter ER-182A balance with an uncertainty of $\pm 1 \times 10^{-4}$ g, covering the whole composition range of the binary mixtures. Before each series of measurements, the instruments were calibrated in accordance with the instructions, no systematic errors being detected in the measurements. The uncertainty in the calculation of excess molar volumes was estimated to be better than $5.6 \times 10^{-3}\,\mathrm{cm^3\cdot mol^{-1}}$.

3. RESULTS AND DATA CORRELATION

3.1. Data Correlation

The densities, refractive indices, and derived properties are given in Tables III and IV. The excess molar volumes were determined using the following equation:

$$V_{\mathrm{m}}^{\mathrm{E}} = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{2}$$

In this equation, ρ is the density, M_i is the molar mass of component i [10], ρ_i is the density of pure component i, and N is the number of components in the mixture. A Redlich–Kister type equation was used to correlate isentropic compressibilities on mixing and excess molar volumes, of the binary mixtures, by the method of least squares with all points weighted equally [11]. This equation can be expressed as

$$\delta Q = x_i x_j \sum_{p=0}^{m} B_p \left(x_i - x_j\right)^p \tag{3}$$

where δQ is $V_m^E / (\mathrm{cm^3\cdot mol^{-1}})$. The degree of this equation (m parameter) was optimized by applying the F-test [12] by means a procedure based on the Marquardt algorithm [13]. Figure 1 shows the experimental points of $V_{\mathrm{m}}^{\mathrm{E}}$ plotted against mole fraction as well as the fitted curves. Table V gives infinite dilution partial excess molar volumes. In this expression the value of the property and the number of experimental data are represented by z and n, respectively.

Table III. Experimental Data of Density of the Binary Mixtures at the Studied Temperatures

x_1	ρ (g·cm^3) 298.15 K	ρ (g·cm^{-3}) 293.15 K	ρ (g·cm^{-3}) 288.15 K	ρ (g·cm^{-3}) 283.15 K	V^E (cm^3·mol^{-1}) 298.15 K	V^E (cm^3·mol^{-1}) 293.15 K	V^E (cm^3·mol^{-1}) 288.15 K	V^E (cm^3·mol^{-1}) 283.15 K	$\alpha^E \times 10^6$ (K^{-1}) 298.15 K	$\alpha^E \times 10^6$ (K^{-1}) 293.15 K	$\alpha^E \times 10^6$ (K^{-1}) 288.15 K	$\alpha^E \times 10^6$ (K^{-1}) 283.15 K
Methanol (1) + soybean oil (2)												
0.0430	0.91570	0.91911	0.92257	0.92604	0.012	0.010	−0.002	−0.018	−0.726	1.165	3.070	4.990
0.0864	0.91542	0.91884	0.92231	0.92579	0.019	0.016	−0.004	−0.029	0.461	2.752	5.061	7.388
0.1538	0.91493	0.91838	0.92185	0.92535	0.030	0.005	−0.010	−0.044	4.370	5.542	6.722	7.912
0.1878	0.91466	0.91812	0.92160	0.92511	0.032	−0.003	−0.020	−0.058	6.686	6.926	7.168	7.412
0.2338	0.91426	0.91775	0.92122	0.92474	0.029	−0.015	−0.031	−0.067	9.690	8.634	7.570	6.498
0.3071	0.91353	0.91704	0.92053	0.92405	0.020	−0.031	−0.047	−0.077	13.426	10.754	8.060	5.347
0.3528	0.91300	0.91652	0.92002	0.92355	0.012	−0.038	−0.055	−0.086	14.887	11.639	8.366	5.067
0.4033	0.91233	0.91586	0.91938	0.92291	0.001	−0.046	−0.069	−0.093	15.809	12.251	8.665	5.052
0.4386	0.91180	0.91533	0.91886	0.92240	−0.009	−0.051	−0.075	−0.099	16.187	12.497	8.777	5.029
0.5018	0.91066	0.91422	0.91776	0.92131	−0.021	−0.063	−0.083	−0.103	16.969	12.746	8.490	4.200
0.5480	0.90965	0.91322	0.91677		−0.029	−0.068	−0.085		18.339	12.975	7.568	
Ethanol (1) + soybean oil (2)												
0.0364	0.91561	0.91904	0.92249	0.92594	0.047	0.029	0.027	0.020	3.178	2.101	1.016	−0.077
0.1054	0.91493	0.91837	0.92183	0.92529	0.084	0.063	0.051	0.044	6.143	4.322	2.487	0.639
0.1530	0.91440	0.91785	0.92131	0.92479	0.110	0.085	0.073	0.060	6.848	5.093	3.324	1.543
0.2127	0.91366	0.91712	0.92060	0.92408	0.136	0.109	0.093	0.078	7.250	5.797	4.333	2.857
0.2557	0.91307	0.91653	0.92002	0.92351	0.150	0.124	0.101	0.085	7.677	6.388	5.089	3.780
0.3043	0.91232	0.91580	0.91930	0.92280	0.161	0.129	0.104	0.086	8.631	7.320	5.999	4.667
0.3424	0.91168	0.91516	0.91867	0.92218	0.162	0.132	0.105	0.088	9.856	8.308	6.749	5.178
0.4161	0.91022	0.91373	0.91725	0.92077	0.159	0.127	0.100	0.082	13.518	10.876	8.214	5.532
0.4435	0.90960	0.91311	0.91664	0.92017	0.157	0.123	0.097	0.077	15.270	12.009	8.723	5.411
0.5108	0.90780	0.91135	0.91490	0.91845	0.148	0.107	0.080	0.059	20.126	14.947	9.727	4.466
0.5551	0.90637	0.90994	0.91352	0.91707	0.136	0.094	0.060	0.046	23.386	16.751	10.063	3.323
0.6107	0.90419	0.90781	0.91141	0.91497	0.119	0.067	0.035	0.026	26.887	18.430	9.905	1.313
0.6466	0.90249	0.90613	0.90974	0.91331	0.100	0.050	0.022	0.015	28.407	18.915	9.346	−0.299
0.7141	0.89840	0.90207	0.90566		0.050	0.013	0.005		28.577	17.850	7.033	

Table III. (*Continued*)

x_1	ρ (g·cm^3) 298.15 K	ρ (g·cm^{-3}) 293.15 K	ρ (g·cm^{-3}) 288.15 K	ρ (g·cm^{-3}) 283.15 K	V^E (cm^3·mol^{-1}) 298.15 K	V^E (cm^3·mol^{-1}) 293.15 K	V^E (cm^3·mol^{-1}) 288.15 K	V^E (cm^3·mol^{-1}) 283.15 K	$\alpha^E \times 10^6$ (K^{-1}) 298.15 K	$\alpha^E \times 10^6$ (K^{-1}) 293.15 K	$\alpha^E \times 10^6$ (K^{-1}) 288.15 K	$\alpha^E \times 10^6$ (K^{-1}) 283.15 K
1-Propanol (1) + soybean oil (2)												
0.0379	0.91553	0.91896	0.92242	0.92588	0.070	0.052	0.034	0.026	4.021	2.933	1.836	0.731
0.1000	0.91480	0.91826	0.92172	0.92520	0.142	0.100	0.087	0.063	7.708	5.851	3.979	2.094
0.1417	0.91428	0.91773	0.92120	0.92468	0.168	0.139	0.120	0.100	8.801	6.901	4.985	3.055
0.1998	0.91348	0.91694	0.92042	0.92390	0.199	0.167	0.144	0.128	9.318	7.677	6.024	4.358
0.2452	0.91279	0.91626	0.91974	0.92323	0.214	0.179	0.160	0.140	9.418	8.048	6.667	5.275
0.3245	0.91139	0.91487	0.91837	0.92188	0.237	0.204	0.178	0.150	10.024	8.853	7.673	6.484
0.3595	0.91068	0.91417	0.91768	0.92119	0.245	0.209	0.180	0.156	10.742	9.438	8.124	6.799
0.3959	0.90987	0.91337	0.91688	0.92040	0.249	0.211	0.187	0.160	11.896	10.260	8.611	6.949
0.4480	0.90856	0.91207	0.91560	0.91913	0.248	0.212	0.182	0.155	14.353	11.855	9.338	6.801
0.5048	0.90688	0.91041	0.91396	0.91749	0.237	0.198	0.165	0.146	18.119	14.140	10.130	6.088
0.5624	0.90482	0.90838	0.91194	0.91548	0.220	0.181	0.147	0.130	22.943	16.913	10.835	4.709
0.5928	0.90353	0.90713	0.91069	0.91424	0.215	0.163	0.135	0.118	25.782	18.480	11.118	3.698
0.6531	0.90047	0.90411	0.90768	0.91125	0.194	0.135	0.113	0.097	31.647	21.547	11.365	1.101
0.7027	0.89724	0.90092	0.90451	0.90808	0.168	0.108	0.089	0.077	36.220	23.716	11.107	−1.602
0.7477	0.89351	0.89723	0.90083	0.90442	0.137	0.078	0.065	0.055	39.639	25.071	10.379	−4.431
0.8019	0.88750	0.89123	0.89486	0.89850	0.085	0.043	0.033	0.019	41.989	25.425	8.721	−8.120
0.8721	0.87529	0.87909	0.88276	0.88642	−0.003	−0.035	−0.037	−0.039	39.992	22.653	5.163	−12.474
0.9338	0.85486	0.85879	0.86254	0.86628	−0.032	−0.057	−0.055	−0.056	29.914	15.604	1.162	−13.407
0.9638	0.83733	0.84134	0.84515	0.84899	−0.029	−0.049	−0.046	−0.050	20.088	9.899	−0.388	−10.769
2-Propanol (1) + soybean oil (2)												
0.0406	0.91542	0.91885	0.92230	0.92576	0.081	0.064	0.057	0.049	1.886	1.767	1.646	1.525
0.1002	0.91457	0.91802	0.92148	0.92495	0.178	0.148	0.136	0.123	4.418	4.031	3.642	3.249
0.1490	0.91382	0.91727	0.92074	0.92422	0.234	0.209	0.192	0.175	6.318	5.668	5.012	4.352
0.1941	0.91306	0.91651	0.91999	0.92349	0.281	0.262	0.240	0.210	7.980	7.067	6.147	5.220
0.2498	0.91201	0.91549	0.91898	0.92249	0.338	0.301	0.277	0.245	9.979	8.723	7.456	6.180
0.2939	0.91109	0.91458	0.91809	0.92160	0.370	0.332	0.298	0.271	11.586	10.035	8.473	6.898
0.3719	0.90922	0.91274	0.91627	0.91980	0.403	0.357	0.320	0.289	14.675	12.508	10.325	8.125
0.4009	0.90843	0.91196	0.91549	0.91903	0.407	0.360	0.328	0.295	15.964	13.516	11.049	8.562
0.4519	0.90687	0.91043	0.91397	0.91752	0.412	0.356	0.326	0.294	18.504	15.453	12.376	9.276
0.4988	0.90522	0.90880	0.91236	0.91592	0.403	0.347	0.313	0.283	21.224	17.455	13.654	9.824

0.5448	0.90333	0.90694	0.91052	0.91409	0.390	0.329	0.294	0.267	24.326	19.653	14.942	10.193
0.6044	0.90038	0.90401	0.90763	0.91123	0.359	0.306	0.265	0.234	29.077	22.867	16.606	10.293
0.6488	0.89770	0.90134	0.90498	0.90860	0.319	0.275	0.236	0.207	33.184	25.513	17.778	9.980
0.7056	0.89333	0.89706	0.90073	0.90438	0.281	0.221	0.186	0.158	39.079	29.118	19.071	8.940
0.7506	0.88884	0.89262	0.89633	0.90002	0.244	0.184	0.149	0.120	44.077	31.990	19.797	7.502
0.7987	0.88254	0.88642	0.89021	0.89391	0.191	0.127	0.088	0.068	49.294	34.758	20.091	5.298
0.8502	0.87308	0.87702			0.107	0.055			53.623	36.642		
					1-Butanol (1) + soybean oil (2)							
0.0459	0.91542	0.91883	0.92228	0.92574	0.037	0.034	0.026	0.018	−0.024	0.540	1.109	1.682
0.0869	0.91489	0.91831	0.92176	0.92522	0.067	0.062	0.056	0.049	0.950	1.415	1.885	2.358
0.1473	0.91402	0.91746	0.92091	0.92438	0.125	0.105	0.102	0.089	3.609	3.191	2.769	2.345
0.1983	0.91321	0.91666	0.92012	0.92360	0.170	0.146	0.128	0.118	6.575	4.977	3.368	1.747
0.2446	0.91240	0.91586	0.91934	0.92281	0.194	0.166	0.144	0.136	9.540	6.709	3.857	0.983
0.3047	0.91122	0.91470	0.91818	0.92166	0.220	0.183	0.165	0.153	13.420	8.968	4.483	−0.037
0.3475	0.91027	0.91377	0.91725	0.92074	0.235	0.189	0.175	0.158	16.009	10.503	4.955	−0.636
0.3959	0.90907	0.91258	0.91607	0.91957	0.250	0.197	0.180	0.166	18.604	12.096	5.536	−1.073
0.4492	0.90755	0.91109	0.91459	0.91808	0.256	0.199	0.181	0.171	20.915	13.608	6.244	−1.176
0.4898	0.90622	0.90977	0.91328	0.91678	0.258	0.202	0.182	0.170	22.221	14.555	6.829	−0.958
0.5446	0.90414	0.90770	0.91122	0.91474	0.254	0.198	0.179	0.165	23.309	15.515	7.659	−0.258
0.6055	0.90133	0.90490	0.90843	0.91196	0.233	0.184	0.167	0.153	23.591	16.119	8.587	0.996
0.6429	0.89924	0.90282	0.90636	0.90991	0.216	0.170	0.154	0.137	23.298	16.238	9.121	1.948
0.6981	0.89551	0.89908	0.90265	0.90621	0.173	0.144	0.124	0.110	22.276	16.056	9.786	3.466
0.7503	0.89090	0.89449	0.89807	0.90165	0.137	0.113	0.098	0.083	20.745	15.482	10.177	4.828
0.7993	0.88514	0.88875	0.89235	0.89595	0.108	0.086	0.074	0.060	18.882	14.560	10.202	5.808
0.8512	0.87668	0.88032	0.88395	0.88757	0.065	0.048	0.036	0.028	16.474	13.090	9.677	6.235
0.9001	0.86480	0.86849	0.87214	0.87578	0.026	0.011	0.006	0.002	13.616	11.010	8.382	5.731
0.9631	0.83740	0.84117	0.84489	0.84861	−0.008	−0.016	−0.018	−0.021	7.627	6.133	4.626	3.105

$$\sigma = \sqrt{\frac{\sum_{i}^{n} \left(z_{\text{exp}} - z_{\text{pred}}\right)^2}{n}} \tag{4}$$

As was reported in previous studies [1–4], this kind of mixture shows phase splitting for molecules with high activated hydroxyl groups, due to the steric hindrance. In fact, three mixtures (soybean oil + methanol, ethanol, or 2-propanol) show inmiscibility at high concentrations of the solvent. The solubility limits applied in this work are reported in a recent publication [14]. The reported data are associated with the homogeneous range at each studied temperature. In almost all cases, an expansive tendency is observed with increasing composition of the solvent, the highest steric hindrance being observed for the 2-propanol mixture due to its branched end and active hydroxyl group. As exceptions, mixtures of methanol show a sigmoid tendency as do solvent-rich mixtures of 1-propanol and 1-butanol. This change in trend is due to the formation of "iceberg" structures among alcohol molecules and a strong ordered structure at infinite dilution of triglyceride.

3.2. Partial Excess Molar Volumes

Partial molar quantities are important in the study of the dependence of an extensive property on the phase composition at constant pressure and temperature, since it shows a variation with mole fraction. They should be applied to any extensive property of a single-phase system such as volume, Gibbs energy, etc. If we let E represent any extensive property of a single phase which is a function of pressure, temperature, and number of moles of the components, the differential of E is expressed as

$$\delta E = \left(\frac{\partial E}{\partial T}\right)_{P,n} \mathrm{d}T + \left(\frac{\partial E}{\partial P}\right)_{T,n} \mathrm{d}P + \sum_{i=1}^{N} \left(\frac{\partial E}{\partial n_i}\right)_{T,P,n} \mathrm{d}n_i \tag{5}$$

where the quantity $\left(\frac{\partial E}{\partial n_i}\right)_{T,P,n}$ is defined as the partial molar quantity of the ith component in the phase, and N refers to all other components, showing the finite change in the property on the addition of 1 mole of component i in an infinite quantity of solution at constant temperature and pressure. For what is referred to as an excess property, the partial excess molar volume of a component in a binary mixture can

Table IV. Experimental Refractive Indices of the Binary Mixtures at the Studied Temperatures

x_1	n_D 298.15 K	n_D 293.15 K	n_D 288.15 K
	Methanol (1) + soybean oil (2)		
0.0430	1.47239	1.47427	1.47615
0.0864	1.47205	1.47399	1.47580
0.1538	1.47154	1.47349	1.47534
0.1878	1.47128	1.47315	1.47504
0.2338	1.47080	1.47275	1.47464
0.3071	1.46999	1.47194	1.47390
0.3528	1.46944	1.47135	1.47332
0.4033	1.46871	1.47060	1.47253
0.4386	1.46789	1.47008	1.47204
0.5018	1.46674	1.46887	1.47070
0.5480	1.46587	1.46801	1.46960
	Ethanol (1) + soybean oil (2)		
0.0364	1.47241	1.47424	1.47612
0.1054	1.47182	1.47368	1.47557
0.1530	1.47152	1.47325	1.47529
0.2127	1.47107	1.47263	1.47473
0.2557	1.47071	1.47234	1.47449
0.3043	1.46970	1.47153	1.47373
0.3424	1.46909	1.47107	1.47310
0.4161	1.46788	1.46986	1.47186
0.4435	1.46733	1.46938	1.47125
0.5108	1.46584	1.46780	1.47004
0.5551	1.46466	1.46656	1.46850
0.6107	1.46275	1.46483	1.46686
0.6466	1.46128	1.46324	1.46522
0.7141	1.45777	1.45962	1.46162
	1-Propanol (1) + soybean oil (2)		
0.0379	1.47238	1.47428	1.47613
0.1000	1.47185	1.47374	1.47557
0.1417	1.47145	1.47335	1.47524
0.1998	1.47085	1.47275	1.47463
0.2452	1.47032	1.47226	1.47414
0.3245	1.46980	1.47125	1.47313
0.3595	1.46876	1.47073	1.47258
0.3959	1.46818	1.47013	1.47201
0.4480	1.46716	1.46913	1.47111
0.5048	1.46584	1.46814	1.46991
0.5624	1.46434	1.46635	1.46832
0.5928	1.46337	1.46527	1.46722
0.6531	1.46096	1.46301	1.46495
0.7027	1.45896	1.46048	1.46245
0.7477	1.45562	1.45767	1.45965

Table IV. (*Continued*)

x_1	n_D 298.15 K	n_D 293.15 K	n_D 288.15 K
0.8019	1.45096	1.45295	1.45485
0.8721	1.44147	1.44354	1.44554
	Methanol (1) + soybean oil (2)		
0.9338	1.42553	1.42756	1.42984
0.9638	1.41189	1.41426	1.41620
	2-Propanol (1) + soybean oil (2)		
0.0406	1.47230	1.47419	1.47604
0.1002	1.47184	1.47382	1.47551
0.1490	1.47120	1.47310	1.47499
0.1941	1.47086	1.47259	1.47453
0.2498	1.46993	1.47199	1.47382
0.2939	1.46928	1.47128	1.47332
0.3719	1.46805	1.47003	1.47194
0.4009	1.46745	1.46941	1.47144
0.4519	1.46632	1.46838	1.47054
0.4988	1.46525	1.46709	1.46917
0.5448	1.46390	1.46590	1.46803
0.6044	1.46180	1.46399	1.46602
0.6488	1.45974	1.46182	1.46376
0.7056	1.45660	1.45884	1.46062
0.7506	1.45316	1.45521	1.45743
0.7987	1.44868	1.45075	1.45286
0.8502	1.44167	1.44391	
	1-Butanol (1) + soybean oil (2)		
0.0459	1.47230	1.47421	1.47604
0.0869	1.47197	1.47383	1.47574
0.1473	1.47135	1.47331	1.47514
0.1983	1.47095	1.47294	1.47464
0.2446	1.47029	1.47223	1.47410
0.3047	1.46951	1.47147	1.47330
0.3475	1.46888	1.47082	1.47283
0.3959	1.46800	1.47003	1.47191
0.4492	1.46702	1.46901	1.47088
0.4898	1.46617	1.46809	1.46998
0.5446	1.46486	1.46664	1.46860
0.6055	1.46283	1.46470	1.46635
0.6429	1.46136	1.46333	1.46532
0.6981	1.45886	1.46087	1.46264
0.7503	1.45562	1.45760	1.45957
0.7993	1.45169	1.45357	1.45555
0.8512	1.44585	1.44775	1.44976
0.9001	1.43758	1.43955	1.44159
0.9631	1.41879	1.42068	1.42261

be determined from the excess molar volume by means of the following expression:

$$\overline{V}_i^{\mathrm{E}} = V^{\mathrm{E}} + (1 - x_i)\left(\frac{\mathrm{d}V^{\mathrm{E}}}{\mathrm{d}x_i}\right) \tag{6}$$

where the differential term is calculated from the Redlich–Kister expression used to correlate the excess molar volumes. Expressions for the partial excess molar volumes are as follows:

$$\overline{V}_1^{\mathrm{E}} = (1 - x_1)^2 \left[\sum_{p=0}^{m} B_p (2x_1 - 1)^p + x_1 \sum_{p=1}^{m} 2pB_p (2x_1 - 1)^{p-1}\right] \tag{7}$$

$$\overline{V}_2^{\mathrm{E}} = (1 - x_2)^2 \left[\sum_{p=0}^{m} B_p (1 - 2x_2)^p + x_2 \sum_{p=1}^{m} (-2)pB_p (1 - 2x_2)^{p-1}\right] \tag{8}$$

where the symbols retain the meaning noted above. From Eqs. (7) and (8), the corresponding limiting partial excess molar volumes can be determined by considering x_i as zero in each expression, such limiting values depending only on these correlation parameters. Figure 2a, b shows plots of partial excess molar volumes with mole fraction for the six binary mixtures. In Table V, the values of limiting partial excess molar volumes at 298.15 K for the binary mixtures are reported. In the figure a similar behavior for all the studied mixtures is observed, showing a strong decreasing negative trend. A lower initial negative effect is observed for a higher chain of alcohol. Only methanol mixtures showed a sigmoid behavior as a consequence of the behavior observed for the excess molar volume (Fig. 3). All mixtures (and methanol) show a maximum (or minimum) for 0.2 mole fraction.

3.3. Derived Properties

A frequently derived property for industrial mixtures is the temperature dependence of volumetry which is expressed as the isobaric expansivity or thermal expansion coefficient (α). The data reported in the literature normally give only values of thermal expansion coefficients for both pure compounds and its mixtures, showing the relative changes in density, calculated by means of $\left(-\Delta\rho/\rho\right)$ as a function of temperature and assuming that α remains constant in any thermal range. As in the case of pure compounds, it can be computed at a given composition by means of the expression:

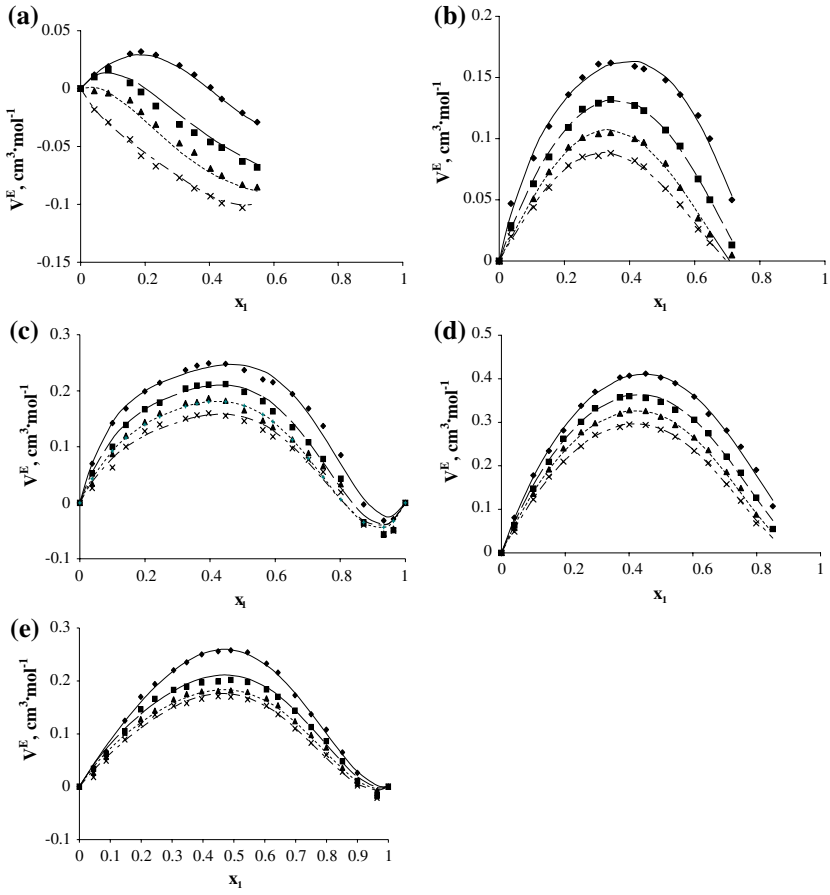

Fig. 1. Curves of constant excess molar volumes ($cm^3 \cdot mol^{-1}$) for mixtures of soybean oil (2) + (a) methanol (1), (b) ethanol (1), (c) 1-propanol (1), (d) 2-propanol (1), and (e) 1-butanol (1), with x_1 the alcohol composition, at temperatures (×)283.15, (▲)288.15, (■)293.15, and (♦)298.15 K. Redlich–Kister curves for each temperature are included.

$$\alpha = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{p,x} \tag{9}$$

taking into account the temperature dependence of the density. However, a more interesting contribution is made to the field of properties in liquid mixtures if this calculation is done taking separately the partial contributions of the thermal expansivities of each component in the mixture, as well as that due to non-ideality in the mixture. To this aim, the basic

Table V. Partial Excess Molar Volumes at Infinite Dilution of the Binary Mixtures

Mixture	$\overline{V}_1^{E,\infty}$ ($cm^3 \cdot mol^{-1}$)	$\overline{V}_2^{E,\infty}$ ($cm^3 \cdot mol^{-1}$)
298.15 K		
Methanol (1) + soybean oil (2)	0.296	0.074
Ethanol (1) + soybean oil (2)	1.185	−1.127
1-Propanol (1) + soybean oil (2)	2.175	−0.983
2-Propanol (1) + soybean oil (2)	2.095	0.304
1-Butanol (1) + soybean oil (2)	0.960	−0.100
293.15 K		
Methanol (1) + soybean oil (2)	0.356	−0.918
Ethanol (1) + soybean oil (2)	0.763	−0.859
1-Propanol (1) + soybean oil (2)	1.652	−1.188
2-Propanol (1) + soybean oil (2)	1.870	−0.203
1-Butanol (1) + soybean oil (2)	0.975	−0.193
288.15 K		
Methanol (1) + soybean oil (2)	0.101	−0.792
Ethanol (1) + soybean oil (2)	0.525	−0.644
1-Propanol (1) + soybean oil (2)	1.304	−1.235
2-Propanol (1) + soybean oil (2)	1.657	−0.473
1-Butanol (1) + soybean oil (2)	0.905	−0.279
283.15 K		
Methanol (1) + soybean oil (2)	−0.468	0.453
Ethanol (1) + soybean oil (2)	0.469	−0.478
1-Propanol (1) + soybean oil (2)	1.132	−1.124
2-Propanol (1) + soybean oil (2)	1.454	−0.507
1-Butanol (1) + soybean oil (2)	0.723	−0.330

expression relating the molar volume of a mixture and its excess molar volume is

$$V = \sum_{i=1}^{N} x_i V_i + V^{E} \tag{10}$$

where V_i and x_i correspond to the molar volume and composition of component i.

From the density data, the excess volume is described as a function of temperature indicating the non-ideality of the mixture. The values of the excess isobaric expansivity computed from the measured densities are reported in Table III. The excess isobaric expansivities of the alcohol mixtures are also shown in Fig. 4. The behavior of the isobaric expansivity could be explained by the additional interactions among alcohol and triglyceride molecules. The excess isobaric expansivities show a sigmoid behavior at low temperatures, with a change in behavior observed at rich

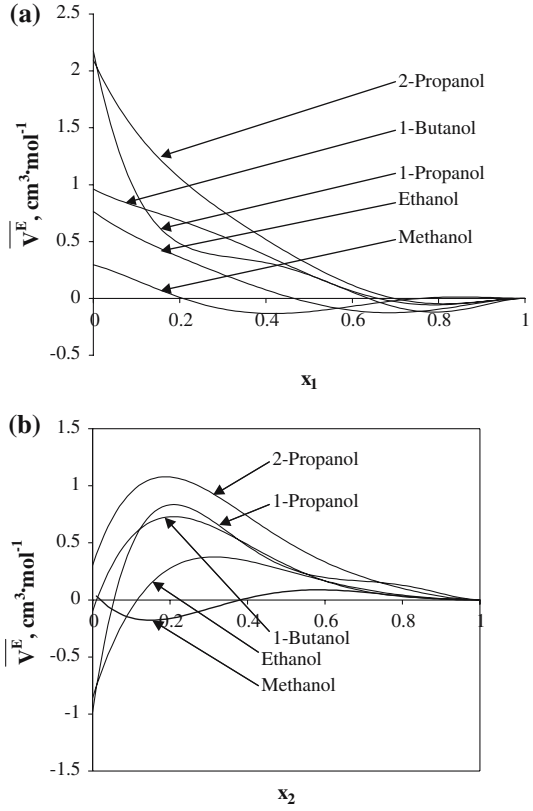

Fig. 2. Partial excess molar volumes ($cm^3 \cdot mol^{-1}$) of the mixtures soybean oil (2) + (a) methanol (1), (b) ethanol (1), (c) 1-propanol (1), (d) 2-propanol (1), and (e) 1-butanol (1), with x_1 the alcohol composition, (a) $\overline{V}_1^E$ and (b) $\overline{V}_2^E$ at 298.15 K.

compositions of the solvent. The non-ideality of the mixture is quite similar at every temperature for low alcohol compositions. Major variations for this excess property occur at high compositions of the solvent, thus, only diluted mixtures of soybean oil show nonlinear variations with temperature. This suggests that fitting values of α directly is inappropriate.

4. PHYSICAL PROPERTY MODELS

The prediction of different thermodynamic properties of multicomponent mixtures have been the subject of study in recent years, applying different empirical or semiempirical models. In this paper, the measured experimental results were compared with calculated values using several

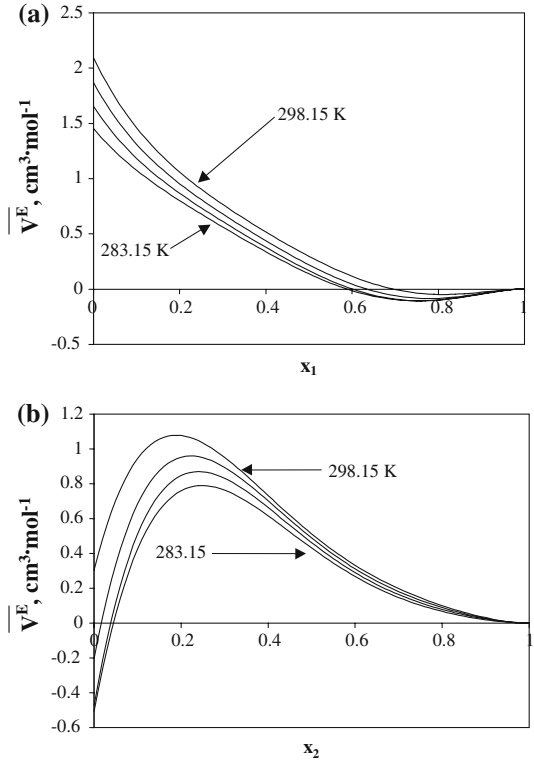

Fig. 3. Partial excess molar volumes (a) $\overline{V}_1^{\mathrm{E}}$ and (b) $\overline{V}_2^{\mathrm{E}}$ of mixtures 2-propanol (1) + soybean oil (2) from 283.15 to 298.15 K, with x_1 the alcohol composition.

models. The density of the mixtures was predicted by application of the equations of state proposed by Rackett (R), the modified equation proposed by Spencer and Danner (SDR) [15] using extended mixing rules proposed by those authors, the Kay (modified Prausnitz–Gunn combination) rule [13], and the pure thermophysical property data [10] (Table VI) or estimation procedures explained earlier. The refractive index is an easily measurable property; however, when it is not available, it is not easy to determine reliable methods of estimation of this property through other available parameters or properties [16]. The use and interest of this property for different applications has been reported earlier [17]. The refractive indices were compared with the predicted results by Lorentz–Lorenz (LL), Gladstone–Dale (GD), Arago–Biot (AB), Eykman (Ey), Newton (N), Oster (O), and Eyring–John (EJ) mixing rules [15]. In Tables VI and VII the root-mean-square deviations of the models are compiled. It is

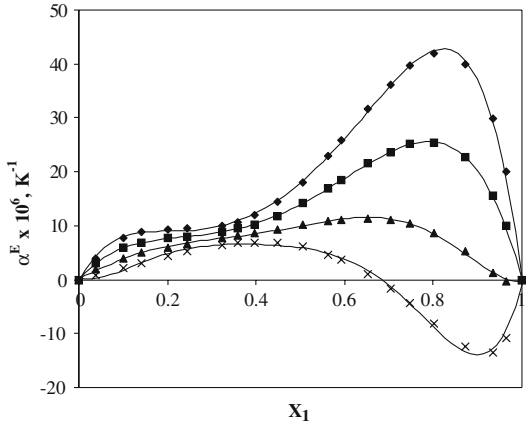

Fig. 4. Curves of constant excess isobaric expansivity (α^E) of the mixture 1-propanol (1) + soybean oil (2), (×)283.15, (▲)288.15, (■)293.15 and (♦)298.15 K, with x_1 the alcohol composition.

Table VI. Root-Mean-Square Deviations of the Experimental Results from Rackett (R) and Spencer, Danner, and Rackett (SDR) Equations of State

	R ($cm^3 \cdot mol^{-1}$)	SDR ($cm^3 \cdot mol^{-1}$)
Methanol + soybean oil	0.0632	0.0945
Ethanol + soybean oil	0.0315	0.0608
1-Propanol + soybean oil	0.0168	0.0340
2-Propanol + soybean oil	0.0070	0.0160
1-Butanol + soybean oil	0.0298	0.0117

observed for density predictions that the SDR method shows smaller deviations for all the mixtures although both give similar results in the binary systems. The best refractive index predictions for the binary mixtures are those obtained by Lorenz–Lorentz, Arabo–Biot, Newton, and Oster equations considering additivity on mixing; all of these procedures are simple and accurate for estimation.

5. CONCLUSIONS

Experimental results for the volumetric and refractive behavior at temperatures from 283.15 to 298.15 K are presented in the scope of investigating the dependence of such properties for a homologous series of

Table VII. Root-Mean-Square Deviations of the Experimental Refractive Indices from the Estimation Results for the Lorentz–Lorenz (L–L), Dale–Gladstone (D–G), Arago–Biot (A–B), Eykman (Eyk), Newton (Nw), Oster (Os), and Eyring-Jhon (E–J) Equations

L–L	D–G	A–B	Eyk	Nw	Os	E–J
			Methanol + soybean oil			
			298.15 K			
0.00037	0.00018	0.00018	0.00024	0.00009	0.00010	0.00027
[a]0.00090	[a]0.00065	[a]0.00171	[a]0.00073	[a]0.00042	[a]0.00053	[a]0.00336
			293.15 K			
0.00047	0.00028	0.00028	0.00034	0.00012	0.00018	0.00037
[a]0.00042	[a]0.00024	[a]0.00017	[a]0.00030	[a]0.00010	[a]0.00015	[a]0.00016
			288.15 K			
0.00041	0.00022	0.00022	0.00028	0.00006	0.00012	0.00032
[a]0.00231	[a]0.00187	[a]0.00543	[a]0.00203	[a]0.00145	[a]0.00167	[a]0.01074
			Ethanol + soybean oil			
			298.15 K			
0.00040	0.00019	0.00019	0.00024	0.00019	0.00015	0.00028
[a]0.00104	[a]0.00073	[a]0.00197	[a]0.00083	[a]0.00048	[a]0.00059	[a]0.00388
			293.15 K			
0.00040	0.00015	0.00015	0.00022	0.00012	0.00006	0.00027
[a]0.00021	[a]0.00035	[a]0.00028	[a]0.00011	[a]0.00011	[a]0.00010	[a]0.00067
			288.15 K			
0.00047	0.00025	0.00025	0.00031	0.00016	0.00016	0.00035
[a]0.00052	[a]0.00029	[a]0.00039	[a]0.00036	[a]0.00018	[a]0.00020	[a]0.00064
			1-Propanol + soybean oil			
			298.15 K			
0.00044	0.00016	0.00016	0.00022	0.00032	0.00020	0.00028
[a]0.00099	[a]0.00065	[a]0.00189	[a]0.00075	[a]0.00045	[a]0.00052	[a]0.00381
			293.15 K			
0.00046	0.00013	0.00013	0.00023	0.00024	0.00012	0.00029
[a]0.00049	[a]0.00019	[a]0.00046	[a]0.00027	[a]0.00027	[a]0.00017	[a]0.00094
			288.15 K			
0.00047	0.00014	0.00014	0.00024	0.00023	0.00011	0.00030
[a]0.00047	[a]0.00015	[a]0.00037	[a]0.00024	[a]0.00024	[a]0.00013	[a]0.00079
			2-Propanol + soybean oil			
			298.15 K			
0.00020	0.00014	0.00014	0.00008	0.00041	0.00029	0.00008
[a]0.00102	[a]0.00066	[a]0.00225	[a]0.00077	[a]0.00039	[a]0.00050	[a]0.00469
			293.15 K			
0.00028	0.00012	0.00012	0.00012	0.00034	0.00023	0.00015
[a]0.00053	[a]0.00024	[a]0.00074	[a]0.00032	[a]0.00022	[a]0.00017	[a]0.00162
			288.15 K			
0.00026	0.00011	0.00011	0.00010	0.00034	0.00024	0.00013
[a]0.00287	[a]0.00224	[a]0.00713	[a]0.00247	[a]0.00165	[a]0.00196	[a]0.01438

Table VII. (*Continued*)

L–L	D–G	A–B	Eyk	Nw	Os	E–J
			1-Butanol + soybean oil			
			298.15 K			
0.00032	0.00009	0.00009	0.00015	0.00021	0.00012	0.00019
[a]0.00090	[a]0.00060	[a]0.00184	[a]0.00070	[a]0.00036	[a]0.00047	[a]0.00376
			293.15 K			
0.00031	0.00008	0.00008	0.00013	0.00022	0.00012	0.00018
[a]0.00209	[a]0.00165	[a]0.00510	[a]0.00181	[a]0.00125	[a]0.00146	[a]0.01022
			288.15 K			
0.00031	0.00010	0.00010	0.00015	0.00023	0.00015	0.00019
[a]0.00205	[a]0.00161	[a]0.00502	[a]0.00176	[a]0.00120	[a]0.00141	[a]0.01010

[a]Assumes non-additivity on mixing

alkanols + soybean oil, which are related to refining technology. In general, the molecular interactions depend mainly on two effects: (a) variation of intermolecular forces when two components come into contact (disperse interactions or H-bonds in these cases) and (b) variation of molecular packing as a consequence of differences in the size, shape, or groups of the molecules of the components, as well as degrees of freedom due to bond nature and molecular backbone.

If the interactions between the molecules of two mixed components are weaker than in the pure component, the volumetric tendency will be positive. This usually occurs when one of the components has polar groups and the other is nonpolar, or shows weakly polar behavior. The triglyceride in soybean oil is weakly polar and alkanols are polar/slighty polar. When the molecules are mixed, the nonpolar triglyceride molecules intersperse among the alcohol molecules, breaking clusters and resulting in decreased interactions among the dipoles of the hydroxyl group. This effect is clearly shown in Fig. 2 (decreasing x_1) in terms of the partial excess molar volume against composition. As polar interactions diminish, the excess volume becomes positive (Fig. 1). The experimental results agree with this explanation since all the studied mixtures show excess volumes that are positive at low concentrations of soybean oil. This result shows that the effects of intermolecular forces are stronger than the packing caused by geometrical effects. This results in the differences of the excess volumes for the different alkanols. If we compare the maximum excess volumes ($x \approx 0.5$), the following observations can be made: lower values correspond to the lowest temperatures and solvents with high activated hydroxyl groups. Based on these observations, the solvents could be grouped according spherical geometry (methanol, ethanol) or flat

geometry (1-propanol, 2-propanol, 1-butanol). The 2-propanol solvent is a secondary alkanol with a flexible structure which could be modified in the aliphatic branch and the hydroxyl group is activated. The results can be interpreted qualitatively as a consequence of the diminution of the probability of effective H-bonds. This interaction will be increasingly difficult to establish the larger the aliphatic chains are. If they have spherical structure, some interactions can persist and the excess volume will not be large. If the alkanol molecules have a bulky substituent or occupy a different plane from the triglyceride chains, the interactions among hydroxyl groups are disabled and the excess volume will be larger than in the previous case but under homogeneous conditions.

Despite the lack of thermodynamic data and the complexity of the mixtures (large differences in molecular volume, mass, and structure), the reliability of predictive models for density and refractive index was demonstrated. The methods are quite simple but the accurate results show that they are adequate for estimation of the properties of these complex mixtures.

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