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Temperature dependence of excess molar volumes in (*n*-alkane (C_6–C_9) or alcohol (C_2–C_4))+olive oil mixtures

C. González[a,*], M. Iglesias[1,b], J. Lanz[a], J.M. Resa[a]

[a]*Dpto. de Ing. Química, Universidad del Pais Vasco, Apto. 450, Vitoria, Spain*
[b]*Dpto. de Ing. Química, Universidad de Vigo, Apto. 36200, Vigo, Spain*

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Abstract

In the scope of investigating physical properties related to equipment design for edible oil industries we present the temperature dependence of excess molar volumes of *n*-alkane (*n*-hexane, *n*-heptane, *n*-octane and *n*-nonane) or alkanol (ethanol, 1-propanol, 2-propanol, 1-butanol) with natural olive oil being measured at the range 283.15–298.15 K and atmospheric pressure. The phase compositions on every partial miscible binary mixture were obtained by measurement of density and application of the fitting polynomials. Application of contribution methods (UNIFAC and UNIFAC-Lyngby) were applied in order to compare its capability in predicting the experimental values. Derived properties such as partial excess molar volumes, isobaric expansibility and isothermal coefficient of pressure excess molar enthalpy were computed due to its importance in the study of specific molecular interactions. Because of current processes, design is strongly computer oriented, consideration was also given to how accurate the corresponding states prediction works. The validity of predicting densities was tested by the Rackett equation, this model being selected attending to ease of use, accuracy and range of application.

Keywords: Derived properties; Temperature dependence; *n*-Alkane; Alkanol; Olive oil

1. Introduction

Knowledge of thermodynamic properties and phase equilibria of fats and oils is of practical interest to the industrial manufacturer since thermal and mechanical procedures applied are closely related to its temperature and pressure dependence. Nowadays, the use of physics methods to mixture analysis (vibrational tube densimeter, scattering refractometry, capillar viscosimetry, etc.) yield better results than current chemistry procedures showing higher accuracy and on-line application capability. In accordance to that in the last few years a considerable effort has been developed in the field of calorimetry and thermodynamic properties of oils and mixtures with different solvents. Such properties are strongly dependent on double bond presence, chain length and isomeric structures of fatty acids and molecular package of triglyceride into solvents. Attending to different origin of fatty substances and the complexity of its composition and structure, currently it can be observed to be a considerable lack of accuracy or thermodynamic consistency in some open data literature. In what is referred to mixtures, the scarce data references are greater due to the recent

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*Corresponding author. Fax: +34-45-130756.

[1] Fax: +34-986-812382; e-mail: migles@uvigo.es

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development of accurate techniques and the relatively important non-ideality of oils+solvents mixture. It is not always possible to obtain proper values at such temperature and pressure, moreover, when it is referred to mixtures in a non-standard condition. In the scope of investigating physical properties related to equipment design of natural oils industries and new environment friendly procedures of extraction and refining such as modified distillation or wintering, we present the temperature dependence of excess molar volumes of the mixtures alkane (*n*-hexane, *n*-heptane, *n*-octane and *n*-nonane) or alcohol (ethanol, 1-propanol, 2-propanol, 1-butanol) with natural olive oil being measured at the range 283.15–298.15 K and atmospheric pressure, as a function of molar fraction. The binodal points on every partial miscible binary mixture were determined by the cloud point method. From the experimental values, the excess molar volumes were computed, a temperature dependent Redlich–Kister type polynomial being fitted to the results. Because of the expense of the experimental measurement of such data and as the current processes design is strongly computer oriented, consideration was also given to how accurate the corresponding states prediction works. The validity of predicting the experimental values of density was tested by the Rackett equation of state which was selected attending to the criteria as ease of use, accuracy and range of application. Temperature and functional dependence of partial molar quantities, isobaric expansibility and isothermal coefficient of pressure excess molar enthalpy are analysed and commented upon. Group contribution methods were applied to liquid–liquid equilibria prediction, only a qualitative description when phase split occurs was obtained due to non-stochiometric triglyceride structure and complex interactions with solvents.

2. Experimental

All solvents used in the preparation of samples were of Fluka quality with richness better than 99.5 mol%. The pure components were stored in sunlight protected form and constant humidity and temperature. In order to reduce molar fraction errors, the vapour space into the vessels was minimized during the samples preparation. Refined olive oils were supplied by Koipe, and the water content and volatile compounds were lower than 0.1%. These oils were analyzed by means of a gas chromatograph Perkin-Elmer model Sigma 3B equipped with a flame detector. Chromatographic technique and fatty acids chemical procedure were described in previous works [1]. The fatty acids composition obtained was palmitic acid, 12.4%; stearic acid, 2.8%; oleic acid 77.8%, and linoleic acid, 7.0%; the uncertainty in mol% for these results were better than ±0.1%. From this composition, the average molar mass of this oil has been computed in accordance with the following expression:

$$M_{\mathrm{oil}} = 3\left(\sum_{i=1}^{N} x_i M_i\right) + 2M_{\mathrm{CH_2}} + M_{\mathrm{CH}}, \qquad (1)$$

x_i being the molar fraction and M_i the molar mass of each fatty acid attending the concentration analysis, N the number of fatty acid found by analysis, and $M_{\mathrm{CH_2}}$ and M_{CH} are the molar mass contributions of triglyceride molecule fraction. The computed average molar mass in olive oil samples were 875.84 g mol^{-1}. The variation in the composition due to different samples affects mainly the mono and polyunsaturated fatty acids, the change in molar mass being lower than ±1 g mol^{-1} and in excess molar volume lower than $\pm 2\times 10^{-3}$ cm^3 mol^{-1}. Mixtures were prepared by mass using a Salter ER-182A balance, the whole composition range of the binary mixtures being covered. The accuracy in molar fractions was obtained to be higher than $\pm 5\times 10^{-4}$. The densities of pure components and their mixtures were measured with an Anton Paar DMA-58 vibrational tube densimeter with a resolution of 10^{-5} g cm^{-3}. Apparatus calibration was performed periodically in accordance with vendor instructions using a double reference (Millipore quality water and ambient air at each temperature). Accuracy in the calculation of excess molar volumes was estimated as better than $\pm 2\times 10^{-2}$ cm^3 mol^{-1} and the temperature of measurement in $\pm 10^{-2}$ K. The experimental and literature densities of solvents and oil are gathered in Table 1.

3. Data correlation

The excess molar volumes of binary mixtures shown in Tables 2–9 were computed by applying

Table 1
Comparison of experimental data with literature data for chemicals at different temperatures

Component	ρ (g cm^{-3})				
	298.15 K	293.15 K	288.15 K	283.15 K	Lit. (298.15 K)[a]
n-Hexane	0.65485	0.65930	0.66385	0.66830	0.65484
n-Heptane	0.67955	0.68367	0.68792	0.69214	0.67946
n-Octane	0.69859	0.70260	0.70664	0.71068	0.69862
n-Nonane	0.71398	0.71777	0.72169	0.72557	0.71381
Ethanol	0.78513	0.78941	0.79364	0.79777	0.78509
1-Propanol	0.79952	0.80341	0.80743	0.81143	0.79975
2-Propanol	0.78095	0.78516	0.78934	0.79341	0.78126
1-Butanol	0.80614	0.80984	0.81368	0.81750	0.80600
Olive oil	0.90928	0.91263	0.91615	0.91960	0.909–0.915[b]

[a] [2].
[b] [3].

Table 2
Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for *n*-hexane+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\ \alpha^E$ (K^{-1})
Temperature (298.15 K)				
0.0517	0.90760	−0.204	2.374	−7.43
0.1214	0.90500	−0.415	3.571	−10.91
0.1712	0.90298	−0.622	4.169	−12.61
0.2138	0.90103	−0.755	4.809	−14.74
0.2679	0.89835	−0.974	5.830	−18.70
0.3271	0.89502	−1.222	7.053	−24.22
0.4290	0.88769	−1.429	8.685	−33.65
0.4594	0.88515	−1.535	8.958	−35.88
0.5039	0.88099	−1.677	9.192	−38.56
0.5413	0.87701	−1.785	9.291	−40.54
0.6024	0.86929	−1.937	9.480	−44.59
0.6378	0.86387	−1.971	9.740	−48.59
0.7501	0.84075	−2.205	12.041	−81.33
0.8523	0.80373	−2.091	14.902	−148.90
0.8996	0.77599	−1.877	14.545	−178.71
0.9472	0.73356	−1.193	10.955	−169.88
Temperature (293.15 K)				
0.0517	0.91094	−0.178	1.568	−4.82
0.1214	0.90835	−0.379	2.850	−8.71
0.1712	0.90631	−0.553	3.593	−11.04
0.2138	0.90438	−0.692	4.217	−13.16
0.2679	0.90168	−0.879	5.004	−16.16
0.3271	0.89832	−1.087	5.810	−19.71
0.4290	0.89099	−1.270	6.871	−25.69
0.4594	0.88854	−1.427	7.099	−27.38
0.5039	0.88434	−1.531	7.387	−29.91
0.5413	0.88036	−1.628	7.620	−32.30
0.6024	0.87271	−1.800	8.084	−37.59
0.6378	0.86731	−1.833	8.451	−42.07
0.7501	0.84417	−2.022	10.205	−68.53
0.8523	0.80700	−1.835	11.338	−109.94
0.8996	0.77910	−1.574	10.472	−124.07
0.9472	0.73778	−1.162	7.491	−111.69
Temperature (288.15 K)				
0.0517	0.91444	−0.144	0.776	−2.07
0.1214	0.91179	−0.271	2.142	−6.37
0.1712	0.90979	−0.470	3.027	−9.37
0.2138	0.90787	−0.606	3.635	−11.49
0.2679	0.90518	−0.788	4.192	−13.47
0.3271	0.90180	−0.966	4.587	−14.93
0.4290	0.89451	−1.152	5.088	−17.26
0.4594	0.89193	−1.217	5.272	−18.38
0.5039	0.88780	−1.356	5.613	−20.74
0.5413	0.88384	−1.457	5.978	−23.57
0.6024	0.87612	−1.579	6.712	−30.16
0.6378	0.87073	−1.612	7.184	−35.15
0.7501	0.84763	−1.799	8.399	−54.96
0.8523	0.81054	−1.624	7.833	−68.68
0.8996	0.78277	−1.393	6.468	−66.21
0.9472	0.74138	−0.960	4.086	−50.01
Temperature (283.15 K)				
0.0517	0.91789	−0.130	−0.003	0.84
0.1214	0.91529	−0.286	1.446	−3.91
0.1712	0.91324	−0.424	2.471	−7.59
0.2138	0.91133	−0.558	3.062	−9.70
0.2679	0.90861	−0.701	3.394	−10.61
0.3271	0.90521	−0.849	3.386	−9.85
0.4290	0.89806	−1.107	3.336	−8.33
0.4594	0.89549	−1.168	3.476	−8.85
0.5039	0.89135	−1.285	3.870	−11.03
0.5413	0.88733	−1.339	4.363	−14.31
0.6024	0.87966	−1.470	5.363	−22.27
0.6378	0.87434	−1.526	5.938	−27.79
0.7501	0.85117	−1.645	6.625	−40.54
0.8523	0.81431	−1.516	4.389	−24.96
0.8996	0.78671	−1.314	2.533	−4.89
0.9472	0.74559	−0.926	0.739	15.42

Table 3
Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for n-heptane+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	10^6 α^E (K^{-1})
Temperature (298.15 K)				
0.0533	0.90747	−0.147	0.552	−1.05
0.0946	0.90592	−0.240	0.925	−1.83
0.1438	0.90395	−0.391	1.416	−3.04
0.1931	0.90172	−0.490	2.002	−4.76
0.2624	0.89824	−0.680	2.972	−8.08
0.3120	0.89539	−0.800	3.719	−11.01
0.3314	0.89420	−0.860	4.010	−12.24
0.4052	0.88905	−1.038	5.042	−17.18
0.4499	0.88539	−1.123	5.569	−20.18
0.5088	0.87986	−1.253	6.113	−23.96
0.5601	0.87417	−1.364	6.440	−27.02
0.6078	0.86796	−1.464	6.628	−29.68
0.6606	0.85961	−1.511	6.721	−32.53
0.7107	0.85000	−1.574	6.705	−35.26
0.7668	0.83623	−1.557	6.546	−38.44
0.7991	0.82639	−1.521	6.357	−40.23
0.8527	0.80549	−1.370	5.782	−42.39
0.8994	0.78053	−1.176	4.843	−41.52
0.9516	0.73975	−0.745	2.971	−31.57
Temperature (293.15 K)				
0.0533	0.91100	−0.125	0.762	−1.94
0.0946	0.90927	−0.218	1.270	−3.36
0.1438	0.90727	−0.330	1.839	−5.07
0.1931	0.90505	−0.428	2.399	−6.90
0.2624	0.90157	−0.603	3.190	−9.77
0.3120	0.89872	−0.714	3.751	−12.07
0.3314	0.89753	−0.769	3.967	−13.02
0.4052	0.89239	−0.939	4.746	−16.91
0.4499	0.88877	−1.041	5.170	−19.45
0.5088	0.88321	−1.138	5.653	−22.95
0.5601	0.87750	−1.227	5.990	−26.11
0.6078	0.87135	−1.350	6.220	−29.09
0.6606	0.86302	−1.394	6.367	−32.35
0.7107	0.85334	−1.415	6.374	−35.27
0.7668	0.83966	−1.424	6.180	−38.02
0.7991	0.82983	−1.385	5.940	−39.09
0.8527	0.80902	−1.253	5.250	−39.21
0.8994	0.78416	−1.078	4.245	−36.10
0.9516	0.74356	−0.682	2.481	−25.20
Temperature (288.15 K)				
0.0533	0.91431	−0.122	0.968	−2.88
0.0946	0.91277	−0.207	1.610	−4.97
0.1438	0.91077	−0.307	2.255	−7.20
0.1931	0.90857	−0.411	2.789	−9.15
0.2624	0.90507	−0.553	3.403	−11.54
0.3120	0.90223	−0.660	3.783	−13.17
0.3314	0.90101	−0.688	3.925	−13.83
0.4052	0.89587	−0.842	4.454	−16.62
0.4499	0.89225	−0.935	4.777	−18.66
0.5088	0.88667	−1.008	5.200	−21.86
0.5601	0.88103	−1.127	5.547	−25.12
0.6078	0.87473	−1.160	5.820	−28.43
0.6606	0.86650	−1.247	6.019	−32.13
0.7107	0.85699	−1.334	6.049	−35.26
0.7668	0.84324	−1.298	5.821	−37.54
0.7991	0.83347	−1.274	5.529	−37.84
0.8527	0.81274	−1.156	4.728	−35.80
0.8994	0.78795	−0.989	3.657	−30.34
0.9516	0.74756	−0.634	1.999	−18.44
Temperature (283.15 K)				
0.0533	0.91780	−0.082	1.171	−3.80
0.0946	0.91627	−0.168	1.943	−6.67
0.1438	0.91426	−0.250	2.664	−9.45
0.1931	0.91205	−0.336	3.173	−11.52
0.2624	0.90855	−0.466	3.613	−13.40
0.3120	0.90571	−0.564	3.814	−14.32
0.3314	0.90449	−0.589	3.883	−14.66
0.4052	0.89944	−0.793	4.167	−16.28
0.4499	0.89575	−0.830	4.390	−17.80
0.5088	0.89019	−0.904	4.755	−20.68
0.5601	0.88457	−1.025	5.112	−24.05
0.6078	0.87831	−1.069	5.427	−27.70
0.6606	0.87006	−1.134	5.677	−31.86
0.7107	0.86046	−1.171	5.730	−35.19
0.7668	0.84684	−1.181	5.468	−36.98
0.7991	0.83709	−1.158	5.126	−36.48
0.8527	0.81644	−1.055	4.214	−32.15
0.8994	0.79178	−0.916	3.079	−24.19
0.9516	0.75152	−0.583	1.526	−11.25

the following equation:

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

where ρ is the density of the mixture, ρ_i the property of the pure components, and x_i is the molar fraction. N stands for the number of components in the mixture. Densities of the mixture are also given in Tables 2–9. The computed excess molar volumes of the binary mixtures were fitted using the following Redlich–Kister expression [4]:

$$\delta Q_{ij} = x_i x_j \sum_{p=0}^{S} B_p (x_i - x_j)^p, \tag{3}$$

where δQ_{ij} is the excess property, B_p are the fitting

Table 4

Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for *n*-octane+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\ \alpha^E$ (K^{-1})
Temperature (298.15 K)				
0.0509	0.90696	−0.147	3.350	−11.17
0.1141	0.90453	−0.301	4.381	−14.87
0.1723	0.90200	−0.419	4.048	−13.64
0.1946	0.90094	−0.452	3.818	−12.72
0.2706	0.89695	−0.567	3.081	−9.50
0.3090	0.89469	−0.638	2.808	−8.14
0.3685	0.89075	−0.728	2.479	−6.30
0.4095	0.88771	−0.802	2.252	−4.92
0.4625	0.88325	−0.878	1.874	−2.49
0.5038	0.87930	−0.934	1.481	0.17
0.5508	0.87417	−0.981	0.937	4.15
0.5991	0.86810	−1.050	0.330	9.10
0.6487	0.86064	−1.064	−0.226	14.44
0.7028	0.85094	−1.126	−0.583	19.14
0.7483	0.84079	−1.100	−0.555	20.62
0.7994	0.82677	−1.105	−0.100	17.67
0.8530	0.80737	−1.005	0.762	7.83
0.8960	0.78682	−0.908	1.473	−4.32
0.9498	0.75046	−0.524	1.680	−16.97
Temperature (293.15 K)				
0.0509	0.91032	−0.106	2.261	7.68
0.1141	0.90787	−0.230	3.320	11.49
0.1723	0.90534	−0.338	3.487	12.10
0.1946	0.90429	−0.377	3.464	11.99
0.2706	0.90036	−0.529	3.301	11.23
0.3090	0.89807	−0.568	3.227	10.84
0.3685	0.89418	−0.685	3.136	10.35
0.4095	0.89113	−0.743	3.071	10.00
0.4625	0.88672	−0.841	2.955	9.38
0.5038	0.88277	−0.886	2.827	8.65
0.5508	0.87766	−0.934	2.642	7.53
0.5991	0.87165	−1.023	2.428	6.14
0.6487	0.86427	−1.063	2.222	4.71
0.7028	0.85459	−1.115	2.072	3.75
0.7483	0.84445	−1.077	2.041	4.02
0.7994	0.83045	−1.072	2.112	6.19
0.8530	0.81110	−0.971	2.225	10.87
0.8960	0.79054	−0.856	2.193	15.55
0.9498	0.75433	−0.500	1.632	17.52
Temperature (288.15 K)				
0.0509	0.91379	−0.067	1.191	4.00
0.1141	0.91134	−0.181	2.277	7.91
0.1723	0.90881	−0.280	2.935	10.47
0.1946	0.90777	−0.324	3.116	11.22
0.2706	0.90382	−0.448	3.518	13.03
0.3090	0.90155	−0.498	3.639	13.68
0.3685	0.89766	−0.605	3.781	14.61
0.4095	0.89461	−0.656	3.876	15.36
0.4625	0.89020	−0.746	4.019	16.63
0.5038	0.88627	−0.798	4.151	17.95
0.5508	0.88118	−0.850	4.319	19.84
0.5991	0.87516	−0.925	4.490	22.18
0.6487	0.86778	−0.957	4.629	24.88
0.7028	0.85811	−1.005	4.682	27.83
0.7483	0.84805	−0.995	4.593	29.93
0.7994	0.83405	−0.980	4.287	31.26
0.8530	0.81478	−0.898	3.664	30.51
0.8960	0.79428	−0.794	2.900	27.32
0.9498	0.75820	−0.464	1.585	18.06
Temperature (283.15 K)				
0.0509	0.91734	−0.078	0.140	0.10
0.1141	0.91485	−0.143	1.251	4.12
0.1723	0.91231	−0.224	2.393	8.73
0.1946	0.91125	−0.248	2.773	10.38
0.2706	0.90732	−0.378	3.731	14.92
0.3090	0.90507	−0.438	4.044	16.66
0.3685	0.90119	−0.544	4.416	19.08
0.4095	0.89812	−0.574	4.668	20.98
0.4625	0.89372	−0.663	5.064	24.25
0.5038	0.88980	−0.715	5.452	27.72
0.5508	0.88471	−0.760	5.967	32.78
0.5991	0.87866	−0.812	6.516	39.05
0.6487	0.87129	−0.843	6.995	46.07
0.7028	0.86169	−0.917	7.247	53.14
0.7483	0.85159	−0.883	7.102	57.16
0.7994	0.83767	−0.892	6.424	57.58
0.8530	0.81844	−0.816	5.077	51.09
0.8960	0.79798	−0.717	3.596	39.64
0.9498	0.76205	−0.423	1.539	18.61

parameters obtained by the unweighted least squared method applying a fitting algorithm due to Marquard [5] and S is the degree of the polynomial expansion, which was optimized by means of the Bevington test [6]. In order to obtain generalized parameters, a temperature polynomial expansion was applied, such fitting parameters being reported in Table 10.

$$B_p = \sum_{q=0}^{2} A_{pq} T^q. \tag{4}$$

In this equation, A_{pq} are the temperature dependent parameters for these binary mixtures and T is the absolute temperature. The standard deviations were computed using Eq. (5), where z is the value

Table 5
Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for *n*-nonane+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\ \alpha^E$ (K^{-1})
Temperature (298.15 K)				
0.0438	0.90726	−0.122	2.343	7.69
0.0948	0.90527	−0.207	3.310	11.06
0.1618	0.90235	−0.303	3.107	10.32
0.1890	0.90105	−0.334	2.834	9.23
0.2424	0.89830	−0.407	2.289	6.85
0.2938	0.89535	−0.473	1.945	5.11
0.3434	0.89218	−0.542	1.877	4.48
0.3982	0.88823	−0.610	2.103	5.26
0.4516	0.88387	−0.695	2.556	7.44
0.5034	0.87899	−0.751	3.114	10.64
0.5457	0.87446	−0.800	3.583	13.77
0.5949	0.86841	−0.852	4.066	17.62
0.6508	0.86022	−0.874	4.454	21.75
0.6959	0.85236	−0.890	4.595	24.52
0.8013	0.82730	−0.855	4.214	27.27
0.8512	0.81041	−0.789	3.655	25.96
0.8998	0.78890	−0.680	2.844	22.29
0.9511	0.75739	−0.378	1.630	14.45
Temperature (293.15 K)				
0.0438	0.91056	−0.083	1.714	−5.76
0.0948	0.90858	−0.171	2.454	−8.35
0.1618	0.90565	−0.249	2.463	−8.27
0.1890	0.90437	−0.294	2.361	−7.80
0.2424	0.90163	−0.367	2.188	−6.91
0.2938	0.89867	−0.417	2.158	−6.57
0.3434	0.89552	−0.494	2.283	−6.98
0.3982	0.89157	−0.554	2.556	−8.24
0.4516	0.88719	−0.615	2.886	−10.05
0.5034	0.88233	−0.678	3.188	−12.03
0.5457	0.87778	−0.708	3.380	−13.60
0.5949	0.87171	−0.741	3.514	−15.15
0.6508	0.86354	−0.768	3.536	−16.40
0.6959	0.85566	−0.769	3.463	−16.98
0.8013	0.83068	−0.757	3.055	−17.40
0.8512	0.81382	−0.696	2.740	−17.33
0.8998	0.79235	−0.595	2.276	−16.55
0.9511	0.76105	−0.350	1.438	−12.69
Temperature (288.15 K)				
0.0438	0.91401	−0.046	1.095	−3.72
0.0948	0.91203	−0.127	1.613	−5.48
0.1618	0.90910	−0.196	1.830	−6.11
0.1890	0.90783	−0.246	1.896	−6.29
0.2424	0.90511	−0.329	2.089	−6.96
0.2938	0.90217	−0.388	2.367	−8.11
0.3434	0.89900	−0.441	2.681	−9.61
0.3982	0.89508	−0.514	3.002	−11.37
0.4516	0.89072	−0.580	3.210	−12.79
0.5034	0.88586	−0.632	3.261	−13.49
0.5457	0.88132	−0.661	3.181	−13.42
0.5949	0.87533	−0.731	2.971	−12.54
0.6508	0.86715	−0.738	2.634	−10.73
0.6959	0.85934	−0.764	2.351	−9.01
0.8013	0.83441	−0.743	1.916	−6.97
0.8512	0.81757	−0.677	1.841	−8.20
0.8998	0.79617	−0.586	1.719	−10.46
0.9511	0.76488	−0.333	1.250	−10.81
Temperature (283.15 K)				
0.0438	0.91753	−0.040	0.487	−1.56
0.0948	0.91554	−0.105	0.787	−2.44
0.1618	0.91262	−0.174	1.207	−3.81
0.1890	0.91134	−0.212	1.439	−4.69
0.2424	0.90863	−0.297	1.992	−7.00
0.2938	0.90567	−0.332	2.572	−9.72
0.3434	0.90251	−0.387	3.072	−12.37
0.3982	0.89855	−0.425	3.441	−14.67
0.4516	0.89419	−0.487	3.529	−15.66
0.5034	0.88936	−0.554	3.332	−15.02
0.5457	0.88482	−0.578	2.986	−13.20
0.5949	0.87884	−0.648	2.437	−9.76
0.6508	0.87069	−0.666	1.748	−4.72
0.6959	0.86287	−0.681	1.258	−0.57
0.8013	0.83798	−0.667	0.797	4.08
0.8512	0.82121	−0.621	0.957	1.46
0.8998	0.79983	−0.532	1.171	−4.01
0.9511	0.76864	−0.304	1.064	−8.81

of the property, and n_{DAT} is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\mathrm{DAT}}} \left(z_{\mathrm{exp}} - z_{\mathrm{pred}} \right)^2}{n_{\mathrm{DAT}}} \right)^{1/2}. \tag{5}$$

In Fig. 1, the excess molar volumes at each binary mixture are shown as a function of solvent molar fraction (as well as at the following figures), where the influence of two factors can be observed, the methylene group contribution for every series and the temperature dependence. In what is referred to *n*-alkanes, the functional variation decreases the excess molar volumes from *n*-hexane to *n*-nonane. These solvents are of complete miscibility with olive oil, the contractive trend being attenuated towards longer chain *n*-alkane. In all *n*-alkane+olive oil mixtures studied, minimum value of excess molar volume are shown at approximately 0.75 in molar fraction of

Table 6
Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for ethanol+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\ \alpha^E$ (K^{-1})
Temperature (298.15 K)				
0.0561	0.90879	0.032	−0.725	2.46
0.1066	0.90830	0.071	−1.314	4.66
0.1520	0.90783	0.090	−1.796	6.68
0.1957	0.90732	0.118	−2.211	8.63
0.2984	0.90595	0.142	−2.907	12.91
0.3492	0.90513	0.151	−3.063	14.58
0.4488	0.90316	0.151	−2.954	16.30
0.5440	0.90059	0.141	−2.389	15.42
0.5968	0.89876	0.114	−1.950	13.85
0.6961	0.89381	0.096	−1.092	9.54
0.7467	0.89018	0.061	−0.728	7.28
Temperature (293.15 K)				
0.0561	0.91216	0.016	−0.530	1.86
0.1066	0.91170	0.031	−0.956	3.48
0.1520	0.91125	0.037	−1.251	4.75
0.1957	0.91075	0.063	−1.447	5.73
0.2984	0.90940	0.087	−1.612	7.13
0.3492	0.90860	0.090	−1.592	7.48
0.4488	0.90666	0.091	−1.478	7.99
0.5440	0.90412	0.086	−1.348	8.59
0.5968	0.90227	0.081	−1.256	8.93
0.6961	0.89738	0.065	−0.967	8.78
0.7467	0.89375	0.045	−0.730	7.72
Temperature (288.15 K)				
0.0561	0.91565	0.020	−0.339	1.21
0.1066	0.91518	0.046	−0.604	2.24
0.1520	0.91473	0.055	−0.715	2.71
0.1957	0.91424	0.074	−0.696	2.66
0.2984	0.91289	0.104	−0.339	1.02
0.3492	0.91211	0.096	−0.145	−0.01
0.4488	0.91017	0.104	−0.027	−0.78
0.5440	0.90765	0.097	−0.324	1.38
0.5968	0.90583	0.083	−0.574	3.72
0.6961	0.90100	0.057	−0.845	7.98
0.7467	0.89739	0.040	−0.732	8.18
Temperature (283.15 K)				
0.0561	0.91908	0.003	−0.150	0.53
0.1066	0.91863	0.015	−0.258	0.92
0.1520	0.91817	0.036	−0.188	0.56
0.1957	0.91770	0.042	0.042	−0.58
0.2984	0.91635	0.082	0.912	−5.43
0.3492	0.91556	0.087	1.277	−7.93
0.4488	0.91363	0.098	1.399	−10.04
0.5440	0.91114	0.086	0.682	−6.23
0.5968	0.90936	0.061	0.097	−1.77
0.6961	0.90458	0.034	−0.725	7.13

Table 7
Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for 1-propanol+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\ \alpha^E$ (K^{-1})
Temperature (298.15 K)				
0.0480	0.90881	0.061	0.129	−0.86
0.0962	0.90828	0.112	0.424	−2.37
0.1524	0.90761	0.156	0.773	−4.26
0.2011	0.90696	0.195	0.984	−5.61
0.2420	0.90638	0.207	1.067	−6.40
0.3186	0.90513	0.229	1.001	−6.90
0.3528	0.90449	0.238	0.899	−6.75
0.3929	0.90367	0.240	0.746	−6.35
0.4473	0.90239	0.244	0.516	−5.54
0.5405	0.89962	0.241	0.173	−4.02
0.5922	0.89767	0.222	0.047	−3.34
0.6515	0.89486	0.200	−0.036	−2.76
0.7042	0.89162	0.181	−0.071	−2.32
0.7527	0.8878	0.143	−0.093	−1.77
0.7970	0.88317	0.110	−0.119	−0.93
0.8537	0.87469	0.062	−0.166	0.97
0.9006	0.86368	0.028	−0.202	3.24
0.9488	0.84444	−0.008	−0.185	5.16
Temperature (293.15 K)				
0.0480	0.91214	0.063	−0.239	0.51
0.0962	0.91162	0.107	−0.315	0.47
0.1524	0.91093	0.173	−0.277	0.00
0.2011	0.91030	0.197	−0.192	−0.62
0.2420	0.90972	0.211	−0.111	−1.17
0.3186	0.90849	0.223	0.009	−2.08
0.3528	0.90785	0.235	0.037	−2.37
0.3929	0.90702	0.247	0.048	−2.60
0.4473	0.90575	0.249	0.025	−2.68
0.5405	0.90301	0.238	−0.085	−2.23
0.5922	0.90107	0.220	−0.158	−1.73
0.6515	0.89829	0.193	−0.224	−1.04
0.7042	0.89507	0.174	−0.250	−0.44
0.7527	0.89127	0.138	−0.239	0.00
0.7970	0.88665	0.110	−0.198	0.23
0.8537	0.87822	0.062	−0.112	0.19
0.9006	0.86727	0.029	−0.032	−0.15
0.9488	0.84810	−0.003	0.024	−0.60
Temperature (288.15 K)				
0.0480	0.91566	0.055	−0.602	1.95
0.0962	0.91515	0.092	−1.041	3.47
0.1524	0.91449	0.134	−1.310	4.48
0.2011	0.91384	0.180	−1.348	4.66
0.2420	0.91325	0.206	−1.269	4.35
0.3186	0.91202	0.223	−0.967	3.01
0.3528	0.91139	0.230	−0.810	2.25
0.3929	0.91058	0.231	−0.638	1.36
0.4473	0.90931	0.239	−0.458	0.35

Table 7 (*Continued*)

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\,\alpha^E$ (K^{-1})
0.5405	0.90659	0.226	−0.338	−0.33
0.5922	0.90466	0.210	−0.359	−0.02
0.6515	0.90189	0.186	−0.409	0.78
0.7042	0.89869	0.167	−0.426	1.55
0.7527	0.89491	0.132	−0.383	1.88
0.7970	0.89034	0.099	−0.276	1.46
0.8537	0.88196	0.051	−0.058	−0.63
0.9006	0.87107	0.020	0.134	−3.73
0.9488	0.85194	−0.003	0.229	−6.68
Temperature (283.15 K)				
0.0480	0.91919	0.047	−0.958	3.47
0.0962	0.91870	0.068	−1.755	6.64
0.1524	0.91805	0.105	−2.325	9.22
0.2011	0.91741	0.146	−2.483	10.22
0.2420	0.91683	0.167	−2.408	10.18
0.3186	0.91561	0.185	−1.925	8.38
0.3528	0.91497	0.203	−1.642	7.12
0.3929	0.91415	0.215	−1.313	5.54
0.4473	0.91289	0.222	−0.932	3.54
0.5405	0.91017	0.219	−0.587	1.68
0.5922	0.90826	0.199	−0.557	1.78
0.6515	0.90552	0.170	−0.591	2.70
0.7042	0.90234	0.151	−0.599	3.65
0.7527	0.89855	0.128	−0.523	3.86
0.7970	0.89401	0.093	−0.352	2.75
0.8537	0.88563	0.057	−0.006	−1.50
0.9006	0.87477	0.028	0.298	−7.51
0.9488	0.85573	0.003	0.431	−13.10

Table 8
Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for 2-propanol+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\,\alpha^E$ (K^{-1})
Temperature (298.15 K)				
0.0514	0.90880	−0.023	−3.190	11.73
0.1115	0.90800	0.053	−4.036	15.31
0.1541	0.90735	0.126	−3.778	14.52
0.2100	0.90643	0.198	−3.157	12.20
0.2543	0.90564	0.233	−2.742	10.59
0.3011	0.90471	0.268	−2.496	9.72
0.3981	0.90242	0.315	−2.529	10.87
0.5116	0.89881	0.343	−2.671	13.74
0.6002	0.89489	0.334	−2.313	13.53
0.7066	0.88789	0.273	−1.505	10.26
0.8020	0.87739	0.160	−1.113	11.33
0.8511	0.86879	0.068	−1.168	16.91
0.0514	0.91222	−0.059	1.006	4.05
0.1115	0.91142	0.024	1.395	5.48
0.1541	0.91079	0.084	1.431	5.44
0.2100	0.90988	0.155	1.391	5.00
0.2543	0.90909	0.196	1.369	4.75
0.3011	0.90817	0.231	1.386	4.80
0.3981	0.90585	0.314	1.526	5.86
0.5116	0.90234	0.301	1.620	7.48
0.6002	0.89843	0.307	1.472	7.68
0.7066	0.89149	0.250	1.067	6.51
0.8020	0.88107	0.142	0.695	6.34
0.8511	0.87252	0.057	0.560	7.73
Temperature (288.15 K)				
0.0514	0.91574	−0.074	1.140	−4.06
0.1115	0.91494	0.013	1.201	−4.89
0.1541	0.91431	0.077	0.875	−4.16
0.2100	0.91341	0.144	0.346	−2.61
0.2543	0.91264	0.173	−0.018	−1.41
0.3011	0.91173	0.205	−0.295	−0.41
0.3981	0.90949	0.247	−0.540	0.58
0.5116	0.90596	0.268	−0.587	0.86
0.6002	0.90208	0.277	−0.646	1.49
0.7066	0.89520	0.220	−0.636	2.54
0.8020	0.88479	0.135	−0.285	1.06
0.8511	0.87633	0.044	0.038	−1.96
Temperature (283.15 K)				
0.0514	0.91922	−0.021	3.250	−12.62
0.1115	0.91842	0.066	3.752	−15.84
0.1541	0.91781	0.112	3.142	−14.29
0.2100	0.91695	0.146	2.053	−10.65
0.2543	0.91617	0.187	1.308	−7.91
0.3011	0.91525	0.229	0.777	−5.90
0.3981	0.91303	0.261	0.429	−5.00
0.5116	0.90953	0.274	0.428	−6.14
0.6002	0.90570	0.267	0.166	−5.04
0.7066	0.89884	0.217	−0.213	−1.65
0.8020	0.88848	0.135	0.119	−4.52
0.8511	0.88004	0.049	0.626	−12.19

solvent. More negative values are observed at high temperatures for *n*-alkane solvents due to a better molecular package (Fig. 1(a)–(d)), although this effect decreases when molecular chain grows. In the alcohol mixtures, it could be observed as the first factor which produces a growing expansive behaviour through the homologous series (ethanol, 1-propanol and 1-butanol) due to molecular mass and package hindrance of aliphatic chain in the presence of oil. The maximum value is shown at equimolar composition of alkanol and olive oil. It is worthwhile to point out the moderated significance of temperature factor in high

Table 9
Densities (ρ), excess molar volumes (V^E), excess isobaric expansibilities (α^E) and isothermal pressure dependence of excess molar enthalpies ($(\partial H^E/\partial P)_T$) on mixing for the binary mixtures at different temperatures for 1-butanol+olive oil

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	$(\partial H^E/\partial P)_T$ (J MPa^{-1} mol^{-1})	$10^6\ \alpha^E$ (K^{-1})
Temperature (298.15 K)				
0.0507	0.90817	0.081	−0.779	2.40
0.0986	0.90759	0.116	−1.228	3.91
0.1563	0.90681	0.162	−1.655	5.57
0.2126	0.90597	0.191	−2.066	7.44
0.2654	0.90507	0.226	−2.449	9.45
0.3050	0.90433	0.244	−2.706	11.01
0.3620	0.90312	0.272	−2.970	13.04
0.4150	0.90184	0.282	−3.046	14.35
0.4603	0.90060	0.279	−2.953	14.76
0.4969	0.89946	0.279	−2.772	14.51
0.5570	0.89728	0.266	−2.297	12.91
0.6022	0.89530	0.253	−1.846	10.83
0.6579	0.89234	0.226	−1.274	7.66
0.6997	0.88958	0.209	−0.901	5.32
0.7462	0.88582	0.166	−0.605	3.42
0.8019	0.87973	0.134	−0.469	3.20
0.8528	0.87183	0.105	−0.538	5.85
0.9001	0.86104	0.059	−0.666	10.63
0.9509	0.84204	0.019	−0.627	14.47
Temperature (293.15 K)				
0.0507	0.91151	0.063	−0.505	1.51
0.0986	0.91092	0.110	−0.707	2.08
0.1563	0.91015	0.151	−0.815	2.38
0.2126	0.90932	0.174	−0.899	2.68
0.2654	0.90845	0.189	−0.998	3.13
0.3050	0.90772	0.203	−1.079	3.57
0.3620	0.90652	0.230	−1.181	4.23
0.4150	0.90525	0.240	−1.227	4.71
0.4603	0.90400	0.249	−1.208	4.87
0.4969	0.90287	0.248	−1.148	4.77
0.5570	0.90070	0.238	−0.971	4.09
0.6022	0.89873	0.226	−0.790	3.18
0.6579	0.89577	0.208	−0.553	1.80
0.6997	0.89301	0.197	−0.396	0.80
0.7462	0.88927	0.154	−0.274	0.09
0.8019	0.8832	0.125	−0.227	0.33
0.8528	0.87534	0.096	−0.275	2.12
0.9001	0.86459	0.052	−0.346	5.04
0.9509	0.84566	0.014	−0.327	7.50
Temperature (288.15 K)				
0.0507	0.91504	0.035	−0.236	0.56
0.0986	0.91444	0.095	−0.195	0.16
0.1563	0.91368	0.129	0.011	−0.99
0.2126	0.91284	0.165	0.247	−2.34
0.2654	0.91197	0.183	0.428	−3.54
0.3050	0.91125	0.192	0.520	−4.29
0.3620	0.91006	0.216	0.578	−5.07
0.4150	0.90879	0.230	0.562	−5.47
0.4603	0.90756	0.230	0.508	−5.57
0.4969	0.90643	0.232	0.448	−5.52
0.5570	0.90426	0.228	0.333	−5.23
0.6022	0.90229	0.221	0.248	−4.89
0.6579	0.89935	0.200	0.156	−4.39
0.6997	0.89661	0.186	0.100	−3.96
0.7462	0.89287	0.149	0.051	−3.43
0.8019	0.88683	0.119	0.010	−2.68
0.8528	0.87900	0.090	−0.016	−1.83
0.9001	0.86829	0.048	−0.032	−0.86
0.9509	0.84942	0.011	−0.032	0.15
Temperature (283.15 K)				
0.0507	0.91858	0.056	0.029	−0.43
0.0986	0.91800	0.097	0.308	−1.88
0.1563	0.91724	0.133	0.823	−4.54
0.2126	0.91640	0.171	1.374	−7.64
0.2654	0.91551	0.206	1.830	−10.57
0.3050	0.91478	0.223	2.091	−12.58
0.3620	0.91360	0.240	2.306	−14.89
0.4150	0.91234	0.249	2.319	−16.21
0.4603	0.91111	0.250	2.195	−16.59
0.4969	0.90999	0.247	2.016	−16.37
0.5570	0.90782	0.245	1.615	−15.05
0.6022	0.90586	0.235	1.268	−13.40
0.6579	0.90294	0.207	0.852	−10.91
0.6997	0.90022	0.191	0.587	−8.99
0.7462	0.89650	0.148	0.371	−7.14
0.8019	0.89048	0.118	0.243	−5.86
0.8528	0.88265	0.095	0.238	−5.98
0.9001	0.87198	0.049	0.278	−7.08
0.9509	0.85316	0.012	0.257	−7.59

Table 10
Phase splitting compositions in solvent molar fraction (x_{oil}, organic phase; $x_{alcohol}$, alcoholic phase) for the binary mixtures ethanol+olive oil and 2-propanol+olive oil at the range 283.15–298.15 K

Mixture	x_{oil}	$x_{alcohol}$	T (K)
Ethanol+olive oil	0.7560	0.9944	298.15
2-Propanol+olive oil	0.8863	0.9803	298.15
Ethanol+olive oil	0.7573	0.9949	293.15
2-Propanol+olive oil	0.8818	0.9817	293.15
Ethanol+olive oil	0.7307	0.9953	288.15
2-Propanol+olive oil	0.8511	0.9870	288.15
Ethanol+olive oil	0.7073	0.9951	283.15
2-Propanol+olive oil	0.8214	0.9866	283.15

molar mass solvents (1-propanol, 2-propanol and 1-butanol) (Fig. 1(f)–(h)) when compared with ethanol. In all cases, temperature produces higher values of excess molar volumes since it difficults the polar

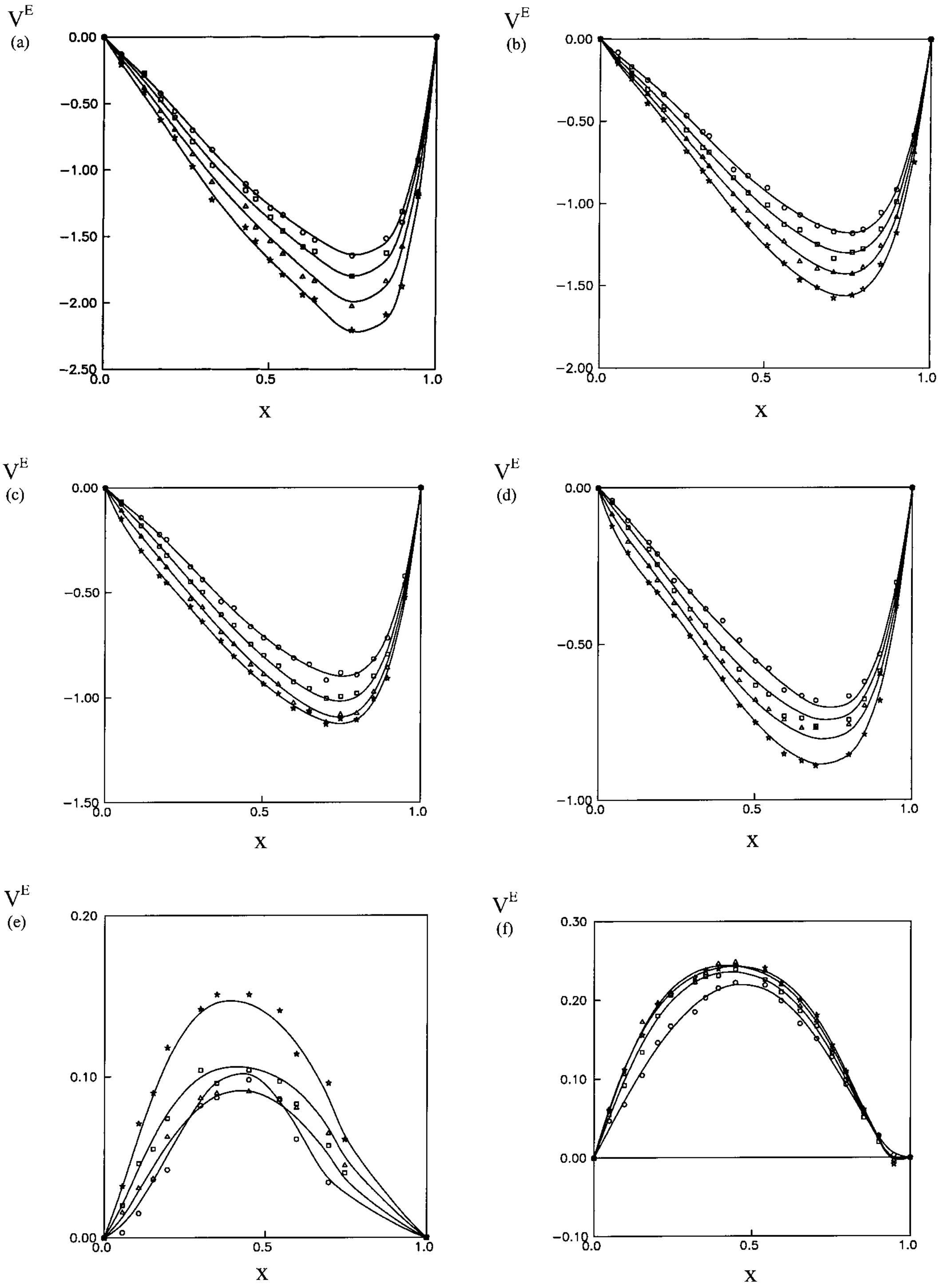

Fig. 1. Curves of constant excess molar volumes (cm^3 mol^{-1}) of (a) *n*-hexane, (b) *n*-heptane, (c) *n*-octane, (d) *n*-nonane, (e) ethanol, (f) 1-propanol, (g) 2-propanol, (h) 1-butanol+olive oil at the temperatures 283.15 (○), 288.15 (□), 293.15 (△) and 298.15 K (☆).

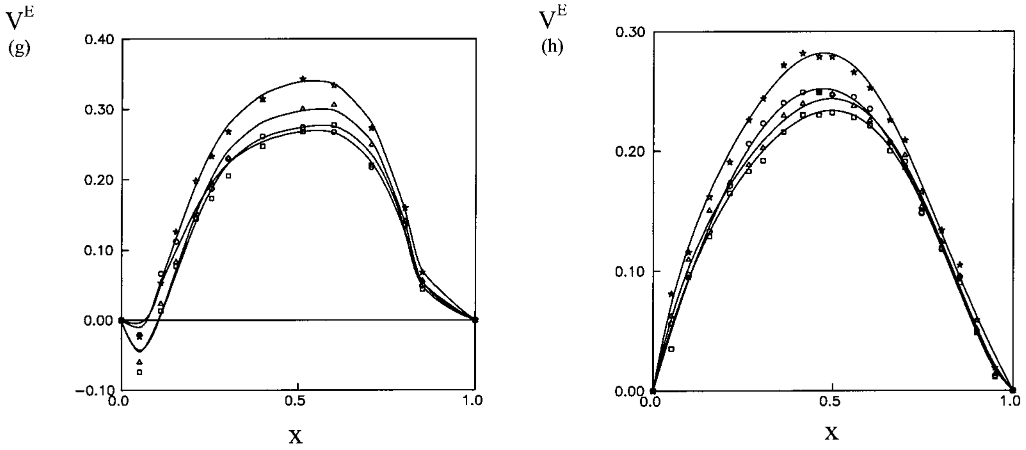

Fig. 1. (*Continued*)

interaction by means of hydrogen bonds. For both the cases (ethanol and 2-propanol), phase splitting occurs, lower composition in alcohol being observed in the functional series due to polar activity of hydroxyl functional group. In Table 11, solubility limits for these alcohol+olive oil mixtures are gathered. For the reasons given above, the same temperature dependence was observed in these mixtures.

4. Derived properties

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

$$\alpha = \left(\frac{\partial \ln \rho}{\partial T}\right)_{P,x}, \tag{6}$$

taking into account the temperature dependence of 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 expansibilities of each component in the mixture, as well as that due to non-ideality in the mixture. To this aim, the basic expression relating the molar volume of a mixture and its excess molar volume will be, in accordance to Eq. (1):

$$V = \sum_{i=1}^{N} x_i V_i + V^{\mathrm{E}}, \tag{7}$$

where V_i and x_i correspond to the molar volume and to the concentration of compound i. By differentiating Eq. (7),

$$\left(\frac{\partial V}{\partial T}\right)_{P,x_i} = \frac{\partial\left(\sum_{i=1}^{N} x_i V_i\right)}{\partial T} + \left(\frac{\partial V^{\mathrm{E}}}{\partial T}\right)_{P,x_i}. \tag{8}$$

Dividing by V and changing by minus sign:

$$\alpha = \frac{1}{V}\left[\left(\frac{\partial V^{\mathrm{E}}}{\partial T}\right)_{P,x_i} + \frac{\partial}{\partial T}\sum_{i=1}^{N}(x_i V_i)\right], \tag{9}$$

and then, we obtain

$$\alpha = V^{-1}\left[\left(\frac{\partial V^{\mathrm{E}}}{\partial T}\right)_{P,x_i} + \sum_{i=1}^{N}(\alpha_i x_i V_i)\right], \tag{10}$$

α and α_i being the isobaric expansivities of mixture and pure compound, respectively. From this expression, the excess isobaric expansibility would be

Table 11
Parameters of Eq. (4) in the range 283.15–298.15 K and σ

V^E (cm^3 mol^{-1})	Parameters			σ
n-Hexane+olive oil				
	$A_{01}=-181.522$	$A_{02}=1.318$	$A_{03}=-0.002$	0.030
	$A_{11}=154.074$	$A_{12}=-1.025$	$A_{13}=0.002$	
	$A_{21}=684.237$	$A_{22}=-4.597$	$A_{23}=0.008$	
	$A_{31}=-1187.639$	$A_{32}=8.309$	$A_{33}=-0.015$	
	$A_{41}=-2370.910$	$A_{42}=16.382$	$A_{43}=-0.028$	
n-Heptane+olive oil				
	$A_{01}=-30.762$	$A_{02}=0.271$	$A_{03}=-0.001$	0.016
	$A_{11}=-15.064$	$A_{12}=0.142$	$A_{13}=0.000$	
	$A_{21}=296.765$	$A_{22}=-2.007$	$A_{23}=0.003$	
	$A_{31}=-246.825$	$A_{32}=1.699$	$A_{33}=-0.003$	
	$A_{41}=-407.592$	$A_{42}=2.802$	$A_{43}=-0.005$	
n-Octane+olive oil				
	$A_{01}=164.846$	$A_{02}=-1.098$	$A_{03}=0.002$	0.012
	$A_{11}=397.002$	$A_{12}=-2.741$	$A_{13}=0.005$	
	$A_{21}=589.663$	$A_{22}=-4.027$	$A_{23}=0.007$	
	$A_{31}=-66.151$	$A_{32}=0.442$	$A_{33}=-0.001$	
	$A_{41}=-1444.274$	$A_{42}=9.995$	$A_{43}=-0.017$	
n-Nonane+olive oil				
	$A_{01}=23.595$	$A_{02}=-0.127$	$A_{03}=0.000$	0.013
	$A_{11}=-329.265$	$A_{12}=2.276$	$A_{13}=-0.004$	
	$A_{21}=-487.493$	$A_{22}=3.317$	$A_{23}=-0.006$	
	$A_{31}=603.638$	$A_{32}=-4.189$	$A_{33}=0.007$	
	$A_{41}=208.298$	$A_{42}=-1.306$	$A_{43}=0.002$	
Ethanol+olive oil				
	$A_{01}=143.906$	$A_{02}=-1.000$	$A_{03}=0.002$	0.009
	$A_{11}=-277.466$	$A_{12}=1.902$	$A_{13}=-0.003$	
	$A_{21}=-421.936$	$A_{22}=2.863$	$A_{23}=-0.005$	
	$A_{31}=469.629$	$A_{32}=-3.179$	$A_{33}=0.005$	
	$A_{41}=592.212$	$A_{42}=-4.004$	$A_{43}=0.007$	
1-Propanol+olive oil				
	$A_{01}=-39.230$	$A_{02}=0.271$	$A_{03}=0.000$	0.004
	$A_{11}=136.299$	$A_{12}=-0.939$	$A_{13}=0.002$	
	$A_{21}=-359.584$	$A_{22}=2.443$	$A_{23}=-0.004$	
	$A_{31}=84.333$	$A_{32}=-0.554$	$A_{33}=0.001$	
	$A_{41}=417.737$	$A_{42}=-2.850$	$A_{43}=0.005$	
2-Propanol+olive oil				
	$A_{01}=116.620$	$A_{02}=-0.814$	$A_{03}=0.001$	0.010
	$A_{11}=-27.833$	$A_{12}=0.191$	$A_{13}=0.000$	
	$A_{21}=-341.658$	$A_{22}=2.356$	$A_{23}=-0.004$	
	$A_{31}=-525.311$	$A_{32}=3.615$	$A_{33}=-0.006$	
	$A_{41}=1597.653$	$A_{42}=-10.981$	$A_{43}=0.019$	
1-Butanol+olive oil				
	$A_{01}=182.725$	$A_{02}=-1.259$	$A_{03}=0.002$	0.005
	$A_{11}=-236.102$	$A_{12}=1.626$	$A_{13}=-0.003$	
	$A_{21}=-307.986$	$A_{22}=2.133$	$A_{23}=-0.004$	
	$A_{31}=307.186$	$A_{32}=-2.108$	$A_{33}=0.004$	
	$A_{41}=355.250$	$A_{42}=-2.486$	$A_{43}=0.004$	

expressed as

$$\alpha^{\mathrm{E}} = \alpha - \sum_{i=1}^{N} \phi_i \alpha_i, \tag{11}$$

where

$$\phi_i = \frac{x_i V_i}{\sum_{i=1}^{N} x_i V_i} \tag{12}$$

is the volumetric fraction of the components of the mixture, such a property could be described as the variation of density with respect to the property at such condition with temperature due to non-ideality of mixture. The values of excess isobaric expansibility computed from the measured densities are gathered in Tables 2–9. For example, the isobaric expansibility (Fig. 2(a), (c), (e) and (g)) and the corresponding excess magnitude (Fig. 2(b), (d), (f) and (h)) of the alcohol mixtures are enclosed in Fig. 2. It could be observed as isobaric expansibility decrease with temperature for every binary system, a higher dependence being shown in the ethanol case. The exponential behaviour could be explained by the more intense interaction among alcohol molecules as the molar fraction increases. The excess isobaric expansibilities are of moderate intensity with positive tendency as temperature increases, although 1-propanol shows inverse trend. Maximum values or sigmoid behaviour are observed when contractive (1- and 2-propanol) (Fig. 2(d) and (f)) or phase splitting occurs (ethanol and 2-propanol) (Fig. 2(b) and (f)). Although the contractive trend is lower in *n*-alkane mixtures, its excess isobaric expansibility are considerable in percentage. They gather the growing behaviour of α when the temperature decreases as well as the negative contribution at high composition and the attenuation of this effect with decreasing temperature. Moreover, the real variation on this excess magnitude occurs in high compositions of solvent, thus only diluted mixtures of olive oil are non-linear and sensitive to temperature (Fig. 2(b)). Similar trend could be observed in the other alkanes except for *n*-octane, showing slightly decreasing negative excess magnitudes. This fact suggests the non-adequate use of α as a linear variation between pure component values and the role of excess values above all in *n*-alkane+olive oil mixtures. The isothermal coefficient of pressure excess molar enthalpy can be derived accurately from volumetric measurements by the application of the following expression:

$$\left(\frac{\partial H^{\mathrm{E}}}{\partial P}\right)_{T,x} = V^{\mathrm{E}} - T\left(\frac{\partial V^{\mathrm{E}}}{\partial T}\right)_{P,x}, \tag{13}$$

this magnitude stands for the dependence of excess molar enthalpy of mixing with pressure at fixed composition and temperature. In Fig. 3, the variation of the pressure coefficient for alcoholic mixtures can be observed, high positive slopes being obtained at low temperature with the exception of 1-propanol which presents an inversion trend point. The maximum difference point is shown to be approximately at equimolar composition for ethanol and 1-butanol but diluted alcohol composition for 1- and 2-propanol. In *n*-alkane mixtures, only positive contributions to pressure coefficients are observed at all temperatures. Partial molar quantities are important in the study of the dependence of an extensive property on phase composition at constant pressure and temperature, showing its trend with composition. The partial excess molar volume of a component in a multicomponent mixture and the limiting pure partial excess molar volumes have been calculated by equations described by Scatchard [7]. Table 12 reports the values of limiting pure partial excess molar volumes for the binary mixtures and Fig. 3 shows the variation of these magnitudes with the corresponding molar fraction of solvent for the mixtures.

In *n*-alkane mixtures, the strong effect of triglyceride molecules on the partial excess magnitude could be observed, the huge values of $\bar{V}_2^{\mathrm{E},\infty}$ being decreased by the increment in methylene groups in the molecular solvent chain. As a slight effect, temperature increases the negative values of $\bar{V}_i^{\mathrm{E}}$ only in *n*-hexane mixtures, being clearly non-negligible. In alcohol mixtures, positive values are observed in almost the whole composition range, decreasing or negative trend being observed at dilution of oil (see $\bar{V}_1^{\mathrm{E}}$ in all the cases, Fig. 4(e)–(h)) due to hydrogen bonds and infinite dilution of alcohol ($\bar{V}_2^{\mathrm{E}}$ in Fig. 4(e), (f) and (h)). The curious trend in 2-propanol limiting values could be caused by the secondary alcohol character and the disruption of oil structure. In two binary systems (ethanol and 2-propanol mixtures), inflection points are observed corresponding to splitting zones. In both the cases, high negative values of partial excess molar volumes are computed since alcohol is the component in greater abundance, and then hydrogen bonds struc-

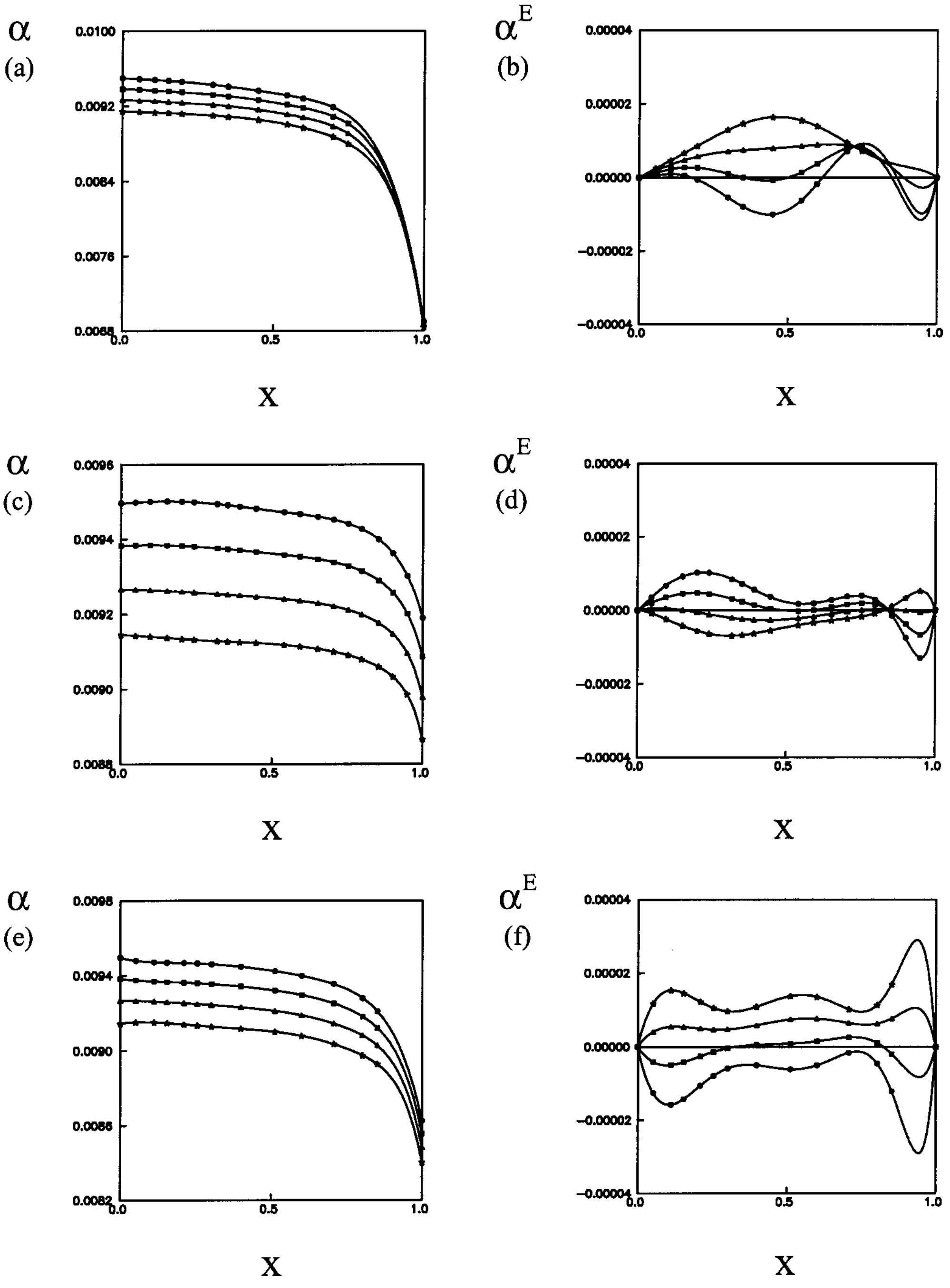

Fig. 2. Curves of constant isobaric expansibility (α, K^{-1}) and excess isobaric expansibility (α^E, K^{-1}) of the mixtures: (a, b) ethanol, (c, d) 1-propanol, (e, f) 2-propanol, (g, h) 1-butanol+olive oil at the range 283.15–298.15 K (same symbols used above).

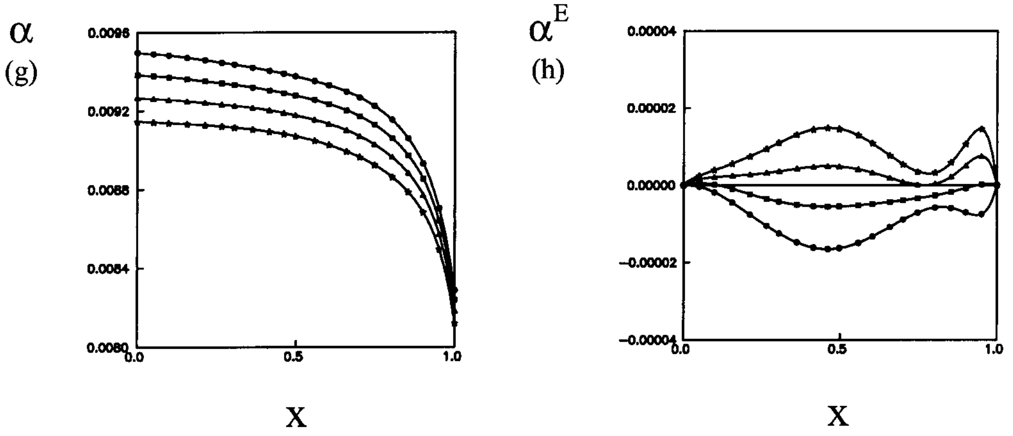

Fig. 2. (*Continued*)

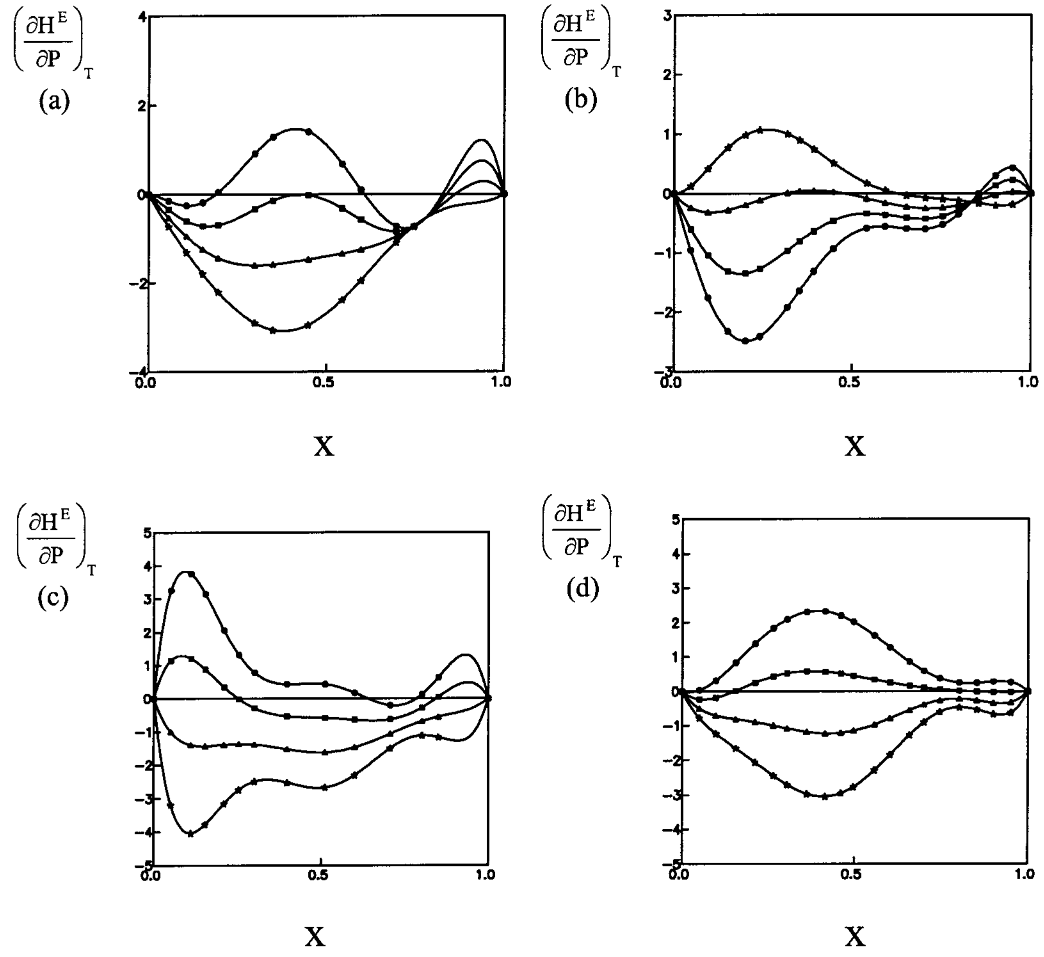

Fig. 3. Curves of constant isothermal coefficient of pressure excess molar enthalpy ($(\partial H^E/\partial P)_T$) (J MPa^{-1} mol^{-1}) of the mixtures: (a) ethanol, (b) 1-propanol, (c) 2-propanol and (d) 1-butanol+olive oil at the range 283.15–298.15 K (same symbols used above).

Table 12
Partial excess molar volumes at infinite dilution of the binary mixtures at the range of temperature 283.15–298.15 K

Mixture	Temperature (K)	$\bar{V}_1^{E,\infty}$ (cm^3 mol^{-1})	$\bar{V}_2^{E,\infty}$ (cm^3 mol^{-1})
n-Hexane+olive oil	298.15	−4.008	−30.028
n-Heptane+olive oil		−3.278	−18.121
n-Octane+olive oil		−3.861	−13.811
n-Nonane+olive oil		−3.488	−10.306
Ethanol+olive oil		0.476	−0.721
1-Propanol+olive oil		1.384	−0.416
2-Propanol+olive oil		−1.246	−2.484
1-Butanol+olive oil		1.668	0.593
n-Hexane+olive oil	293.15	−3.026	−25.314
n-Heptane+olive oil		−2.984	−16.649
n-Octane+olive oil		−2.432	−12.648
n-Nonane+olive oil		−2.336	−9.478
Ethanol+olive oil		0.275	−0.661
1-Propanol+olive oil		1.296	−0.447
2-Propanol+olive oil		−2.267	−2.836
1-Butanol+olive oil		1.345	0.296
n-Hexane+olive oil	288.15	−2.554	−22.402
n-Heptane+olive oil		−2.629	−15.448
n-Octane+olive oil		−1.633	−11.721
n-Nonane+olive oil		−1.524	−8.662
Ethanol+olive oil		0.150	−0.313
1-Propanol+olive oil		1.094	−0.340
2-Propanol+olive oil		−2.151	−2.706
1-Butanol+olive oil		1.123	0.181
n-Hexane+olive oil	283.15	−2.589	−21.295
n-Heptane+olive oil		−2.213	−14.518
n-Octane+olive oil		−1.464	−11.033
n-Nonane+olive oil		−1.052	−7.858
Ethanol+olive oil		0.101	0.323
1-Propanol+olive oil		0.780	−0.095
2−Propanol+olive oil		−0.898	−2.093
1-Butanol+olive oil		1.003	0.249

ture the mixture. The local maxima observed near diluted mixtures point out the role of short alcohols in the substantial change in molecular interactions.

5. Prediction of excess molar volumes

Due to the strong dependence of design and optimization of chemical processes on computer calculations, the availability of accurate and tested methods as well as related parameters is of increasing relevance. In this case, consideration was given to the Rackett equation [8,9] in order to analyze how accurate densities are predicted. This method is described by the following expression:

$$V = (RT_c/P_c)\beta^{[1+(1-T_r)^{2/7}]}, \tag{14}$$

where V is the molar volume, T_r is the reduced temperature, T_c and P_c are the critical properties and β is the compressibility factor or an acentric factor dependent parameter which varies attending to the molecular structure parameter [10]. The selected mixing rule to compute molar volumes in mixtures and then excess molar volumes by Eq. (1) was that proposed by Kay (modified combination of Prausnitz–Gunn) [10–12]. In order to predict mixture

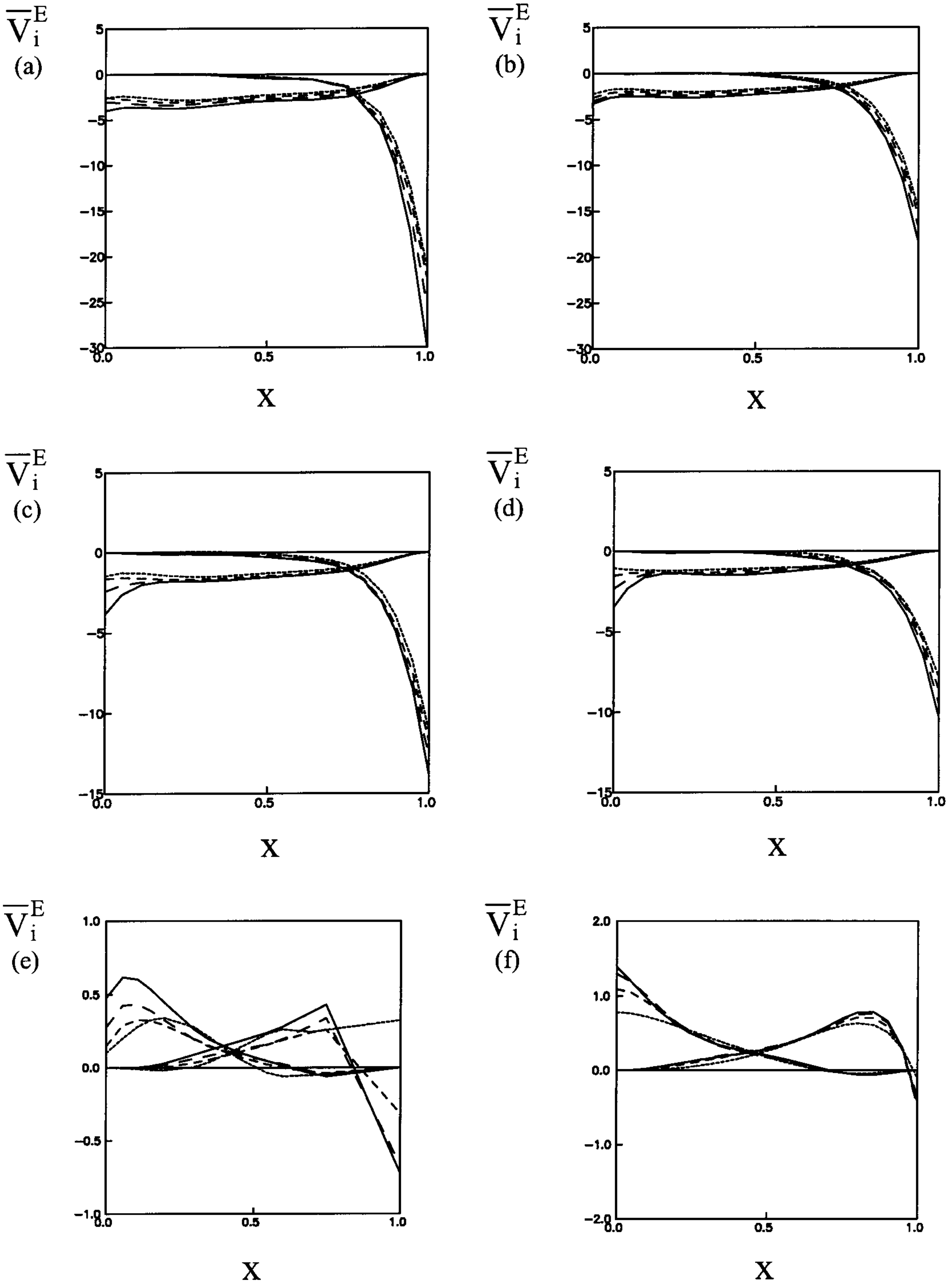

Fig. 4. Partial excess molar volumes (cm^3 mol^{-1}) ($\bar{V}_1^E$ (right axis) and $\bar{V}_2^E$ (left axis)) of (a) *n*-hexane, (b) *n*-heptane, (c) *n*-octane, (d) *n*-nonane, (e) ethanol, (f) 1-propanol, (g) 2-propanol, (h) 1-butanol+olive oil at the temperatures 283.15 (· · ·), 288.15 (- - -), 293.15 (— — —) and 298.15 K (———).

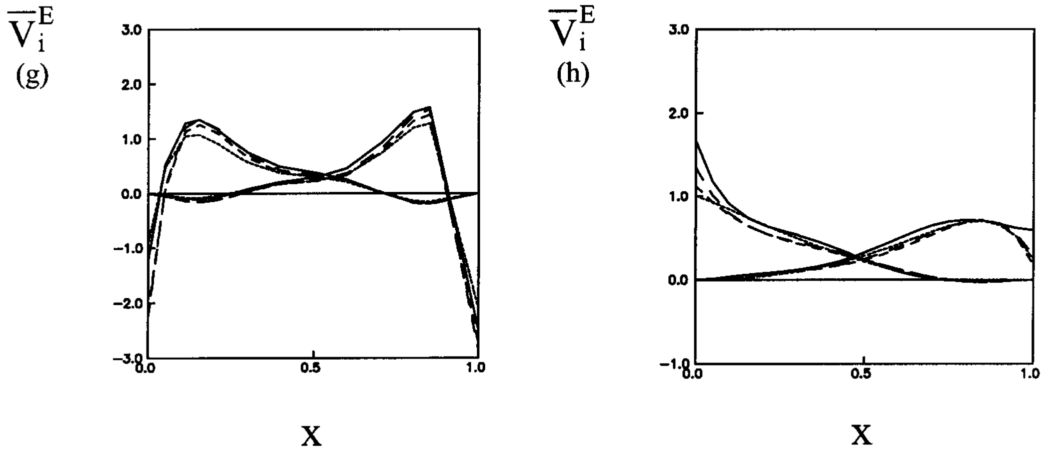

Fig. 4. (*Continued*)

excess volumes, critical properties are needed for each compound, open literature or estimative methods could be applied. Currently available values are found for *n*-alkanes or alkanols but a considerable lack of thermodynamic data occurs for natural substances. The procedures for the estimation of critical constants have been reviewed by several authors [10,13] and among such methods, those developed by Lydersen [14], Ambrose [15–17], Kreglewski [18–20] and Somayajulu [21,22] have gained recognition by simplicity and general accurate results in a wide range of compounds. While the procedures developed by Lydersen and Ambrose yield satisfactory predictions for organics of low molecular weight, Kreglewski yields accurate values in homogeneous series of compounds of high molecular weight. In spite of that, such methods lack sufficient group contributions or use extrapolated values. More recently, Somayajulu has proposed a generalization of former methods looking for theoretical support and finer values by the means of application of molecular index concept. Such a magnitude was obtained on the basis of group contributions listed by both Lydersen and Ambrose in many cases. In accordance with this procedure, the following equation was applied:

$$G_i = a_i + b_i N_i, \tag{15}$$

where i stands for t (temperature), p (pressure) or v (volume) depending on the magnitude estimation, G is a parameter $((T_b/(T_c-T_b))$, $(M/P_c)^{1/2}$ or V_c, respectively, accordingly above explained symbols), N is the group indices depending on molecular index, and a and b are the procedure parameters. In Table 13, open literature and estimated critical values are gathered for the compounds enclosed in studied mixtures. In Fig. 5, comparison between the binary experimental and predicted densities is shown in terms of root square deviations. Table 14 gathers deviation values at each temperature, non-definitively better results being obtained by either Rackett or modified Rackett, although their adequate predictive (better than 5%) capabilities are slightly better at low temperatures.

Table 13
Open literature and estimated critical values for compounds enclosed binary mixtures

Compound	P_c (MPa)	T_c (K)	Z_c	ω
n-Hexane	3.01	507.5	0.264	0.299
n-Heptane	2.74	540.3	0.263	0.349
n-Octane	2.49	568.8	0.259	0.398
n-Nonane	2.29	594.6	0.260	0.445
Ethanol	6.14	513.9	0.240	0.644
1-Propanol	5.17	536.8	0.253	0.623
2-Propanol	4.76	508.3	0.248	0.665
1-Butanol	4.42	563.1	0.259	0.593
Olive oil	0.48	701.3	0.256	0.432

6. Phase equilibria models

Liquid–liquid equilibria is of interest in extraction operation or modified heterogeneous distillation use-

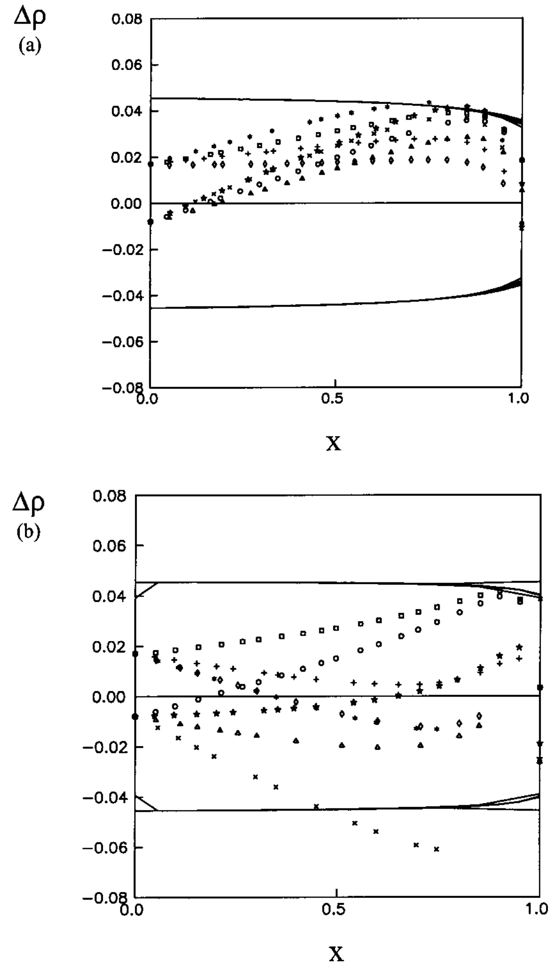

Fig. 5. Deviations (g cm^{-3}) ($\Delta\rho$ (5%), solid line; experimental values for each case, dashed line) from predicted values for (a) *n*-alkanes (*n*-hexane (R, ∗; mR, ×), *n*-heptane (R, +; mR, ☆), *n*-octane (R, ◇; mR, △) and *n*-nonane (R, □; mR, ○)) and alkanols (ethanol (R, ∗; mR, ×), 1-propanol (R, +; mR, ☆), 2-propanol (R, ◇; mR, △) and 1-butanol (R, □ ; mR, ○)) at 298.15 K.

ful to develop thermodynamic predictive methods and compute new sets of contribution parameters. The Universal Function-group Activity Coefficients model have been successfully applied for the prediction of a large number of liquid–liquid systems. This model depends on the interaction parameters between each pair of main functional groups present in the mixture, which were obtained by selecting a division of molecules in representative functional groups and then regressing the experimental data to the models, and

Table 14
Root square deviations for predictive density values by Rackett (R) or modified Rackett (mR) with respect to corresponding experimental data for binary mixtures at the range 283.15–298.15 K

Mixture	Temperature (K)	R	mR
n-Hexane+olive oil	298.15	0.03254	0.02248
n-Heptane+olive oil		0.02287	0.02630
n-Octane+olive oil		0.01681	0.01713
n-Nonane+olive oil		0.02919	0.02119
Ethanol+olive oil		0.03943	0.05355
1-Propanol+olive oil		0.01169	0.00892
2-Propanol+olive oil		0.01179	0.01592
1-Butanol+olive oil		0.02823	0.02081
n-Hexane+olive oil	293.15	0.03205	0.02196
n-Heptane+olive oil		0.02237	0.02586
n-Octane+olive oil		0.01643	0.01686
n-Nonane+olive oil		0.02879	0.02084
Ethanol+olive oil		0.01464	0.04541
1-Propanol+olive oil		0.01131	0.00883
2-Propanol+olive oil		0.01220	0.01667
1-Butanol+olive oil		0.02765	0.02024
n-Hexane+olive oil	288.15	0.03168	0.02154
n-Heptane+olive oil		0.02203	0.02557
n-Octane+olive oil		0.01610	0.01657
n-Nonane+olive oil		0.02864	0.02072
Ethanol+olive oil		0.01506	0.04625
1-Propanol+olive oil		0.01112	0.00877
2-Propanol+olive oil		0.01265	0.01732
1-Butanol+olive oil		0.02724	0.01979
n-Hexane+olive oil	283.15	0.03143	0.02126
n-Heptane+olive oil		0.02173	0.02531
n-Octane+olive oil		0.01681	0.01649
n-Nonane+olive oil		0.02846	0.02054
Ethanol+olive oil		0.01550	0.04537
1-Propanol+olive oil		0.01098	0.00875
2-Propanol+olive oil		0.01313	0.01800
1-Butanol+olive oil		0.02686	0.01936

obtaining numerical values for the interaction parameters [23,24]. Liquid–liquid equilibrium calculations were performed by solving the isoactivity relation of each component in two liquid phases as follows:

$$\gamma_i^{\mathrm{E}} x_i^{\mathrm{E}} = \gamma_i^{\mathrm{R}} x_i^{\mathrm{R}}, \tag{16}$$

$$N_i = N_i^{\mathrm{E}} + N_i^{\mathrm{R}}, \tag{17}$$

where E is the extract (solvent phase), R the raffinatte (oil phase), and N_i is the number of moles, γ_i being the corresponding activity coefficient of component i in

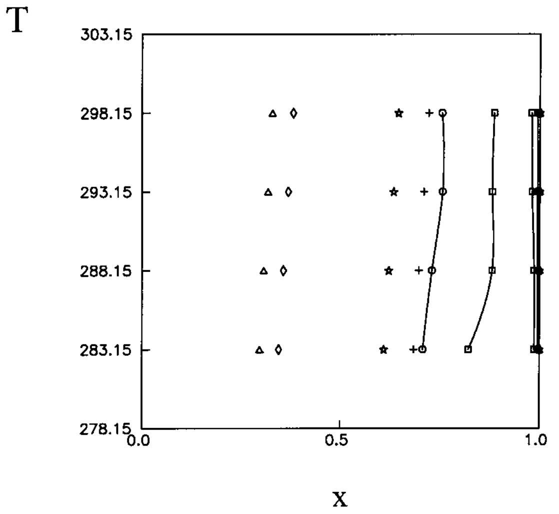

Fig. 6. Predictive (△, modified UNIFAC for ethanol; ◇, modified UNIFAC for 2-propanol; ☆, UNIFAC for ethanol; +, UNIFAC for 2-propanol) and experimental (○, ethanol; □, 2-propanol) data of liquid–liquid equilibria at the range 283.15–298.15 K.

the different liquid phases, as calculated from the equilibrium model. The interaction parameters between the *n*-alkanes, alcohols and linearized triglyceride of the group contribution models were used to predict the activity coefficients. Eqs. (16) and (17) are solved to calculate the mole fraction for component *i* in each liquid phase, a single tie line being obtained by this method of calculation. The applicability of these models was tested by comparing, as shown in Fig. 6, the calculated phase equilibrium compositions determined by the application of the corresponding polynomials which were gathered above. Only liquid phase split was observed in two binaries and all temperatures measured, such immiscibility covering lower composition range as the polar character of the solvent increases. A poor description is obtained by such methods, better values being computed by the means of the original model in both phases.

7. Conclusions

Experimental values of volumetric behaviour in the temperature range 283.15–298.15 K are presented in the scope of investigating the dependence of such property with homologous series of alkanols and *n*-alkanes, which are related to refining procedures of vegetable oil. In spite of thermodynamic data lack and the complexity of the mixtures (great difference in molecular volume, mass and structure as well as a linearized composition in fatty acids), the application of predictive equations for density was proved and tested. Group contribution methods were applied to liquid–liquid equilibria prediction, only a qualitative description when phase split occurs were obtained due to non-stochiometric triglyceride structure and complex interactions with solvents.

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