Densities, Surface Tensions, and Refractive Indexes of Propyl Propanoate + Hexane + *m*-Xylene at 298.15 K

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This paper reports experimental densities, surface tensions, and refractive indexes of the ternary system (propyl propanoate + hexane + *m*-xylene) at the temperature 298.15 K and atmospheric pressure over the whole composition range. Also, the corresponding binary mixtures not published before are presented. The excess molar volumes, surface tension deviations, and changes in the refractive index on mixing have been calculated. Finally, we will compare the experimental data of surface tension and refractive index with different theoretical and empirical approximations.

Introduction

This work continues our studies about the excess thermodynamic properties for ternary mixtures containing propyl propanoate, hexane, and aromatic hydrocarbon.[1,2] We present here experimental densities, surface tensions, and refractive indexes of the ternary system (propyl propanoate + hexane + *m*-xylene) and of the corresponding binary mixture (hexane + *m*-xylene) at 298.15 K. For the binary mixture (propyl propanoate + *m*-xylene), we present here only the refractive index because the densities and surface tensions were published previously by us in ref 3. Also the corresponding magnitudes for the binary mixture {propyl propanoate + hexane} have been already published by us.[1,2] We will compare the experimental data with different theoretical and empirical approximations. In the case of the surface tensions, we will test the empirical relation of Brock and Bird[4] and the theories of Hildebrand and Scott,[5] which are extensions of the classical Guggenheim's ideal solution theory, one of them for ideal solutions containing molecules of similar size (HSIS) and the other one for mixtures of molecules with different size (HSEG). To correlate the refractive index of a mixture with its corresponding density, we will use the empirical approximations due to Lorentz−Lorenz, Wiener, Heller, Gladstone−Dale, and Newton, all of them summarized in ref 6.

From the measured data we will extract the excess molar volumes, surface tension deviations, and changes in the refractive indexes on mixing. These last results will be fitted with a Redlich−Kister type equation[7] for the binary mixtures, while for the ternary one we used Cibulka's equation[8] in the case of the excess molar volumes and the surface tensions and the equation of Morris and Nagata[9,10] for the changes in the refractive indexes. Finally, the data for the calculated excess magnitudes in the ternary system will be compared with those obtained from several empirical equations based on the experimental data obtained for the corresponding binary mixtures. Among the many empirical equations, we have checked our data to those of Jacob−Fitzner,[11] Kohler,[12] Colinet,[13] Knobeloch−Schwartz,[14] Tsao−Smith,[15] Toop,[16] Scatchard,[17] Hillert,[18] and Mathieson−Thynne.[19] The four first approximations are symmetrical, and the last five are asymmetric, which means that the order of the components is relevant in the results obtained.

Experimental Section

The chemicals employed were supplied by Fluka and Sigma-Aldrich. Their mass purities were propyl propanoate (Sigma-Aldrich, > 99 %), hexane (Fluka, ≥ 99.5 %), and *m*-xylene (Fluka, ≥ 99 %). The substances were degassed by ultrasound and dried over molecular sieves (Sigma type 0.4 nm) and were otherwise used as supplied.

All the mixtures were prepared by mass using a Mettler AT 201 balance, the uncertainty of the mole fraction is estimated to be about $\pm 1 \cdot 10^{-5}$. Densities (ρ) of pure liquids and their corresponding mixtures were measured using an Anton Paar digital densimeter (model 60/602) thermostated with a Schott-Gërate CT 1450 circulating-water bath, with a precision in the temperature control of 0.01 K. The uncertainties of the densities are about $\pm 1 \cdot 10^{-5}$ $g \cdot cm^{-3}$. Calibration is performed daily with Milli-Q water and heptane (Sigma, > 99 %). Surface tension (σ) was determined using a Lauda TVT1 automated tensiometer, which employs the principle of the drop volume. This technique consists of measuring the volume of a drop detaching from a capillary with a known circular cross-section. The uncertainty of the surface tension measured with this method is $\pm 1 \cdot 10^{-2}$ $mN \cdot m^{-1}$. A Lauda RC6CP thermostatic bath controlled the temperature to better than 0.1 K. Detailed instrument design and experimental procedure have been described elsewhere.[20] Refractive indexes (n_D) were measured with an Atago RX-1000 automatic refractometer with a reproducibility in the refractive index of $1 \cdot 10^{-4}$, and the temperature was regulated using a PolyScience 9101 thermostat, with an uncertainty lower that 0.1 K.

Results

The measured densities, surface tensions, and refractive indexes of the three pure liquids used at $T = 298.15$ K are listed in Table 1 with literature values. The agreement, within the experimental uncertainties, between both sets of data indicates the high quality of our compounds and that our experimental equipment has good accuracy.

Densities, surface tensions, and refractive indexes of the binary systems obtained in this work and not published before are shown, respectively, in Tables 2 to 4. In Tables 5 to 7, we include the same magnitudes for the ternary system.

The excess molar volumes (V_m^E), surface tension deviations ($\delta\sigma$), and changes in the refractive index on mixing (Δn_D) were

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10.1021/je0504111 CCC: $33.50

Table 1. Density, Surface Tension, and Refractive Index of the Pure Components at 298.15 K

	ρ/g·cm^{-3}		σ/mN·m^{-1}		n_D	
component	exp.	lit.	exp.	lit.	exp.	lit.
propyl propanoate	0.87553	0.87553[21]	24.10	24.21[23]	1.3905	1.3920[22]
hexane	0.65470	0.65471[22]	17.91	17.90[22]	1.3723	1.3723[24]
m-xylene	0.85978	0.8600[22]	28.03	28.10[22]	1.4945	1.4946[24]

Table 2. Densities, ρ, and Excess Molar Volumes, V_m^E, for Binary Mixture Hexane (1) + *m*-Xylene (2) at 298.15 K

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}
0.0431	0.85057	−0.039	0.5167	0.75198	−0.252
0.0825	0.84228	−0.077	0.5833	0.73831	−0.242
0.1572	0.82664	−0.142	0.6294	0.72897	−0.232
0.2093	0.81569	−0.170	0.6769	0.71932	−0.217
0.2575	0.80559	−0.191	0.7318	0.70821	−0.193
0.2997	0.79680	−0.211	0.7817	0.69813	−0.163
0.3563	0.78503	−0.234	0.8329	0.68789	−0.136
0.4278	0.77024	−0.248	0.8914	0.67622	−0.101
0.4830	0.75886	−0.251	0.9446	0.66565	−0.062

Table 3. Surface Tensions, σ, and Surface Tension Deviations, $\delta\sigma$, for Binary Mixture Hexane (1) + *m*-Xylene (2) at 298.15 K

x_1	σ / mN·m^{-1}	$\delta\sigma$ / mN·m^{-1}	x_1	σ / mN·m^{-1}	$\delta\sigma$ / mN·m^{-1}
0.0522	27.13	−0.37	0.5086	21.50	−1.38
0.0797	26.69	−0.53	0.5677	21.01	−1.27
0.1442	25.66	−0.91	0.6431	20.41	−1.11
0.2008	24.85	−1.14	0.6771	20.15	−1.03
0.2281	24.48	−1.24	0.7418	19.70	−0.82
0.3075	23.50	−1.42	0.7668	19.54	−0.73
0.3603	22.91	−1.47	0.8545	18.99	−0.39
0.4106	22.39	−1.48	0.8802	18.83	−0.29
0.4174	22.33	−1.47	0.9600	18.29	−0.02

Table 4. Refractive Indexes, n_D, and Changes in the Refractive Indexes, Δn_D, for Binary Mixtures at 298.15 K

x_1	n_D	Δn_D	x_1	n_D	Δn_D
Propyl Propanoate (1) + *m*-Xylene (2)					
0.0448	1.4894	−0.0003	0.5421	1.4358	−0.0023
0.1176	1.4814	−0.0008	0.5906	1.4308	−0.0022
0.1702	1.4756	−0.0011	0.6442	1.4254	−0.0020
0.2173	1.4704	−0.0014	0.7474	1.4151	−0.0016
0.3134	1.4599	−0.0019	0.7982	1.4101	−0.0014
0.3923	1.4515	−0.0021	0.8483	1.4052	−0.0011
0.4461	1.4458	−0.0022	0.8942	1.4008	−0.0007
0.4902	1.4412	−0.0023	0.9522	1.3952	−0.0003
Hexane (1) + *m*-Xylene (2)					
0.0431	1.4891	−0.0001	0.5167	1.4300	−0.0015
0.0830	1.4840	−0.0004	0.5798	1.4223	−0.0014
0.1562	1.4748	−0.0007	0.6769	1.4106	−0.0013
0.2093	1.4682	−0.0009	0.7318	1.4040	−0.0012
0.2997	1.4569	−0.0012	0.8329	1.3920	−0.0009
0.3521	1.4502	−0.0013	0.8836	1.3860	−0.0007
0.4276	1.4409	−0.0014	0.9325	1.3803	−0.0004

Table 5. Densities, ρ, and Excess Molar Volumes, V_m^E, for the Ternary Mixture Propyl Propanoate (1) + Hexane (2) + *m*-Xylene (3) at 298.15 K

x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}
0.8500	0.0658	0.85970	0.046	0.2546	0.0616	0.85129	−0.065
0.7714	0.0625	0.85927	0.022	0.2515	0.1547	0.83158	−0.078
0.7554	0.1607	0.83831	0.113	0.2555	0.2447	0.81275	−0.072
0.6939	0.0652	0.85752	0.009	0.2513	0.3342	0.79399	−0.051
0.6764	0.1589	0.83750	0.078	0.2557	0.4128	0.77772	−0.006
0.6762	0.2387	0.82067	0.171	0.2525	0.4913	0.76139	0.052
0.5934	0.0626	0.85656	−0.014	0.2548	0.5863	0.74190	0.141
0.5948	0.1654	0.83476	0.071	0.2531	0.6671	0.72534	0.231
0.5956	0.2406	0.81904	0.125	0.1765	0.0677	0.84862	−0.070
0.6055	0.3107	0.80453	0.210	0.1774	0.1627	0.82858	−0.097
0.5210	0.0639	0.85516	−0.030	0.1799	0.3319	0.79318	−0.090
0.4985	0.1563	0.83524	0.016	0.1741	0.4043	0.77811	−0.088
0.4988	0.2365	0.81835	0.073	0.1744	0.5709	0.74372	0.015
0.5070	0.4100	0.78233	0.248	0.1807	0.7374	0.70991	0.181
0.4322	0.0647	0.85358	−0.049	0.0945	0.0835	0.84384	−0.082
0.4274	0.1557	0.83427	−0.020	0.0969	0.1599	0.82785	−0.127
0.4227	0.2355	0.81739	0.020	0.0775	0.2433	0.80996	−0.154
0.4271	0.3106	0.80179	0.068	0.0729	0.3299	0.79178	−0.163
0.4240	0.4108	0.78083	0.165	0.0758	0.4200	0.77316	−0.168
0.3392	0.0576	0.85357	−0.060	0.0743	0.5840	0.73944	−0.130
0.3979	0.1752	0.82966	−0.019	0.0733	0.6652	0.72283	−0.082
0.3427	0.3229	0.79781	0.021	0.0775	0.7582	0.70412	−0.015
0.3407	0.4041	0.78086	0.081	0.0777	0.8416	0.68737	0.060
0.3374	0.5799	0.74467	0.235				

Table 6. Surface Tensions, σ, and Surface Tension Deviations, $\delta\sigma$, for the Ternary Mixture Propyl Propanoate (1) + Hexane (2) + *m*-Xylene (3) at 298.15 K

x_1	x_2	σ / mN·m^{-1}	$\delta\sigma$ / mN·m^{-1}	x_1	x_2	σ / mN·m^{-1}	$\delta\sigma$ / mN·m^{-1}
0.8633	0.0568	23.89	−0.18	0.2296	0.5140	21.09	−0.84
0.7393	0.0871	23.92	−0.32	0.2713	0.1406	24.63	−0.91
0.7758	0.1526	23.06	−0.37	0.2645	0.2183	23.76	−1.02
0.6640	0.1544	23.34	−0.52	0.2613	0.3146	22.77	−1.05
0.6909	0.2289	22.42	−0.57	0.2734	0.3780	22.10	−1.03
0.5722	0.0833	24.43	−0.51	0.2629	0.4824	21.23	−0.88
0.5925	0.1537	23.54	−0.61	0.2782	0.5399	20.75	−0.72
0.5769	0.2436	22.60	−0.70	0.2644	0.6613	19.90	−0.40
0.4917	0.0824	24.70	−0.57	0.1607	0.1508	24.95	−0.92
0.5110	0.1206	24.21	−0.59	0.1668	0.2234	24.07	−1.04
0.4903	0.2463	22.81	−0.80	0.1701	0.2783	23.37	−1.17
0.5103	0.3050	22.15	−0.79	0.1634	0.4118	22.08	−1.14
0.5030	0.4116	21.15	−0.74	0.1704	0.4620	21.61	−1.07
0.4207	0.0851	24.90	−0.61	0.1613	0.5846	20.71	−0.77
0.4353	0.1269	24.35	−0.69	0.1709	0.6375	20.31	−0.59
0.4394	0.2002	23.43	−0.85	0.1635	0.7612	19.57	−0.12
0.4795	0.2398	22.93	−0.79	0.0974	0.2347	24.09	−1.18
0.4170	0.4056	21.44	−0.85	0.0958	0.2995	23.37	−1.25
0.4362	0.4839	20.73	−0.69	0.0968	0.4515	21.87	−1.21
0.3576	0.1166	24.71	−0.74	0.1024	0.5282	21.22	−1.06
0.3319	0.2294	23.48	−0.93	0.1106	0.6165	20.54	−0.81
0.3522	0.2843	22.79	−0.98	0.0926	0.7321	19.83	−0.43
0.3343	0.4800	21.06	−0.80	0.1017	0.8161	19.33	−0.04
0.3607	0.5604	20.34	−0.60				

computed using eqs 1 to 3, respectively: In these equations ρ,

$$V_m^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{-1}) \qquad (1)$$

$$\delta\sigma = \sigma - \sum_{i=1}^{N} x_i \sigma_i \qquad (2)$$

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{D,i} \qquad (3)$$

σ, and n_D are respectively the density, the surface tension, and the refractive index in the mixture; ρ_i, σ_i, and n_i are the properties of the pure components; and N is the number of the components in the mixture (so $N = 2$ in the case of a binary mixture and $N = 3$ for a ternary one). The calculated values of V_m^E, $\delta\sigma$, or Δn_D appear respectively in Tables 2 to 4 for the binary mixtures not published before and in Tables 5 to 7 for the ternary system.

Table 7. Refractive Indexes, n_D, and Changes in the Refractive Indexes, Δn_D, for the Ternary Mixture Propyl Propanoate (1) + Hexane (2) + *m*-Xylene (3) at 298.15 K

x_1	x_2	n_D	Δn_D	x_1	x_2	n_D	Δn_D
0.8500	0.0658	1.3971	−0.0011	0.3374	0.5799	1.3871	−0.0016
0.7714	0.0625	1.4052	−0.0015	0.2546	0.0616	1.4584	−0.0021
0.7554	0.1607	1.3953	−0.0011	0.2555	0.2447	1.4357	−0.0023
0.6939	0.0652	1.4125	−0.0020	0.2513	0.3342	1.4254	−0.0021
0.6764	0.1589	1.4033	−0.0015	0.2557	0.4128	1.4153	−0.0022
0.6762	0.2387	1.3937	−0.0014	0.2525	0.4913	1.4066	−0.0016
0.5934	0.0626	1.4229	−0.0023	0.2548	0.5863	1.3947	−0.0017
0.5948	0.1654	1.4107	−0.0018	0.2531	0.6671	1.3853	−0.0014
0.5956	0.2406	1.4016	−0.0017	0.1765	0.0677	1.4664	−0.0014
0.6055	0.3107	1.3923	−0.0014	0.1777	0.2319	1.4459	−0.0017
0.5210	0.0639	1.4301	−0.0025	0.1799	0.3319	1.4330	−0.0022
0.4985	0.1563	1.4213	−0.0024	0.1741	0.4043	1.4250	−0.0020
0.4988	0.2365	1.4116	−0.0022	0.1769	0.4892	1.4145	−0.0018
0.5156	0.3121	1.4010	−0.0019	0.1744	0.5709	1.4047	−0.0019
0.5070	0.4100	1.3904	−0.0015	0.1846	0.6768	1.3914	−0.0012
0.4322	0.0647	1.4392	−0.0025	0.1807	0.7374	1.3844	−0.0013
0.4274	0.1557	1.4287	−0.0024	0.0945	0.0835	1.4732	−0.0013
0.4227	0.2355	1.4196	−0.0022	0.0969	0.1599	1.4634	−0.0015
0.4271	0.3106	1.4101	−0.0021	0.0775	0.2433	1.4553	−0.0014
0.4240	0.4108	1.3984	−0.0019	0.0729	0.3299	1.4450	−0.0016
0.4319	0.4812	1.3894	−0.0015	0.0758	0.4200	1.4335	−0.0018
0.3392	0.0576	1.4500	−0.0022	0.0732	0.5131	1.4223	−0.0019
0.3979	0.1752	1.4294	−0.0024	0.0743	0.5840	1.4136	−0.0018
0.3427	0.3229	1.4173	−0.0022	0.0733	0.6652	1.4041	−0.0015
0.3407	0.4041	1.4077	−0.0021	0.0775	0.7582	1.3926	−0.0012
0.3456	0.4902	1.3974	−0.0014	0.0777	0.8416	1.3828	−0.0008

The derived excess functions of the binary systems can be represented by a Redlich−Kister equation:[7]

$$Q_{ij}^{E} = x_i x_j \sum_{k=0}^{m} A_k (x_i - x_j)^k \tag{4}$$

where Q_{ij}^{E} represents any of the following properties: V_m^E, $\delta\sigma$, or Δn_D; x_i and x_j are the mole fractions of components *i* and *j*, respectively; and A_k denotes the polynomial coefficients. The degree (m) of the polynomial Redlich−Kister equation was optimized by applying the F-test.[25] The coefficients A_k for eq 4 and the standard deviations, *s*, obtained for the three magnitudes appear in Table 8, where we also include the parameters already published for some of the binary mixtures.

To correlate the excess magnitudes of the ternary mixture, we have employed as usual the following equation:

$$Q_{123}^{E} = Q_{bin}^{E} + x_1 x_2 (1 - x_1 - x_2) \Delta_{123} \tag{5}$$

where

$$Q_{bin}^{E} = Q_{12}^{E} + Q_{13}^{E} + Q_{23}^{E} \tag{6}$$

Here the symbol Q_{123}^{E} represents $V_{m,123}^{E}$, $\delta\sigma_{123}$, or $\Delta n_{D,123}$; Q_{ij}^{E} is given by eq 4; and the term $x_1 \cdot x_2 \cdot x_3 \cdot \Delta_{123}$ is the ternary contribution. The term Δ_{123} can be fitted to an expression given by Cibulka[8] that reads

$$\Delta_{123} = B_1 + B_2 x_1 + B_3 x_2 \tag{7}$$

where B_i are fitting parameters. Equation 7 is appropriate to fit the ternary contribution of $V_{m,123}^{E}$ and $\delta\sigma_{123}$. For fitting Δ_{123} obtained from changes in the refractive indexes on mixing, $\Delta n_{D,123}$, eq 7 is not fine, so they were correlated in terms of the following equation due to Morris et al.[9] and Nagata and Tamura:[10]

$$\Delta_{123} = RT(B_1 + B_2 x_1 + B_3 x_2 + B_4 x_1^{2} + B_5 x_2^{2}) \tag{8}$$

The parameters B_i for eqs 7 and 8 with the corresponding standard deviations of the fit, *s*, are given in Table 8.

Discussion

The excess molar volume versus mole fraction of hexane for the binary mixture (hexane + *m*-xylene) is plotted in Figure 1. The continuous line corresponds to the fit of a Redlich−Kister type equation (eq 4) with the parameters given in Table 8. This binary system shows negative values of the excess molar volume over the whole composition range, with a minimum at nearly equimolecular composition. This graph is similar in sign and shape with the results obtained for the binary mixture (hexane + ethylbenzene),[2] while the absolute value is around 40 % higher here. This same mixture and magnitude was published previously at 293.15 K[26] and 298.15 K.[27] The results given in those two references are very similar between them, although the temperature of measurement was different. The data presented here match in sign and shape with that published

Table 8. Coefficients A_k from Equation 4 and B_p from Equations 7 and 8 with Standard Deviations, *s*

	A_0	A_1	A_2	A_3	A_4	A_5	s
			Propyl Propanoate + Hexane				
V_m^E/cm^3·mol^{-1} [a]	1.366	−0.652	0.300				0.005
$\delta\sigma$/mN·m^{-1} [b]	−2.58	−1.92	4.88	−1.31			0.01
Δn_D [a]	−0.0042	0.0015					0.00003
			Propyl Propanaote + *m*-Xylene				
V_m^E/cm^3·mol^{-1} [c]	−0.266	0.101					0.0006
$\delta\sigma$/mN·m^{-1} [c]	−1.23	0.18	−0.28				0.002
Δn_D	−0.0092	0	0.0014	0	0.0021	0.0003	0.00003
			Hexane + *m*-Xylene				
V_m^E/cm^3·mol^{-1}	−1.009	0	0.128	0.368	−0.287	−0.615	0.0023
$\delta\sigma$/mN·m^{-1}	−5.58	2.67	−0.78	0	3.03	1.16	0.01
Δn_D	−0.0059	0	0	−0.0019			0.00002

	B_1	B_2	B_3	B_4	B_5	*s*
			Propyl Propanoate + Hexane + *m*-Xylene			
$V_{m,123}^E$/cm^3·mol^{-1}	0.354	1.612	−1.641			0.0067
$\delta\sigma_{123}$/mN·m^{-1}	1.08	1.21	1.04			0.02
$\Delta n_{D,123}$	−0.1288	−1.2657	1.9801	1.6738	−2.4909	0.0017

[a] Ref 1. [b] Ref 2. [c] Ref 3.

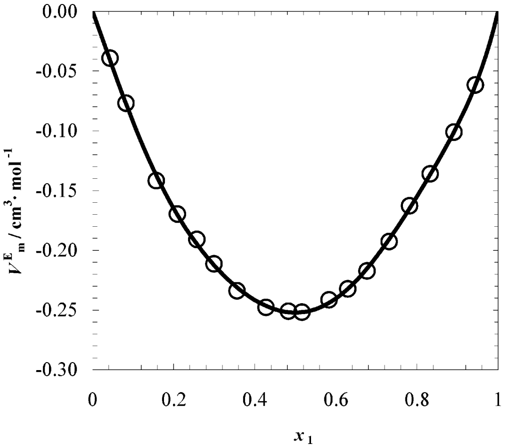

Figure 1. Excess molar volumes of hexane (1) + *m*-xylene (2) at 298.15 K. The continuous line corresponds to the fit of a Redlich−Kister equation (eq 4).

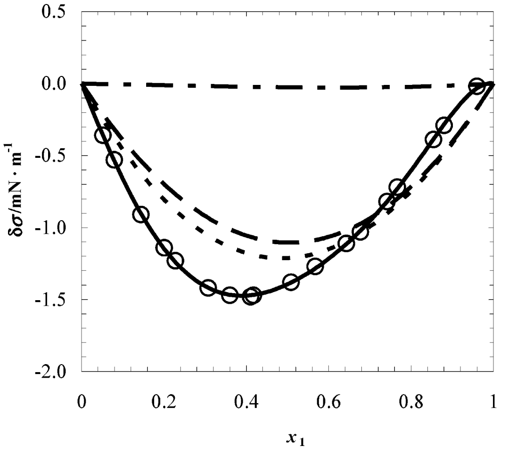

Figure 2. Surface tension deviations of hexane (1) + *m*-xylene (2) at 298.15 K. The continuous line corresponds to the fit of a Redlich−Kister equation (eq 4), the dotted line represents the HSEG approximation, the dashed line represents the HSIS empirical model, and the dot−dashed line represents the Brock and Bird theory.

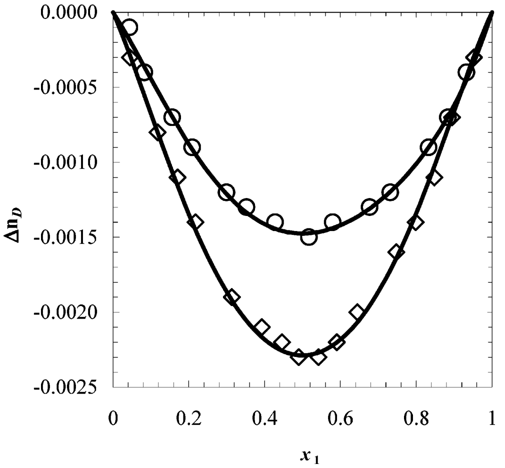

Figure 3. Changes in the refractive index of ◇, propyl propanoate (1) + *m*-xylene (2); ○, hexane (1) + *m*-xylene (2) at 298.15 K. The continuous lines correspond to the fit of a Redlich−Kister equation (eq 4).

before, but the absolute value of V^E_m is about 20 % higher in our case for the equimolar composition.

Surface tension deviation versus mole fraction of hexane for the binary system (hexane + *m*-xylene) is shown in Figure 2. The values of the surface tension deviations are negative, and the minimum is skewed toward the mixtures rich in the second component. This curve observed is very similar to that presented before for the mixture (hexane + ethylbenzene)[2] even in absolute value. The continuous line corresponds to the fit of a Redlich−Kister type equation (eq 4) with the fitting parameters given in Table 8. The other lines that appear in Figure 2 correspond to the different empirical approximations used: thus

Table 9. Standard Deviations, *s*, of the Experimental n_D Results from the Predicted Ones Using the Lorentz−Lorenz (L−L), Gladstone−Dale (G−D), Newton (N), Heller (H), and Wiener (W) Equations

	L−L	G−D	N	H	W
propyl propanoate + hexane[a]	0.0011	0.0001	0.0002	0.0010	0.0010
propyl propanoate + *m*-xylene	0.0002	0.0005	0.0012	0.0006	0.0001
hexane + *m*-xylene	0.0007	0.0001	0.0009	0.0016	0.0008

[a] Ref 1.

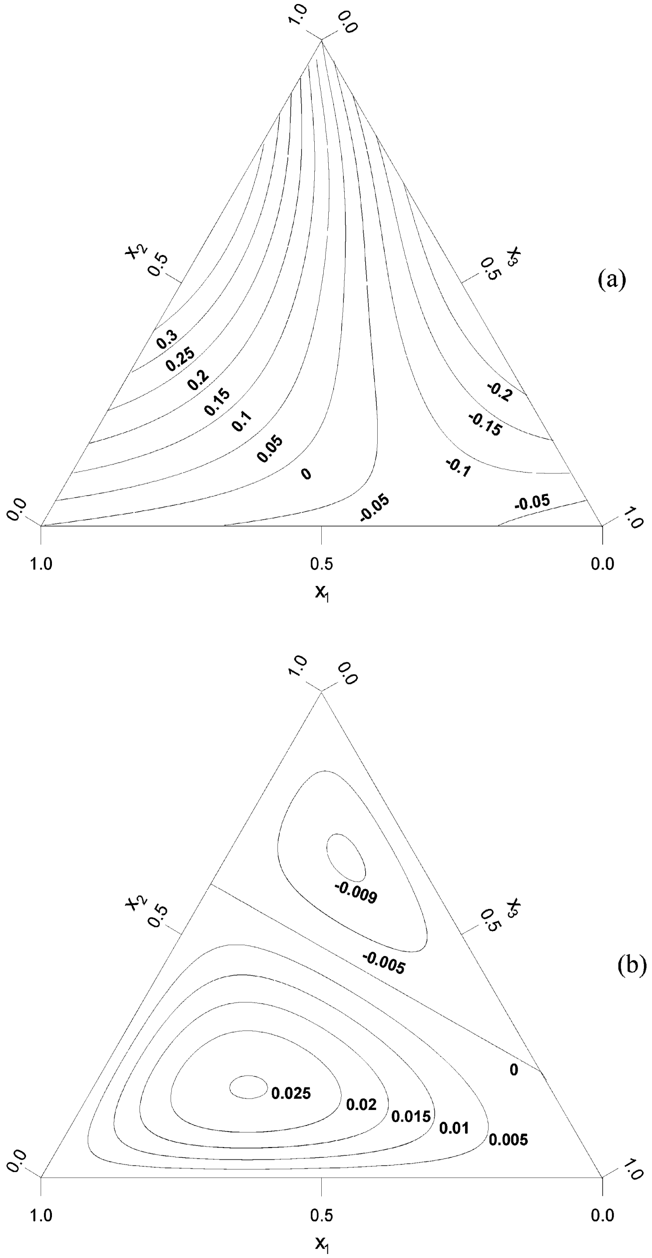

Figure 4. (a) Curves of constant $V^E_{m,123}$/cm^3·mol^{-1} for the ternary system propyl propanoate (1) + hexane (2) + *m*-xylene (3) calculated from eq 5. (b) Ternary contribution, ($V^E_{m,123}$ − $V^E_{m,bin}$)/cm^3·mol^{-1} for the ternary system.

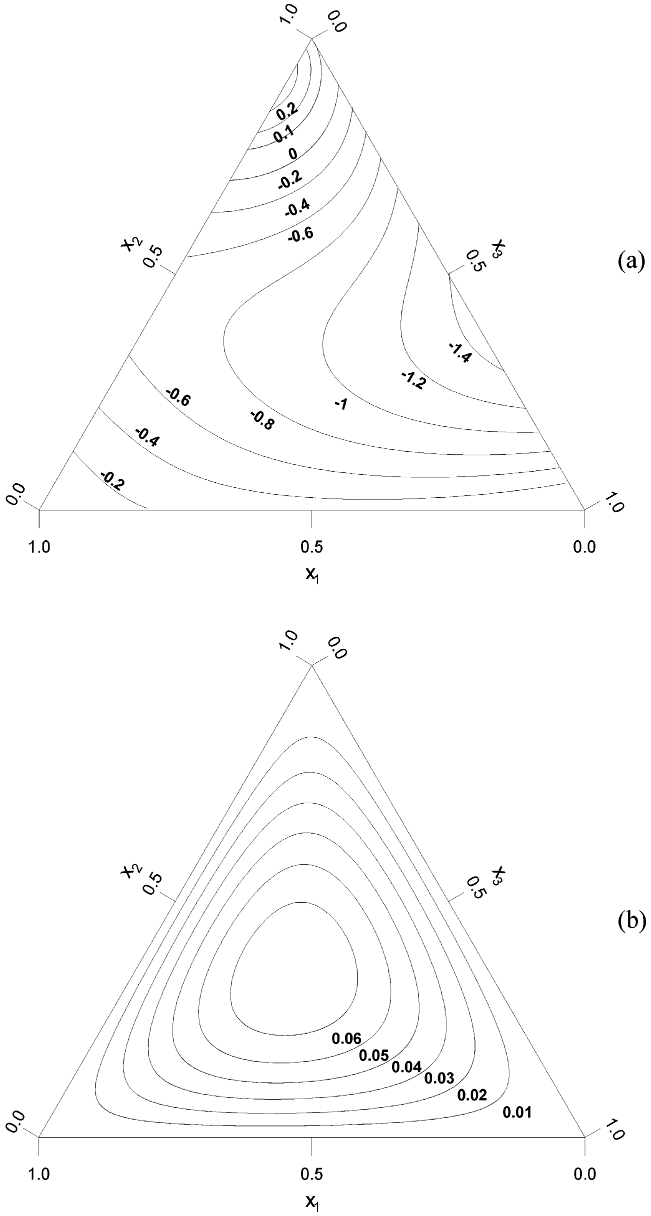

Figure 5. (a) Curves of constant $\delta\sigma_{123}$/mN·m^{-1} for the ternary system propyl propanoate (1) + hexane (2) + *m*-xylene (3) calculated form eq 5. (b) Ternary contribution, $(\delta\sigma_{123} - \delta\sigma_{\text{bin}})$/mN·m^{-1} for the ternary system.

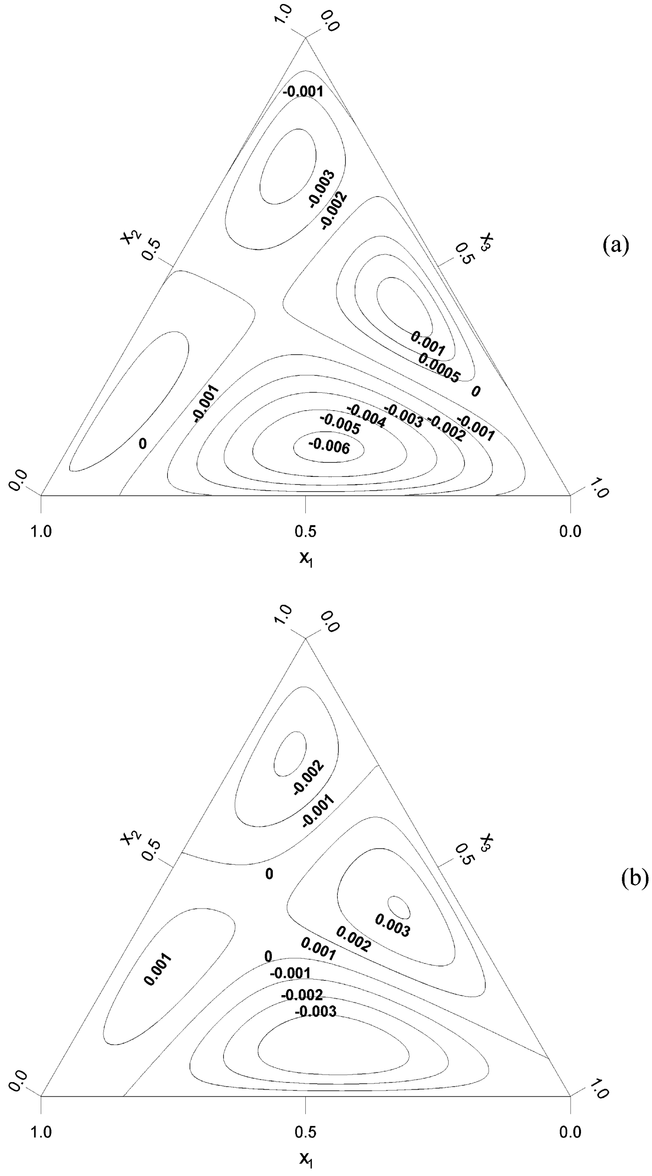

Figure 6. (a) Curves of constant $\Delta n_{\text{D},123}$ for the ternary system propyl propanoate (1) + hexane (2) + *m*-xylene (3) calculated from eq 5. (b) Ternary contribution, $(\Delta n_{\text{D},123} - \Delta n_{\text{D,bin}})$ for the ternary system.

the dotted line represents the HSEG approximation, the dashed line represents the HSIS empirical model, and the dot−dashed line corresponds to the Brock and Bird theory. All of these equations have been compiled in ref 3. As observed, none of the empirical models predict the exact value of $\delta\sigma$, but the HSEG equation is the most accurate to predict this binary mixture.

Figure 3 shows the changes in the refractive index versus mole fraction of propyl propanoate and hexane, respectively, for the binary systems (propyl propanoate + *m*-xylene) and (hexane + *m*-xylene). Both binary systems present negative values of changes in the refractive index over the whole composition, with a minimum for equimolar composition. If we compare with the result for the same mixtures but with ethylbenzene as second component published previously[2], we observe that the results are also very similar in sign and shape. The absolute value of the mixture with propyl propanoate is also similar while for the mixture with hexane it is about 20 % lower for the mixture with *m*-xylene as second component. We have tested five empirical models to predict Δn_{D} from the density data and the n_{D} values of the pure components. These models are those of Lorentz−Lorenz, Gladstone−Dale, Newton, Heller, and Wiener that are compiled in ref 6. The standard deviations for the calculated data from the experimental measurements and that obtained from the models are included in Table 9. As observed all five models predict the experimental changes of n_{D} with good accuracy. The Gladstone−Dale model is the most accurate to predict the data for the mixtures containing hexane, while for the remaining binary mixture (propyl propanoate + *m*-xylene) the most appropriate model is that from Wiener.

In Figures 4 to 6, we present the results obtained for the ternary mixture studied here. Thus, in Figures 4a, 5a, and 6a we show lines of constant $V^{\text{E}}_{\text{m},123}$, $\delta\sigma_{123}$, and $\Delta n_{\text{D},123}$, respectively. While in Figures 4b, 5b, and 6b we show lines of ternary contribution $(V^{\text{E}}_{\text{m},123} - V^{\text{E}}_{\text{m,bin}})$, $(\delta\sigma_{123} - \delta\sigma_{\text{bin}})$, and $(\Delta n_{\text{D},123} - \Delta n_{\text{D,bin}})$, respectively. If we compare the results for the ternary mixture {propyl propanoate + hexane + *m*-xylene} with that published previously with ethylbenzene,[2] we observe that the results for $V^{\text{E}}_{\text{m},123}$ are very similar for the two systems, both in shape and in absolute value, but for the ternary contribution

Table 10. Standard Deviations, *s*, of Empirical Expressions for (a) Propyl Propanoate + Hexane + *m*-Xylene, (b) Hexane + *m*-Xylene + Propyl Propanoate, and (c) *m*-Xylene + Propyl Propanoate + Hexane at 298.15 K

	a	b	c
	$V^{E}_{m,123}$, *s*/cm^3·mol^{-1}		
Jacob−Fitzner	0.012		
Kohler	0.014		
Colinet	0.011		
Knobeloch−Schwartz	0.026		
Tsao−Smith	0.038	0.031	0.052
Toop	0.013	0.022	0.014
Scatchard	0.013	0.022	0.011
Hillert	0.013	0.022	0.010
Mathieson−Thynne	0.010	0.017	0.011
	$\delta\sigma_{123}$, *s*/mN·m^{-1}		
Jacob−Fitzner	0.05		
Kohler	0.06		
Colinet	0.03		
Knobeloch−Schwartz	0.21		
Tsao−Smith	0.23	0.19	0.09
Toop	0.10	0.14	0.08
Scatchard	0.08	0.14	0.04
Hillert	0.09	0.14	0.08
Mathieson−Thynne	0.04	0.10	0.02
	$\Delta n_{D,123}$, *s*		
Jacob−Fitzner	0.0002		
Kohler	0.0002		
Colinet	0.0002		
Knobeloch−Schwartz	0.0004		
Tsao−Smith	0.0002	0.0003	0.0002
Toop	0.0002	0.0002	0.0002
Scatchard	0.0002	0.0002	0.0002
Hillert	0.0002	0.0002	0.0002
Mathieson−Thynne	0.0002	0.0002	0.0002

the results differ between both systems. Thus, while the system with ethylbenzene has all values negative, with a minimum about −0.08, the system with *m*-xylene has positive and negative values with maximum and minimum values about 0.025 and −0.01, respectively, as shown in Figure 4b. The curves for $\delta\sigma_{123}$- and ($\delta\sigma_{123} - \delta\sigma_{\text{bin}}$) are very similar in shape for both systems, but the absolute value is about 40 % higher for $\delta\sigma_{123}$ and around 10 times lower for the ternary contribution for the system with *m*-xylene with respect to that with ethylbenzene as third component. Finally, the curves for $\Delta n_{D,123}$ are different for both systems, for the constant lines as for the ternary contribution. Let us note that the changes in the refractive index on mixing are near the experimental uncertainty and also that the data for the system with ethylbenzene was fitted with the Cibulka expression given in eq 7, while *m*-xylene was fitted with the Morris and Nagata equation given in eq 8.

The data of the three physical magnitudes of the ternary mixture have been compared with nine empirical models that predict the ternary excesses from the corresponding binary ones. These theories are those of Jacob−Fitzner,[11] Kohler,[12] Colinet,[13] Knobeloch−Schwartz,[14] Tsao−Smith,[15] Toop,[16] Scatchard,[17] Hillert,[18] and Mathieson−Thynne.[19] The four first approximations are symmetric, and the last five are asymmetric, which means that the order of the components is relevant in the results obtained. In Table 10, we present the obtained standard deviations, *s*, from the calculated data using each theory and the experimental results. We can observe in Table 10 that the empirical approximation of Colinet presents the lower *s* for the three magnitudes among the symmetric equations. For the asymmetric equations, the value of *s* depends on the order of the components taken to perform the calculations, and that from Mathieson−Thynne presents the lowest *s* value for selected order of components, followed by the approximation given by Scatchard. Note that for $\Delta n_{D,123}$ the standard deviation is about the experimental uncertainties of the refractometer used, and so all the models present a very similar *s* value.

Conclusions

From the measured data presented in this paper about densities, surface tensions, and refractive indexes of the ternary system (propyl propanoate + hexane + *m*-xylene) at the temperature 298.15 K and atmospheric pressure, we extract the corresponding excess magnitudes. After comparing the data of the excesses of the three magnitudes for the ternary mixture, we conclude that the best model to predict the ternary contribution among the nine tested is that of Colinet. In the case of the binary mixtures, each magnitude must be compared with different empirical models. For the surface tension deviations, none of the three models tested predicts the magnitude and shape of the data measured, mainly because the models give a symmetrical curve while the measured one is slighty skewed toward mixtures rich in *m*-xylene. For the changes in the refractive index on mixing all of the five models tested fit the measured data, with the Gladstone−Dale model being the one with the lowest deviation.

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Received for review October 5, 2005. Accepted November 11, 2005.

JE0504111