Mixing properties of propyl acetate+aromatic hydrocarbons at 298.15 K

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Abstract−We present experimental data of speed of sound, refractive index on mixing and density for the binaries of propyl acetate+(toluene, ethylbenzene, *p*-xylene, isopropylbenzene, butylbenzene, isobutylbenzene, mesitylene, or *t*-butylbenzene) at T=298.15 K and 1 atm, and the corresponding computed derived magnitudes (change of isentropic compressibility, change of refractive index on mixing, and excess molar volume). The mixtures show a clear expansive tendency for the highest molar weight compounds, and the steric hindrance role of the aromatic chemicals was analyzed to the light of the non ideality on mixing. Values of physical properties were compared with the results obtained by theoretical estimation procedures.

Key words: Excess Volumes, Change of Refractive Indices, Change of Isentropic Compressibility, Propyl Acetate, Aromatic Hydrocarbon, Estimation

INTRODUCTION

As a continuation of previous works [Resa et al., 1998, 2001, 2002], this paper is devoted to the study of different thermodynamic properties of mixtures with chemicals containing the ester group in aromatic environment. To this aim, we presented experimental data of the binaries of propyl acetate+(toluene, ethylbenzene, *p*-xylene, isopropylbenzene, butylbenzene, isobutylbenzene, mesitylene, or *t*-butylbenzene) measured at standard condition (T=298.15 K, P=1 atm). The speed of sound, refractive index on mixing and density were measured and then applied to compute the corresponding derived magnitudes (change of isentropic compressibility, change of refractive index on mixing, and excess molar volume). The mixtures show a rising expansive tendency for increasing molar weight compounds, and the steric hindrance role of the aromatic chemicals was analyzed to the light of the non ideality on mixing. In what is referred to as the estimation of these magnitudes, different procedures were applied (equation of state for density, mixing rule for refractive indices and the Collision Factor Theory for isentropic compressibilities), and an accurate agreement among the experimental and theoretical values both in magnitude and sign was obtained.

EXPERIMENTAL SECTION

All the chemicals were supplied by Riedel de Haën and their mole fraction purities were better than 0.995, as checked by gas chromatography. The mixtures were prepared by mass with a Salter ER-182A balance with a precision of $\pm 1 \cdot 10^{-4}$ g. The liquids were degassed in an ultrasonic bath for four hours and stored into inert argon (N55, less than 3 ppmv in water) atmosphere to avoid ambient water contamination. At least 48 hours before use of the chemicals, they were dried over molecular sieves type 3 Å for acetone and methanol and 4 Å for n-alkanes, 1/16 inch (Aldrich cat. n° 20.860-4 or 20.858-2, respectively). The chemicals were checked by using gas chroma-

tography and better purities were obtained than those from vendor specifications. The pure properties of the chemicals were measured and compared with other recent literature values at 298.15 K and atmosphere at Table 1. The experimental procedure of measurement in our laboratory was explained previously [Resa et al., 2002].

DATA PROCEDURE

1. Correlation of Derived Magnitudes

The excess molar volumes, changes of refractive indices and changes of isentropic compressibilities on mixing values are presented in Table 2 and were computed from Eqs. (1), (2) and (3):

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

$$\delta n_D = n_D - \sum_{i=1}^{n} x_i n_{Di} \tag{2}$$

$$\delta \kappa_S = \frac{1}{\rho u^2} - \sum_{i=1}^{n} \frac{x_i}{\rho_i u_i^2} \tag{3}$$

In these equations, ρ is the density, n_D the refractive index on mixing and κ_S the isentropic compressibility on mixing. The ρ_i, n_{Di}, u_i and κ_{Si} symbols are the properties of pure chemicals and n is the number of components in the mixture. A Redlich-Kister [Redlich and Kister, 1948] type equation was used to correlate the derived properties of the binary mixtures; by using the unweighted least squares method, all experimental points weighted equally [Marquardt, 1963]. The Redlich-Kister equation can be expressed as:

$$\delta Q = x_i x_j \cdot \sum_{p=0}^{m} B_p (x_i - x_j)^p, \tag{4}$$

where δQ is $V^E/(cm^3 \cdot mol^{-1})$, δn_D or $\delta \kappa_S/(TPa^{-1})$. The degree of this equation (m parameter) was optimized by applying an F-test [Bevington, 1969]. The fitting parameters are gathered in Table 3, with the corresponding root mean square deviations (σ). The root mean square deviations were computed by using Eq. (5), where z is the value of the property, and n_{DAT} is the number of experimental data.

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Table 1. Physical properties of the pure solvents at T = 298.15 K

Compound	$\rho/\text{g}\cdot\text{cm}^{-3}$ (Expt)	$\rho/\text{g}\cdot\text{cm}^{-3}$ (Lit.)[a]	n_D (Expt)	n_D (Lit.)[a]	u (Expt)	u (Lit.)[b]
Propyl acetate	0.88201	0.88303	1.38176	1.3828	1,165.5	1,172
Toluene	0.86214	0.86219	1.49400	1.49413	1,305.0	1,305.0
Ethylbenzene	0.86258	0.86253	1.49315	1.49320	1,319.0	1,319.0
p-Xylene	0.85659	0.85661	1.49308	1.49325	1,309.7	1,309.7
Isopropylbenzene	0.85752	0.85743	1.48862	1.48890	1,307.7	1,307.7
Mesitylene	0.86129	0.86111	1.49675	1.49684	1,336.8	1,336.8
Butylbenzene	0.85625	0.85607	1.4873	1.48740	1,334.1	1,334.1
Isobutylbenzene	0.84896	0.84907	1.4840	1.48393	1,296.9	1,296.9
t-Butylbenzene	0.86227	0.86240	1.4902	1.49011	1,315.6	1,315.6

[a]*TRC Thermodynamic Tables*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994.
[b]Resa et al., 2003.

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

Only previously published data have been found in open literature for the excess molar volumes of propyl acetate+(ethyl benzene or *p*-xylene) at 293.15 K [Qin et al., 1992]. Figs. 1-3 show the derived properties plotted against x_1 (propyl acetate composition) as well as the curves fitted by Eq. (4). Almost the whole mixtures show an expansive trend at any composition, due to the increasing dispersive interactions and show a maximum for equimolar mixtures. As an exception providing the tendency, the mixtures propyl acetate+(*p*-xylene, ethylbenzene or toluene) show a negative or sigmoid trend, due to their relatively low steric hindrance trend atten-

dant to the molecular structure.

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, because it shows their trend with molar fraction variation. They should be applied to any extensive property of a single-phase system such as volume, Gibbs energy or any other. If we let E represent any extensive property of a single phase which is a function of pressure, temperature and mole numbers of the components, the differential of E should be expressed as:

$$\delta E = \left(\frac{\partial E}{\partial T}\right)_{P,n} dT + \left(\frac{\partial E}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{N}\left(\frac{\partial E}{\partial n_i}\right)_{T,P,n} dn_i \tag{6}$$

where the quantity $(\partial E/\partial n_i)_{T,P,n}$ is defined as the partial molar quan-

Table 2. Thermodynamic properties of propyl acetate+(toluene, ethylbenzene, *p*-xylene, isopropylbenzene, mesitylene, butylbenzene, isobutylbenzene, or *t*-butylbenzene) at T = 298.15 K

			Propyl acetate+toluene				
x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\text{mol}^{-1}$	n_D	δn_D	$u/(\text{ms}^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/\text{TPa}^{-1}$
0.0398	0.86320	−0.0232	1.48895	−0.0006	1299.3	686.3	−0.9
0.0866	0.86434	−0.0411	1.48312	−0.0011	1292.3	692.7	−1.6
0.1199	0.86515	−0.0545	1.47911	−0.0014	1287.4	697.4	−2.1
0.1694	0.86633	−0.0723	1.47331	−0.0017	1280.3	704.2	−2.9
0.2127	0.86734	−0.0860	1.46805	−0.0021	1273.8	710.5	−3.2
0.2538	0.86826	−0.0950	1.46332	−0.0022	1268.1	716.3	−3.8
0.3066	0.86941	−0.1033	1.45701	−0.0026	1260.3	724.1	−4.0
0.3505	0.87036	−0.1106	1.45199	−0.0026	1253.9	730.7	−4.2
0.3980	0.87127	−0.1047	1.44653	−0.0028	1247.2	737.9	−4.3
0.4515	0.87238	−0.1096	1.44043	−0.0029	1239.7	745.8	−4.6
0.4987	0.87335	−0.1139	1.43507	−0.0029	1232.9	753.3	−4.4
0.5483	0.87428	−0.1080	1.42966	−0.0028	1226.1	760.8	−4.4
0.6032	0.87525	−0.0948	1.42357	−0.0027	1218.4	769.6	−4.1
0.6510	0.87615	−0.0914	1.41842	−0.0025	1211.9	777.1	−4.0
0.7081	0.87719	−0.0839	1.41209	−0.0024	1204.1	786.2	−3.6
0.7717	0.87831	−0.0721	1.40534	−0.0020	1195.5	796.6	−3.0
0.8207	0.87913	−0.0585	1.40018	−0.0017	1188.9	804.8	−2.4
0.8887	0.88023	−0.0361	1.3931	−0.0012	1179.9	816.1	−1.4
0.9393	0.88103	−0.0179	1.38783	−0.0007	1173.3	824.5	−0.8

Table 2. Continued

Propyl acetate+ethylbencene							
x_1	$\rho/g \cdot cm^{-3}$	$V^E/cm^3 mol^{-1}$	n_D	δn_D	$u/(ms^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/TPa^{-1}$
0.054	0.86372	−0.0038	1.48724	0.0001	1310.7	673.9	−1.5
0.120	0.86497	−0.0090	1.48005	0.0003	1300.6	683.4	−3.1
0.157	0.86566	−0.0106	1.47605	0.0004	1295.0	688.8	−3.9
0.214	0.86673	−0.0122	1.46982	0.0005	1286.2	697.4	−5.0
0.266	0.86770	−0.0120	1.46417	0.0006	1278.2	705.4	−5.7
0.317	0.86866	−0.0125	1.45858	0.0007	1270.4	713.3	−6.4
0.362	0.86950	−0.0111	1.45362	0.0008	1263.4	720.5	−6.8
0.434	0.87085	−0.0088	1.44568	0.0008	1252.3	732.2	−7.2
0.482	0.87176	−0.0063	1.44030	0.0008	1244.8	740.3	−7.3
0.514	0.87236	−0.0051	1.43679	0.0008	1239.9	745.6	−7.2
0.568	0.87340	−0.0023	1.43065	0.0008	1231.5	755.0	−7.1
0.611	0.87421	0.0002	1.42590	0.0008	1224.9	762.4	−6.8
0.655	0.87507	0.0020	1.42087	0.0007	1218.0	770.3	−6.5
0.707	0.87606	0.0045	1.41509	0.0006	1210.1	779.5	−5.9
0.764	0.87718	0.0062	1.40865	0.0006	1201.3	789.9	−5.1
0.808	0.87807	0.0065	1.40358	0.0005	1194.5	798.2	−4.3
0.855	0.87900	0.0071	1.39828	0.0004	1187.4	807.0	−3.4
0.897	0.87986	0.0066	1.39344	0.0002	1180.9	815.0	−2.5
0.956	0.88106	0.0044	1.38684	0.0001	1172.0	826.2	−1.1
Propyl acetate+p-xylene							
x_1	$\rho/g \cdot cm^{-3}$	$V^E/cm^3 mol^{-1}$	n_D	δn_D	$u/(ms^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/TPa^{-1}$
0.048	0.85789	−0.0236	1.48796	0.0003	1302.9	686.7	−1.3
0.097	0.85919	−0.0432	1.48273	0.0004	1295.9	693.0	−2.4
0.158	0.86077	−0.0583	1.47630	0.0008	1287.2	701.2	−3.7
0.193	0.86172	−0.0700	1.47242	0.0009	1282.1	706.0	−4.3
0.245	0.86304	−0.0759	1.46698	0.0012	1274.6	713.3	−5.2
0.300	0.86446	−0.0847	1.46096	0.0013	1266.6	721.1	−5.8
0.353	0.86580	−0.0890	1.45528	0.0015	1259.0	728.7	−6.3
0.413	0.86732	−0.0927	1.44863	0.0015	1250.3	737.6	−6.7
0.455	0.86839	−0.0920	1.44395	0.0016	1244.2	743.9	−6.8
0.504	0.86959	−0.0884	1.43854	0.0015	1237.1	751.4	−6.9
0.565	0.87112	−0.0844	1.43169	0.0015	1228.3	760.9	−6.7
0.598	0.87196	−0.0812	1.42789	0.0014	1223.4	766.3	−6.6
0.650	0.87328	−0.0776	1.42193	0.0012	1215.8	774.7	−6.2
0.695	0.87438	−0.0690	1.41692	0.0012	1209.3	782.0	−5.7
0.757	0.87595	−0.0590	1.40969	0.0009	1200.2	792.5	−4.9
0.801	0.87701	−0.0479	1.40478	0.0008	1194.0	799.9	−4.2
0.849	0.87823	−0.0406	1.39922	0.0006	1187.1	808.1	−3.4
0.902	0.87953	−0.0253	1.39321	0.0005	1179.5	817.2	−2.4
0.949	0.88072	−0.0141	1.38772	0.0003	1172.7	825.6	−1.3

tity of the ith component in the phase, and the value N refers to all the other components present, showing a finite change in the property by the addition of 1 mol of the component i in an infinite quantity of solution at constant temperature and pressure. The expression for the partial excess molar volume should be written as:

$$\overline{V}_i^E = (1-x_i)^2 \left[\sum_{p=0}^m B_p (2x_1-1)^p + x_i \sum_{p=1}^m (-2)^{i-1} p B_p (2x_1-1)^{p-1} \right] \qquad (7)$$

where the symbols have the meaning explained above. From Eq.

(7), the corresponding limiting partial excess molar volumes should be determined by considering x_i null for each case, and such limiting values depend only on these correlation parameters. In Table 4, the values of limiting partial excess molar volumes at 298.15 K for the binary mixtures are enclosed. These values show the strong influence of propyl acetate on mesitylene liquid phase. A similar behaviour for these aromatic chemicals could be observed with propyl acetate, but attending to structural differences, a rising difficult package could be observed as propyl acetate abundance was in-

Table 2. Continued

			Propyl acetate+isopropylbencene				
x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\text{mol}^{-1}$	n_D	δn_D	$u/(\text{ms}^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/\text{TPa}^{-1}$
0.046	0.85852	0.0010	1.48444	0.0007	1301.7	687.5	−1.4
0.095	0.85954	0.0009	1.47962	0.0012	1295.4	693.4	-3.1
0.151	0.86070	0.0038	1.47461	0.0021	1288.1	700.3	−4.7
0.196	0.86167	0.0030	1.47038	0.0027	1281.8	706.4	−5.5
0.256	0.86299	−0.0006	1.46453	0.0032	1274.1	713.9	−7.1
0.300	0.86394	0.0037	1.46030	0.0037	1267.8	720.2	−7.5
0.364	0.86537	0.0074	1.45394	0.0042	1259.3	728.7	−8.8
0.418	0.86665	0.0057	1.44828	0.0044	1251.4	736.9	−9.0
0.448	0.86729	0.0131	1.44536	0.0046	1247.4	741.0	−9.3
0.496	0.86844	0.0129	1.44011	0.0044	1240.5	748.3	−9.4
0.551	0.86980	0.0132	1.43426	0.0046	1232.5	756.8	−9.4
0.598	0.87093	0.0157	1.42897	0.0042	1225.7	764.3	−9.0
0.647	0.87216	0.0180	1.42351	0.0040	1218.8	771.8	−9.0
0.695	0.87337	0.0225	1.41832	0.0040	1211.7	779.9	−8.3
0.754	0.87494	0.0211	1.41154	0.0035	1202.9	789.9	−7.3
0.805	0.87632	0.0201	1.40551	0.0029	1195.3	798.7	−6.2
0.852	0.87760	0.0198	1.40005	0.0024	1188.4	806.9	−5.2
0.891	0.87874	0.0170	1.39512	0.0018	1182.2	814.3	−3.9
0.954	0.88059	0.0094	1.38736	0.0007	1172.6	825.9	−1.9

			Propyl acetate+butylbenzene				
x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\text{mol}^{-1}$	n_D	δn_D	$u/(\text{ms}^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/\text{TPa}^{-1}$
0.052	0.85721	0.0150	1.48330	0.0013	1326.2	663.3	−2.1
0.095	0.85801	0.0258	1.47934	0.0019	1319.9	669.0	−4.2
0.151	0.85906	0.0407	1.47488	0.0034	1311.4	676.9	−6.3
0.199	0.86002	0.0468	1.47025	0.0038	1304.1	683.7	−8.1
0.255	0.86115	0.0589	1.46568	0.0052	1295.0	692.4	−9.4
0.311	0.86231	0.0708	1.46078	0.0062	1286.5	700.6	−11.1
0.352	0.86323	0.0712	1.45656	0.0063	1279.8	707.3	−11.8
0.400	0.86430	0.0791	1.45199	0.0068	1272.0	715.1	−12.5
0.470	0.86596	0.0831	1.44529	0.0075	1260.9	726.3	−13.9
0.496	0.86663	0.0786	1.44236	0.0074	1256.2	731.3	−13.6
0.546	0.86786	0.0818	1.43705	0.0073	1247.7	740.2	−13.5
0.601	0.86932	0.0801	1.43085	0.0069	1238.1	750.4	−13.2
0.647	0.87058	0.0760	1.42571	0.0066	1230.0	759.2	−12.5
0.694	0.87185	0.0796	1.42058	0.0065	1222.4	767.6	−12.5
0.765	0.87396	0.0709	1.41217	0.0056	1209.5	782.2	−10.6
0.805	0.87517	0.0669	1.40737	0.0050	1202.3	790.4	−9.5
0.850	0.87663	0.0597	1.40157	0.0040	1193.7	800.6	−7.5
0.901	0.87836	0.0409	1.39513	0.0029	1184.4	811.6	−5.4
0.948	0.88001	0.0276	1.38884	0.0016	1175.3	822.6	−2.8

creased in mesitylene mixtures. On the other hand, propyl acetate+ (*p*-xylene or toluene) mixtures present a greater tolerance for the inert solvent (weak polar ether group, molecular structural similarity), and a slightly contractive character was observed at any composition.

3. Estimation of Physical Properties

Due to strong dependence of design and optimization of chemical processes on computer calculations, the availability of accurate, simple and tested methods, as well as related parameters is of increasing relevance. In this case, consideration was given to the Rackett equation of state [Rackett, 1970; Spencer and Danner, 1972] in order to analyze how accurate densities are predicted. According to this model, the density could be described as:

$$\rho=\left(\frac{MP_C}{RT_C}\right)\beta^{-[1+(1-T_r)^{2/7}]} \tag{8}$$

where T_r is the reduced temperature, T_C and P_C are the pseudocritical properties of mixture, M is the average molecular weight in mix-

Table 2. Continued

			Propyl acetate+isobutylbenzene				
x_1	$\rho/g \cdot cm^{-3}$	V^E/cm^3mol^{-1}	n_D	δn_D	$u/(ms^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/TPa^{-1}$
0.045	0.85006	0.0039	1.48010	0.0008	1291.7	705.0	−1.4
0.094	0.85126	0.0087	1.47656	0.0023	1286.1	710.2	−2.8
0.141	0.85245	0.0133	1.47239	0.0029	1280.5	715.4	−3.9
0.203	0.85400	0.0272	1.46750	0.0043	1273.5	722.1	−5.5
0.252	0.85535	0.0293	1.46334	0.0052	1267.6	727.6	−6.6
0.297	0.85655	0.0361	1.45960	0.0060	1262.1	732.9	−7.3
0.360	0.85841	0.0336	1.45369	0.0066	1254.4	740.4	−8.3
0.403	0.85968	0.0372	1.44973	0.0070	1248.8	745.9	−8.6
0.452	0.86116	0.0408	1.44517	0.0074	1242.7	751.9	−9.2
0.512	0.86305	0.0436	1.43926	0.0077	1234.8	759.9	−9.3
0.548	0.86420	0.0500	1.43555	0.0077	1230.1	764.7	−9.4
0.600	0.86594	0.0490	1.42975	0.0071	1223.1	772.0	−9.0
0.648	0.86764	0.0469	1.42459	0.0069	1216.5	778.9	−8.7
0.702	0.86959	0.0450	1.41845	0.0063	1209.0	786.8	−8.0
0.749	0.87135	0.0426	1.41313	0.0058	1202.4	793.8	−7.3
0.802	0.87335	0.0441	1.40721	0.0052	1195.1	801.7	−6.4
0.854	0.87549	0.0387	1.40113	0.0045	1187.8	809.6	−5.6
0.903	0.87755	0.0283	1.39448	0.0028	1180.2	818.1	−3.6
0.951	0.87970	0.0172	1.38827	0.0015	1172.9	826.3	−1.9
			Propyl acetate+mesitylene				
x_1	$\rho/g \cdot cm^{-3}$	V^E/cm^3mol^{-1}	n_D	δn_D	$u/(ms^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/TPa^{-1}$
0.049	0.86195	0.0406	1.49148	0.0004	1320.8	665.0	6.3
0.098	0.86258	0.0756	1.48632	0.0008	1319.7	665.7	−2.1
0.153	0.86330	0.1154	1.48106	0.0018	1310.2	674.8	−3.1
0.199	0.86398	0.1395	1.47631	0.0024	1302.5	682.3	−4.2
0.260	0.86490	0.1714	1.46968	0.0028	1291.7	692.9	−4.8
0.308	0.86562	0.1983	1.46474	0.0034	1283.5	701.2	−5.4
0.360	0.86648	0.2188	1.45901	0.0037	1274.3	710.7	−5.6
0.415	0.86747	0.2304	1.45295	0.0040	1265.1	720.3	−6.2
0.462	0.86836	0.2347	1.44743	0.0038	1256.6	729.3	−5.9
0.497	0.86899	0.2432	1.44377	0.0041	1251.0	735.3	−6.3
0.543	0.86996	0.2398	1.43816	0.0039	1242.7	744.4	−5.9
0.615	0.87145	0.2407	1.42995	0.0040	1230.7	757.6	−6.0
0.662	0.87248	0.2338	1.42435	0.0037	1222.5	767.0	−5.2
0.696	0.87327	0.2261	1.42017	0.0034	1216.8	773.4	−5.1
0.749	0.87454	0.2111	1.41373	0.0031	1207.7	783.9	−4.3
0.798	0.87585	0.1828	1.40744	0.0025	1199.4	793.7	−3.7
0.852	0.87736	0.1455	1.40084	0.0021	1190.2	804.7	−2.8
0.898	0.87864	0.1160	1.39514	0.0016	1182.6	813.9	−2.0
0.953	0.88042	0.0571	1.38777	0.0006	1173.2	825.3	−0.9

ture and β is the compressibility factor or an acentric factor dependent parameter which varies according to a molecular structure parameter [Reid et al., 1988]. The selected mixing rule to compute densities was proposed by Kay (modified combination of Prausnitz-Gunn) [Kay, 1936; Prausnitz and Gunn, 1958]. In order to predict this property, the critical values are required for each compound, and open literature or estimative methods were used. In Table 5, critical values from the open literature are gathered for the compounds enclosed in the studied mixtures [Reid et al., 1988]. In Table

6, a comparison between the binary experimental and predicted densities is shown in terms of root mean square deviations. From these values, it was observed that the Rackett equation predicts more adequately for these binary mixtures, only in the heaviest aromatic mixtures showing similar results with the modified equation.

In what is referred to as refractive indices on mixing, the experimental data were compared with the estimated results for the mixing rule proposed by Lorentz-Lorenz [Iglesias et al., 1996], which is expressed by the equation:

Table 2. Continued

				Propyl acetate+*t*-butylbenzene			
x_1	$\rho/\text{g·cm}^{-3}$	$V^E/\text{cm}^3\text{mol}^{-1}$	n_D	δn_D	$u/(\text{ms}^{-1})$	κ_S/TPa^{-1}	$\delta\kappa_S/\text{TPa}^{-1}$
0.042	0.86297	−0.0025	1.48646	0.0010	1310.2	675.1	−1.9
0.100	0.86381	0.0040	1.48172	0.0025	1302.9	681.9	−4.5
0.154	0.86470	−0.0054	1.47703	0.0036	1295.7	688.9	−6.4
0.222	0.86582	−0.0081	1.47086	0.0048	1286.8	697.6	−9.0
0.248	0.86624	−0.0060	1.46868	0.0055	1283.1	701.2	−9.7
0.307	0.86725	−0.0069	1.46292	0.0061	1275.1	709.3	−11.3
0.350	0.86804	−0.0130	1.45877	0.0066	1268.9	715.5	−12.2
0.405	0.86902	−0.0114	1.45320	0.0070	1261.0	723.7	−13.1
0.447	0.86979	−0.0115	1.44901	0.0074	1254.7	730.3	−13.4
0.500	0.87079	−0.0095	1.44354	0.0077	1247.0	738.5	−14.0
0.549	0.87175	−0.0119	1.43810	0.0075	1239.8	746.3	−14.1
0.595	0.87264	−0.0046	1.43294	0.0074	1232.5	754.4	−13.8
0.650	0.87377	−0.0030	1.42668	0.0071	1224.0	763.9	−13.3
0.727	0.87545	−0.0062	1.41768	0.0064	1211.9	777.8	−12.1
0.749	0.87592	−0.0051	1.41495	0.0060	1208.4	781.9	−11.5
0.800	0.87707	−0.0014	1.40852	0.0051	1199.8	792.0	−9.9
0.851	0.87821	0.0055	1.40208	0.0042	1191.3	802.3	−7.9
0.906	0.87955	0.0045	1.39474	0.0028	1182.0	813.8	−5.4
0.952	0.88072	0.0054	1.38922	0.0023	1173.7	824.2	−2.7

$$\frac{n_D^2-1}{n_D^2+2}=\sum_{i=1}^{N}\left[\phi_i\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}\right)\right] \tag{9}$$

where ϕ is the volumetric fraction of the components. In Table 7, the root mean square deviations for the binary mixtures are enclosed, and similar accurate deviations were obtained for all the mixtures.

The Schaffs-Nutsch-kuhnkies (Collision Factor Theory) [Nutsch-kuhnkies, 1965; Schaffs, 1975] method was applied to isentropic compressibilities prediction for the binary mixtures. In Table 8, the root mean square deviations of the estimations are gathered. The application of the Collision Factor Theory (CFT) presents slight deviation values when predicting the isentropic compressibilities by using B (geometrical volume) and S (collision factor) values determined from measured pure data.

$$\kappa_S=\left(\frac{1}{\rho^3}\right)\cdot\left(\frac{M}{u_\infty\cdot\sum_i^N x_i S_s\cdot\sum_i^N x_i B_s}\right)^2 \tag{10}$$

where u_∞ is taken as 1,600 ms^{-1} and the other symbols are analogous to those explained above.

The Collision Factor Theory (CFT) is dependent on the collision factors among molecules as a function of temperature into pure solvent or mixture. The pertinent relations in these calculations and its theoretical basis were described by Nutsch-kuhnkies, 1965, and Schaffs, 1975. The collision factors (S) and the characteristic molecular volumes (B) of the pure solvents used in the CFT calculations were estimated by using the experimental ultrasonic velocities and the molar volumes in this paper.

RESULTS AND DISCUSSION

Many chemical, food, pharmacologic and other industries present

non ideal mixtures involved in their processes. For this reason it is necessary to pay attention to the device and equipment design and operational magnitudes to obtain an adequate and optimized process. The propyl acetate is currently used as flavouring agent in perfumes and cosmetics, as well as solvent for the manufacture of resins, lacquers and plastics, paint coating and printing ink industry. Its presence in aromatic environment is usual and the interactions in mixture are of interest in order to understand and define solubility limits and mechanisms of solvation. As a continuation of previous works, this paper is devoted to the study of different thermodynamic properties of chemicals containing the ester group in aromatic environment. To this aim, we present experimental data of speed of sound, refractive index on mixing and density for the binaries of propyl acetate+(toluene, ethylbenzene, *p*-xylene, isopropylbenzene, butylbenzene, isobutylbenzene, mesitylene, or *t*-butylbenzene), which were measured and then applied to compute the corresponding derived magnitudes (change of isentropic compressibility, change of refractive index on mixing, and excess molar volume) at T=298.15 and 1 atm. These mixtures show a rising expansive tendency for the highest molar weight compounds, because the steric hindrance of the aromatic chemicals plays an important role.

In general, the expansibility trend on mixing mainly depends on two effects: a) variation of intermolecular forces when two components come into contact, and b) variation of molecular packing as a consequence of differences in the size and shape of the molecules of the components. If the interactions between the molecules of two mixed components are weaker than in the pure component, the excess volume will be positive. This usually occurs when one of the components has polar groups and the other has a non-polar, or weakly polar behaviour. Propyl acetate is weakly polar and aromatic hydrocarbons are nearly non-polar. When the pure compounds are mixed, the non-polar hydrocarbon molecules intersperse among the pro-

Table 3. Fitting parameters of Eq. (4) and root mean square deviations (σ)

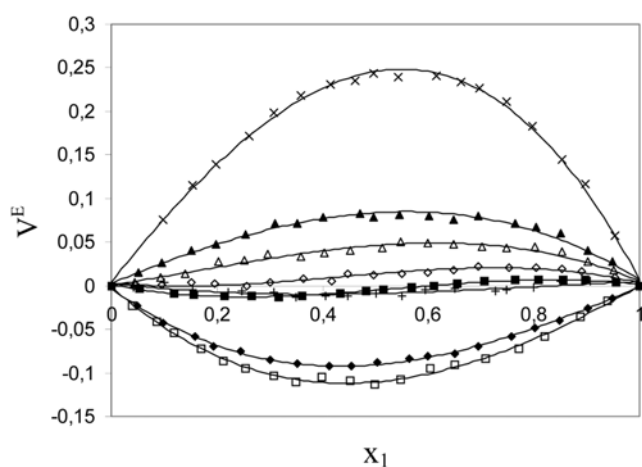|		Propyl acetate+toluene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=-0.438019$	$B_1=0.103494$	$B_2=-0.029585$	$B_3=-0.004793$	$\sigma=2.56 \cdot 10^{-3}$
δn_D	$B_0=-0.011384$	$B_1=0.000584$	$B_2=-0.001755$	$B_3=0.000432$	$\sigma=5.07 \cdot 10^{-5}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-17.953742$	$B_1=1.563449$	$B_2=-0.169483$	$B_3=3.393022$	$\sigma=7.73 \cdot 10^{-2}$
		Propyl acetate+ethylbenzene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=-0.023119$	$B_1=0.097556$	$B_2=0.023746$	$B_3=-0.000521$	$\sigma=2.56 \cdot 10^{-3}$
δn_D	$B_0=0.003289$	$B_1=-0.000126$	$B_2=-0.000761$	$B_3=0.000368$	$\sigma=5.07 \cdot 10^{-5}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-29.121329$	$B_1=1.193258$	$B_2=1.242943$	$B_3=0.455908$	$\sigma=7.73 \cdot 10^{-2}$
		Propyl acetate+p-xylene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=-0.358238$	$B_1=0.090608$	$B_2=-0.043495$	$B_3=0.037426$	$\sigma=1.15 \cdot 10^{-3}$
δn_D	$B_0=0.006128$	$B_1=-0.001755$	$B_2=-0.001513$	$B_3=0.002591$	$\sigma=4.58 \cdot 10^{-5}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-27.464070$	$B_1=1.059711$	$B_2=0.616863$	$B_3=-0.465116$	$\sigma=3.38 \cdot 10^{-2}$
		Propyl acetate+isopropylbenzene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=0.047411$	$B_1=0.098933$	$B_2=0.073716$	$B_3=0.001114$	$\sigma=1.57 \cdot 10^{-3}$
δn_D	$B_0=0.018149$	$B_1=0.000291$	$B_2=-0.001537$	$B_3=0.003033$	$\sigma=9.49 \cdot 10^{-5}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-37.726580$	$B_1=-2.507066$	$B_2=-0.786782$	$B_3=-1.900086$	$\sigma=1.19 \cdot 10^{-1}$
		Propyl acetate+mesitylene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=0.969904$	$B_1=0.171029$	$B_2=0.128853$	$B_3=0.100724$	$\sigma=2.53 \cdot 10^{-3}$
δn_D	$B_0=0.016323$	$B_1=0.000077$	$B_2=-0.003320$	$B_3=0.004830$	$\sigma=1.16 \cdot 10^{-4}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-25.922932$	$B_1=11.152722$	$B_2=15.044848$	$B_3=-38.763803$	$\sigma=1.47 \cdot 10^{0}$
		Propyl acetate+butylbenzene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=0.324330$	$B_1=0.036146$	$B_2=0.111666$	$B_3=0.138061$	$\sigma=1.93 \cdot 10^{-3}$
δn_D	$B_0=0.029238$	$B_1=0.002075$	$B_2=-0.001761$	$B_3=0.005636$	$\sigma=1.56 \cdot 10^{-4}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-54.317136$	$B_1=-7.615417$	$B_2=-0.019262$	$B_3=-0.329782$	$\sigma=2.05 \cdot 10^{-1}$
		Propyl acetate+isobutylbenzene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=0.177026$	$B_1=0.065848$	$B_2=0.076689$	$B_3=0.103321$	$\sigma=2.25 \cdot 10^{-3}$
δn_D	$B_0=0.029961$	$B_1=0.002004$	$B_2=-0.001648$	$B_3=0.006866$	$\sigma=1.61 \cdot 10^{-4}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-36.988547$	$B_1=-3.622427$	$B_2=-0.606885$	$B_3=-4.627176$	$\sigma=1.29 \cdot 10^{-1}$
		Propyl acetate+t-butylbenzene			
$V^E/(cm^3 \cdot mol^{-1})$	$B_0=-0.044069$	$B_1=0.024952$	$B_2=0.086926$	$B_3=0.015931$	$\sigma=2.56 \cdot 10^{-3}$
δn_D	$B_0=0.030060$	$B_1=0.002436$	$B_2=0.001341$	$B_3=0.004311$	$\sigma=1.69 \cdot 10^{-4}$
$\delta \kappa_S/(TPa^{-1})$	$B_0=-55.969414$	$B_1=-9.095222$	$B_2=-1.008802$	$B_3=0.989522$	$\sigma=1.02 \cdot 10^{-1}$

Fig. 1. Dependence of excess molar volumes (cm³·mol⁻¹) with mole fraction at 298.15 K for propyl acetate+((■) toluene, (□) ethylbenzene, (◆) *p*-xylene, (◇) isopropylbenzene, (▲) butylbenzene, (△) isobutylbenzene, (×) mesitylene, or (+) *t*-butylbenzene) and (——, Eq. (4)) fitting curves.
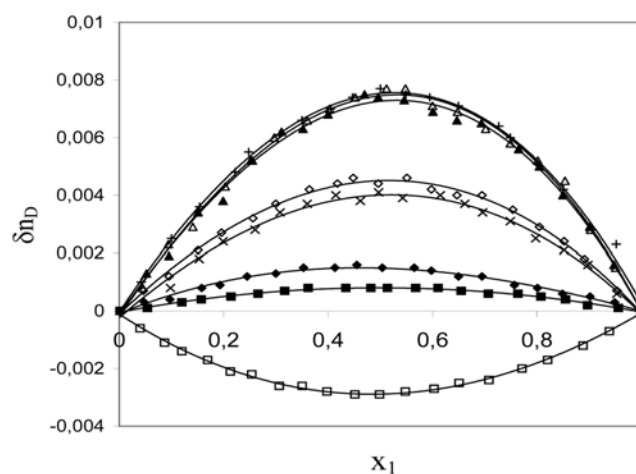

Fig. 2. Dependence of change of refractive index with mole fraction at 298.15 K for propyl acetate+((■) toluene, (□) ethylbenzene, (◆) *p*-xylene, (◇) isopropylbenzene, (▲) butylbenzene, (△) isobutylbenzene, (×) mesitylene, or (+) *t*-butylbenzene) and (——, Eq. (4)) fitting curves.
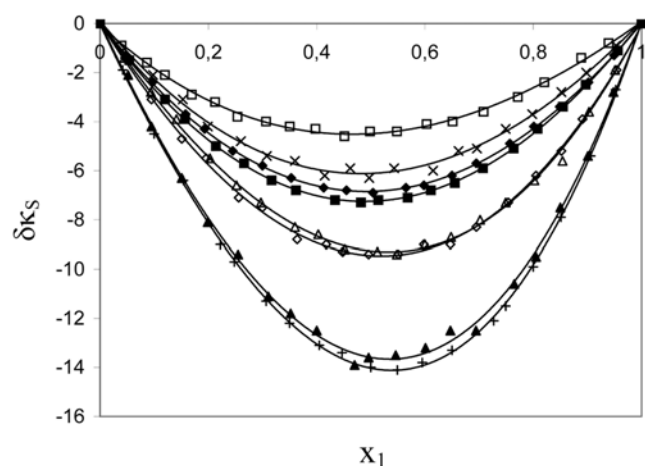
Fig. 3. Dependence of change of isentropic compressibilities (TPa⁻¹) with mole fraction at 298.15 K for propyl acetate+((■) toluene, (□) ethylbenzene, (◆) p-xylene, (◇) isopropylbenzene, (▲) butylbenzene, (△) isobutylbenzene, (✕) mesitylene, or (+) t-butylbenzene) and (———, Eq. (4)) fitting curves.

Table 4. Partial excess molar volumes at infinite dilution of the binary mixtures at 298.15 K

	$\overline{V}_1^{E,\infty}$/(cm³mol⁻¹)	$\overline{V}_2^{E,\infty}$/(cm³mol⁻¹)
Propyl acetate+toluene	−0.379	−0.573
Propyl acetate+ethylbenzene	0.098	−0.097
Propyl acetate+p-xylene	−0.298	−0.505
Propyl acetate+isopropylbenzene	0.220	0.022
Propyl acetate+mesitylene	0.519	0.353
Propyl acetate+butylbenzene	0.354	0.153
Propyl acetate+isobutylbenzene	1.303	0.895
Propyl acetate+t-butylbenzene	0.073	0.013

Table 5. Open literature critical values for compounds enclosed into binary mixtures [Riddick et al., 1986]

Compound	P_c (bar)	T_c (K)	Z_c	ω
Propyl acetate	33.632	549.73	0.254	0.464
Toluene	41.047	591.80	0.264	0.339
Ethylbenzene	36.053	617.15	0.263	0.348
p-Xylene	35.100	616.23	0.259	0.401
Isopropylbenzene	32.082	631.13	0.262	0.359
Mesitylene	31.261	637.25	0.253	0.474
Butylbenzene	28.860	660.50	0.261	0.373
Isobutylbenzene	31.504	657.87	0.282	0.110
t-Butylbenzene	29.580	647.30	0.269	0.271

Table 6. Root square deviations for predictive density values by rackett (R) or modified rackett (mR) with respect to corresponding experimental data for the binary mixtures

	R	mR
Propyl acetate+toluene	0.0030	0.0244
Propyl acetate+ethylbenzene	0.0031	0.0229
Propyl acetate+p-xylene	0.0047	0.0282
Propyl acetate+isopropylbenzene	0.0056	0.0265
Propyl acetate+mesitylene	0.0169	0.0432
Propyl acetate+butylbenzene	0.0144	0.0203
Propyl acetate+isobutylbenzene	0.0290	0.0263
Propyl acetate+t-butylbenzene	0.0213	0.0194

Table 7. Root mean square deviations for estimation of refractive index on mixing (Lorentz-Lorenz Rule) with respect to corresponding experimental data for the binary mixtures

Propyl acetate+toluene	0.00034
Propyl acetate+ethylbenzene	0.00018
Propyl acetate+p-xylene	0.00055
Propyl acetate+isopropylbenzene	0.00032
Propyl acetate+mesitylene	0.00028
Propyl acetate+butylbenzene	0.00025
Propyl acetate+isobutylbenzene	0.00035
Propyl acetate+t-butylbenzene	0.00043

Table 8. Root mean square deviations (TPa⁻¹) obtained by applying the methods of Schaaffs-Nutsch-Kuhnkies (CFT) for the binary mixtures isentropic compressibilities

Propyl acetate+toluene	0.005
Propyl acetate+ethylbenzene	0.001
Propyl acetate+p-xylene	0.001
Propyl acetate+isopropylbenzene	0.003
Propyl acetate+mesitylene	0.003
Propyl acetate+butylbenzene	0.007
Propyl acetate+isobutylbenzene	0.001
Propyl acetate+t-butylbenzene	0.005

pyl acetate molecules, resulting in a decreased interaction among the dipoles of the acetate group. This effect is clearly shown in terms of the partial molar volume at infinite dilution. As polar interactions diminish, the partial excess molar volume becomes positive (infinite dilution) at almost the whole cases. The experimental results agree with this explanation since almost all the studied mixtures show positive excess volumes. This fact shows that the change of

intermolecular forces is higher than that of the packing caused by geometrical effects. This causes the differences of the excess volumes from some hydrocarbons to others. If we compare the maximum excess volumes at equimolar composition, the following observations can be made: negative values correspond to mixtures of flat geometry hydrocarbons with small substituents or separated ones (ethylbenzene, p-xylene); intermediate values correspond to mixtures with no-flat geometry hydrocarbons (t-butylbenzene, isopropylbenzene, ethylbenzene); and the highest values correspond to (propyl acetate+mesitylene). Mesitylene has a flat geometry and three methyl groups in the meta position around the aromatic ring. The results can be interpreted qualitatively as a consequence of the diminution of the molecular interaction among acetate and aromatic structure. The heaviest aromatic hydrocarbon molecules will have rising difficulties in establishing interactions. If the molecules are flat or with few bulky substituents, toluene, p-xylene, some interactions can persist and the excess volume becomes slightly posi-

tive, sigmoid or negative. If the hydrocarbon molecules have bulky substituents, they will be placed at a different plane than the one for the benzenic ring, the interactions among acetate molecules are disabled and the excess volume will be higher than in the previous case. The presence of three methylene groups in the meta position obstructs the approach of the acetate group towards the ring and the steric volume is higher and the excess volume increases. A similar trend in the excess volume with the size of molecules has been shown in other (non-polar+polar compounds), such as methyl, ethyl or vinyl acetate with aromatic compounds [Resa et al., 1998, 2001, 2002].

CONCLUSIONS

As a conclusion, it is important to point out that as the rising of chain in the solvent acetate produces a lower non-ideality on mixing, then higher solvent power could be observed for these kinds of mixtures for non polar substances. The obtained results show the importance of steric hindrance to establish dispersive interactions on mixing and the progressive occultation of the polar effect of ester molecular group, when the chain is increased. Due to the strong dependence of adequate industrial design on computation and simulation, an estimation of physical properties was made by different theoretical procedures, with mainly accurate results being obtained, showing the practical application of the simple models used.

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