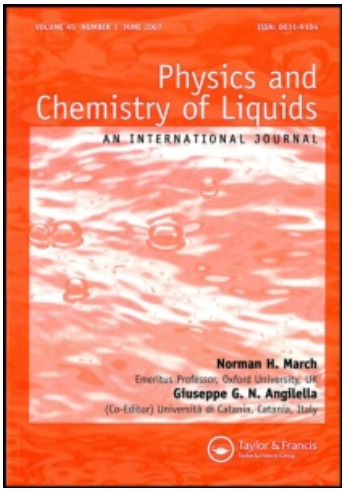

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Influence of temperature on excess molar volumes for butyl acetate + aromatic hydrocarbons

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To cite this Article Resa, J. M. , Gonzalez, C. , Concha, R. G. and Iglesias, M.(2004) 'Influence of temperature on excess molar volumes for butyl acetate + aromatic hydrocarbons', Physics and Chemistry of Liquids, 42: 5, 493 — 520
To link to this Article: DOI: 10.1080/00319100410001724557
URL: http://dx.doi.org/10.1080/00319100410001724557

Physics and Chemistry of Liquids
Vol. 42, No. 5, October 2004, pp. 493–520

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INFLUENCE OF TEMPERATURE ON EXCESS MOLAR VOLUMES FOR BUTYL ACETATE + AROMATIC HYDROCARBONS

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(Received 30 July 2003)

Excess molar volumes dependence with temperature for the mixtures butyl acetate + aromatic hydrocarbons (toluene, ethylbenzene, *p*-xylene, mesitylene, isopropylbenzene, butylbenzene, isobutylbenzene, and *t*-butylbenzene) were determined from density measurements by a vibrating-tube densimeter. The excess molar volumes are positive or slightly negative in the studied mixtures over the whole composition range, attending to the solvent molecular weight, only the isobutylbenzene showing a sigmoid trend. Steric hindrance in these mixtures was analyzed in the light of partial excess molar volumes behavior. The experimental data were used to test semiempirical procedures of density prediction, and compute the binary interaction parameters of the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state, which are of general interest in multicomponent thermodynamic functions estimation. The obtained results point out the interest of the equations of state to study complex mixtures and as a tool for predicting other magnitudes of general application for theoretical studies or processes calculations.

Keywords: Excess volume; Binary mixtures; Butyl acetate; Aromatic hydrocarbon; Equation of state; Estimation; Temperature.

1. INTRODUCTION

As a continuation of previous works [1–5], this article is devoted to the study of thermodynamics of mixtures with chemicals containing the ester group into aromatic environment. With this aim, our research team is carrying out a collection of studies focused on acetate mixtures to analyze the influence of the position of alkyl groups in the aromatic ring and the temperature influence on thermophysical properties. In this work, excess molar volumes of butyl acetate + aromatic hydrocarbons (toluene, ethylbenzene, *p*-xylene, isopropylbenzene, butylbenzene, isobutylbenzene, mesitylene, or *t*-butylbenzene) were determined from density measurements by vibrating-tube technique as a function of temperature (293.15 K–313.15 K). Steric hindrance in these mixtures was analyzed by examining the partial excess molar volumes behavior.

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ISSN 0031-9104 print: ISSN 1029-0451 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00319100410001724557

Experimental data were used to test semiempirical methods and to compute the binary interaction parameters of the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state, which are of interest in order to predict derived multicomponent thermodynamic functions.

2. EXPERIMENTAL

All the chemicals were supplied by Fluka, except butyl acetate, which was supplied by Panreac, and with mole fraction purities better than 0.990, as checked by gas chromatography. The mixtures were prepared by mass using a Salter ER-182A balance with a precision of $\pm 1 \times 10^{-4}$ g. The liquids were degassed in an ultrasonic bath for at least 4 h. The densities were measured with a precision of $\pm 10^{-5}\,\mathrm{g\,cm^{-3}}$ by an Anton Paar DSA 48 digital vibrating-tube densimeter. The pure density of the chemicals was measured and compared (Table I) with other recent literature values at 298.15 K and atmospheric temperature. The experimental procedure of measurement in our laboratory was explained previously [3].

The densimeter was calibrated with milli-Q water and ambient air. The air density was calculated using equation:

$$\rho(T,p) = \frac{0.131024 \cdot (p)}{1 + 0.00367 \cdot (T - 273.15)}, \tag{1}$$

where T is the temperature (measured with an accuracy of $\pm 1 \times 10^{-2}$ K) and p is the pressure. The excess volumes had an accuracy of $\pm 2 \times 10^{-3}\,\mathrm{cm^{-3}\,mol^{-1}}$ and was computed from the experimental data in accordance with Eq. (2):

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

where M_i is the molecular weight, x_i is the molar fraction, ρ_i is the density of the component i, and ρ is the density of the mixture.

TABLE I Experimental measured data and comparison with literature data for pure liquids at 298.15 K

Compound	M ($\mathrm{g\,mol^{-1}}$)	*Density* ($\mathrm{g\,cm^{-3}}$)					
		293.15 K	*Exptl. 298.15 K*	*Lit*[a] *298.15 K*	*303.15 K*	*308.15 K*	*313.15 K*
Butyl Acetate	116.16	0.88116	0.87614	0.87636	0.87103	0.86583	0.86062
Toluene	92.14	0.86687	0.86232	0.86219	0.85785	0.85330	0.84873
Ethylbenzene	106.167	0.86707	0.86273	0.86253	0.85839	0.85398	0.84958
p-Xylene	106.167	0.86078	0.85646	0.85661	0.85213	0.84779	0.84343
Mesitylene	120.194	0.86523	0.86116	0.86111	0.85709	0.85295	0.84885
Isopropylbenzene	120.194	0.86188	0.85763	0.85743	0.85342	0.84915	0.84485
Butylbenzene	134.221	0.86002	0.85606	0.85607	0.85210	0.84808	0.84406
Isobutylbenzene	134.221	0.85288	0.84891	0.84907	0.84489	0.84082	0.83670
t-Butylbenzene	134.221	0.86623	0.86216	0.86240	0.85812	0.85403	0.84992

[a]Organic solvents (1986).

3. DATA PROCEDURE

3.1. Correlation of Derived Magnitudes

The densities and excess molar volumes of the studied mixtures are listed in Table II as a function of temperature (293.15–313.15 K). The excess molar volumes of the binary mixtures were fitted to a modified Redlich–Kister polynomial of the form [7]:

$$V^E = x_1 x_2 \sum_{p=0}^{2} B_p (x_1 - x_2)^p \tag{3}$$

$$B_p = \sum_{q=0}^{2} B_{pq} \cdot T^q, \tag{4}$$

where B_{pq} are fitting parameters obtained by a least-squares method (Marquard algorithm [8]), with all the data being weighted equally. Table III shows the values of these parameters together with the root mean square deviations σ. Equation (3) was used to calculate the solid curves in Fig. 1, in which the excess molar volumes of butyl acetate + aromatic hydrocarbon (toluene, ethylbenzene, *p*-xylene, isopropylbenzene, butylbenzene, isobutylbenzene, mesitylene, or *t*-butylbenzene) are plotted against the mole fraction of butyl acetate at the studied temperatures. The root mean square deviations were computed using Eq. (5), in which z is the value of the excess volume, and n is the number of experimental data:

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

3.2. Partial Excess Molar Volumes

Partial molar quantities are important in the study of the dependence of an extensive property like volume on phase composition at constant pressure and temperature, showing the contractive or expansive behavior into a mixture along composition. The partial excess molar volume of a component in a multicomponent mixture can be computed from the excess molar volume by means of the following expression:

$$\bar{V}_i^E = V^E + (1 - x_i) \cdot \left(\frac{\partial V^E}{\partial x_i} \right), \tag{6}$$

with the excess volume expressed by a Redlich–Kister equation. Accordingly, the partial excess molar volume is therefore:

$$\bar{V}_i^E = (1 - x_i)^2 \left\{ \sum_{p=0}^{M} B_p (2x_1 - 1)^p + x_i \sum_{p=1}^{M} (-1)^{i-1} 2p B_p (2x_1 - 1)^{p-1} \right\}, \tag{7}$$

TABLE II Values of densities and excess molar volumes on mixing for the binary mixtures butyl acetate (1) + aromatic hydrocarbons (toluene, ethylbenzene, *p*-xylene, mesitylene, isopropylbenzene, butylbenzene, isobutylbenzene, *t*-butylbenzene) (2) at the temperature range 293.15–313.15 K

x_1	*Density* ($g\,cm^{-3}$)					V^E ($cm^3\,mol^{-1}$)				
	293.15 K	*298.15 K*	*303.15 K*	*308.15 K*	*313.15 K*	*293.15 K*	*298.15 K*	*303.15 K*	*308.15 K*	*313.15 K*
Butyl acetate + toluene										
0.9449	0.88081	0.87589	0.87094	0.86592	0.86085	−0.023	−0.025	−0.027	−0.031	−0.033
0.8971	0.88036	0.87546	0.87053	0.86551	0.86047	−0.041	−0.044	−0.046	−0.048	−0.050
0.8404	0.87983	0.87495	0.87002	0.86504	0.86002	−0.065	−0.067	−0.067	−0.070	−0.072
0.7972	0.87937	0.87450	0.86960	0.86464	0.85965	−0.076	−0.078	−0.079	−0.082	−0.086
0.7516	0.87889	0.87404	0.86916	0.86421	0.85923	−0.089	−0.092	−0.092	−0.095	−0.098
0.7000	0.87829	0.87346	0.86861	0.86369	0.85874	−0.099	−0.101	−0.103	−0.106	−0.109
0.6517	0.87771	0.87290	0.86809	0.86318	0.85824	−0.106	−0.109	−0.113	−0.114	−0.117
0.5999	0.87706	0.87227	0.86748	0.86259	0.85769	−0.111	−0.115	−0.118	−0.119	−0.123
0.5524	0.87643	0.87166	0.86689	0.86205	0.85715	−0.115	−0.118	−0.121	−0.125	−0.126
0.4994	0.87570	0.87096	0.86622	0.86140	0.85653	−0.116	−0.121	−0.124	−0.127	−0.128
0.4468	0.87495	0.87023	0.86550	0.86071	0.85589	−0.115	−0.120	−0.121	−0.126	−0.128
0.4011	0.87428	0.86957	0.86487	0.86010	0.85530	−0.115	−0.119	−0.121	−0.124	−0.126
0.3447	0.87339	0.86870	0.86404	0.85929	0.85452	−0.108	−0.112	−0.114	−0.116	−0.119
0.2985	0.87264	0.86796	0.86332	0.85860	0.85386	−0.102	−0.105	−0.107	−0.108	−0.111
0.2502	0.87178	0.86714	0.86252	0.85784	0.85311	−0.090	−0.093	−0.094	−0.097	−0.098
0.2001	0.87090	0.86627	0.86169	0.85703	0.85233	−0.079	−0.081	−0.083	−0.085	−0.086
0.1500	0.86994	0.86534	0.86080	0.85615	0.85150	−0.061	−0.064	−0.067	−0.067	−0.069
0.0998	0.86898	0.86440	0.85986	0.85527	0.85065	−0.046	−0.048	−0.048	−0.051	−0.053
0.0499	0.86794	0.86338	0.85888	0.85430	0.84971	−0.023	−0.025	−0.025	−0.025	−0.027
Butyl acetate + ethylbenzene										
0.9505	0.88055	0.87556	0.87048	0.86531	0.86015	−0.006	−0.006	−0.005	−0.004	−0.006
0.9009	0.87993	0.87497	0.86993	0.86480	0.85967	−0.011	−0.010	−0.011	−0.011	−0.010
0.8511	0.87929	0.87436	0.86937	0.86427	0.85918	−0.014	−0.015	−0.015	−0.014	−0.015
0.8016	0.87865	0.87376	0.86880	0.86374	0.85870	−0.017	−0.018	−0.019	−0.019	−0.020
0.7555	0.87805	0.87318	0.86826	0.86324	0.85823	−0.021	−0.021	−0.022	−0.023	−0.024
0.7003	0.87731	0.87250	0.86761	0.86263	0.85767	−0.023	−0.025	−0.026	−0.025	−0.028
0.6456	0.87658	0.87179	0.86695	0.86202	0.85709	−0.025	−0.026	−0.028	−0.029	−0.029
0.6041	0.87602	0.87126	0.86645	0.86156	0.85666	−0.028	−0.029	−0.030	−0.031	−0.032
0.5505	0.87529	0.87057	0.86579	0.86096	0.85610	−0.030	−0.031	−0.032	−0.035	−0.036
0.5021	0.87463	0.86994	0.86521	0.86039	0.85558	−0.033	−0.034	−0.035	−0.036	−0.037
0.4448	0.87383	0.86917	0.86449	0.85972	0.85495	−0.033	−0.034	−0.035	−0.037	−0.038
0.3989	0.87318	0.86856	0.86390	0.85917	0.85444	−0.035	−0.035	−0.036	−0.037	−0.038
0.3526	0.87252	0.86793	0.86331	0.85861	0.85392	−0.035	−0.035	−0.036	−0.037	−0.038

0.2929	0.87165	0.86710	0.86253	0.85788	0.85324	−0.033	−0.034	−0.035	−0.036	−0.038
0.2540	0.87107	0.86655	0.86200	0.85740	0.85278	−0.032	−0.032	−0.033	−0.036	−0.035
0.2024	0.87029	0.86581	0.86131	0.85672	0.85216	−0.028	−0.029	−0.030	−0.029	−0.031
0.1488	0.86948	0.86503	0.86057	0.85603	0.85151	−0.024	−0.025	−0.026	−0.025	−0.026
0.1008	0.86872	0.86430	0.85988	0.85539	0.85091	−0.019	−0.019	−0.019	−0.020	−0.020
0.0544	0.86798	0.86360	0.85921	0.85477	0.85031	−0.012	−0.013	−0.013	−0.014	−0.013
Butyl acetate + p-xylene										
0.9489	0.88029	0.87529	0.87020	0.86503	0.85986	−0.015	−0.014	−0.010	−0.009	−0.009
0.8979	0.87943	0.87446	0.86941	0.86429	0.85915	−0.034	−0.032	−0.029	−0.029	−0.027
0.8519	0.87863	0.87369	0.86867	0.86357	0.85847	−0.047	−0.045	−0.042	−0.040	−0.038
0.7990	0.87772	0.87281	0.86782	0.86277	0.85771	−0.065	−0.062	−0.058	−0.057	−0.055
0.7490	0.87684	0.87196	0.86701	0.86200	0.85698	−0.080	−0.078	−0.073	−0.072	−0.070
0.6993	0.87595	0.87111	0.86619	0.86122	0.85624	−0.094	−0.091	−0.086	−0.084	−0.083
0.6518	0.87507	0.87026	0.86539	0.86046	0.85552	−0.103	−0.100	−0.098	−0.096	−0.095
0.5991	0.87409	0.86932	0.86449	0.85960	0.85470	−0.114	−0.112	−0.109	−0.108	−0.105
0.5505	0.87314	0.86840	0.86361	0.85877	0.85390	−0.119	−0.115	−0.113	−0.112	−0.109
0.4999	0.87213	0.86743	0.86268	0.85788	0.85306	−0.120	−0.118	−0.116	−0.115	−0.113
0.4519	0.87116	0.86649	0.86177	0.85702	0.85223	−0.121	−0.119	−0.116	−0.115	−0.113
0.4040	0.87016	0.86553	0.86086	0.85615	0.85141	−0.120	−0.118	−0.116	−0.116	−0.113
0.3519	0.86907	0.86448	0.85985	0.85519	0.85049	−0.117	−0.116	−0.114	−0.114	−0.111
0.3077	0.86812	0.86355	0.85895	0.85433	0.84967	−0.112	−0.110	−0.107	−0.107	−0.104
0.2480	0.86681	0.86230	0.85774	0.85318	0.84856	−0.104	−0.103	−0.100	−0.100	−0.097
0.2012	0.86574	0.86125	0.85673	0.85221	0.84764	−0.093	−0.090	−0.087	−0.087	−0.084
0.1494	0.86454	0.86010	0.85563	0.85114	0.84662	−0.078	−0.077	−0.075	−0.074	−0.070
0.1014	0.86338	0.85898	0.85455	0.85010	0.84564	−0.059	−0.057	−0.056	−0.053	−0.053
0.0494	0.86213	0.85777	0.85339	0.84900	0.84457	−0.041	−0.039	−0.039	−0.038	−0.035
Butyl acetate + mesitylene										
0.9494	0.88004	0.87504	0.86997	0.86481	0.85967	0.041	0.046	0.050	0.052	0.052
0.8998	0.87899	0.87403	0.86901	0.86392	0.85885	0.076	0.082	0.087	0.088	0.085
0.8531	0.87806	0.87316	0.86819	0.86317	0.85814	0.099	0.103	0.109	0.108	0.108
0.8007	0.87704	0.87220	0.86726	0.86232	0.85733	0.123	0.128	0.137	0.132	0.136
0.7495	0.87612	0.87133	0.86646	0.86155	0.85666	0.136	0.141	0.148	0.146	0.145
0.7020	0.87534	0.87060	0.86578	0.86093	0.85606	0.138	0.141	0.148	0.146	0.149
0.6518	0.87451	0.86982	0.86508	0.86025	0.85544	0.141	0.143	0.147	0.150	0.153
0.5990	0.87364	0.86900	0.86430	0.85956	0.85480	0.144	0.148	0.154	0.152	0.156
0.5517	0.87291	0.86832	0.86367	0.85897	0.85425	0.140	0.142	0.149	0.149	0.155
0.5012	0.87215	0.86758	0.86298	0.85833	0.85368	0.133	0.141	0.146	0.147	0.151
0.4499	0.87133	0.86683	0.86230	0.85768	0.85310	0.134	0.138	0.142	0.146	0.147

(*continued*)

TABLE II Continued

x_1	*Density* ($g\,cm^{-3}$)					V^E ($cm^3\,mol^{-1}$)				
	293.15 K	*298.15 K*	*303.15 K*	*308.15 K*	*313.15 K*	*293.15 K*	*298.15 K*	*303.15 K*	*308.15 K*	*313.15 K*
0.3998	0.87064	0.86616	0.86167	0.85713	0.85259	0.119	0.126	0.132	0.132	0.136
0.3481	0.86991	0.86549	0.86106	0.85656	0.85207	0.107	0.113	0.116	0.119	0.123
0.2995	0.86924	0.86487	0.86049	0.85604	0.85165	0.093	0.097	0.101	0.103	0.100
0.2516	0.86865	0.86437	0.86002	0.85562	0.85124	0.069	0.067	0.072	0.073	0.077
0.2009	0.86802	0.86375	0.85949	0.85516	0.85081	0.044	0.047	0.047	0.045	0.052
0.1506	0.86736	0.86316	0.85893	0.85462	0.85034	0.026	0.025	0.028	0.031	0.035
0.1002	0.86668	0.86252	0.85832	0.85409	0.84990	0.012	0.012	0.017	0.015	0.013
0.0516	0.86598	0.86189	0.85775	0.85357	0.84941	0.005	0.001	0.005	0.003	0.003
Butyl acetate + isopropylbenzene										
0.9500	0.88016	0.87517	0.87011	0.86497	0.85980	−0.002	−0.001	0.000	−0.003	−0.002
0.8992	0.87913	0.87419	0.86918	0.86409	0.85898	−0.002	−0.001	−0.002	−0.004	−0.003
0.8497	0.87814	0.87325	0.86828	0.86325	0.85818	−0.003	−0.004	−0.004	−0.007	−0.006
0.8007	0.87718	0.87231	0.86740	0.86241	0.85739	−0.005	−0.004	−0.005	−0.008	−0.008
0.7493	0.87616	0.87134	0.86648	0.86155	0.85659	−0.005	−0.006	−0.007	−0.011	−0.013
0.6996	0.87519	0.87041	0.86559	0.86071	0.85580	−0.009	−0.007	−0.008	−0.013	−0.015
0.6500	0.87422	0.86949	0.86472	0.85988	0.85503	−0.010	−0.010	−0.012	−0.015	−0.019
0.6017	0.87329	0.86859	0.86387	0.85907	0.85426	−0.010	−0.012	−0.013	−0.017	−0.020
0.5550	0.87239	0.86774	0.86306	0.85831	0.85353	−0.012	−0.014	−0.016	−0.020	−0.022
0.4994	0.87132	0.86671	0.86208	0.85738	0.85265	−0.012	−0.015	−0.017	−0.019	−0.022
0.4514	0.87040	0.86584	0.86125	0.85659	0.85191	−0.013	−0.017	−0.018	−0.021	−0.023
0.4021	0.86946	0.86493	0.86039	0.85576	0.85114	−0.013	−0.016	−0.018	−0.019	−0.024
0.3578	0.86861	0.86412	0.85962	0.85504	0.85044	−0.013	−0.016	−0.018	−0.020	−0.022
0.3036	0.86758	0.86312	0.85867	0.85415	0.84959	−0.011	−0.015	−0.017	−0.019	−0.021
0.2496	0.86655	0.86214	0.85774	0.85325	0.84875	−0.009	−0.013	−0.016	−0.016	−0.019
0.2043	0.86568	0.86132	0.85695	0.85251	0.84805	−0.006	−0.012	−0.013	−0.015	−0.018
0.1510	0.86469	0.86034	0.85602	0.85162	0.84722	−0.005	−0.008	−0.010	−0.011	−0.015
0.0998	0.86373	0.85943	0.85513	0.85079	0.84642	−0.003	−0.007	−0.006	−0.009	−0.012
0.0521	0.86285	0.85856	0.85430	0.85000	0.84568	−0.004	−0.004	−0.001	−0.003	−0.009

Butyl acetate + butylbenzene										
0.9493	0.87987	0.87488	0.86985	0.86471	0.85960	0.005	0.010	0.010	0.011	0.007
0.8999	0.87861	0.87369	0.86873	0.86367	0.85862	0.015	0.018	0.016	0.015	0.013
0.8489	0.87733	0.87247	0.86758	0.86261	0.85763	0.024	0.027	0.026	0.022	0.020
0.8010	0.87615	0.87137	0.86654	0.86162	0.85670	0.032	0.033	0.031	0.030	0.029
0.7517	0.87497	0.87027	0.86549	0.86064	0.85579	0.039	0.036	0.036	0.034	0.032
0.6998	0.87377	0.86912	0.86441	0.85962	0.85483	0.043	0.042	0.041	0.040	0.039
0.6499	0.87265	0.86806	0.86341	0.85866	0.85395	0.045	0.043	0.043	0.045	0.041
0.6004	0.87157	0.86703	0.86244	0.85777	0.85310	0.045	0.044	0.043	0.042	0.042
0.5496	0.87047	0.86599	0.86146	0.85685	0.85224	0.046	0.044	0.043	0.043	0.042
0.4993	0.86941	0.86499	0.86051	0.85596	0.85141	0.045	0.042	0.043	0.042	0.041
0.4500	0.86840	0.86403	0.85960	0.85510	0.85061	0.043	0.041	0.042	0.043	0.041
0.3997	0.86739	0.86306	0.85871	0.85427	0.84982	0.040	0.039	0.036	0.036	0.038
0.3501	0.86642	0.86214	0.85783	0.85345	0.84906	0.036	0.036	0.035	0.034	0.035
0.3023	0.86550	0.86127	0.85700	0.85268	0.84834	0.031	0.031	0.031	0.031	0.032
0.2515	0.86453	0.86034	0.85614	0.85187	0.84759	0.029	0.028	0.027	0.026	0.026
0.1989	0.86355	0.85942	0.85526	0.85104	0.84684	0.023	0.022	0.022	0.023	0.019
0.1545	0.86273	0.85864	0.85454	0.85037	0.84620	0.019	0.018	0.017	0.016	0.015
0.1016	0.86180	0.85775	0.85370	0.84957	0.84546	0.011	0.012	0.009	0.011	0.010
0.0490	0.86088	0.85687	0.85287	0.84880	0.84474	0.004	0.005	0.002	0.004	0.002
Butyl acetate + isobutylbenzene										
0.9482	0.87936	0.87438	0.86935	0.86424	0.85910	0.011	0.014	0.013	0.009	0.010
0.8995	0.87776	0.87280	0.86784	0.86279	0.85774	0.011	0.021	0.020	0.016	0.013
0.8469	0.87608	0.87123	0.86633	0.86133	0.85633	0.009	0.013	0.011	0.011	0.010
0.7981	0.87453	0.86970	0.86486	0.85994	0.85502	0.012	0.021	0.019	0.016	0.013
0.7510	0.87309	0.86830	0.86351	0.85867	0.85379	0.009	0.019	0.019	0.013	0.011
0.6954	0.87141	0.86674	0.86200	0.85721	0.85239	0.006	0.009	0.011	0.009	0.008
0.6485	0.87004	0.86538	0.86071	0.85599	0.85123	0.001	0.011	0.010	0.006	0.004
0.5973	0.86853	0.86397	0.85935	0.85467	0.84996	0.003	0.005	0.007	0.004	0.004
0.5506	0.86719	0.86264	0.85808	0.85346	0.84883	0.003	0.011	0.011	0.007	0.003
0.5056	0.86584	0.86139	0.85687	0.85228	0.84769	0.015	0.015	0.016	0.016	0.013
0.4537	0.86449	0.86005	0.85560	0.85108	0.84654	−0.002	0.007	0.006	0.004	0.000
0.3994	0.86303	0.85868	0.85428	0.84981	0.84532	−0.006	−0.003	−0.003	−0.004	−0.005
0.3619	0.86204	0.85767	0.85332	0.84889	0.84447	−0.009	0.002	0.001	−0.001	−0.007
0.3027	0.86044	0.85619	0.85189	0.84752	0.84313	−0.004	−0.002	−0.003	−0.003	−0.006
0.2486	0.85910	0.85484	0.85059	0.84628	0.84196	−0.014	−0.002	−0.002	−0.005	−0.009
0.2010	0.85790	0.85372	0.84951	0.84524	0.84094	−0.018	−0.012	−0.011	−0.011	−0.011
0.1619	0.85691	0.85273	0.84856	0.84435	0.84011	−0.016	−0.005	−0.004	−0.007	−0.011
0.1042	0.85548	0.85141	0.84728	0.84310	0.83889	−0.017	−0.014	−0.011	−0.010	−0.011
0.0560	0.85433	0.85025	0.84617	0.84205	0.83794	−0.021	−0.008	−0.007	−0.009	−0.018

(*continued*)

TABLE II Continued

x_1	*Density* ($g\,cm^{-3}$)					V^E ($cm^3\,mol^{-1}$)				
	293.15 K	*298.15 K*	*303.15 K*	*308.15 K*	*313.15 K*	*293.15 K*	*298.15 K*	*303.15 K*	*308.15 K*	*313.15 K*
Butyl acetate + t-butylbenzene										
0.9500	0.88034	0.87538	0.87034	0.86521	0.86007	−0.007	−0.008	−0.009	−0.010	−0.010
0.9005	0.87954	0.87464	0.86965	0.86458	0.85950	−0.015	−0.016	−0.016	−0.016	−0.017
0.8509	0.87875	0.87390	0.86897	0.86397	0.85896	−0.021	−0.022	−0.022	−0.024	−0.025
0.8013	0.87797	0.87317	0.86831	0.86337	0.85842	−0.028	−0.029	−0.029	−0.031	−0.033
0.7489	0.87714	0.87240	0.86761	0.86273	0.85784	−0.032	−0.033	−0.035	−0.037	−0.039
0.7006	0.87640	0.87172	0.86697	0.86215	0.85732	−0.037	−0.040	−0.041	−0.042	−0.045
0.6496	0.87564	0.87100	0.86632	0.86156	0.85679	−0.043	−0.045	−0.048	−0.049	−0.051
0.6070	0.87499	0.87039	0.86575	0.86105	0.85632	−0.045	−0.047	−0.048	−0.051	−0.053
0.5499	0.87413	0.86959	0.86501	0.86037	0.85571	−0.047	−0.050	−0.051	−0.054	−0.055
0.4994	0.87338	0.86889	0.86438	0.85978	0.85517	−0.048	−0.051	−0.054	−0.055	−0.056
0.4489	0.87264	0.86819	0.86372	0.85919	0.85464	−0.048	−0.050	−0.052	−0.054	−0.056
0.4061	0.87201	0.86760	0.86318	0.85869	0.85418	−0.047	−0.049	−0.052	−0.053	−0.055
0.3516	0.87121	0.86686	0.86248	0.85806	0.85361	−0.045	−0.047	−0.048	−0.050	−0.053
0.3008	0.87047	0.86617	0.86185	0.85747	0.85307	−0.040	−0.044	−0.046	−0.048	−0.049
0.2511	0.86976	0.86549	0.86123	0.85690	0.85256	−0.036	−0.039	−0.042	−0.043	−0.045
0.1995	0.86903	0.86481	0.86058	0.85630	0.85200	−0.032	−0.034	−0.035	−0.035	−0.037
0.1522	0.86835	0.86416	0.85998	0.85576	0.85150	−0.025	−0.026	−0.026	−0.028	−0.029
0.1000	0.86762	0.86348	0.85934	0.85517	0.85097	−0.017	−0.018	−0.019	−0.021	−0.023
0.0517	0.86695	0.86284	0.85876	0.85463	0.85047	−0.010	−0.010	−0.012	−0.013	−0.015

TABLE III Fitting parameters of Eq. (4), and root mean square deviation, σ ($cm^3\,mol^{-1}$)

Butyl acetate + toluene			
$B_{00} = 4.222166$	$B_{01} = -0.028575$	$B_{02} = 0.000043$	
$B_{10} = -3.948839$	$B_{11} = 0.025916$	$B_{12} = -0.000042$	
$B_{20} = -23.312032$	$B_{21} = 0.149768$	$B_{22} = -0.000241$	$\sigma = 0.002$
$B_{30} = -5.538533$	$B_{31} = 0.038572$	$B_{32} = -0.000067$	
$B_{40} = 24.469713$	$B_{41} = -0.150649$	$B_{42} = 0.000230$	
Butyl acetate + ethylbenzene			
$B_{00} = -0.854417$	$B_{01} = 0.005634$	$B_{02} = -0.000011$	
$B_{10} = 4.477747$	$B_{11} = -0.028938$	$B_{12} = 0.000047$	
$B_{20} = -3.623357$	$B_{21} = 0.024293$	$B_{22} = -0.000041$	$\sigma = 0.001$
$B_{30} = -10.429856$	$B_{31} = 0.067781$	$B_{32} = -0.000110$	
$B_{40} = 13.402412$	$B_{41} = -0.090916$	$B_{42} = 0.000154$	
Butyl acetate + p-xylene			
$B_{00} = -1.901063$	$B_{01} = 0.007871$	$B_{02} = -0.00001$	
$B_{10} = -4.451105$	$B_{11} = 0.028623$	$B_{12} = -0.000045$	
$B_{20} = -18.678827$	$B_{21} = 0.121603$	$B_{22} = -0.000197$	$\sigma = 0.004$
$B_{30} = -3.923384$	$B_{31} = 0.028848$	$B_{32} = -0.00005$	
$B_{40} = 17.797890$	$B_{41} = -0.121130$	$B_{42} = 0.000205$	
Butyl acetate + mesitylene			
$B_{00} = -7.530926$	$B_{01} = 0.050504$	$B_{02} = -0.000078$	
$B_{10} = 4.139031$	$B_{11} = -0.024535$	$B_{12} = 0.000038$	
$B_{20} = -0.011158$	$B_{21} = 0.003645$	$B_{22} = -0.000012$	$\sigma = 0.007$
$B_{30} = -71.466395$	$B_{31} = 0.468506$	$B_{32} = -0.000763$	
$B_{40} = -48.059311$	$B_{41} = 0.308703$	$B_{42} = -0.000496$	
Butyl acetate + isopropylbenzene			
$B_{00} = -2.909204$	$B_{01} = 0.020687$	$B_{02} = -0.000037$	
$B_{10} = -25.677746$	$B_{11} = 0.169694$	$B_{12} = -0.000280$	
$B_{20} = 29.580615$	$B_{21} = -0.193531$	$B_{22} = 0.000317$	$\sigma = 0.002$
$B_{30} = 53.534534$	$B_{31} = -0.356526$	$B_{32} = 0.000593$	
$B_{40} = -65.993768$	$B_{41} = 0.434261$	$B_{42} = -0.000714$	
Butyl acetate + butylbenzene			
$B_{00} = 2.834408$	$B_{01} = -0.017200$	$B_{02} = 0.000028$	
$B_{10} = 1.922777$	$B_{11} = -0.011248$	$B_{12} = 0.000017$	
$B_{20} = 13.068293$	$B_{21} = -0.083408$	$B_{22} = 0.000133$	$\sigma = 0.002$
$B_{30} = -32.140242$	$B_{31} = 0.210122$	$B_{32} = -0.000344$	
$B_{40} = -81.298181$	$B_{41} = 0.534002$	$B_{42} = -0.000877$	
Butyl acetate + isobutylbenzene			
$B_{00} = -20.676884$	$B_{01} = 0.136776$	$B_{02} = -0.000226$	
$B_{10} = -8.870706$	$B_{11} = 0.058631$	$B_{12} = -0.000096$	
$B_{20} = -7.763516$	$B_{21} = 0.048137$	$B_{22} = -0.000075$	$\sigma = 0.008$
$B_{30} = 46.790609$	$B_{31} = -0.303569$	$B_{32} = 0.000494$	
$B_{40} = -116.029749$	$B_{41} = 0.768487$	$B_{42} = -0.001271$	
Butyl acetate + t-butylbenzene			
$B_{00} = 1.492566$	$B_{01} = -0.009553$	$B_{02} = 0.000013$	
$B_{10} = -5.294953$	$B_{11} = 0.035168$	$B_{12} = -0.000058$	
$B_{20} = 1.700969$	$B_{21} = -0.011235$	$B_{22} = 0.000019$	$\sigma = 0.002$
$B_{30} = 9.494027$	$B_{31} = -0.063896$	$B_{32} = 0.000107$	
$B_{40} = -9.416420$	$B_{41} = 0.063996$	$B_{42} = -0.000109$	

showing the finite change in the property on the addition of 1 mol of the component i in an infinite quantity of solution at constant temperature and pressure. The limiting partial excess molar volume is determined from Eq. (7) by considering infinite dilution, considering x_i mole for each case, such limiting values being dependent only on these

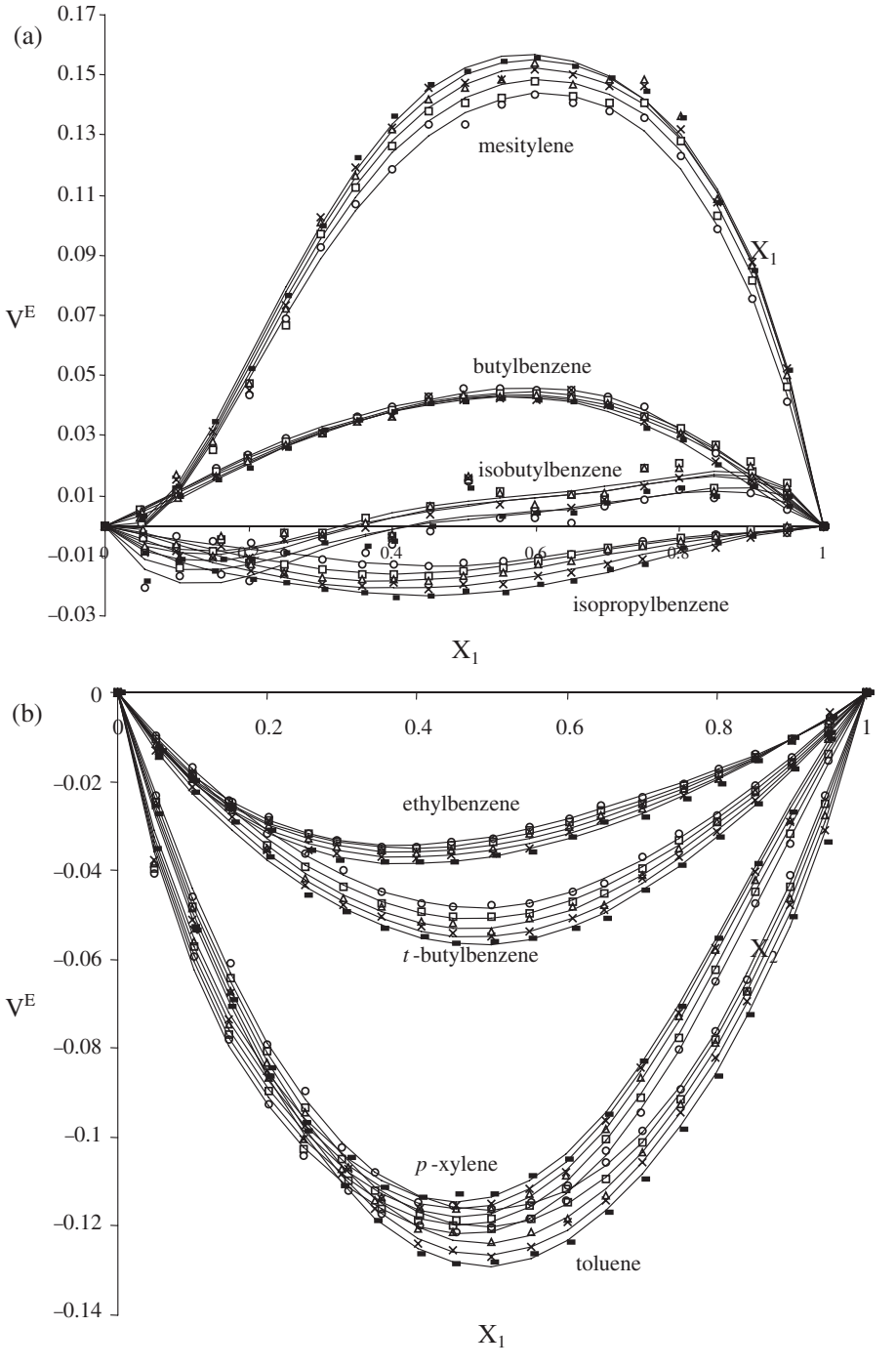

FIGURE 1 Excess volumes V^E as a function of temperature, for butyl acetate + aromatic hydrocarbons (toluene, ethylbenzene, *p*-xylene, mesitylene, isopropylbenzene, butylbenzene, isobutylbenzene, or *t*-butylbenzene) at the temperatures (○) 293.15 K, (□) 298.15 K, (△) 303.15 K, (×) 308.15 K and (–) 313.15 K and Redlich–Kister fitting curves at the same range of temperature (—) 293.15 K, (— – —) 298.15 K, (– – –) 303.15 K, (– –) 308.15 K, and (– – — – –) 313.15 K.

correlation parameters. In Table IV, the values of limiting partial excess molar volumes as a function of temperature for the binary mixtures are enclosed.

$$V_i^{E,\infty} = \sum_{p=0}^{M} B_p(-1)^{p_i} \tag{8}$$

The variation of the partial excess molar volumes with mole fraction is shown in Fig. 2(a) and (b) for the binary mixtures at $T = 298.15\,\mathrm{K}$ and in Fig. 3(a)–(d) for the mixtures butyl acetate + *p*-xylene and mesitylene as a function of temperature. In these figures it can be observed the extreme negative values for the systems containing toluene and *p*-xylene as well as the attenuation for increasing molar fraction. It is interesting to point out the inflexion for the curve of mesitylene due to an inversion of the main intermolecular force in mixing. The maximum appears at 0.2 molar fraction, changing the interaction from dispersive attraction among benzenic rings toward interactions among polar ester groups and π electrons. This fact is affected by steric hindrance due to the globular size of the molecules. From the Fig. 3(a)–(d) it is obvious that the temperature dependence is low although a rising of the expansive trend appears when the temperature is increased.

3.3. Estimation of Physical Properties

Due to the 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 [9,10] in order to analyze how accurate densities are predicted. Attending to this model, the density could be described as:

$$\rho = \left(\frac{MP_C}{RT_C}\right)\beta^{-\left[1+(1-T_r)^{2/7}\right]}, \tag{9}$$

where T_r is the reduced temperature, T_c and P_c are the critical properties of mixture, M is the average molecular weight in mixture, and β is the compressibility factor or an acentric factor dependent parameter which varies with a molecular structure parameter [11]. The selected mixing rule to compute densities was proposed by Kay (modified combination of Prausnitz-Gunn) [11]. In order to predict this property, the critical values are required for each compound, open literature or estimative methods being used (as for *t*-butylbenzene, where Ambrose method was applied [11]). In Table V, open literature critical values are gathered for the compounds enclosed in the studied mixtures [11]. In Table VI, a comparison between the binary experimental and predicted densities are gathered in terms of root mean square deviations. In accordance to these results, the following points could be concluded: (a) the estimation by modified Rackett equation is closer to the experimental values at all cases, (b) both deviations (σ and σ^*) decrease as temperature increases, and (c) the lowest molar weight compounds (toluene, *p*-xylene, etc.) show better deviations, giving mesitylene the poorest results.

TABLE IV Partial excess molar volumes at infinite dilution of the binary mixtures (butyl acetate + aromatic hydrocarbon) as function of temperature in the range 293.15–313.15 K

Aromatic	*T* = *293.15 K*		*T* = *298.15 K*		*T* = *303.15 K*		*T* = *308.15 K*		*T* = *313.15 K*	
	$\overline{V}_1^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_2^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_1^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_2^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_1^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_2^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_1^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_2^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_1^{E,\infty}$ ($cm^3\,mol^{-1}$)	$\overline{V}_2^{E,\infty}$ ($cm^3\,mol^{-1}$)
Toluene	−0.4632	−0.4224	−0.5129	−0.4737	−0.5555	−0.5289	−0.5910	−0.5880	−0.6193	−0.6507
Ethylbenzene	−0.2499	−0.1461	−0.2627	−0.1409	−0.2673	−0.1335	−0.2635	−0.1243	−0.2516	−0.1130
p-Xylene	−0.8674	−0.3010	−0.8398	−0.2622	−0.8075	−0.2283	−0.7699	−0.2003	−0.7294	−0.1754
Mesitylene	−0.1968	0.9618	−0.1945	1.1211	−0.1852	1.2148	−0.1691	1.2429	−0.1462	1.2058
Isopropylbenzene	−0.0719	−0.0477	−0.0428	−0.0342	−0.0509	−0.0267	−0.0965	−0.0253	−0.1794	−0.0300
Butylbenzene	0.0715	0.0797	0.0914	0.1566	0.0920	0.1814	0.0731	0.1539	0.0349	0.0743
Isobutylbenzene	−0.3668	0.2670	−0.1985	0.3391	−0.1287	0.3525	−0.1573	0.3073	−0.2846	0.2034
tert-Butylbenzene	−0.1952	−0.1582	−0.2092	−0.1676	−0.2295	−0.1785	−0.2561	−0.1907	−0.2890	−0.2044

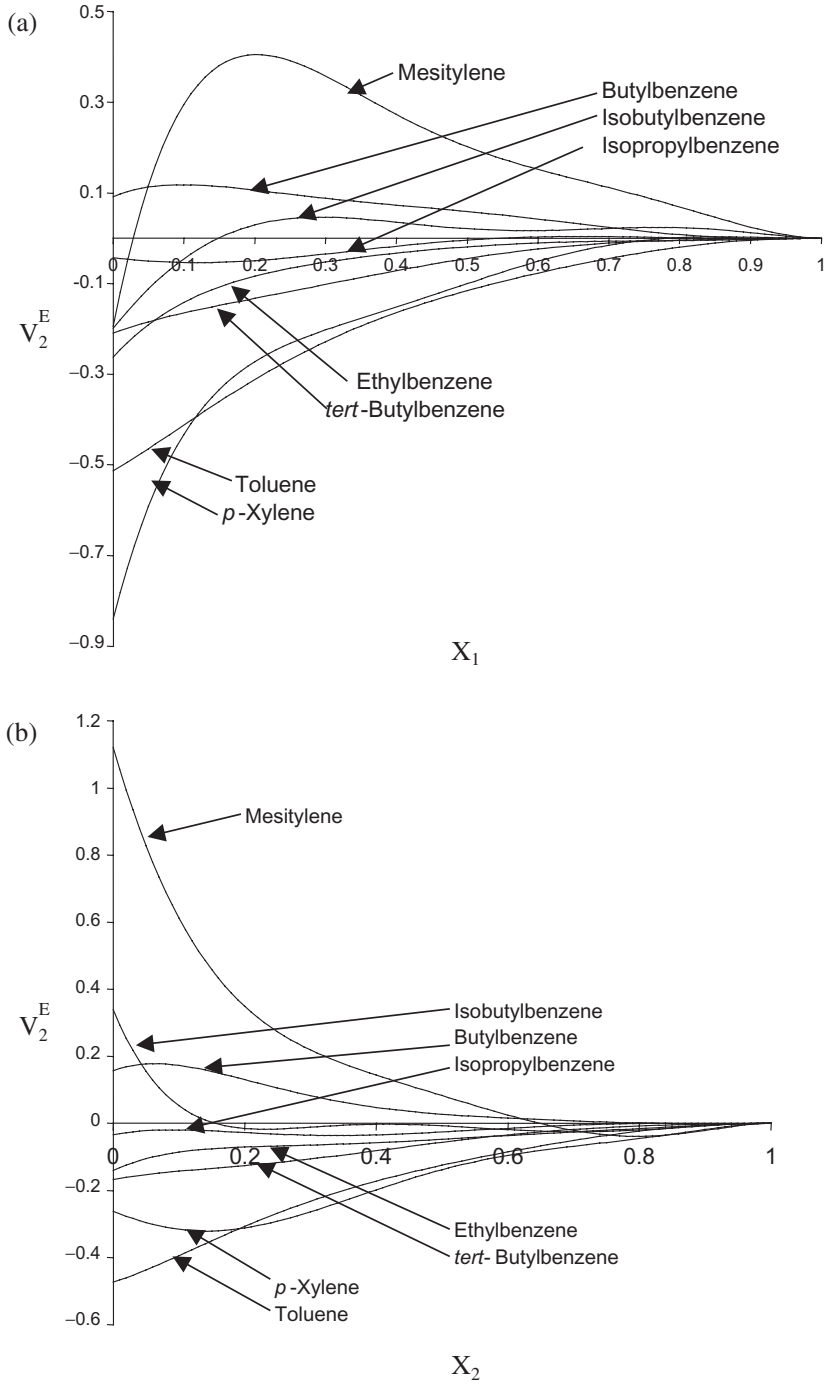

FIGURE 2 Partial excess molar volumes (a) $\bar{V}_1^E$ and (b) $\bar{V}_2^E$ of butyl acetate + aromatic hydrocarbons as a function of the mole fraction of butyl acetate at $T = 298.15\,\mathrm{K}$.

TABLE V Open literature critical values for compounds enclosed into binary mixtures

Compound	P_c (bar)	T_c (K)	V_c ($cm^3\,mol^{-1}$)	ω	Z_c	Z_{RA}
Butyl acetate	30.90	579.00	412.8	0.407	0.253	0.255
Toluene	41.08	591.75	316.0	0.264	0.264	0.267
Ethylbenzene	36.09	617.15	374.0	0.304	0.263	0.264
p-Xylene	35.11	616.20	378.0	0.322	0.259	0.262
Mesitylene	31.27	637.30	430.0	0.399	0.252	0.255
Isopropylbenzene	32.09	631.00	434.7	0.326	0.261	0.262
Butylbenzene	28.90	660.50	497.0	0.393	0.262	0.256
Isobutylbenzene	30.50	650.00	480.0	0.383	0.271	0.257
t-Butylbenzene[a]	29.60	660.00	517.5	0.265	0.270	0.267

Ref. [11]
[a] V_c and Z_c were estimated by the Ambrose method [15].

As a conclusion, the use of the acentric factor dependence parameter (Z_{RA}) as an indicator of ideality deviation for mixtures is more adequate than Z_C, as it was observed in previously publications where these equations of state were compared. The tendency of σ and σ^* in these mixtures as well as their evolution with temperature is in accordance with the values of density. The deviations decrease with temperature as well as the values of the magnitude. Not surprisingly the greatest deviations are showed by the mixtures of mesitylene and *tert*-butylbenzene, because of their high nonideality.

3.4. Equations of State

In the last few years, interest on equations of state for the prediction of thermodynamic properties (excess molar volumes, partial excess and partial molar volumes, phase equilibria, excess molar enthalpies, etc.) has increased. This fact is due to its simplicity as a model, low data, and versatility in operation conditions without a solid theoretical basis. Their response are robust and accurate in a wide range of conditions and requirements. A considerable number of equations of state are available in the literature, most of them being adequate to obtain acceptable results by simple rules if the parameters are obtained from enclosed binary mixtures in the multicomponent system. In this case, the Soave–Redlich–Kwong (SRK) and the Peng–Robinson (PR) equations [12,13] were applied in combination with the mixing rule of two parameters in the copressure and covolume factors. For a binary mixture, at constant p and T, the excess molar volume is expressed as follows:

$$V^E = \Delta V = V_m - \sum_{i=1}^{n} x_i V_i = \sum_{i=1}^{n} x_i \left(-\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}} \left(\frac{\partial p}{\partial V}\right)^{-1}_{T,n_i} - V_i \right), \tag{10}$$

where the partial derivatives and the molar volume are obtained from the selected equation of state. A general expression of the mentioned equation of state could be:

$$p = \frac{RT}{V-b} - \frac{a}{(V+\delta_1 b)(V+\delta_2 b)}, \tag{11}$$

where R is the universal constant of gases, T is the temperature, a is the copressure, b is the covolume, and $\delta_1 = 1$ and $\delta_2 = 0$ for the SRK equation and $(1 \pm \sqrt{2})$ for the PR

TABLE VI Standard deviations of the experimental results from those estimated for densities (σ and σ^* were estimated with Racket and Spencer and Danner modified Racket equations, respectively) for the binary mixtures (butyl acetate + aromatic hydrocarbon) as function of temperature in the range 293.15–313.15 K

Aromatic	$T = 293.15$ K σ ($cm^3\,mol^{-1}$)	$T = 298.15$ K σ^* ($cm^3\,mol^{-1}$)	$T = 303.15$ K σ ($cm^3\,mol^{-1}$)	$T = 308.15$ K σ^* ($cm^3\,mol^{-1}$)	$T = 313.15$ K σ ($cm^3\,mol^{-1}$)	σ^* ($cm^3\,mol^{-1}$)	σ ($cm^3\,mol^{-1}$)	σ^* ($cm^3\,mol^{-1}$)	σ ($cm^3\,mol^{-1}$)	σ^* ($cm^3\,mol^{-1}$)
Toluene	0.013	0.008	0.013	0.008	0.013	0.008	0.013	0.008	0.013	0.008
Ethylbenzene	0.013	0.006	0.013	0.006	0.013	0.006	0.013	0.006	0.013	0.006
p-Xylene	0.015	0.008	0.015	0.008	0.015	0.008	0.015	0.008	0.015	0.008
Mesitylene	0.027	0.012	0.027	0.012	0.027	0.012	0.027	0.012	0.027	0.012
Isopropylbenzene	0.017	0.009	0.017	0.009	0.017	0.009	0.017	0.009	0.017	0.009
Butylbenzene	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016
Isobutylbenzene	0.015	0.046	0.016	0.045	0.016	0.045	0.016	0.045	0.016	0.045
tert-Butylbenzene	0.025	0.018	0.025	0.018	0.025	0.018	0.024	0.018	0.024	0.018

equation. Three different combining rules for binary parameters were enclosed into this model, which show different correlation dependence (Eqs. (12), (13) and (14)):

$$\text{Mixing rule R1:} \quad l_{ij} = m_{ij} = 0 \tag{12}$$

$$\text{Mixing rule R2:} \quad l_{ij} = 0 \tag{13}$$

$$\text{Mixing rule R3:} \quad k_{ij}, l_{ij}, m_{ij} \neq 0, \tag{14}$$

these parameters being a constant value over the whole range of composition diagrams for every mixture and temperatures. The general equations for the applied combining rules are:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (1 - k_{ij} - l_{ij} z_i)(a_i a_j)^{0.5} \tag{15}$$

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (1 - m_{ij}) \left(\frac{b_i + b_j}{2} \right), \tag{16}$$

where $z = (x_i - x_j)$. This rule is analogous to that proposed by Panagiotopoulos and Reid [11], introducing a second interaction parameter, which is called in a general form "general non-cuadratic mixing rule". This R3 rule suffers from the so-called Michelsen–Kistenmacher syndrome, which has been applied with relative success to binary mixtures and for multicomponent prediction.

All these rules use the common temperature dependence of the attractive term in the equation of state proposed by Soave [11]. In Table V the critical magnitudes applied in the calculations are enclosed [11]. In order to compute the binary interaction parameters for each mixing rule, a common correlation procedure was applied such as the minimization of an objective function (Eq. (17)), which ensures the relative accuracy of predicted and experimental values and deals to zero.

$$OF = \frac{\sum_{i=1}^{n} (z_{\text{exp}} - z_{\text{pred}})^2}{z_{\text{exp}}} \tag{17}$$

A Marquard routine were applied to correlate the interaction parameters in combination with the Newton–Raphson method. In what is referred to as the capability to correlate experimental data, a good response is obtained for the mixtures and conditions studied here.

After some algebra the objective function F will be:

$$F = V^E_{\text{exp}} - \sum_{i=1}^{n} x_i \left(- \frac{\begin{pmatrix} ((RT/V - nb) - (nRT/(V - nb)^2)(\partial/\partial n_i)(V - nb) \\ -(1/\mu)(\partial(an^2)/\partial n_i) + (an^2/\mu^2)(\partial\mu/\partial n_i) \end{pmatrix}}{-(nRT/(V - nb)^2) + (an^2/\mu^2)(\partial\mu/\partial n_i)} - V_i \right), \tag{18}$$

where $\mu = \{(V + n\delta_1 b)(V + n\delta_2 b)\}$, V is the mixture molar volume, and n is the number of moles in the mixture. In Tables VII and VIII the binary coefficients for Eqs. (15) and

TABLE VII Binary interaction parameters computed for the described mixing rules (Eqs. (15) and (16)), applied in combination with the SRK equation of state, and, in brackets, root mean square deviations

	R1	*R2*	*R3*
Butyl acetate + toluene			
293.15 K	$k_{12} = -2.160 \times 10^{-2}$ (0.0026)	$k_{12} = -1.160 \times 10^{-2}$ m_{12}=1.387 $\times$ 10^{-3} (0.0016)	$k_{12} = -9.374 \times 10^{-1}$ l_{12}=5.686 $\times$ 10^{-3} m_{12}=7.456 $\times$ 10^{-3} (0.0014)
298.15 K	$k_{12} = -2.150 \times 10^{-2}$ (0.0024)	$k_{12} = -1.222 \times 10^{-2}$ $m_{12} = 1.327 \times 10^{-3}$ (0.0014)	$k_{12} = -9.299 \times 10^{-1}$ $l_{12} = 6.113 \times 10^{-3}$ $m_{12} = 8.231 \times 10^{-3}$ (0.0010)
303.15 K	$k_{12} = -2.127 \times 10^{-2}$ (0.0024)	$k_{12} = -1.185 \times 10^{-2}$ $m_{12} = 1.327 \times 10^{-3}$ (0.0014)	$k_{12} = -9.283 \times 10^{-1}$ $l_{12} = 6.020 \times 10^{-3}$ $m_{12} = 8.577 \times 10^{-3}$ (0.0009)
308.15 K	$k_{12} = -2.107 \times 10^{-2}$ (0.0028)	$k_{12} = -1.141 \times 10^{-2}$ $m_{12} = 1.468 \times 10^{-3}$ (0.0020)	$k_{12} = -9.183 \times 10^{-1}$ $l_{12} = 6.444 \times 10^{-3}$ $m_{12} = 9.607 \times 10^{-3}$ (0.0013)
313.15 K	$k_{12} = -2.086 \times 10^{-2}$ (0.0037)	$k_{12} = -8.514 \times 10^{-3}$ $m_{12} = 1.938 \times 10^{-3}$ (0.0027)	$k_{12} = -9.012 \times 10^{-1}$ $l_{12} = 7.005 \times 10^{-3}$ $m_{12} = 1.127 \times 10^{-2}$ (0.0015)
Butyl acetate + ethylbenzene			
293.15 K	$k_{12} = -2.908 \times 10^{-3}$ (0.0048)	$k_{12} = 4.105 \times 10^{-2}$ $m_{12} = 5.988 \times 10^{-3}$ (0.0006)	$k_{12} = -9.096 \times 10^{-1}$ $l_{12} = -3.479 \times 10^{-4}$ $m_{12} = 6.563 \times 10^{-3}$ (0.0006)
298.15 K	$k_{12} = -2.779 \times 10^{-3}$ (0.0047)	k_{12}=3.697 $\times$ 10^{-2} $m_{12} = 5.574 \times 10^{-3}$ (0.0009)	$k_{12} = -9.091 \times 10^{-1}$ $l_{12} = -7.092 \times 10^{-4}$ $m_{12} = 6.788 \times 10^{-3}$ (0.0007)
303.15 K	$k_{12} = -2.666 \times 10^{-3}$ (0.0047)	$k_{12} = 3.407 \times 10^{-2}$ $m_{12} = 5.304 \times 10^{-3}$ (0.0009)	$k_{12} = -9.110 \times 10^{-1}$ $l_{12} = -8.782 \times 10^{-4}$ $m_{12} = 6.839 \times 10^{-3}$ (0.0006)
308.15 K	$k_{12} = -2.550 \times 10^{-3}$ (0.0050)	$k_{12} = 3.245 \times 10^{-2}$ $m_{12} = 5.206 \times 10^{-3}$ (0.0012)	$k_{12} = -9.253 \times 10^{-1}$ $l_{12} = -4.188 \times 10^{-4}$ $m_{12} = 5.947 \times 10^{-3}$ (0.0012)
313.15 K	$k_{12} = -2.433 \times 10^{-3}$ (0.0048)	$k_{12} = 2.898 \times 10^{-2}$ $m_{12} = 4.808 \times 10^{-3}$ (0.0009)	$k_{12} = -9.257 \times 10^{-1}$ $l_{12} = -7.089 \times 10^{-4}$ $m_{12} = 6.080 \times 10^{-3}$ (0.0007)
Butyl acetate + p-xylene			
293.15 K	$k_{12} = -9.860 \times 10^{-3}$ (0.0123)	$k_{12} = 6.443 \times 10^{-2}$ $m_{12} = 1.012 \times 10^{-2}$ (0.0042)	$k_{12} = -9.066 \times 10^{-1}$ $l_{12} = 2.058 \times 10^{-3}$ $m_{12} = 7.655 \times 10^{-3}$ (0.0039)
298.15 K	$k_{12} = -9.103 \times 10^{-3}$ (0.0126)	$k_{12} = 6.120 \times 10^{-2}$ $m_{12} = 9.869 \times 10^{-3}$ (0.0043)	$k_{12} = -9.287 \times 10^{-1}$ $l_{12} = 2.900 \times 10^{-3}$ $m_{12} = 6.222 \times 10^{-3}$ (0.0038)
303.15 K	$k_{12} = -8.330 \times 10^{-3}$ (0.0132)	$k_{12} = 5.858 \times 10^{-2}$ $m_{12} = 9.676 \times 10^{-3}$ (0.0050)	$k_{12} = -1.051$ $l_{12} = 8.910 \times 10^{-3}$ $m_{12} = -2.420 \times 10^{-3}$ (0.0039)

(*continued*)

TABLE VII Continued

	R1	*R2*	*R3*
308.15 K	$k_{12} = -7.789 \times 10^{-3}$ (0.0134)	$k_{12} = 5.612 \times 10^{-2}$ $m_{12} = 9.520 \times 10^{-3}$ (0.0048)	$k_{12} = -1.033$ $l_{12} = 7.954 \times 10^{-3}$ $m_{12} = -1.271 \times 10^{-3}$ (0.0036)
313.15 K	$k_{12} = -7.124 \times 10^{-3}$ (0.0131)	$k_{12} = 5.147 \times 10^{-2}$ $m_{12} = 8.980 \times 10^{-3}$ (0.0047)	$k_{12} = -1.018$ $l_{12} = 6.829 \times 10^{-3}$ $m_{12} = -2.900 \times 10^{-4}$ (0.0034)
Butyl acetate + mesitylene			
293.15 K	$k_{12} = 1.834 \times 10^{-2}$ (0.0183)	$k_{12} = 5.029 \times 10^{-2}$ $m_{12} = 4.133 \times 10^{-3}$ (0.0066)	$k_{12} = -8.571 \times 10^{-1}$ $l_{12} = -6.832 \times 10^{-3}$ $m_{12} = 6.907 \times 10^{-3}$ (0.0064)
298.15 K	$k_{12} = 1.847 \times 10^{-2}$ (0.0195)	$k_{12} = 5.013 \times 10^{-2}$ $m_{12} = 4.224 \times 10^{-3}$ (0.0082)	$k_{12} = -8.599 \times 10^{-1}$ $l_{12} = -6.480 \times 10^{-3}$ $m_{12} = 6.915 \times 10^{-3}$ (0.0082)
303.15 K	$k_{12} = 1.874 \times 10^{-2}$ (0.0200)	$k_{12} = 4.984 \times 10^{-2}$ $m_{12} = 4.279 \times 10^{-3}$ (0.0081)	$k_{12} = -8.861 \times 10^{-1}$ $l_{12} = -2.328 \times 10^{-3}$ $m_{12} = 5.263 \times 10^{-3}$ (0.0083)
308.15 K	$k_{12} = 1.851 \times 10^{-2}$ (0.0193)	$k_{12} = 4.652 \times 10^{-2}$ $m_{12} = 3.967 \times 10^{-3}$ (0.0088)	$k_{12} = -8.778 \times 10^{-1}$ $l_{12} = -4.794 \times 10^{-3}$ $m_{12} = 6.047 \times 10^{-3}$ (0.0090)
313.15 K	$k_{12} = 1.850 \times 10^{-2}$ (0.0180)	$k_{12} = 4.372 \times 10^{-2}$ $m_{12} = 3.677 \times 10^{-3}$ (0.0080)	$k_{12} = -8.700 \times 10^{-1}$ $l_{12} = -7.033 \times 10^{-3}$ $m_{12} = 6.808 \times 10^{-3}$ (0.0079)
Butyl acetate + isopropylbenzene			
293.15 K	$k_{12} = 8.806 \times 10^{-4}$ (0.0017)	$k_{12} = 4.604 \times 10^{-3}$ $m_{12} = 4.866 \times 10^{-4}$ (0.0014)	$k_{12} = -1.0038$ $l_{12} = 1.131 \times 10^{-3}$ $m_{12} = -3.616 \times 10^{-4}$ (0.0014)
298.15 K	$k_{12} = 8.390 \times 10^{-4}$ (0.0030)	$k_{12} = 9.897 \times 10^{-3}$ $m_{12} = 1.223 \times 10^{-3}$ (0.0011)	$k_{12} = -1.0038$ $l_{12} = 2.093 \times 10^{-3}$ $m_{12} = -3.672 \times 10^{-4}$ (0.0011)
303.15 K	$k_{12} = 8.815 \times 10^{-4}$ (0.0033)	$k_{12} = 1.005 \times 10^{-2}$ $m_{12} = 1.276 \times 10^{-3}$ (0.0014)	$k_{12} = -1.0037$ $l_{12} = 2.157 \times 10^{-3}$ $m_{12} = -3.742 \times 10^{-4}$ (0.0014)
308.15 K	$k_{12} = 8.018 \times 10^{-4}$ (0.0025)	$k_{12} = 7.310 \times 10^{-3}$ $m_{12} = 9.325 \times 10^{-4}$ (0.0010)	$k_{12} = -1.0045$ $l_{12} = 1.751 \times 10^{-3}$ $m_{12} = -4.305 \times 10^{-4}$ (0.0010)
313.15 K	$k_{12} = 7.944 \times 10^{-4}$ (0.0037)	$k_{12} = 1.018 \times 10^{-2}$ $m_{12} = 1.387 \times 10^{-3}$ (0.0013)	$k_{12} = -1.0089$ $l_{12} = 2.733 \times 10^{-3}$ $m_{12} = -7.635 \times 10^{-4}$ (0.0013)
Butyl acetate + butylbenzene			
293.15 K	$k_{12} = 7.819 \times 10^{-3}$ (0.0027)	$k_{12} = 6.032 \times 10^{-3}$ $m_{12} = -2.186 \times 10^{-4}$ (0.0024)	$k_{12} = -9.233 \times 10^{-1}$ $l_{12} = -1.346 \times 10^{-2}$ $m_{12} = 3.729 \times 10^{-3}$ (0.0018)

(*continued*)

TABLE VII Continued

	R1	*R2*	*R3*
298.15 K	$k_{12} = 7.900 \times 10^{-3}$ (0.0012)	$k_{12} = 6.589 \times 10^{-3}$ $m_{12} = -1.653 \times 10^{-4}$ (0.0006)	$k_{12} = -9.678 \times 10^{-1}$ $l_{12} = -4.002 \times 10^{-3}$ $m_{12} = 1.021 \times 10^{-3}$ (0.0006)
303.15 K	$k_{12} = 8.027 \times 10^{-3}$ (0.0019)	$k_{12} = 6.700 \times 10^{-3}$ $m_{12} = -1.726 \times 10^{-4}$ (0.0016)	$k_{12} = -9.372 \times 10^{-1}$ $l_{12} = -1.046 \times 10^{-2}$ $m_{12} = 3.020 \times 10^{-3}$ (0.0011)
308.15 K	$k_{12} = 8.206 \times 10^{-3}$ (0.0029)	$k_{12} = 5.723 \times 10^{-3}$ $m_{12} = -3.326 \times 10^{-4}$ (0.0021)	$k_{12} = -9.350 \times 10^{-1}$ $l_{12} = -1.141 \times 10^{-2}$ $m_{12} = 3.234 \times 10^{-3}$ (0.0017)
313.15 K	$k_{12} = 8.344 \times 10^{-3}$ (0.0037)	$k_{12} = 5.110 \times 10^{-3}$ $m_{12} = -4.462 \times 10^{-4}$ (0.0026)	$k_{12} = -9.143 \times 10^{-1}$ $l_{12} = -1.620 \times 10^{-2}$ $m_{12} = 4.754 \times 10^{-3}$ (0.0011)
Butyl acetate + isobutylbenzene			
293.15 K	$k_{12} = 5.831 \times 10^{-3}$ (0.0101)	$k_{12} = 1.907 \times 10^{-2}$ $m_{12} = 1.660 \times 10^{-3}$ (0.0066)	$k_{12} = -8.762 \times 10^{-1}$ $l_{12} = -1.515 \times 10^{-2}$ $m_{12} = 7.100 \times 10^{-3}$ (0.0061)
298.15 K	$k_{12} = 6.770 \times 10^{-3}$ (0.0087)	$k_{12} = 1.776 \times 10^{-2}$ $m_{12} = 1.421 \times 10^{-3}$ (0.0055)	$k_{12} = -1.0915 \times 10^{-1}$ $l_{12} = 2.291 \times 10^{-2}$ $m_{12} = -6.538 \times 10^{-3}$ (0.0055)
303.15 K	$k_{12} = 7.022 \times 10^{-3}$ (0.0077)	$k_{12} = 1.646 \times 10^{-2}$ $m_{12} = 1.257 \times 10^{-3}$ (0.0047)	$k_{12} = -1.0842$ $l_{12} = 2.128 \times 10^{-2}$ $m_{12} = -6.311 \times 10^{-3}$ (0.0047)
308.15 K	$k_{12} = 7.044 \times 10^{-3}$ (0.0067)	$k_{12} = 1.444 \times 10^{-2}$ $m_{12} = 1.014 \times 10^{-3}$ (0.0045)	$k_{12} = -9.440 \times 10^{-1}$ $l_{12} = -4.927 \times 10^{-3}$ $m_{12} = 2.871 \times 10^{-3}$ (0.0045)
313.15 K	$k_{12} = 7.072 \times 10^{-3}$ (0.0075)	$k_{12} = 1.504 \times 10^{-2}$ $m_{12} = 1.126 \times 10^{-3}$ (0.0050)	$k_{12} = -9.223 \times 10^{-1}$ $l_{12} = -8.718 \times 10^{-3}$ $m_{12} = 4.499 \times 10^{-3}$ (0.0049)
Butyl acetate + tert-butylbenzene			
293.15 K	$k_{12} = -7.017 \times 10^{-3}$ (0.0038)	$k_{12} = 2.515 \times 10^{-3}$ $m_{12} = 1.220 \times 10^{-3}$ (0.0011)	$k_{12} = -1.0054$ $l_{12} = 1.138 \times 10^{-3}$ $m_{12} = 5.568 \times 10^{-4}$ (0.0011)
298.15 K	$k_{12} = -6.912 \times 10^{-3}$ (0.0042)	$k_{12} = 3.139 \times 10^{-3}$ $m_{12} = 1.326 \times 10^{-3}$ (0.0009)	$k_{12} = -1.0057$ $l_{12} = 1.348 \times 10^{-3}$ $m_{12} = 5.344 \times 10^{-4}$ (0.0009)
303.15 K	$k_{12} = -6.713 \times 10^{-3}$ (0.0046)	$k_{12} = 3.447 \times 10^{-3}$ $m_{12} = 1.382 \times 10^{-3}$ (0.0012)	$k_{12} = -1.0059$ $l_{12} = 1.466 \times 10^{-3}$ $m_{12} = 5.169 \times 10^{-4}$ (0.0013)
308.15 K	$k_{12} = -6.514 \times 10^{-3}$ (0.0046)	$k_{12} = 3.202 \times 10^{-3}$ $m_{12} = 1.361 \times 10^{-3}$ (0.0010)	$k_{12} = -1.0066$ $l_{12} = 1.525 \times 10^{-3}$ $m_{12} = 4.545 \times 10^{-4}$ (0.0010)
313.15 K	$k_{12} = -6.304 \times 10^{-3}$ (0.0049)	$k_{12} = 3.352 \times 10^{-3}$ $m_{12} = 1.393 \times 10^{-3}$ (0.0011)	$k_{12} = -1.0076$ $l_{12} = 1.720 \times 10^{-3}$ $m_{12} = 3.643 \times 10^{-4}$ (0.0012)

TABLE VIII Binary interaction parameters computed for the described mixing rules (Eqs. (15) and (16)), applied in combination with the PR equation of state, and, in brackets, root mean square deviations

	R1	*R2*	*R3*
Butyl acetate + toluene			
293.15 K	$k_{12} = -2.317 \times 10^{-2}$ (0.0025)	$k_{12} = -1.234 \times 10^{-2}$ $m_{12} = 1.467 \times 10^{-3}$ (0.0016)	$k_{12} = -1.082$ $l_{12} = -3.7521 \times 10^{-3}$ $m_{12} = -2.377 \times 10^{-3}$ (0.0014)
298.15 K	$k_{12} = -2.305 \times 10^{-2}$ (0.0023)	$k_{12} = -1.301 \times 10^{-2}$ $m_{12} = 1.396 \times 10^{-3}$ (0.0014)	$k_{12} = -1.090$ $l_{12} = -4.403 \times 10^{-3}$ $m_{12} = -3.046 \times 10^{-3}$ (0.0010)
303.15 K	$k_{12} = -2.278 \times 10^{-2}$ (0.0023)	$k_{12} = -1.263 \times 10^{-2}$ $m_{12} = 1.466 \times 10^{-3}$ (0.0014)	$k_{12} = -1.092$ $l_{12} = -4.170 \times 10^{-3}$ $m_{12} = -3.315 \times 10^{-3}$ (0.0009)
308.15 K	$k_{12} = -2.253 \times 10^{-2}$ (0.0027)	$k_{12} = -1.212 \times 10^{-2}$ $m_{12} = 1.552 \times 10^{-3}$ (0.0020)	$k_{12} = -1.103$ $l_{12} = -4.804 \times 10^{-3}$ $m_{12} = -4.277 \times 10^{-3}$ (0.0013)
313.15 K	$k_{12} = -2.229 \times 10^{-2}$ (0.0036)	$k_{12} = -8.776 \times 10^{-3}$ $m_{12} = 2.082 \times 10^{-3}$ (0.0027)	$k_{12} = -1.123$ $l_{12} = -6.193 \times 10^{-3}$ $m_{12} = -5.894 \times 10^{-3}$ (0.0015)
Butyl acetate + ethylbenzene			
293.15 K	$k_{12} = -3.395 \times 10^{-3}$ (0.0048)	$k_{12} = 4.601 \times 10^{-2}$ $m_{12} = 6.585 \times 10^{-3}$ (0.0006)	$k_{12} = -1.107$ $l_{12} = 6.758 \times 10^{-3}$ $m_{12} = -6.404 \times 10^{-3}$ (0.0006)
298.15 K	$k_{12} = -3.258 \times 10^{-3}$ (0.0047)	$k_{12} = 4.176 \times 10^{-2}$ $m_{12} = 6.184 \times 10^{-3}$ (0.0008)	$k_{12} = -1.108$ $l_{12} = 6.754 \times 10^{-3}$ $m_{12} = -6.701 \times 10^{-3}$ (0.0007)
303.15 K	$k_{12} = -3.140 \times 10^{-3}$ (0.0048)	$k_{12} = 3.864 \times 10^{-2}$ $m_{12} = 5.916 \times 10^{-3}$ (0.0008)	$k_{12} = -1.106$ $l_{12} = 6.777 \times 10^{-3}$ $m_{12} = -6.812 \times 10^{-3}$ (0.0006)
308.15 K	$k_{12} = -3.020 \times 10^{-3}$ (0.0051)	$k_{12} = 3.666 \times 10^{-2}$ $m_{12} = 5.794 \times 10^{-3}$ (0.0011)	$k_{12} = -1.091$ $l_{12} = 6.435 \times 10^{-3}$ $m_{12} = -5.977 \times 10^{-3}$ (0.0011)
313.15 K	$k_{12} = -2.899 \times 10^{-3}$ (0.0049)	$k_{12} = 3.288 \times 10^{-2}$ $m_{12} = 5.382 \times 10^{-3}$ (0.0008)	$k_{12} = -1.090$ $l_{12} = 6.366 \times 10^{-3}$ $m_{12} = -6.156 \times 10^{-3}$ (0.0007)
Butyl acetate + p-xylene			
293.15 K	$k_{12} = -1.158 \times 10^{-2}$ (0.0124)	$k_{12} = 7.085 \times 10^{-2}$ $m_{12} = 1.099 \times 10^{-2}$ (0.0044)	$k_{12} = -1.112$ $l_{12} = 1.269 \times 10^{-2}$ $m_{12} = -5.630 \times 10^{-3}$ (0.0037)
298.15 K	$k_{12} = -1.071 \times 10^{-2}$ (0.0127)	$k_{12} = 6.732 \times 10^{-2}$ $m_{12} = 1.073 \times 10^{-2}$ (0.0045)	$k_{12} = -1.091$ $l_{12} = 1.176 \times 10^{-2}$ $m_{12} = -4.584 \times 10^{-3}$ (0.0036)
303.15 K	$k_{12} = -9.818 \times 10^{-3}$ (0.0133)	$k_{12} = 6.433 \times 10^{-2}$ $m_{12} = 1.052 \times 10^{-2}$ (0.0052)	$k_{12} = -1.055$ $l_{12} = 1.011 \times 10^{-2}$ $m_{12} = -2.376 \times 10^{-3}$ (0.0039)

(*continued*)

TABLE VIII Continued

	R1	*R2*	*R3*
308.15 K	$k_{12} = -9.201 \times 10^{-3}$ (0.0135)	$k_{12} = 6.171 \times 10^{-2}$ $m_{12} = 1.037 \times 10^{-2}$ (0.0051)	$k_{12} = -1.036$ $l_{12} = 9.084 \times 10^{-3}$ $m_{12} = -1.221 \times 10^{-3}$ (0.0036)
313.15 K	$k_{12} = -8.439 \times 10^{-3}$ (0.0132)	$k_{12} = 5.674 \times 10^{-2}$ $m_{12} = 9.818 \times 10^{-3}$ (0.0049)	$k_{12} = -1.020$ $l_{12} = 7.832 \times 10^{-3}$ $m_{12} = -2.108 \times 10^{-4}$ (0.0034)
Butyl acetate + mesitylene			
293.15 K	$k_{12} = 2.006 \times 10^{-2}$ (0.0185)	$k_{12} = 5.730 \times 10^{-2}$ $m_{12} = 4.717 \times 10^{-3}$ (0.0065)	$k_{12} = -8.494 \times 10^{-1}$ $l_{12} = -5.905 \times 10^{-3}$ $m_{12} = 7.032 \times 10^{-3}$ (0.0065)
298.15 K	$k_{12} = 2.016 \times 10^{-2}$ (0.0198)	$k_{12} = 5.703 \times 10^{-2}$ $m_{12} = 4.821 \times 10^{-3}$ (0.0082)	$k_{12} = -8.526 \times 10^{-1}$ $l_{12} = -5.517 \times 10^{-3}$ $m_{12} = 7.035 \times 10^{-3}$ (0.0082)
303.15 K	$k_{12} = 2.042 \times 10^{-2}$ (0.0203)	$k_{12} = 5.656 \times 10^{-2}$ $m_{12} = 4.879 \times 10^{-3}$ (0.0081)	$k_{12} = -8.804 \times 10^{-1}$ $l_{12} = -1.082 \times 10^{-3}$ $m_{12} = 5.321 \times 10^{-3}$ (0.0083)
308.15 K	$k_{12} = 2.011 \times 10^{-2}$ (0.0196)	$k_{12} = 5.276 \times 10^{-2}$ $m_{12} = 4.539 \times 10^{-3}$ (0.0088)	$k_{12} = -8.716 \times 10^{-1}$ $l_{12} = -3.815 \times 10^{-3}$ $m_{12} = 6.144 \times 10^{-3}$ (0.0090)
313.15 K	$k_{12} = 2.005 \times 10^{-2}$ (0.0184)	$k_{12} = 4.954 \times 10^{-2}$ $m_{12} = 4.226 \times 10^{-3}$ (0.0080)	$k_{12} = -8.634 \times 10^{-1}$ $l_{12} = -6.292 \times 10^{-3}$ $m_{12} = 6.945 \times 10^{-3}$ (0.0080)
Butyl acetate + isopropylbenzene			
293.15 K	$k_{12} = 7.030 \times 10^{-4}$ (0.0018)	$k_{12} = 5.155 \times 10^{-3}$ $m_{12} = 5.673 \times 10^{-4}$ (0.0014)	$k_{12} = -1.0034$ $l_{12} = 1.206 \times 10^{-3}$ $m_{12} = -3.037 \times 10^{-4}$ (0.0014)
298.15 K	$k_{12} = 6.341 \times 10^{-4}$ (0.0031)	$k_{12} = 1.112 \times 10^{-2}$ $m_{12} = 1.392 \times 10^{-3}$ (0.0011)	$k_{12} = -1.0035$ $l_{12} = 2.319 \times 10^{-3}$ $m_{12} = -3.082 \times 10^{-4}$ (0.0011)
303.15 K	$k_{12} = 6.618 \times 10^{-4}$ (0.0034)	$k_{12} = 1.134 \times 10^{-2}$ $m_{12} = 1.454 \times 10^{-3}$ (0.0014)	$k_{12} = -1.0031$ $l_{12} = 2.361 \times 10^{-3}$ $m_{12} = -2.916 \times 10^{-4}$ (0.0014)
308.15 K	$k_{12} = 5.476 \times 10^{-4}$ (0.0025)	$k_{12} = 8.211 \times 10^{-3}$ $m_{12} = 1.075 \times 10^{-3}$ (0.0010)	$k_{12} = -1.0042$ $l_{12} = 1.913 \times 10^{-3}$ $m_{12} = -3.670 \times 10^{-4}$ (0.0010)
313.15 K	$k_{12} = 5.164 \times 10^{-4}$ (0.0038)	$k_{12} = 1.146 \times 10^{-2}$ $m_{12} = 1.586 \times 10^{-3}$ (0.0013)	$k_{12} = -1.0090$ $l_{12} = 3.020 \times 10^{-3}$ $m_{12} = -7.180 \times 10^{-4}$ (0.0013)
Butyl acetate + butylbenzene			
293.15 K	$k_{12} = 8.283 \times 10^{-3}$ (0.0025)	$k_{12} = 6.621 \times 10^{-3}$ $m_{12} = -1.979 \times 10^{-4}$ (0.0024)	$k_{12} = -9.182 \times 10^{-1}$ $l_{12} = -1.432 \times 10^{-2}$ $m_{12} = 3.882 \times 10^{-3}$ (0.0018)
298.15 K	$k_{12} = 8.319 \times 10^{-3}$ (0.0009)	$k_{12} = 7.228 \times 10^{-3}$ $m_{12} = -1.341 \times 10^{-4}$ (0.0006)	$k_{12} = -9.656 \times 10^{-1}$ $l_{12} = -4.215 \times 10^{-3}$ $m_{12} = 1.078 \times 10^{-3}$ (0.0006)

(*continued*)

TABLE VIII Continued

	R1	*R2*	*R3*
303.15 K	$k_{12} = 8.406 \times 10^{-3}$ (0.0017)	k_{12}=7.327 × 10^{-3} $m_{12} = -1.370 \times 10^{-4}$ (0.0016)	$k_{12} = -9.331 \times 10^{-1}$ $l_{12} = -1.112 \times 10^{-2}$ m_{12}=3.165 × 10^{-3} (0.0011)
308.15 K	$k_{12} = 8.552 \times 10^{-3}$ (0.0027)	$k_{12} = 6.174 \times 10^{-3}$ $m_{12} = -3.112 \times 10^{-4}$ (0.0021)	$k_{12} = -9.308 \times 10^{-1}$ l_{12}=−1.217 × 10^{-2} $m_{12} = 3.390 \times 10^{-3}$ (0.0017)
313.15 K	$k_{12} = 8.648 \times 10^{-3}$ (0.0035)	$k_{12} = 5.441 \times 10^{-3}$ $m_{12} = -4.327 \times 10^{-4}$ (0.0026)	$k_{12} = -9.090 \times 10^{-1}$ $l_{12} = -1.728 \times 10^{-2}$ $m_{12} = 4.972 \times 10^{-3}$ (0.0011)
Butyl acetate + isobutylbenzene			
293.15 K	$k_{12} = 5.691 \times 10^{-3}$ (0.0104)	$k_{12} = 2.157 \times 10^{-2}$ $m_{12} = 1.940 \times 10^{-3}$ (0.0066)	$k_{12} = -8.687 \times 10^{-1}$ $l_{12} = -1.570 \times 10^{-2}$ $m_{12} = 7.410 \times 10^{-3}$ (0.0061)
298.15 K	$k_{12} = 6.733 \times 10^{-3}$ (0.0090)	$k_{12} = 1.999 \times 10^{-2}$ $m_{12} = 1.672 \times 10^{-3}$ (0.0055)	$k_{12} = -1.0946$ $l_{12} = 2.446 \times 10^{-2}$ $m_{12} = -6.543 \times 10^{-3}$ (0.0055)
303.15 K	$k_{12} = 6.978 \times 10^{-3}$ (0.0080)	$k_{12} = 1.845 \times 10^{-2}$ $m_{12} = 1.493 \times 10^{-3}$ (0.0047)	$k_{12} = -1.0865$ $l_{12} = 2.259 \times 10^{-2}$ $m_{12} = -6.286 \times 10^{-3}$ (0.0047)
308.15 K	$k_{12} = 6.955 \times 10^{-3}$ (0.0070)	$k_{12} = 1.611 \times 10^{-2}$ $m_{12} = 1.228 \times 10^{-3}$ (0.0044)	$k_{12} = -9.405 \times 10^{-1}$ $l_{12} = -4.991 \times 10^{-3}$ $m_{12} = 3.057 \times 10^{-3}$ (0.0045)
313.15 K	$k_{12} = 6.938 \times 10^{-3}$ (0.0078)	$k_{12} = 1.677 \times 10^{-2}$ $m_{12} = 1.361 \times 10^{-3}$ (0.0050)	$k_{12} = -9.175 \times 10^{-1}$ $l_{12} = -9.015 \times 10^{-3}$ $m_{12} = 4.756 \times 10^{-3}$ (0.0049)
Butyl acetate + tert-butylbenzene			
293.15 K	$k_{12} = -7.596 \times 10^{-3}$ (0.0037)	$k_{12} = 3.090 \times 10^{-3}$ $m_{12} = 1.334 \times 10^{-3}$ (0.0011)	$k_{12} = -1.0051$ $l_{12} = 1.250 \times 10^{-3}$ $m_{12} = 6.280 \times 10^{-4}$ (0.0011)
298.15 K	$k_{12} = -7.500 \times 10^{-3}$ (0.0041)	$k_{12} = 3.786 \times 10^{-3}$ $m_{12} = 1.453 \times 10^{-3}$ (0.0009)	$k_{12} = -1.0056$ $l_{12} = 1.489 \times 10^{-3}$ $m_{12} = 6.055 \times 10^{-4}$ (0.0009)
303.15 K	$k_{12} = -7.298 \times 10^{-3}$ (0.0045)	$k_{12} = 4.113 \times 10^{-3}$ $m_{12} = 1.516 \times 10^{-3}$ (0.0012)	$k_{12} = -1.0055$ $l_{12} = 1.592 \times 10^{-3}$ $m_{12} = 6.053 \times 10^{-4}$ (0.0013)
308.15 K	$k_{12} = -7.097 \times 10^{-3}$ (0.0045)	$k_{12} = 3.811 \times 10^{-3}$ $m_{12} = 1.494 \times 10^{-3}$ (0.0010)	$k_{12} = -1.0066$ $l_{12} = 1.663 \times 10^{-3}$ $m_{12} = 5.336 \times 10^{-4}$ (0.0010)
313.15 K	$k_{12} = -6.886 \times 10^{-3}$ (0.0048)	$k_{12} = 3.958 \times 10^{-3}$ $m_{12} = 1.532 \times 10^{-3}$ (0.0011)	$k_{12} = -1.0076$ $l_{12} = 1.874 \times 10^{-3}$ $m_{12} = 4.412 \times 10^{-4}$ (0.0012)

(16) are gathered, together with the root mean square deviations (σ) from the experimental data by means of Eq. (4), for SRK and PR EOS respectively. It can be observed that a high accuracy is achieved from the measured data, almost the same deviations being obtained for both equations. The similarity of predictions for different formulations of cubic equations of state has been taken into account in much of the literature. The mixing rules applied showed a good response in all cases, although R2 and R3 present a closer trend.

4. RESULTS AND CONCLUSIONS

Many chemicals, food, pharmacologic, and other industries present nonideal mixtures enclosed in their processes. For this reason it is necessary to pay attention to device and equipment design and operational magnitudes to obtain adequate and optimized processes. Butyl acetate is used widely in the perfume industry and also applied as a solvent in the production of different synthetic products (nitrocellulose, artificial leather, synthetic resins, print inks, agricultural chemicals, adhesives, paint, butyl glycol, butyl acrylate, etc.) and flavoring agent for foods and pharmaceuticals. This paper is focused on the study and measurement of physical properties of mixtures containing ester groups in an aromatic environment, as a continuation of previous work [1–5].

In general, excess volumes mainly depend 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 as it occurs for the greatest compounds in this work. This usually occurs when one of the components has polar groups and the other a nonpolar, or weakly polar behavior. Butyl acetate is weakly polar and aromatic hydrocarbons are nearly nonpolar. When the pure compounds are mixed, the nonpolar hydrocarbon molecules intersperse among the butyl acetate molecules, resulting in a decreased interaction among the dipoles of the acetate and the destruction of dispersive interactions among benzenic rings. The new interaction among unalike molecules is less strong and produces an expansion with maxima at almost equimolecular compositions for compounds of high molecular volume. This effect is clearly shown in Fig. 2(a) and (b) in terms of the partial molar volume against composition. This fact shows that the change of intermolecular forces is higher than the packing caused by geometrical effects for these chemicals (mesitylene, butylbenzene, etc.). If we pay attention to the mixtures containing light solvents the opposite effect will be noted, the inclusion of the aromatic molecules with small volume destroy neither π electron dispersive forces nor ester polar attraction. The mixture of these compounds reforces the molecular package, a slight contractive trend taking place. Only the mixtures containing isobutylbenzene show sigmoid tendencies; contractive values for diluted ester (intense dispersive forces) and expansive for concentrated ester (steric hindrance among aliphatic ends). If we compare the maximum excess volumes ($x \approx 0.5$) the following observations can be made: lower values correspond to mixtures of flat geometry hydrocarbons with small substituents or separated ones (toluene, *p*-xylene), intermediate values correspond to mixtures with no-flat geometry hydrocarbons (*t*-butylbenzene, isopropylbenzene, ethylbenzene) and the highest values correspond to 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 butyl acetate and aromatic structure. Hydrocarbon molecules will have increasingly rising difficulties in establishing interactions the larger they are, due to the steric hindrance with the aliphatic end of butyl acetate. If the molecules are flat or with few bulky substituents (toluene, *p*-xylene), some interactions can persist and negative excess volumes appear. If the hydrocarbon molecules have a bulky substituent or occupy 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, as occurs in the highest hydrocarbons. The presence of three methylene groups in the meta position obstructs the approach of the acetate toward the ring and the steric volume is higher. In this case, the interaction among acetate molecules will be lower and the excess volume increases.

The extreme behavior of butyl acetate + mesitylene is clearly showed in Fig. 3(c) and (d) where an inflexion point is observed at 0.2 molar fraction of butyl acetate showing a change of intermolecular interactions. From Figs. 1 and 3 it is concluded that temperature effect is moderated in the studied range although this factor produces a more expansive trend for those mixtures like butyl acetate + mesitylene when temperature is increased and more contractive effect for mixtures like butyl acetate + toluene. Only previously published data were found for the mixtures butyl acetate + (toluene, ethylbenzene, or *p*-xylene) at 293.15 K. For comparison, we refer the reader to the deviations from the experimental presented in this work (Fig. 4), the data of Qin *et al.* [14], and the equations of state of modified Rackett and SRK (mixing rule R3) for the

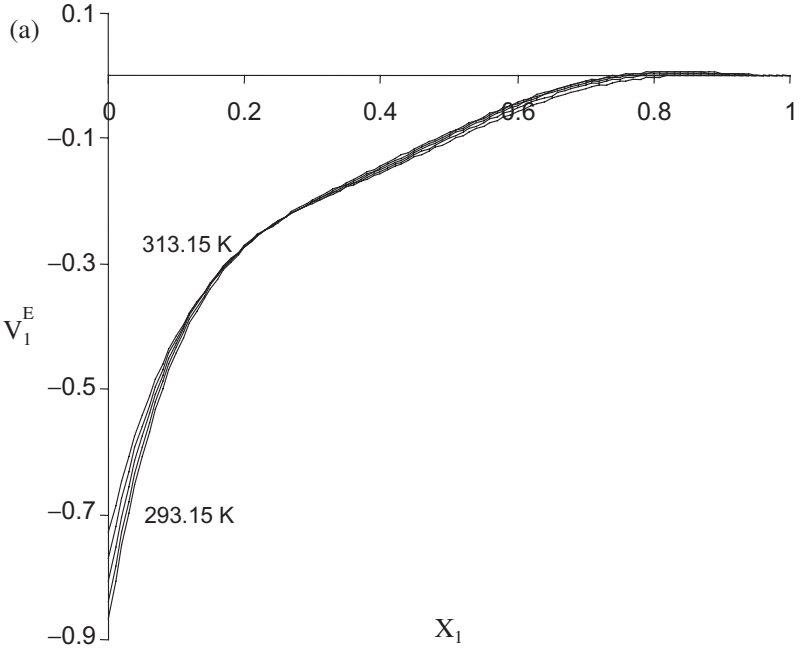

FIGURE 3 Partial excess molar volumes (a) $\bar{V}_1^E$ and (b) $\bar{V}_2^E$ of butyl acetate + *p*-xylene and (c) $\bar{V}_1^E$ and (d) $\bar{V}_2^E$ of butyl acetate + mesitylene as a function of the temperature in the range 293.15–313.15 K.

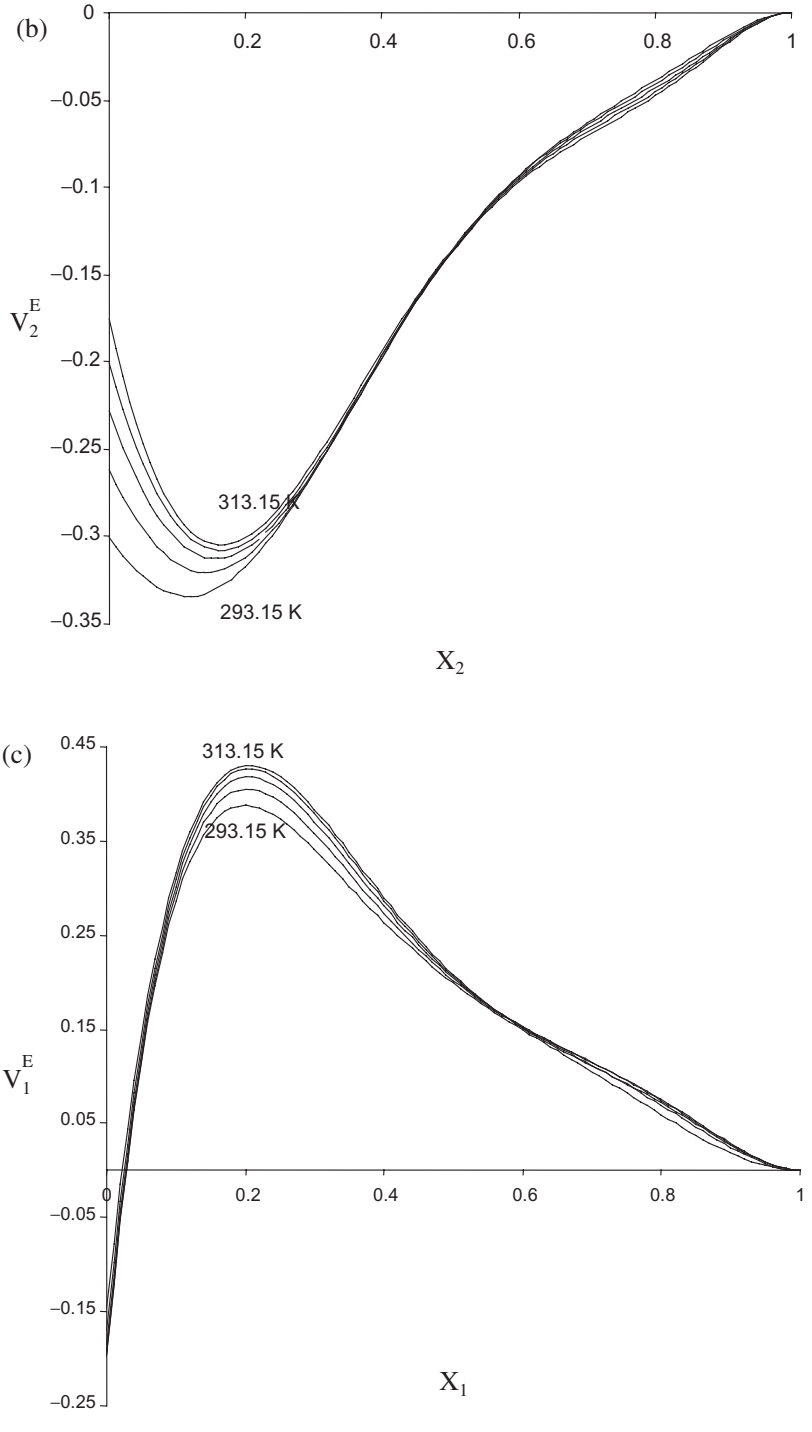

FIGURE 3 Continued.

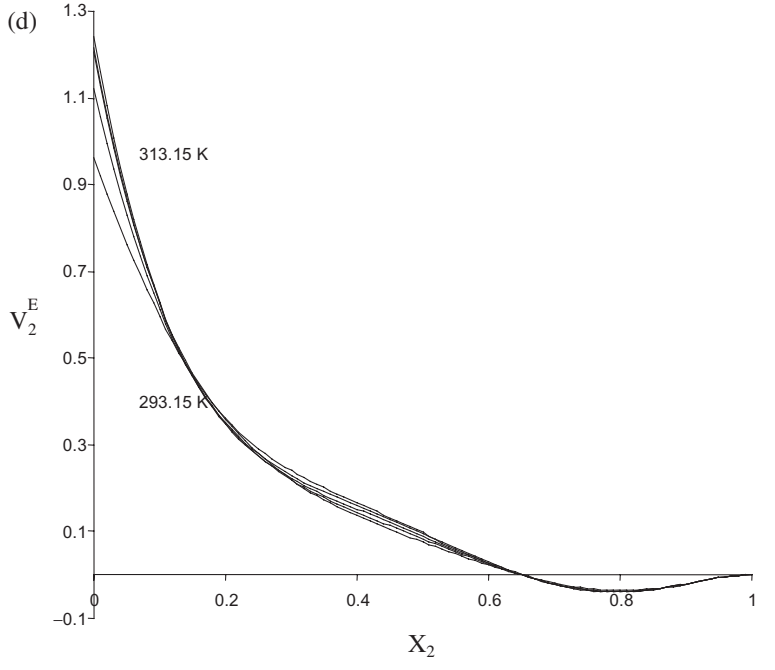

FIGURE 3 Continued.

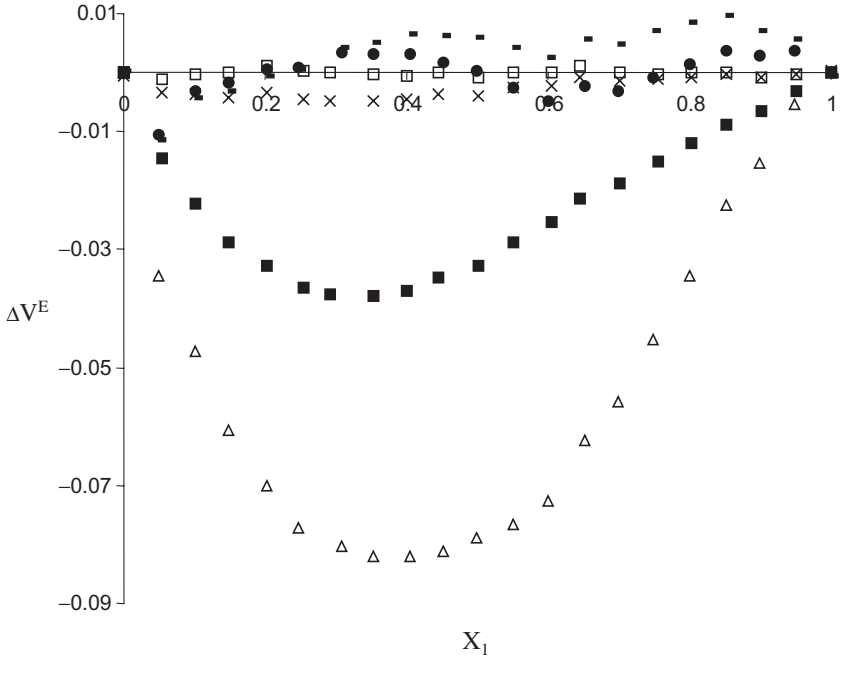

FIGURE 4 Deviation of excess molar volumes on mixing in literature [14], of our estimated values applying Spencer–Danner–Rackett equation and of those calculated with SRK EOS using R3, from experimental results for the systems butyl acetate + ethylbenzene (× Qin, ■ *m*-Rackett, and □ SRK) and + *p*-Xylene (− Qin, △ *m*-Rackett, and ● SRK) at 293.15 K.

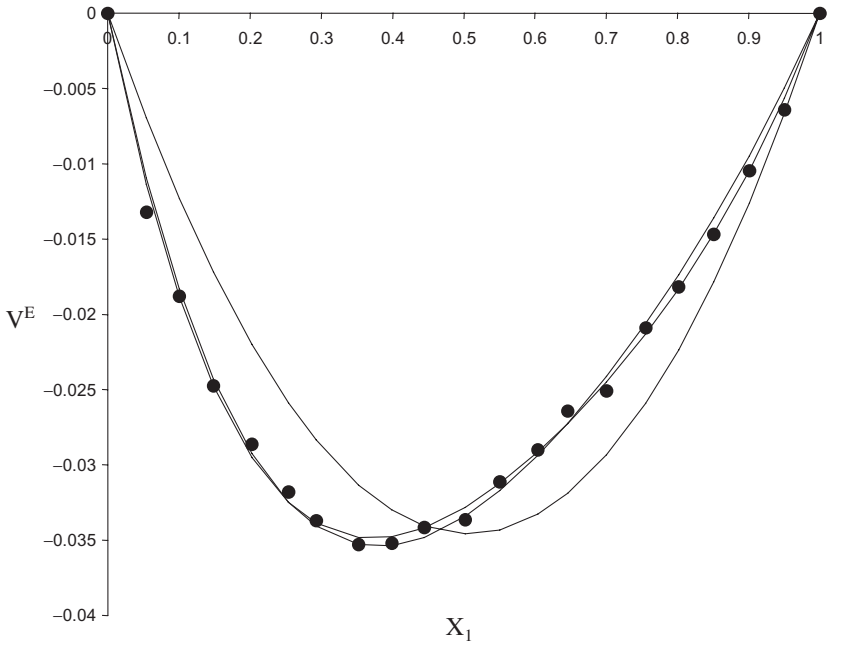

FIGURE 5 Comparison of experimental values of V^E (●) and those estimated by application of the 3 mixing rules in the SRK EOS (— – — R1, – – R2, and — R3), for the binary mixture butyl acetate + ethylbenzene at 298.15 K.

systems butyl acetate + (ethylbenzene and *p*-xylene) at 293.15 K. From this figure high deviations of modified Rackett equation, in terms of excess molar volume, are observed. The previous literature [14] shows moderate deviations, underestimating the negative values of these mixtures. Only the equations of state of SRK or PR show real capability of prediction. As an example, this accuracy could be observed for butyl acetate + ethylbenzene at 298.15 K (Fig. 5), only the R1 mixing rule showing slight deviation toward a symmetric tendency due to its low molar fraction dependence. Nowadays, our work is being focused towards the application of more complex mixing rules (noncuadratic or G^E dependent rules) in order to predict accurately complex mixtures as high-order multicomponent or heterogeneous systems.

Acknowledgments

Miguel Iglesias wishes to thank the Basque Country Government, Departamento de Educación, Universidades e Investigación, Dirección de Política Científica (Eusko Jaurlaritza, Hezkuntza, Unibertsitate eta Ikerketa Saila) for its support in the development of his research.

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