International Journal of Thermophysics, Vol. 26, No. 5, September 2005 (© 2005)
DOI: 10.1007/s10765-005-8096-3

Effect of Temperature on the Change of Refractive Index on Mixing for Butyl Acetate + Aromatic Hydrocarbons

J. M. Resa,[1,2] C. Gonzalez,[1] R. G. Concha,[1] and M. Iglesias[1]

Received June 6, 2003

In this work experimental data for the refractive index on mixing for butyl acetate + (toluene, ethylbenzene, *p*-xylene, isopropylbenzene, butylbenzene, isobutylbenzene, mesitylene, or *t*-butylbenzene) binary mixtures, and some computed derived properties, as a function of temperature, are presented. The mixtures show a clear expansive trend for the highest molar mass compounds. Values of measured properties were compared with results obtained by semiempirical relations and equations of state with simple mixing rules. Accurate results were obtained with the latter, and such parameters could be used in the prediction of multicomponent refractive indices or other thermodynamic properties using standard thermodynamic expressions.

KEY WORDS: aromatic hydrocarbons; binary mixtures; butyl acetate; equation of state; refractive index; temperature.

1. INTRODUCTION

Many chemical, food, pharmacological, and other industries involve nonideal mixtures in their processes. For this reason it is necessary to optimize the equipment design and operational parameters to obtain an adequate and efficient process. 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.)

[1] Dpto. de Ingenieria Química, Facultad de Farmacia, Universidad del Pais Vasco, Apto. 450, Vitoria, Spain.
[2] To whom correspondence should be addressed. E-mail: iqpredij@vc.ehu.es

and is a flavoring agent for foods and pharmaceuticals. As a result, butyl acetate is a component of all the binary mixtures considered in this study.

As a continuation of previous work [1–4], this paper is devoted to the study of the thermodynamic properties of mixtures with components consisting of the ester group + aromatic compounds. With this aim, we have carried out a series of studies focussed on acetate mixtures to analyze the influence of the position of alkyl groups in the aromatic ring and the influence of temperature on thermophysical mixing properties. To this end, the refractive indices on mixing for butyl acetate + (toluene, ethylbenzene, *p*-xylene, mesitylene, isopropylbenzene, butylbenzene, isobutylbenzene, or *t*-butylbenzene) binary mixtures were measured at several temperatures and atmospheric pressure. The mixtures show an expansive trend for increasing molar mass compounds. For the case of refractive index estimation, different semiempirical models from Ref. 5 and a cubic equation of state [2] have been adapted, from a derivation of the Heller equation, to obtain an expression for refractive indices on mixing. By means of such a derivation, the Soave–Redlich–Kwong (SRK) cubic equation of state has been applied to compute binary interaction parameters from experimental data. The temperature dependence of this derived property was analyzed in terms of functional groups; agreement between the experimental and theoretical results was achieved. The results demonstrate the value of this procedure as a tool for estimating multicomponent mixture properties using refractive indices or various binary or multicomponent mixture thermophysical properties by adequate derivations of the equations of state.

2. EXPERIMENTAL SECTION

All chemicals were supplied by Fluka, except for butyl acetate, which was supplied by Panreac, and all have 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 a ultrasonic bath for four hours to minimize water contamination. The purities of the chemicals were checked using gas chromatography, and these purities were compared with those from vendor specifications. The properties of the pure compounds were measured and compared (Table I) with recent literature values at 298.15 K and atmospheric pressure. Experimental procedures for these measurements were described in detail previously [3]. The experimental techniques used for n_D and T measurements and the uncertainties involved in obtaining the experimental data in Table II are also described in Ref. 3.

Table I. Comparison of Measured Refractive Indices with Literature Data for Pure Liquids at 298.15 K

	n_D	
Compound	Exptl.	Lit[a].
Butyl acetate	1.39176	1.39180
Toluene	1.49399	1.49413
Ethylbenzene	1.49316	1.49320
p-Xylene	1.49298	1.49325
Mesitylene	1.49682	1.49684
Isopropylbenzene	1.48869	1.48890
Butylbenzene	1.48735	1.48742
Isobutylbenzene	1.48397	1.48400
t-Butylbenzene	1.49003	1.49024

[a] TRC Thermodynamic Tables (1994) [6].

3. DATA ANALYSIS

3.1. Correlation of Derived Properties

The changes of refractive indices on mixing are presented in Table II and were computed from the following equation:

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

In this equation, n_D is the refractive index on mixing, n_{Di} is the refractive index of pure component i, x_i is the mole fraction of component i, and n is the number of components in the mixture. A Redlich–Kister [7] type equation was used to correlate the derived properties of the binary mixtures, by using the unweighted least-squares method, with all experimental points weighted equally [8]. The Redlich–Kister equation can be expressed as

$$\delta Q = x_i x_j \cdot \sum_{p=0}^{m} B_p \left(x_i - x_j\right)^p, \tag{2}$$

where δQ is δn_D in this case. The degree of this equation (m parameter) was optimized by applying the F-test [9]. The B_p parameters were expanded as a quadratic function of temperature as expressed in the following equation:

$$B_p = \sum_{q=0}^{2} B_{pq} \cdot T^q, \tag{3}$$

Table II. Refractive Indices and Changes of Refractive Indices on Mixing for the Binary Mixtures Butyl Acetate (1) + (Toluene, Ethylbenzene, *p*-Xylene, Mesitylene, Isopropylbenzene, Butylbenzene, Isobutylbenzene, *t*-butylbenzene) (2) in the Temperature Range of 293.15–313.15 K

	n_D (K)					δn_D (K)				
x_1	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
Butyl acetate + Toluene										
0.9449	1.39881	1.39630	1.39384	1.39133	1.38884	−0.0010	−0.0011	−0.0011	−0.0011	−0.0011
0.8971	1.40273	1.40025	1.39777	1.39518	1.39265	−0.0020	−0.0020	−0.0020	−0.0021	−0.0021
0.8404	1.40760	1.40508	1.4025	1.39992	1.39741	−0.0030	−0.0030	−0.0031	−0.0031	−0.0031
0.7972	1.41141	1.40888	1.40629	1.40371	1.40120	−0.0036	−0.0036	−0.0037	−0.0037	−0.0037
0.7516	1.41545	1.41287	1.41026	1.40773	1.40511	−0.0042	−0.0043	−0.0043	−0.0043	−0.0044
0.7000	1.42017	1.41756	1.41498	1.41233	1.40974	−0.0048	−0.0049	−0.0049	−0.0049	−0.0050
0.6517	1.42468	1.42207	1.41943	1.41676	1.41415	−0.0052	−0.0053	−0.0053	−0.0054	−0.0054
0.5999	1.42964	1.42695	1.42432	1.42164	1.41904	−0.0056	−0.0057	−0.0057	−0.0058	−0.0058
0.5524	1.43430	1.43166	1.42902	1.42632	1.42368	−0.0058	−0.0059	−0.0059	−0.0059	−0.0059
0.4994	1.43964	1.43696	1.43430	1.43157	1.42895	−0.0059	−0.0060	−0.0060	−0.0060	−0.0060
0.4468	1.44504	1.44235	1.43970	1.43691	1.43423	−0.0059	−0.0060	−0.0059	−0.0060	−0.0060
0.4011	1.44980	1.44705	1.44430	1.44161	1.43890	−0.0058	−0.0059	−0.0060	−0.0060	−0.0060
0.3447	1.45590	1.45318	1.45041	1.44769	1.44494	−0.0055	−0.0056	−0.0056	−0.0056	−0.0057
0.2985	1.46100	1.45826	1.45547	1.45277	1.45010	−0.0052	−0.0052	−0.0053	−0.0052	−0.0052
0.2502	1.46644	1.46358	1.46079	1.45814	1.45535	−0.0047	−0.0048	−0.0048	−0.0047	−0.0048
0.2001	1.47222	1.46948	1.46668	1.46382	1.46101	−0.0040	−0.0041	−0.0041	−0.0041	−0.0042
0.1500	1.47815	1.47538	1.47251	1.46966	1.46684	−0.0033	−0.0033	−0.0033	−0.0034	−0.0034
0.0998	1.48428	1.48149	1.47861	1.47573	1.47285	−0.0023	−0.0023	−0.0023	−0.0024	−0.0025
0.0499	1.49044	1.48757	1.48472	1.48180	1.47891	−0.0012	−0.0013	−0.0013	−0.0014	−0.0015
Butyl acetate + Ethylbenzene										
0.9505	1.39875	1.39633	1.39386	1.39139	1.38895	−0.0005	−0.0005	−0.0005	−0.0005	−0.0004
0.9009	1.40339	1.40097	1.39849	1.39597	1.39349	−0.0009	−0.0008	−0.0008	−0.0009	−0.0009

0.8511	1.40813	1.40566	1.40320	1.40068	1.39815	−0.0012	−0.0012	−0.0012	−0.0012	−0.0012
0.8016	1.41282	1.41035	1.40784	1.40537	1.40283	−0.0015	−0.0015	−0.0015	−0.0015	−0.0015
0.7555	1.41729	1.41481	1.41224	1.40974	1.40720	−0.0017	−0.0017	−0.0018	−0.0018	−0.0018
0.7003	1.42266	1.42015	1.41759	1.41507	1.41252	−0.0020	−0.0020	−0.0020	−0.0020	−0.0020
0.6456	1.42806	1.42552	1.42292	1.42036	1.41779	−0.0021	−0.0022	−0.0022	−0.0022	−0.0023
0.6041	1.43221	1.42967	1.42703	1.42449	1.42191	−0.0022	−0.0022	−0.0023	−0.0023	−0.0023
0.5505	1.43764	1.43508	1.43242	1.42983	1.42720	−0.0022	−0.0023	−0.0023	−0.0024	−0.0024
0.5021	1.44254	1.43999	1.43733	1.43472	1.43207	−0.0022	−0.0023	−0.0023	−0.0023	−0.0024
0.4448	1.44842	1.44582	1.44315	1.44053	1.43785	−0.0022	−0.0022	−0.0023	−0.0023	−0.0024
0.3989	1.45314	1.45054	1.44782	1.44526	1.44253	−0.0021	−0.0022	−0.0023	−0.0022	−0.0024
0.3526	1.45799	1.45536	1.45263	1.45000	1.44729	−0.0020	−0.0020	−0.0021	−0.0021	−0.0022
0.2929	1.46417	1.46155	1.45890	1.45623	1.45354	−0.0019	−0.0019	−0.0019	−0.0019	−0.0020
0.2540	1.46832	1.46568	1.46302	1.46037	1.45768	−0.0017	−0.0017	−0.0017	−0.0017	−0.0018
0.2024	1.47382	1.47116	1.46843	1.4658	1.46310	−0.0014	−0.0015	−0.0015	−0.0015	−0.0016
0.1488	1.4796	1.47693	1.47418	1.47152	1.46884	−0.0011	−0.0011	−0.0012	−0.0012	−0.0012
0.1008	1.48485	1.48219	1.47946	1.47673	1.47401	−0.0007	−0.0007	−0.0007	−0.0008	−0.0009
0.0544	1.48984	1.48716	1.48442	1.48172	1.47899	−0.0004	−0.0005	−0.0005	−0.0005	−0.0006
Butyl acetate + *p*-Xylene										
0.9489	1.39894	1.39654	1.39405	1.39155	1.38910	−0.0004	−0.0004	−0.0004	−0.0005	−0.0004
0.8979	1.40384	1.40137	1.39885	1.39641	1.39390	−0.0007	−0.0007	−0.0008	−0.0007	−0.0008
0.8519	1.40830	1.40578	1.40327	1.40076	1.39826	−0.0009	−0.0010	−0.0010	−0.0010	−0.0010
0.7990	1.41333	1.41087	1.40834	1.40581	1.40327	−0.0012	−0.0012	−0.0013	−0.0013	−0.0013
0.7490	1.41825	1.41572	1.41319	1.41066	1.40812	−0.0014	−0.0014	−0.0014	−0.0015	−0.0015
0.6993	1.42315	1.42063	1.41806	1.41551	1.41295	−0.0016	−0.0016	−0.0016	−0.0017	−0.0017
0.6518	1.42787	1.42531	1.42272	1.42021	1.41762	−0.0017	−0.0017	−0.0017	−0.0017	−0.0018
0.5991	1.43317	1.43060	1.42798	1.42546	1.42286	−0.0017	−0.0017	−0.0018	−0.0018	−0.0019
0.5505	1.43808	1.43550	1.43288	1.43034	1.42775	−0.0017	−0.0018	−0.0018	−0.0018	−0.0018
0.4999	1.44322	1.44061	1.43796	1.43542	1.43282	−0.0017	−0.0018	−0.0018	−0.0019	−0.0019
0.4519	1.44815	1.44554	1.44286	1.44032	1.43770	−0.0017	−0.0017	−0.0018	−0.0018	−0.0018

Table II. *(Continued)*

	n_D (K)					δn_D (K)				
x_1	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
0.4040	1.45307	1.45044	1.44776	1.44522	1.44259	−0.0016	−0.0016	−0.0017	−0.0017	−0.0017
0.3519	1.45847	1.45583	1.45312	1.45058	1.44789	−0.0015	−0.0015	−0.0016	−0.0016	−0.0017
0.3077	1.46309	1.46041	1.45768	1.45514	1.45247	−0.0014	−0.0014	−0.0015	−0.0015	−0.0015
0.2480	1.46931	1.46663	1.46387	1.46134	1.45863	−0.0012	−0.0012	−0.0013	−0.0013	−0.0014
0.2012	1.47424	1.47153	1.46878	1.46623	1.46356	−0.0010	−0.0011	−0.0011	−0.0012	−0.0012
0.1494	1.47980	1.47710	1.47436	1.47174	1.46903	−0.0007	−0.0008	−0.0008	−0.0009	−0.0009
0.1014	1.48487	1.48216	1.47940	1.47685	1.47409	−0.0005	−0.0006	−0.0006	−0.0006	−0.0007
0.0494	1.49045	1.48779	1.48504	1.48238	1.47977	−0.0002	−0.0002	−0.0002	−0.0003	−0.0002
Butyl acetate + Mesitylene										
0.9494	1.39954	1.39710	1.39467	1.39225	1.38972	5.3E-05	2.7E-05	3.8E-05	8.1E-05	1.8E-05
0.8998	1.40482	1.40240	1.39997	1.39751	1.39502	0.0001	0.0001	0.0001	0.0001	0.0001
0.8531	1.40984	1.40738	1.40488	1.40245	1.39998	0.0002	0.0002	0.0001	0.0002	0.0002
0.8007	1.41541	1.41296	1.41050	1.40803	1.40553	0.0003	0.0003	0.0003	0.0003	0.0002
0.7495	1.42089	1.41842	1.41595	1.41342	1.41096	0.0004	0.0003	0.0003	0.0003	0.0003
0.7020	1.42599	1.42348	1.42096	1.41847	1.41604	0.0005	0.0004	0.0003	0.0003	0.0004
0.6518	1.43134	1.42882	1.42637	1.42379	1.42135	0.0006	0.0005	0.0005	0.0004	0.0004
0.5990	1.43693	1.43440	1.43191	1.42937	1.42693	0.0006	0.0005	0.0005	0.0004	0.0005
0.5517	1.44194	1.43941	1.43693	1.43441	1.43194	0.0006	0.0006	0.0005	0.0005	0.0005
0.5012	1.44725	1.44474	1.44227	1.43973	1.43728	0.0006	0.0006	0.0006	0.0005	0.0006
0.4499	1.45266	1.45014	1.44772	1.44513	1.44264	0.0007	0.0006	0.0006	0.0005	0.0006
0.3998	1.45790	1.45539	1.45292	1.45039	1.44787	0.0006	0.0006	0.0006	0.0005	0.0005
0.3481	1.46333	1.46081	1.45838	1.45580	1.45332	0.0006	0.0006	0.0006	0.0005	0.0006
0.2995	1.46840	1.46588	1.46345	1.46088	1.45835	0.0006	0.0005	0.0006	0.0005	0.0005
0.2516	1.47339	1.47090	1.46844	1.46589	1.46337	0.0005	0.0005	0.0005	0.0005	0.0005
0.2009	1.47870	1.47618	1.47366	1.47112	1.46860	0.0005	0.0005	0.0004	0.0004	0.0004
0.1506	1.48392	1.48139	1.47885	1.47632	1.47373	0.0004	0.0004	0.0003	0.0003	0.0003

0.1002	1.48903	1.48660	1.48406	1.48160	1.47894	0.0003	0.0003	0.0002	0.0003	0.0002
0.0516	1.49409	1.49160	1.48907	1.48654	1.48399	0.0002	0.0002	0.0001	0.0001	0.0002
Butyl acetate + Isopropylbenzene										
0.9500	1.39913	1.39675	1.39426	1.39185	1.3894	0.0001	0.0001	0.0001	0.0002	0.0002
0.8992	1.40425	1.40180	1.39931	1.39691	1.39437	0.0003	0.0003	0.0002	0.0003	0.0002
0.8497	1.40920	1.40674	1.40425	1.40180	1.39927	0.0004	0.0004	0.0004	0.0004	0.0004
0.8007	1.41410	1.41161	1.40915	1.40668	1.40412	0.0006	0.0005	0.0006	0.0005	0.0005
0.7493	1.41919	1.41670	1.41421	1.41175	1.40924	0.0007	0.0006	0.0006	0.0006	0.0007
0.6996	1.42417	1.42165	1.41914	1.41673	1.41413	0.0008	0.0008	0.0008	0.0008	0.0007
0.6500	1.42906	1.42655	1.42403	1.42154	1.41898	0.0009	0.0009	0.0009	0.0008	0.0008
0.6017	1.43384	1.43130	1.42878	1.42629	1.42372	0.0010	0.0009	0.0009	0.0009	0.0009
0.5550	1.43843	1.43587	1.43334	1.43083	1.42824	0.0010	0.0010	0.0010	0.0009	0.0009
0.4994	1.44384	1.44127	1.43873	1.43623	1.43363	0.0010	0.0010	0.0010	0.0010	0.0009
0.4514	1.44850	1.44593	1.44338	1.44086	1.43827	0.0010	0.0010	0.0010	0.0009	0.0009
0.4021	1.45329	1.45068	1.44815	1.44562	1.44301	0.0010	0.0010	0.0010	0.0009	0.0009
0.3578	1.45755	1.45496	1.45242	1.44988	1.44725	0.0010	0.0010	0.0010	0.0009	0.0009
0.3036	1.46273	1.46014	1.45758	1.45505	1.45243	0.0009	0.0009	0.0009	0.0008	0.0008
0.2496	1.46790	1.46525	1.46266	1.46014	1.45753	0.0008	0.0008	0.0008	0.0007	0.0007
0.2043	1.47219	1.46954	1.46694	1.46442	1.46178	0.0007	0.0007	0.0007	0.0006	0.0006
0.1510	1.47724	1.47459	1.47198	1.46948	1.46680	0.0006	0.0005	0.0005	0.0005	0.0005
0.0998	1.48203	1.47941	1.47677	1.47424	1.47156	0.0004	0.0004	0.0004	0.0003	0.0003
0.0521	1.48648	1.48385	1.48124	1.47872	1.47599	0.0002	0.0002	0.0002	0.0002	0.0001
Butyl acetate + Butylbenzene										
0.9493	1.39969	1.39734	1.39484	1.39244	1.39000	0.0007	0.0007	0.0007	0.0007	0.0007
0.8999	1.40499	1.40257	1.40021	1.39782	1.39529	0.0013	0.0012	0.0013	0.0014	0.0013
0.8489	1.41049	1.40806	1.40567	1.40319	1.40078	0.0019	0.0019	0.0019	0.0019	0.0019
0.8010	1.41551	1.41312	1.41060	1.40817	1.40574	0.0023	0.0023	0.0022	0.0023	0.0023
0.7517	1.42070	1.41819	1.41576	1.41331	1.41084	0.0028	0.0027	0.0027	0.0027	0.0027

Table II. *(Continued)*

	n_D (K)					δn_D (K)				
x_1	293.15	298.15	303.15	308.15	313.15	293.15	298.15	303.15	308.15	313.15
0.6998	1.42593	1.42345	1.42099	1.41852	1.41609	0.0031	0.0030	0.0029	0.0030	0.0029
0.6499	1.43099	1.42852	1.42607	1.42354	1.42107	0.0034	0.0033	0.0033	0.0032	0.0031
0.6004	1.43586	1.43342	1.43102	1.42848	1.42602	0.0035	0.0035	0.0035	0.0034	0.0033
0.5496	1.44082	1.43837	1.43591	1.43351	1.43104	0.0036	0.0036	0.0035	0.0036	0.0035
0.4993	1.44563	1.44318	1.44078	1.43832	1.43589	0.0036	0.0036	0.0035	0.0036	0.0035
0.4500	1.45031	1.44787	1.44547	1.44298	1.44055	0.0036	0.0035	0.0035	0.0035	0.0035
0.3997	1.45505	1.45258	1.45018	1.44769	1.44526	0.0035	0.0034	0.0034	0.0034	0.0034
0.3501	1.45956	1.45713	1.45470	1.45232	1.44977	0.0033	0.0032	0.0032	0.0033	0.0031
0.3023	1.46389	1.46143	1.45905	1.45651	1.45403	0.0030	0.0030	0.0030	0.0029	0.0028
0.2515	1.46838	1.46596	1.46358	1.46100	1.45858	0.0027	0.0027	0.0026	0.0026	0.0025
0.1989	1.47295	1.47054	1.46814	1.46556	1.46318	0.0022	0.0022	0.0022	0.0021	0.0020
0.1545	1.47686	1.47443	1.47201	1.46946	1.46708	0.0019	0.0018	0.0018	0.0017	0.0017
0.1016	1.48141	1.47885	1.47649	1.47387	1.47154	0.0014	0.0012	0.0012	0.0011	0.0011
0.0490	1.48578	1.48339	1.48091	1.47847	1.47595	0.0007	0.0007	0.0006	0.0007	0.0005
Butyl acetate + Isobutylbenzene										
0.9482	1.39966	1.3973	1.39479	1.39237	1.38994	0.0007	0.0008	0.0007	0.0007	0.0008
0.8995	1.40482	1.40235	1.39997	1.39757	1.39493	0.0014	0.0013	0.0014	0.0015	0.0013
0.8469	1.41021	1.40779	1.40535	1.40290	1.40036	0.0019	0.0019	0.0019	0.0020	0.0019
0.7981	1.41525	1.41278	1.41030	1.40782	1.40532	0.0024	0.0024	0.0024	0.0024	0.0024
0.7510	1.41999	1.41754	1.41506	1.41255	1.41004	0.0028	0.0028	0.0028	0.0028	0.0027
0.6954	1.42551	1.42300	1.42052	1.41799	1.41549	0.0032	0.0032	0.0032	0.0031	0.0031
0.6485	1.43012	1.42758	1.42505	1.42256	1.42003	0.0035	0.0034	0.0034	0.0034	0.0033
0.5973	1.43506	1.43254	1.43002	1.42750	1.42498	0.0037	0.0036	0.0036	0.0036	0.0035
0.5506	1.43942	1.43693	1.43443	1.43187	1.42940	0.0038	0.0037	0.0037	0.0037	0.0037

0.5056	1.44366	1.44110	1.43853	1.43602	1.43356	0.0039	0.0038	0.0037	0.0037	0.0037
0.4537	1.44838	1.44587	1.44328	1.44077	1.43826	0.0038	0.0037	0.0037	0.0037	0.0036
0.3994	1.45330	1.45072	1.44816	1.44564	1.44310	0.0037	0.0036	0.0035	0.0035	0.0035
0.3619	1.45664	1.45401	1.45147	1.44897	1.44641	0.0036	0.0034	0.0034	0.0034	0.0033
0.3027	1.46180	1.45922	1.45658	1.45405	1.45156	0.0033	0.0032	0.0031	0.0030	0.0030
0.2486	1.46644	1.46384	1.46128	1.45868	1.45618	0.0029	0.0028	0.0028	0.0027	0.0027
0.2010	1.47035	1.46781	1.46524	1.46268	1.46015	0.0024	0.0024	0.0024	0.0023	0.0023
0.1619	1.47345	1.47097	1.46850	1.46595	1.46350	0.0019	0.0019	0.0020	0.0020	0.0020
0.1042	1.47812	1.47565	1.47310	1.47066	1.46813	0.0013	0.0013	0.0013	0.0014	0.0013
0.0560	1.48206	1.47965	1.47708	1.47442	1.47211	0.0008	0.0008	0.0008	0.0007	0.0009
Butyl acetate + *t*-Butylbenzene										
0.9500	1.39982	1.39742	1.3949	1.39263	1.39007	0.0007	0.0007	0.0007	0.0009	0.0008
0.9005	1.40535	1.40288	1.40048	1.39799	1.39547	0.0014	0.0013	0.0014	0.0014	0.0013
0.8509	1.41079	1.40829	1.40593	1.40331	1.4009	0.0020	0.0019	0.0020	0.0018	0.0019
0.8013	1.41615	1.41367	1.41122	1.40871	1.40625	0.0024	0.0024	0.0024	0.0023	0.0023
0.7489	1.42175	1.41927	1.41683	1.41427	1.41174	0.0029	0.0028	0.0028	0.0028	0.0027
0.7006	1.42687	1.42436	1.42195	1.41938	1.41686	0.0032	0.0032	0.0032	0.0031	0.0030
0.6496	1.43209	1.42958	1.42717	1.42461	1.42212	0.0034	0.0034	0.0034	0.0033	0.0033
0.6070	1.43649	1.43400	1.43155	1.42904	1.42656	0.0036	0.0036	0.0036	0.0036	0.0036
0.5499	1.44227	1.43976	1.43736	1.43476	1.43237	0.0038	0.0038	0.0038	0.0037	0.0038
0.4994	1.44728	1.44477	1.44234	1.43978	1.43736	0.0038	0.0038	0.0038	0.0038	0.0038
0.4489	1.45221	1.44966	1.44727	1.44470	1.44226	0.0038	0.0037	0.0038	0.0037	0.0037
0.4061	1.45636	1.45381	1.45141	1.4488	1.44635	0.0037	0.0037	0.0037	0.0036	0.0036
0.3516	1.46145	1.45891	1.45652	1.45387	1.45137	0.0035	0.0034	0.0034	0.0034	0.0033
0.3008	1.46621	1.46360	1.46120	1.45859	1.45614	0.0032	0.0031	0.0031	0.0031	0.0031
0.2511	1.47077	1.46811	1.46570	1.46309	1.46062	0.0029	0.0028	0.0027	0.0027	0.0027
0.1995	1.47531	1.47273	1.47031	1.46770	1.46521	0.0024	0.0023	0.0023	0.0022	0.0022
0.1522	1.4795	1.47702	1.47452	1.47204	1.46953	0.0019	0.0019	0.0018	0.0019	0.0019
0.1000	1.48411	1.48154	1.47905	1.47649	1.47384	0.0014	0.0013	0.0012	0.0013	0.0010
0.0517	1.48818	1.48564	1.48328	1.48061	1.47812	0.0007	0.0007	0.0007	0.0006	0.0006

where B_{pq}'s are the fitting parameters and T is the temperature in K. The fitting parameters are presented in Table III, with the corresponding root-mean-square deviations (σ). The deviations were computed using the following equation:

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\mathrm{DAT}}} \left(z_{\mathrm{exp}} - z_{\mathrm{pred}} \right)^2}{n_{\mathrm{DAT}}} \right)^{1/2}, \tag{4}$$

where z is the value of the property and n_{DAT} is the number of experimental data. Figure 1 shows the derived properties (δn_{D}) plotted against x_1 (butyl acetate composition), as well as the curves fitted by Eqs. (2) and (3). The mixtures show different trends depending on their molecular structure and molar mass, clearly expansive or moderately expansive (tert-butyl benzene, iso-butyl benzene or butyl benzene and isopropyl benzene or mesitylene, respectively) due to increases in the dispersive interactions; all mixtures show a maximum in δn_{D} at the equimolar composition. The butyl acetate + (toluene, ethylbenzene, or *p*-xylene) mixtures show a negative δn_{D} trend, due to their lower hindrance based on their molecular structure. The temperature dependence is small for all the mixtures. Although small, the change of refractive index on mixing decreases with increasing temperature. The only published data found in the open literature for any of the systems were those of Qin et al. [10] for excess molar volumes of butyl acetate + (toluene, ethylbenzene or *p*-xylene) at 293.15 K, which were used for comparison.

3.2. Estimation of Refractive Index on Mixing

For many practical purposes it is necessary to predict the nonideality of binary or multicomponent liquid mixtures from physical parameters or by means of pure component properties using adequate models. The estimation of different thermodynamic properties of binary or multicomponent mixtures has been a subject of study in recent years, applying different empirical or semiempirical models used to optimize industrial equipment and to understand the behavior of liquids on mixing. In this work, we tested the applicability of several semiempirical models as direct tools for refractive index estimation (Lorentz–Lorenz, Dale–Gladstone, Arago–Biot, Eykman, Newton, Oster, Eyring–John, Wiener, and Heller [5] models) and an equation of state for indirect predictions based on excess molar volume data. Due to the linear dependence of the refractive index on mixing, small deviations were obtained in the first case as observed in Table IV. For the studied mixtures, very accurate results were computed by the Lorentz–Lorenz, Eykman, and Eyring–John rules, better results being obtained when nonadditivity on mixing is taken on account.

Table III. Fitting Parameters of Eq. (3) and Root-Mean-Square Deviations (σ)

Butyl acetate + Toluene			
$B_{00} = 0.047722$	$B_{01} = -0.000445$	$B_{02} = 6.85 \times 10^{-7}$	$\sigma = 8.29 \times 10^{-5}$
$B_{10} = -0.195981$	$B_{11} = 0.001354$	$B_{12} = -2.31 \times 10^{-6}$	
$B_{20} = 0.805962$	$B_{21} = -0.005389$	$B_{22} = 9.00 \times 10^{-6}$	
$B_{30} = 0.846030$	$B_{31} = -0.005682$	$B_{32} = 9.55 \times 10^{-6}$	
$B_{40} = -1.847346$	$B_{41} = 0.012462$	$B_{42} = -0.000021$	
Butyl acetate + Ethylbenzene			
$B_{00} = -0.025565$	$B_{01} = 0.000151$	$B_{02} = -3.20 \times 10^{-7}$	$\sigma = 5.72 \times 10^{-5}$
$B_{10} = 0.195726$	$B_{11} = -0.001315$	$B_{12} = 2.20 \times 10^{-6}$	
$B_{20} = 0.214884$	$B_{21} = -0.001551$	$B_{22} = 2.77 \times 10^{-6}$	
$B_{30} = -0.383939$	$B_{31} = 0.002515$	$B_{32} = -4.11 \times 10^{-6}$	
$B_{40} = -0.452057$	$B_{41} = 0.003192$	$B_{42} = -5.60 \times 10^{-6}$	
Butyl acetate + *p*-Xylene			
$B_{00} = 0.018354$	$B_{01} = -0.000141$	$B_{02} = 1.88 \times 10^{-6}$	$\sigma = 5.29 \times 10^{-5}$
$B_{10} = -0.184127$	$B_{11} = 0.001201$	$B_{12} = -1.97 \times 10^{-6}$	
$B_{20} = -0.080718$	$B_{21} = 0.000581$	$B_{22} = -1.05 \times 10^{-6}$	
$B_{30} = 0.620146$	$B_{31} = -0.004099$	$B_{32} = 6.76 \times 10^{-6}$	
$B_{40} = -0.060952$	$B_{41} = -0.000379$	$B_{42} = -5.64 \times 10^{-7}$	
Butyl acetate + Mesitylene			
$B_{00} = 0.230443$	$B_{01} = -0.001487$	$B_{02} = 2.42 \times 10^{-6}$	$\sigma = 5.06 \times 10^{-5}$
$B_{10} = 0.332604$	$B_{11} = -0.002174$	$B_{12} = 3.54 \times 10^{-6}$	
$B_{20} = 0.129034$	$B_{21} = -0.000832$	$B_{22} = 1.33 \times 10^{-6}$	
$B_{30} = -0.777710$	$B_{31} = 0.005032$	$B_{32} = -8.14 \times 10^{-6}$	
$B_{40} = -0.472483$	$B_{41} = 0.003116$	$B_{42} = -5.13 \times 10^{-6}$	
Butyl acetate + Isopropylbenzene			
$B_{00} = -0.019104$	$B_{01} = -0.00169$	$B_{02} = -3.08 \times 10^{-7}$	$\sigma = 4.02 \times 10^{-5}$
$B_{10} = -0.090941$	$B_{11} = 0.00597$	$B_{12} = -9.84 \times 10^{-7}$	
$B_{20} = 0.458943$	$B_{21} = -0.003048$	$B_{22} = 5.05 \times 10^{-6}$	
$B_{30} = 0.302283$	$B_{31} = -0.002040$	$B_{32} = 3.44 \times 10^{-6}$	
$B_{40} = -0.913491$	$B_{41} = 0.006067$	$B_{42} = -0.000010$	
Butyl acetate + Butylbenzene			
$B_{00} = 0.025945$	$B_{01} = -0.000054$	$B_{02} = 5.14 \times E^{-8}$	$\sigma = 7.60 \times 10^{-5}$
$B_{10} = 0.433726$	$B_{11} = -0.002825$	$B_{12} = 4.60 \times 10^{-6}$	
$B_{20} = 0.107126$	$B_{21} = -0.000630$	$B_{22} = 9.02 \times 10^{-7}$	
$B_{30} = -0.815239$	$B_{31} = 0.005146$	$B_{32} = -8.09 \times 10^{-6}$	
$B_{40} = -0.110274$	$B_{41} = 0.000682$	$B_{42} = -1.04 \times 10^{-6}$	
Butyl acetate + Isobutylbenzene			
$B_{00} = 0.208356$	$B_{01} = -0.001242$	$B_{02} = 1.99 \times 10^{-6}$	$\sigma = 7.60 \times 10^{-5}$
$B_{10} = -0.274847$	$B_{11} = 0.001772$	$B_{12} = -2.85 \times 10^{-6}$	
$B_{20} = -0.342145$	$B_{21} = 0.002353$	$B_{22} = -4.05 \times 10^{-6}$	
$B_{30} = 0.124930$	$B_{31} = -0.000725$	$B_{32} = 1.03 \times 10^{-6}$	
$B_{40} = -0.360054$	$B_{41} = 0.002080$	$B_{42} = -2.93 \times 10^{-6}$	

Table III. *(Continued)*

Butyl acetate + *t*-Butylbenzene			
$B_{00} = 0.056997$	$B_{01} = -0.000261$	$B_{02} = 4.04 \times 10^{-7}$	$\sigma = 8.47 \times 10^{-5}$
$B_{10} = -0.340296$	$B_{11} = 0.002254$	$B_{12} = -3.73 \times 10^{-6}$	
$B_{20} = 0.250097$	$B_{21} = -0.001519$	$B_{22} = 2.26 \times 10^{-6}$	
$B_{30} = 0.913484$	$B_{31} = -0.006100$	$B_{32} = 0.000011$	
$B_{40} = -1.076907$	$B_{41} = 0.006983$	$B_{42} = -0.000011$	

In recent years, interest in equations of state for prediction of excess molar volumes, partial excess molar and partial molar volumes, phase equilibria or excess molar enthalpies, and other properties has increased. This is due to their simplicity, relative high accuracy, low input data information requirements, and wide versatility in operating conditions. In order to apply these models to estimate the thermodynamic properties of mixtures, the use of mixing rules is necessary.

In addition to semi-empirical models, we also employed cubic equations of state from a derivation of the Heller [11] equation, to obtain an expression for refractive indices on mixing [2]. By means of such a derivation, the SRK cubic equation of state [12] has been applied to compute binary interaction parameters from experimental data for volumetric measurements [13]. We have divided this discussion into three parts: the first is a brief explanation of the rules and development of expressions, the second part presents the correlation procedure of binary values to obtain physical parameters, and the third part is the evaluation of the obtained results. The methods applied to these mixtures relate the refractive indices on mixing, based on different applications of the Heller equation, and a mixing rule for refraction [5]. It has been pointed out that the mixing rules for refractive indices are functions of the volume fractions of the mixture, since it is possible to generalize them as a function of the density of the mixture and of the pure components [6]:

$$\frac{f(n_D)}{\rho} = \sum_{i=1}^{N} \frac{w_i f(n_{D_i})}{\rho_i} \tag{5}$$

In this equation, w_i is the mass fraction, and f is a mathematical function of the refractive indices of the mixture (n_D) and the refractive index of each component (n_{Di}). Applying a previously explained substitution, it is possible to obtain an implicit expression for the refractive index as

$$\sum_{i=1}^{N}\left[(f(n_{\mathrm{D}})-f(n_{\mathrm{D}}))\left(\frac{\mathrm{x}_{ii}}{(f(n_{\mathrm{D}})\,V_i}\right)\right]=\sum_{i=1}^{N}x_i\left(\frac{-\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n}}{\left(\frac{\partial P}{\partial V_{\mathrm{m}}}\right)_{T,n}}-V_i\right), \quad (6)$$

where f has been substituted by the empirical mixing rule of Dale–Gladstone [5] and the partial quantities and molar volumes were computed from the corresponding equation of state, the former being dependent on the applied mixing rule, and the latter on the selected equation of state, which could be written in a general form as

$$P=\frac{\mathrm{R}T}{V-b}-\frac{a}{(V+\delta_1 b)(V+\delta_2 b)}, \quad (7)$$

where V is the mixture molar volume, n is the number of moles in the mixture, and δ_1 and δ_2 are a couple of parameters which have the following values: $\delta_1=1, \delta_2=0$ for SRK. Three different combining rules for binary parameters were incorporated in this model, as follows:

$$\text{Mixing rule R1:} \quad l_{ij}=m_{ij}=0, \quad (8)$$

$$\text{Mixing rule R2:} \quad l_{ij}=0, \quad (9)$$

$$\text{Mixing rule R3:} \quad k_{ij}, l_{ij}, m_{ij}\neq 0. \quad (10)$$

These parameters are assumed to be constant over the whole range of composition for each mixture. The general equations for the applied combining rules are

$$a=\sum_{i=1}^{N}\sum_{j=1}^{N}x_i x_j(1-k_{ij}-l_{ij}z_i)(a_i a_j)^{0.5}, \quad (11)$$

$$b=\sum_{i=1}^{N}\sum_{j=1}^{N}x_i x_j(1-m_{ij})\left(\frac{b_i+b_j}{2}\right), \quad (12)$$

where $z=(x_i-x_j)$. In Table V, the critical properties used in the calculations are reported [14]. In order to compute the binary interaction parameters for each mixing rule, a common fitting procedure was applied to minimize an objective function (OF);

$$OF=\frac{\sum_{i=1}^{n}(z_{\mathrm{exp}}-z_{\mathrm{pred}})^2}{z_{\mathrm{exp}}}. \quad (13)$$

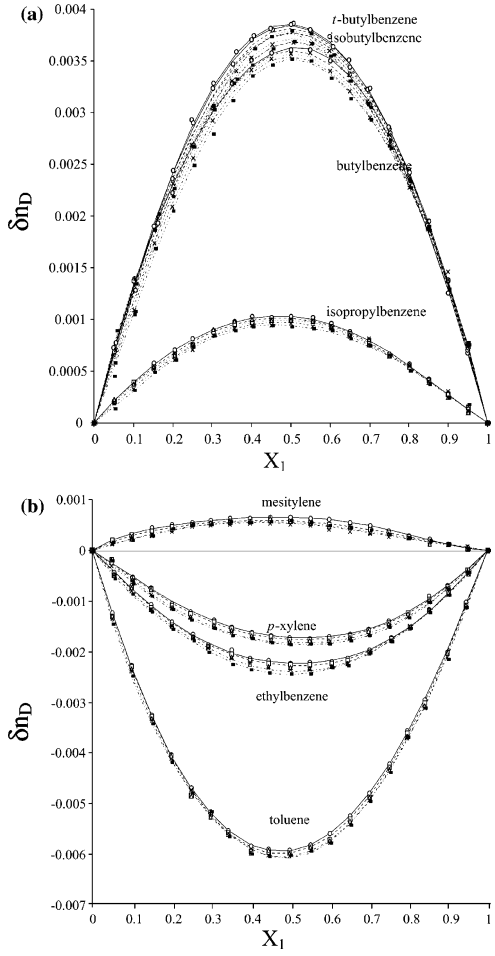

Fig. 1. Change of refractive index with mole fraction as a function of temperature: (a) butyl acetate + (isopropylbenzene, butylbenzene, isobutylbenzene, or *t*-butylbenzene) at the temperatures (□) 293.15 K, (□) 298.15 K, (X) 303.15 K, (×) 308.15 K and (-) 313.15 K and Redlich-Kister fitting curves over the same range of temperature (—) 293.15 K, (— – —) 298.15 K, (– – –) 303.15 K, (– –) 308.15 K, and (– – — – –) 313.15 K. (b) butyl acetate + (toluene, ethylbenzene, *p*-xylene, or mesitylene) at the temperatures (□) 293.15 K, (□) 298.15 K, (X) 303.15 K, (×) 308.15 K, and (-) 313.15 K and Redlich-Kister fitting curves over the same range of temperature (—) 293.15 K, (— – —) 298.15 K, (– – –) 303.15 K, (– –) 308.15 K, and (– – — – –) 313.15 K.

Table IV. Root-Mean-Square Deviations of the Experimental Refractive Indices from the Calculated Results for the Lorentz–Lorenz (L–L), Dale–Gladstone (D–G), Arago–Biot (A–B), Eykman (Ey), Newton (Nw), Oster (Os), Eyring-Jhon (E–J), Wiener (Wi), and Heller (He) models at the Temperature Range 293.15–313.15 K (nonadditivity values marked with asterisk)

	L–L	D–G	A–B	Ey	Nw	Os	E–J	Wi	He
Butyl acetate + Toluene									
293.15 K	0.00040	0.00032	0.00032	0.00011	0.00100	0.00072	0.00004	0.00546	0.00052
	*0.00004	*0.00065	*0.00139	*0.00046	*0.00128	*0.00103	*0.00213	*0.00550	*0.00050
298.15 K	0.00032	0.00039	0.00039	0.00018	0.00106	0.00078	0.00007	0.00549	0.00048
	*0.00009	*0.00073	*0.00150	*0.00054	*0.00135	*0.00110	*0.00227	*0.00553	*0.00046
303.15 K	0.00029	0.00042	0.00042	0.00021	0.00109	0.00081	0.00010	0.00548	0.00047
	*0.00012	*0.00076	*0.00153	*0.00057	*0.00138	*0.00113	*0.00232	*0.00552	*0.00044
308.15 K	0.00026	0.00045	0.00045	0.00024	0.00111	0.00083	0.00013	0.00547	0.00045
	*0.00017	*0.00079	*0.00159	*0.00060	*0.00141	*0.00116	*0.00240	*0.00551	*0.00043
313.15 K	0.00023	0.00048	0.00048	0.00028	0.00114	0.00086	0.00016	0.00548	0.00041
	*0.00021	*0.00083	*0.00164	*0.00064	*0.00144	*0.00119	*0.00248	*0.00553	*0.00039
Butyl acetate + Ethylbenzene									
293.15 K	0.00043	0.00029	0.00029	0.00011	0.0095	0.00067	0.00010	0.00551	0.00060
	*0.00032	*0.00037	*0.0057	*0.00018	*0.00103	*0.0076	*0.00053	*0.00553	*0.00059
298.15 K	0.00039	0.00031	0.00031	0.00012	0.00098	0.00070	0.00007	0.00553	0.00056
	*0.00029	*0.00040	*0.00060	*0.00020	*0.00105	*0.00078	*0.00057	*0.00554	*0.00055
303.15 K	0.00037	0.00034	0.00034	0.00014	0.00100	0.00072	0.00007	0.00552	0.00055
	*0.00026	*0.00043	*0.00063	*0.00023	*0.00107	*0.00080	*0.00060	*0.00553	*0.00054
308.15 K	0.00036	0.00033	0.00033	0.00013	0.00099	0.00071	0.00006	0.00551	0.00054
	*0.00025	*0.00042	*0.00063	*0.00022	*0.00107	*0.00080	*0.00061	*0.00552	*0.00053
313.15 K	0.00031	0.00037	0.00037	0.00017	0.00103	0.00075	0.00006	0.00554	0.00051
	*0.00020	*0.00047	*0.00069	*0.00027	*0.00111	*0.00084	*0.00068	*0.00555	*0.00050
Butyl acetate + *p*-Xylene									
293.15 K	0.00068	0.00010	0.00010	0.00020	0.00071	0.00043	0.00032	0.00530	0.00078
	*0.00030	*0.00035	*0.00107	*0.00017	*0.00097	*0.00073	*0.00179	*0.00534	*0.00074
298.15 K	0.00066	0.00011	0.00011	0.00019	0.00072	0.00045	0.00030	0.00528	0.00076

Table IV. *(Continued)*

	L–L	D–G	A–B	Ey	Nw	Os	E–J	Wi	He
	*0.00029	*0.00036	*0.00106	*0.00018	*0.00098	*0.00073	*0.00175	*0.00532	*0.00073
303.15 K	0.00063	0.00012	0.00012	0.00017	0.00074	0.00046	0.00028	0.00527	0.00074
	*0.00028	*0.00037	*0.00105	*0.00019	*0.00099	*0.00074	*0.00171	*0.00531	*0.00071
308.15 K	0.00060	0.00013	0.00013	0.00015	0.00076	0.00048	0.00026	0.00530	0.00071
	*0.00026	*0.00039	*0.00106	*0.00020	*0.00101	*0.00075	*0.00170	*0.00534	*0.00068
313.15 K	0.00140	0.00109	0.00109	0.00115	0.00115	0.00108	0.00120	0.00523	0.00139
	*0.00132	*0.00115	*0.00150	*0.00117	*0.00131	*0.00122	*0.00201	*0.00527	*0.00137
Butyl acetate + Mesitylene									
293.15 K	0.00021	0.00056	0.00056	0.00034	0.00127	0.00098	0.00021	0.00632	0.00055
	*0.00058	*0.00022	*0.00056	*0.00004	*0.00098	*0.00066	*0.00202	*0.00629	*0.00056
298.15 K	0.00018	0.00059	0.00059	0.00037	0.00130	0.00101	0.00024	0.00634	0.00055
	*0.00055	*0.00024	*0.00057	*0.00002	*0.00101	*0.00068	*0.00206	*0.00631	*0.00056
303.15 K	0.00019	0.00058	0.00058	0.00036	0.00130	0.00100	0.00023	0.00635	0.00054
	*0.00057	*0.00023	*0.00062	*0.00005	*0.00100	*0.00067	*0.00214	*0.00632	*0.00055
308.15 K	0.00016	0.00060	0.00060	0.00038	0.00132	0.00102	0.00025	0.00637	0.00053
	*0.00054	*0.00025	*0.00060	*0.00004	*0.00102	*0.0069	*0.00212	*0.00634	*0.00054
313.15 K	0.00022	0.00054	0.00054	0.00032	0.00125	0.00092	0.00019	0.00632	0.00054
	*0.00061	*0.00019	*0.00066	*0.00008	*0.00095	*0.00062	*0.00220	*0.00628	*0.00055
Butyl acetate + Isopropylbenzene									
293.15 K	0.00038	0.00028	0.00028	0.00010	0.00089	0.00063	0.00007	0.00523	0.00054
	*0.00034	*0.00030	*0.00036	*0.00012	*0.00091	*0.00066	*0.00015	*0.00524	*0.00054
298.15 K	0.00036	0.00029	0.00029	0.00010	0.00089	0.00064	0.00006	0.00523	0.00053
	*0.00032	*0.00032	*0.00039	*0.00013	*0.00092	*0.00067	*0.00019	*0.00523	*0.00053
303.15 K	0.00038	0.00027	0.00027	0.00009	0.00087	0.00062	0.00008	0.00519	0.00054
	*0.00033	*0.00030	*0.00039	*0.00012	*0.00091	*0.00065	*0.00021	*0.00520	*0.00054
308.15 K	0.00037	0.00027	0.00027	0.00008	0.00088	0.00062	0.00006	0.00522	0.00052
	*0.00031	*0.00031	*0.00041	*0.00013	*0.00092	*0.00066	*0.00026	*0.00522	*0.00052
313.15 K	0.00037	0.00027	0.00027	0.00009	0.00087	0.00062	0.00007	0.00520	0.00052
	*0.00031	*0.00032	*0.00044	*0.00013	*0.00092	*0.00066	*0.00030	*0.00521	*0.00052
Butyl acetate + Butylbenzene									
293.15 K	0.00033	0.00031	0.00031	0.00013	0.00089	0.00065	0.00007	0.00524	0.00055

	*0.00044	*0.00021	*0.00008	*0.00007	*0.00081	*0.00055	*0.00067	*0.00522	*0.00055
298.15 K	0.00030	0.00033	0.00033	0.00015	0.00092	0.00067	0.00007	0.00528	0.00052
	*0.00041	*0.00023	*0.00005	*0.00007	*0.00084	*0.00058	*0.00062	*0.00527	*0.00053
303.15 K	0.00029	0.00034	0.00034	0.00016	0.00093	0.00068	0.00007	0.00532	0.00050
	*0.00040	*0.00024	*0.00005	*0.00007	*0.00085	*0.00059	*0.00060	*0.00531	*0.00050
308.15 K	0.00031	0.00032	0.00032	0.00014	0.00091	0.00066	0.00007	0.00531	0.00050
	*0.00042	*0.00023	*0.00007	*0.00007	*0.00083	*0.00057	*0.00061	*0.00530	*0.00050
313.15 K	0.00027	0.00036	0.00036	0.00017	0.00095	0.00070	0.00008	0.00539	0.00045
	*0.00037	*0.00027	*0.00010	*0.00010	*0.00088	*0.00061	*0.00055	*0.00538	*0.00045
Butyl acetate + Isobutylbenzene									
293.15 K	0.00040	0.00022	0.00022	0.00011	0.00076	0.00053	0.00014	0.00481	0.00055
	*0.00039	*0.00022	*0.00022	*0.00009	*0.00076	*0.00053	*0.00020	*0.00482	*0.00055
298.15 K	0.00034	0.00026	0.00026	0.00011	0.00081	0.00057	0.00009	0.00485	0.00052
	*0.00036	*0.00024	*0.00020	*0.00008	*0.00079	*0.00055	*0.00022	*0.00485	*0.00052
303.15 K	0.00034	0.00025	0.00025	0.00010	0.00080	0.00057	0.00008	0.00484	0.00053
	*0.00036	*0.00023	*0.00019	*0.00007	*0.00078	*0.00055	*0.00021	*0.00484	*0.00052
308.15 K	0.00034	0.00025	0.00025	0.00009	0.00080	0.00056	0.00007	0.00485	0.00051
	*0.00035	*0.00023	*0.00020	*0.00007	*0.00078	*0.00055	*0.00019	*0.00485	*0.00051
313.15 K	0.00033	0.00026	0.00026	0.00011	0.00081	0.00057	0.00009	0.00484	0.00053
	*0.00033	*0.00025	*0.00024	*0.00010	*0.00081	*0.00057	*0.00014	*0.00485	*0.00053
Butyl acetate + *t*-Butylbenzene									
293.15 K	0.00055	0.00014	0.00014	0.00011	0.00075	0.00049	0.00022	0.00538	0.00069
	*0.00042	*0.00024	*0.00048	*0.00008	*0.00084	*0.00059	*0.00052	*0.00540	*0.00068
298.15 K	0.00052	0.00016	0.00016	0.00010	0.00077	0.00051	0.00019	0.00540	0.00067
	*0.00039	*0.00026	*0.00052	*0.00009	*0.00087	*0.00062	*0.00058	*0.00541	*0.00066
303.15 K	0.00053	0.00015	0.00015	0.00010	0.00076	0.00050	0.00020	0.00542	0.00066
	*0.00039	*0.00026	*0.00052	*0.00009	*0.00086	*0.00061	*0.00059	*0.00543	*0.00065
308.15 K	0.00052	0.00016	0.00016	0.00011	0.00077	0.00050	0.00020	0.00541	0.00067
	*0.00038	*0.00027	*0.00054	*0.00010	*0.00087	*0.00062	*0.00062	*0.00542	*0.00066
313.15 K	0.00052	0.00018	0.00018	0.00012	0.00078	0.00052	0.00020	0.00545	0.00064
	*0.00038	*0.00029	*0.00056	*0.00013	*0.00088	*0.00063	*0.00065	*0.00547	*0.00063

Table V. Literature Values of Critical Properties of Pure Components of Binary Mixtures[a]

Compound	P_c(bar)	T_c (K)	ω-acentric factor
Butyl acetate	30.90	579	0.407
Toluene	41.08	591.75	0.264
Ethylbenzene	36.09	617.15	0.304
p-Xylene	35.11	616.20	0.322
Mesitylene	31.27	637.30	0.399
Isopropylbenzene	32.09	631.00	0.326
Butylbenzene	28.90	660.50	0.393
Isobutylbenzene	30.50	650.00	0.383
t-Butylbenzene	29.60	660.00	0.265

[a] Poling et al. [14].

The Marquard routine was applied in combination with a Newton–Raphson method to fit the interaction parameters [13]. Good results were obtained for almost all the binary mixtures, with deviations close to the uncertainty of the measurements. The largest deviations were obtained for the mixtures where mesitylene was a component. No systematic trend with temperature was observed for the deviations. Somewhat better results were obtained with the R3 mixing rule at high temperatures, but all of them showed similar behavior, which can be observed in Table III.

4. DISCUSSION AND CONCLUSIONS

As discussed above, this paper is devoted to the study of the thermodynamic properties of chemicals containing the ester group in an aromatic structure [1–4] in order to analyze the steric hindrance effect on thermophysical properties. To this aim, we have presented experimental data for the refractive index on mixing for the following binaries: butyl acetate + (toluene, ethylbenzene, *p*-xylene, mesitylene, isopropylbenzene, butylbenzene, isobutylbenzene, and *t*-butylbenzene). These results were used to compute corresponding derived properties. These mixtures show an increasing expansion tendency for the highest molar mass compounds, with the steric hindrance of the aromatic chemicals playing an important role.

In general, the expansion trend on mixing depends mainly on two effects: (a) intermolecular forces in mixtures and (b) molecular packing as a consequence of differences in the size and shape of the molecules as is the case here. If the interactions between molecules of two mixed components are weaker than in the pure components, the excess volume will be positive and the refractive index lower. This usually occurs when one of

the components is polar and the other is nonpolar, or weakly polar. Butyl acetate is weakly polar, and the aromatic hydrocarbons are nearly nonpolar. When the pure compounds are mixed, the nonpolar hydrocarbon molecules are interspersed among the acetate molecules, resulting in decreased interactions among the dipoles of the acetate group. This effect is clearly shown in terms of the derived properties. The experimental results agree with this explanation since almost all the studied mixtures show excess volumes that are either always positive or both positive and negative [4]. This fact shows that the change of intermolecular forces is larger than the packing caused by geometrical effects. This causes differences in the change of refractive index from some hydrocarbons to others. If we compare the maxima of the derived magnitude at the equimolar composition, the following observations can be made: negative values correspond to mixtures of linear hydrocarbons with small substituents or separated ones (toluene, ethylbenzene, and *p*-xylene), intermediate values correspond to mixtures with nonlinear hydrocarbons (isopropylbenzene and mesitylene), and the highest values correspond to butylbenzene, isobutylbenzene, and *t*-butylbenzene. 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 interactions among acetates and aromatic compounds. The aromatic hydrocarbon molecules will have increasing difficulties in establishing interactions as they increase in size. If the molecules are flat or have a few bulky substituents (toluene, *p*-xylene, and ethylbenzene), some interactions can persist and the expansion character becomes negative (as for a toluene mixture). If the hydrocarbon molecules have bulky substituents placed in a different plane than the one for the ring, the interactions among acetate molecules are disabled and the expansion trend will be higher than in the previous case. The presence of three methylene groups in the meta position hinders the approach of the acetate group towards the ring, and the steric volume is higher and the refraction decreases. A similar trend with the size of molecules has been shown in other nonpolar + polar compounds, such as methyl, ethyl, propyl, or vinyl acetate with aromatic compounds [1–4].

As a conclusion, it is important to point out that an increase in the chain length in the solvent acetate produces a higher nonideality on mixing; then a higher solvent power could be observed for these kinds of mixtures for nonpolar substances. The obtained results show the importance of the steric hindrance to establish dispersive interactions on mixing and the progressive screening of the polar effect of the ester molecular group, when the molar mass of the solvent is increased. Due to the strong dependence of an adequate industrial design on computation and simulation,

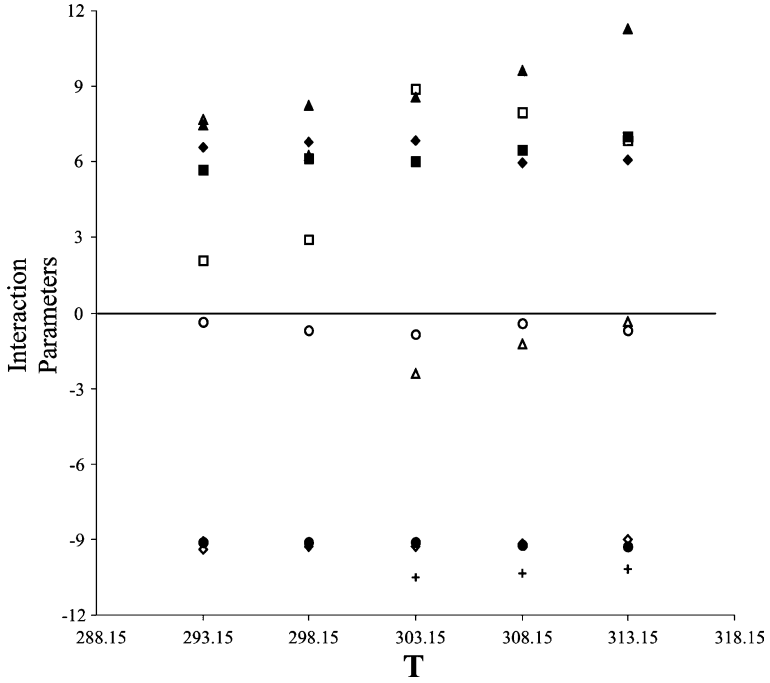

Fig. 2. Influence of temperature on mixing rule R3 parameters corresponding to the SRK equation of state ($k \times 10, l \times 10^3$, $m \times 10^3$) for the binary mixtures of butyl acetate + toluene ((◇) k, (■) l, (▲) m), + ethylbenzene ((●) K, (□) l, (♦) m), and + *p*-xylene ((+) k, (□) l, (△) m).

an estimation of physical properties was made by different theoretical procedures. Combining rules applied to cubic equations of state showed good results to correlate experimental values of refraction from parameters obtained by excess molar volumes. In Fig. 2, the evolution of the SRK–R3 interaction parameters for the butyl acetate + (toluene, ethylbenzene or *p*-xylene) mixture is shown as a function of temperature and shows a moderate dependence (slight variation of slope with temperature), and the values of the interaction parameters are dependent on the molecular structure, but mainly on the molar mass. The obtained results point out two facts: first, the importance of k_{ij} is greater than the influence of m_{ij}. The negative trend of k_{ij} suggests a compression factor of larger magnitude than expected from simple additivity. Second, the m_{ij} parameter decreases when the molar mass increases as the solvent is added to butyl acetate. This fact is in accordance with the obtained experimental data, due to the globular structure adopted by the aromatic solvents by branched chains on

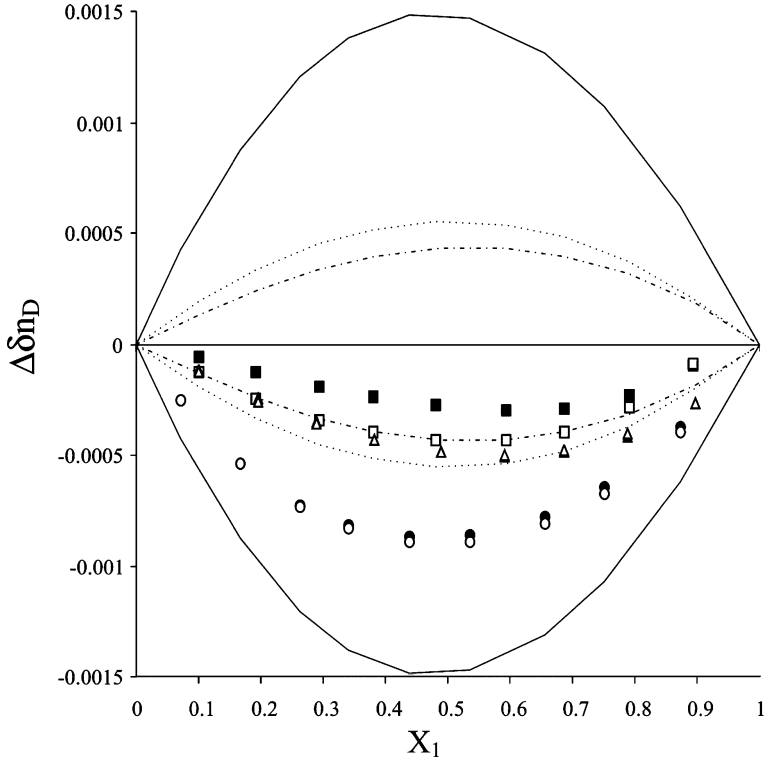

Fig. 3. Deviations of change of refractive index on mixing of literature values [10] (full symbols) and of our estimated values from excess molar volumes of these mixtures [4] (empty symbols) by means of Eqs. (6), (11), and (12), from experimental results for the systems butyl acetate + ((●, □) toluene, (■, □) ethylbenzene, and (▲, △) *p*-xylene) at 293.15 K. Deviation curves of 25% are shown for each mixture ((—) toluene, (– – –) ethylbenzene, and (– — –) *p*-xylene).

the ring. Extrapolating this tendency, m_{ij} becomes zero for ideal spherical molecules at each temperature.

As an example of applications of the EOS parameters obtained in this section, in Fig. 3 a comparison is shown between the experimental data of Qin et al. [1992] and those derived from our experimental refractive index data; a deviation of 25% is computed for the butyl acetate + (toluene, ethylbenzene, *p*-xylene) mixtures at 293.15 K.

The comparison was made in terms of the change of refractive index on mixing. It is interesting to point out that the accuracy of predictions of changes of refractive index on mixing is higher by this procedure than

Table VI. Root-Mean-Square Deviations of the Experimental Data Presented in this Work with Respect to the Estimated Values Obtained by Application of the Equation of State and the Combining Rule R3

	$\sigma/(\delta n_D) \times 10^4$				
Mixture	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Butyl acetate + Toluene	6.47	7.25	7.56	7.91	8.28
Butyl acetate + Ethylbenzene	3.73	4.02	4.26	4.24	4.70
Butyl acetate + *p*-Xylene	3.54	3.60	3.70	3.86	3.86
Butyl acetate + Mesitylene	2.22	2.46	2.29	2.51	1.88
Butyl acetate + Isopropylbenzene	3.01	3.17	3.02	3.11	3.17
Butyl acetate + Butylbenzene	2.08	2.35	2.46	2.29	2.69
Butyl acetate + Isobutylbenzene	2.14	2.35	2.28	2.31	2.53
Butyl acetate + *t*-Butyllbenzene	2.36	2.62	2.56	2.65	2.86

by use of the experimental literature data (Qin et al., 1992) by means of Eqs. (6), (11), and (12) as can be observed in Fig. 3 and Table IV.

ACKNOWLEDGMENTS

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

REFERENCES

1. J. M. Resa, C. González, J. Lanz, and J. A. Mtz. de Ilarduya, *J. Therm. Anal. Calorim.* **52**:895 (1998).
2. J. M. Resa, M. Iglesias, C. González, J. Lanz, and J. A. Mtz de Ilarduya, *J. Chem. Thermodyn.* **33**:723 (2001).
3. J. M. Resa, C. González, S. Ortiz de Landaluce, and J. Lanz, *J. Chem. Thermodyn.* **34**:995 (2002).
4. J. M. Resa, C. Gonzalez, S. Prieto, E. Díez, and M. Iglesias, *Korean J. Chem. Eng.* **21**:1015 (2004).
5. M. Iglesias, B. Orge, and J. Tojo, *Fluid Phase Equilib.* **126**:203 (1996).
6. *TRC Thermodynamic Tables*, Thermodynamic Research Center, Texas A&M University, College Station, Texas (1994).
7. O. Redlich and A. T. Kister, *Ind. Eng. Chem.* **40**:345 (1948).
8. D. W. Marquard, *J. Soc. Indust. Appl. Math.* **11**:431 (1963).
9. P. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
10. A. Qin, D. E. Hoffman, and P. Munk, *J. Chem. Eng. Data.* **37**:66 (1992).
11. W. Heller, *J. Phys. Chem.* **69**:1123 (1965).
12. G. Soave, *Chem Eng. Sci.* **27**:1197 (1972).

13. J. M. Resa, C. Gonzalez, R. G. Concha, and M. Iglesias, *Phys. Chem. Liq.* **42**:493 (2004).
14. B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 2001).