

Experimental VLE Data of Binary Systems of Ester + Alcohol at 0.6 MPa. Verification using new Association Parameters for the Point-to-Point Test

Pedro Susial Badajoz*; **Diego García-Vera**; **Isabel Montesdeoca**; **Dunia E. Santiago**; **Anibal Marrero-Pérez**; **Patricia Herrera-Vega**; **Gwendolyn Pérez-Riverol**

Escuela de Ingenierías Industriales y Civiles. Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Canary Islands, Spain.

Datos experimentales de VLE de sistemas binarios de éster + alcohol a 0,6 MPa. Verificación usando nuevos parámetros de asociación para la prueba punto a punto

Dades experimentals de VLE de sistemes binaris d'èster + alcohol a 0,6 MPa. Verificació mitjançant nous paràmetres d'associació per a la prova punt a punt

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SUMMARY

Experimental data of vapor–liquid equilibria (VLE) are reported for the following binary systems: butyl acetate+ethanol, butyl acetate+1–propanol and butyl acetate+1–butanol at 0.6 MPa. No azeotrope was found in the butyl acetate+1–butanol system at 0.6 MPa. The thermodynamic consistency of the obtained data was analyzed using some equations of state (EOS) in the point–to–point test. The phase behavior was satisfactorily modelled using the Peng–Robinson EOS. The new association parameter of the Hayden–O'Connell method was determined from 144 pure substances and the influence of the second virial coefficient calculations in the point–to–point test was evaluated.

Keywords: VLE isobaric data, Butyl acetate, Alcohol, Association parameter

RESUMEN

Se informan datos experimentales de equilibrio vapor–líquido (VLE) para los siguientes sistemas binarios: acetato de butilo+etanol, acetato de butilo+1-propanol y acetato de butilo+1-butanol a 0,6 MPa. No se encontró azeótropo en el sistema acetato de butilo + 1-butanol a 0,6 MPa. La consistencia termodinámica de los datos obtenidos se analizó utilizando algunas ecuaciones de estado (EOS) en la prueba punto a punto. El comportamiento de la fase se modeló satisfactoriamente utilizando el EOS de Peng-Robinson. Se determinó el

nuevo parámetro de asociación del método Hayden-O'Connell a partir de 144 sustancias puras y se evaluó la influencia de los cálculos del segundo coeficiente virial en la prueba punto a punto

Palabras clave: Datos isobáricos de VLE, acetato de butilo, alcohol, parámetro de asociación

RESUM:

S'informen dades experimentals d'equilibris vapor–líquid (VLE) per als sistemes binaris següents: acetat de butil+etanol, acetat de butil+1-propanol i acetat de butil+1-butanol a 0,6 MPa. No es va trobar cap azeòtrop al sistema d'acetat de butil + 1-butanol a 0,6 MPa. La consistència termodinàmica de les dades obtingudes es va analitzar mitjançant algunes equacions d'estat (EOS) en la prova punt a punt. El comportament de la fase es va modelar satisfactòriament mitjançant l'EOS Peng-Robinson. El nou paràmetre d'associació del mètode Hayden-O'Connell es va determinar a partir de 144 substàncies pures i es va avaluar la influència dels càlculs del segon coeficient virial en la prova punt a punt.

Paraules clau: Dades isobàriques VLE, acetat de butil, alcohol, paràmetre d'associació

*Corresponding author: pedro.susial@ulpgc.es

INTRODUCTION

Alcohols, such ethanol, 1-propanol or 1-butanol and esters such butyl acetate, are solvents used in several industries. Alcohols are frequently used as oxygenated additives to improve the octane number in reformulated gasoline^{1,2}. Esters are commonly employed as biofuel additives^{3,4}. Therefore, as a consequence of the industrial importance of these substances, the VLE of some ester/alcohol binary systems have been studied in this paper.

On the other side, almost 50 years have passed since the original association parameters from the Hayden-O'Connell⁵ procedure was first published, reason why it seems appropriate to redetermine these parameters to be applied in the point-to-point consistency test and to analyze the second virial coefficients effect in verifying VLE data.

The T-x₁-y₁ VLE data were obtained by using a dynamic recirculating ebulliometer at 0.6 MPa for the binary mixtures of butyl acetate + ethanol, or 1-propanol, or 1-butanol. These systems have been studied isothermally and isobarically by different authors⁶⁻¹⁴.

The butyl acetate + ethanol (BAE) system has been studied isothermally⁶⁻⁸ and isobarically at 101.3 kPa by Beregovykh et al.⁷, Shono et al.⁷, Gonzalez and Ortega⁸ and Polyakova et al.⁸ The butyl acetate + 1-propanol (BAP) system has been reported isobarically at 101.3 kPa by Beregovykh et al.⁷, Gonzalez and Ortega⁹ and also by Ortega et al.⁹ The butyl acetate + 1-butanol (BAB) system has been informed isothermally¹⁰ and isobarically at 6.67, 19.99, 39.99, 79.99 and 101.3 kPa by Figurski and Von Weber¹⁰, isobarically at 6.67, 22.06 and 101.3 kPa by Sheinker and Peresleni¹¹, isobarically at 13.33, 26.66, 39.99, 53.33, 66.66, 79.99, 93.33 and 101.3 kPa by Shim et al.¹⁰, also isobarically at 101.3 kPa by Belousov et al.¹⁰, Brunjes and Furnas¹¹, Beregovykh et al.¹², Gonzalez and Ortega¹⁰, Lladosa et al.¹⁰, Mato and Cepeda¹³ and Ortega et al.¹⁰ In addition, these systems (BAE, BAP and BAB) have been recently studied at 0.15 MPa by Susial et al.¹⁴

VLE data of BAE, BAP and BAB at 0.6 MPa have been verified considering the γ - ϕ approach. The point-to-point test of Van Ness¹⁵ was applied using the Fredenslund et al.¹⁶ routines. The Fredenslund et al.¹⁶ subroutine SVIR was modified and the Tsonopoulos¹⁷ procedure was also used for the second virial coefficient calculations. The molar volume of the pure liquid compound was calculated by the Yen-Woods¹⁸ equation. The global results of mean deviation of y₁ was the criterion applied in the Fredenslund et al.¹⁶ subroutine by using both procedures at the point-to-point test. Next, the experimental data were correlated by employing the ϕ - ϕ approximation. The equation of state (EOS) of Peng-Robinson-Stryjek-Vera^{19,20} (PRSV) with quadratic mixing rules was applied. In addition, the PRSV^{19,20} EOS was also used in the Fredenslund et al.¹⁶ point-to-point test to check the thermodynamic consistency of the analyzed data.

MATERIALS AND EXPERIMENTAL METHODS

The pure substances were used in this work as received from the manufacturer. The properties of the chemicals employed in this paper did not differ from those previously published by us¹⁴. The normal boiling point (T_{bp}), density (ρ_{li}) and refractive index (n_D) were determined at 298.15 K and atmospheric pressure for pure substances.

For boiling point, density and refractive index determinations of pure components and mixtures, a stainless steel ebulliometer, a Mettler Toledo DM40 vibrating tube density meter and an Atago 7000 Alpha digital refractometer were used.

In the experimental determination of VLE data, an ebulliometer included in an experimental installation, described in previous studies^{21,22}, was employed. The ebulliometer is made of stainless steel, and allows to work with dynamic recirculation of both liquid and vapor phases by means of the Cottrell-pump effect. This equipment operates with fluids circulating in co-current flow. The VLE data are obtained after a mass transfer process is developed by the contact between the phases.

RESULTS AND DISCUSSION

The experimental data of the VLE obtained in this work at 0.6 MPa are presented in Table 1. Figure 1 shows the disposition of the isobaric data from this work when compared with data obtained by us at 0.15 MPa¹⁴. In all cases, the correlation curves presented in Fig. 1, were obtained as previously indicated^{21,23} by using the fitting functions together with the results of data correlations.

The adequate development of data was verified by considering, on the one hand, the increase in the alcohol chain and, on the other, different pressures. Thus, the azeotropic point in the BAB system, observed previously¹⁴, disappears at 0.6 MPa.

The activity coefficients of the liquid phase (γ_i) were calculated for each system using the following equation:

$$\gamma_i = \frac{y_i \phi_i P}{x_i \phi_i^o p_i^o} \exp \left[\frac{(p_i^o - p) v_i^L}{RT} \right] \quad (1)$$

The virial equation of state truncated at the second term was employed in Eq. 1 for fugacity coefficient (ϕ_i) calculations according to Eq.2:

$$\phi_i = \phi_i^o \exp \left[\frac{p}{RT} \left(2 \sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij} \right) - \frac{p_i^o B_{ii}}{RT} \right] \quad (2)$$

The Hayden and O'Connell⁵ procedure and Yen-Woods¹⁷ equation were employed, respectively, for the determination of second virial coefficients (B_{ii}, B_{ij}) and liquid molar volumes of pure compounds (v_i^L). Results, including the excess Gibbs energy function (G^E/RT) are presented in Table 1.

Table 1. Experimental VLE data at 0.6 MPa and calculated values^a

T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT
Butyl Acetate (1) + Ethanol (2)						Butyl Acetate (1) + 1-Propanol (2)						Butyl Acetate (1) + 1-Butanol (2)					
405.3	0.000	0.000		1.00		427.0	0.000	0.000		1.00		452.2	0.000	0.000		1.00	
406.3	0.037	0.016	2.20	1.00	0.033	428.9	0.049	0.029	1.61	0.98	0.004	452.3	0.024	0.022	1.44	0.99	0.001
406.9	0.053	0.023	2.17	1.00	0.038	429.6	0.084	0.045	1.43	0.98	0.014	452.7	0.053	0.045	1.32	0.99	0.004
407.7	0.078	0.034	2.13	0.99	0.050	430.4	0.106	0.054	1.34	0.98	0.010	453.0	0.078	0.064	1.27	0.99	0.008
408.5	0.098	0.042	2.05	0.98	0.054	433.6	0.203	0.102	1.22	0.96	0.007	453.6	0.122	0.098	1.23	0.99	0.012
409.3	0.153	0.056	1.70	1.01	0.089	435.7	0.278	0.143	1.18	0.96	0.017	453.9	0.143	0.115	1.22	0.98	0.015
410.8	0.201	0.071	1.57	1.01	0.100	437.4	0.334	0.172	1.14	0.96	0.018	454.5	0.190	0.151	1.19	0.98	0.020
412.7	0.252	0.089	1.49	1.01	0.106	438.1	0.361	0.190	1.14	0.97	0.026	455.0	0.227	0.177	1.15	0.99	0.024
415.5	0.331	0.119	1.40	1.01	0.120	439.1	0.393	0.210	1.13	0.97	0.029	456.2	0.309	0.237	1.10	1.00	0.029
418.1	0.397	0.146	1.33	1.02	0.125	439.5	0.402	0.216	1.13	0.97	0.028	456.6	0.336	0.253	1.08	1.01	0.029
419.0	0.423	0.161	1.35	1.02	0.138	440.3	0.429	0.232	1.11	0.97	0.030	457.6	0.393	0.298	1.06	1.01	0.030
421.8	0.485	0.188	1.27	1.03	0.133	442.0	0.480	0.268	1.10	0.98	0.036	458.3	0.435	0.332	1.05	1.02	0.032
423.9	0.532	0.209	1.22	1.05	0.128	443.3	0.515	0.291	1.08	0.99	0.034	458.6	0.458	0.348	1.04	1.03	0.033
424.5	0.552	0.218	1.21	1.07	0.133	444.9	0.556	0.320	1.06	0.99	0.031	459.6	0.502	0.390	1.04	1.02	0.032
425.8	0.585	0.232	1.17	1.10	0.131	446.4	0.597	0.352	1.05	1.01	0.034	460.8	0.561	0.444	1.03	1.03	0.032
426.7	0.603	0.241	1.15	1.11	0.127	448.2	0.645	0.393	1.04	1.03	0.038	462.0	0.615	0.497	1.03	1.04	0.031
428.3	0.633	0.261	1.14	1.12	0.126	449.7	0.673	0.418	1.03	1.04	0.031	462.6	0.641	0.524	1.03	1.04	0.031
429.7	0.665	0.277	1.11	1.16	0.122	452.9	0.737	0.487	1.02	1.06	0.029	463.1	0.658	0.545	1.03	1.03	0.030
431.4	0.697	0.299	1.10	1.20	0.120	455.8	0.780	0.541	1.01	1.06	0.018	464.6	0.718	0.613	1.03	1.03	0.030
432.5	0.716	0.312	1.08	1.22	0.115	458.5	0.823	0.605	1.01	1.07	0.018	465.7	0.760	0.663	1.03	1.03	0.029
433.1	0.727	0.318	1.07	1.24	0.111	460.7	0.861	0.660	1.00	1.12	0.018	466.4	0.780	0.687	1.03	1.02	0.025
433.8	0.738	0.327	1.07	1.26	0.109	462.8	0.889	0.712	1.00	1.14	0.017	467.1	0.812	0.727	1.03	1.03	0.028
434.8	0.753	0.335	1.05	1.29	0.097	466.4	0.925	0.800	1.01	1.09	0.013	468.2	0.851	0.777	1.03	1.04	0.027
435.4	0.759	0.340	1.04	1.29	0.090	468.0	0.942	0.838	1.00	1.10	0.009	469.5	0.892	0.834	1.02	1.04	0.025
436.5	0.777	0.355	1.03	1.33	0.088	470.1	0.961	0.891	1.00	1.06	0.006	470.7	0.926	0.882	1.02	1.05	0.021
438.4	0.803	0.383	1.03	1.38	0.086	471.4	0.975	0.927	1.00	1.08	0.005	471.8	0.954	0.925	1.02	1.05	0.017
440.2	0.822	0.404	1.01	1.42	0.074	472.6	0.986	0.961	1.01	1.00	0.005	473.8	0.988	0.980	1.00	1.03	0.000
443.9	0.856	0.459	1.02	1.47	0.068	474.6	1.000	1.000	1.00			474.6	1.000	1.000	1.00		
448.5	0.892	0.534	1.02	1.52	0.063												
452.6	0.915	0.591	1.00	1.56	0.042												
456.9	0.938	0.663	1.00	1.61	0.032												
462.0	0.959	0.750	1.00	1.64	0.017												
474.6	1.000	1.000	1.00														

^a Expanded uncertainties U(k=2) are: U(T)=0.4 K, U(p)=0.003 MPa, U(x_1)=U(y_1)=0.004. T, x_1 , y_1 , γ_1 and γ_2 represent: temperature, liquid phase ester mole fraction, vapor phase ester mole fraction, liquid phase activity coefficient of ester and liquid phase activity coefficient of alcohol.

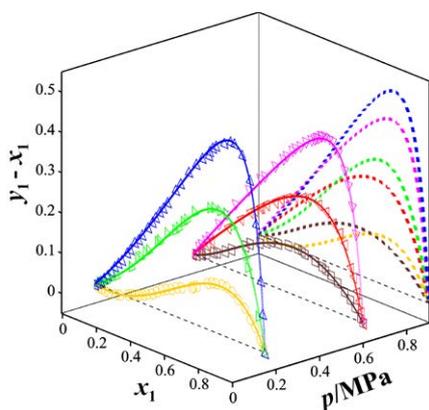


Fig. 1 Plot of ($y_1 - x_1$) vs x_1 of experimental data of isobaric systems and fitting curves. The data are represented by symbols, from this work at 0.6 MPa (∇) for BAE; at 0.6 MPa (\triangle) for BAP and at 0.6 MPa (\square) for BAB and from bibliography¹⁴ at 0.15 MPa (\triangle) for BAE; at 0.15 MPa (\triangleright) for BAP and at 0.15 MPa (\circ) for BAB. The projections of the correlation curves (dashed lines) have been plotted in two-dimensional representation.

Verification of experimental VLE data

Several of the different and frequently used consistency tests have been applied to verify the obtained data. In this work, VLE data at 0.6 MPa showed positive thermodynamic consistency, when verified with the point to point test of Van Ness et al.¹⁵, and considering the global criteria of Fredenslund et al.¹⁶ The Hayden and O'Connell⁵ procedure and Yen-Woods¹⁸ equation were employed in the FORTRAN program of Fredenslund et al.¹⁶ The association parameter (ETA) indicated by Fredenslund et al.¹⁶, the critical properties²⁴ and the vapor pressures^{21,23,25,26} from the bibliography (range from 4 to 1650 kPa) were used in this Fredenslund-Hayden^{5,16,18} (FH) test (see Table 2).

In addition, the acentric factors (w_i) calculated using these properties^{21,23,25,26} were: 0.410, 0.636, 0.620 and 0.600, for butyl acetate, ethanol, 1-propanol and 1-butanol, respectively. The errors were 0.03%, 0.16%, 1.26% and 0.92%, respectively. The w_i of bibliography²⁴ was taken as reference. Lastly, the Tsonopoulos¹⁷ procedure

Table 2. Results of point-to-point consistency test for the binary systems at 0.6 MPa^a

Parameter\method	FH test old ETA ^b			FHN test new ETA ^c			FT test (K _{ij} =0.05) ^d			FMD test ^e			FD test ^f			FPRSV test ^g		
	BAE	BAP	BAB	BAE	BAP	BAB	BAE	BAP	BAB	BAE	BAP	BAB	BAE	BAP	BAB	BAE	BAP	BAB
10 ³ BIAS(y _i)	8.6	8.1	7.9	8.3	7.8	7.6	9.0	9.5	8.7	8.6	9.2	8.7	5.8	7.1	7.5	-4.3	7.1	8.6
10 ³ MAD(y _i)	8.8	8.6	7.9	8.7	8.3	7.6	9.2	9.8	8.7	8.8	9.5	8.7	7.3	7.7	7.5	6.7	7.7	8.6
MPD(y _i)	9.68	7.00	4.80	9.72	6.90	4.73	9.91	7.52	5.06	9.71	7.39	5.03	8.79	6.64	4.69	8.36	6.62	5.01
BIAS(p/kPa)	0.0	-0.2	-0.1	0.0	-0.2	-0.1	0.0	-0.2	-0.1	0.0	-0.2	-0.1	0.0	-0.2	-0.1	-0.0	-0.2	-0.1
MAD(p/kPa)	1.8	1.9	0.7	1.8	1.9	0.7	1.8	1.9	0.7	1.8	1.9	0.7	1.8	1.9	0.7	1.8	1.9	0.7
MPD(p)	0.30	0.31	0.11	0.30	0.31	0.11	0.30	0.31	0.11	0.30	0.31	0.11	0.30	0.31	0.11	0.29	0.31	0.11
Van Ness et al. test ^h	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes	passes

^a average of residuals (BIAS); mean absolute deviation (MAD); mean proportional deviation (MPD) calculated as follow:

$$\text{BIAS}(F) = \frac{1}{n-2} \sum_1^n (F_{\text{exp}} - F_{\text{cal}}); \text{MAD}(F) = \frac{1}{n-2} \sum_1^n |F_{\text{exp}} - F_{\text{cal}}|; \text{MPD}(F) = \frac{100}{n-2} \sum_1^n \frac{|F_{\text{exp}} - F_{\text{cal}}|}{F_{\text{exp}}}$$

of data. ^b Ref [5,16,18]. ^c Ref [5,16,18]. ^d Ref [16–18]. ^e Ref [16,18,27]. ^f Ref [16,18,33,54]. ^g Ref [16–20].

(K_{ij}=0.05 as mixing parameter) was applied in the SVIR subroutine of Fredenslund et al.¹⁶ FORTRAN program.

The results obtained with the Fredenslund-Tsonopoulos¹⁶⁻¹⁸ (FT) test using the Tsonopoulos¹⁷ procedure for second virial coefficient calculations, the Yen-Woods¹⁸ equation, the critical properties²⁴ and the vapor pressures^{21,23,25,26} from bibliography, are presented in Table 2. Next, the same procedure was used and the virial coefficients were calculated by the Meng-Duan²⁷ equations. For this, the SVIR subroutine of Fredenslund et al.¹⁶ was replaced, but the same original FORTRAN program was employed. Results obtained with the Fredenslund-Meng-Duan^{16,18,27} (FMD) test are presented in Table 2. The same properties from bibliography^{21,23-26} and identical degrees in the Legendre polynomials than those used in the previous tests in this paper were used in each system.

After analyzing the residuals and plotting the results of the previous tests (FH, FT and FMD), we observe that the data globally satisfies the criteria of Fredenslund et al.¹⁶ No preferential trend is observed and the distribution of the residuals is random throughout the composition range.

PRSV modeling

The Peng-Robinson¹⁹ (PR) equation of state (EOS) is a two-constant equation which is able to describe accurately fluid properties and the behavior of the equilibrium vapor phase for non-polar mixtures by using the following equation:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (3)$$

The Mathias-Copeman²⁸ modification of the attraction parameter was revised, modified and expanded by Stryjek-Vera²⁰ by including one generalized parameter and one adjustable parameter. After this, the PRSV^{19,20} equation can be applied to polar compounds or associating substances as well as heavy hydrocarbons.

However, when extending the PRSV^{19,20} EOS to polar mixtures or strongly non-ideal mixtures, the one-parameter in the mixing rules of van der Waals is not enough. It is hence necessary to use the two-parameters in quadratic mixing rules.

The attraction and repulsion parameters in Eq. 3 are both expressed as a function of the composition of the substances in the mixture. In this sense, the following equations were used:

$$a_m = \sum_i^n \sum_j^n x_i x_j [a_i(T) a_j(T)]^{0.5} (1 - k_{12});$$

$$b_m = \sum_i^n \sum_j^n x_i x_j \left(\frac{b_i + b_j}{2} \right) (1 - k_{21}) \quad (4)$$

Therefore, in this work the quadratic van der Waals mixing rules with two parameters (k₁₂) and (k₂₁) were applied. These parameters can be obtained from the fitting of experimental data.

To check the modeling of the binary systems using PRSV^{19,20} EOS, the critical properties were taken from literature²⁴ and w₁ was calculated as indicated in the previous section. The specific parameters (k_i) of Stryjek-Vera²⁰ were calculated by using the vapor pressures^{21,23,25,26} and the critical properties from bibliography²⁴; and the results were: 0.0184, -0.0558, 0.2837 and 0.4938 for butyl acetate, ethanol, 1-propanol and 1-butanol, respectively.

An isobaric bubble point algorithm (p-x₁ scheme) was applied to check the data predictions for BAE, BAP and BAB systems at 0.6 MPa. The simplex method of Nelder-Mead²⁹ was applied. The uncertainties informed in Table 1 were applied to carry out the minimization procedure for all the binary systems of this work. The estimation of parameters was performed at each temperature by minimizing the following objective function (OF):

$$\text{OF} = \frac{1}{U(T)} \sum_1^n |T^{\text{exp}} - T^{\text{calc}}| + \frac{1}{U(y_1)} \sum_1^n |y_1^{\text{exp}} - y_1^{\text{calc}}| \quad (5)$$

Table 3 includes the results of the modeling of BAE, BAP and BAB systems at 0.6 MPa by applying the PRSV^{19,20} EOS and using the two-parameters classical mixing rules (see Eq. 4), with the binary parameters k_{12} and k_{21} , which are determined by the VLE data fitting.

The prediction results are presented in Fig. 2 as correlations of T vs x_1 and T vs y_1 as well as x_1 vs $y_1 - x_1$ from PRSV^{19,20} EOS in the binary systems BAE, BAP and BAB at 0.6 MPa. It can be observed that the y_1 are properly reproduced by PRSV^{19,20} EOS.

On the other side, significant differences are observable when reproducing the T in the BAE and BAP systems at 0.6 MPa (see Table 3 and Fig. 2). Such differences are not appreciable in the graphical representation of T for the BAB system at 0.6 MPa, which are globally similar to the uncertainty of the experimental data.

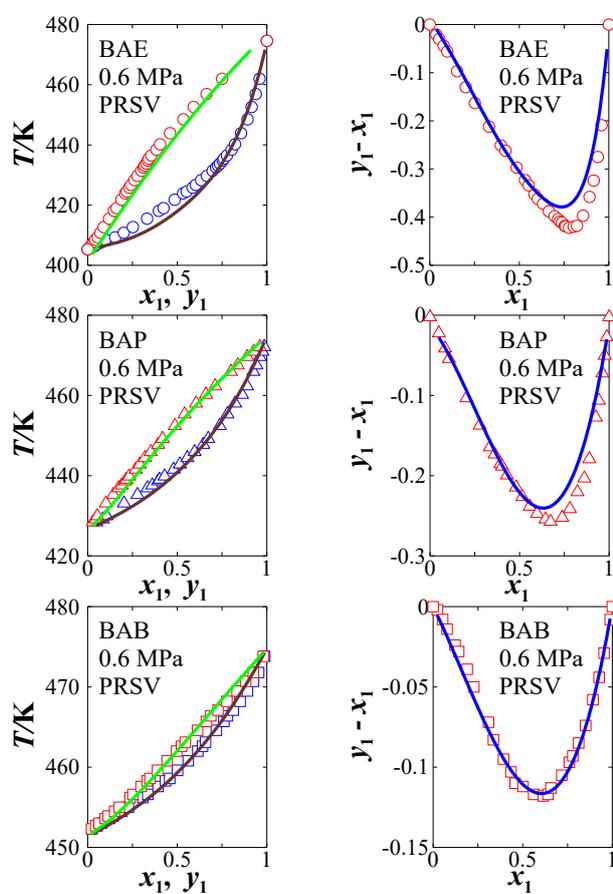


Fig. 2 Comparison of the VLE data with the EOS predictions for the binary system butyl acetate (1) + ethanol (2) (○, ○) at 0.6 MPa (BAE), butyl acetate (1) + 1-propanol (2) (△, △) at 0.6 MPa (BAP) and butyl acetate (1) + 1-butanol (2) (□, □) at 0.6 MPa (BAB). The predictions from the PRSV^{19,20} EOS are plotted by the curves of data correlations.

Point-to-point test analysis

Considered consistency tests. Observed differences

In this work, some differences previously indicated²⁵ are observed in the results after applying the FH, FT and FMD tests. The differences are associated to the procedure for calculating the second virial coefficients (B_{ii} , B_{ij}).

Note that all the point-to-point tests were applied (see FH, FT and FMD in Table 2) by using the method suggested by Van Ness et al.¹⁵ in the Fredenslund et al.¹⁶ FORTRAN program. Consequently, the different results obtained are only a function of the procedures and equations used to calculate B_{ii} , B_{ij} . That is, they are a function of the quality of the selected experimental data of B_{ii} , which were used to deduce the procedures and correlations, as well as the different mixing and combining rules.

Procedures for calculating the B_{ii} coefficients

In recent years the available experimental information related to the second virial coefficients has increased. However, it can be said that the bibliography^{24,30-36} is mostly a compilation, and therefore, based on this, the same shortcomings and procedures are not always adequate for the experimental determination of the virial coefficients^{37,38}, are used.

Regarding the calculation procedures of B_{ii} , B_{ij} , which will be used later in the virial equation of state, the same could be said. That is, in practice, one of the following two procedures is used: the Hayden-O'Connell⁵ method, with a strong base in both chemical theory; or some of the correlations fundamentally based on the serial development of the potential of Lennard Jones (the Vetere³⁹ or Meng-Duan²⁷ equations, or the most widely used Tsonopoulos¹⁷ equations).

Therefore, it is paradoxical that much attention is paid to procedures for verifying VLE data using the virial EOS, while on the contrary, the proper attention does not seem to be given to obtain the experimental data about the B_{ii} and B_{mix} ^{37,40}. These data are necessary to apply and verify the different correlations, the mixing rules and the combining rules, which will be subsequently used also to verify the experimental data of the VLE and to check the quality of such VLE data. Consequently, it seems reasonable to analyze which procedure may be more suitable to calculate the B_{ii} , due to the limitations in the experimental data and the scarcity of experimental data of the B_{mix} ^{33,38}.

Frequently, it has been considered that the Hayden-O'Connell⁵ method generally showed better reproductions of B_{ii} ^{41,42} for the different types of substances when it is compared with the Tsonopoulos¹⁶ procedure. In addition, it has been observed that the Tsonopoulos¹⁷ correlations has some drawbacks^{40,43,44}, which may have been solved with the modifications made in subsequent years^{45,46}. This has enabled to obtain equivalent and even better predictions of B_{ii} than those obtained with the Hayden-O'Connell⁵ method, except perhaps for some polar and/or strongly associated substances, as well as for long-chain substances.

Therefore, it can be said that much attention has been paid to the different procedures, as well as to their different extensions and/or modifications^{40,45-47}, and more frequently to the Tsonopoulos⁴⁴⁻⁴⁶ procedure. However, fewer revisions, modifications or updates have been reported for the Hayden-O'Connell⁵ method. These are the reasons why, in this work, we decided to update the association parameters (ETA) used in the Hayden-O'Connell⁵ procedure, taking as reference the bibliography^{17,24,27,34,44,45,48}.

Table 3. Results of VLE predictions using PRSV^{19, 20} EOS

Butyl Acetate (1) + Ethanol (2)								
EOS/Parameters	k ₁₂	k ₂₁	MAD(y ₁)	MPD(y ₁)	SD(y ₁)	MAD(T/K)	MPD(T)	SD(T/K)
PRSV ^{19,20}	-0.132	-0.229	0.029	14.37	0.037	2.52	0.59	2.79
Butyl Acetate (1) + 1-Propanol (2)								
EOS/Parameters	k ₁₂	k ₂₁	MAD(y ₁)	MPD(y ₁)	SD(y ₁)	MAD(T/K)	MPD(T)	SD(T/K)
PRSV ^{19,20}	-0.027	-0.048	0.011	2.65	0.016	1.49	0.34	1.66
Butyl Acetate (1) + 1-Butanol (2)								
EOS/Parameters	k ₁₂	k ₂₁	MAD(y ₁)	MPD(y ₁)	SD(y ₁)	MAD(T/K)	MPD(T)	SD(T/K)
PRSV ^{19,20}	0.121	0.143	0.003	2.61	0.004	0.58	0.13	0.65

$$SD(F) = \sqrt{\frac{\sum_1^n (F_{exp} - F_{cal})^2}{n-2}}$$
 with F being (y₁) or (T/K); n is the number of data.

UPDATE OF THE ETA OF THE HAYDEN-O'CONNELL METHOD

In order to achieve the association parameters (ETA), in addition to the thermodynamic properties^{26,54-56}, the data of the virial coefficients from the bibliography^{17,24,27,34,44,45,48} were used as reference. The number of data and the selected range of temperature are both indicated in Tables 4 for each of the substances (see columns 4-5 and 9-10).

The Hayden-O'Connell⁵ routine extracted from the bibliography¹⁶ was applied to obtain the ETA parameters. The obtained ETA parameters (see columns 3 and 8 in Table 4) are the result of considering the SD that minimizes the differences between the data from the bibliography^{17,24,27,34,44,45,48} and those obtained using the Hayden-O'Connell⁵ procedure.

PRM1 parameter

When taking the properties from the bibliography²⁴ as reference, some deficiencies were observed in the Radius of Gyration (RD), which motivated us to search for a relationship between the properties that would allow us to reproduce them. As a result, the parameter (PRM1),

$$PRM1 = (MM)^{0.15149} \cdot (\omega \cdot Z_c)^{0.03985} \cdot \left(\frac{P_c}{T_c}\right)^{-0.21518} \quad (6)$$

was obtained by correlating the thermodynamic properties of the 144 substances presented in Table 4. The thermodynamic properties used in the Eq. 6 were taken from literature^{24,49-51}.

The PRM1 data of the aforementioned substances were fitted using a RD vs PRM1 polynomial equation. The minimization statistical parameters were obtained from the following equation:

$$RD_{PRED} = A0 \cdot PRM1^3 + A1 \cdot PRM1^2 + A2 \cdot PRM1 + A3 \quad (7)$$

The overall results obtained for the 144 substances were: A0=-0.041, A1=0.162, A2=5.687, A3=-3.416, MAD_{TOTAL}=0.126 and SD_{TOTAL}=0.157. The errors for the prediction of RD/Angstroms were less than 1.8%. Furthermore, only a single substance (line 39 column 2 in Table 4) of those studied showed an error greater than 5%, which indicates that acceptable results were

obtained for the different individual correlations of each groups of substances.

Eq. 7 should not be considered as a predictive relationship of the RD. Consequently, the results obtained using Eq. 7 enable to provide a qualitative orientation of the property within the set of thermodynamic properties. For this reason, all 144 pairs of data of RD vs PRM1 were plotted, and the error curves were calculated by considering a 95% confidence level. The obtained results showed that only 3% of the data were outside the error correlation curves (see Fig. 3).

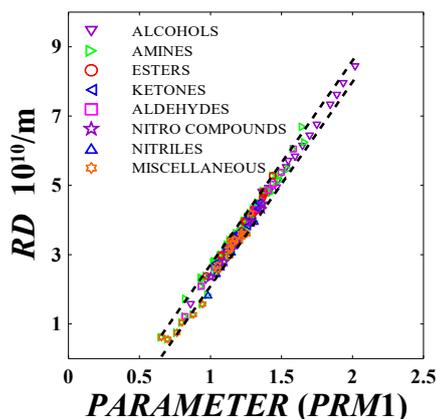


Fig. 3 Representation of Radius of Gyration (RD) vs Molecular Weight (MM), Acentric Factor (w) and Critical Properties [Compressibility Coefficient (Z_c), Pressure (P_c) and Temperature (T_c)] all included in the PRM1 parameter.

PRM2 parameter

The aforementioned procedure motivated the search of a parameter (PRM2) that related the new association parameters (ETA), for each of the 144 substances in Table 4, by applying the Hayden-O'Connell⁵ routine extracted from the bibliography¹⁶. For this, the thermodynamic properties from the bibliography^{24,49-51} were used. The following expression for the 142 substances, in which the ETA parameter was not null, was obtained:

$$PRM2 = (\omega \cdot ETA)^{-0.00075} \cdot \left(\frac{MM \cdot T_c \cdot Z_c}{RD}\right)^{0.23035} \cdot \left(\frac{T_c}{P_c}\right)^{0.27107} \quad (8)$$

After the above, the parameter PRM2 shown in Eq. 8 was correlated with the Molecular Weight (MM) for all the 142 pairs of data using the following polynomial equation:

$$MM_{\text{PRED}} = A0 \cdot PRM2^3 + A1 \cdot PRM2^2 + A2 \cdot PRM2 + A3 \quad (9)$$

The overall results obtained from the 142 substances accounting for the MAD and SD statistical parameters, were: $A0=0.810$, $A1=-2.506$, $A2=37.457$, $A3=-69.342$, $MAD_{\text{TOTAL}}=4.187$ and $SD_{\text{TOTAL}}=5.293$. The relationship between MM and the parameter PRM2 were plotted for all substances. The correlation results by using the error curves were plotted (see Fig. 4). A confidence level of a 95% was estimated. As can be seen in Fig. 4, only 2% of the data are outside the range established by the error correlation curves.

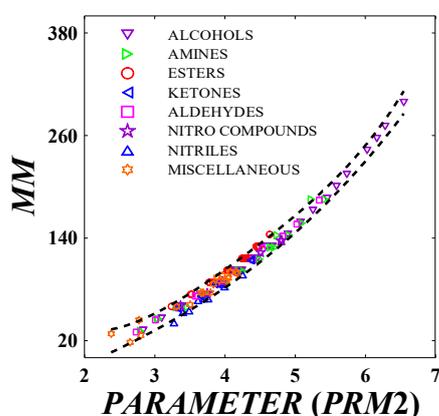


Fig. 4 Representation of Radius of Gyration (RD) vs Molecular Weight (MM), Acentric Factor (w) and Critical Properties [Compressibility Coefficient (Z_c), Pressure (P_c) and Temperature (T_c)] all included in the PRM1 parameter.

PRM3 parameter

In order to verify the quality and the reproducibility of the new ETA parameter of the substances in the different groups and subgroups, a similar relationship to the previous ones was studied. It was possible to deduce an explicit global relationship for the 142 substances in which ETA was different from zero, using the PRM3 parameter:

$$PRM3 = \left(\frac{ETA}{\omega} \right)^{A2} \cdot \left(\frac{MM \cdot RD \cdot Z_c}{P_c} \right)^{A3} \cdot \left(\frac{P_c}{T_c} \right)^{A4} \quad (10)$$

Using Eq. 10 the association parameter was correlated for all the different subgroups of substances with the following relationship:

$$Ln(ETA_{\text{PRED}}) = A0 + A1 \cdot Ln(PRM3) \quad (11)$$

The overall results obtained from the 142 data were: $A0=0.096$, $A1=-13.072$, $A2=-0.083$, $A3=0.002$, $A4=0.044$, $MAD_{\text{TOTAL}}=0.330$ and $SD_{\text{TOTAL}}=0.553$. The results of the correlation using Eq. 11 as well as the error curves with a confidence level of 95% (see Fig. 5), show that only 10 data are outside the range established by the error curves.

The errors shown in the ETA parameter prediction regarding the previously cited substances are the result of correlating substances that do not belong to a specific group or subgroup. Considering this, it is observed that about 90% of the data the association parameter is adequately reproduced.

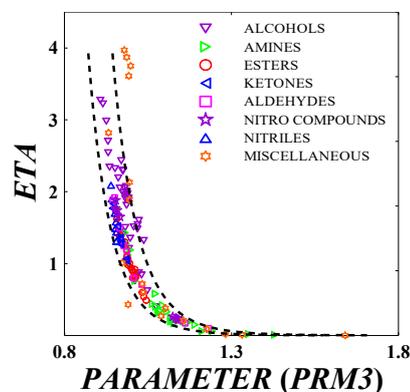


Fig. 5 Representation of Association Parameter (ETA) of Hayden-O'Connell⁵ method vs. Molecular Weight (MM), Acentric Factor (w), Radius of Gyration (RD) and Critical Properties [Compressibility Coefficient (Z_c), Pressure (P_c) and Temperature (T_c)] all included in the PRM3 parameter, with fitting of error curves.

APPLICATION OF THE FH TEST WITH THE NEW ETA (FHN TEST)

After this update and verification of ETA, the routine of Fredenslund et al.¹⁶ was employed using the new parameters. Results for ethanol, 1-propanol, 1-butanol and butyl acetate are shown in Table 4. The Hayden-O'Connell⁵ procedure and Yen-Woods¹⁸ equation were employed in the FORTRAN program of Fredenslund et al.¹⁶ The critical properties²⁴, the vapor pressures from literature^{21,23,25,26} and the new ETA parameters were used in this FHN test (see Table 2).

Considering the results presented in Table 2, it is clear that when B_{ii} is calculated using the Hayden-O'Connell⁵ routine with the recalculated ETA, the differences between these calculated B_{ii} and those obtained from literature^{17,24,27,34,44,45,48} decrease. Therefore, it is reasonable to analyze all the calculated B_{ii} for the substances in this work, since after applying the verification tests (see Table 2) the differences observed in the results are still significant.

COMPARISON OF THE PROCEDURES TO OBTAIN B_{ii}

The B_{ii} used in the different tests (FT and FMD), obtained through the procedures described in bibliography^{17,27,45,47}, and the B_{ii} obtained by applying the Hayden-O'Connell⁵ method using both the association parameter of the bibliography¹⁶ and the new ETA parameter determined in this work, were compared with the experimental data of B_{ii} found in literature^{34,44}, as well as with calculated values obtained from the correlations of experimental data^{24,45,48}.

Table 4. Association parameters calculated from Hayden and O'Connell⁵ method

1	2	3	4	5	6	7	8	9	10	11
	SUBSTANCES	ETA	ΔT	N° Data	CAS N°	SUBSTANCES	ETA	ΔT	N° Data	CAS N°
	ALCOHOLS					ESTERS				
4	METHANOL	1.32	320-500	10	67-56-1	METHYL FORMATE	0.54	290-470	10	107-31-3
5	ETHANOL	1.6	320-500	10	64-17-5	METHYL ACETATE	0.89	280-500	12	79-20-9
6	PROPANOL	1.48	300-520	12	71-23-8	ETHYL FORMATE	0.49	280-490	12	109-94-4
7	BUTANOL	2.05	320-560	13	71-36-3	METHYL PROPIONATE	0.94	280-520	13	554-12-1
8	1-PENTANOL	1.98	280-580	16	71-41-0	ETHYL ACETATE	0.91	280-520	13	141-78-6
9	1-HEXANOL	2.05	290-610	17	111-27-3	PROPYL FORMATE	0.8	280-520	13	110-74-7
10	1-HEPTANOL	2.32	290-630	18	111-70-6	BUTYL FORMATE	1.09	280-540	14	592-84-7
11	1-OCTANOL	0.84	520-650	14	111-87-5	PROPYL ACETATE	1.06	280-540	14	109-60-4
12	1-NONANOL	0.87	540-670	13	143-08-8	ETHYL PROPIONATE	1	280-540	14	105-37-3
13	1-DECANOL	1.21	390-680	16	112-30-1	METHYL n-BUTYRATE	0.8	280-540	14	623-42-7
14	1-UNDECANOL	0.85	540-700	17	112-42-5	ISOPROPYL ACETATE	0.6	280-540	14	108-21-4
15	1-DODECANOL	0.62	540-710	18	112-53-8	BUTYL ACETATE	1.51	290-570	15	123-86-4
16	1-TRIDECANOL	1.23	360-720	19	112-70-9	PROPYL PROPIONATE	1.42	290-570	15	106-36-5
17	1-TETRADECANOL	1.65	300-740	23	112-72-1	sec-BUTYL ACETATE	1.4	290-550	14	105-46-4
18	1-HEXADECANOL	2.34	300-760	24	36653-82-4	ETHYL n-BUTYRATE	1.1	290-570	15	105-54-4
19	1-HEPTADECANOL	2.54	300-760	24	1454-85-9	ISOBUTYL ACETATE	0.92	290-550	14	110-19-0
20	1-OCTADECANOL	2.7	300-760	24	112-92-5	ETHYL ISOBUTYRATE	0.82	280-540	14	97-62-1
21	1-EICOSANOL	2.98	300-780	24	629-96-9	PENTYL ACETATE	1.3	300-580	15	628-63-7
23	2-PROPANOL	1.54	280-500	12	67-63-0	PROPYL n-BUTYRATE	1.27	310-590	15	105-66-8
24	sec-BUTYL ALCOHOL	1.81	290-530	13	78-92-2	BUTYL PROPIONATE	1.19	300-580	15	590-01-2
25	2-PENTANOL	1.97	280-540	14	6032-29-7	ISOPENTYL ACETATE	0.98	300-580	15	123-92-2
26	3-PENTANOL	1.91	280-540	14	584-02-1	BUTYL n-BUTYRATE	1.62	310-610	16	109-21-7
27	2-HEPTANOL	2.43	300-580	15	543-49-7	ALDEHYDES				
28	2-OCTANOL	3.27	320-620	16	123-96-6	METHANAL	0.17	280-410	8	50-00-0
29	2-METHYL 1-PROPANOL	1.95	310-530	12	78-83-1	ACETALDEHYDE	0.71	280-450	10	75-07-0
31	2-METHYL 1-BUTANOL	2.07	290-550	14	137-32-6	PROPIONALDEHYDE	0.8	280-490	12	123-38-6
32	3-METHYL 1-BUTANOL	2	290-570	15	123-51-3	BUTYRALDEHYDE	1.05	280-510	13	123-72-8
33	2,2-DIMETHYL 1-PROPANOL	1.9	280-540	14	75-84-3	ISOBUTYRALDEHYDE	1.17	280-500	12	78-84-2
34	3-METHYL 2-BUTANOL	1.35	280-540	14	598-75-4	VALERALDEHYDE	1.25	280-550	15	110-62-3
35	2-METHYL 1-PENTANOL	2.29	300-580	15	105-30-6	HEXANAL	1.49	290-570	15	66-25-1
36	2-ETHYL 1-BUTANOL	2.29	310-570	14	97-95-0	HEPTANAL	1.88	310-610	16	111-71-7
37	4-METHYL 2-PENTANOL	2.19	290-570	15	108-11-2	2-ETHYL HEXANAL	1.92	310-590	15	123-05-7
38	3-METHYL 1-PENTANOL	1.88	300-580	15	589-35-5	NONANAL	0.22	330-650	17	124-19-6
39	2-METHYL 1-HEXANOL	2.3	300-590	16	624-22-6	DECANAL	0.21	350-670	17	112-31-2
40	2-ETHYL 1-HEXANOL	3.22	320-620	16	104-76-7	DODECANAL	0.1	350-690	18	112-54-9
41	tert-BUTYL ALCOHOL	1.51	350-500	9	75-65-0	KETONES				
43	2-METHYL 2-BUTANOL	1.5	280-540	14	75-85-4	ACETONE	1.04	280-490	12	67-64-1
44	3-METHYL 3-PENTANOL	1.4	290-570	15	77-74-7	2-BUTANONE	1.06	280-530	14	78-93-3
45	AMINES					2-PENTANONE	1.27	280-550	15	107-87-9
46	METHYLAMINE	0.22	280-430	9	74-89-5	DIETHYL KETONE	1.28	280-550	15	96-22-0
47	ETHYLAMINE	0.4	280-450	10	75-04-7	METHYL ISOPROPYL KETONE	1.36	280-550	15	563-80-4
48	PROPYLAMINE	0.76	280-490	12	107-10-8	2-HEXANONE	1.52	290-570	15	591-78-6
49	BUTYLAMINE	1.01	290-530	13	109-73-9	ISOBUTYL METHYL KETONE	1.36	280-570	16	108-10-1
50	ISOBUTYLAMINE	0.89	280-510	13	78-81-9	2-HEPTANONE	1.77	310-610	16	110-43-0
51	PENTYLAMINE	1.12	280-530	14	110-58-7	5-METHYL 2-HEXANONE	1.83	310-590	15	110-12-3
52	HEXYLAMINE	1.28	290-570	15	111-26-2	NITRO COMPOUNDS				
53	1-AMINO HEPTANE	1.77	310-590	15	111-68-2	NITROMETHANE	1.65	310-550	13	75-52-5
54	1-OCTYLAMINE	0.33	330-610	15	111-86-4	NITROETHANE	1.74	310-590	15	79-24-3
55	1-NONYLAMINE	0.2	350-630	15	112-20-9	1-NITROPROPANE	1.88	310-590	15	108-03-2
56	1-DECYLAMINE	0.18	350-650	16	2016-57-1	2-NITROPROPANE	1.77	310-590	15	79-46-9
57	DODECYLAMINE	0.15	370-690	17	124-22-1	m-NITROTOLUENE	0.22	370-730	19	99-08-1
58	DIMETHYLAMINE	0.25	280-430	9	124-40-3	o-NITROTOLUENE	0.23	370-710	18	88-72-2
59	ETHYL METHYL AMINE	0.34	280-470	11	624-78-2	p-NITROTOLUENE	0.24	370-730	19	99-99-0
60	DIETHYLAMINE	0.31	280-490	12	109-89-7	NITROBENZENE	0.26	370-710	18	98-95-3
61	DIPROPYLAMINE	1.19	280-550	15	142-84-7	MISCELLANEOUS CHEMICALS				
62	DIISOPROPYLAMINE	0.44	280-510	13	108-18-9	CARBON OXIDE SULFIDE	0.02	190-640	16	463-58-1
63	DIBUTYLAMINE	0.42	310-590	15	111-92-2	CARBON MONOXIDE	0.01	60-330	19	630-08-0
64	ISOPROPYLAMINE	0.06	280-470	11	75-31-0	CARBON DIOXIDE	0.09	160-610	16	124-38-9
65	tert-BUTYLAMINE	0.01	280-470	11	75-64-9	CARBON DISULFIDE	0.43	280-550	16	75-15-0
66	sec-BUTYLAMINE	0.02	280-510	13	13952-84-6	ETHYLEN GLYCOL	3.75	330-630	16	107-21-1
67	1,1-DIMETHYL PROPYL AMINE	0.2	280-510	13	594-39-8	1,2-PROPYLENE GLYCOL	3.61	330-610	15	57-55-6
68	TRIMETHYLAMINE	0.06	290-430	8	75-50-3	1,3-PROPYLENE GLYCOL	3.87	330-650	17	504-63-2
69	TRIETHYLAMINE	0.17	300-530	13	121-44-8	1,4-BUTANEDIOL	3.97	350-650	16	110-63-4
70	BUTYL DIMETHYL AMINE	0.2	280-530	14	927-62-8	2-ETHOXYETHANOL	2.13	290-550	14	110-80-5
71	TRIPROPYLAMINE	0.58	350-570	12	102-69-2	PHENOL	0.21	330-670	18	108-95-2
72	TRIBUTYLAMINE	1.43	330-630	16	102-82-9	CYCLOHEXANOL	2.82	320-620	16	108-93-0
73	NITRILES					FURFURAL	0.38	330-650	17	98-01-1
74	ACETONITRILE	1.7	280-530	14	75-05-8	ETHYNE	0.27	160-580	15	74-86-2
75	PROPENENITRILE	1.35	280-530	14	107-13-1	ANILINE	0.72	280-690	22	62-53-3
76	PROPIONITRILE	1.44	280-550	15	107-12-0	CYCLOHEXANONE	1.01	330-650	17	108-94-1
77	METHACRYLONITRILE	1.31	280-550	15	126-98-7	VINYL ACETATE	0.6	270-510	13	108-05-4
78	BUTYRONITRILE	1.58	290-570	15	109-74-0	WATER	1.89	330-630	16	7732-18-5
79	ISOBUTYRONITRILE	1.49	290-550	14	78-82-0	METHYL METHACRYLATE	0.002	290-550	14	80-62-6
80	VALERONITRILE	1.9	310-590	15	110-59-8	ETHYL METHACRYLATE	0.000	290-570	15	97-63-2
81	HEXANENITRILE	2.09	310-610	16	628-73-9	TETRAHYDROFURAN	0.000	305-530	13	109-99-9

We observed that as a consequence of the update of ETA, the differences with respect to these references have been notably reduced in the prediction of B_{ii} . On the other hand, the temperatures of the BAE, BAP and BAB systems are in the range 405-475 K. Therefore, this range of temperatures is interesting for the analysis of the B_{ii} for the substances in this work, with respect to the results of the tests presented in Table 2.

Within the temperature range indicated above, for ethanol, 1-propanol, 1-butanol and butyl acetate, the global differences in the $B_{ii}/(\text{mL/mol})$, calculated by the Hayden-O'Connell⁵ method and using the new association parameter were: 28.4, 5.3, 23.1 and 159.8, respectively. Considering the Tsonopoulos^{17,45} procedure the mean values of the differences in the $B_{ii}/(\text{mL/mol})$ were: 10.9, 8.6, 29.3 and 79.9, and using the Meng-Duan^{27,47} procedure the mean values of the differences in the $B_{ii}/(\text{mL/mol})$ were: 6.5, 24.8, 157.8 and 113.0, respectively. The bibliography^{24,34,44,45,48} was taken as a reference for calculations in all cases.

It can hence be seen that the average differences between the different B_{ii} prediction procedures are not excessive, except for 1-butanol. Thus, the magnitude of these differences does not seem to explain the different results obtained by applying the point-to-point tests of FHN, FT and FMD (see Table 2). Basically, such differences in the mean values of the B_{ii} , which were calculated by the Hayden-O'Connell⁵ procedure using the new ETA parameter are within the range of variability of the experimental data used as a reference (less than 30 mL/mol for all alcohols), except for the B_{ii} of butyl acetate.

OTHER INFLUENCES ON B_{ii} PREDICTIONS

The question of the differences in the results regarding the point-to-point tests of FHN, FT and FMD (see Table 2) may not be only limited to the estimations made when using the different procedures for determining B_{ii} . Thus, it could be assumed that, for the substances used in this work, the second virial coefficients were predicted adequately, with any of the procedures employed in this study. However, the Hayden-O'Connell⁵ procedure returned best results for B_{ii} after the update of the ETA parameter.

Therefore, the results shown in Table 2 are the result of the different procedures that have been used to obtain B_{ii} as well as the use of the different combination rules that lead to obtaining B_{mix} ^{52,53}. That could be due to the poor updating and lack of experimental data of both B_{ii} and B_{mix} . To verify the above, we proceeded to evaluate the B_{ii} and B_{ij} used during the tests to verify the data of the VLE by using the different types of tests indicated in Table 2.

The statistical results show that, as the temperature increases, the differences between the B_{ii} values calculated using the procedures cited in Table 2 are random, increasing in some cases and decreasing in others, and hence, the trend is not uniform. However, the differences in the resulting B_{ii} values for ethanol when the Hayden-O'Connell⁵ vs Tsonopoulos¹⁷ (HT) procedures are compared, and when the Tsonopoulos¹⁷ vs Meng-Duan²⁷ (TMD) procedures are compared, are

within the range of variability of the B_{ii} experimental data. Identically, the differences in B_{ii} for 1-propanol when HT procedures and when Hayden-O'Connell⁵ vs Meng-Duan²⁷ (HMD) procedures are compared, are within the range of variability of the B_{ii} experimental data. This can also be affirmed regarding the differences between the TMD procedures with respect to the B_{ii} of butyl acetate.

However, considering HT and HMD, the differences in the B_{ii} values of butyl acetate present errors greater than 8% and 6%, respectively. In addition, between the HMD procedures the errors in B_{ii} for ethanol is greater than 7%. For 1-propanol and TMD procedures the error in the differences of B_{ii} is greater than 8%. Remarkable differences are also seen for the calculation of B_{ii} for 1-butanol with the three mentioned procedures: the HT procedures show an error greater than 8%, and with both the HMD and TMD procedures, important errors are observed, close to 26% and 16% respectively.

On the other hand, regarding the second cross virial coefficients (B_{ij}), when checking the predictions with the procedures indicated above, some discrepancies were observed, such as: errors close to 4.9% considering HMD and 8% considering HT for the B_{ij} between butyl acetate and 1-propanol as well as errors of 6% considering HT and TMD for the B_{ij} between butyl acetate and 1-butanol.

However, when the TMD procedures were applied, for the B_{ij} between butyl acetate and ethanol and between butyl acetate and 1-propanol, the errors obtained are close to 2% and 3%, respectively.

OTHERS SUGGESTED PROCEDURES

From the aforementioned, it seems reasonable to indicate that the problem, caused by applying the different procedures in the point-to-point test, is not only related to the B_{ii} prediction. That is, the differences observed after applying the point-to-point test could be a consequence of the random uncertainty in the point deviations, and the different ways of predicting the second crossed virial coefficients.

These are the reasons why, instead of using general or generalized procedures to find out about the B_{ii} of the different substances in the FORTRAN¹⁶ program, individual procedures should be used for each of the substances. However, the general procedures are attractive and even preferable from the point of view of using a single function that can be applied to all substances.

If the virial EOS were to be used in the point-to-point test, then individual, simple and easy to manipulate and integrate relationships, such as the one suggested by Dymond et al.³³ could solve the problem. That is the reason why the B_{ii} data of butyl acetate, obtained using the bibliography⁴⁸, were correlated to the equation reported by Dymond et al.³³,

$$B_{ii} / \text{mL} \cdot \text{mol}^{-1} = \sum_{k=0}^{k=N} A_k \cdot \left(\frac{29815}{T/K} - 1 \right)^k \quad (12)$$

resulting: $A_0 = -5152.9$, $A_1 = -22307.6$, $A_2 = -42061.6$, $A_3 = -32143.3$; while the equations for alcohols were taken

from the bibliography⁴⁵. The classical Lorentz expression (the Lorentz cube-root rule) was used to calculate the cross virial coefficients⁵⁴:

$$B_{ij} = \frac{[(B_{ii})^{1/3} + (B_{jj})^{1/3}]^3}{8} \quad (13)$$

Eqs. 12 and 13 together with the ratio of the mixing virial coefficients (B_{mix}),

$$B_{mix} = \sum_{i=1}^{i=N} \sum_{j=1}^{j=N} y_i y_j B_{ij} \quad (14)$$

were applied in the subroutine SVIR of the FORTRAN program from Fredenslund et al.¹⁶ Therefore, that was the only modification of the FORTRAN program to verify again the results of the point-to-point test of Van Ness et al.¹⁵ with respect to the other procedures.

The results obtained for the deviations in the y_1 by applying the Fredenslund et al.¹⁶ routine, the equations of Dymond et al.³³ and the Lorentz cube-root rule⁵⁴ for B_{ij} , present at the FD test are included in Table 2. Therefore, even though there are differences with respect to the results obtained with the FHN test, in which the new ETA were used, the trend of the results is to present smaller deviations in the mole fraction of the vapor phase than those obtained when applying the other procedures (see Table 2).

While these types of equations are developed for all substances and their mixtures, a different EOS can be used in the procedure¹⁶, preferably validated by both engineering applications and in the reproduction of VLE data.

USING A DIFFERENT EOS IN THE POINT-TO-POINT TEST

In this work, the PRSV^{19,20} EOS used to correlate VLE data was applied in the FORTRAN program by Fredenslund et al.¹⁶, specifically in the PHIB subroutine. The constants for the binary systems are shown in Table 3. Therefore, a different EOS (PRSV^{19,20} EOS) was used in the Van Ness et al.¹⁵ thermodynamic consistency test.

Consequently, the reference fugacity coefficients and the fugacity coefficients were calculated by using the PRSV^{19,20} EOS and substituted in Eq. 1, to obtain the activity coefficients in order to apply the point-to-point test of Van Ness.¹⁵ The mixing rules expressed by Eq. 4 were applied. The results obtained when applying the Fredenslund et al.¹⁶ routine and the PRSV^{19,20} EOS (FPRSV test) are shown in Table 2 for the systems in this work.

Taking into account the listed objections regarding the mixtures and mixing rules^{52,53}, it is observed that in two of the studied systems, the FPRSV test procedure produces differences in the y_1 equal (BAE system) or smaller (BAP system) than when applying the FHN test with new ETA. In the BAB system, deviations similar to those obtained by the application of the FT test are generated. The same applies to the FMD

test with the Meng-Duan²⁷ procedure, for which the differences in B_{ii} , as previously indicated, were of a similar order of magnitude to those generated with the Hayden-O'Connell⁵ method.

In any case, the data corresponding to the systems presented in this work seem to be of sufficient quality. Furthermore, after updating the association parameter, it may be evident that the Hayden-O'Connell⁵ method can still be used to determine the second virial coefficients with the same reliability than with other procedures, and therefore this method is adequate for the evaluation of VLE data in the test of Van Ness et al.¹⁵ and the point-to-point version of Fredenslund et al.¹⁶

Finally, as a consequence of insufficient information on B_{ij} , of which only a very small part has been recommended^{33-38,44,45}, as well as the significant lack of experimental data on B_{ij} , the use of other different EOS could be adequate for the determination of f_i , which are subsequently applied in the approximation g-f, and in order to evaluate the VLE data in the point-to-point test version of Fredenslund et al.¹⁵

CONCLUSIONS

The experimental VLE data corresponding to the binary systems of butyl acetate with ethanol, 1-propanol or 1-butanol at 0.6 MPa have been determined and checked by using the different thermodynamic consistency tests. The point-to-point test of Van Ness et al. applied in the Fredenslund et al. FORTRAN routine was modified in the PHIB and SVIR subroutines. In general, after considering the differences observed by applying the different point-to-point consistency tests, the VLE data can be accepted as good quality data.

After this, the Peng-Robinson-Stryjek-Vera EOS with quadratic mixing rules was employed for data prediction. The predictions generated by this model in y_1 are not very different from the experimental data, but when considering the reproduction of temperature the differences are more significant.

In order to evaluate the differences observed in the results when applying distinct point-to-point tests, the obtained data were analyzed by using several prediction procedures for the B_{ii} coefficients. In addition, new association parameters were determined to be used in the Hayden-O'Connell method. For these purposes, the data and correlations recommended in the bibliography have been used.

While it is considered desirable to use a general procedure to predict the B_{ii} coefficients for any substance, the limitations of the different correlations become evident, since they are a consequence of the quantity and the high-quality of experimental data, and such data are insufficient. In contrast, the Hayden-O'Connell procedure can be considered an accurate and fully generalized method for predicting B_{ii} by using only critical properties and molecular parameters. This procedure only needed updating the association parameter to properly reproduce the B_{ii} coefficients that were taken from the bibliography and used as reference.

NOMENCLATURE

BAE	Butyl Acetate+Ethanol system	MPD	Mean proportional deviation
BAP	Butyl Acetate+1-Propanol system	OF	Objective function
BAB	Butyl Acetate+1-Butanol system	P_c	Critical pressure/kPa
ETA	Association parameter (see η in ref. 22)	PRM1	Parameter PRM1 in Eq. 6
FD test	Fredenslund+Dymond test	PRM2	Parameter PRM2 in Eq. 8
FH test	Fredenslund+Hayden-O'Connell test with ETA in ref. 15	PRM3	Parameter PRM3 in Eq. 10
FHN test	Fredenslund+Hayden-O'Connell test with new ETA	PRSV	Peng-Robinson+Stryjek-Vera equation
FMD test	Fredenslund+Meng-Duan test	RD	Radius of gyration/Angstroms
FPRSV test	Fredenslund+Peng-Robinson-Stryjek-Vera test	RMS	The root-mean-square
FT test	Fredenslund+Tsonopoulos test	SD	Standard deviation
HMD	Hayden-O'Connell+Meng-Duan	T_c	Critical temperature/K
HT	Hayden-O'Connell+Tsonopoulos	TMD	Tsonopoulos+Meng-Duan
MAD	Mean absolute deviation	w	Acentric factor
MM	Molecular weight/(g/mol)	Z_c	Critical compressibility coefficient

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