Experimental VLE data of methyl acetate or ethyl acetate + 1-butanol at 0.6 MPa. Predictions with Peng-Robinson EOS and group contribution models

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Datos experimentales del ELV para acetato de metilo o acetato de etilo + 1-butanol a 0.6 MPa. Predicciones utilizando Peng-Robinson EoS y los modelos de contribución por grupos.

Dades experimentals de l'ELV per l'acetat de metil o acetat d'etil + 1-butanol a 0,6 MPa. Prediccions utilitzant Peng-Robinson EoS i els models d'aportació per grups.

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SUMMARY

Vapor-liquid equilibrium data were obtained with a stainless steel ebulliometer at 0.6 MPa for methyl acetate + 1-butanol and ethyl acetate + 1-butanol. The experimental data for the binary systems were tested and verified thermodynamically, showed positive consistency when the point-to-point test of Van Ness was applied. The group contribution models ASOG and three versions of the UNIFAC were applied to calculate the vapor-liquid equilibrium data and after, these values were compared to the experimental data. The approach ϕ-ϕ was applied by using the Peng-Robinson equation of state, the classical attractive term was employed. The quadratic and Wong-Sandler mixing rules were verified and the adjustable parameter of Stryjek-Vera was also applied.

Keywords VLE isobaric data, Methyl Acetate, Ethyl Acetate, 1-Butanol

RESUMEN

Los datos del equilibrio líquido-vapor para el acetato de metilo + 1-butanol y el acetato de etilo + 1-butanol fueron obtenidos a 0.6 MPa utilizando un ebullómetro de acero inoxidable. Los datos experimentales de los sistemas binarios fueron comprobados y verificados termodinámicamente, observándose que presentan consistencia positiva al ser aplicado el test punto a punto de Van Ness. Los modelos de contribución por grupos ASOG y tres versiones de UNIFAC fueron empleados para calcular los datos del equilibrio líquido-vapor, posteriormente los valores calculados fueron comparados con los datos experimentales. La aproximación ϕ-ϕ fue utilizada aplicando la ecuación de estado de Peng-Robinson, utilizando el término atractivo clásico. Las reglas de mezclado cuadráticas y las de Wong-Sandler fueron verificadas y se empleó el parámetro ajustable de Stryjek-Vera.

Palabras clave: Datos isobáricos del ELV; acetato de metilo; acetato de etilo; 1-butanol.

RESUM

Les dades de l'equilibri líquid-vapor per a l'acetat de metil + 1-butanol i l'acetat d'etil + 1-butanol es van obtenir a 0,6 MPa utilitzant un ebulloscopi d'acer inoxidable. Les dades experimentals dels sistemes binaris es van comprovar i verificar termodinàmicament, i es va observar que presenten consistència positiva a l'aplicació del test de Van Ness punt a punt. Els models d'aportació per grups ASOG i les tres versions de UNIFAC van ser empleats per calcular les dades de l'equilibri líquid-vapor, i posteriorment els valors calculats van ser comparats amb els dades experimentals. L'aproximació ϕ-ϕ es va utilitzar aplicant

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l'equació d'estat de Peng-Robinson, utilitzant el terme atractiu clàssic. Les regles de barrejat quadràtiques i les de Wong-Sandler van ser verificades i es va utilitzar el paràmetre ajustable de Stryjek-Vera.

Paraules clau: Dades isobàriques de l'ELV; acetat de metil; acetat de etil; 1-butanol.

IINTRODUCTION

Esters and alcohols are frequently used in different industrial processes. Methyl acetate is used in organic synthesis and is also an excellent solvent for resin and paints, while ethyl acetate is used in the food, photographic, textile and paper industries. 1-butanol is employed in chlorination processes, as a dehydrating agent, in paints, lacquers and varnishes; in the pharmaceutical industry, for tanning of hides, in the photographic industry and in perfumes. 1-butanol has also been studied as biodiesel due to the energy demand.

Consequently, the study of the behavior of these substances, mixtures and the determination of the vapor-liquid equilibrium (VLE) has a scientific interest and is necessary in many industrial processes. That is why as in previous works[1,2] we determined VLE data for ester/alcohol binary mixtures at moderate pressure. Data were determined at 0.6 MPa for (1) methyl acetate + (2) 1-butanol (MA1B) and (1) ethyl acetate + (2) 1-butanol (EA1B). These systems were previously studied by different authors[3-6] under several operating conditions.

VLE of MA1B has been studied at 74.66 and 127.99 kPa by Susial and Ortega[3], at 101.3 kPa by Belousov et al.[3], Esteller et al.[3], Ortega and Susial[3], and Patlasov et al.[4]; and at 0.3 MPa by Susial et al.[5]. VLE of EA1B has been studied isothermally by Alsmeyer and Marquardt[3] and isobarically at 70.5 and 94 kPa by Darwish and Al-Khateib[3], at 97.3 kPa by Mainkar and Mene[6] at 101.3 kPa by Belousov et al.[3], Ortega et al.[4] and Shono et al.[4]; and at 0.3 MPa by Susial et al.[5]. Azeotropes have not been reported in these systems.

In this study experimental data were verified by applying the test of Van Ness[7] using the FORTRAN program[8] of Fredenslund et al. The γ-ϕ approach enables to analyze the efficiency of the different group contribution models[9-12]. In addition, by using the ϕ-ϕ approach, experimental data were correlated with the Peng-Robinson[13] (PR) equation of state (EOS) using quadratic mixing rules or Wong-Sandler[14] (WS) mixing rules. The classical attractive term or the adjustable parameter of Stryjek-Vera[15] (SV) were also used in both cases.

EXPERIMENTAL

Chemicals

Methyl acetate, ethyl acetate and 1-butanol (99%, 99.9% and 99.9% mass purity, respectively) from Panreac Química S.A. were used. The physical properties, normal boiling point (T_{bp}), density (ρ_{ii}) and refractive index (n_D) at 298.15 K have been previously published[1,2,5]. These products were used as received.

A Kyoto Electronics DA-300 vibrating tube density meter with an uncertainty of ±0.1 kg·m^{-3} was employed for density determinations of both pure components and VLE data. In addition, a Zusi 315RS Abbe refractometer with an uncertainty of ±0.0002 units was used for the refractive index determinations of pure components.

Equipment and procedures

An ebulliometer made of stainless steel (2 mm thickness) was employed (Fig. 1) to obtain experimental VLE data. The apparatus operates with a 400 cm^3 capacity. It has been built to work at moderate or high pressures. Flooding does not occur when working with about 800 cm^3 of mixing liquid. The liquid mixture is heated in a double-walled inverted vessel (E). Liquid and vapor circulate due to the Cotrell pump effect that takes place when the liquid is heated inside the boiling flask (E). The liquid phase is circulated across the funnel (B) to be collected in the C valve. The condensed vapor in the cooler (F) is circulated to be collected in the D valve.

The general description of the equilibrium ebulliometer and the disposal of the different elements in the installation can be consulted in previous papers[1,2,5].

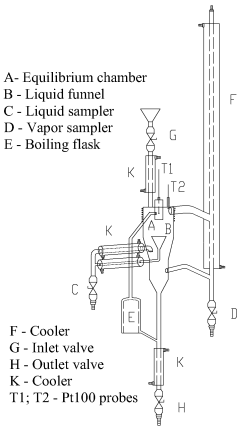

Fig. 1. *Schematic diagram of the equilibrium recirculation still used for VLE measurements.*

The experiments began with the cleaning of the equipment. For this, about 500 cm^3 of ethanol were introduced in the ebulliometer and the electric resistance located at E (see Fig. 1) was switched on; ethanol was boiled and kept under recirculation at atmospheric pressure for 45 min. After this, ethanol was removed and, with the equipment still hot, the system was left under vacuum at 10 kPa (absolute pressure) for 45 min. Next, the ebulliometer was loaded with about 500 cm^3 of acetone and the electric resistance located at E (see Fig. 1) was turned on; boiling of acetone was maintained under recirculation for 45 min at atmospheric pressure. Thereafter, acetone was removed and before the equipment cooled, vacuum was applied at 10 kPa (absolute pressure) for 45 min. Finally, the ebulliometer was closed at negative pressure (taking manometric pressure as reference), and dry nitrogen was introduced using a separate line[1] until a pressure of about 150 kPa was reached. Before loading the equipment with the substances to be studied, pressure was reduced to 101 kPa; this enables to introduce the substances without contamination. Next, the equip-

ment was closed and charged with dry nitrogen, ready to operate at moderate pressure[1,2,5,16].

The equilibrium still typology is of those in which both phases are recirculated. The ebulliometer operates dynamically by using the vapor lift pump effect. The equipment is made to work in co-currents flow, and thus, the equilibrium condition depends on the contact time between the non-miscible phases: the mass transfer process is a function of residence time. In other words, the equilibrium condition does not only depend on constant temperature and pressure. Consequently, the statistical value of these two properties cannot be taken as the equilibrium criterion; the constant composition of both phases must be also verified.

For this ebulliometer, the input/output flow of each phase was evaluated under different operating conditions and with different binary mixtures[16]. With a flow around 25 cm^3/min it was possible to obtain a composition in each phase that remained practically constant when the renovation time was greater than 75 min. For this reason, the mixtures studied in this work were kept at boiling conditions for 90 min to ensure the stationary state. Once the steady state was reached the vapor and liquid phase were both sampled. Next, the equilibrium was disturbed by adding one of the substances to the mixture in the ebulliometer.

A digital recorder Dostmann Electronic GmbH p655 and two Pt100 probes with ±0.03 K uncertainty were employed. The calibration of the system was done by Dostmann Electronic GmbH. Proper operation of the probes installed in the equipment was verified by measuring the boiling point of distilled water. Pressure was controlled with a pressure regulating valve (Binks MFG Co.) included in the nitrogen supply line. Pressure was measured with a digital transducer 8311 from Burket Fluid Control Systems, with an operating range from 0.0 to 4.0 MPa (uncertainty ±0.004 MPa).

A calibration curve of composition vs. density had been previously obtained at 298.15 K for the systems of this work[5]. Mole fraction (x_i) vs. density (ρ_{ij}) data were verified by the adequate correlation of the excess volumes. The uncertainty was estimated to be less than 0.003 in mole fraction of vapor phase.

RESULTS AND DISCUSSION

Treatment and Prediction of VLE data

The VLE data T-x_1-y_1 for MA1B and EA1B at 0.6 MPa are shown in Table 1. The activity coefficients of the liquid phase (γ_i) for each system were determined by using the following equation:

$$\gamma_i = \frac{y_i p}{x_i p_i^{o}} exp\left[\frac{p}{RT}\left(2\sum_j y_j B_{ij} - \sum_i\sum_j y_i y_j B_{ij}\right) - \frac{p_i^{o} B_{ii}}{RT} + \frac{\left(p_i^{o} - p\right) v_i^{L}}{RT}\right] \quad (1)$$

The virial state equation truncated at the second term was employed and the second virial coefficients (B_{ii}, B_{ij}) were obtained by means of the Hayden and O'Connell[17] method (see Table 1). The liquid molar volumes of pure compounds were estimated from the equation of Yen and Woods[18]. Table 1 includes the γ_i values calculated from VLE data and using Eq. 1 as was previously indicated and by using the properties of Table 2. Literature data[1,20,21] were employed to obtain the Antoine constants (see Table 2). A moderate positive deviation from Raoult's Law can be observed, probably due to a molecular association via hydrogen bonds.

Table 1 *Experimental VLE data for binary systems at 0.6 MPa. Calculated values of second virial coefficients and activity coefficients of the liquid phase*[a]

T / K	x_1	y_1	B_{11} / L/mol	B_{22} / L/mol	B_{12} / L/mol	γ_1	γ_2
methyl acetate (1) + 1-butanol (2)							
452.24	0.000	0.000	-0.4855	-0.5675			1.00
448.61	0.034	0.108	-0.4958	-0.5855	-0.5426	1.05	1.00
448.17	0.036	0.116	-0.4970	-0.5877	-0.5442	1.07	1.00
447.31	0.044	0.140	-0.4995	-0.5921	-0.5474	1.08	1.00
446.09	0.054	0.175	-0.5031	-0.5985	-0.5520	1.12	1.00
444.77	0.068	0.213	-0.5070	-0.6056	-0.5570	1.11	1.00
444.40	0.072	0.224	-0.5081	-0.6076	-0.5584	1.11	1.00
443.38	0.084	0.251	-0.5111	-0.6132	-0.5624	1.08	1.01
441.51	0.100	0.290	-0.5168	-0.6236	-0.5697	1.08	1.02
439.49	0.120	0.343	-0.5230	-0.6353	-0.5778	1.11	1.02
436.74	0.151	0.416	-0.5317	-0.6517	-0.5891	1.12	1.00
435.16	0.166	0.437	-0.5368	-0.6615	-0.5957	1.10	1.03
433.67	0.186	0.476	-0.5416	-0.6710	-0.6021	1.10	1.02
433.02	0.192	0.486	-0.5438	-0.6752	-0.6049	1.11	1.03
427.78	0.259	0.599	-0.5614	-0.7108	-0.6284	1.11	1.01
425.72	0.288	0.635	-0.5686	-0.7257	-0.6380	1.11	1.01
423.03	0.323	0.678	-0.5782	-0.7459	-0.6509	1.11	1.01
417.51	0.418	0.761	-0.5987	-0.7907	-0.6786	1.07	1.03
417.11	0.425	0.762	-0.6002	-0.7941	-0.6807	1.07	1.05
415.14	0.456	0.784	-0.6078	-0.8114	-0.6911	1.06	1.07
413.56	0.492	0.802	-0.6140	-0.8257	-0.6996	1.04	1.10
413.19	0.501	0.801	-0.6155	-0.8291	-0.7017	1.03	1.14
410.07	0.578	0.837	-0.6281	-0.8588	-0.7191	1.00	1.22
406.15	0.659	0.880	-0.6444	-0.8988	-0.7420	1.00	1.26
404.97	0.690	0.893	-0.6495	-0.9115	-0.7491	0.99	1.29
402.47	0.753	0.914	-0.6604	-0.9394	-0.7645	0.98	1.41
401.16	0.790	0.926	-0.6662	-0.9546	-0.7728	0.98	1.49
400.18	0.812	0.937	-0.6707	-0.9662	-0.7791	0.98	1.47
397.34	0.895	0.963	-0.6837	-1.0013	-0.7978	0.98	1.70
396.45	0.920	0.971	-0.6879	-1.0128	-0.8038	0.98	1.81
396.02	0.931	0.974	-0.6899	-1.0184	-0.8067	0.98	1.91
395.56	0.943	0.977	-0.6921	-1.0244	-0.8099	0.98	2.08
395.01	0.956	0.984	-0.6947	-1.0318	-0.8137	0.99	1.91
394.91	0.961	0.986	-0.6952	-1.0331	-0.8144	0.98	1.89
394.33	0.974	0.990	-0.6979	-1.0409	-0.8184	0.99	2.07
394.10	0.979	0.991	-0.6991	-1.0441	-0.8200	0.99	2.32
393.01	1.000	1.000	-0.7043	-1.0592		1.00	

[a] Expanded uncertainties U(0.95 level of confidence) are: U(T)=0.03 K, U(p)= 0.004 MPa, $U(x_1)=U(y_1)=0.003$

VLE data were tested for thermodynamic consistency by using the point-to-point test of Van Ness et al.[7] Results indicate that the experimental data for MA1B and EA1B binary systems at 0.6 MPa satisfy the Fredenslund et al.[8] criterion. Results of the Redlich-Kister and Herington test were respectively: D=75.97 > 10% and ABS(D-J)=53.36 > 10 for MA1B; D=59.50 > 10% and ABS(D-J)=46.83 > 10 for EA1B. Therefore both system fails with area test. In addition, bibliographic[3-5] data were employed for data verification of this work, and for this purpose all data were correlated to a polynomial equation presented in a previous paper[16] as follows,

$$y_1 - x_1 = x_1(1-x_1)\sum_{k=0} A_k Z_T^k \qquad \text{with} \qquad Z_T = \frac{x_1}{x_1 + R_T(1-x_1)} \quad (2)$$

being A_k and R_T adjustable parameters. The fitting curves and experimental data are shown in Figs. 2 and

3. A significant compressive effect can be observed as a consequence of the applied pressure. Data from this study agrees with that in literature[3-5].

Table 1 *Continued*[a]

T / K	x_1	y_1	B_{11} / L/mol	B_{22} / L/mol	B_{12} / L/mol	Υ_1	Υ_2
ethyl acetate (1) + 1-butanol (2)							
452.24	0.000	0.000	-0.6539	-0.5675			1.00
451.47	0.008	0.018	-0.6566	-0.5712	-0.6220	1.13	1.00
451.31	0.013	0.025	-0.6571	-0.5720	-0.6227	0.97	1.00
450.82	0.018	0.044	-0.6588	-0.5744	-0.6247	1.24	1.00
450.66	0.023	0.049	-0.6594	-0.5752	-0.6253	1.08	1.00
450.11	0.034	0.073	-0.6613	-0.5779	-0.6276	1.10	1.00
449.13	0.050	0.108	-0.6648	-0.5828	-0.6317	1.13	1.00
447.81	0.069	0.147	-0.6695	-0.5896	-0.6373	1.14	1.01
446.97	0.089	0.180	-0.6726	-0.5939	-0.6409	1.10	1.01
445.99	0.105	0.214	-0.6761	-0.5991	-0.6452	1.13	1.01
445.12	0.123	0.245	-0.6793	-0.6037	-0.6490	1.12	1.01
444.25	0.139	0.268	-0.6825	-0.6084	-0.6528	1.11	1.02
443.27	0.158	0.298	-0.6861	-0.6138	-0.6572	1.10	1.03
441.18	0.202	0.365	-0.6940	-0.6255	-0.6666	1.10	1.04
437.30	0.284	0.478	-0.7089	-0.6483	-0.6848	1.11	1.05
436.66	0.301	0.506	-0.7114	-0.6522	-0.6878	1.12	1.03
434.05	0.363	0.570	-0.7218	-0.6685	-0.7005	1.10	1.06
431.25	0.433	0.642	-0.7331	-0.6869	-0.7146	1.10	1.07
429.17	0.496	0.691	-0.7417	-0.7010	-0.7253	1.08	1.10
427.48	0.565	0.738	-0.7488	-0.7129	-0.7341	1.05	1.13
426.96	0.584	0.749	-0.7527	-0.7195	-0.7390	1.05	1.16
425.24	0.649	0.790	-0.7584	-0.7292	-0.7462	1.02	1.20
424.6	0.674	0.808	-0.7612	-0.7340	-0.7497	1.02	1.20
423.98	0.701	0.829	-0.7639	-0.7387	-0.7531	1.02	1.18
423.83	0.709	0.827	-0.7645	-0.7398	-0.7539	1.01	1.24
423.49	0.727	0.835	-0.7660	-0.7424	-0.7558	1.00	1.27
423.07	0.750	0.854	-0.7679	-0.7456	-0.7581	1.00	1.24
422.52	0.777	0.863	-0.7703	-0.7499	-0.7612	0.99	1.33
422.05	0.798	0.879	-0.7724	-0.7536	-0.7639	0.99	1.31
421.89	0.806	0.887	-0.7731	-0.7548	-0.7648	0.99	1.28
421.30	0.830	0.899	-0.7757	-0.7595	-0.7681	0.99	1.33
420.02	0.880	0.925	-0.7814	-0.7698	-0.7755	0.99	1.45
418.70	0.938	0.957	-0.7874	-0.7807	-0.7831	0.99	1.68
418.00	0.964	0.976	-0.7906	-0.7866	-0.7873	0.99	1.64
417.82	0.976	0.983	-0.7915	-0.7881	-0.7883	0.99	1.76
417.58	0.982	0.988	-0.7926	-0.7901	-0.7898	1.00	1.67
417.33	0.990	0.994	-0.7937	-0.7923	-0.7912	1.00	1.51
417.02	1.000	1.000	-0.7951	-0.7923		1.00	

[a] *Expanded uncertainties U(0.95 level of confidence) are: U(T)=0.03 K, U(p)= 0.004 MPa, U(x_1)=U(y_1)=0.003*

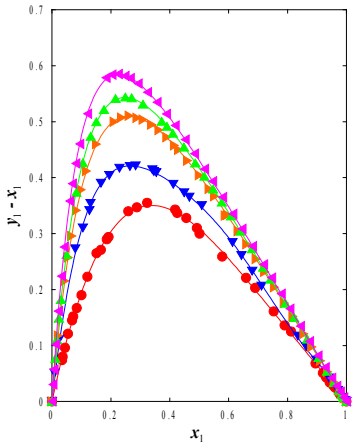

Fig. 2 *Plot of experimental (y_1–x_1) vs. x_1 data for MA1B (●) at 0.6 MPa. Literature data at 74.66 (◀) and 127.99 (▶) kPa by Susial and Ortega[3], 101.3 (▲) kPa by Ortega and Susial[3], and 0.3 (▼) MPa by Susial et al.[5] with fitting curves.*

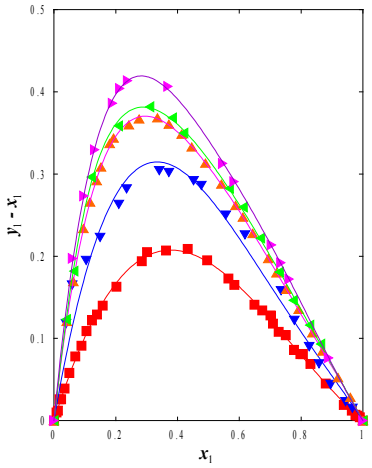

Fig. 3 *Experimental points of (y_1–x_1) vs. x_1 for EA1B (■) at 0.6 MPa. Literature data at 70.5 (▶) and 94.0 (◀) kPa by Darwish and Al-Khateib[3], 101.3 (▲) kPa by Ortega et al.[4] and 0.3 (▼) MPa by Susial et al.[5] with fitting curves.*

Next, considering the excess Gibbs function,

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (3)$$

the activity coefficients were correlated with the following thermodynamic models: the Wilson[22] model, the NRTL[23] model and the UNIQUAC[24] model.

In the Wilson model[22] the excess Gibbs function is represented by the following equation,

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \quad \text{with} \quad \Lambda_{ij} = \frac{V_j}{V_i} exp\left(-\frac{\Delta\lambda_{ij}}{RT}\right) \qquad (4)$$

where the Wilson functions Λ_{ij} depends on the adjustable interaction energy parameters $\Delta\lambda_{ij}$ and the molar volumes of pure components, V_i and V_j, which have been calculated with the Yen and Woods[18] equation (see Table 2).

The NRTL model[23] applies the following equation for the excess Gibbs free energy,

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{G_{21}\tau_{21}}{x_1 + G_{21}x_2} + \frac{G_{12}\tau_{12}}{x_2 + G_{12}x_1}\right) \quad \text{with } G_{ij} = exp(-\alpha_{ij}\tau_{ij}) \text{ and } \tau_{ij} = \frac{\Delta g_{ij}}{RT} \qquad (5)$$

where $\alpha_{ij}=\alpha_{ji}$ is a non-random parameter of the mixture which is associated with molecular organization. The adjustable parameters, τ_{ij}, depend on a temperature function with interaction energies Δg_{ij} between an *i-j* pair of molecules.

In the UNIQUAC model[24] the excess Gibbs function is composed of the combinatorial and residual parts as follow,

$$\frac{G^E}{RT} = \frac{G^E_{Comb}}{RT} + \frac{G^E_{Resid}}{RT} \qquad (6)$$

$$\frac{G^E_{Comb}}{RT} = x_1 \ln\left(\frac{\Phi_1}{x_1}\right) + x_2 \ln\left(\frac{\Phi_2}{x_2}\right) + \left(\frac{Z}{2}\right)\left[q_1 x_1 \ln\left(\frac{\theta_1}{\Phi_1}\right) + q_2 x_2 \ln\left(\frac{\theta_2}{\Phi_2}\right)\right] \qquad (7)$$

Table 2 *Properties of literature[19] and from this work.*

Tc[19]	Pc[19]	RD[19]	μ[19]	Zc[19]	A	B	C	V_+	r	q
K	MPa	Å	D					L/mol		
methyl acetate										
506.80	4.69	2.996	1.679	0.254	6.7347	1529.38	6.59	0.0798	2.8042	2.576
ethyl acetate										
523.25	3.83	3.468	1.781	0.252	7.0337	1869.43	-22.19	0.0985	3.4786	3.116
1-butanol										
562.93	4.4127	3.251	1.66	0.259	6.4296	1261.325	106.43	0.0936	3.4543	3.052

$$log_{10}\, P_i^o/\text{kPa} = A - \frac{B}{T/\text{K} - C}$$

Table 3 *Correlation parameters of G^E/RT vs. x_1, mean absolute deviations and standard deviations*

model	parameters		MAD(y_1)	MAD(T)/K	SD(γ_1)	SD(γ_2)	SD(G^E/RT)
methyl acetate (1) + 1-butanol (2) at 0.6 MPa							
Wilson[22]	$\Delta\lambda_{12}$ = -2824.4 J·mol^{-1}	$\Delta\lambda_{21}$ = 6962.7 J·mol^{-1}	0.019	2.04	0.11	0.14	0.015
NRTL (α = 0.47)[23]	Δg_{12} = 5996.6 J·mol^{-1}	Δg_{21} = -2183.6 J·mol^{-1}	0.018	2.04	0.10	0.12	0.018
UNIQUAC (Z = 10)[24]	Δu_{12} = 3935.6 J·mol^{-1}	Δu_{21} = -2104.9 J·mol^{-1}	0.020	2.07	0.11	0.14	0.016
ethyl acetate (1) + 1-butanol (2) at 0.6 MPa							
Wilson[22]	$\Delta\lambda_{12}$ = -1693.4 J·mol^{-1}	$\Delta\lambda_{21}$ = 4206.9 J·mol^{-1}	0.013	0.53	0.07	0.09	0.010
NRTL (α = 0.47)[23]	Δg_{12} = 4396.8 J·mol^{-1}	Δg_{21} = -1896.1 J·mol^{-1}	0.013	0.61	0.07	0.08	0.012
UNIQUAC (Z = 10)[24]	Δu_{12} = 3185.2 J·mol^{-1}	Δu_{21} = -1922.2 J·mol^{-1}	0.014	0.57	0.07	0.09	0.011

$$\text{MAD}(F) = \frac{1}{n-2}\sum_1^n \left|F_{\text{exp}} - F_{\text{cal}}\right|;\quad \text{SD}(F) = \sqrt{\frac{\sum_1^n (F_{\text{exp}} - F_{\text{cal}})^2}{n-2}};\qquad F \equiv y_1, T, p, \gamma_1, \gamma_2, G^E/RT$$

$$\frac{G^E_{Resid}}{RT} = -q_1 x_1\, ln(\theta_1 + \theta_2\tau_{21}) - q_2 x_2\, ln(\theta_2 + \theta_1\tau_{12}) \tag{8}$$

$$\Phi_i = \frac{x_i r_i}{x_i r_i + x_j r_j};\qquad \theta_i = \frac{x_i q_i}{x_i q_i + x_j q_j}\quad \text{and}\quad \tau_{ij} = exp\left(-\frac{\Delta u_{ij}}{RT}\right) \tag{9}$$

being Z the coordination number, **Φ** the molecular fraction of segments and θ the molecular fraction of surfaces. t_{ij} are the adjustable parameters and Δu_{ij} represents the average interaction energy of molecules. The volume and area of groups of van der Waals are used to calculate r and q, volume and area parameters, of the UNIQUAC model (see Table 2).

The adjustable parameters in each of these models (Table 3) were obtained using the Nelder and Mead method[25]. Deviation in the sum of the squares of activity coefficient was minimized for both substances during optimization of the parameters. For MA1B the NRTL equation[23] yielded the lowest mean absolute deviations (MAD) as well as standard deviations (SD) between experimental and calculated values for temperature and vapor compositions. However, the Wilson model[22] yields the best correlation for EA1B, with the lowest MAD in both temperature and vapor phase mole fraction.

Temperature, pressure, vapor phase composition and the calculated activity coefficients were compared with the theoretical predictions of VLE obtained with the ASOG model[9], the mod. UNIFAC-Lyngby model[10] proposed by Larsen et al., the original UNIFAC model[8] with Hansen et al. parameters[11] and the mod. UNIFAC-Dortmund model[12] proposed by Gmehling et al.

In the group contribution models the activity coefficient of the liquid phase are calculated with the following equation:

$$ln\,\gamma_i = ln\,\gamma_i^{Comb} + ln\,\gamma_i^{Resid} \tag{10}$$

Differences in the models arise from the interpretation given in each one about the combinatorial and residual contributions. In the ASOG[9] model the combinatorial part is obtained by using the Flory-Huggins equation

$$ln\,\gamma_i^{Comb} = 1 + ln\left(\frac{\vartheta_i^c}{\sum_j x_j \vartheta_j^c}\right) - \frac{\vartheta_i^c}{\sum_j x_j \vartheta_j^c} \tag{11}$$

being ϑ_j^c the number of atoms (non hydrogen atoms) in the molecule *j*. The residual part is determined as follow,

$$ln\,\gamma_i^{Resid} = \sum \vartheta_{ki}\left(ln\,\Gamma_k - ln\,\Gamma_k^i\right) \tag{12}$$

being ϑ_{ki} the number of atoms (non hydrogen atoms) in group *k* in molecule *i*, Γ_k the group activity coefficient of group *k* and Γ_k^i the activity coefficient of group *k* in a standard state (pure component *i*). The ASOG model considers the group activity coefficient is given by the Wilson equation as follows,

$$ln\,\Gamma_k = 1 - ln\left(\sum_l X_l a_{lk}\right) - \sum_l \frac{X_l a_{lk}}{\sum_m X_m a_{lm}} \tag{13}$$

where X_l represent the group fraction of group *l* in the liquid solution. In the above expression (Eq. 13) the summations extend over all groups and a_{lk}, a_{lm} are the group interaction parameters.

The UNIFAC[8,10-12] models are generally based on the equations of the UNIQUAC model for the combinatorial part, being for the clasical UNIFAC[8] model,

$$ln\,\gamma_i^{Comb} = ln\left(\frac{\Phi_i}{x_i}\right) + q_i\left(\frac{Z}{2}\right) ln\left(\frac{\theta_i}{\Phi_i}\right) + l_i - \left(\frac{\Phi_i}{x_i}\right)\sum_j x_j l_j \tag{14}$$

θ represents the molecular surface area fraction (see Eq. 9), **Φ** is the molecular volume fraction (see Eq. 9) and the pure-component lattice parameter, *l,* is function of van der Waals surface area (*q*) and van der Waals volume (*r*). For the mod. UNIFAC-Larsen[10] model,

$$ln\,\gamma_i^{Comb} = ln\left(\frac{\psi_i}{x_i}\right) + 1 - \frac{\psi_{i_i}}{x_i} \tag{15}$$

Table 4 *Results of predictions using group contribution models and PR-EOS*

	mod. UNIFAC-Lyngby[10] OH/COOC	UNIFAC-1991[8,11] OH/CCOO	mod. UNIFAC-Dortmund[12] OH/CCOO	ASOG-1979[9] OH/COO	PR[13]	PRSV[13,15]	PRWS[13,14]	PRSVWS[13-15]
			methyl acetate (1) + 1-butanol (2) at 0.6 MPa					
MAD(y_1)	0.011	0.028	0.023	0.046	0.007	0.014	0.012	0.013
MAD(T)/K	0.93	3.32	2.76	5.93	0.82	0.47	0.37	0.45
MAD(p)/MPa	0.011	0.044	0.036	0.078				
MPD(γ_1)	4.12	17.81	12.78	32.96				
MPD(γ_2)	12.75	4.13	3.70	4.31				
			ethyl acetate (1) + 1-butanol (2) at 0.6 MPa					
MAD(y_1)	0.012	0.020	0.012	0.023	0.008	0.008	0.012	0.006
MAD(T)/K	1.17	2.16	0.70	2.39	0.74	0.38	0.55	0.26
MAD(p)/MPa	0.011	0.028	0.009	0.031				
MPD(γ_1)	5.33	17.45	6.16	21.18				
MPD(γ_2)	10.74	4.13	3.51	4.2				

$$\mathrm{MPD}(F) = \frac{100}{n-2}\sum_{1}^{n}\frac{\left|F_{\exp} - F_{\mathrm{cal}}\right|}{F_{\exp}}$$

where ψ represent the modified group volume fraction. For the mod. UNIFAC-Gmehling[12] model,

$$\ln\gamma_i^{Comb} = \ln\delta_i + 1 - \delta_i - q_i\left(\frac{Z}{2}\right)\left[\ln\left(\frac{\Phi_i}{\eta_i}\right) + 1 - \frac{\Phi_i}{\eta_i}\right] \qquad (16)$$

being η the modified molecular surface area fraction and δ the modified molecular volume fraction. In the UNIFAC models, the residual part of the activity coefficient (Eq. 12 being ϑ_{ki} the number of groups of type k in molecule i,) is replaced by the solution-of-groups concept. The following equation is used for the group activity coefficient,

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \Theta_m\xi_{mk}\right) - \sum_m\frac{\Theta_m\xi_{mk}}{\sum_n\Theta_n\xi_{mn}}\right] \qquad (17)$$

where Q_k is the van der Waals surface area of group k, Θ represents the group surface area fraction and ξ is defined by an equation that includes the group contribution parameters. Both Θ and ξ have different expressions in the UNIFAC versions.

Table 4 shows prediction results from the group contribution models. Figs. 4 and 5 show the experimental data and the fitting curves of predictions when using these group contribution models.

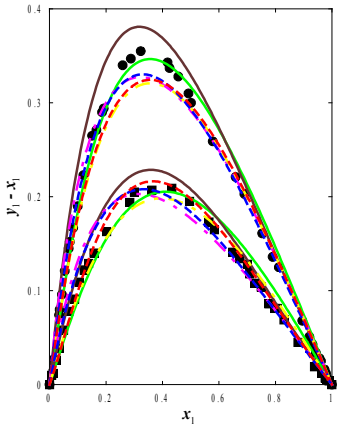

Fig. 4 *Plot of experimental VLE data for MA1B (●) and EA1B (■) at 0.6 MPa together with predictions of mod. UNIFAC-Larsen[10] (— —, green color line); mod. UNIFAC-Gmehling[12] (— —, dark brown color line); PR-EOS[13] (— —, blue color line); PRSVWS-EOS[13-15] (—, red color line); PRWS-EOS[13,14] (— • — •, magenta color line) and PRSV-EOS[13,15] (— • — •, yellow color line).*

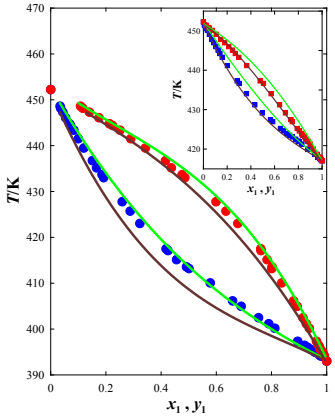

Fig. 5 *Representation of experimental T-x_1-y_1 data for the binary systems MA1B (●, ●) and EA1B (■, ■) at 0.6 MPa together with (green color lines) mod. UNIFAC-Larsen[10] and (dark brown color lines) mod. UNIFAC-Gmehling[12] predictions.*

In general terms, the best prediction for γ_i was obtained with the mod. UNIFAC model proposed by Gmehling et al.[12] However, most accurate results in composition were found using the mod. UNIFAC model proposed by Larsen et al.[10] The Gmehling et al.[12] version also returns a good prediction for EA1B. The UNIFAC model[8] with the Hansen et al.[11] parameters and the ASOG model[9] yield poor predictions and higher deviations in pressure and temperature, being the mean proportional deviation (MPD) for the prediction of the vapor phase mole fraction, respectively: 9% and 16% for MA1B and 12% and 14% for EA1B.

Results indicate that with the current parameters, some of the group contribution models do not reproduce adequately the VLE at moderate pressures; however, it is often observed that predictions given by the models proposed by Larsen et al.[10] and Gmehling et al.[12] are more successful.

Modelling with PR-EOS

The reliability in VLE modelling for mixtures that have hydrogen bonding via proton donor and proton acceptor is low if proper binary interaction parameters are not employed, especially at high pressure. Consequently, the prediction of phase equilibrium can be done by using EOS; if necessary, using the appropriate mixing rules. This is why in this work the

PR-EOS[13] using quadratic mixing rules and the WS[14] mixing rules have been used. The adjustable parameter employed by SV[15] in the attractive term was also applied. The PR-EOS[13] has the following equation:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (18)$$

where p, T and R represent pressure, temperature and the ideal gas constant. Furthermore, a is the temperature-dependant attractive parameter and b is the temperature-independent repulsive parameter, which are determined by the following equations:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (19)$$

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (20)$$

being T_c and P_c respectively, the critical temperature and pressure of each pure component. The classical correlation for temperature-dependant β function is:

$$\beta(T) = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2 \quad (21)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (22)$$

When the SV[15] equation is employed, in PRSV-EOS m is modified according to Eq. 23, where κ0 is a function of the acentric factor, and ω and κ1 are adjustable parameters for each pure component, as follows:

$$m = \kappa 0 + \kappa 1\left(1 + T_r^{0.5}\right)\left(0.7 - T_r\right) \quad (23)$$

$$\kappa 0 = \left(0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3\right) \quad (24)$$

The classical mixing rules, with the binary interaction parameter $k1_{ij}$ and $k2_{ij}$ were employed. Therefore, the a_m and b_m parameters were:

$$a_m = \sum_i^N \sum_j^N x_i x_j \left(a_i a_j\right)^{0.5} \left(1 - k1_{ij}\right) \quad (25)$$

$$b_m = \sum_i^N \sum_j^N x_i x_j \left(\frac{b_i + b_j}{2}\right) \left(1 - k2_{ij}\right) \quad (26)$$

However, for non-ideal mixtures like those this paper the quadratic mixing rules can not to be adequate. Therefore, the WS[14] mixing rules were also applied. The WS mixing rules are given by:

$$b_m = \frac{\sum_i^N \sum_j^N x_i x_j \left(b_{ij} - a_{ij}/(RT)\right)}{\left(1 - A_\infty^E/(CRT) - \sum_i^N x_i a_i/(RTb_i)\right)} \quad (27)$$

$$\left(b_{ij} - a_{ij}/(RT)\right) = \frac{1}{2}\left[\left(b_i - a_i/(RT)\right) + \left(b_j - a_j/(RT)\right)\right]\left(1 - k_{ij}\right) \quad (28)$$

$$a_m = b_m\left(\sum_i^N x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C}\right) \quad (29)$$

where C is a numerical constant equal to and $k_{ij} = k_{ji}$ is the binary interaction parameter for each system. A_∞^E is an excess Helmholtz free energy model at infinite pressure that can be equated to a low-pressure excess Gibbs energy model[26]. In this study, the NRTL model[23] was used, as follows:

$$\frac{A_\infty^E}{RT} = \sum_i^N x_i \frac{\sum_j^N x_j G_{ji}\tau_{ji}}{\sum_r^N x_r G_{ri}} \quad \text{with} \quad G_{ij} = exp\left(-\alpha_{ij}\tau_{ij}\right) \quad (30)$$

being $\alpha_{ij}=\alpha_{ji}$ as well as τ_{ij} and τ_{ji} adjustable parameters to obtain agreement between theory and experiment for VLE. The non-randomness parameter (α) of the NRTL model[23] was fixed to 0.47 in this study.

Vapor pressures reported in literature[1,20,21] were used to obtain the k1 adjustable parameter of SV[15] using the PR equation. The critical properties employed (see Table 2) were taken from Daubert and Danner[19]. SD was used for minimization parameters.

The Matlab program from Martin et al.[27] is an educational program with a library of different EOS's including PR[13], PRSV[13,15], PRWS[13,14] and PRSVWS[13-15]. We developed a FORTRAN code, based on a simplified version of the above-mentioned Matlab program, but related by separate to PR-EOS[13], PRSV-EOS[13,15], PRWS-EOS[13,14] and PRSVWS-EOS[13-15].

Martin's Matlab program[27] uses inner functions, such as fzero, fsolve or fminsearch. These inner math functions of Matlab are robust and reliable but they imply long times of computer use. We substitute them for our own FORTRAN subroutines that lead us to similar accuracy. At the same time, we change Matlab programs structure, avoiding unnecessary loops, and eliminating redundant assignment sentences, improving our FORTRAN code in speed of execution.

Using these new programs, our results are k1=0.0234 (k1=0.05791[28]) with SD=3.27 and MPD=1.6 for methyl acetate; k1=0.0692 (k1=0.06464[28]) with SD=5.40 and MPD=1.2 for ethyl acetate and k1=0.4874 (k1=0.33431[15]) with SD=4.43 and MPD=1.7 for 1-butanol.

When comparing the results with those cited in the literature[15,28], a good match for the ethyl acetate and discrepancies in the other two substances is observed. However, while in the case of 1-butanol the temperature range used in this study for correlations is wider, in all cases the number of data used in this paper to obtain the SV parameter, is also much higher; this, along with the considerable differences in both the critical properties and acentric factor used in the case of methyl acetate and 1-butanol, can explain the differences.

The binary interaction parameters for the systems of this work were treated as fitting parameters of VLE data. The physical properties from literature[19] were used for data processing by PR-EOS[13] considering the classical b(T) function for the attractive interaction and also by PRSV-EOS[13,15] using the SV modification. In both cases, the numerical values of $k1_{ij}$, $k2_{ij}$ with quadratic mixing rules were obtained. In addition, the numerical values of $k1_{ij}$, $k2_{ij}$ were also calculated when the WS[14] mixing rules and κ_{ij}, τ_{ij}, τ_{ji} parameters were employed in PRWS-EOS[13,14] and PRSVWS-EOS[13-15]. All calculated values were obtained by using the FORTRAN programs above mentioned.

To systematize data analysis of the MA1B and EA1B binary systems, it was decided to obtain the acentric factor, since the models are highly dependent on this parameter. Vapor pressures from literature[1,20,21] and the critical properties of Daubert and Danner[19] were used. The Nelder and Mead method[25] was employed for data correlation. Results were: ω=0.328 (ω=0.3253[19]) with SD=0.0004; ω=0.362 (ω=0.3611[19]) with SD=0.0012 and ω=0.599 (ω=0.5945[19]) with SD=0.0003, for methyl acetate, ethyl acetate and 1-butanol, respectively.

To predict the compositions of the MA1B and EA1B binary systems at 0.6 MPa it was considered the p-x_1 bubble point scheme. The simplex method[25] was used, and the objective function (OF) was as follows:

$$OF = \frac{1}{U(T)}\sum_{1}^{n}\left|T^{exp} - T^{calc}\right| + \frac{1}{U(y_1)}\sum_{1}^{n}\left|y_1^{exp} - y_1^{calc}\right| \qquad (31)$$

Often for the Eq. 31 the maximum-likelihood principle is considered. Therefore, the standard deviations (SD) are employed. However, in this work uncertainties U(T); U(y1) have been used in Eq. 31. This amendment arises when considering that SD is a standard uncertainty, and therefore, its use may be sufficient when the experimental data are correlated with the equations of the thermodynamic-mathematical models that enable the production of adjustable parameters. In addition, when the models can predict VLE data, it seems more reasonable to consider a higher level of confidence. That is why we have selected the expanded uncertainty, because in this way we ensure a higher quality prediction by the models.

Temperature and composition of vapor phase were compared with the theoretical predictions of VLE using the PR-EOS[13], PRSV-EOS[13,15], PRWS-EOS[13,14] and PRSVWS-EOS[13-15]. Table 4 presents the global results obtained for MAD(y_1) and MAD(T). On the other side, the results for binary interaction parameters and objective function obtained using PR-EOS[13] were kl=0.0345, k2=-0.0354, OF=2.9 for MA1B system, and k1=0.0319, k2=0.0109, OF=2.8 for EA1B system; using PRSV-EOS[13,15] the results were k1=0.0231, k2=0.0234, OF=2.0 for MA1B system, and k1=0.0099, k2=0.0901, OF=1.6 for EA1B system; using PRWS-EOS[13,14] the results were kij=0.1519, α=0.47, τ_{ij}=-0.7693, τ_{ji}=1.4983, OF=1.6 for MA1B system, and kij=0.0588, α=0.47, τ_{ij}=-0.2311, τ_{ji}=0.8075, OF=2.3 for EA1B system. and using PRSVWS-EOS[13-15] the results were kij=0.1269, α=0.47, τ_{ij}=0.0183, τ_{ji}=0.0258, OF=1.9 for MA1B system, and kij=0.4896, α=0.47, τ_{ij}=-0.4529, τ_{ji}=-0.7123, OF=1.1 for EA1B system. Figs. 4, 6, 7 show the experimental data and the correlation curves obtained by using these EOS.

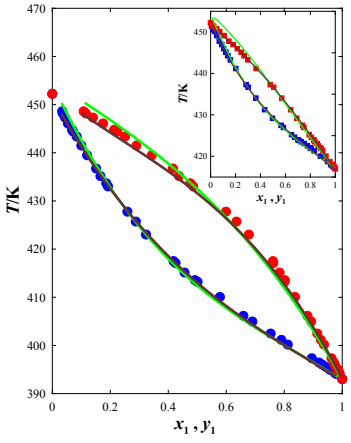

Fig. 6 *Representation of experimental T-x_1-y_1 data for the binary systems MA1B (●,●) and EA1B (■,■) at 0.6 MPa. Predictions represented by green color lines and dark brown color lines using PR-EOS[13] and PRSVWS-EOS[13-15] respectively.*

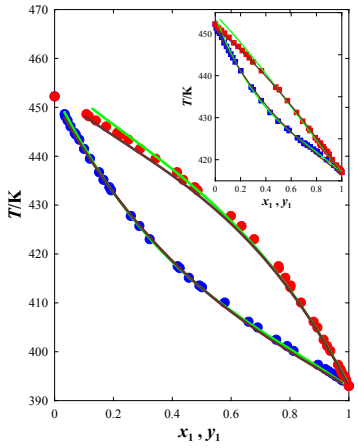

Fig. 7 *Representation of experimental T-x_1-y_1 data for the binary systems MA1B (●,●) and EA1B (■,■) at 0.6 MPa. Predictions represented by green color lines and dark brown color lines using PRWS-EOS[13,14] and PRSV-EOS[13,15] respectively.*

Results indicate that the best overall prediction of the experimental VLE data in both systems is obtained with the PRSVWS-EOS model[13-15] as can be seen in Table 3 and Figs. 4 and 6. The PR-EOS model[13] returns reasonably good predictions when considering the composition of the vapor phase (see Fig. 4). The prediction of temperature for both systems is poor (see Fig. 6), when compared to the results obtained with models that use the SV equation[15]. This can be observed in Figs. 4, 6, 7. On the other hand, in Fig. 4 a similar prediction of the composition of the vapor phase is observed with the PR-EOS[13] and PRSVWS-EOS[13-15] models. Fig. 6 shows that best temperature predictions are archived by using the SV equation[15]. A similar behavior can be seen in Figs. 4 and 7.

Therefore, in general, when the SV equation is employed, better predictions are obtained than when the PR model is used. However, this does not seem enough to describe the thermodynamic behavior, nor for VLE calculations. Nevertheless, when using the WS mixing rules, results show that the PRSVWS model can satisfactorily represent the VLE, for non-ideal polar organic systems, such as the ester + alcohol mixtures of this work.

CONCLUSIONS

Experimental data for the binary mixtures methyl acetate/1-butanol and ethyl acetate/1-butanol at 0.6 MPa were obtained. The thermodynamic consistency was verified by using the point-to-point test. Results satisfy the global criterion of this test. In addition, data obtained in this work shows good agreement with bibliographic data.

Predictions by using the ASOG and UNIFAC group contribution models were obtained. Results show that the mod. UNIFAC-Lingby version returns satisfactory and best predictions, although the mod. UNIFAC-Dortmund model returns a good prediction of EA1B.

Experimental data were correlated with PR-EOS using quadratic mixing rules and the Wong-Sandler mixing rules. The effect on the attractive term using

the Stryjek-Vera parameter was also verified. Globally, results show the best predictions were obtained by using the Stryjek-Vera parameter and Wong-Sandler mixing rules simultaneously.

AUTHOR INFORMATION

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The authors declare no competing financial interest.

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