
Isobaric VLE for the binary systems Isobutyl Acetate + Methanol or +1-Propanol at 0.15 MPa

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ELV isobárico para el binario de sistemas Acetato de isobutil + Metanol o Acetato de Isobutil + 1-Propanol a 0,15 MPa

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RESUMEN

Se ha determinado el Equilibrio Líquido-Vapor a 0.15 MPa para las mezclas binarias Acetato de Isobutilo + Metanol y Acetato de Isobutilo + 1-Propanol utilizando un ebullicómetro de acero inoxidable en el que las dos fases se recirculan. Los datos isobáricos T-x-y son informados, incluyendo el punto azeotrópico del sistema binario Acetato de Isobutilo + 1-Propanol. Se han realizado los cálculos considerando la fase vapor no ideal, empleando los segundos coeficientes de virial obtenidos al utilizar el método de Hayden-O'Connell. La correlación de Yen-Woods fue empleada para los cálculos del factor de Poynting. Los coeficientes de actividad de la fase líquida han sido obtenidos. La consistencia termodinámica de los sistemas fue verificada con el test punto-a-punto of Van Ness. Los modelos de contribución por grupos ASOG y diferentes versiones de UNIFAC fueron utilizados.

Palabras clave: ASOG; Azeótropo; Sistemas Binarios; UNIFAC; Equilibrio Líquido-Vapor.

SUMMARY

Vapor-Liquid Equilibria were measured at 0.15 MPa for binary mixtures of Isobutyl Acetate + Methanol and Isobutyl Acetate + 1-Propanol using a stainless-steel ebulliometer in which both phases are recirculated. The isobaric T-x-y data are reported, including the azeotropic point for the binary mixture of Isobutyl Acetate + 1-Propanol. Calculations of the non-ideality of the vapor phase were made with the second virial coefficients determined by the Hayden and O'Connell method. The Yen and Woods correlation was employed for the Poynting factor calculations. The activity coefficients of the liquid phase have been calculated.

Thermodynamic consistency with the point-to-point test of Van Ness were examined on these systems. The ASOG and several UNIFAC group contribution models were used.

Keywords: ASOG; Azeotrope; Binary system; UNIFAC; Vapor-Liquid Equilibria.

RESUM

S'ha determinat el Equilibri Líquid-Vapor a 0.15 MPa per a les mesclures binàries Acetat de isobutil + Metanol i Acetat de Isobutil + 1-Propanol utilitzant un ebullicòmetre d'acer inoxidable en el que les dues fases es recirculen. S'introdueixen les dades isobàriques T-x-y, incloent el punt azeotrópic del sistema binari Acetat de Isobutil + 1-Propanol. S'han realitzat els càlculs considerant la fase de vapor no ideal, emprant els segons coeficients de virial obtinguts en utilitzar el mètode de Hayden-O'Connell. La correlació de Yen-Woods va ser emprada per als càlculs del factor de Poynting. S'han obtingut els coeficients d'activitat de la fase líquida. La consistència termodinàmica dels sistemes va ser verificada amb el test punt-a-punt de Van Ness. Es van utilitzar els models de contribució per grups ASOG i diferents versions de UNIFAC.

Paraules clau: ASOG, azeòtrop, sistemes binaris, UNIFAC, equilibri líquid-vapor.

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INTRODUCTION

The modelling of phase equilibria have been one of the most compelling problems of chemical engineering. Even though a great variety of methods have been developed to understand and design the different separation processes of substances, these models exhibit certain limitations in their predictions, mostly for complex mixtures and for those processes that take place at over-atmospheric pressures.

Distillation is one of the most important processes in chemical industries. As a consequence of the limitations presented by the prediction models, experimental vapor liquid equilibria (VLE) data are needed for the dimensioning of the equipments required for this unit operation. This is particularly necessary for substances such as esters or alcohols, which must be provided with high purity degrees for many processes and industries.

This is the reason why, using like in previous works (Susial et al., 2010a) a dynamic ebullimeter, we have determined VLE data corresponding to the systems isobutyl acetate + methanol (IBAM) and isobutyl acetate + 1-propanol (IBAP) at 0.15 MPa.

We have only found the system IBAM at 101.3 kPa in literature (Resa et al., 1998). The azeotrope of the IBAP system has not been found to be described in bibliography. Consequently, in order to verify the quality of the experimental data obtained in this work, we proceeded to their thermodynamic validation by applying the test of Van Ness (Van Ness et al., 1973). After this, the experimental data were employed to test the predictive capacity of the group contribution models ASOG (Kojima and Tochigi, 1979) and UNIFAC (Gmehling et al., 1993; Hansen et al., 1991; Larsen et al., 1987).

EXPERIMENTAL SECTION

Chemicals.

The chemicals used in this work were purchased from Panreac Química S.A. Methanol and 1-Propanol were high-purity grade, 99.9 and 99.8%, respectively; but the Isobutil Acetate employed was purum grade higher than 99%. All chemicals were used without further purification. The properties of the pure compounds were measured in this study, and the comparison with literature data is shown in Table 1. The refractive index of the pure compounds was measured at 298.15 K by a Zusi Abbe refractometer, model 315RS, with an accuracy of ± 0.0002 units. The densities of pure chemicals were measured at 298.15 K using a Kyoto Electronics DA-300 vibrating tube density meter with an accuracy of $\pm 0.1 \text{ kg}\cdot\text{m}^{-3}$.

Apparatus and Procedures.

The apparatus used was a stainless-steel ebullimeter with the recirculation of both phases, which has been described previously (Susial et al., 2010a). This equipment has a heating unit which ensures the complete mixing of the liquid mixtures. This design also prevents liquid drop entrainment and partial condensation of the vapor phase. Temperature was measured with $\pm 0.02 \text{ K}$ of uncertainty

using a Pt-100 probe with a digital Dostmann Electronic P655 thermometer. The Pt-100 probes were calibrated by Dostmann Electronic GmbH following laboratory standards calibration procedures, according to the international NPL and NIST standards. Pressure was maintained at 0.15 MPa through a controller valve of Binks MFG Co. Working pressure was measured using a pressure transmitter with a 0.0 to 4.0 MPa range (uncertainty of $\pm 0.002 \text{ MPa}$) of Burket Fluid Control Systems, model 8311. Equilibrium was usually reached after 1.5 h. After this, small volumes of samples from the equilibrium phases were collected in external sealed recipients and were analyzed with a density meter at 298.15 K. A calibration curve composition vs. density had been previously obtained. The greatest uncertainty found for these systems with this method of composition analysis was better than 0.002 units in the vapour and liquid phase mole fraction.

Table 1: Physical properties of pure substances and literature data.

	purity	T _{bp}	ρ (298.15K)	n_D (298.15K)
		K	($\text{kg}\cdot\text{m}^{-3}$)	
Methanol	puriss. p.a.	337.85 ^(A)	786.8 ^(A)	1.3270 ^(A)
	w > 0.999	337.9 ^(D)	786.56 ^(D)	1.32634 ^(D)
		337.696 ^(E)	786.37 ^(E)	1.32652 ^(E)
1-Propanol	puriss. p.a.	370.35 ^(A)	799.6 ^(A)	1.3837 ^(A)
	w > 0.998	370.03 ^(C)	799.44 ^(C)	1.3835 ^(C)
		370.301 ^(E)	799.60 ^(E)	1.3837 ^(E)
Isobutyl Acetate	purum	389.44 ^(A)	866.2 ^(A)	1.3882 ^(A)
	w > 0.99	389.80 ^(E)	867.7 ^(E)	1.3880 ^(E)
		389.85 ^(F)	866.29 ^(G)	1.3876 ^(F)

^(A) this work; ^(C) Ortega et al., 2000; ^(D) Resa et al., 2001;

^(E) Riddick et al., 1986; ^(F) Montón et al., 2005; ^(G) Resa et al., 1998.

RESULTS AND DISCUSSION

VLE calculations were performed using the so-called γ - ϕ approach. Fugacity coefficients are used to account for the non-ideality of the vapor phase. These were obtained from the virial equation of state truncated at the second term, with pure and cross virial coefficients predicted from the Hayden and O'Connell method (Hayden and O'Connell, 1975) and using the properties and critical constants from literature (Fredenslund et al., 1977) for these calculations. The Poynting correction was calculated using the Yen and Woods procedure (Yen and Woods, 1966) for the molar volume of pure liquids and the Antoine constants equation for the vapour pressures of pure compounds in Table 2. The activity coefficients used to describe the real behavior of the liquid phase were calculated from the following expression:

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

The activity coefficients of the liquid phase (see Table 3), calculated from VLE data as previously indicated, showed a positive deviation from ideal behavior. The hydrogen bonding in the alcohol and the dipolar force with the π -electrons in the ester group may be the reason of this positive deviation. The VLE data T - x_1 - y_1 of IBAM and IBAP at 0.15 MPa are shown in Table 3. The experimental data

Table 2: The Antoine constants of this work with literature data.

$\log_{10}(p_i^0/\text{kPa}) = A - \frac{B}{T/K - C}$	A	$\sigma(A)$	B	$\sigma(B)$	C	$\sigma(C)$	$\frac{\Delta T}{K}$	$\frac{\sigma(p_i^0)}{\text{MPa}}$	Lit
Methanol	7.4336	0.0001	1761.29	0.02	13.75	0.01	290-432	0.001	(A)
	7.1592		1547.71		37.42		315-345		(B)
	7.20519		1581.993		33.439				(E)
1-Propanol	7.0930	0.0001	1626.72	0.03	50.29	0.01	313-470	0.002	(A)
	6.77153		1380.23		80.41		340-390		(C)
	6.87613		1441.71		74.29				(E)
Isobutyl Acetate	6.4101	0.0001	1487.45	0.03	51.07	0.01	300-516	0.001	(A)
	6.3546		1462.4		53.45				(E)
	6.4088		1500.59		49.088		307-392		(F)

(A) this work; (B) Orchilles et al., 2007; (C) Ortega et al., 2000;
(E) Riddick et al., 1986; (F) Montón et al., 2005;

Table 3: Experimental VLE data (T - x_1 - y_1) and calculated values for activity coefficients of liquid phase.

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
Isobutyl Acetate (1) + Methanol (2) at 0.15 MPa									
349.15	0.000	0.000		1.000	353.12	0.348	0.111	1.592	1.168
349.18	0.019	0.014	4.300	0.990	353.67	0.379	0.118	1.521	1.193
349.19	0.032	0.022	4.008	0.995	354.22	0.417	0.126	1.446	1.236
349.20	0.044	0.030	3.972	0.999	354.99	0.458	0.136	1.380	1.279
349.21	0.057	0.035	3.574	1.007	355.80	0.503	0.145	1.299	1.342
349.55	0.069	0.039	3.246	1.003	356.60	0.545	0.152	1.220	1.415
349.61	0.082	0.046	3.213	1.008	357.76	0.585	0.163	1.167	1.471
349.73	0.096	0.05	2.969	1.015	359.63	0.650	0.186	1.119	1.593
349.99	0.116	0.058	2.820	1.019	360.86	0.688	0.203	1.103	1.679
350.18	0.127	0.062	2.733	1.021	361.87	0.713	0.215	1.087	1.738
350.22	0.147	0.068	2.585	1.037	365.74	0.776	0.261	1.056	1.846
350.55	0.158	0.073	2.548	1.032	367.95	0.81	0.293	1.052	1.939
350.72	0.180	0.080	2.434	1.046	374.77	0.871	0.388	1.028	1.996
351.03	0.199	0.087	2.365	1.051	386.99	0.934	0.600	1.005	1.777
351.23	0.209	0.088	2.261	1.055	399.07	0.987	0.899	0.999	1.639
352.53	0.287	0.105	1.868	1.098	403.32	1.000	1.000	1.000	
352.51	0.316	0.106	1.714	1.144					
Isobutyl Acetate (1) + 1-Propanol (2) at 0.15 MPa									
381.41	0.000	0.000		1.000	380.99	0.261	0.204	1.469	1.089
381.03	0.006	0.010	3.132	1.006	381.93	0.383	0.277	1.319	1.148
380.84	0.008	0.012	2.835	1.012	382.46	0.475	0.324	1.224	1.239
380.78	0.012	0.016	2.525	1.014	383.65	0.577	0.379	1.135	1.357
380.65	0.017	0.019	2.125	1.021	383.99	0.608	0.396	1.114	1.409
380.65	0.063	0.062	1.871	1.024	384.55	0.645	0.420	1.095	1.466
380.67	0.090	0.083	1.752	1.030	385.30	0.679	0.450	1.089	1.500
380.73	0.100	0.092	1.744	1.029	385.75	0.709	0.473	1.081	1.562
380.75	0.108	0.101	1.772	1.027	387.67	0.772	0.532	1.053	1.662
380.77	0.127	0.114	1.699	1.034	389.96	0.838	0.609	1.037	1.815
380.82	0.145	0.130	1.694	1.035	392.07	0.885	0.676	1.024	1.981
380.85	0.167	0.146	1.651	1.042	395.66	0.936	0.794	1.025	2.022
380.87	0.196	0.166	1.598	1.053	399.25	0.973	0.905	1.015	1.980
380.93	0.230	0.184	1.506	1.074	403.32	1.000	1.000	1.000	

Table 4: Results obtained from VLE correlations using the FF equations.

FF	R_T	A_0	A_1	A_2	A_3	
Isobutyl Acetate (1) + Methanol (2) at 0.15 MPa						
Eq. (2)	3.945	-0.43	-4.84	0.16	-2.99	$\sigma(y_1-x_1) = 0.005$
Eq. (3)	3.945	-49.92	-84.66	-421.63	329.79	$\sigma(T)/K = 0.22$
Eq. (4)	1.239	-61.48	526.65	-1005.01	575.21	$\sigma(T)/K = 0.39$
Eq. (5)	3.945	1.34	-1.32	1.24		$\sigma(G^E/RT) = 0.008$
Isobutyl Acetate (1) + 1-Propanol (2) at 0.15 MPa						
Eq. (2)	2.039	0.05	-2.52	1.97	-2.59	$\sigma(y_1-x_1) = 0.003$
Eq. (3)	2.039	-30.78	-0.70	-51.26	-45.57	$\sigma(T)/K = 0.27$
Eq. (4)	1.079	-33.41	8.33	56.21	-56.23	$\sigma(T)/K = 0.21$
Eq. (5)	2.039	0.91	-0.55	0.86		$\sigma(G^E/RT) = 0.007$

$$\sigma(F) = \sqrt{\frac{\sum_1^n (F_{\text{exp}} - F_{\text{cal}})^2}{n-m}}$$

Table 5: Mean errors and average deviations in the prediction of VLE data using ASOG and UNIFAC models.

	UNIFAC ^(A)	UNIFAC ^(B)	UNIFAC ^(C)	ASOG ^(D)
Isobutyl Acetate (1) + Methanol (2) at 0.15 MPa				
	CH ₃ OH/COOC	CH ₃ OH/COOC	CH ₃ OH/COOC	OH/COO
$\delta(y_1)$	0.007	0.008	0.009	0.009
$\bar{\epsilon}(y_1)$	4.06	5.13	6.92	5.46
$\delta(T)/K$	0.37	0.41	0.55	0.52
Isobutyl Acetate (1) + 1-Propanol at 0.15 MPa				
	OH/COOC	OH/COOC	OH/COOC	OH/COO
$\delta(y_1)$	0.017	0.008	0.022	0.014
$\bar{\epsilon}(y_1)$	9.02	4.77	11.31	7.06
$\delta(T)/K$	1.83	0.34	2.18	1.61
Azeotropic data				
$x_{1\text{az exp}} = 0.046$	0.016	0.120	0.007	0.027
$T_{\text{az exp}} = 380.35$	381.37	380.71	381.42	381.31

^(A) Larsen *et al.*, 1987; ^(B) Hansen *et al.*, 1991; ^(C) Gmehling *et al.*, 1993;

^(D) Kojima and Tochigi, 1979

$$\delta(F) = (1/n) \sum_1^n |F_{\text{exp}} - F_{\text{cal}}| \quad ; \quad \bar{\epsilon}(F) = (100/n) \sum_1^n |F_{\text{exp}} - F_{\text{cal}}| / F_{\text{exp}}$$

were verified in order to evaluate the thermodynamic consistency by using the Fortran routine described in literature (Fredenslund *et al.*, 1977). The Legendre polynomials were used to correlate the excess Gibbs free energy. According to the Fredenslund criterion (Fredenslund *et al.*, 1977), the experimental data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase is less than 0.01. In the present study, the values obtained are $\delta y = 0.0098$ for IBAM system and $\delta y = 0.0095$ for IBAP system.

Next, as in previous papers (Ortega *et al.*, 2000; Susial *et al.*, 2010b) the data from every system were correlated to a fitting function (FF) with a polynomial structure:

$$(y_1 - x_1) [x_1(1-x_1)]^{-1} = \sum_{k=0}^m A_k Z_T^k \quad (2)$$

$$[T - x_1 T_{\text{bp1}}^o - (1-x_1) T_{\text{bp2}}^o] [x_1(1-x_1)]^{-1} = \sum_{k=0}^m A_k Z_T^k \quad (3)$$

$$[T - y_1 T_{\text{bp1}}^o - (1-y_1) T_{\text{bp2}}^o] [y_1(1-y_1)]^{-1} = \sum_{k=0}^m A_k Z_T^k \quad (4)$$

$$(G^E/RT) [x_1(1-x_1)]^{-1} = \sum_{k=0}^m A_k Z_T^k \quad (5)$$

In Eqs. (2-5) the Ocón active fraction (Ocón, 1969; Ocón *et al.*, 1973) is given by the following equation:

$$Z_T = \frac{x_1}{x_1 + R_T(1-x_1)} \quad (6)$$

The Ocón parameter R_T in Eq. (6) has been established (Ocón, 1969; Ocón *et al.*, 1973) to be pressure and temperature dependant, as it is related with molar volumes of the pure compounds. Results of the experimental data treatment for the FF equations obtained using the Nelder and Mead procedure (Nelder and Mead, 1965), and considering the summatory of square deviations by minimization, are shown in Table 4. A similar mathematical treatment was performed on literature data (Resa *et al.*, 1998).

The T-x-y diagrams of IBAM and IBAP binary systems are shown in Figures 1-2. Both Figures show the good correspondence of IBAM at 0.15 MPa with bibliographic data (Resa *et al.*, 1998) at 101.32 kPa, as well as the azeotropic point of IBAP ($x_{1\text{az exp}} = 0.046$, $T_{\text{az exp}} = 380.35$ K) at 0.15 MPa. The small differences found in the molar range 0.6-0.8 (see Figure 2) can be attributed to a higher systematic error present in this work for pressure measurements.

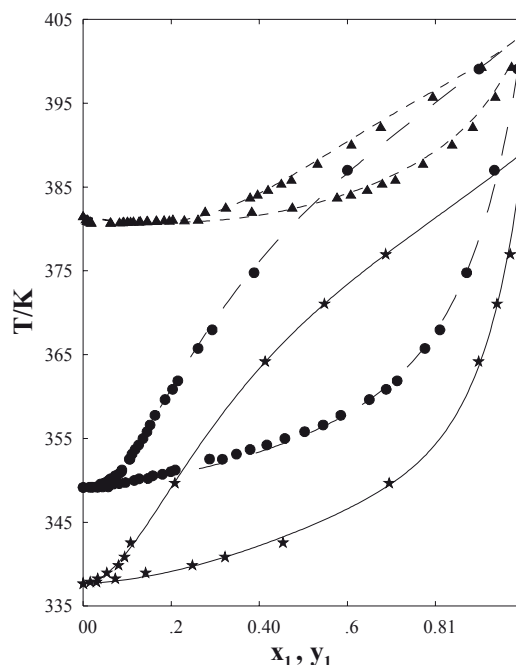


Figure 1: Representation of (*) literature data (Resa *et al.*, 1998) and FF curve with experimental data for the (●) IBAM and (▲) IBAP systems at 0.15 MPa and predictions from UNIFAC (Larsen *et al.*, 1987) (—) for the IBAM system and UNIFAC (Hansen *et al.*, 1991) (- -) for the IBAP system.

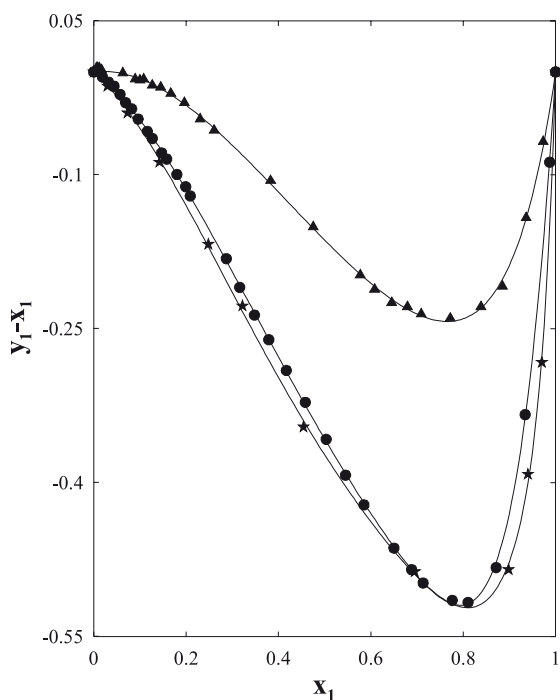


Figure 2: Plot of experimental data (●) IBAM and (▲) IBAP systems at 0.15 MPa together with (*) literature data (Resa et al., 1998) and FF curves.

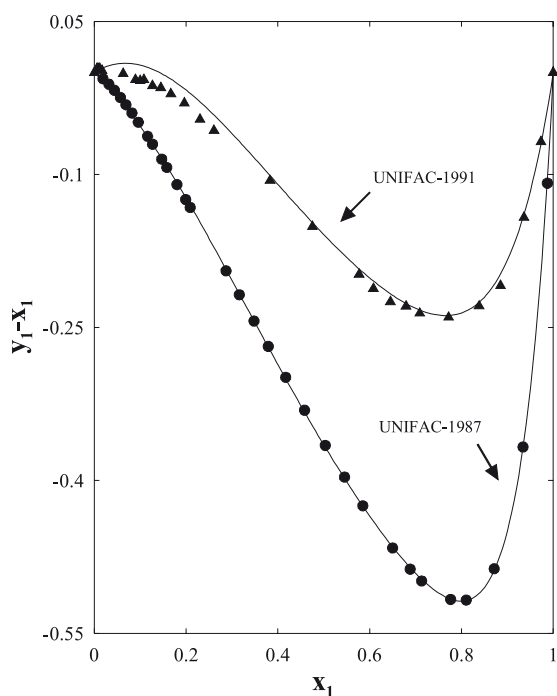


Figure 3: Comparison between the measured data of (●) IBAM and (▲) IBAP systems at 0.15 MPa with predictions from UNIFAC (Larsen et al., 1987) for the IBAM system and UNIFAC (Hansen et al., 1991) for the IBAP system.

The verified data from this work were used to test the predictive behavior of the group contribution models, due to the application potential of these in the modeling of VLE. The global results of this study are shown in Table 5. We can observe that the ASOG (Kojima and Tochigi, 1979) model seems to return, generally, the best mean results.

However, when specifying the predictions, the UNIFAC (Larsen et al., 1987) model gives a perfect prediction of the IBAM system, both for the T-x-y diagram (see Figure 1), and for y_1-x_1 vs. x_1 (see Figure 3). On the other hand, the IBAP system is well predicted by the UNIFAC (Hansen et al., 1981) model, both for y_1-x_1 vs. x_1 (see Figure 3) and T-x-y (see Figure 1). In any case, the ASOG model generates a correct estimation of the IBAP azeotrope (see Table 5).

CONCLUSIONS

Vapor-Liquid equilibria of the binary mixtures Isobutyl Acetate + Methanol and Isobutyl Acetate + Propanol were measured at 0.15 MPa. The results of all binary mixtures satisfied the thermodynamic consistency test of Van Ness (Van Ness et al., 1973) by applying the Fredenslund routine (Fredenslund et al., 1977). A new azeotrope has been presented for the Isobutyl Acetate/Propanol system. Various activity coefficient group contribution models have been used for VLE predictions. The models UNIFAC (Larsen et al., 1987) for Isobutyl Acetate/Methanol system and UNIFAC (Hansen et al., 1991) for Isobutyl Acetate/Propanol system are suitable to correlate the experimental data, as the deviations in vapor phase compositions and equilibrium temperatures are reasonably small.

List of Symbols

A, B, C	Antoine equation parameters
A_k	parameter of Eqs. 2-5
B_{ii}	second virial coefficient of pure component ($\text{m}^3 \cdot \text{mol}^{-1}$)
B_{ij}	cross second virial coefficient ($\text{m}^3 \cdot \text{mol}^{-1}$)
\bar{e}	average error (%)
F	property ($F=y_1$; $F=(y_1-x_1)$; $F=\gamma_1$; $F=\gamma_2$; $F=T$; $F=G^E/RT$)
G^E	excess free energy ($\text{J} \cdot \text{mol}^{-1}$)
m	number of equation parameters
n	number of experimental data
n_D	refractive index
p_i^0	vapor pressure for pure substance (kPa)
p	total pressure (kPa)
R	universal gas constant ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
RT	parameter of Eq. 6
T	temperature (K)
v_i^L, v_i^G	pure substances liquid and gas molar volumes ($\text{m}^3 \cdot \text{mol}^{-1}$)
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Z_T	active fraction of vapor phase or liquid phase

Greek symbols

γ	activity coefficient
ϕ	fugacity coefficient
δ	mean deviation
ρ	density ($\text{kg} \cdot \text{m}^{-3}$)
σ	standard deviation

Subscripts

az	azeotrope
bp	normal boiling point
cal	calculated
exp	experimental
i, j	chemical substances
Lit	literature
1	ester

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