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Chemical Engineering Research and Design

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Vapor–liquid equilibria for ethyl acetate + methanol and ethyl acetate + ethanol mixtures: Experimental verification and prediction

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A B S T R A C T

This work aims of the determination of a series of vapor–liquid equilibrium (VLE) experimental data at low pressure (70 kPa) for binary mixtures of ethyl acetate with methanol and ethanol. The Fischer's ebulliometer was used for the measurements of VLE data. A complete series of equilibrium data was obtained such as pressure, temperature and compositions of the liquid and vapor phases (PTxy). The two VLE data sets were submitted to a thermodynamic consistence test, where the deviations were evaluated in all variables, using the UNIQUAC activity coefficient equation. The magnitude of the average deviations was within the experimental uncertainty satisfying the Gibbs–Duhen equation. The data sets were also used to test the prediction of the UNIFAC model in its original and modified editions and the results were also within experimental uncertainties. Then a series of binary systems containing alcohols (methanol and ethanol) and esters (methyl and ethyl acetate) were collected from the literature for testing systematically the capability of the UNIFAC contribution method for this type of mixtures.

Keywords: Vapor–liquid; Equilibrium data; UNIQUAC; UNIFAC; Group contribution; ester + alcohol

1. Introduction

Measurements of reliable vapor–liquid equilibrium data is of essential importance for the elaboration of phase diagrams, supplying not only the primary information to the engineer for the design and operation of units of separation, but also to develop new methods of calculation and theory of mixtures. The proper use of simulators with these models can result in successful process optimizations. The phase behavior description of binary mixtures of ethyl acetate with methanol and ethanol presents industrial interest. The study of these systems has particular interest in the production of biodiesel, especially in the stage of separation and recovery of the alcohol from ester. This separation of the alcohol from ester may be performed by distillation, which consists of an important stage of the process of biodiesel production, and therefore it demands accurate data and consequently modeling for design purposes.

Various experimental works concerning the obtainment of vapor–liquid equilibrium data for alcohol and ester mixtures at different experimental conditions has been reported in literature (Kumar and Rajendran, 2000; Kuramochi et al., 2009; Navarro-Espinosa et al., 2010; Susial et al., 2010, 2012; Dhanalakshmi et al., 2013; Veneral et al., 2013), which the experimental data were predicted by different models such as UNIQUAC, UNIFAC, van Laar, Wilson, NRTL and others. However, reports covering the application and quantitative comparison of different versions of UNIFAC model to predict the VLE at low pressure of ester and alcohol binary systems are scarce. Herein, it is also demonstrated that both original and modified editions of UNIFAC model can be used to predict the vapor–liquid equilibrium data at low pressure for alcohol (methanol and ethanol) and ester (methyl and ethyl acetates) mixtures, with the aid of literature reports also.

In this context, the aim of this work is to provide new and accurate measurements of vapor–liquid equilibrium and also to test the

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Available online 24 July 2014
http://dx.doi.org/10.1016/j.cherd.2014.07.010

Table 1 – Sources, purities and density ρ_i of the pure components.

Component	CAS-RN	Supplier	Purity (%)	ρ (g cm^{-3})[a] (298.15 K)	ρ (g cm^{-3})[b] (298.15 K)
Ethyl acetate	141-78-6	Quimex	≥99%	0.8936	0.8934
Methanol	67-56-1	Nuclear	≥99%	0.7896	0.7895
Ethanol	64-17-5	Nuclear	≥99%	0.7859	0.7858

[a] Literature (Daubert and Danner, 1995).
[b] Experimental.

UNIFAC model in its original and modified editions for binary mixtures of methyl and ethyl acetates with methanol and ethanol.

2. Experimental

2.1. Apparatus and procedures

The measurements of VLE data were carried out in a Fischer apparatus. The experimental set up is composed of an ebulliometer Fischer model 602, digital controller Fischer System 101, bomb of vacuous Edwards E2M1, controller of pressure model Edwards 600 Barocel and thermostatic bath, Tecnal model TE-184. The temperatures of equilibrium were measured through thermometer PT-100 with resolution of 0.1 K (Fischer Labor-UND, 1997). The calibration of the sensor of pressure was carefully made with mercury barometer (Hála et al., 1967). The Fischer ebulliometer presented in Fig. 1 has as principle of operation the recirculation of the liquid and vapor phases in contact, until that the steady state is reached. It also provides conditions for sampling both phases for analysis.

The liquid mixture is placed in the mixture flask (1) (see Fig. 1). It is heated up until entering in ebullition in the camera (2). The generated vapor, together with drops of liquid, arise through the tube (3), denominated of Cottrell pump. During this transport and inside the equilibrium cell vapor–liquid contact is taken place promoting the required interchanges of mass and energy to establish the condition of steady-state, which may be considered very close to the equilibrium condition. At the end of the Cottrell pump the mixture enters into the equilibrium chamber where a thermometer (4) registers the equilibrium temperature in that moment. Vapor continues to arise and, later on, it crosses the condenser (5) and it comes back to the flask of the mixture. The liquid drops come back to the mixture flask (1). The apparatus is coupled to a thermostatic bath with cooling, to condense the vapor coming from the equilibrium cell for sampling and recirculation to the mixture flask (1). After some time, when both phases are continually recirculating and there is no more sensitive variation in the equilibrium temperature, samples of the liquid (6.1) and vapor (6) phases are simultaneously withdrawn, through activation of the valves (7.1) and (7), respectively. These samples were analyzed by gas chromatography with a Varian Star 3400CX instrument equipped with flame ionization detector. The capillary column was BD5 (length = 30 m and i.d. = 0.25 mm) and helium was used as carried gas.

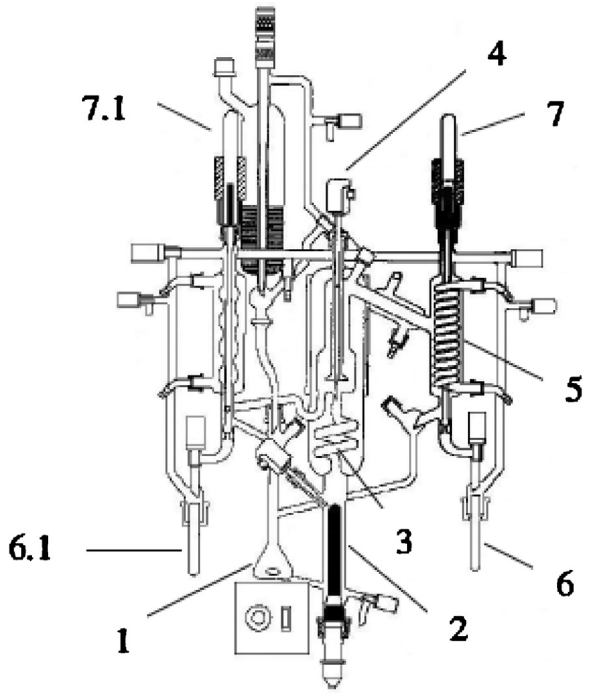

Fig. 1 – Scheme of the Fischer cell: (1) mixture flask; (2) ebullition camera; (3) Cottrell pump; (4) thermometer; (5) condenser; (6) sampler of vapor phase and (6.1) sampler of liquid phase; (7) and (7.1) electromagnetic for sampling valves of vapor and liquid phases, respectively.

3. Results and discussion

3.1. Vapor pressures for the pure components

The components with degree of purity P.A. were used in the preparation of the binary mixtures, without further purification. The densities were measured with a digital densimeter (Anton Paar Model DMA-60) to check this degree of purity, and the results are shown in Table 1. The results show good concordance between experimental and literature (Daubert and Danner, 1995) data for all the compounds.

The vapor pressure data, P^s, as a function of temperature T for the pure components ethyl acetate, methanol and ethanol, were also determined with the aid of the Fischer cell. The vapor pressure data are presented in Table 2. They are in

Table 2 – Vapor pressure, P^S, of ethyl acetate, methanol and ethanol as a function of temperature T.

Ethyl acetate		Methanol		Ethanol	
T (K)	P^S (kPa)	T (K)	P^S (kPa)	T (K)	P^S (kPa)
308.54	20.00	302.29	20.00	316.21	20.00
317.51	30.00	310.10	30.00	324.12	30.00
324.32	40.00	316.11	40.00	330.02	40.00
329.92	50.00	321.01	50.00	334.83	50.00
334.73	60.00	325.12	60.00	338.94	60.00
338.94	70.00	328.67	70.00	342.49	70.00
342.64	80.00	331.83	80.00	345.65	80.00
346.05	90.00	334.68	90.00	348.45	90.00
349.15	100.00	337.68	100.00	351.10	100.00
349.50	101.74	337.79	102.02	351.45	101.74

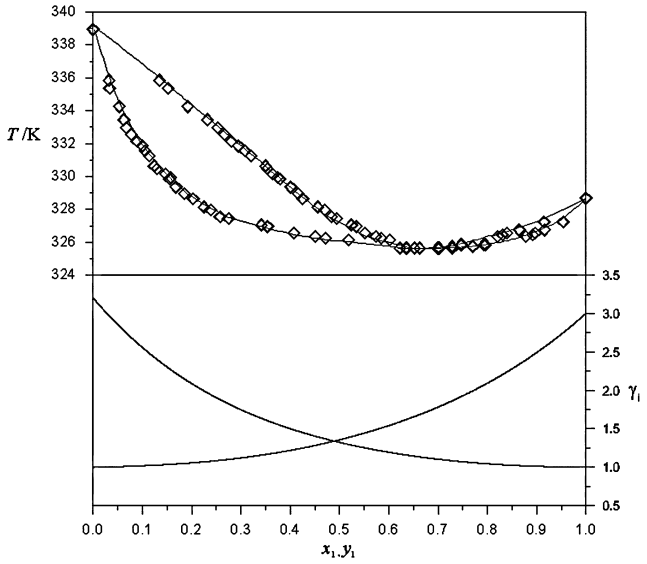

Fig. 2 – T–x,y and γ–x diagrams for the system methanol (1) + ethyl acetate (2) at 70 kPa; (◊) experimental values and (—) UNIQUAC.

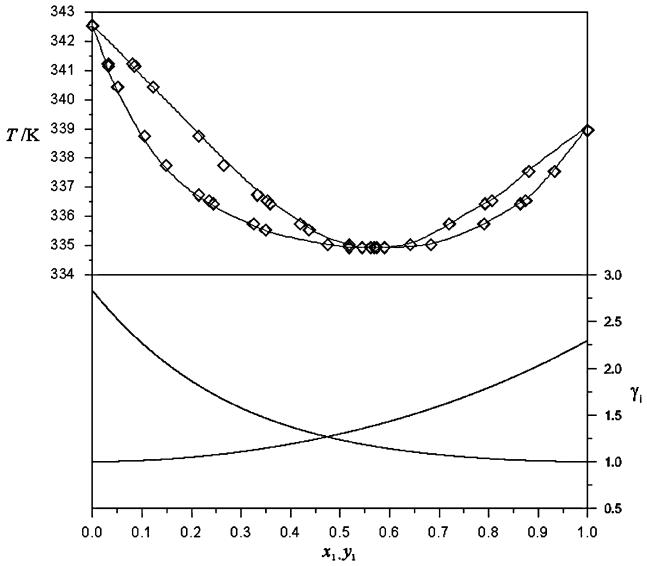

Fig. 4 – T–x,y and γ–x diagrams for the system ethyl acetate (1) + ethanol (2) at 70 kPa; (◊) experimental values and (—) UNIQUAC.

quantitative agreement with literature, as it has been demonstrated in the Antoine parameters estimation.

3.2. *Determination of VLE data*

The measurements of the liquid–vapor equilibrium for the systems methanol + acetate of ethyl and acetate of ethyl + ethanol were determined at constant pressure of 70 kPa. These experimental data are presented in the Tables 3 and 4, respectively. For each experimental point, a period of about 30 min has been waited until the stabilization of temperature was indicated at continuous flow (Oliveira et al., 2002). Then the liquid and vapor samples were collected simultaneously and conditioned in appropriate flasks for refrigeration before chromatographic analysis. Figs. 2–5 demonstrates the behavior of the studied binary systems and also UNIQUAC correlation of the experimental data (Abrams and Prausnitz, 1975).

3.3. *Correlation of the experimental data*

For the thermodynamic evaluation of the VLE data, it was first needed the vapor pressure correlations of the pure components (Table 2) that covered the temperature range used for each binary mixture. Therefore, literature data were also joined to the observed data for the Antoine correlation, providing at the same time a test of coherence and accuracy of the data.

The determination of the ANTOINE parameters was made with a Levemberg–Marquadt method, and the form presented in Eq. (1) was used. Literature vapor pressures data were collected in the DIPPR compilation (Kretschmer and Wiebe, 1949; Polak and Mertl, 1965; Timmermans, 1965; Ambrose and

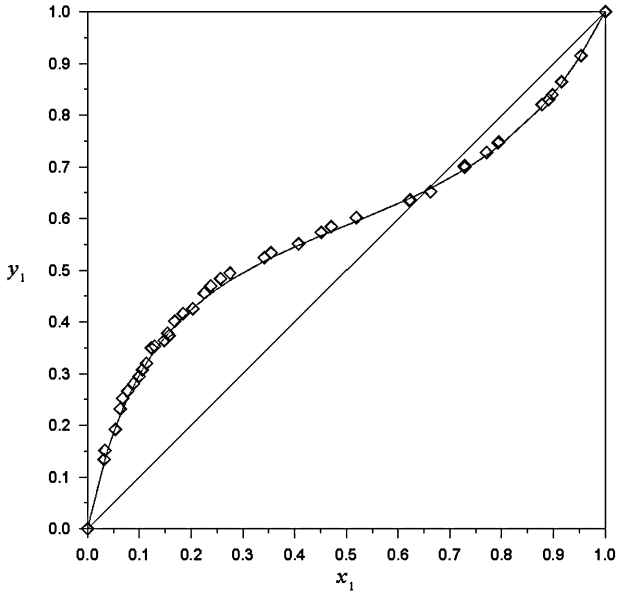

Fig. 3 – Diagram y-x for the system methanol (1) + ethyl acetate (2) at 70 kPa; (◊) experimental values and (—) UNIQUAC.

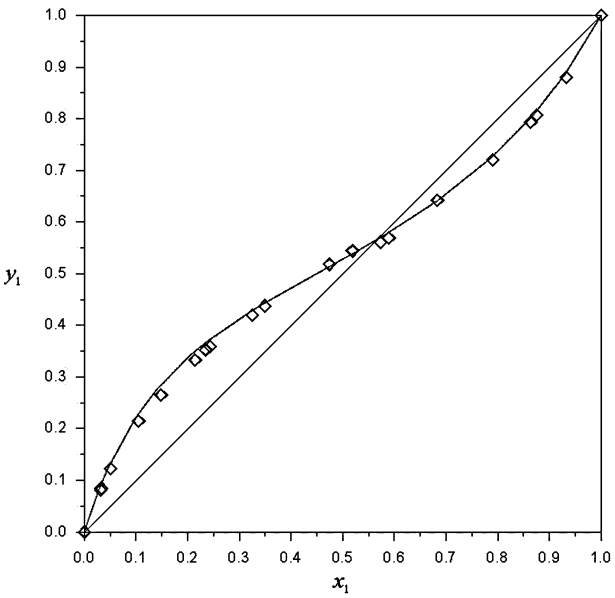

Fig. 5 – Diagram y-x for the system ethyl acetate (1) + ethanol (2) at 70 kPa; (◊) experimental values and (—) UNIQUAC.

Table 3 – Vapor–liquid equilibrium data for the system methanol (1) + ethyl acetate (2), liquid mole fraction x_1, temperature T, vapor mole fraction y_1, and pressure P.

x_1	T (K)	y_1	P (kPa)	x_1	T (K)	y_1	P (kPa)
1.0000	328.67	1.0000	70.0	0.2746	327.45	0.4945	70.0
0.9534	327.25	0.9150	70.0	0.2571	327.55	0.4838	70.0
0.9158	326.75	0.8647	70.0	0.2382	327.95	0.4697	70.0
0.8913	326.45	0.8302	70.0	0.2252	328.15	0.4559	70.0
0.8978	326.55	0.8395	70.0	0.2031	328.65	0.4255	70.0
0.8785	326.35	0.8203	70.0	0.1846	328.95	0.4159	70.0
0.8784	326.35	0.8202	70.0	0.1683	329.35	0.4011	70.0
0.7954	325.85	0.7483	70.0	0.1548	329.85	0.3787	70.0
0.7934	325.85	0.7465	70.0	0.1571	329.95	0.3738	70.0
0.7936	325.85	0.7467	70.0	0.1472	330.15	0.3640	70.0
0.7708	325.75	0.7281	70.0	0.1298	330.45	0.3530	70.0
0.7280	325.65	0.7021	70.0	0.1235	330.65	0.3498	70.0
0.7285	325.65	0.7016	70.0	0.1139	331.25	0.3201	70.0
0.7292	325.65	0.6987	70.0	0.1054	331.55	0.3075	70.0
0.6631	325.65	0.6515	70.0	0.0998	331.85	0.2949	70.0
0.6223	325.65	0.6351	70.0	0.0889	332.15	0.2807	70.0
0.6231	325.65	0.6357	70.0	0.0778	332.55	0.2670	70.0
0.5187	326.15	0.6018	70.0	0.0675	332.95	0.2527	70.0
0.4713	326.25	0.5842	70.0	0.0624	333.45	0.2318	70.0
0.4511	326.35	0.5733	70.0	0.0533	334.25	0.1923	70.0
0.4074	326.55	0.5511	70.0	0.0335	335.35	0.1516	70.0
0.3543	326.95	0.5336	70.0	0.0321	335.85	0.1345	70.0
0.3412	327.05	0.5243	70.0	0.0000	338.94	0.0000	70.0

Table 4 – Vapor–liquid equilibrium data for the system ethyl acetate (1) + ethanol (2), liquid mole fraction x_1, temperature T, vapor mole fraction y_1, and pressure P.

x_1	T (K)	y_1	P (kPa)	x_1	T (K)	y_1	P (kPa)
1.0000	338.94	1.0000	70.0	0.3251	335.73	0.4199	70.0
0.9325	337.54	0.8808	70.0	0.2440	336.43	0.3590	70.0
0.8750	336.53	0.8070	70.0	0.2353	336.53	0.3526	70.0
0.8641	336.43	0.7933	70.0	0.2147	336.73	0.3333	70.0
0.7902	335.73	0.7205	70.0	0.1487	337.74	0.2653	70.0
0.6835	335.03	0.6420	70.0	0.1053	338.74	0.2142	70.0
0.5896	334.93	0.5686	70.0	0.0506	340.44	0.1227	70.0
0.5732	334.93	0.5610	70.0	0.0327	341.14	0.0850	70.0
0.5189	334.93	0.5441	70.0	0.0314	341.24	0.0814	70.0
0.4745	335.03	0.5180	70.0	0.0000	342.54	0.0000	70.0
0.3493	335.53	0.4376	70.0				

Sprake, 1970; Boublík et al., 1973; Wilhoit and Zwolinski, 1973; Ambrose et al., 1981; Smith and Srivastava, 1986; Daubert and Danner, 1995) covering the whole temperature range.

$$\log_{10} P_i^S(\text{kPa}) = A_i - \frac{B_i}{T(\text{K}) + C_i} \quad (1)$$

The estimated parameters along with the temperature ranges are given in Table 5. It is noteworthy that the correlation of the various data sets together presented deviations within the experimental uncertainties, as it may be observed by the values of the standard deviations.

To check the consistency of the observed data, the program PARMOD (Larsen, 1986) that uses the model UNIQUAC (Abrams and Prausnitz, 1975) was used for the correlation. Results are presented in Table 6, where the deviations demonstrate the degree of consistence of the observed data. The uncertainties attributed to each variable were: $\sigma_x = 0.002$; $\sigma_y = 0.002$; $\sigma_T = 0.1$ K and $\sigma_P = 0.01$ kPa.

3.4. *Prediction of the experimental data with UNIFAC*

Table 7 shows the results of bubble calculations using two versions of the UNIFAC model (Fredenslund et al., 1977; Larsen et al., 1987) for the studied alcohol + ester systems. It may be pointed out that the deviations are reasonably low

Table 5 – Antoine estimated parameters for the Eq. (1), T in K and P in kPa.

Substance	*Ai*	*Bi*	*Ci*	T (K)[a] literature	T (K)[a] Exp.	Exp.points	σ (kPa)std dev
Ethyl acetate	6.150076	1195.257	−61.632	302–359	308–349	45	0.0011
Methanol	6.908169	1405.643	−50.960	301–351	302–338	40	0.0009
Ethanol	7.531538	1759.721	−32.976	308–359	316–351	36	0.0013

[a] Data from this work (Table 3) and from literature (Kretschmer and Wiebe, 1949; Polak and Mertl, 1965; Timmermans, 1965; Ambrose and Sprake, 1970; Boublík et al., 1973; Wilhoit and Zwolinski, 1973; Ambrose et al., 1981; Smith and Srivastava, 1986; Daubert and Danner, 1995) to cover T range of the VLE data.

Table 6 – UNIQUAC estimated parameters and mean deviations[a] for the systems methanol + ethyl acetate and ethyl acetate + ethanol at 70 kPa.

a_{ij} (K)	T (K)	AADx[a]	ΔT (%)[b]	AADy[a]	ΔP (%)[b]
Methanol (1) (r = 1.4320, q = 1.4311) + ethyl acetate (2) (r = 3.4786, q = 3.1160)					
a_{12} = −74.01; a_{21} = 422.9	325–339	0.0035	0.06	0.0044	0.01
Ethyl acetate (1) (r = 3.4786, q = 3.1160) + ethanol (2) (r = 2.1055, q = 1.9720)					
a_{12} = 158.6; a_{21} = 2.110	334–343	0.0043	0.01	0.0060	0.21

[a] $AAD = \left(\frac{1}{N}\right)\sum_{i=1}^{N}|\exp - \mathrm{calc}|_i$.
[b] $\Delta = \left(\frac{100}{N}\right)\sum_{i=1}^{N}\left|\frac{\exp - \mathrm{calc}}{\exp}\right|_i$.

Table 7 – UNIFAC test of prediction for a systematic series of binary mixtures of methanol or ethanol with esters (methyl and ethyl acetate), based on the mean deviations.

System	Reference	T (K)	P (kPa)	n	UNIFAC (Fredenslund et al., 1977)		Mod. UNIFAC (Larsen et al., 1987)	
					AADy[a]	ΔP (%)[b]	AADy[a]	ΔP (%)[b]
Methanol + methyl acetate	Susial et al. (2010)	386–378	500	24	0.0153	0.85	0.0192	2.05
Methanol + methyl acetate	Blanco and Ortega (1996)	335–346	141.3	22	0.0111	3.05	0.0208	2.71
Methanol + methyl acetate	Nagata (1969)	326–337	101.3	16	0.0096	1.44	0.0270	4.82
Methanol + Methyl Acetate	Bernatová et al. (2006)	323.15	56–89	14	0.0197	4.44	0.0210	2.46
Methanol + ethyl acetate	[This work]	325–339	70	46	0.0223	3.87	0.0336	6.81
Methanol + ethyl acetate	Susial et al. (2012)	378–385	300	26	0.0079	2.07	0.0114	5.13
Methanol + ethyl Acetate	Murti and Winkle (1958)	338–350	101.3	19	0.0074	0.59	0.0322	7.93
Methanol + Ethyl acetate	Tu et al. (1997a)	328–334	99.44	21	0.0046	1.06	0.0313	7.82
Methanol + ethyl acetate	Nakanishi et al. (1976)	337–337	101.3	22	0.0088	0.82	0.0313	8.26
Ethanol + Methyl Acetate	Susial et al. (2010)	399–384	500	19	0.0069	2.32	0.0340	5.87
Ethanol + ethyl acetate	[This work]	334–342	70	21	0.0133	1.07	0.0080	1.75
Ethanol + ethyl acetate	Susial et al. (2012)	378–388	300	24	0.0110	5.08	0.0068	3.69
Ethanol + ethyl acetate	Dhanalakshmi et al. (2013)	346–353	101.3	15	0.0309	3.85	0.0272	2.69
Ethanol + ethyl acetate	Murti and Winkle (1958)	350–352	101.3	15	0.0133	2.89	0.0112	0.98
Ethanol + ethyl acetate	Li et al. (2009)	351–350	101.3	13	0.0129	2.42	0.0089	1.39
Ethanol + ethyl acetate	Calvar et al. (2005)	345–350	101.3	26	0.0075	2.88	0.0102	0.84
Ethanol + ethyl acetate	Tu et al. (1997b)	345–351	101.3	12	0.0143	3.91	0.0034	0.86

[a] $AAD = \left(\frac{1}{N}\right)\sum_{i=1}^{N}|\exp - \mathrm{calc}|_i$.
[b] $\Delta = \left(\frac{100}{N}\right)\sum_{i=1}^{N}\left|\frac{(\exp - \mathrm{calc})}{\exp}\right|_i$.

demonstrating the applicability of the UNIFAC models for these systems.

It was performed a verification of the azeotropic behavior of the studied systems as function of the pressure. Actually, increasing the pressure the azeotropic point is shifted. For the system methanol(1) + ethyl acetate(2) at 70 kPa it was determined experimentally in this work an azeotropic of c.a. 65% molar of alcohol. At 300 kPa the azeotropic concentration is changed to 81% molar of alcohol, as observed in Susial et al. (2012). The same behavior is also observed with the literature data (Susial et al., 2010; Blanco and Ortega, 1996; Nagata, 1969; Bernatová et al., 2006) for the system methanol(1) + methyl acetate(2). In this case the azeotropic shift from atmospheric pressure to 500 kPa is 33–53% molar of alcohol. This difference may allow a separation design strategy for the regeneration of methanol with two distillation columns, where the first is at higher pressure.

4. Conclusions

The use of inert gas was necessary to avoid the introduction of humid air in the system during the sampling procedure, otherwise interferences and degradations could be obtained in the samples. The precision of the data of the measured VLE data for the systems methanol + acetate of ethyl and acetate of ethyl + ethanol has been verified with the test of thermodynamic consistency of the deviations. Furthermore, the values of vapor pressure of the pure compounds validate the precision of the method. The series of experimental data collected served as a basis to test the applicability of the UNIFAC model for the studied systems. It has also been shown that both the original and modified versions of UNIFAC presented good performances of prediction for the binary mixtures of alcohol and esters studied.

Acknowledgments

Brazilian financial support provided by ANP, CAPES, CNPq and INCT of Enviromental Studies is gratefully acknowledged.

References

Abrams, D.S., Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J. 21, 116–128.
Ambrose, D., Ellender, J.H., Gundry, H.A., Lee, D.A., Townsend, R., 1981. Thermodynamic properties of organic oxygen compounds LI. The vapour pressures of some esters and fatty acids. J. Chem. Thermodyn. 13, 795–802.
Ambrose, D., Sprake, C.H.S., 1970. Vapor pressure of alcohols. J. Chem. Thermodyn. 2, 631–645.

Bernatová, S., Aim, K., Wichterle, I., 2006. Isothermal vapour–liquid equilibrium with chemical reaction in the quaternary water + methanol + acetic acid + methyl acetate system, and in five binary subsystems. Fluid Phase Equilib. 247, 96–101.

Blanco, A.M., Ortega, J., 1996. Isobaric vapor–liquid equilibria of methanol + methyl ethanoate, + methyl propanoate, and + methyl butanoate at 141.3 kPa. J. Chem. Eng. Data 41, 566–570.

Boublík, T., Fried, V., Hála, E., 1973. The Vapor Pressures of Pure Substances. Elsevier, Amsterdam.

Calvar, N., Domınguez, A., Tojo, J., 2005. Vapor–liquid equilibria for the quaternary reactive system ethyl acetate + ethanol + water + acetic acid and some of the constituent binary systems at 101.3 kPa. Fluid Phase Equilib. 235, 215–222.

Daubert, T.E., Danner, R.P., 1995. DIPPR (Design Institute for Physical Property Data) Data Compilation Version 12.4. AIChE, New York.

Dhanalakshmi, J., Sai, P.S.T., Balakrishnan, A.R., 2013. Effect of inorganic salts on the isobaric vapor–liquid equilibrium of the ethyl acetate–ethanol system. J. Chem. Eng. Data 58, 560–569.

Fischer Labor-UND, 1997. Manual of operation of the apparatus Fischer 10, 602.

Fredenslund, A., Gmehling, J., Rasmussen, P., 1977. Vapor–Liquid Equilibria Using UNIFAC. Elsevier, Amsterdam.

Hála, E., Pick, J., Vilím, O., 1967. Vapour–Liquid Equilibrium, 2nd ed. Pergamon Press, Oxford.

Kretschmer, C.B., Wiebe, R., 1949. Liquid–vapor equilibrium of ethanol – toluene solutions. J. Am. Chem. Soc. 71, 1793–1797.

Kumar, M.D., Rajendran, M., 2000. Salt effect on enthalpy of mixing of methanol + ethyl acetate at 303.15 K. J. Chem. Eng. Data 45, 11–14.

Kuramochi, H., Maeda, K., Kato, S., Osako, M., Nakamura, K., Sakai, S., 2009. Application of UNIFAC models for prediction of vapor–liquid and liquid–liquid equilibria relevant to separation and purification processes of crude biodiesel fuel. Fuel 88, 1472–1477.

Larsen, B.L., 1986. A Parameter Estimation Program for the Modified UNIFAC and UNIFAC Models, IVC-SEP Program Package Manual 8605. Technical University of Denmark, DTU/IKT, Lyngby.

Larsen, B.L., Rasmussen, P., Fredenslund, A., 1987. A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing. Ind. Eng. Chem. Res. 26, 2274–2286.

Li, Q., Zhang, J., Lei, Z., Zhu, J., Xing, F., 2009. Isobaric vapor–liquid equilibrium for ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium tetrafluoroborate. J. Chem. Eng. Data 54, 193–197.

Murti, P.S., Winkle, M.V., 1958. Vapor–liquid equilibria for binary systems of methanol, ethyl alcohol, 1-propanol, and 2-propanol with ethyl acetate and 1-propanol-water. Ind. Eng. Chem. Chem. Eng. Data Ser. 3, 72–81.

Nagata, I., 1969. Vapor–liquid equilibrium data for the binary systems methanol–benzene and methyl acetate–methanol. J. Chem. Eng. Data 14, 418–420.

Nakanishi, K., Nakasato, K., Toba, R., Shirai, H., 1976. Vapor–liquid equilibria of binary systems containing alcohols methanol–ethyl acetate and methanol–isopropyl ether. J. Chem. Eng. Data 12, 440–442.

Navarro-Espinosa, R., Cardona, C.A., López, J.A., 2010. Experimental measurements of vapor–liquid equilibria at low pressure: systems containing alcohols, esters and organic acids. Fluid Phase Equilib. 287, 141–145.

Oliveira, H.N.M., Lopes, F.W.B., Dantas Neto, A.A., Chiavone-Filho, O., 2002. Vapor–liquid equilibria for pentane + dodecane and heptane + dodecane at low pressures. J. Chem. Eng. Data 47, 1384–1387.

Polak, K., Mertl, I., 1965. Saturated vapour pressure of methyl acetate, ethyl acetate, n-propyl acetate, methyl propionate, and ethyl propionate. Collect. Czechoslovak Chem. Commun. 30, 3526–3528.

Smith, B.D., Srivastava, R., 1986. Data for Pure Compounds. Part B. Halogenated Hydrocarbons and Alcohols. Elsevier, Amsterdam.

Susial, P., Rodriguez-Henriquez, J.J., Sosa-Rosario, A., Rios-Santana, R., 2012. Vapor–liquid equilibrium of ethyl acetate + $C_nH_{2n+1}OH$ (n = 1,2,3) binary systems at 0.3 MPa. Chin. J. Chem. Eng. 20, 723–730.

Susial, P., Sosa-Rosario, A., Rios-Santana, R., 2010. Vapour–liquid equilibrium with a new ebulliometer: ester + alcohol system at 0.5 MPa. Chin. J. Chem. Eng. 18, 1000–1007.

Timmermans, J., 1965. Physico-Chemical Constants of Pure Organic Substances, vol. 2., 2nd ed. Elsevier, New York.

Tu, C.H., Wu, Y.S., Liu, T.L., 1997a. Isobaric vapor–liquid equilibria of the methanol methyl acetate and methyl acrylate system at atmospheric pressure. Fluid Phase Equilib. 135, 97–108.

Tu, C.H., Wu, Y.S., Ou, F.C., 1997b. Effect of 1,2-propanediol on the vapor–liquid equilibria of the ethyl acetate + ethanol system at 101.3 kPa. Fluid Phase Equilib. 130, 243–252.

Veneral, J.G., Junior, D.L.R., Mazutti, M.A., Voll, F.A.P., Cardozo-Filho, L., Corazza, M.L., Oliveira, J.V., 2013. Thermophysical properties of biodiesel and related systems: low-pressure vapour–liquid equilibrium of methyl/ethyl *Jatropha curcas* biodiesel. J. Chem. Thermodyn. 60, 46–51.

Wilhoit, R.C., Zwolinski, B.J., 1973. Physical and thermodynamic properties of aliphatic alcohols. J. Phys. Chem. Ref. Data 2 (Suppl. 1).