CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci
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Experimental determination of vapour-liquid equilibrium data for the binary mixtures isobutyl alcohol/dibutyl ether, isobutyl acetate/dibutyl ether and isobutyl alcohol/isobutyl acetate at 101.3 kPa

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The thermodynamic data are essential for the development, design and simulation of any process, including the distillation to separate reactants and products. Sometimes, the experimental vapour-liquid equilibrium data are not available at the literature and must be obtained. This paper shows some of these data required in an extractive distillation process related to the transesterification of methyl acetate by isobutyl alcohol (IBOH) to isobutyl acetate (IBAC) and methanol determined in our laboratory. The use of dibutyl ether (DBE) as extractive agent is evaluated. This process could be useful to revalorize the residual methyl acetate from the polyvinyl alcohol industry.

Isobaric data at 101.3 kPa are determined using a recirculating still. The activity coefficients were found to be thermodynamically consistent, and they were correlated with the Wilson, van Laar, NRTL and UNIQUAC equations for which the parameters are reported. The activity coefficients were compared with the results of the modified UNIFAC group contribution methods. The results indicate that the three binary systems deviate from the ideality. IBOH-DBE and IBOH-IBAC systems show pinch zone near of pure IBOH and the IBAC-DBE system, near of pure IBAC.

1. Introduction

The polyvinyl alcohol is a polymer non flammable, non toxic and biodegradable by several adapted microorganisms. Unfortunately, in his industrial production, a huge amount of residue is collected: 1.68 kg of residue for each kilogram of polymer. The residue is unavoidable as is generated by the main reaction of vinyl alcohol with methanol. The recirculation of the non reacted methanol is difficult because it forms an azeotrope with the residual methyl acetate. The residual organic streams of the industry are a potential source of hydrocarbons, but the solution must be adapted to each particular case requiring experimental data which are sometimes unavailable. For similar reasons, there are some reticence to use the reactive distillation and other process intensification which produce a higher efficiency with lower investment.

The transesterification reaction of methyl acetate with an alcohol can produce methanol and acetate of higher commercial value than the methyl acetate. The reaction with ethanol produces ethyl acetate; this reaction can be performed in a reactive distillation pressure swing system (Bonet et al. 2006 a, b). The reaction with butanol produces butyl acetate; this reaction can be performed in a reactive distillation pervaporation system (Steinigeweg and Gmehling, 2004). This paper deals with the vapour-liquid equilibrium data required to evaluate the reaction with isobutyl alcohol to produce isobutyl acetate. The extractive distillation is the method more widely used at the industry and it should be take into account in the comparison with other alternatives. The success of the extractive distillation depends on a right choice of the extractive agent. Our goal is to determine the unavailable vapour-liquid equilibrium data required to study the transesterification with isobutyl alcohol using extractive distillation with dibutyl ether as extractive agent. The separation of IBAC and IBOH by other extractive agent (N.N-dimethylformamide) is already available at the literature (Muñoz et al, 2005).

The dibutyl ether seems a good extractive agent according a previous extractive agent selection by the modified UNIFAC using the method proposed by Gmehling and Mollmann (1998). The DBE does not introduce further azeotrope and the selectivity at infinite dilution is also right although its boiling point would be preferable to be higher than 40 K from the IBAC and IBOH boiling points.

2. Material and method

The reagents provided by Fluka were used without further purification after the gas chromatographic analysis showed no significant impurities (table 1).

Table 1. Properties of the reactants.

		MW	bp (ºC)	d420 (g/mL)	Assay (GC)
isobutyl alcohol	$C_4H_{10}O$	74.12	107-108	0.801	>99.5
isobutyl acetate	$C_6H_{12}O_2$	116.16	116-118	0.870	>98.5
dibutyl ether	$C_8H_{18}O$	130.23	140-142	0.767	>99.5

The vapor-liquid equilibrium is determined by a dynamic recirculating still all-glass commercial apparatus, manufactured by Fischer Labor und Verfahrenstechnik (Germany). The equilibrium temperature is measured by means of a Pt-100 thermometer with an accuracy of 0.05 ºC. A Fischer phase equilibrium control system is used to measure and control the pressure and heating power. The pressure in the still is at 101.3+/- 0.1; controlled by a vacuum pump and a nitrogen source; the dry nitrogen source is used as inert atmosphere.

The mixture is heated to its boiling point and after 1-2 hours the system becomes totally stationary to begin the experiments. Then, samples are taken by syringing 0.5 mL of liquid and vapour in equilibrium without disruption of the operation. After the first sample, the other sample conditions are obtained by small and proximately equidistant steps. The system is in equilibrium when the temperature of vapour and liquid are very close and constants. The equilibrium is verified by taking some samples and checking that the value is constant. The stabilization time is usually around 15 - 20 min.

The samples analysis are performed on a Hewlett Packard gas chromatograph (model 5890 II Plus) with an autoinjector. The capillary column, 30 m by 0.32 mm diameter, from Supelco (column 2-4159) is packed with 1.00 micrometer FILN. The column temperature ranges are from 80 to 155 ºC with a temperature ramp after the minute 5. The detection is carried out using FID (Flame Ionization Detector). The carrier gas is hydrogen and the helium flow rate is adjusted to 30 mL·min-1. The response peaks are integrated using a HP 3365 integrator. The gas chromatograph is calibrated with gravimetrically prepared solutions, each sample is analysed 3 times.

3. Results

The experimental vapor-liquid equilibrium data and the activity coefficients for the binary mixtures isobutyl alcohol/dibutyl ether, isobutyl acetate/dibutyl ether and isobutyl alcohol/isobutyl acetate at 101.3 kPa are tabulated as additional information.

The vapour pressures for each compound are obtained from the extended Antoine equation (equation 1) with the parameters implemented in the simulator (table 2). The functional group parameters used at the UNIFAC estimation are retrieved from the simulator data base (Appendix).

$$\ln p_I^* = C_{1i} + \frac{C_{2i}}{(T + C_{3i})} + C_{4i}T + C_{5i} \cdot \ln(T) + C_{6i} \cdot T^{C_{7i}} \qquad (1)$$

Table 2. Parameters of the extended Antoine equation implemented in the data base of the simulator, P (bar), T (K).

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	Bounds (K)
IBOH	114.9	-10504.0	0	0	-13.921	$1.69 \cdot 10^{-17}$	6	165-548
IBAC	65.4	-6944.3	0	0	-7.298	$3.79 \cdot 10^{-6}$	2	174-561
DBE	65.3	-7537.6	0	0	-7.060	$9.14 \cdot 10^{-18}$	6	175-584

The activity coefficients were calculated as

$$\gamma_i = \frac{\Phi_i P y_i}{f_i^0 x_i} \qquad (2)$$

Fugacity calculation f_i^0

$$f_i^0 = \Phi_i P_i^0 \exp\left[\frac{V_{mi}(P - P_i^0)}{RT}\right] \qquad (3)$$

Fugacity coefficient calculation Φ_i

$$\ln \Phi_i = (Z-1)\frac{D_i}{F} - \ln(Z - FP) - \frac{E^2}{F}\left(\frac{2C_i}{E} - \frac{D_i}{F}\right)\ln\left(1 + \frac{FP}{Z}\right) \quad (4)$$

Compressibility calculation Z

$$Z^3 + Z^2 + \left[E^2P - FP(1+FP)\right]Z + (E^2P)(FP) = 0 \quad (5)$$

where: $C_i^2 = 0.062/T_{ri}^{2.5}\,P_{ci}$
$D_i = 0.0126/T_{ri}\,P_{ci}$
$E = \sum y_i\,C_i$
$F = \sum y_i\,D_i$
T_{ri} = reduced temperature of component i (T/T_{ci})
T_{ci} = critical temperature of component i (consistent units)
P_{ci} = critical pressure of component i (kPa)
P = working pressure (kPa)
V_{mi} = molar volume of component i (m^3/mol)
T = temperature of data point (consistent units)
R = 0.008314 kPa m^3/mol K

The activity coefficients were test to be thermodynamically consistent using two area methods (table 3): the Herrington test (1951), from Haslego (2005), establish that for an isobaric system, the net area under the obtained curve graphing ln (γ_1/γ_2) versus x_1 should be between the values -0,10 and 1.5 ($\Delta T_{max}/T_{min}$), where ΔT_{max} is the maximum difference in boiling points in the total composition range and T_{min} is the lowest boiling temperature in the system; and the Wisniak test (1993), who requires the evaluation of the integrals L and W as described. The deviation value, D, defined as D = 100[|L-W|/(L+W)], indicate thermodynamic consistency for values under 5.

Table 3. Thermodynamic consistency test

	Herrington			Wisniak	
	1.5 ΔT_{max} / T_{min}	Net area	Consistency	D	Consistency
IBOH-DBE	0.4483	0.07754	+	2.2808	+
IBAC-DBE	0.3078	0.14479	+	5.0000	+
IBOH-IBAC	0.1276	0.04557	+	7.0478	-

The activity coefficients were correlated with the Wilson, van Laar, NRTL and UNIQUAC equations. The adjusted parameters are shown in table 4. Similar good adjustments were obtained by the Wilson, NRTL and UNIQUAC equations. The van Laar equation, also adjust well the data. The modified UNIFAC group contribution method presents a good estimation for the IBOH-DBE and IBAC-DBE mixtures but it is not so good for the IBOH-IBAC mixture. Diagrams T-x-y for the three binary systems, show the experimental data points with a continuous line for the NRTL model regression and a discontinuous line for the UNIFAC estimation (Figure 1).

Table 4. Correlation parameters for activity coefficients and average of absolute temperature residuals

	IBOH-DBE	IBAC-DBE	IBOH-IBAC
Wilson, λ_{12} (J/mol)	-1547.8178	-347.10675	-40.92606
Wilson, λ_{21} (J/mol)	-203.00513	141.98167	-111.23221
$\lvert\Delta T_{aver}\rvert$ (K)	0.56	0.49	0.22
Van Laar, λ_{12} (dimensionless)	414.94072	221.34254	167.73477
Van Laar, λ_{21} (dimensionless)	380.2349	120.66974	167.69498
$\lvert\Delta T_{aver}\rvert$ (K)	0.93	1.12	0.60
NRTL, λ_{12} (J/mol)	-256.50995	-244.09693	132.3636
NRTL, λ_{21} (J/mol)	1774.82461	468.41156	17.71793
NRTL, $\alpha_{12} = \alpha_{21}$	0.3	0.3	0.3
$\lvert\Delta T_{aver}\rvert$ (K)	0.57	0.49	0.22
UNIQUAC, λ_{12} (J/mol)	204.98536	170.76761	14.8511
UNIQUAC, λ_{21} (J/mol)	-767.93851	-255.98968	-63.03282
$\lvert\Delta T_{aver}\rvert$ (K)	0.57	0.48	0.20

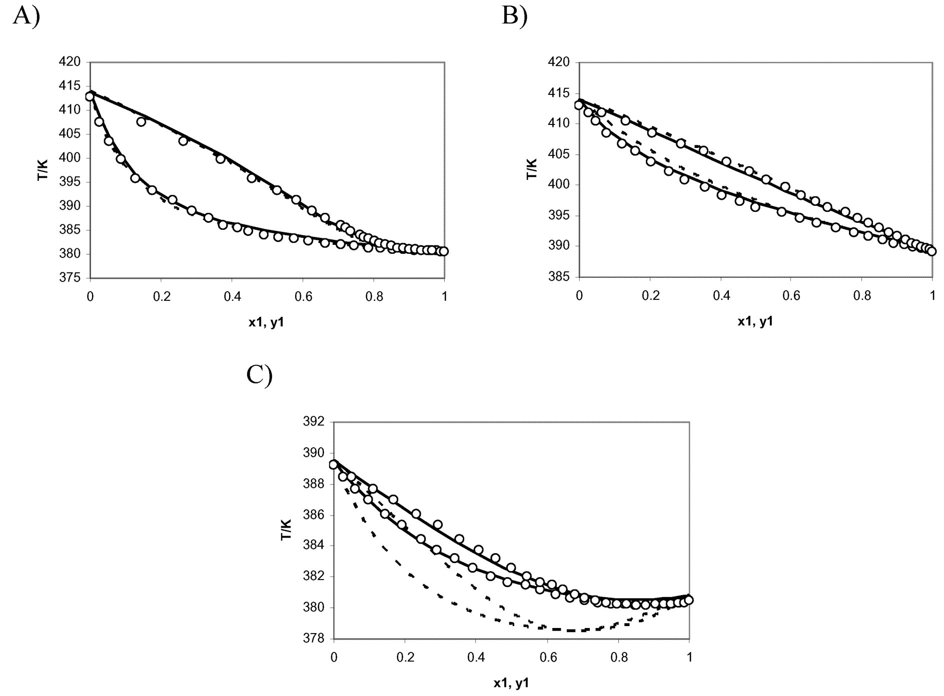

Figure 1. T-x_1-y_1 diagram at constant pressure, P = 101.3 kPa, for the binary system (A) isobutyl alcohol (1)- dibutyl ether (2); (B) isobutyl acetate (1)- dibutyl ether (2) and (C) isobutyl alcohol (1)- isobutyl acetate (2). (o) Experimental data; (—) NRTL model; (---) UNIFAC.

References

Bonet, J., Thery, R., Meyer, X.M., Meyer, M., Reneaume, J.M., Galan, M.I., Costa, J. 2006a. Infinite/Infinite Analysis as a Tool for an Early Oriented Synthesis of a Reactive Pressure Swing Process, Computers and Chemical Engineering, doi:10.1016/j.compchemeng. 2006.06.004.

Bonet, J., Galan M.I., Costa, J., Thery, R., Meyer, X.M., Meyer, M., Reneaume, J.M. 2006 b. Pressure optimisation o fan original system of pressure swing with a reactive column, Institution of Chemical Engineers Symposium Series, 152, 344.

Gmehling, J., Mollmann, C. 1998. Synthesis of Distillation Processes Using Thermodynamic Models and the Dortmund Data Bank. Industrial and Engineering Chemistry Research, 37, 3112-3123.

Hasslego,C. (2005) Chemical Engineers' Resource Page (http://www.cheresources.com)

Herrington, E.F.G. 1951. Test for the consistency of experimental isobaric vapour-liquid equilibrium data. J. Inst. Pet., 37, 457-470.

Muñoz, R., Monton, J.B., Burguet, M.C., de la Torre, J. 2005. Phase equilibria in the systems isobutyl alcohol + N.N-dimethylformamide, isobutyl acetate + N.N-dimethylformamide, and isobutyl alcohol + isobutyl acetate + N.N-dimethylformamide at 101.3 kPa, Fluid Phase Equilibria, 232, 62-69.

Steinigeweg, S., Gmehling, J. 2004. Transesterification processesby combination of reactive distillation and pervaporation, Chem. Eng. and Proc., 43, 447-456.

Wisniak, J. 1993. A new test for thermodynamic consistency of vapor-liquid equilibrium. Industrial and Engineering Chemistry Research, 32, 1531-1533.

Appendix - Data retrieved from the simulator data base:

Table A1. UNIFAC functional group Q_k and R_k parameters.

	>CH-	>CH2	-CH3	-OH	-AC	-CH2-O-
Aspen ID	1005	1010	1015	1200	1505	1610
Q_k	0.228	0.540	0.848	1.200	1.728	0.780
R_k	0.4469	0.6744	0.9011	1.000	1.9031	0.9183

Table A2. UNIFAC functional group b_{kn} parameters.

	>CH-	>CH2	-CH3	-OH	-AC	-CH2-O-
>CH-	0	0	0	986.5	232.1	251.5
>CH2	0	0	0	986.5	232.1	251.5
-CH3	0	0	0	986.5	232.1	251.5
-OH	156.4	156.4	156.4	0	101.1	28.06
-Ac	114.8	114.8	114.8	245.4	0	-235.7
-CH2-O-	83.36	83.36	83.36	237.7	461.3	0