VAPOUR–LIQUID EQUILIBRIA OF PYRIDINE + ACETATE MIXTURES AT 101·325 kPa

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Experimental vapour–liquid equilibrium data for the binary mixtures ethyl acetate + pyridine, n-propyl acetate + pyridine and n-butyl acetate + pyridine have been determined at 101·325 kPa. The Wilson, NRTL, LEMF, UNIQUAC and Effective UNIQUAC equations have been fitted to the data, which have also been used to establish UNIFAC parameters for interaction between CCOO and PYRIDINE groups.

Distillation is one of the commonest ways of separating liquid mixtures in chemical plants. The design of distillation columns requires knowledge of phase equilibria of the components to be separated under given operating conditions. Such data must either be obtained experimentally, or by some reliable prediction method such as the UNIFAC group contribution method. Hitherto, no UNIFAC group interaction parameters have been available for CCOO/PYRIDINE interactions. In this article we report experimental vapour–liquid equilibrium data for the binary mixtures ethyl acetate + pyridine, n-propyl acetate + pyridine and n-butyl acetate + pyridine at 101·325 kPa, and the corresponding CCOO/PYRIDINE UNIFAC parameters. The densities and refractive indices of the mixtures at 25°C, which were subsequently used for analysis of both phases, are likewise reported as are excess molar volumes and refractions to which we fitted Redlich–Kister equations of the form

$$M^{\mathrm{E}}/x(1-x) = \sum_{i=1}^{m} A_i(2x-1)^{i-1}\,, \qquad (1)$$

where M^{E} is the excess property in question.

EXPERIMENTAL

All the chemicals used were Carlo Erba RPE grade products. None were purified further except for pyridine, which was treated with potassium hydroxide and distilled under argon to reduce

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its water content. The criteria of purity used were density at 25°C, refractive index at 25°C and boiling point at 101·325 kPa. Table I lists the values of these parameters determined experimentally in this work, together with previously published values.

TABLE I

Physical properties of pure components

Component	Data experimental	Data literature	Data ref.
Pyridine			
ϱ	0·9782	0·97824	1
		0·97810	2
n_D	1·5072	1·50745	1
		1·5033	2
t_B	115·0	115·256	1
		114·9	2
Ethyl acetate			
ϱ	0·8945	0·89455	1
		0·8944	4
n_D	1·3697	1·36979	1
		1·3697	4
t_B	77·1	77·114	1
		77·1	4
n-Propyl acetate			
ϱ	0·8827	0·88303	1
		0·8825	4
n_D	1·3838	1·3840	5
		1·3844	4
t_B	101·4	101·546	1
		101·6	5
n-Butyl acetate			
ϱ	0·8762	0·87636	1
		0·8758	6
n_D	1·3936	1·3941	6
		1·3939	4
t_B	125·9	126·114	1
		126·15	6

TABLE II

Densities and refractive indices of binary mixtures at 25°C

Ethyl acetate + + pyridine			n-Propyl acetate + + pyridine			Pyridine + n-butyl + acetate		
x	ϱ	n_D	x	ϱ	n_D	x	ϱ	n_D
0·000	0·9782	1·5072	0·000	0·9782	1·5072	0·000	0·8762	1·3936
0·018	0·9764	1·5028	0·032	0·8742	1·5012	0·030	0·8781	1·3959
0·042	0·9741	1·4987	0·077	0·9686	1·4931	0·077	0·8812	1·3994
0·079	0·9707	1·4927	0·109	0·9647	1·4876	0·117	0·8840	1·4025
0·096	0·9692	1·4900	0·133	0·9619	1·4836	0·135	0·8853	1·4040
0·137	0·9654	1·4836	0·160	0·9587	1·4792	0·165	0·8875	1·4064
0·172	0·9622	1·4782	0·198	0·9544	1·4733	0·214	0·8911	1·4105
0·202	0·9595	1·4736	0·224	0·9515	1·4693	0·249	0·8938	1·4135
0·228	0·9572	1·4697	0·256	0·9480	1·4646	0·269	0·8954	1·4153
0·261	0·9542	1·4648	0·283	0·9451	1·4606	0·288	0·8969	1·4170
0·291	0·9516	1·4604	0·326	0·9406	1·4546	0·322	0·8997	1·4201
0·313	0·9497	1·4572	0·362	0·9369	1·4497	0·353	0·9023	1·4230
0·348	0·9467	1·4522	0·384	0·9347	1·4467	0·378	0·9045	1·4255
0·378	0·9441	1·4480	0·410	0·9321	1·4433	0·413	0·9076	1·4290
0·400	0·9422	1·4449	0·460	0·9272	1·4370	0·448	0·9108	1·4236
0·431	0·9396	1·4406	0·499	0·9235	1·4322	0·476	0·9134	1·4356
0·478	0·9357	1·4342	0·548	0·9189	1·4265	0·519	0·9176	1·4404
0·497	0·9341	1·4316	0·598	0·9144	1·4209	0·565	0·9222	1·4457
0·556	0·9292	1·4237	0·628	0·9117	1·4177	0·601	0·9259	1·4500
0·622	0·9238	1·4151	0·690	0·9063	1·4113	0·634	0·9294	1·4541
0·669	0·9200	1·4091	0·722	0·9037	1·4081	0·667	0·9331	1·4584
0·713	0·9165	1·4036	0·752	0·9012	1·4051	0·697	0·9365	1·4624
0·741	0·9142	1·4001	0·783	0·8987	1·4021	0·731	0·9405	1·4671
0·765	0·9122	1·3971	0·810	0·8965	1·3996	0·760	0·9440	1·4712
0·787	0·9104	1·3994	0·841	0·8941	1·3968	0·811	0·9505	1·4787
0·804	0·9091	1·3923	0·873	0·8917	1·3940	0·850	0·9557	1·4847
0·837	0·9064	1·3883	0·907	0·8891	1·3911	0·875	0·9592	1·4885
0·880	0·9031	1·3832	0·931	0·8873	1·3891	0·903	0·9632	1·4928
0·923	0·8999	1·3782	0·951	0·8858	1·3875	0·919	0·9665	1·4954
0·945	0·8983	1·3757	0·974	0·8843	1·3857	0·941	0·9688	1·4987
0·977	0·8960	1·3721	1·000	0·8827	1·3838	0·970	0·9733	1·5029
1·000	0·8945	1·3697				1·000	0·9782	1·5072

TABLE III

Correlation parameters for the excess properties

A_i	Ethyl acetate + pyridine		n-Propyl acetate + pyridine		Pyridine + n-butyl acetate	
	V^E	R^E	V^E	R^E	V^E	R^E
A_1	−6·264 . 10^{-1}	6·671 . 10^{-2}	−5·872 . 10^{-1}	−3·721 . 10^{-1}	−4·060 . 10^{-1}	5·005 . 10^{-1}
A_2	−1·763 . 10^{-1}	1·134 . 10^{-1}	2·054 . 10^{-1}	−5·742 . 10^{-2}	−2·174 . 10^{-1}	3·522 . 10^{-1}
A_3	3·074 . 10^{-1}	−1·712 . 10^{-1}	1·404 . 10^{-1}	−6·483 . 10^{-2}	2·743 . 10^{-1}	3·777 . 10^{-1}
A_4	9·450 . 10^{-1}	1·413 . 10^{-1}	1·686 . 10^{-1}	4·895 . 10^{-2}		4·847 . 10^{-1}
A_5	2·520 . 10^{-1}	−3·998 . 10^{-1}	4·118 . 10^{-1}			6·177 . 10^{-1}
A_6	−3·317 . 10^{-1}	3·111 . 10^{-1}	2·843 . 10^{-1}			
σ	1·61 . 10^{-3}	1·38 . 10^{-3}	7·04 . 10^{-4}	4·51 . 10^{-4}	4·89 . 10^{-4}	1·03 . 10^{-3}

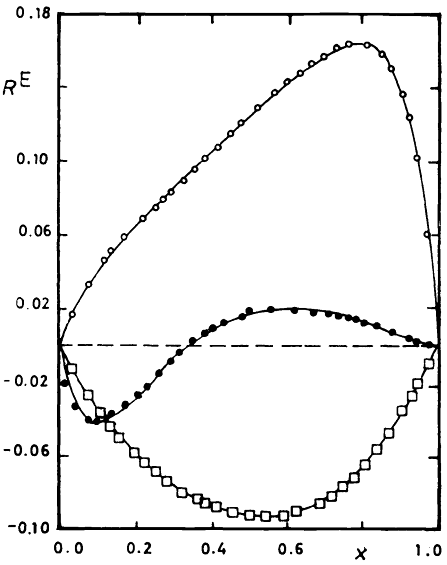

FIG. 1

Excess molar volumes at 25°C: ○ ethyl acetate + pyridine; □ n-propyl acetate + pyridine; ● pyridine + n-butyl acetate; —— Redlich–Kister correlation

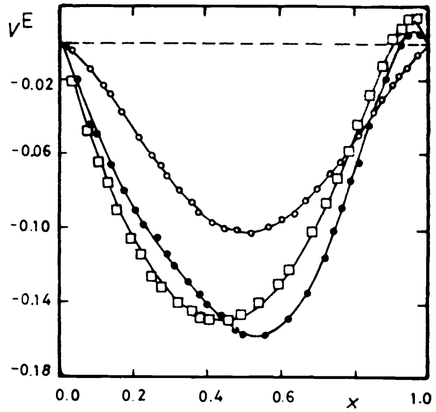

FIG. 2

Excess molar refractions at 25°C: ○ ethyl acetate + pyridine; □ n-propyl acetate + pyridine; ● pyridine + n-butyl acetate; —— Redlich–Kister correlation

Vapour–liquid equilibrium data were obtained using the still designed by Ocón and Espantoso[7] which is similar to the Othmer apparatus but achieves more homogeneous liquid phase by secondary recycling. Analysis of equilibrium liquid and vapour phases was performed by measuring the densities and refractive indices of samples and interpolating them among the previously tabulated values (Table II).

Excess molar volume and refraction data were fitted to Redlich–Kister equations (Eq. (*1*)) a test function being used to determine the optimal number of coefficients. The coefficients and standard deviations for each mixture and property are listed in Table III, and Figs 1 and 2 show the experimental data together with the fitted equations.

Table IV lists the experimental vapour–liquid equilibrium data obtained for each of the binary mixtures studied.

TABLE IV

Experimental vapour–liquid equilibrium data of binary systems at 101·325 kPa

Ethyl acetate + pyridine			n-Propyl acetate + pyridine			Pyridine + n-butyl acetate		
x	y	t	x	y	t	x	y	t
0·000	0·000	115·0	0·000	0·000	115·0	0·000	0·000	125·9
0·051	0·155	110·7	0·050	0·076	113·7	0·035	0·052	125·3
0·103	0·279	106·8	0·096	0·143	112·7	0·081	0·112	124·6
0·143	0·380	104·0	0·142	0·214	111·6	0·147	0·189	123·7
0·187	0·450	101·5	0·188	0·271	110·8	0·181	0·233	123·2
0·239	0·528	98·5	0·232	0·325	110·0	0·221	0·277	122·7
0·285	0·597	96·5	0·275	0·381	109·3	0·250	0·314	122·3
0·335	0·648	94·2	0·325	0·436	108·5	0·299	0·368	121·7
0·387	0·689	92·5	0·377	0·484	107·8	0·328	0·397	121·4
0·441	0·741	90·5	0·429	0·536	107·1	0·368	0·438	120·9
0·502	0·782	88·2	0·481	0·587	106·4	0·415	0·483	120·4
0·543	0·811	87·1	0·534	0·631	105·8	0·489	0·558	119·5
0·588	0·831	85·7	0·582	0·672	105·2	0·527	0·593	119·1
0·627	0·854	84·6	0·628	0·712	104·7	0·565	0·627	118·7
0·673	0·875	83·5	0·682	0·756	104·1	0·611	0·666	118·3
0·747	0·910	81·7	0·735	0·798	103·6	0·671	0·719	117·7
0·785	0·929	80·7	0·791	0·837	103·1	0·735	0·776	117·1
0·825	0·939	80·0	0·845	0·881	102·6	0·787	0·819	116·6
0·865	0·955	79·2	0·905	0·927	102·1	0·851	0·872	116·0
0·901	0·965	78·5	0·965	0·973	101·6	0·914	0·928	115·5
0·967	0·988	77·6	1·000	1·000	101·4	0·959	0·965	115·2
1·000	1·000	77·1				1·000	1·000	115·0

RESULTS AND DISCUSSION

Processing of Equilibrium Data

In processing the equilibrium data, the non-ideality of both phases was taken into account using Hayden and O'Connell's[8] method for calculating the second virial coefficient and hence the fugacity coefficient of the vapour phase.

Table V lists the properties of the pure components used in fitting the semi-theoretical equations and in the UNIFAC calculations. Following Reid et al.[9], we calculated the radius of gyration of n-propyl acetate from parachor. The parameters *r*

TABLE V

Properties and parameters of the components used in the correlation and the prediction of vapour–liquid equilibrium values (PC critical pressure, RD mean gyration radius, DMU dipole moment, ETA association parameter, TC critical temperature, ZC critical compressibility factor)

Quantity	Pyridine	Ethyl acetate	n-Propyl acetate	n-Butyl acetate
PC, kPa	5 640·8	3 830·1	3 333·6	3 109·7
RD, μm	3·05 . 10^{-4}[a]	3·35 . 10^{-4}[a]	3·70 . 10^{-4}	4·17 . 10^{-4}[a]
DMU, Cm	7·67 . 10^{-30}[a]	5·93 . 10^{-30}[a]	6·00 . 10^{-30}[b]	6·33 . 10^{-30}[a]
ETA	0·00[a]	0·53[a]	0·53	0·53[a]
TC, K	620·0[a]	523·3[a]	549·4[b]	579·1[a]
ZC	0·277[b]	0·252[b]	0·252[b]	0·260[b]
r	3·00[a]	3·48[a]	4·15	4·83[a]
q	2·16[a]	3·12[a]	3·66	4·20[a]
A[c]	9·16634	9·22723	9·14210	9·17600
B[c]	1 373·990	1 245·329	1 282·873	1 385·800
C[c]	215·001	217·911	208·664	206·100

[a] Prausnitz et al.[12]; [b] Reid et al.[9]; [c] $3 + \log P = A - B/(t + C)$. Riddick and Bunger[1].

TABLE VI

Results of thermodynamic consistency test

System	Number of points	$\langle \Delta P \rangle$ kPa	$\langle \Delta y \rangle$
Pyridine + ethyl acetate	22	0·3141	0·0076
n-Propyl acetate + pyridine	21	0·1419	0·0044
Pyridine + n-butyl acetate	22	0·1824	0·0094

Table VII

Correlation of vapour–liquid equilibrium data

Equation	Parameters	Root mean square deviation				
		RMS P	RMS t	RMS x	RMS y	S
	Ethyl acetate + pyridine system					
WILSON	$\Delta\lambda_{12}$ = −2 166·25	0·113	0·19	0·0008	0·0074	223·60
	$\Delta\lambda_{21}$ = 4 117·73					
NRTL	Δg_{12} = 3 812·06	0·117	0·21	0·0009	0·0083	269·28
(α = 0·30)	Δg_{21} = −2 032·22					
LEMF	Δg_{12} = −1 315·41	0·115	0·19	0·0008	0·0095	306·84
(α = −1)	Δg_{21} = 1 548·11					
UNIQUAC	Δu_{12} = 3 966·40	0·087	0·16	0·0007	0·0065	161·68
	Δu_{21} = −2 371·08					
Effective	Δu_{12} = 8 783·19	0·077	0·13	0·0015	0·0083	235·50
UNIQUAC	Δu_{21} = −4 323·72					
	Propyl acetate + pyridine system					
WILSON	$\Delta\lambda_{12}$ = −1 384·06	0·075	0·12	0·0004	0·0039	65·67
	$\Delta\lambda_{21}$ = 1 989·35					
NRTL	Δg_{12} = 702·08	0·053	0·12	0·0004	0·0050	66·81
(α = 0·30)	Δg_{21} = −108·21					
LEMF	Δg_{12} = 1 625·59	0·076	0·11	0·0004	0·0050	85·17
(α = −1)	Δg_{21} = −2 170·94					
UNIQUAC	Δu_{12} = 2 519·05	0·073	0·10	0·0004	0·0036	55·29
	Δu_{21} = −1 839·33					
Effective	Δu_{12} = 8 110·04	0·091	0·07	0·0009	0·0065	124·46
UNIQUAC	Δu_{21} = −5 023·83					
	Pyridine + butyl acetate system					
WILSON	$\Delta\lambda_{12}$ = 2 295·06	0·115	0·19	0·0008	0·0063	186·46
	$\Delta\lambda_{21}$ = −1 849·08					
NRTL	Δg_{12} = −795·34	0·117	0·19	0·0007	0·0061	184·10
(α = 0·30)	Δg_{21} = 1 314·78					
LEMF	Δg_{12} = 1 196·53	0·128	0·20	0·0007	0·0059	183·91
(α = −1)	Δg_{21} = −1 214·78					
UNIQUAC	Δu_{12} = −1 715·51	0·115	0·19	0·0008	0·0067	198·74
	Δu_{21} = 2 296·77					
Effective	Δu_{12} = 527·27	0·097	0·17	0·0009	0·0083	241·06
UNIQUAC	Δu_{21} = −319·06					

and q were determined from van der Waals group volumes and surface areas respectively (Bondi[10]). As suggested by Fredenslund et al.[11], on account of structural similarity the association parameter of n-propyl acetate has been assumed to be the same as for the other esters. The value of the pyridine/ester solvatation parameter has been taken to be 0·30 (Prausnitz et al.[12]).

All the experimental vapour–liquid equilibrium data satisfactorily passed Fredenslund et al.[11] thermodynamic consistency test. Table VI lists the corresponding mean deviations of vapour phase composition and pressure.

The Wilson[13], NRTL (Renon and Prausnitz[14]), LEMF (Marina and Tassios[15]), UNIQUAC (Abrams and Prausnitz[16]) and Effective UNIQUAC (Nagata and Katoh[17]) equations were fitted to the experimental equilibrium data using the method proposed by Prausnitz et al.[12] in which the relevant parameters are estimated by a maximum likelihood non-linear regression procedure. Specifically, all the experimental data are treated as subject to error, and the optimal parameter values are taken to be those minimizing the objective function

$$S = \sum^{j} \left(\frac{(P_i^c - P_i^e)^2}{\sigma_{P_i}^2} + \frac{(T_i^c - T_i^e)^2}{\sigma_{T_i}^2} + \frac{(x_{1i}^c - x_{1i}^e)^2}{\sigma_{x_{1i}}^2} + \frac{(y_{1i}^c - y_{1i}^e)^2}{\sigma_{y_{1i}}^2} \right), \qquad (2)$$

where superscripts c and e indicate calculated and experimental values respectively, the sum is taken over all j experimental points for the mixture in question and the σ's are the estimated standard deviations of the variables, which were as follows: $\sigma_P = 0{\cdot}13$ kPa, $\sigma_T = 0{\cdot}1$°C, $\sigma_x = 0{\cdot}001$ m.f. and $\sigma_y = 0{\cdot}003$ m.f. The estimated parameters for each of the above equations, together with the corresponding root mean square errors in pressure, temperature and phase compositions, are listed in Table VII for all three mixtures studied.

UNIFAC *Parameters*

The basic idea of a group contribution method such as UNIFAC (Fredenslund et al.[11,18]) is to use phase equilibrium data that have been determined experimentally

TABLE VIII

Root mean square deviations for the binary systems

System	t	y
Pyridine + ethyl acetate	0·91	0·010
n-Propyl acetate + pyridine	0·25	0·005
Pyridine + n-butyl acetate	0·24	0·009

for a relatively small number of systems to predict phase equilibrium data for other systems in which the same atom groups occur. We have used the experimental data obtained in this study to estimate UNIFAC CCOO/PYRIDINE group interaction parameters, for which no values have hitherto been published. The other UNIFAC parameters values used were those published by Gmehling et al.[19].

In the UNIFAC method, group interaction parameters are estimated using experimental data for T, x_i and y_i where i indicates one of the components present

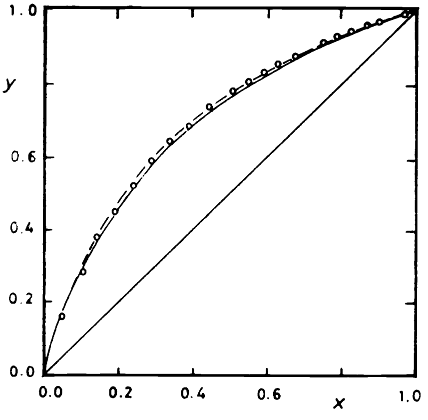

Fig. 3

Equilibrium diagram of ethyl acetate + pyridine system at 101·325 kPa: — — — UNIQUAC correlation; ——— UNIFAC prediction

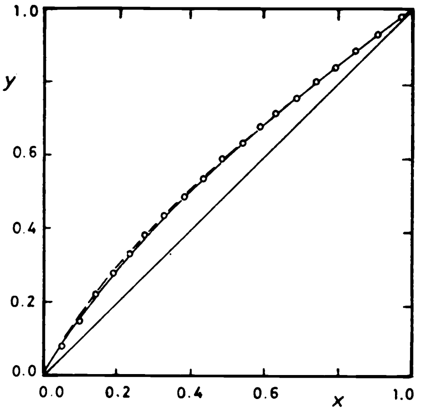

Fig. 4

Equilibrium diagram of the n-propyl acetate + pyridine system at 101·325 kPa: — — — UNIQUAC correlation; ——— UNIFAC prediction

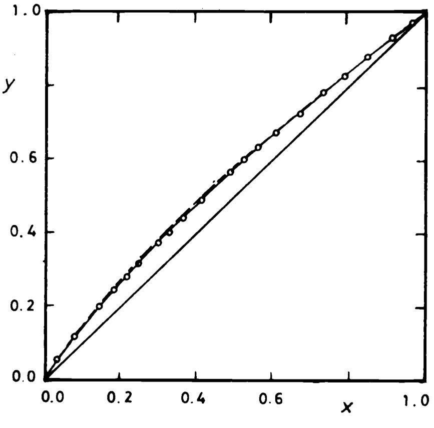

Fig. 5

Equilibrium diagram of the pyridine + n-butyl acetate system at 101·325 kPa: — — — LEMF correlation; ——— UNIFAC prediction

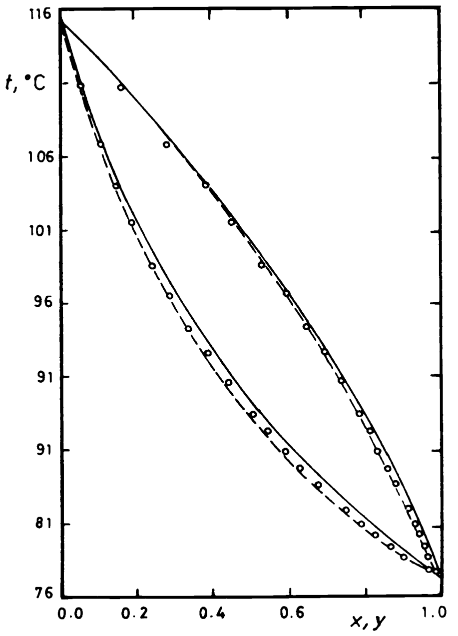

Fig. 6

Boiling-point diagram of the ethyl acetate + pyridine system at 101·325 kPa: — — — UNIQUAC correlation; ——— UNIFAC prediction

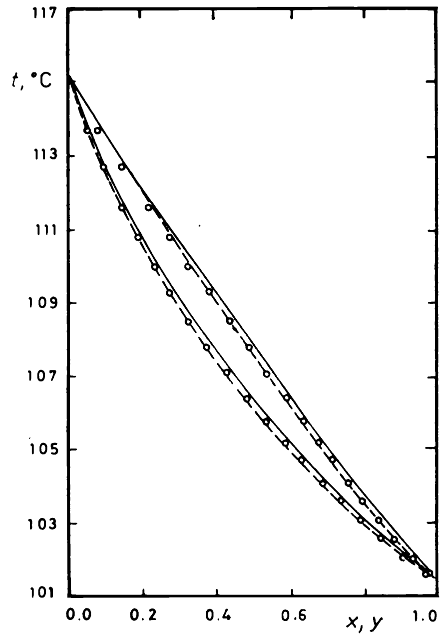

Fig. 7

Boiling-point diagram of the n-propyl acetate + pyridine system at 101·325 kPa: — — — UNIQUAC correlation; ——— UNIFAC prediction

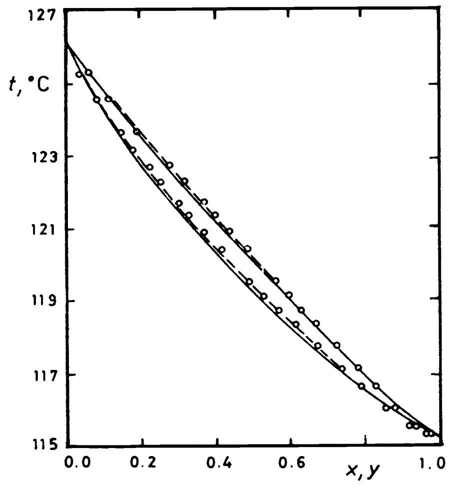

Fig. 8

Boiling-point diagram of the pyridine + n-butyl acetate system at 101·325 kPa: — — — LEMF correlation: ——— UNIFAC prediction and the activity coefficients γ_i are given by

$$\gamma_i = \frac{\phi_i y_i P}{x_i \phi_i^s P_i^s \exp\left(V_i(P - P_i^s)/RT\right)} . \qquad (3)$$

In this study, parameter estimation was performed as per Fredenslund et al.[11] by using Nelder and Mead's[20] simplex method to minimize the objective function

$$F = \sum_i \sum_j (\ln \gamma_{i,\mathrm{exp}} - \ln \gamma_{i,\mathrm{UNIFAC}})_j^2 , \qquad (4)$$

where i indicates a component and j an experimental point. Table VIII lists the parameter values obtained in such a way together with the corresponding root mean square deviations of temperature and vapour phase composition for each of the mixtures studied. Graphs of y against x for these mixtures are shown in Figs 3–5, and boiling point graphs in Figs 6–8.

CONCLUSIONS

The vapour–liquid equilibria of pyridine + acetate mixtures exhibit positive deviations from Raoult's law, the least ideal of those studied here being pyridine + ethyl acetate. Of the semiempirical equations considered, the UNIQUAC equation best fitted the experimental data for ethyl acetate + pyridine and n-propyl acetate + pyridine, while the Wilson, NRTL and LEMF equations gave slightly better results for n-butyl acetate + pyridine, the best of the three being the LEMF equation.

The experimental data obtained led to the UNIFAC group interaction parameter values $a_{\mathrm{CCOO/PYRIDINE}} = 116{\cdot}30$ and $a_{\mathrm{PYRIDINE/CCOO}} = -89{\cdot}41$. The vapour–liquid equilibria "predicted" for the three systems studied using these values are quite close to the experimental values, as was to be expected. Unfortunately, we have not found in the literature any vapour–liquid equilibrium data for other pyridine + ester systems, which would constitute a stronger test of the parameters' worth.

SYMBOLS

A_i	parameters in Eq. (*1*)
A, B, C	Antoine parameters
F	objective function, Eq. (*4*)
$\Delta g_{12}, \Delta g_{21}$	NRTL and LEMF parameters, J mol^{-1}
j	number of experimental data, Eqs (*2*) and (*4*)
m	number of Redlich–Kister parameters, Eq. (*1*)
M^E	excess property, Eq. (*1*)
n_D	refractive index at 25°C
P	pressure, kPa

q	parameter of the UNIQUAC and Effective UNIQUAC equations
R	gas constant
R^E	excess molar refraction
r	parameter of the UNIQUAC and Effective UNIQUAC equations
S	objective function, Eq. (*2*)
t	temperature, °C
t_B	boiling point at 101·325 kPa
Δu_{12}, Δu_{21}	parameters of the UNIQUAC and Effective UNIQUAC equations, J mol^{-1}
V	molar volume of the liquid, cm^3 mol^{-1}
V^E	excess molar volume, cm^3 mol^{-1}
x	liquid phase mole fraction
y	vapour phase mole fraction
α	nonrandomness parameters, NRTL and LEMF equations
γ	activity coefficient
$\Delta\lambda_{12}$, $\Delta\lambda_{21}$	Wilson equation parameters, J mol^{-1}
ϕ	vapour phase fugacity coefficient
ϱ	density at 25°C, g cm^{-3}
σ	standard deviation

Superscripts

c	calculated value
e	experimental value
E	excess
s	saturation condition value

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