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TECHNICAL NOTE

Extractive Distillation of *p*-Cresol/2,6-Xylenol Mixtures in the Presence of Alkanolamines

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ABSTRACT

The separation of *p*-cresol/2,6-xylenol mixtures has been investigated by extractive distillation in the presence of alkanolamines. The interaction parameters of liquid phase models, such as Wilson, NRTL, and UNIQUAC, have been estimated from binary vapor–liquid equilibrium data. The predicted relative volatility values for the *p*-cresol/2,6-xylenol mixtures in the presence of the alkanolamines were compared with experimental data.

Key Words. *p*-Cresol; 2,6-Xylenol; Alkanolamines; Reactive entrainers; Reactive distillation

INTRODUCTION

The separation of close boiling point isomers/nonisomeric mixtures is difficult by conventional distillation. The separation, if achieved by extractive distillation in the presence of a reactive entrainer, may be termed reactive extractive distillation (RED). This process is effective if the original components are different in their chemical natures and the reactive entrainer preferentially reacts with one of the components to form a higher boiling point complex or product, so that the unreacted component is

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removed as the distillate and the reaction complex/product and entrainer are the bottoms products from which the other component can be recovered.

Literature reports are available in which a complexation reaction has been imposed on distillation to improve the separation efficiency. For example, distillation of *m*-/*p*-xylenes has been conducted in the presence of either aluminum chloride under mild alkylating conditions (1) or sodium-*p*-xylene-18-crown ether in cumene as reactive entrainers (2, 3).

Separation of alkylphenols obtained as tar acids is difficult because of their close boiling points. Several strategies have been applied for the separation of *m*-/*p*-cresols and 2,6-xylenol/cresols mixtures. Some of these are based on the formation of an inclusion compound with cyclodextrin followed by distillation from alcoholic alkaline solutions (4, 5). It is expected that a stronger phenol will have a lower volatility in the presence of the alkali. Gassend et al. (6) separated alcohols and phenols using reactive distillation by partial conversion of alcohols or phenols into tin or aluminum alkoxides or phenoxides. Since these alkoxides are nonvolatile, the vapor phase is enriched with the less reactive alcohol/phenol. The separation factor depends on the pK_a values and the steric hindrance of alcohols and phenols, with the less-hindered component preferentially forming the complex. Using a similar strategy, Duprat et al. (7) reported separation of β-/γ-picolines mixtures in the presence of trifluoroacetic acid added in stoichiometric deficiency where a preferential complexation of the acid with γ-picoline took place.

Mahapatra et al. (8) separated mixtures of 2,6-xylenol/*p*-cresol and of chlorophenols by extractive distillation using aqueous solutions of *p*-toluene sulfonic acid and organic bases (methyl diethanolamine and diethanolamine). This new class of solvents provides sufficiently high relative volatility ($\alpha \sim 3.0$). No efforts were made, however, by these authors to develop a predictive strategy for these mixtures. Recently, Ningoo and Gaikar (9) reported that *p*-cresol can be separated from mixture of *m*-/*p*-cresols in the presence of organic amines by extractive distillation. Due to its higher acidity, *m*-cresol forms a higher boiling complex with the organic amine and remains in the liquid phase; the vapor phase is enriched with unreacted *p*-cresol.

The present work deals with the separation of another close boiling point mixture, *p*-cresol (pK_a = 10.14) and 2,6-xylenol (pK_a = 10.60) by reactive extractive distillation in the presence of alkanolamines. An acid–base complex formation is expected between *p*-cresol and the organic amine, and therefore the vapor phase should be enriched with 2,6-xylenol.

EXPERIMENTAL

Binary and ternary isobaric vapor–liquid equilibrium data were obtained for 2,6-xylenol/monoethanolamine (MEA), *p*-cresol/MEA, 2,6-xylenol/diethanolamine (DEA), *p*-cresol/DEA, 2,6-xylenol/triethanolamine (TEA), *p*-cresol/TEA, 2,6-xylenol/*p*-cresol (at 15 and 135 mmHg), 2,6-xylenol/*p*-cresol/MEA, 2,6-xylenol/*p*-cresol/DEA, and 2,6-xylenol/*p*-cresol/TEA mixtures in a modified Othmer recirculation still (10). The pressures were 760, 135, and 15 mmHg for systems involving MEA, DEA, and TEA, respectively. The analysis of liquid and vapor phases for binary mixtures was done by acid–base titration and for ternary mixtures by both acid–base titration and gas–liquid chromatography.

RESULTS AND DISCUSSION

Distillation in the presence of reactive entrainers is usually treated in terms of complexation constants, assuming the formation of nonvolatile complexes. The remaining noncomplexed amount is then treated as an ideal liquid phase to represent vapor–liquid equilibria. However, we recently showed that such distillation can be treated as multicomponent distillation, and the specific interactions can be expressed in terms of activity coefficients of liquid-phase models (9). This approach gives a better predictive ability for treating the distillation process in the presence of the reactive entrainer and in the absence of the formation of a new compound.

The liquid-phase activity coefficients (γ) were calculated from experimental VLE data and were fitted into three thermodynamic liquid phase models (Wilson, NRTL, UNIQUAC) to estimate the model interaction parameters. A nonlinear least-square technique was used to estimate the adjustable parameters. The objective function selected for minimization was

$$\text{O.F.} = \sum^{n} (\gamma_1^{\text{e}} - \gamma_1^{\text{p}})^2 + (\gamma_2^{\text{e}} - \gamma_2^{\text{p}})^2$$

where n is the number of data points. The superscripts p and e represent the predicted and experimental activity coefficients, respectively. The fugacity coefficients were estimated using the virial equation of state, and the vapor pressures of the pure components were obtained from published literature (11, 12).

Table 1 gives the model parameters obtained, and Fig. 1 to 6 show the experimental points and estimated T–x–y curves using the three models.

TABLE 1
Interaction Parameters of Binary Systems[a] (in cal/gmole)

System	Wilson		NRTL		UNIQUAC	
	a_{12}	a_{21}	a_{12}	a_{21}	a_{12}	a_{21}
p-Cresol (1)/MEA (2)	578.16	−263.38	44.39	44.39	−86.38	−46.56
2,6-Xylenol (1)/MEA (2)	195.49	91.94	−30.0	−28.76	−139.62	−362.34
p-Cresol (1)/DEA (2)	173.65	−128.78	732.96	−1050.81	3061.77	−574.99
2,6-Xylenol (1)/DEA (2)	23.52	22.66	−150.71	156.86	1249.79	−359.86
2,6-Xylenol (1)/*p*-Cresol (2) at 135 mmHg	−30.0	−35.0	−42.50	−32.98	−10.85	−14.69
p-Cresol (1)/TEA (2)	−1869.1	−245.9	−1349.0	−299.90	−1097.0	−1924.0
2,6-Xylenol (1)/TEA (2)	1225.68	−1400	480.0	−579.00	185.21	−150.83
2,6-Xylenol (1)/*p*-Cresol (2) at 15 mmHg	−4.99	6.00	−9.95	−5.95	−12.0	−13.00

[a] Wilson: $a_{12} = \lambda_{12} - \lambda_{11}$; $a_{21} = \lambda_{21} - \lambda_{22}$. NRTL: $a_{12} = g_{12} - g_{11}$; $a_{21} = g_{21} - g_{22}$. UNIQUAC: $a_{12} = \Delta u_{12}$; $a_{21} = \Delta u_{21}$.

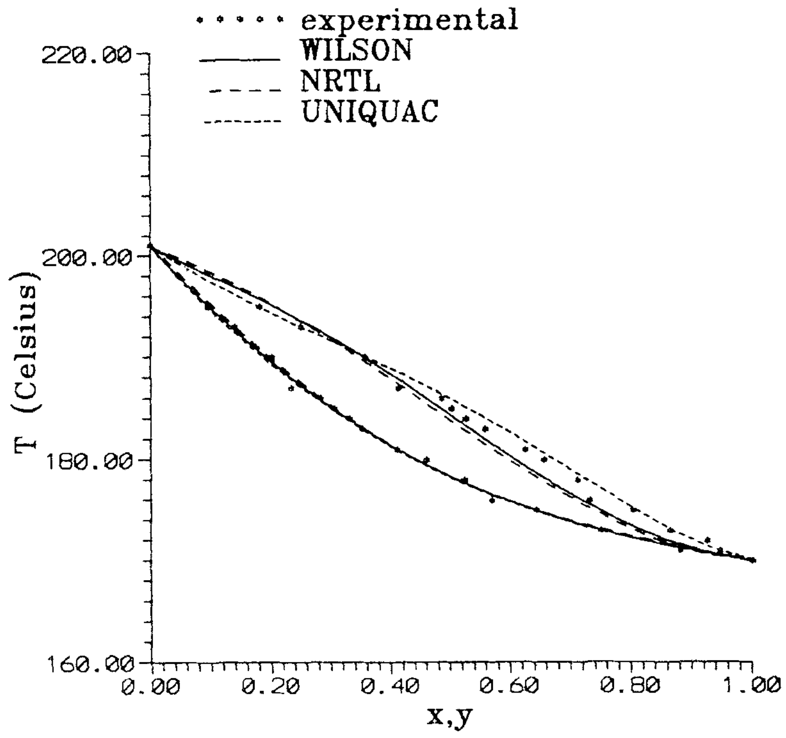

FIG. 1 *T–x–y* plot (2,6-xylenol/MEA).

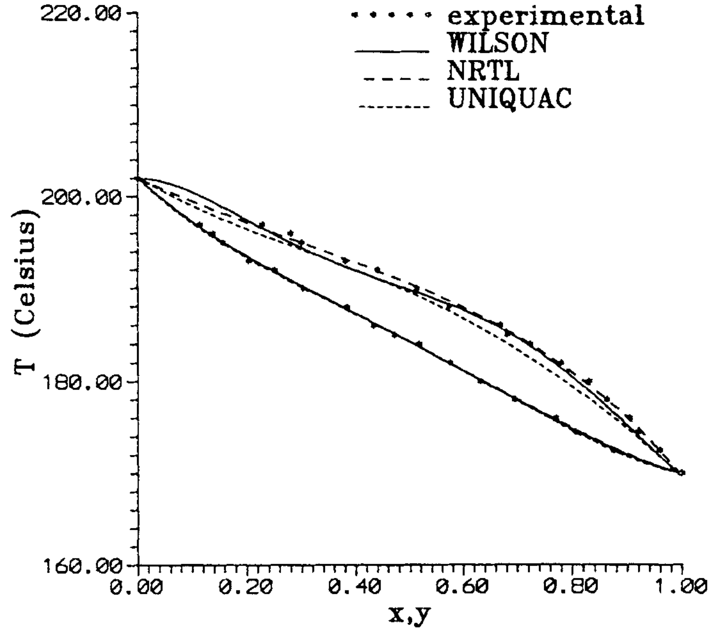

FIG. 2 *T–x–y* plot (*p*-cresol/MEA).

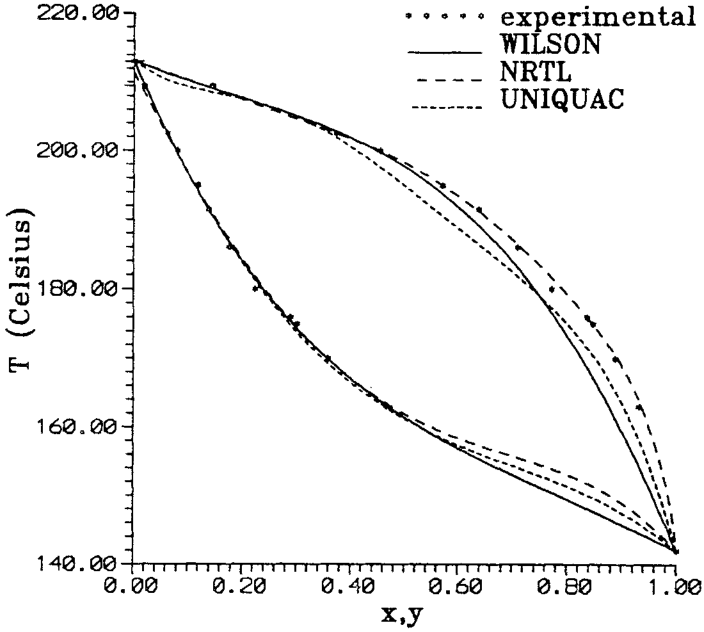

FIG. 3 *T–x–y* plot (2,6-xylenol/DEA).

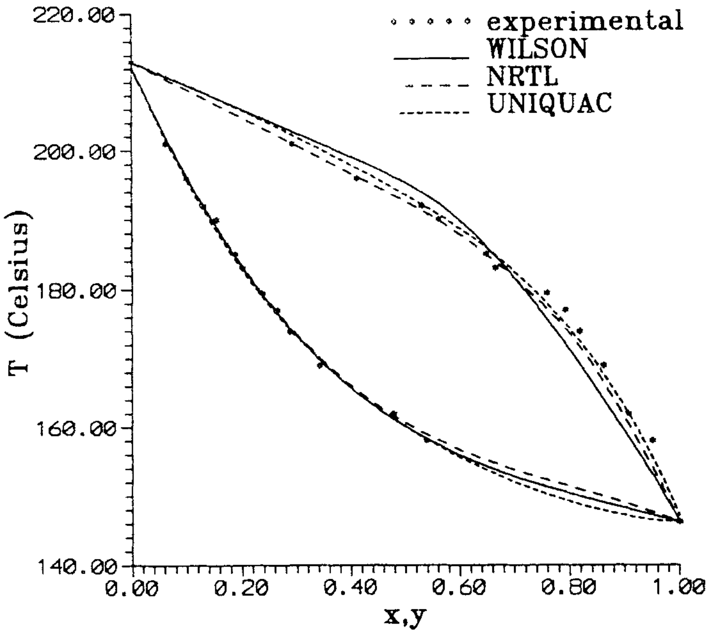

FIG. 4 *T–x–y* plot (*p*-cresol/DEA).

The NRTL and UNIQUAC models gave better fits of the VLE data than the Wilson model. For *p*-cresol and 2,6-xylenol with DEA and TEA, the γ values are less than unity. The vapor-phase fugacity coefficients show considerable negative deviations from unity in the case of systems involving MEA. Because monoethanolamine is a more volatile component, strong interactions, even in the vapor phase, cannot be ruled out. Conversely, with other alkanolamines at reduced pressures, the vapor phase shows an almost ideal behavior.

The advantage of using these models to express the specific interactions existing between the phenols and amines is in their predictive capacity for ternary mixtures. Assuming that the binary parameters are the same in the ternary mixtures, the relative volatility can be predicted for *p*-cresol/2,6-xylenol mixtures in the presence of alkanolamines.

The estimated binary specific interaction parameters were used to predict the ternary vapor–liquid equilibria and the relative volatility of 2,6-xylenol/*p*-cresol in the presence of MEA, DEA, and TEA.

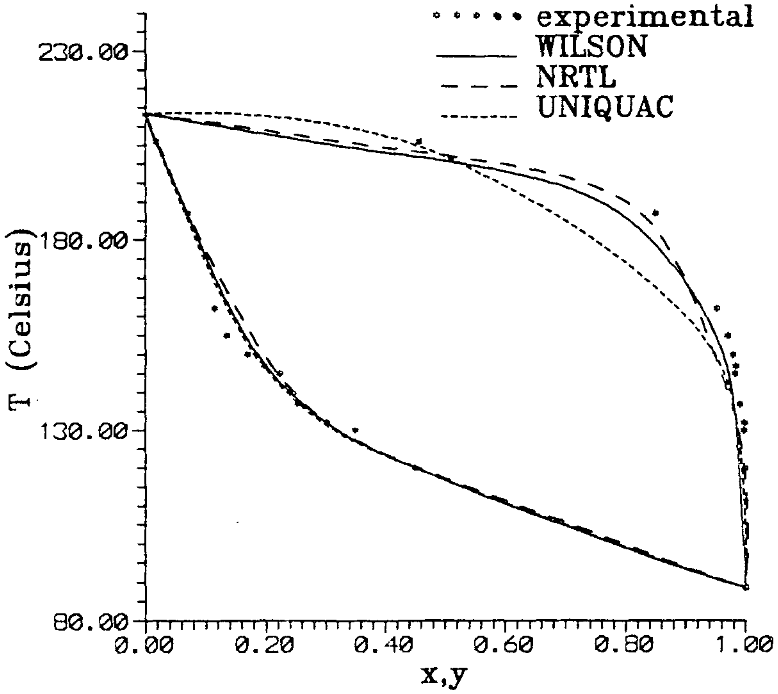

FIG. 5 T–x–y plot (2,6-xylenol/TEA).

Table 2 compares the experimental and estimated vapor-phase compositions and relative volatility values for the best models. Predictions using the Wilson model for systems involving MEA and the NRTL model for the other two alkanolamines match the experimental values satisfactorily. The relative volatility values of *p*-cresol/2,6-xylenol mixtures in the presence of the amines are significantly higher than unity in the absence of the amines. The efficiency of separation increases in the order MEA < DEA < TEA.

TEA, although a weak base compared to DEA, gives better separations, indicating the significance of steric hindrance in the phenol–amine interactions, 2,6-Xylenol also has the phenolic OH group sterically hindered by the two neighboring —CH_3 groups. TEA, the most sterically hindered, is unable to interact efficiently with 2,6-xylenol. For the organic compounds the acid–base interactions involve hydrogen bonding and/or dipole–dipole

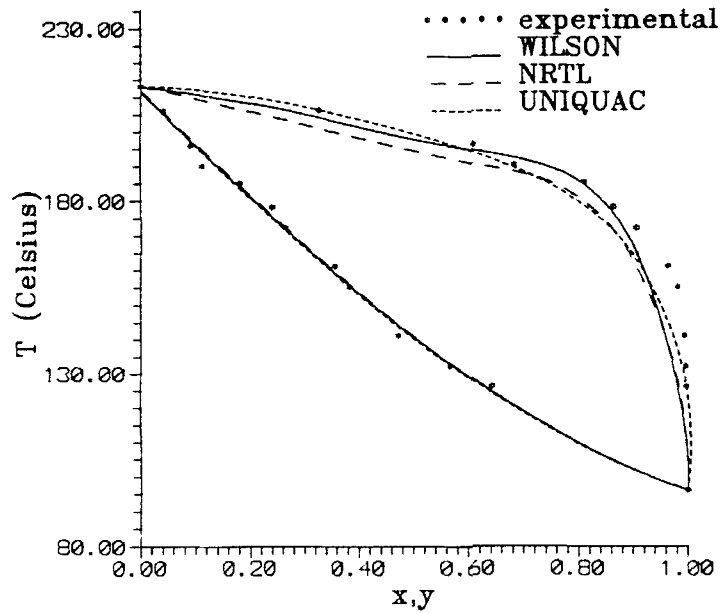

FIG. 6 *T*–*x*–*y* plot (*p*-cresol/TEA).

TABLE 2
Estimated Ternary VLE and Its Comparison with the Experimental Data

x_1	x_2	y_1^e	y_2^e	y_1^p	y_2^p	α_{12}	α_{12}^p
		2,6-Xylenol (1)/*p*-Cresol (2)/MEA (3): Wilson					
0.08	0.09	0.04	0.03	0.045	0.035	1.50	1.446
0.15	0.18	0.08	0.07	0.086	0.077	1.37	1.340
0.19	0.20	0.10	0.08	0.117	0.104	1.31	1.257
0.23	0.24	0.14	0.12	0.153	0.146	1.37	1.23
0.27	0.30	0.16	0.14	0.192	0.179	1.27	1.192
		2,6-Xylenol (1)/*p*-Cresol (2)/DEA (3): NRTL					
0.08	0.10	0.45	0.28	0.476	0.302	1.99	1.970
0.15	0.17	0.52	0.34	0.553	0.355	1.73	1.765
0.17	0.22	0.49	0.37	0.464	0.395	1.71	1.520
0.29	0.27	0.50	0.43	0.527	0.455	1.65	1.646
0.26	0.29	0.54	0.44	0.524	0.421	1.36	1.388
		2,6-Xylenol (1)/*p*-Cresol (2)/TEA (3): NRTL					
0.06	0.10	0.59	0.38	0.578	0.386	2.59	2.495
0.11	0.23	0.54	0.45	0.531	0.452	2.51	2.456
0.17	0.26	0.60	0.39	0.612	0.381	2.35	2.445
0.18	0.32	0.56	0.44	0.556	0.441	2.26	2.241
0.19	0.35	0.53	0.47	0.522	0.476	2.08	2.020

interactions, unlike the proton transfer reactions in the aqueous phase. Thus, the selectivity is decided by the efficiency of interactions between phenolic OH and the nitrogen of the amino group.

CONCLUSIONS

The interaction parameters were obtained from binary VLE experiments and were used successfully for the prediction of ternary VLE data in the presence of the reactive entrainers. The higher relative volatility values for 2,6-xylenol/*p*-cresol mixtures compared to unity in the absence of the amines indicate the possibility of separation using these amines as extractive solvents. By considering the assumption of the temperature-independent nature of the interaction parameters, the match of experimental values with predicted values is satisfactory. Although this approach seems more appropriate from the thermodynamic point of view, it does not give any information regarding the nature of interactions between the components.

NOMENCLATURE

a_{ij}	interaction parameter between components i and j, cal/gmol
O.F.	objective function
x_i	mole fraction of i in the liquid phase
y_i	mole fraction of i in the vapor phase

Superscripts

e	experimental value
p	predicted value

Greek Symbols

α	relative volatility
γ_i	activity coefficient of i in the liquid phase

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