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Vapor−Liquid Equilibrium in Extractive Distillation of the Acetone/Methanol System Using Water as Entrainer and Pressure Reduction

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Displacement of the azeotropic composition of acetone/methanol system by using water as entrainer has been studied for different solvent:feed molar ratios (S/F = 1.0, 2.5, and 3.0) combined with pressure reduction, at 75.0 kPa. The vapor−liquid equilibrium data were compared to ASPEN Plus simulations using Wilson, NRTL, and UNIQUAC models. To determine the composition of the liquid and vapor phases, headspace-gas chromatography was used. For a solvent:feed molar ratio of 1.0 was obtained a complete azeotrope elimination. The obtained relative volatilities between 1.6 and 3.2 were for the assayed S/F ratios. Experimental data were well-represented by simulation with the UNIQUAC model, obtaining a vapor molar composition and temperature mean error of 0.009−0.027 and 0.80−1.70 K, respectively.

Introduction

Separation of azeotropic mixtures is one process of interest in the chemical industry because it is not possible to use conventional separation methods. Extractive distillation is a common process used to separate this kind of mixture where a third component, a salt solution or a solvent, is used as entrainer. The entrainer function is to increase the relative volatility of the mixture; in this way, the components boil separately, allowing the collection of heavier components (solvent and heavy key) at the distillation column bottom and the light key at the top.[1] Its selection involves a vapor−liquid equilibrium (VLE) study to establish solvent−mixture component interactions, and separation process effectiveness.[2] Higher boiling point with respect to the mixture components, capability to change the relative volatility between the key components, thermal stability, financial viability, and feasibility of recovery are desired properties in an entrainer.[3]

Acetone and methanol are solvents commonly used in industry, and their mixtures are common. For example, they are the major components in the aqueous product obtained from hydrocarbon synthesis by the Fischer−Tropsch process.[4] This mixture (acetone−methanol) presents a minimum boiling point azeotrope,[5] and a possible way to separate this azeotropic mixture is by extractive distillation. Studies using water as entrainer at 101.325 kPa,[4,6–8] or salts like cadmium acetate[9] and calcium bromide,[10] have been reported to determine the displacement of the acetone−methanol azeotrope. Because industrially acetone−methanol mixtures are concentrated up to azeotropic composition and then they are submitted to the azeotropic separation processes to reduce energy consumption and size in this type of separations, it is important to establish an economical and operational feasibility with regard to a specific entrainer, and facts relating to the necessary amount of entrainer to displace the binary azeotrope. It has been shown that a feasible entrainer used to displace the methanol−acetone azeotrope is water.[4,6,7,11]

Although there are several reports with regard to the VLE for the methanol−acetone−water system at 101.325 kPa, no reports evaluate both the effect of the solvent:feed molar ratio and the pressure reduction to displace the azeotropic point. Although pressure reduction could be an alternative to improve the separation process, it is a cost-demanding operation. However, when plant location at different sea levels is possible, the atmospheric pressure reduction can be considered as a noncost design parameter with technical consequences. For instance, in some South America important cities, the atmospheric pressure can be even of 75.0 kPa (2600 mts osl).

The aim of this work is to determine the effect of water as entrainer on the displacement of the binary (acetone−methanol) azeotrope, evaluating the vapor−liquid equilibrium for different solvent:feed molar ratios (S/F) combined with an operating pressure of 75.0 kPa, and to compare experimental results with predicted data by ASPEN Plus v. 2006 using Wilson, NRTL, and UNIQUAC models.

Materials and Methods

Chemicals. Solutions were prepared with acetone (J.T. Baker, 99.57%) and methanol (Panreac, 99.8%) analytical grade. Water content in reagents was determined by Karl Fischer titration (DL32 Coulometric Titrators, Mettler Toledo DL32). The quantity of water obtained was 0.24% and 0.26% for acetone and methanol, respectively. Deionized water was purified using an ion-exchanger filter.

Apparatus and Procedure. The designed equipment was a modification of the still described by Othmer[12] (Figure 1). Briefly, the still consisted of a 500 mL round-bottom flask, placed over a stirring hot plate surrounded by a heating tape. The top of the vapor line extended above the level of the central and outlet vapor tube leading to the condenser. To prevent vapor condensate from running back into the still, the vapor line was isolated with glass fiber, and a tempering controlled resistance (350 W − 110 V) was settled along the ascending line to minimize the temperature difference between both liquid and vapor phases. Condensed vapor was recycled into the still body to be mixed with the liquid phase by a condensed loop. Liquid samples were removed from the sampling port, while condensed vapor was removed from the condensate receiver. Temperature measurements were made by a RTD PT-100 sensor (±0.2 K precision) connected to a PID Autonics TZN4S controller.

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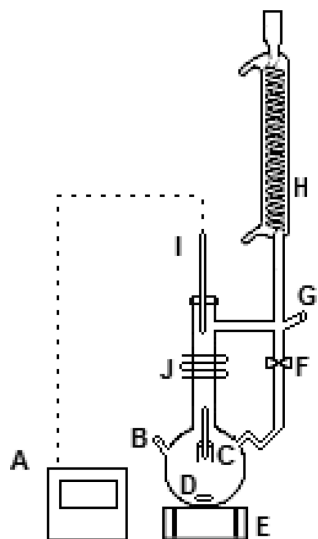† Universidad de los Andes.
‡ Universidad Nacional de Colombia.

$$\gamma_i = \phi_i y_i P / \{\phi_i^\circ x_i P_i^\circ \exp[\upsilon_i^L (P - P_i^\circ)/RT]\} \qquad (1)$$

where R is the gas constant, T is the temperature (K), and P is the pressure (kPa); x, y are the vapor and liquid mole compositions, the liquid molar volume υ_i^L was calculated from the Yen and Woods equation,[14] the pure-component vapor pressures Pi° were obtained using the Antoine equation with coefficients in Table 2, and fugacity coefficients, φ_i and φ_i°, were obtained using the second virial coefficients estimated by the method of Hayden−O'Connell (eq 2).[16]

$$\ln(\phi_i) = (2 \sum_j y_i B_{ij} - \sum_i \sum_j y_i y_j B_{ij}) P/RT \qquad (2)$$

For both binary and ternary data, the thermodynamic consistency was checked by the McDermott test.[17] The acceptance criterion ($D < D_{max}$) is based on a two-point test where a maximum local deviation (D_{max}) is calculated using estimated errors in composition, temperature, and pressure measurements. Next, for two experimental points, a and b, the local deviations D and D_{max} are given by eqs 3 and 4, respectively.

$$D = \sum_{i=1}^{n} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \qquad (3)$$

$$D_{max} = \sum_{i=1}^{n} (x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x +$$

$$2 \sum_{i=1}^{n} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{n} (x_{ia} + x_{ib})\frac{\Delta P}{P} \qquad (4)$$

$$+ \sum_{i=1}^{n} (x_{ia} + x_{ib})B_i\left(\frac{1}{[T_a + C_i]^2} + \frac{1}{[T_b + C_i]^2}\right)\Delta T$$

where n refers to the number of compounds, x_i and y_i refer to liquid and mole fractions of the species, respectively, γ_i refers to the overall liquid activity of component i, and B_i and C_i are Antoine parameters. In this work, errors were determined to be $\Delta P = 0.3$ kPa, $\Delta T = 0.3$ K, and $\Delta x = 0.015$ mol fraction. Although under these conditions all binary and ternary data were thermodynamically consistent, some experimental data for the ternary system were excluded because they present a $\Delta x > 0.015$ (Table 4). It is noted that the error in concentration was the most deciding factor in evaluating consistency of experimental data.

Meanwhile, to determine the overall agreement of experimental data and calculated data by the selected models (Wilson,

Figure 1. Vapor−liquid equilibrium equipment sketch. Controller, A; liquid sampling, B; liquid temperature, C; magnetic agitation, D; heating plate, E; valve, F; condensate sampling, G; condenser, H; vapor temperature, I; and resistance, J.

Assays were isobarically carried out at 75.0 kPa, measured with a GPB 1300 barometer with a precision of ±0.3 kPa. To evaluate entrainer effect on the acetone−methanol azeotrope displacement, feed acetone−methanol mixtures with acetone concentrations in the range of 50−98% and water:feed molar ratios of 1.0, 2.5, and 3.0 were prepared. Subsequently, 3 mL of both liquid and condensed vapor were removed in sealed devices and refrigerated to prevent evaporation leakage. Each experiment was performed in duplicate.

Solvents (methanol and acetone) were analyzed by headspace-gas chromatography (GC-HS, GC-2010, Shimadzu, USA) equipped with a SHRX5 column (15 m, 0.25 mm i.d., 0.25 μm) capillary column and flame ionization detector (FID). The inlet temperature was set at 423.15 K, and helium served as the carrier gas with a flow of 1.0 cm^3 min^{-1} with a split 100:1. The oven temperature was isotherm programmed at 323 K for 6 min. The detector temperature was 423.15 K with hydrogen flow of 40 mL min^{-1} and air flow of 400 cm^3 min^{-1} with constant makeup flow at 40 cm^3 min^{-1}. Samples were preheated for 10 min at 353 K and 500 rpm in the HS, and injection temperature was 353 K. Concentrations were calculated from calibration curves using stock solutions of pure compounds. Water content was determined by difference among compositions.

Simulation of the Acetone−Methanol−Water Extractive Distillation. Simulation of the acetone−methanol azeotropic mixture separation was carried out in ASPEN Plus v. 2006. This involves two columns: the extractive distillation and recovery one in which acetone and methanol are recovered, respectively. The used process flow-sheet of the extractive distillation process was described previously.[13] A comparison between the configuration proposed by Luyben[11] and our previous work[13] (Table 1) for the extractive and recovery columns using S/F ratios of 1.0 and 1.5 was made.

Results and Discussion

Vapor−liquid equilibrium results for the binary (methanol−acetone) and ternary (methanol−water−acetone) systems are presented in Tables 3 and 4, with activity coefficients γ_i calculated using eq 1.

Table 1. Configuration of Extractive and Recovery Columns and Operational Conditions

parameter	Luyben[11]		Gil et al.[13]	
column configuration	extractive	recovery	extractive	recovery
number of stages	57	26	52	26
feed stage	40	14	48	14
entrainer feed stage	25		22	
reflux ratio	3.44	1.61	5	3
condenser	total	total	total	total
pressure drop per tray (kPa)			1.013	1.013
Operational Conditions for Both Configurations				
binary feed composition (% mol)				
acetone	77.25			
methanol	22.25			
distillate mole flow (kmol h^{-1})	76	25		
entrainer feed temperature (K)	320.15			
binary feed temperature (K)	293.15	363.15		
pressure (kPa)	75.0	75.0		
top stage pressure (kPa)	75.0	75.0		

Table 2. Antoine Equation Constants, $\log_{10} P_i^S = A - ((B)/(C + T))$ with T in K and P_i^S in kPa[15]

	A	B	C
acetone	6.35647	1277.030	−35.92
methanol	7.02240	1474.080	−44.02
water	7.13653	1695.167	−42.74

NRTL, and UNIQUAC), Tan et al.[18] equations for determining mean absolute deviation between experimental and predicted temperature and vapor composition (eqs 5 and 6) were used.

$$|\Delta T| = \frac{1}{n}\left[\sum_{i=1}^{n} |T_i^c - T_i^e|\right] \qquad (5)$$

$$|\Delta y_{1,2}| = \frac{1}{2n}\left[\sum_{i=1}^{n} |y_{1,i}^c - y_{1,i}^e| - |y_{2,i}^c - y_{2,i}^e|\right] \qquad (6)$$

where n is the total number of points, T_i^c is the boiling temperature calculated by the model at ith point, and T_i^e is the experimental boiling temperature at ith point; y_i^c and y_i^e are the vapor mole fractions calculated by the model and obtained experimentally, respectively, at point ith. Subscripts 1 and 2 correspond to acetone and methanol vapor mole fractions, respectively.

Table 3 presents experimental data for the binary acetone−methanol system 75.0 kPa, and calculated and experimental $x-y$ and $T-x,y$ plots of the system are presented in Figure 2. It is observed that VLE prediction using Wilson, NRTL, and UNIQUAC models in ASPEN Plus v. 2006 for the binary system overlapped and presented a minimum boiling point azeotrope. Experimental data were suitably predicted by all of the selected models; the obtained mean absolute deviation between calculated and experimental data for temperature and acetone vapor composition was 0.71 ± 0.6 K and 0.10 ± 0.07, respectively. Experimentally was characterized a point in the vicinity of the azeotropic point, obtaining a temperature of 320.30 K and acetone mole fraction of 0.81, which is in agreement with calculated temperature and acetone mole fraction for azeotrope 320.20 K and 0.821. Although there are no VLE reports at 75.0 kPa, results are in agreement with expected performance when a decrease of pressure occurs; at 101.32 kPa, the azeotropic point has been reported at 328.55 K and acetone mole fraction of 0.783.[19]

Table 4 presents the experimental VLE data for acetone−methanol and entrainer (water) system at solvent:feed (S/F) molar ratios of 1.0, 2.5, and 3.0, and Figure 3 presents the pseudobinary acetone (1) + methanol (2) (x_1-y_1) phase diagram for experimental and predicted data by the UNIQUAC model. In Figure 3, NRTL and Wilson model prediction profiles were
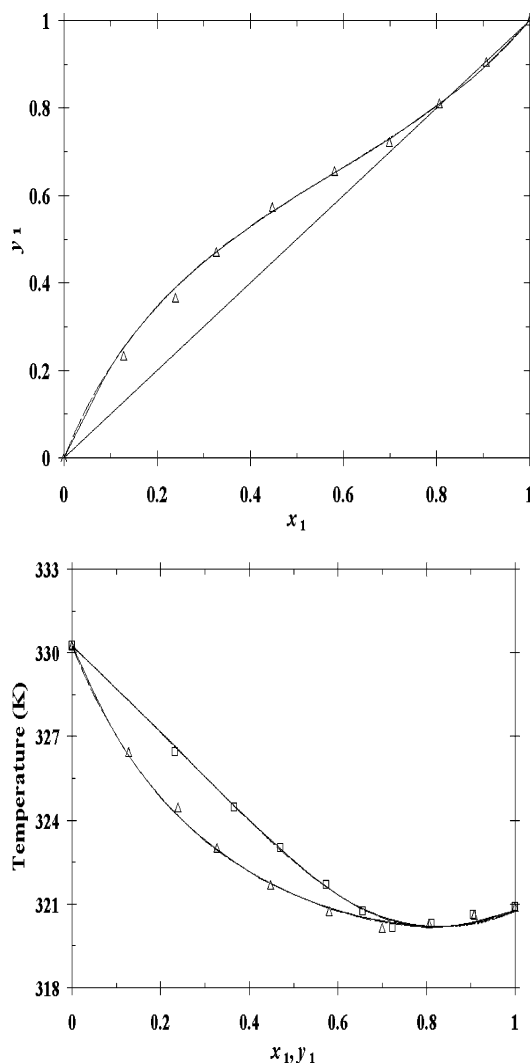
Figure 2. Vapor−liquid equilibrium x_1-y_1 and $T-x_1,y_1$ plot for the binary system acetone (1) + methanol (2) at 75.0 kPa. Nomenclature: simulated results with Wilson (· · ·), NRTL (− − −), and UNIQUAC (−) models.

not included because visual overlapping did not allow differentiation among the models. When water was added in the still at the selected S/F, it was observed that the azeotrope was eliminated at all assayed S/F ratios. As S/F was increased, separation was improved gradually. This effect is caused by the high boiling point of water, and water affinity with methanol (because of the polar group OH) that decreases its volatility in the mixture, allowing the acetone−methanol separation. These results indicate that is not necessary to use large amounts of

Table 3. Experimental Vapor−Liquid Equilibrium Data for the System Acetone (1) + Methanol (2) at 75.0 kPa[a]

T (K)	δ (T)	x_1	δ (x_1)	y_1	δ (y_1)	ϕ_1	γ_1	ϕ_2	γ_2
320.9	0.071	0.994	0.002	0.993	0.003	0.9686	1.001	0.9786	1.803
320.6	0.071	0.908	0.012	0.905	0.004	0.9690	1.026	0.9781	1.602
320.3	0.071	0.807	0.027	0.812	0.010	0.9695	1.046	0.9780	1.535
320.2	0.000	0.700	0.014	0.723	0.021	0.9700	1.081	0.9780	1.460
320.8	0.141	0.581	0.010	0.656	0.024	0.9706	1.154	0.9783	1.267
321.7	0.071	0.448	0.020	0.573	0.013	0.9715	1.264	0.9786	1.145
323.0	0.071	0.327	0.017	0.470	0.007	0.9726	1.355	0.9790	1.102
324.5	0.141	0.239	0.003	0.366	0.002	0.9738	1.431	0.9795	1.052
326.5	0.141	0.128	0.009	0.233	0.005	0.9752	1.525	0.9800	1.063
330.2[b]	0.000	N.D		N.D		0.9776	1.832	0.9815	1.010

[a] Temperature (T), liquid-phase (x_i), and vapor-phase (y_i) mole fractions, activity coefficient (γ_i), fugacity coefficient (ϕ_i), and standard deviation (δ). The standard deviation was defined as $\sigma = [(1/N)\sum_{i=1}^{N}(z_i - \bar{z})^2]^{1/2}$, where N is the total number of data, z_i is the ith data, and $\bar{z}$ is the data mean of each studied variable (temperature, T; liquid (x) or vapor (y) mole fraction). ND: not detectable. [b] This measure corresponds to pure methanol. Composition in both phases x and y 0.997 ± 0.000.

Table 4. Experimental Vapor−Liquid Equilibrium Data for the System Acetone (1) + Methanol (2) + Water (3) at 75.0 kPa and Solvent to Molar Feed Ratios (S/F) of 3.0, 2.5, and 1.0[a]

T (K)	$\delta(T)$	x_1	$\delta(x_1)$	x_2	$\delta(x_2)$	y_1	$\delta(y_1)$	y_2	$\delta(y_2)$	γ_1	γ_2	γ_3
					S/F = 3.0							
334.15	0.00	0.097	0.002	0.122	0.004	0.356	0.063	0.150	0.031	2.348	1.073	2.232
332.45[b]	0.42	0.138	0.021	0.120	0.025	0.494	0.045	0.151	0.013	2.419	1.179	1.894
330.95	0.14	0.154	0.005	0.080	0.001	0.632	0.019	0.140	0.056	2.925	1.729	1.261
329.9	0.21	0.170	0.008	0.069	0.002	0.531	0.008	0.081	0.004	2.300	1.227	2.267
329.25	0.28	0.180	0.005	0.054	0.000	0.565	0.022	0.067	0.002	2.356	1.314	2.210
329.2	0.07	0.190	0.012	0.052	0.002	0.577	0.048	0.065	0.004	2.289	1.318	2.176
328.6	0.07	0.227	0.013	0.050	0.005	0.745	0.021	0.058	0.008	2.520	1.269	1.294
327.95	0.14	0.244	0.007	0.031	0.001	0.612	0.060	0.031	0.001	1.972	1.114	2.409
327.55[b]	0.28	0.431	0.016	0.025	0.019	0.733	0.017	0.014	0.004	1.333	0.649	2.324
327.1	0.07	0.269	0.010	0.005	0.000	0.671	0.104	0.006	0.003	2.019	1.516	2.265
					S/F = 2.5							
334.25	0.14	0.080	0.005	0.125	0.005	0.346	0.148	0.195	0.012	2.748	1.355	2.104
331.45[b]	0.70	0.106	0.022	0.109	0.063	0.417	0.114	0.128	0.052	2.754	1.144	2.401
329.85	0.28	0.129	0.015	0.078	0.013	0.612	0.339	0.128	0.087	3.479	1.702	1.468
329.4	0.07	0.157	0.010	0.067	0.011	0.492	0.175	0.078	0.031	2.336	1.232	2.528
328.6	0.07	0.157	0.006	0.053	0.002	0.452	0.015	0.054	0.002	2.216	1.114	2.958
328.1	0.07	0.163	0.005	0.047	0.002	0.470	0.005	0.050	0.001	2.258	1.177	2.944
327.85[b]	0.00	0.198	0.033	0.046	0.004	0.473	0.008	0.039	0.002	1.879	0.970	3.169
327.15	0.00	0.193	0.007	0.029	0.000	0.579	0.016	0.029	0.004	2.424	1.166	2.553
327.15	0.14	0.204	0.004	0.016	0.001	0.770	0.033	0.022	0.002	3.043	1.617	1.353
326.45	0.00	0.215	0.007	0.006	0.000	0.548	0.081	0.006	0.001	2.104	1.141	3.008
					S/F = 1.0							
331.9	0.35	0.069	0.001	0.177	0.006	0.287	0.043	0.283	0.017	2.847	1.531	2.313
329.5	0.34	0.118	0.000	0.151	0.007	0.327	0.002	0.136	0.009	2.059	0.953	3.334
327.6	0.48	0.117	0.007	0.106	0.008	0.314	0.073	0.105	0.008	2.131	1.130	3.711
327.4	0.64	0.158	0.003	0.089	0.001	0.321	0.001	0.072	0.002	1.626	0.931	4.040
325.95	0.14	0.214	0.003	0.072	0.009	0.287	0.077	0.043	0.008	1.128	0.717	5.055
325.83	0.99	0.210	0.001	0.070	0.004	0.402	0.002	0.050	0.001	1.616	0.880	4.116
325.6	0.64	0.229	0.002	0.049	0.002	0.347	0.002	0.042	0.004	1.291	1.055	4.632
325.65[b]	0.99	0.219	0.062	0.034	0.012	0.413	0.098	0.039	0.021	1.601	1.426	4.000
325.2[b]	0.35	0.233	0.027	0.019	0.039	0.418	0.038	0.016	0.000	1.548	1.057	4.222
325.0	0.07	0.163	0.000	0.008	0.010	0.380	0.012	0.015	0.002	1.243	2.188	4.697

[a] Temperature (T), liquid-phase (x_i) and vapor-phase (y_i) mole fractions, activity coefficient (γ_i), and standard deviation (δ). The standard deviation was defined as $\sigma = [(1/N)\sum_{i=1}^{N}(z_i - \bar{z})^2]^{1/2}$, where N is the total number of data, z_i is the ith data, and $\bar{z}$ is the data mean of each studied variable (temperature, T; liquid (x) or vapor (y) mole fraction). [b] Excluded data.
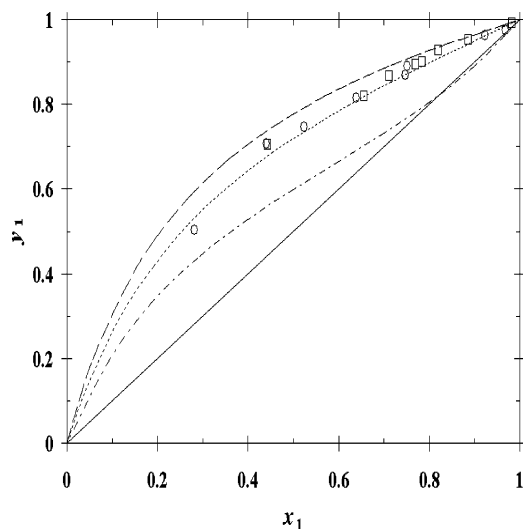

Figure 3. Comparison between calculated UNIQUAC and experimental phase diagram (x_1-y_1) for acetone (1)−methanol (2) system on a solvent-free basis at 75.0 kPa (binary system, − · −). Solvent:molar feed ratios of 3.0 (predicted, − −; experimental, □) and 1.0 (predicted, - - -; experimental, ○).

solvent to achieve the desired separation. Using a S/F molar ratio slightly higher than 1.0 is enough to guarantee the azeotropic point elimination with a low solvent consumption at 75.0 kPa. This favors economically the process and probably equipment maintenance. Nevertheless, an increment of the S/F ratio to 3.0 showed that predicted data were overestimated in regard to experimental. This observed difference in the pseudo-

binary diagram showed to be greater when the acetone mole fraction was lower than 0.80.

Different authors have reported in large plant simulation S/F ratios between 1.5 and 4.0 at 101.25 kPa.[1,11,20] This implies that pressure decrease has a positive effect on the reduction of the solvent:feed molar ratio to eliminate the azeotropic point. Other authors have reported the elimination of the azeotropic point using 5% of monoethanolamine (MEA) in the feed or inorganic salts such as KCSN and LiCl. The fact that water can be used in a lower ratio to displace the azeotrope completely presents advantages like low process cost regarding the salts and MEA cost, and a lower corrosive effect on equipment than that caused by salt solutions at high temperature.

The mean absolute deviation of temperature and vapor molar composition obtained between experimental and calculated data by Wilson, NRTL, and UNIQUAC models in ASPEN Plus v. 2006 are presented in Table 5. The lowest temperature mean absolute error was obtained with the UNIQUAC model, and it is observed that the mean absolute error increased as S/F ratio decreased, obtaining the highest deviation between experimental and predicted data at S/F 1.0. Although a similar performance is observed for the mean absolute error of composition, at S/F 1.0 the mean error is the same for different models. For these reasons, the UNIQUAC model was selected as the most suitable model to predict the ternary system VLE. These results are in agreement with the Luyben report,[11] who proposed this model to separate acetone−methanol mixture by extractive distillation using water as entrainer.

Figures 4 and 5 present the comparison between experimental temperature and liquid and vapor molar composition with those

Table 5. Mean Absolute Deviation (MAD) and Standard Deviation (SD) for Experimental versus Calculated Vapor−Liquid Equilibrium Using Wilson, NRTL, and UNIQUAC Models for Solvent to Molar Feed Ratios (S/F) of 3.0, 2.5, and 1.0

	Wilson		NRTL		UNIQUAC	
	MAD	SD	MAD	SD	MAD	SD
			S/F = 3.0			
$|\Delta y_{1,2}|$	0.012	0.015	0.011	0.015	0.009	0.015
$|\Delta T|$	0.417	0.190	0.494	0.213	0.246	0.114
			S/F = 2.5			
$|\Delta y_{1,2}|$	0.016	0.028	0.011	0.020	0.030	0.028
$|\Delta T|$	0.704	0.396	0.709	0.381	0.523	0.329
			S/F = 1.0			
$|\Delta y_{1,2}|$	0.029	0.066	0.029	0.065	0.029	0.056
$|\Delta T|$	1.728	0.893	1.364	0.935	0.767	0.713

calculated by the UNIQUAC model. It is noted that for acetone mole fractions higher than 0.80, in a solvent-free basis, the model presents a good correlation with experimental data, but predicted acetone liquid mole fraction is underestimated by the
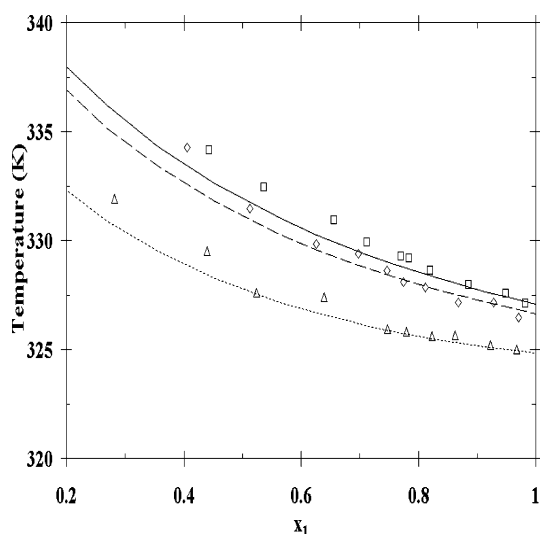
Figure 4. $T-x$ diagram for acetone (1) + methanol (2) system on a solvent-free basis at 75.0 kPa. UNIQUAC model for a solvent:molar feed ratio of 3.0 (calculated, −; experimental, □), 2.5 (calculated, − −; experimental, ◊), and 1.0 (calculated, · · ·; experimental, △).
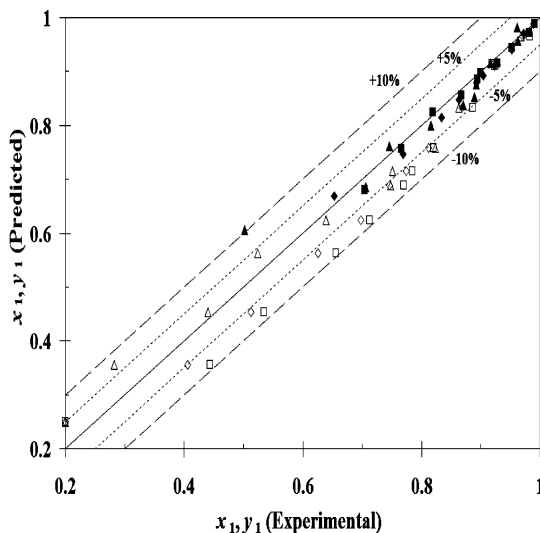

Figure 5. Parity plot for vapor (filled symbols) and liquid (empty symbols) composition for the acetone (1) + methanol (2) + water (3) system for solvent:molar feed ratios of 3.0 (□), 2.5 (◊), and 1.0 (△).
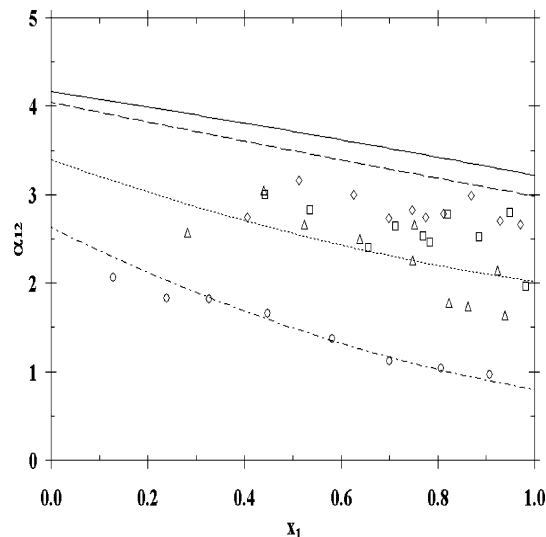

Figure 6. Relative volatility−x diagram for acetone (1) + methanol (2) system on a solvent-free basis at 75.0 kPa. UNIQUAC model for binary system (calculated, − · −; experimental, ○) and solvent:molar feed ratios of 3.0 (calculated, −; experimental, □), 2.5 (calculated, − −; experimental, ◊), and 1.0 (calculated, · · ·; experimental, △).

model, and the difference is notable mainly at high S/F ratios. The increase of water fraction in the mixture caused a higher boiling point, although at S/F of 2.5 and 3.0 no significant differences were observed (maximum ΔT 1 K). Although the overall mean absolute deviation calculated for vapor mole fraction and temperature using Tan et al.[18] equations showed the highest mean error deviations at low S/F ratios (Table 5), the comparison of experimental data and predicted data (Figure 3) showed that at S/F of 1.0 predicted data had a good representation of experimental. The differences observed between predicted and experimental data for the different S/F molar ratios suggest that an adjustment of UNIQUAC residual parameters might be suitable to improve the predicted data.

Entrainer effect on the relative volatility of the mixture was determined by the ratio of vapor and liquid composition of acetone (1) and methanol (2) in a solvent-free basis (eq 7).

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\gamma_1 P_1^0}{\gamma_2 P_2^0} \tag{7}$$

Figure 6 presents the solvent:feed molar ratio effect on the relative volatility. The lowest relative volatility obtained was 1.63 at S/F 1.0, while the highest was 3.1 at S/F 2.5. It is noticeable that relative volatility predicted by the UNIQUAC model is mainly overestimated at S/F 2.5 and 3.0, while at S/F 1.0 there is not a definitive performance. Nevertheless, for the binary system (acetone−methanol), predicted relative volatility by UNIQUAC and experimental data are well-correlated, with a correlation coefficient of 96.9%. In Figure 7 is presented the predicted effect of the increase of water mole fraction on relative volatility for different acetone to methanol ratios. It can be observed that the entrainer increased the relative volatility as it increased its mole fraction in the mixture, but for the different acetone to methanol ratios at water mole fraction of 0.73 a notable increase of the relative volatility that favors the mixture separation was presented. Experimental water mole fraction in feed was between 0.5 and 0.75 with relative volatilities in the range of 1.63 and 3.1 for the binary mixture. This result is in agreement with that predicted by the UNIQUAC model for different acetone−methanol ratios with the same water mole fraction.
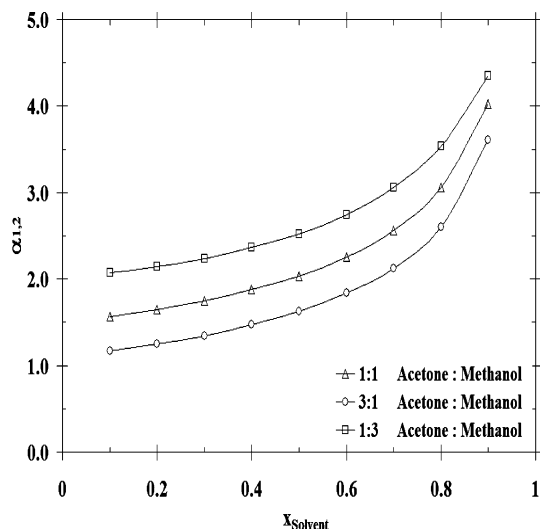
Figure 7. Simulation of the solvent and acetone (1):methanol (2) ratio effect on the relative volatility by UNIQUAC model at 75.0 kPa.
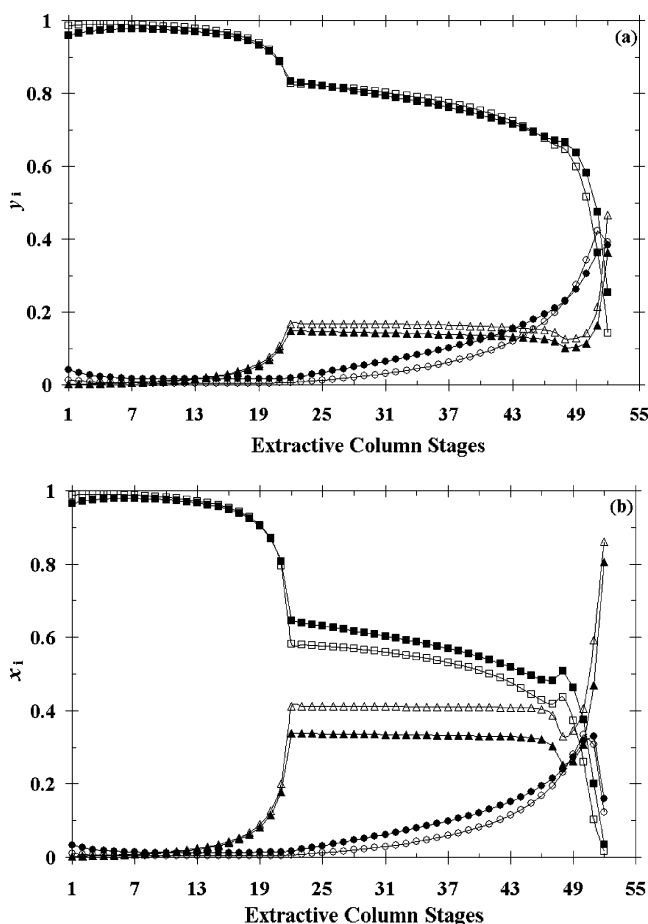

Figure 8. Simulated vapor (a) and liquid (b) molar composition profiles for the extractive column at 75.0 kPa for S/F ratios of 1.0 (close symbols) and 1.5 (open symbols). Acetone (□), methanol (○), and water (△). Stage 1 is regarded to condenser, while stages 25 and 40 are regarded to the entrainer and the azeotropic mixture feed, respectively.

Figures 8 and 9 present vapor and liquid molar composition profiles, temperature, and vapor and liquid molar flow profiles obtained by simulating an extractive column at 75.0 kPa for the acetone−methanol separation with water as entrainer. Simulations were carried out using the extractive and recovery columns configuration proposed by Gil et al.[13] with S/F ratios
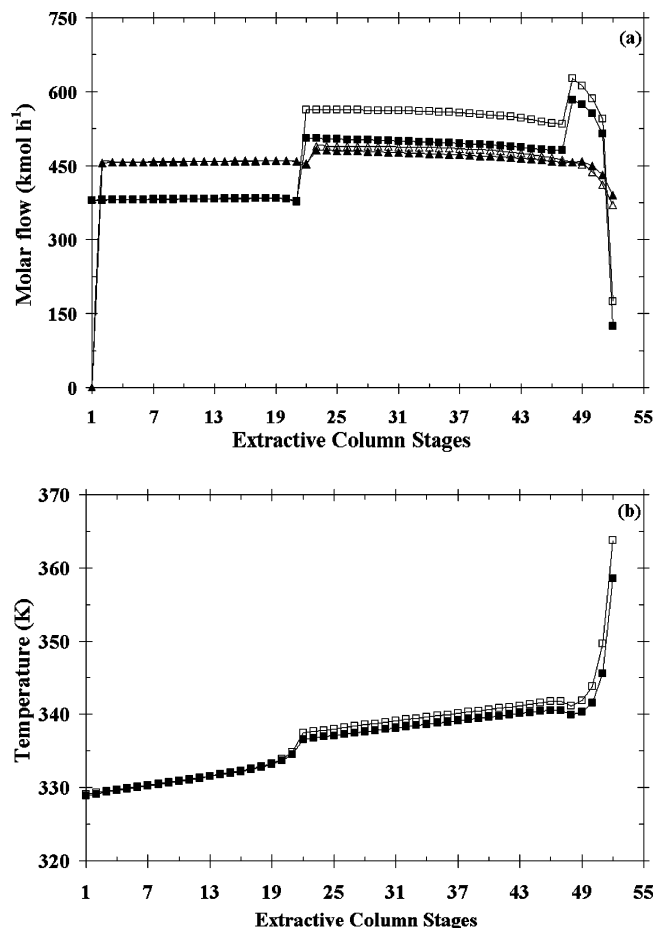

Figure 9. Simulated vapor (△) and liquid (□) molar flows (a) and temperature (b) profiles for the extractive column at 75.0 kPa for S/F ratios of 1.0 (close symbols) and 1.5 (open symbols). Stage 1 is regarded to condenser, while stages 25 and 40 are regarded to the entrainer and the azeotropic mixture feed, respectively.

of 1.0 and 1.5. In addition that at these S/F ratios the process is energetically favored, the UNIQUAC model showed a suitable correlation between experimental and predicted data as discussed above. Molar composition profiles for both vapor and liquid are in agreement with those reported.[11,13] The obtained vapor molar fractions of acetone were 0.957 and 0.985 for S/F of 1.0 and 1.5, respectively. These fractions were higher than those reported by Pradhan and Kannan[20] (0.921), who simulated the process using an UNIFAC model, a S/F ratio 1.5 at 101.25 kPa, and a rate-based model. Nevertheless, these results are lower than those reported by Luyben,[11] who obtained a 0.994 of acetone in distillate using a S/F ratio 2.0 at 101.25 kPa using an equilibrium model. These differences could be due to the columns configurations and the operational conditions. Nevertheless, simulations using the configuration of columns proposed by Luyben,[11] but at 75.0 kPa and under the feed conditions proposed by Gil et al.[13] at S/F ratios of 1.0 and 1.5, allowed one to obtain a vapor molar fraction of 0.9964 and 0.9967 (data not shown). These results suggest that, to obtain vapor molar fractions of acetone higher than or equal to 0.99 at 75.0 kPa, a column with at least 57 stages would be required.

The obtained profiles for the liquid molar composition show a normal performance where acetone and water had an important change at stage 22, in which the acetone composition decreased significantly and water increased due to the entrainer introduction. Also, it is observed a notable change in the liquid molar composition profiles mainly after stage 22 when the S/F ratio
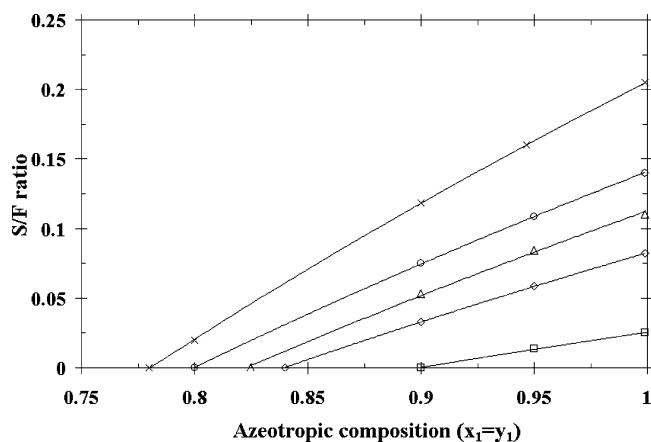
Figure 10. Simulated pressure and solvent to feed molar ratio effect on azeotropic composition displacement (pressure in kPa: 101, ×; 85, ○; 75.0, △; 65, ◇; and 40, □).

is increased, from 1.0 to 1.5 (Figure 8b). The liquid molar flow showed two significant changes due to the entrainer and the azeotropic mixture feed at stages 22 and 48, respectively. Meanwhile, the vapor molar flow remained constant along the column, except at stage 22 in which the entrainer was fed (Figure 8a). This change was caused by the liquid phase vaporization due to the water inlet temperature. It is notable that the increase of the S/F ratio increases meanly the liquid molar flow (Figure 9a). Temperature profiles presented a similar performance for both S/F ratios, but nevertheless entrainer increment caused temperature difference up to 5 K at bottom (Figure 9b). Predicted profiles showed that the use of water as entrainer at 75.0 kPa at S/F ratio of 1.0 is a feasible industrial alternative to break down the azeotropic point of the acetone−methanol mixture.

The combined effect of reduction pressure and water:feed molar ratio is evidenced in Figure 10. Calculations were performed in ASPEN Plus[21] software using the UNIQUAC model. The azeotropic composition is shifted by the entrainer presence, and, at 101 kPa, the azeotrope is eliminated when the S/F ratio reaches a value near 0.21. Meanwhile, at 75.0 kPa the azeotrope is eliminated at S/F ratio of 0.11. Calculations show that a total pressure of 7.0 kPa can produce theoretical azeotropic elimination without water entrainer additions. Interestingly, the pressure reduction plus water addition has a synergistic effect on azeotrope composition displacement. The slopes of the isobars diminished with pressure, indicating that entrainer effect is enhanced at lower pressures. However, it is important to take into account that the operating pressure in the extractive distillation column will be limited by the boiling point of the high purity acetone obtained at the overhead, to make possible the use of cooling water as condensing medium and without demanding another different and expensive refrigerant at the condenser. In this way, the operating pressure range has a practical limit that is a function of the inlet temperature of the cooling fluid, in this case, water, and the temperature difference with regard to acetone condensation. Based on this fact, a typical condenser design establishes that the minimum temperature difference can be 10 °C. Although the pressure reduction is a cost-demanding operation, it becomes an important alterna-

tive during the industrial design process when plant location is possible at different sea levels.

Conclusions

The designed Othmer still allowed the establishment of the vapor−liquid equilibrium for the binary (acetone−methanol) and ternary systems (acetone−methanol−water). Experimental results have been correlated using Wilson, NRTL, and UNIQUAC models, but nevertheless the best accuracy was shown by UNIQUAC. Obtained results presented thermodynamic consistency and suggest that the realized experimental procedure was a rapid and effective method to determine VLE of different types of mixtures, including azeotropic, with close boiling points like acetone−methanol. For that reason, its use can be extended to other ternary systems.

Using water in a solvent:feed molar ratio of 1.0 showed the azeotropic point elimination, suggesting a cost saving that can be achieved using lower quantities of water. This implies that pressure diminution in the extractive column favors the separation and allows operations with low entrainer:feed molar ratios. The UNIQUAC model is presented as one of the best alternatives to predict the process performance of the system using acetone−methanol and water. A good correlation was obtained at low S/F ratios, but the effect of water is overestimated at higher S/F values. However, to propose modifications to UNIQUAC parameters and obtain a better correlation between predicted and experimental data is necessary to carry out further experimental data on all of the composition scale.

Literature Cited

(1) Langston, P.; Hilal, N.; Shingfield, S.; Webb, S. Simulation and optimization of extractive distillation with water as solvent. *Chem. Eng. Process.* **2005**, *44*, 345–351.

(2) Tan, T. C.; Gan, S. H. Vapour−liquid equilibrium of water-ethanol-1-butanol-salt: Prediction and experimental verification. *Chem. Eng. Res.* **2005**, *83*, 1361–1371.

(3) Van Winkle, M. *Distillation*; McGraw Hill: New York, 1972.

(4) Griswold, J.; Buford, C. B. Separation of synthesis mixtures. Vapor−liquid equilibria of acetone-methanol-water. *Ind. Eng. Chem.* **1949**, *41*, 2347–2351.

(5) Vercher, E.; Orchillés, A. V.; Miguel, P. J.; González-Alfaro, V.; Martínez-Andreu, A. Isobaric vapor−liquid equilibria for acetone + methanol + lithium nitrate at 100 kPa. *Fluid Phase Equilib.* **2006**, *250*, 131–137.

(6) Iglesias, M.; Orge, B.; Marino, G.; Tojo, J. Vapor−liquid equilibria for the ternary system acetone + methanol + water at 101.325 kPa. *J. Chem. Eng. Data* **1999**, *44*, 661–665.

(7) Bunch, D. W.; James, W. J.; Ramalho, R. S. Rapid method for obtaining vapor−liquid equilibrium data. Distillate analysis technique as applied to ternary system. *Ind. Eng. Chem. Process Des. Dev.* **1963**, *2*, 282–284.

(8) Verhoeye, L.; Schepper, H. The vapour−liquid equilibria of the binary, ternary and quanternary systems formed by acetone, methanol, propan-2-ol, and water. *J. Appl. Chem. Biotechnol.* **1973**, *23*, 607–619.

(9) Natarajan, T. S.; Srinivasan, D. Vapor−liquid equilibrium data for the systems acetone−methanol and methanol−benzene in the presence of dissolved salts. *J. Chem. Eng. Data* **1980**, *25*, 215–218.

(10) Al-Asheh, S.; Banat, F. Isobaric vapor−liquid equilibrium of acetone + methanol system in the presence of calcium bromide. *J. Chem. Eng. Data* **2005**, *50*, 1789–1793.

(11) Luyben, W. L. Comparison of extractive distillation and pressure-swing distillation for acetone−methanol separation. *Ind. Eng. Chem. Res.* **2008**, *47*, 2696–2707.

(12) Sada, E.; Morisue, T.; Miyahara, K. Salt effects on vapor−liquid equilibrium of tetrahydrofuran−water system. *J. Chem. Eng. Data* **1975**, *20*, 283–287.

(13) Gil, I. D.; Botía, D. C.; Ortiz, P.; Sánchez, O. F. Extractive distillation of acetone/methanol mixture using water as entrainer. *Ind. Eng. Chem. Res.* **2009**, *48*, 4858–4865.

(14) Yen, L. C.; Woods, S. S. A generalized equation for computer calculations of liquid densities. *AIChE J.* **1966**, *12*, 95–99.

(15) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(16) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Res.* **1975**, *14*, 209–216.

(17) Wisniak, J.; Tamir, A. Vapor−liquid equilibria in the ternary systems water-formic acid-acetic acid and water-acetic acid-propionic acid. *J. Chem. Eng. Data* **1977**, *22*, 253–260.

(18) Tan, T. C.; Tan, R.; Soon, L. H.; Ong, S. H. P. Prediction and experimental Vverification of the effect of salt on the vapour−liquid equilibrium of ethanol/1-propanol/water mixture. *Fluid Phase Equilib.* **2005**, *234*, 84–93.

(19) Iliuta, M. C.; Thyrion, F. C. Vapour−liquid equilibrium for the acetone-methanol-inorganic salt system. *Fluid Phase Equilib.* **1995**, *103*, 257–284.

(20) Pradhan, S.; Kannan, A. Simulation and analysis of extractive distillation process in a valve tray column using the rate based model. *Korean J. Chem. Eng.* **2005**, *22*, 441–451.

(21) *Aspen Plus, Version 2006*; Aspen Technology Inc.: Burlington, MA, 2006.