

Vapor Liquid Equilibria of Binary and Ternary Systems with Water, 1,3-Propanediol, and Glycerol

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Isobaric vapor–liquid equilibrium data for the binary system water + 1,3-propanediol and for the ternary system water + 1,3-propanediol + glycerol were determined at 30 kPa. All the experimental data reported were thermodynamically consistent. The activity coefficients were correlated with the Wilson, NRTL, and UNIQUAC equations. A distillation column was simulated to study the removal of water from a fermentation broth containing 1,3-propanediol and glycerol.

Introduction

1,3-Propanediol is commonly used in the synthesis of polyesters, refrigeration applications, paints, plastic industries, and so forth. Presently, 1,3-propanediol is being manufactured by two chemical processes and a biochemical one for a share of a 30 million lb per year market.¹

1,3-Propanediol (1,3-PD) may be obtained by fermentation of renewable substrates such as glycerol and sugars.^{2–4} The recovery of 1,3-PD from the fermentation broth can be carried out by distillation, as this technique is the most widely used for separation of alcohol–water mixtures.⁵ Other alternatives to recover 1,3-PD from fermentation broths by converting it into a substance without hydroxyl groups have been studied by Malinowski et al.⁶

This study was undertaken to obtain the necessary VLE data to carry out the recovery of 1,3-PD, obtained by fermentation of glycerol, by distillation. Previous data on VLE were only found for the binary system water + glycerol.^{7–9} In this work, VLE data for the binary system water + 1,3-propanediol are reported. Accurate data for the system 1,3-propanediol + glycerol could not be obtained with the available still due to an unstable boiling of this system. Therefore, to obtain the necessary parameters of the activity coefficient equations for computer simulation of the distillation process, the VLE of the ternary system, water + 1,3-propanediol + glycerol, was determined. The results obtained were used for the simulation of a distillation column for removal of the solvent, water.

Experimental Section

Chemicals. 1,3-Propanediol (97 wt %) and glycerol (99.5 wt %) were purchased from Fluka. 1,3-Propanediol was purified by vacuum distillation, and the final purity was 99.9 wt %, as determined by gas chromatography (GC) that failed to show any significant impurities other than water. Glycerol and 1,3-propanediol are very hygroscopic; glycerol may absorb water up to 50 wt %. Both products were stored over activated 3 Å molecular sieves in order to keep them dried. The water content of glycerol and 1,3-propanediol

Table 1. Physical Properties of Pure Compounds

compound	ρ (298.15 K)/kg·m ⁻³		$n(D, 298.15 K)$		$T_b(30 kPa)/K$	
	exp	lit. ^a	exp	lit. ^a	exp	lit.
water	997.05	997.047	1.3325	1.3325	342.31	342.25 ^b
1,3-propanediol	1049.65	1050	1.4387	1.4386	451.65	451.36 ^b
glycerol	1257.76	1255.12	1.4730	1.4730		519.86 ^c

^a Riddick et al.²³ ^b Daubert and Danner.²⁴ ^c (PRO/II) Library.²⁵

was determined, before being used, with a Karl-Fisher apparatus (Mitsubishi Kasei CA-20) and was found to be below 0.005 and 0.003 wt %, respectively. Ultrapure water, with a resistivity of 18.2 MΩ·cm, obtained with a Milli-Q system (Millipore), was used. As an additional purity check, some physical properties of the pure components were measured and compared with values reported in the literature. The results are reported in Table 1.

Apparatus and Procedure. An all-glass circulation still of the Gillespie¹⁰ type modified by Röck and Sieg¹¹ was used in this work. This apparatus has been previously described and used in our laboratory to obtain VLE data.^{12,13} The still was operated under a nitrogen atmosphere, to avoid decomposition of glycerol due to the presence of air. The total pressure of the system was monitored with a digital manometer (± 0.1 kPa) and controlled at 30 kPa. Atmospheric pressure was measured with a Lambrecht type barometer. The boiling point temperature in the equilibrium still was measured with a mercury-in-glass thermometer with an accuracy of ± 0.05 K. The still was silanized prior to operation in order to avoid recirculation problems of the condensed vapor phase through the parts of the still with small internal diameter due to the high surface tension of some of the components. The high viscosity of the mixture may lead to uneven boiling. To minimize this effect, a very low flow of nitrogen was allowed in the liquid phase through the bottom of the still. This nitrogen current was dispersed with a magnetic stirrer to form small bubbles that promoted even boiling. Slow heating also avoided bumping of the liquid during boiling.

Sample Analysis. The liquid and vapor phases of the binary and ternary systems were analyzed using a Hewlett-

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Table 2. Antoine Equation^a Parameters, A, B, and C

compound	Antoine constants			region/K
	A	B	C	
water ^b	7.070 30	1655.70	-46.230	314–460
1,3-propanediol ^b	8.319 90	2984.20	-15.250	314–460
glycerol ^c	7.366 20	2529.08	-90.409	292–723

^a Antoine equation: $\log(P/\text{kPa}) = A - B/[(TK) + C]$. ^b Daubert and Danner.²⁴ ^c (PRO II) Library.²⁵

Table 3. Experimental VLE Data for the Binary System Water (1) + 1,3-Propanediol (2) at 30 kPa: Liquid-Phase Mole Fraction, x_1 , Vapor-Phase Mole Fraction, y_1 , Temperature, T , Activity Coefficients, γ_i , and Fugacity Coefficients, Φ_i

x_1	y_1	TK	γ_1	γ_2	Φ_1	Φ_2
0.0000	0.0000	451.65		0.9753	0.9817	0.9857
0.0128	0.2961	442.35	0.8789	0.9755	0.9843	0.9814
0.0723	0.8412	410.95	1.0188	0.8364	0.9906	0.9777
0.1032	0.9220	399.95	1.0846	0.6967	0.9922	0.9756
0.1529	0.9613	389.15	1.0724	0.6110	0.9928	0.9724
0.2582	0.9908	374.65	1.0695	0.3460	0.9930	0.9664
0.3651	0.9910	365.75	1.0443	0.6392	0.9920	0.9611
0.3872	0.9921	364.25	1.0427	0.6318	0.9920	0.9602
0.4890	0.9949	358.55	1.0299	0.6754	0.9914	0.9562
0.5211	0.9958	356.90	1.0320	0.6529	0.9913	0.9550
0.5739	0.9952	354.45	1.0320	0.9678	0.9909	0.9530
0.6412	0.9971	351.90	1.0259	0.8078	0.9907	0.9510
0.6778	0.9971	350.50	1.0276	0.9783	0.9905	0.9497
0.7010	0.9978	349.65	1.0297	0.8419	0.9904	0.9490
0.7551	0.9981	348.15	1.0176	0.9724	0.9902	0.9476
0.7889	0.9983	347.45	1.0031	1.0535	0.9901	0.9470
0.8392	0.9988	345.85	1.0092	1.0773	0.9899	0.9455
0.9080	0.9989	344.50	0.9879	1.8769	0.9897	0.9441
0.9428	0.9989	343.85	0.9727	3.4717	0.9896	0.9435
0.9631	0.9991	343.35	0.9786	4.1143	0.9895	0.9430
1.0000	1.0000	342.31	0.9869		0.9895	0.9427

Packard gas chromatograph (Model 6890) equipped with thermal conductivity (TCD) and flame ionization detectors (FID) connected in series. The FID allows the analysis of 1,3-PD and glycerol, while the TCD was used for water analysis. The GC column was a 25 m by 0.25 mm bonded-phase fused silica capillary column and was operated at variable, programmed temperature, from 443.15 K to 473.15 K. The injector and both detectors were operated at 598.1 K. Helium, 99.999% purity, was used as carrier gas. 1,4-Butanediol was used as internal standard to determine peak areas in ternary mixtures. Concentration measurements were accurate to better than ± 0.0005 mole fraction.

Results and Discussion

Vapor Pressure. Vapor pressures for the pure components were calculated according to the Antoine equation. Vapor pressures for water and 1,3-PD were experimentally determined in the pressure range allowed by the still described in the Experimental Section, that is, from 7 to 133 kPa. The vapor pressure of glycerol could not be measured with the still, due to unstable boiling conditions. At the pressure of 133 kPa, water boils near 381 K, well below the boiling temperature of most of the mixtures of two or three components studied in this work. Therefore, the Antoine equation parameters, A_i , B_i , and C_i , used for VLE data treatment, were selected from the literature to cover the temperature range of interest in this work, and are reported in Table 2.

A comparison of the experimental vapor pressures and those obtained from the Antoine constants taken from the literature gives an average absolute deviation of 0.15 kPa, which is close to the accuracy of the digital manometer used

Table 4. Correlation Parameters of the Activity Coefficient Equations for the Binary System Water (1) + 1,3-Propanediol (2): A_{12} , A_{21} , and α_{12} , and Root-Mean-Squared Deviations for Equilibrium Pressure, Temperature, and Vapor and Liquid Compositions

	root-mean-squared deviations						
	A_{12}	A_{21}	α_{12}	P/kPa	TK	x_1	y_1
Wilson ^a	296.64	-13.12		0.05	0.23	0.0012	0.0099
NRTL ^a	878.17	-521.18	0.4	0.05	0.24	0.0010	0.0099
UNIQUAC ^a	-195.09	309.81		0.05	0.25	0.0008	0.0099

^a A_{12} and A_{21} are in $\text{J}\cdot\text{mol}^{-1}$.

Table 5. Experimental VLE Data for the Ternary System Water (1) + 1,3-Propanediol (2) + Glycerol (3) at 30 kPa: Liquid-Phase Mole Fraction, x_i , Vapor-Phase Mole Fraction, y_i , Temperature, T , and Activity Coefficients, γ_i

TK	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
451.65	0.0000	1.0000	0.0000	0.0000		0.9895	
425.55	0.0762	0.4719	0.9078	0.0917	0.7043	0.5235	0.0502
425.35	0.0726	0.5141	0.9067	0.0894	0.7422	0.4723	0.4330
422.65	0.0650	0.4835	0.9389	0.0556	0.9226	0.3490	0.6438
418.50	0.0739	0.4931	0.9380	0.0560	0.9077	0.4100	0.9141
414.10	0.1116	0.5692	0.9478	0.0514	0.6865	0.3935	0.2105
413.05	0.1027	0.5300	0.9640	0.0358	0.7815	0.3080	0.0485
411.65	0.0951	0.5455	0.9578	0.0421	0.8726	0.3740	0.0268
411.65	0.1257	0.4972	0.9760	0.0210	0.6727	0.2047	0.7663
410.60	0.1095	0.6202	0.9666	0.0329	0.7882	0.2692	0.1894
410.45	0.1071	0.6045	0.9646	0.0344	0.8076	0.2907	0.3575
408.85	0.1173	0.5772	0.9647	0.0341	0.7723	0.3239	0.4437
404.15	0.1292	0.6135	0.9754	0.0245	0.8139	0.2704	0.0577
401.55	0.1394	0.6224	0.9789	0.0200	0.8185	0.2450	0.8012
397.95	0.2050	0.3798	0.9815	0.0174	0.6228	0.4130	0.5722
396.55	0.1525	0.6075	0.9810	0.0189	0.8738	0.2996	0.0981
394.95	0.1730	0.3754	0.9759	0.0240	0.8055	0.6641	0.0576
394.80	0.1730	0.3890	0.9854	0.0143	0.8172	0.3846	0.1800
394.15	0.1893	0.3382	0.9873	0.0126	0.7637	0.4021	0.0579
393.60	0.1886	0.3472	0.9873	0.0126	0.7800	0.4021	0.0611
393.45	0.1894	0.3445	0.9861	0.0137	0.7794	0.4439	0.1228
392.80	0.1848	0.3640	0.9867	0.0132	0.8159	0.4176	0.0661
392.60	0.2304	0.3464	0.9906	0.0090	0.6612	0.3021	0.2854
391.40	0.1789	0.6948	0.9782	0.0217	0.8737	0.3849	0.2582
388.95	0.1897	0.7218	0.9813	0.0186	0.8945	0.3580	0.4319
387.80	0.2010	0.6180	0.9883	0.0115	0.8827	0.2736	0.4555
387.35	0.1953	0.7045	0.9842	0.0157	0.9181	0.3350	0.4238
387.20	0.2061	0.6049	0.9890	0.0109	0.8785	0.2729	0.2269
385.15	0.2280	0.6141	0.9898	0.0101	0.8504	0.2760	0.3113
382.85	0.2210	0.6625	0.9870	0.0129	0.9447	0.3670	0.4929
382.75	0.2557	0.6012	0.9917	0.0082	0.8232	0.2584	0.4040
382.25	0.2683	0.2803	0.9927	0.0072	0.7987	0.4991	0.1325
381.25	0.2437	0.6204	0.9933	0.0066	0.9101	0.2176	0.4714
377.85	0.2591	0.6071	0.9956	0.0043	0.9642	0.1727	0.6068
377.80	0.3113	0.2520	0.9960	0.0039	0.8042	0.3784	0.1866
375.75	0.3836	0.1886	0.9948	0.0049	0.7002	0.7076	0.6609
375.55	0.2835	0.5987	0.9942	0.0057	0.9535	0.2621	0.8115
375.15	0.3320	0.2335	0.9958	0.0041	0.8271	0.4937	0.2264
374.85	0.3567	0.2300	0.9958	0.0041	0.7780	0.5092	0.2432
374.85	0.3563	0.1958	0.9957	0.0042	0.7788	0.6128	0.2244
372.25	0.3747	0.1733	0.9962	0.0037	0.8128	0.7010	0.2686
342.35	1.0000	0.0000	1.0000	0.0000	0.9956		

in this work. This indicates that the Antoine constants selected from the literature would also fit the experimental P versus T data obtained in this work for the pure components.

Binary System: Water (1) + 1,3-Propanediol (2). The results of the VLE measurements at 30 kPa for the binary system water (1) + 1,3-propanediol (2) are presented in Table 3. An inversion in Raoult's law deviation may be observed for 1,3-PD, which has been previously observed for similar systems.^{7,14} When the systems consist of molecules of very different size, such as 1,3-PD and water, the number of water molecules surrounding a 1,3-PD molecule changes with concentration. At low water concentration,

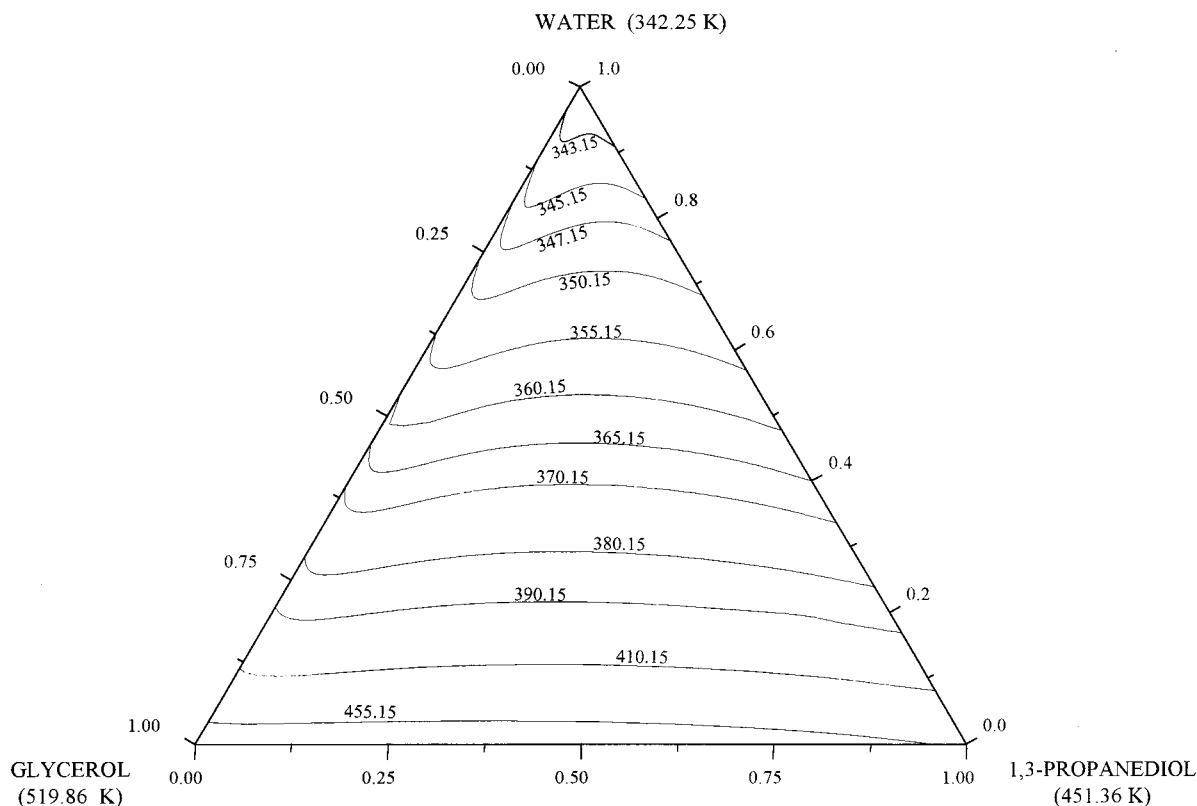


Figure 1. Isotherms for the ternary system water (1) + 1,3-propanediol (2) + glycerol (3) at 30 kPa obtained using the NRTL ($\alpha = 0.8$) equation.

hydrogen bonds between 1,3-PD and water are predominant ($\gamma_{1,3-PD} < 1$), while increasing water concentration favors a self-association of water molecules to a fairly stable ring structure of four or six water molecules⁹ that results in positive Raoult's law deviations ($\gamma_{1,3-PD} > 1$).

Vapor-phase fugacity coefficients for each component in the mixture, Φ_i and Φ_i° , were estimated by the virial equation of state,¹⁵ and second virial coefficients were calculated with the Hayden and O'Connell¹⁶ correlation.

Experimental (P , T , x , y) data were correlated with a nonlinear regression method based on the maximum likelihood principle.¹⁷ The models used for the liquid-phase activity coefficients were Wilson, NRTL, and UNIQUAC. The parameter α_{12} in the NRTL equation was fixed to a value of $\alpha_{12} = 0.4$. Table 4 reports the data regression results, that is, adjustable parameters, A_{12} and A_{21} , for the activity coefficient equations and root-mean-squared deviations for pressure, temperature, and vapor- and liquid-phase compositions.

The Fredenslund et al. test¹⁸ was applied to the experimental data for thermodynamic consistency. The average value of the residuals, $\Delta y = |y_{\text{exp}} - y_{\text{calc}}|$ (y = mole fraction), was $\Delta y = 0.0060$, indicating that the system is thermodynamically consistent. Since there is a large difference in the boiling points of water and 1,3-propanediol, pressure deviation was also taken into account. The average value for $\Delta P = |P_{\text{exp}} - P_{\text{calc}}|$ was $\Delta P = 0.183$ kPa, similar to the accuracy of the digital manometer (0.1 kPa). Residuals for P and y were randomly distributed along the entire composition range. The system was also thermodynamically consistent according to the L-W method of the Wisniak¹⁹ point to point consistency test.

The relative volatility for the system water (1) + 1,3-PD (2) is fairly high, so that only a few distillation stages would be needed to separate the mixture into its components.

Ternary System: Water (1) + 1,3-Propanediol (2) + Glycerol (3). VLE experimental values for the ternary system water (1) + 1,3-propanediol (2) + glycerol (3) at 30 kPa are reported in Table 5. Negative deviations from Raoult's law may be inferred from the activity coefficients ($\gamma < 1$) for this system. This may be due to the low water concentration range studied, that favors hydrogen bonding between different molecules. High water concentration may reverse this behavior, as occurred in the binary system water + 1,3-PD. Vapor-phase fugacity coefficients were calculated by using the virial equation of state, and the second coefficient was estimated by the Hayden and O'Connell¹⁶ correlation. Vapor-phase fugacity coefficients were in the range of 0.99–1.00; therefore, vapor-phase nonideality was not taken into account for VLE data reduction.

Experimental VLE data were correlated by the Wilson, UNIQUAC, and NRTL equations. In the NRTL model several values for the nonrandomness parameter, α , have been set, since the highest variations of that parameter appear in aqueous systems.²⁰ The six adjustable binary parameters contained in these equations were estimated by using the computer program (PRO/II). The subroutine REGRESS of this program uses a weighed orthogonal distance regression algorithm developed by the National Institute of Standards and Technology (NIST).

Table 6 reports the results of data regression, that is, adjustable parameters of the activity coefficient equations (A_{ij} and A_{ji}) and average absolute deviations for equilibrium pressure, temperature, and vapor-phase composition. Figure 1 shows equilibrium isotherms for the ternary system water (1) + 1,3-PD (2) + glycerol (3) calculated by using the NRTL ($\alpha = 0.8$) equation that gives a slightly better data fit.

Table 6. Results of the Correlation of the Experimental VLE Data for the System Water (1) + 1,3-Propanediol (2) + Glycerol (3): Activity Coefficient Equation Parameters and Average Absolute Deviations for Equilibrium Pressure, Temperature, and Vapor-Phase Composition

equation	parameters of the activity coefficient equations ^a						average absolute deviations				
	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	P/kPa	T/K	y_1	y_2	y_3
UNIQUAC	891.23	-2076.34	-930.95	-644.01	-3137.94	-4503.48	2.67	2.65	0.0170	0.0165	0.0006
Wilson	2574.07	-5694.76	-761.20	-4903.84	-9060.43	-7591.29	2.92	3.41	0.0094	0.0093	0.0005
NRTL($\alpha=0.3$)	9751.18	-5172.54	6165.06	-6497.39	-11590.11	-14944.44	1.99	1.97	0.0150	0.0145	0.0006
NRTL($\alpha=0.47$)	9092.78	-3743.42	-6293.75	-1354.69	-8449.95	-9230.73	2.92	3.03	0.0114	0.0112	0.0005
NRTL($\alpha=0.8$)	14090.24	-867.67	3785.20	-2530.48	-9256.44	-7684.92	1.60	2.04	0.0103	0.0099	0.0006

^a Units of the parameters A_{ij} : $\text{J}\cdot\text{mol}^{-1}$.

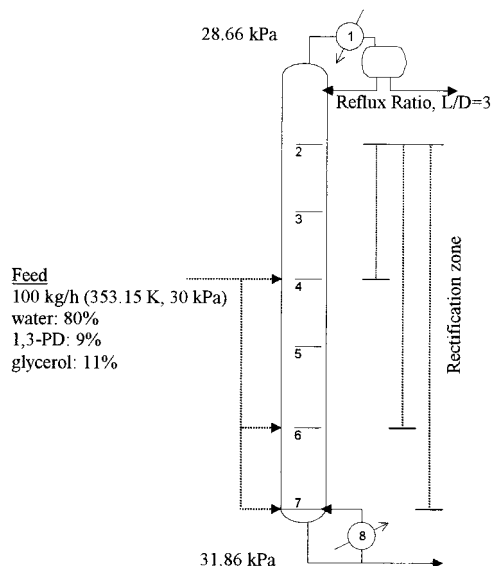


Figure 2. Configuration of the distillation column used for computer simulation.

The thermodynamic consistency of the ternary system water (1) + 1,3-propanediol (2) + glycerol (3) was checked by the McDermott–Ellis²¹ method modified by Wisniak and Tamir.²² According to this test, two experimental points a and b are considered to be thermodynamically consistent if $D < D_{\max}$, where D is a local deviation and D_{\max} a maximum deviation, both related to the equilibrium data a and b . For the experimental data reported, D never exceeded 1.784 while the smallest value for D_{\max} was 3.567; hence, the system may be considered thermodynamically consistent.

Computer Simulation of the Distillation Process

A distillation column for water removal from a fermentation broth containing 1,3-PD and glycerol was studied by computer simulation. The simulation was carried out, assuming ideal equilibrium stages, with a simulation program (PRO/II). The Inside-Out algorithm was used, as it is the preferred option for most distillation problems. The design was carried out for a fermentation broth feed with a composition of 9 wt % 1,3-PD, 11 wt % glycerol, and 80 wt % water. The liquid-phase activity coefficients were calculated by means of the NRTL ($\alpha = 0.8$) equation whose parameters are reported in Table 6.

The column configuration chosen for the simulation is shown in Figure 2. The total number of trays including a bubble temperature type condenser and a kettle (conventional) type reboiler was eight. The top tray pressure was 28.66 kPa, and the pressure drop per tray was chosen to be 0.53 kPa (4 mmHg). The reflux ratio was 3, which solves most of the columns. The influence of the feed location on water removal was studied as a function of the heat duty

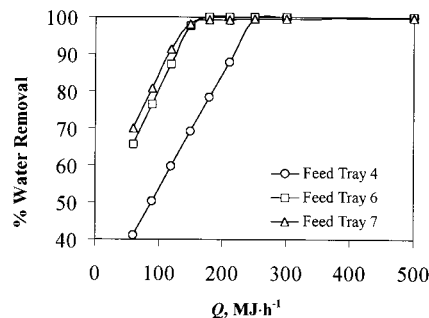


Figure 3. Plot of water removal as a function of the heat duty in the reboiler for different feed trays; data obtained by using the NRTL ($\alpha = 0.8$) equation.

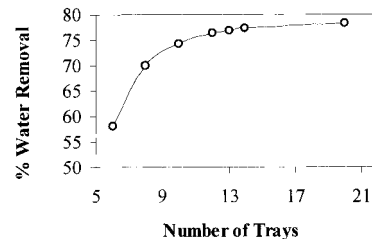


Figure 4. Plot of the water removal as a function of the total number of trays; heat duty $6 \times 10^4 \text{ kJ}\cdot\text{h}^{-1}$; the feed tray was the one just above the reboiler in all cases; data obtained by using the NRTL ($\alpha = 0.8$) equation.

for such a column. The results are presented in Figure 3, where it is observed that, for a fixed heat duty, water removal increases when the rectification zone increases, as expected, since water is removed as the overhead product of the column.

Some assays were also made increasing the rectification zone by increasing the total number of trays. The feed was introduced in the tray just above the reboiler in all cases. The effect of the number of plates on water removal is shown in Figure 4 for a heat duty of $6 \times 10^4 \text{ kJ}\cdot\text{h}^{-1}$. The asymptotic shape of the curve indicates that increasing the number of trays above 12 does not cause further water removal.

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