Activity Coefficient Parameters Determination for various VLE models for Propionic Acid-Water-Salt Mixture at isobaric conditions

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Abstract: Azeotropic systems of low molecular organic acids and water are very common as well as their separation a huge pain. Several methods have been suggested and utilized for avoiding the formation of such azeotropes or breaking the formed ones; one such method is by using salts. In this study, we have chosen Propionic Acid – Water system and LiBr, CaCl₂ and CH₃COOK as salts. The paper focuses on providing the VLE data for these systems along with the identification of activity coefficient parameters for four different models, namely, van Laar Equations, NRTL, Tan – NRTL and UNIQUAC. The study will ease the work for those who are interested in using Propionic Acid – Water system and break their azeotropic composition using salts.

Keywords — Activity coefficient parameters, Azeotropic systems, Inorganic salts, Propionic Acid-Water-Salt mixture, VLE

I. INTRODUCTION

Propionic acid is the third acid in the carboxylic acid group, is an oily liquid with slightly pungent order, finding its usage in esterification, production of propionates such as cellulose propionate, calcium propionate and others, and in manufacturing of ester solvents, fruit flavours, and perfume bases. [1] It is very common to find Propionic Acid and Water as constant boiling mixtures in industry, more profoundly in the manufacturing of Propionic Acid itself from ethylene, water and carbon monoxide or of ethanol and carbon monoxide using catalyst systems formed on mixing of a rhodium or iridium component and an iodine component in the presence of carbon monoxide. [2] The system forms a minimum boiling azeotrope at 0.053 acid mole fraction and 99.98^0C under atmospheric pressure, under these conditions the acid deviates from ideal conditions and separation of the mixture becomes a great concern from cost as well as ease of operation. [3] Several methods have been identified till date for separation of this azeotropic mixture; freeze crystallization [4], extractive distillation [5], ionic liquid separation [6], azeotropic distillation, pressure swing distillation [7] and hybrid technologies. One other common approach for separating this azeotropic system is via salts. Several studies related to determination of VLE for the Propionic Acid – Water – Salt has been done in the past. [3], [8]–[11] In one such study by Banat *et al.*, the researchers tried to identify effect of the Propionic acid – Water – Salt mixtures at isothermal conditions, they chose four different salts viz. sodium

chloride, calcium chloride, ammonium chloride, and aluminum chloride and generated the VLE data using headspace gas chromatography (HSGC). There study was limited to isothermal conditions as well as generation of x,y data alone. [10]

This study incorporates determination of various thermodynamic parameters related to activity coefficient models, such as Parameters A and B in van Laar Equations (equation set 1), τ_{12} and τ_{21} in NRTL model (equation set 2), τ_{12}, τ_{21} and τ_{is} in Tan - NRTL model (equation set 3) [12] and τ_{12} and τ_{21} in UNIQUAC model (equation set 4), all the parameters have been identified by minimizing the Objective function (equation 4) using MS Excel 2007 add-in Solver's regression module.   The salts taken into consideration are LiBr and CaCl₂, although experiments were even conducted with CH₃COOK but disheartening results were obtained.

II. MATERIALS AND METHODS

The chemicals used were Propionic Acid (Merck, LR grade) with a stated minimum purity of 99.0 wt.% (maximum 0.05 wt.% water), distilled water (Merck, HPLC grade) and Lithium Bromide anhydrous (powder,$\geq$ 99.0 %)).Calcium chloride ,anhydrous (powder, $\geq$97.0 %), Sodium chloride anhydrous (powder,$\geq$ 99.0 %) and Potassium acetate anhydrous (powder,$\geq$ 99.0 %).The salts were dried in an oven at 150 °C before use and cooled in the desiccator.

The still which is used in the present work is a modified Othmer Still, designed to avoid and reduce faults and errors. The still volume is 250 ml and is thoroughly washed with water and then with the solution. It is mounted over the hot plate magnetic stirrer. A condenser is mounted over the condensate chamber. A magnetic stirrer is used for stirring thereby maintaining homogeneity of the liquid to improve salt dissolution. The condenser is open to atmosphere. The temperatures of the vapor phase and liquid phase are measured using thermometers with $\pm$ 0.1 °C of uncertainty.

The main characteristic of the present design is that the pot volume is much higher than the liquid condensate volume and at steady state, only a few drops of condensate were collected and analyzed for the determination of the vapor composition. Due to which the composition of the liquid prior to the addition of the salt could well be taken as the equilibrium liquid composition without introducing appreciable error. The still was charged with 100 ml of Propionic acid and water solution of the desired composition

The experimental VLE data for Propionic acid - were measured starting from 10 % concentration of Propionic acid to 90 % concentration of Propionic acid, without the addition of salt. Than VLE data was taken for Propionic acid –water (Azeotropic composition) and different concentration of salt (10, 20,30,40,50 wt % of water) and minimum concentration of salt to eliminate azeotrope was calculated. After that VLE data for Propionic acid –water + salt (minimum quantity required to break azeotrope) was taken.
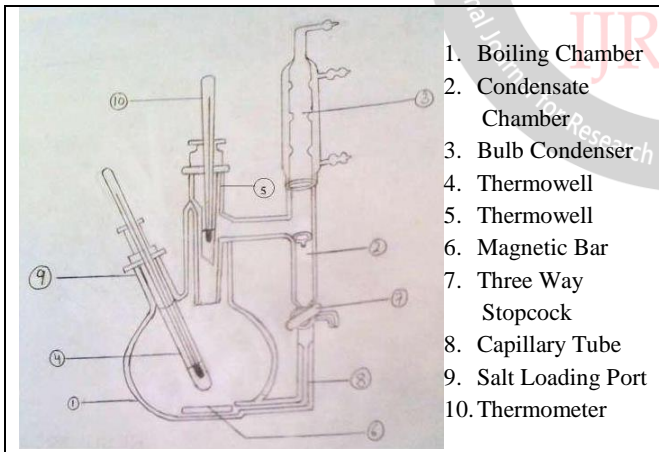

1. Boiling Chamber
2. Condensate Chamber
3. Bulb Condenser
4. Thermowell
5. Thermowell
6. Magnetic Bar
7. Three Way Stopcock
8. Capillary Tube
9. Salt Loading Port
10. Thermometer

Figure 1: The experimental setup – Modified Othmer Still

In the current study, we assumed complete isobaric conditions with total pressure same as that of atmospheric pressure throughout the experiment. The detailed stepwise procedure for identifying the activity parameters goes as follows:

1. First of all the experimental values of T-x,y were obtained for the system at varying salt concentrations.
2. The minimum salt concentration at which the azeotrope broke was considered for further studies.

3. Then at that salt concentration and with varying concentration of acid, T-xy data was obtained.
4. Using Antoine's equation for the known temperature partial pressure data was calculated.
5. Then, by using Raoult's law and assuming fugacity coefficient as 1 and considering total pressure as 760mmHg, activity coefficients were calculated.
6. Now, for each data point molar excess Gibbs free energy was computed, which was then equated with various activity coefficient models.
7. The set of equations so obtained were double summed and a minimum objective function was allowed to undergo regression, to solve the equations to obtain the theoretical values of activity parameters and thus, activity coefficients.

$$Min\ OF = \sum_{i=1}^{np} \sum_{j=1}^{nc} \left(\frac{\gamma_{exp} - \gamma_{cal}}{\gamma_{exp}}\right)^2 \qquad (5)$$

8. Next, to calculate theoretical values of T and y, first of all assume an arbitrary value of temperature was assumed (suppose 100^{0}C), at 100^{0}C the respective partial pressures were calculated, summation of these partial pressures must be equal to total pressure i.e., 760 mmHg, thus, the equations were simulated in such a way that temperature was variable and constraint was total pressure. This gave the theoretical value temperature.
9. At, this temperature we already knew the partial pressure, and considering that the mole fraction composition in liquid phase same as that of experimental values, we computed the calculated values of y, again by regression and setting constraint as the sum of vapour phase composition as 1.
10. To identify the deviation of data obtained from experimental values, error in y was calculated by the following equation. As mentioned in earlier literature source the deviation in values is accepted to 10%.

$$\overline{|\Delta y|} = \sum \frac{|y_{exp} - y_{cal}|}{k} \qquad (6)$$

11. To validate the data, data consistency test was used. We used area integral test, as suggested by equation 7.

$$I = \frac{\int_0^1 \left(\ln\left(\frac{\gamma_1}{\gamma_2}\right)\right)^2 dx}{\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right)^2 dx} \qquad (7)$$

III. RESULTS AND DISCUSSION

For the first system i.e. Water (1) – Propionic Acid (2) – LiBr (3) the concentration versus acid-water mole fraction has been depicted in table (2). It was found that 20% w/w of

salt concentration gave better separation results and the same was considered for further calculations; thus 16.4 g of salt was used for separation. The T-xy values for the system with varying acid concentrations are shown in table (3).

Using the temperature data and Antonie's Constant (Given in Table (2)) partial pressure was calculated by equation (5); also the experimental values of activity coefficients is obtained by modified Raoult's Law given in equation (6). The partial pressure data and the activity coefficients are given in table (5). The various parameters obtained for the system for various models is enlisted in table (6). The values of activity coefficients for all models obtained after simulation are mentioned in table (7).

The deviation of calculated values of activity coefficients from the experimental values of activity coefficients is found out to identify the best suitable model also the same is identified using error in estimation of y_{acid} values and by data consistency test (equation (7)). The deviation of activity coefficients is tabulated in table (8), and it clearly identifies Tan – NRTL Model as the best suited among the models considered for determining VLE of Water (1) – Propionic Acid (2) – LiBr (3).

The vapour phase mole fraction calculations for all models is given in table (9) and the comparison for vapour phase mole fraction of Propionic Acid in the system is given in figure (2).
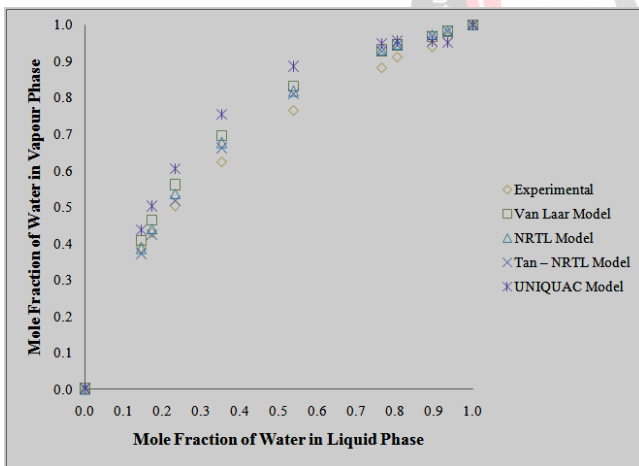

Figure 2: Mole fraction of Water in Vapour Phase versus Liquid Phase in the Water (1) - Propionic Acid (2) - LiBr (3)

The error in calculation of vapour phase mole fraction of Water in the system is shown in table (10). The results of data consistency test direct towards suitability of van Laar Model for salt systems, the results of data consistency test for all models are given in table (11).

$$\log_{10} P_s = A_i - \frac{B_i}{t + C_i} \qquad (5)$$

$$y_k \varphi_k P = x_k \gamma_k p_k^{sat} \qquad (6)$$

The second system i.e. Water (1) – Propionic Acid (2) – $CaCl_2$ (3) the concentration versus acid-water mole fraction has been depicted in table (12). It was found that 10% w/w of salt concentration gave better separation results and the same was considered for further calculations; thus 8.25 g of salt was used for separation. The T-xy values for the system with varying acid concentrations are shown in table (13). The partial pressure data and the activity coefficients are given in table (14). The various parameters obtained for the system for various models is enlisted in table (15). The values of activity coefficients for all models obtained after simulation are mentioned in table (16). The deviation of activity coefficients is tabulated in table (17), and it clearly identifies Tan – NRTL Model as the best suited among the models considered for determining VLE of Water (1) – Propionic Acid (2) – $CaCl_2$ (3). The vapour phase mole fraction calculations for all models is given in table (18) and the comparison for vapour phase mole fraction of Propionic Acid in the system is given in figure (3). The error in calculation of vapour phase mole fraction of Water in the system is shown in table (19). The results of data consistency test direct towards suitability of van Laar Model for salt systems, the results of data consistency test for all models are given in table (20).
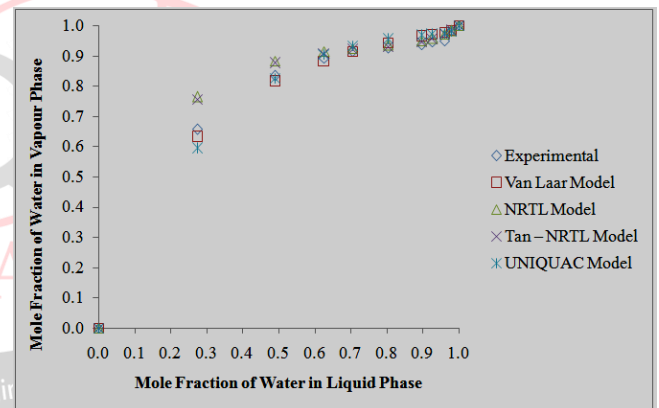
Figure 3: Mole fraction of Water in Vapour Phase versus Liquid Phase in the Water (1) - Propionic Acid (2) - $CaCl_2$ (3)

The last set of experiments was conducted with Water (1) – Propionic Acid (2) – CH_3COOK (3) the concentration versus acid-water mole fraction has been depicted in table (21). It was found that even for salt concentration of upto 50% azeotrope was not broken; experiments with higher salt concentrations were not performed as at commercial scale it won't be economically viable. The failure of this test can be explained with partial solubility of Potassium Acetate with both Water as well as Propionic acid, this did not allow the salt to dissolve in one component and alter the composition.

IV. CONCLUSION

It is found that inorganic salts such as Lithium Bromide and Calcium Chloride gives promising results for breaking of azeotropes at isobaric conditions, while organic salt was not able to break azeotrope at all. Also, azeotrope was

eliminated by using only 10% CaCl2, more amount of LiBr (20%) was required to eliminate azeotrope. Thus it can be concluded that CaCl2 gives the best result among three salts. The parameters required by various models such as van Laar Model, NRTL, Tan – NRTL and UNIQUAC has been identified and it is found that Tan – NRTL model (which is modified version of NRTL model) is best suited for Water – Propionic Acid – Salt Systems.

V. NOMENCLATURE

VLE	Vapour – Liquid Equilibria
NRTL	Non-Random Two-Liquid Model
UNIQUAC	UNIversal QUAsiChemical
LiBr	Lithium Bromide
CaCl$_2$	Calcium Chloride
CH$_3$COOK	Potassium Acetate
Temp, T	Temperature
Conc	Concentration
P	Pressure
x	Liquid Phase Mole Fraction
y	Vapour Phase Mole Fraction
γ	Activity Coefficient
τ, G	Adjustable parameter
φ, θ, r, l, q	UNIQUAC Parameters
sat	Saturation

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Table 1: Models used for study of non-ideal systems

Model	Equation	
van Laar Model	$$\ln \gamma_1 = \frac{A}{[1 + (Ax_1/Bx_2)]^2}$$ $$\ln \gamma_2 = \frac{B}{[1 + (Bx_2/Ax_1)]^2}$$	(1)

NRTL Model	$\ln \gamma_1 = x_2^2 \left[\dfrac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \dfrac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$ $\ln \gamma_2 = x_1^2 \left[\dfrac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \dfrac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$	(2)
Tan – NRTL Model	$\ln \gamma_{io} = \left[\dfrac{\sum_{j=1}^{j=3} \tau_{ji} G_{ji} X_j}{\sum_{k=1}^{k=3} G_{ki} X_k} + \sum_{j=1}^{j=3} \dfrac{X_j G_{ij}}{\sum_{k=1}^{k=3} G_{ki} X_k} \left(\tau_{ij} - \dfrac{\sum_{m=1}^{m=3} X_m \tau_{mj}}{\sum_{k=1}^{k=3} G_{kj} X_k} \right) \right]$	(3)
UNIQUAC Model	$\ln \gamma_1 = \ln\left(\dfrac{\varphi_1}{x_1}\right) + \dfrac{z}{2} q_1 \ln\left(\dfrac{\theta_1}{\varphi_1}\right) + \varphi_2 \left(l_1 - \dfrac{r_1}{r_2} l_2\right) - q_1' \ln(\theta_1' + \theta_2' \tau_{21}) + \theta_2' q_1' \left(\dfrac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} - \dfrac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} \right)$ $\ln \gamma_2 = \ln\left(\dfrac{\varphi_2}{x_2}\right) + \dfrac{z}{2} q_2 \ln\left(\dfrac{\theta_2}{\varphi_2}\right) + \varphi_1 \left(l_2 - \dfrac{r_2}{r_1} l_1\right) - q_2' \ln(\theta_2' + \theta_1' \tau_{12}) + \theta_1' q_2' \left(\dfrac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} - \dfrac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} \right)$	(4)

Table 2: Antonie's Constant for Water and Propionic Acid

Component	A	B	C
Water	8.14019	1810.94	244.49
Propionic Acid	7.99064	1929.30	236.43

Table 3: T-xy data for Water (1) - Propionic Acid (2) - LiBr (3) system for varying salt concentrations

Salt %(wt)	Temp (°C)	y_{acid}	y_{water}	x_{acid}	x_{water}
10	104.90	0.047	0.953	0.107	0.893
20	105.03	0.060	0.940	0.105	0.895
30	105.40	0.068	0.932	0.033	0.967
40	106.72	0.069	0.931	0.028	0.972
50	107.81	0.071	0.929	0.023	0.977

Table 4: T-xy data for Water (1) - Propionic Acid (2) - LiBr (3) system for varying acid concentrations for 16.4 g of LiBr

Conc. of Acid (wt%)	Temp (°C)	y_{acid}	y_{water}	x_{acid}	x_{water}
0	102.70	0.000	1.000	0.000	1.000
10	103.34	0.035	0.965	0.064	0.936
17.8	105.03	0.060	0.940	0.105	0.895
30	106.90	0.088	0.912	0.194	0.806
40	108.85	0.118	0.882	0.235	0.765
50	115.87	0.234	0.766	0.462	0.538
60	123.40	0.376	0.624	0.647	0.353
70	128.87	0.497	0.503	0.767	0.233
80	131.75	0.570	0.430	0.827	0.173
90	133.24	0.611	0.389	0.856	0.144
100	142.40	1.000	0.000	1.000	0.000

Table 5: Partial Pressure and Experimental Determination of Activity Coefficients for Water-Propionic Acid-LiBr System

Temp. (°C)	Partial Pressure Water (1) mmHg	Partial Pressure Propionic Acid (2) mmHg	$\gamma(1)$	$\gamma(2)$
102.70	839.699	200.295	--	--
103.34	858.339	205.266	0.913	2.028
105.03	909.549	218.984	0.878	1.977
106.90	969.189	235.070	0.888	1.462
108.85	1034.864	252.912	0.847	1.509
115.87	1302.567	326.881	0.831	1.178
123.40	1650.295	425.478	0.814	1.038
128.87	1948.687	511.953	0.842	0.962
131.75	2122.549	563.026	0.890	0.930
133.24	2217.483	591.107	0.927	0.918
142.40	2879.835	790.413	--	--

Table 6: Various Parameter Values obtained from Regression for Water (1) - Propionic Acid (2) - LiBr (3) System

Model Name	Parameters	Values
Van Laar's Model	A	0.867
	B	0.422
NRTL Model	τ_{12}	0.00111
	τ_{21}	0.00525

Tan – NRTL Model	τ_{1s}	-0.099
	τ_{2s}	-0.039
UNIQUAC Model	τ_{12}	1.012074
	τ_{21}	1.600791

Table 7: The values of activity coefficients obtained from various models for the Water (1) - Propionic Acid (2) - LiBr (3)

Experimental		Van Laar Model		NRTL Model		Tan – NRTL Model		UNIQUAC Model	
$\gamma(1)$	$\gamma(2)$	$\gamma(1)$	$\gamma(2)$	$\gamma(1)$	$\gamma(2)$	$\gamma(1s)$	$\gamma(2s)$	$\gamma(1)$	$\gamma(2)$
0.913	2.028	1.005	1.269	1.000	0.995	0.905	0.957	1.020	3.215
0.878	1.977	1.012	1.187	1.000	0.995	0.905	0.956	1.066	1.830
0.888	1.462	1.026	1.093	0.999	0.993	0.905	0.955	1.183	1.021
0.847	1.509	1.032	1.070	0.999	0.991	0.904	0.953	1.230	0.915
0.831	1.178	1.058	1.016	0.788	0.808	0.713	0.777	1.356	0.858
0.814	1.038	1.073	1.004	0.970	0.994	0.878	0.956	1.318	0.934
0.842	0.962	1.080	1.001	0.987	0.999	0.893	0.961	1.259	0.972
0.890	0.930	1.083	1.001	0.990	1.000	0.896	0.961	1.224	0.985
0.927	0.918	1.084	1.000	0.991	1.000	0.897	0.961	1.207	0.990

Table 8: The deviations of activity coefficients from experimental values for Water (1) - Propionic Acid (2) - LiBr(3) system

Van Laar Model		NRTL Model		Tan – NRTL Model		UNIQUAC Model	
$\Delta\gamma_1$	$\Delta\gamma_2$	$\Delta\gamma_1$	$\Delta\gamma_2$	$\Delta\gamma_1$	$\Delta\gamma_2$	$\Delta\gamma_1$	$\Delta\gamma_2$
0.0920	0.7590	0.0870	1.0330	0.0080	1.0710	0.1070	1.1870
0.1340	0.7900	0.1220	0.9820	0.0270	1.0210	0.1880	0.1470
0.1380	0.3690	0.1110	0.4690	0.0170	0.5070	0.2950	0.4410
0.1850	0.4390	0.1520	0.5180	0.0570	0.5560	0.3830	0.5940
0.2270	0.1620	0.0430	0.3700	0.1180	0.4010	0.5250	0.3200
0.2590	0.0340	0.1560	0.0440	0.0640	0.0820	0.5040	0.1040
0.2380	0.0390	0.1450	0.0370	0.0510	0.0010	0.4170	0.0100
0.1930	0.0710	0.1000	0.0700	0.0060	0.0310	0.3340	0.0550
0.1570	0.0820	0.0640	0.0820	0.0300	0.0430	0.2800	0.0720
0.1803	**0.3050**	**0.1089**	**0.4006**	**0.0420**	**0.4126**	**0.3370**	**0.3256**

Table 9: The vapour phase compositions for Water (1) - Propionic Acid (2) - LiBr(3) system

Experimental		Van Laar Model		NRTL Model		Tan – NRTL Model		UNIQUAC Model	
y(1)	y(2)	y(1)	y(2)	y(1)	y(2)	y(1)	y(2)	y(1)	y(2)
1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000
0.965	0.035	0.980	0.020	0.984	0.016	0.983	0.017	0.952	0.048
0.940	0.060	0.968	0.032	0.973	0.027	0.971	0.029	0.955	0.045
0.912	0.088	0.942	0.058	0.946	0.054	0.942	0.058	0.953	0.047
0.882	0.118	0.929	0.071	0.931	0.069	0.927	0.073	0.949	0.051
0.766	0.234	0.831	0.169	0.817	0.183	0.810	0.190	0.884	0.116
0.624	0.376	0.697	0.303	0.676	0.324	0.660	0.340	0.755	0.245
0.503	0.497	0.559	0.441	0.536	0.464	0.518	0.482	0.605	0.395
0.430	0.570	0.464	0.536	0.441	0.559	0.424	0.576	0.500	0.500
0.389	0.611	0.409	0.591	0.386	0.614	0.370	0.630	0.438	0.562
0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000

Table 10: Error in values of Mole fraction of Water in Vapour Phase for Water (1) - Propionic Acid (2) - LiBr (3) System

Experimental	van Laar Δy	NRTL Δy	Tan - NRTL Δy	UNIQUAC Δy
1.0000	0.0000	0.0000	0.0000	0.0000
0.9650	0.0150	0.0191	0.0180	0.0133
0.9402	0.0281	0.0328	0.0308	0.0145
0.9121	0.0299	0.0334	0.0297	0.0411
0.8820	0.0469	0.0495	0.0446	0.0669
0.7660	0.0652	0.0509	0.0438	0.1182
0.6240	0.0733	0.0521	0.0363	0.1313
0.5030	0.0559	0.0329	0.0151	0.1024
0.4302	0.0336	0.0106	0.0065	0.0695
0.3890	0.0197	0.0027	0.0188	0.0494
0.0000	0.0000	0.0000	0.0000	0.0000
$|\Delta y|$	**0.0408**	**0.0315**	**0.0270**	**0.0674**

Table 11: The data consistency test results for Water (1) - Propionic Acid (2) - LiBr (3) System

	Van Laar	NRTL	Tan – NRTL	UNIQUAC
Value of Area Integral Test	0.0014	0.0135	0.0758	0.515

Remarks	Perfectly Consistent	Fairly Consistent	Fairly Consistent	Least Consistent

Table 12: T-xy data for Water (1) - Propionic Acid (2) - CaCl2 (3) system for varying salt concentrations

Salt %(wt)	Temp (°C)	y_{acid}	y_{water}	x_{acid}	x_{water}
10	102.6	0.051	0.949	0.040	0.960
20	102.8	0.074	0.926	0.042	0.958
30	103.4	0.089	0.911	0.041	0.959
40	103.8	0.117	0.883	0.039	0.961
50	104.2	0.126	0.874	0.032	0.968

Table 13: T-xy data for Water (1) - Propionic Acid (2) - CaCl2 (3) system for varying acid concentrations for 8.25 g of CaCl2

Conc. of Acid (wt%)	Temp (°C)	y_{acid}	y_{water}	x_{acid}	x_{water}
0	101.4	0.000	1.000	0.000	1.000
10	101.7	0.017	0.983	0.021	0.979
17.8	102.6	0.051	0.949	0.040	0.961
30	105.3	0.053	0.947	0.073	0.927
40	107.3	0.062	0.938	0.105	0.896
50	109.5	0.074	0.926	0.196	0.804
60	111.7	0.085	0.915	0.294	0.706
70	113.4	0.106	0.894	0.373	0.627
80	120.4	0.166	0.834	0.511	0.489
90	129.9	0.343	0.657	0.726	0.274
100	142.3	1.000	0.000	1.000	0.000

Table 14: Partial Pressure and Experimental Determination of Activity Coefficients for Water-Propionic Acid-CaCl2 System

Temp. (°C)	Partial Pressure Water (1) mmHg	Partial Pressure Propionic Acid (2) mmHg	$\gamma(1)$	$\gamma(2)$
101.4	802.64	190.45	--	--
101.7	811.07	192.68	0.941	3.148
102.6	836.80	199.52	0.912	3.472
105.3	918.11	221.29	0.897	4.918
107.3	982.49	238.67	0.810	1.889
109.5	1057.61	259.12	0.828	1.106
111.7	1137.42	281.02	0.866	0.782
113.4	1202.47	299.00	0.901	0.722
120.4	1503.65	383.59	0.862	0.643
129.9	2009.48	529.76	0.908	0.678
142.3	2871.82	787.97	--	--

Table 15: Various Parameter Values obtained from Regression for Water (1) - Propionic Acid (2) - CaCl2 (3) System

Model Name	Parameters	Values
Van Laar's Model	A	0.266
	B	2.864
NRTL Model	τ_{12}	1.689
	τ_{21}	-1.063
Tan – NRTL Model	τ_{1s}	-0.055
	τ_{2s}	-0.036
UNIQUAC Model	τ_{12}	0.986
	τ_{21}	1.648

Table 16: The values of activity coefficients obtained from various models for the Water (1) - Propionic Acid (2) - CaCl2 (3)

Experimental		Van Laar Model		NRTL Model		Tan – NRTL Model		UNIQUAC Model	
$\gamma(1)$	$\gamma(2)$	$\gamma(1)$	$\gamma(2)$	$\gamma(1)$	$\gamma(2)$	$\gamma(1s)$	$\gamma(2s)$	$\gamma(1)$	$\gamma(2)$
0.941	3.148	1.010	6.545	1.000	3.382	0.947	3.262	1.005	3.566
0.912	3.472	1.025	3.953	1.001	2.946	0.948	2.946	1.014	2.622
0.897	4.918	1.058	2.308	1.003	2.330	0.950	2.330	1.039	1.728
0.810	1.889	1.086	1.753	1.006	1.912	0.953	1.912	1.066	1.329
0.828	1.106	1.150	1.242	1.018	1.192	0.964	1.192	1.133	0.919
0.866	0.782	1.194	1.100	1.029	0.828	0.975	0.828	1.165	0.837
0.901	0.722	1.220	1.053	1.037	0.668	0.981	0.668	1.161	0.843
0.862	0.643	1.251	1.019	1.040	0.523	0.985	0.523	1.108	0.893
0.908	0.678	1.281	1.003	1.021	0.447	0.967	0.447	0.972	0.967

Table 17: The deviations of activity coefficients from experimental values for Water (1) - Propionic Acid (2) - CaCl2(3)

Van Laar Model		NRTL Model		Tan – NRTL Model		UNIQUAC Model	
$\Delta\gamma_1$	$\Delta\gamma_2$	$\Delta\gamma_1$	$\Delta\gamma_2$	$\Delta\gamma_1$	$\Delta\gamma_2$	$\Delta\gamma_1$	$\Delta\gamma_2$

0.069	3.397	0.059	0.234	0.006	0.114	0.064	0.418
0.113	0.481	0.089	0.526	0.036	0.526	0.102	0.85
0.161	2.61	0.106	2.588	0.053	2.588	0.142	3.19
0.276	0.136	0.196	0.023	0.143	0.023	0.256	0.56
0.322	0.136	0.19	0.086	0.136	0.086	0.305	0.187
0.328	0.318	0.163	0.046	0.109	0.046	0.299	0.055
0.319	0.331	0.136	0.054	0.08	0.054	0.26	0.121
0.389	0.376	0.178	0.12	0.123	0.12	0.246	0.25
0.373	0.325	0.113	0.231	0.059	0.231	0.064	0.289
0.2611	**0.9011**	**0.1367**	**0.4342**	**0.0827**	**0.4209**	**0.1931**	**0.6578**

Table 18: The vapour phase compositions for Water (1) - Propionic Acid (2) - CaCl2(3) system

Experimental		Van Laar Model		NRTL Model		Tan – NRTL Model		UNIQUAC Model	
y(1)	y(2)	y(1)	y(2)	y(1)	y(2)	y(1)	y(2)	y(1)	y(2)
1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000
0.983	0.017	0.984	0.016	0.983	0.017	0.983	0.017	0.982	0.018
0.949	0.051	0.978	0.022	0.972	0.028	0.970	0.030	0.976	0.024
0.947	0.053	0.971	0.029	0.958	0.042	0.955	0.045	0.970	0.030
0.938	0.062	0.964	0.036	0.950	0.050	0.946	0.054	0.967	0.033
0.926	0.074	0.943	0.057	0.936	0.064	0.931	0.069	0.955	0.045
0.915	0.085	0.914	0.086	0.925	0.075	0.920	0.080	0.933	0.067
0.894	0.106	0.884	0.116	0.914	0.086	0.908	0.092	0.905	0.095
0.834	0.166	0.815	0.185	0.883	0.117	0.876	0.124	0.827	0.173
0.657	0.343	0.632	0.368	0.765	0.235	0.756	0.244	0.594	0.406
0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000

Table 19: Error in values of Mole fraction of Water in Vapour Phase for Water (1) - Propionic Acid (2) - CaCl2 (3) System

Experimental	van Laar Δy	NRTL Δy	Tan - NRTL Δy	UNIQUAC Δy
1.000	0.0000	0.0000	0.0000	0.0000
0.983	0.0007	0.0001	0.0005	0.0179
0.949	0.0291	0.0232	0.0214	0.0074
0.947	0.0238	0.0115	0.0085	0.0210
0.938	0.0264	0.0120	0.0082	0.0198
0.926	0.0168	0.0098	0.0050	0.0172
0.915	0.0015	0.0099	0.0046	0.0072
0.894	0.0101	0.0200	0.0145	0.0096
0.834	0.0189	0.0493	0.0419	0.0667
0.657	0.0249	0.1079	0.0987	0.2395
0.000	0.0000	0.0000	0.0000	0.0000
$|\Delta y|$	**0.0169**	**0.0244**	**0.0226**	**0.0451**

Table 20: The data consistency test results for Water (1) - Propionic Acid (2) - CaCl2 (3) System

	Van Laar	NRTL	Tan – NRTL	UNIQUAC
Value of Area Integral Test	0.061	0.352	0.029	0.2198
Remarks	Fairly Consistent	Least Consistent	Most Consistent	Poorly Consistent

Table 21: T-xy data for Water (1) - Propionic Acid (2) - CH3COOK (3) system for varying salt concentrations

Salt %(wt)	Temp (°C)	y_{acid}	y_{water}	x_{acid}	x_{water}
10	100.3	0.034	0.966	0.051	0.949
20	100.5	0.033	0.967	0.049	0.951
30	100.9	0.044	0.956	0.048	0.952
40	101.3	0.027	0.973	0.049	0.950
50	101.4	0.039	0.962	0.049	0.951