a. TITLE OF THESIS AND ABSTRACT:

PHASE EQUILIBRIUM STUDIES FOR REACTIVE DISTILLATION OF ESTERIFICATION BASED SYSTEMS

ABSTRACT

Esterification is an important reaction for the production of various types of esters to be used as solvents or precursors for manufacturing other chemicals. It is an equilibrium limiting reaction with water as one of the products. With the advent of technology, esterification is usually carried out by combining reaction and separation in single unit which is called reactive distillation. The fact that it involves separation, vapour-liquid equilibrium becomes an integral part of it. Several Excess Gibbs energy models are used for the modelling of VLE data. UNIFAC is one of these models based on functional group contribution for the prediction when experimental data is not available. It is called an empirical model since the predictions may significantly deviate from the experimental data in some cases because the calculation is based on the interaction between the functional groups which may vary for different binary or multicomponent mixtures having the same functional groups. However, this model can be made predictive for a family of alcohol-ester systems by regressing the functional group parameters using the experimental data sets for these systems. The present work includes C2-C6 alcohol-ester system for which VLE data has been generated at six different pressures using a modified differential ebulliometer, and C1 based system for which modelling has been done given the fact that sufficient data is available for this system. This data is modelled using Margules 3 suffix, Wilson, NRTL and UNIQUAC models. The UNIFAC parameters have been regressed based on the experimental data for these systems at all the pressures using ASPEN (ver. 10). Additionally, pure species boiling points of C2 to C6 alcohols and esters have been generated. The parameters of Antoine equation have been regressed based on this data. The experimental data was compared with the available literature data. The model predictions show a good match with the experimental data and the later shows a good comparison with the literature data. The VLE data based on regressed UNIFAC parameters fits the experimental data much better than the conventional UNIFAC parameters.

b. Brief description of the research topic:

Reactive distillation is an emerging technology that combines chemical reaction with phase separation using distillation. This combination can lead to process intensification, energy

optimization and significant green engineering attributes. New applications and deeper understanding have favoured growth in the use of reactive distillation for a variety of chemical synthesis especially esterification and etherification. These reactions are typically reversible in nature. To enable complete conversion, it becomes necessary to remove one of the products formed (predominantly water) simultaneously.

The fact that reactive distillation can facilitate this makes it a promising technology. Simulation and design of reactive distillation process requires a sound knowledge of kinetics and authentic vapour-liquid equilibrium data. This necessitates VLE data generation and modelling using various models.

For some azeotropic systems, the column is operated at sub atmospheric conditions with the objective of breaking the azeotrope. Authentic VLE data at these pressures is required to validate whether the change in pressure can break the azeotrope or not. Practically all alcohol-ester systems form azeotrope. There is a possibility of addressing this condition by doing the separation at lower pressures. For this reason, the VLE data has been generated at different sub-atmospheric pressures.

Various researchers have carried out work in VLE of alcohol-ester systems. The same is summarized in Table 1.

Table 1: Summary of Literature Review

AUTHOR	SYSTEM	TEMPERATURE /PRESSURE	EQUILIBRIUM STILL	MODEL	REMARKS
Nagata et al. (1969)	methanol-methyl acetate	101.325 kPa	Colburn equilibrium still	Van Laar equation	Agreement with experimental data
Tu et al. (1997)	methanol-methyl acetate	101.3kPa	Hunsmann equilibrium still	Margules, Wilson, NRTL and UNIQUAC	Fitted Well

Cao et al. (2017)	methanol-methyl acetate	101.3kPa	Othmer equilibrium still	Electrolyte NRTL model	Fitted Well
Cai et al. (2011)	methanol-methyl acetate	101.3kPa	modified equilibrium still	NRTL	Fitted well and binary parameters were obtained
Peiza et al. (1986)	ethanol-ethyl acetate	101.3kPa	recirculating still	NRTL, Margules, Van Laar, Wilson and UNIQUAC	Margules, Van Laar, Uniquac shows less deviation
Figurski et al. (1998)	ethanol-ethyl acetate	100kPa to 3.5kPa	Van Nes Ebulliometer	AEOS	results are accurate and thermodynamically consistent
Li et al. (2009)	ethanol-ethyl acetate	101.325 kPa	Othmer Still	-	
Orchilles et al. (2007)	ethanol-ethyl acetate	100kPa	dynamic recirculating still	-	-
Gonzalez et al. (1996)	1-Butanol-n-butyl acetate	101.325 kPa	Ebulliometer	ASOG and UNIFAC model, modified UNIFAC	Modified UNIFAC best
Liadosa et al. (2008)	1-Butanol-n-butyl acetate	101.325 kPa	dynamic recirculating still	NRTL, UNIQUAC	Both give good prediction

Cepeda et al. (2010)	1-pentanol + pentyl acetate	101.3 kPa	equilibrium still	NRTL,	Satisfactorily results were obtained
Kirss et al. (2011)	1-pentanol + pentyl acetate	101.3 kPa, 79.99kPa, 53.33kPa, 26.66 kPa	semimicro ebulliometer.	Wilson	Satisfactorily results were obtained
Schmitt et al. (2005)	1-hexanol + n-hexyl acetate	90kPa, 60kPa, 30kPa	circulation still	NRTL	Satisfactorily results were obtained
Susial et al. (2013)	1-Propanol+ n-Propyl acetate	600 kPa	metal ebulliometer with recirculation of both the phase.	ASOG and different versions of UNIFAC	UNIFAC-Dortmund gives good prediction
Ortega et al. (2000)	1-Propanol+ n-Propyl acetate	101.32kPa and 160kPa	equilibrium still	ASOG and different versions of UNIFAC	UNIFAC model by Nitta gives good prediction n

c. Definition of the problem:

The present research work is based on determination of pure component boiling points for C2 to C6 alcohols and esters at six different pressures and modelling the same with Antoine equation and generating partial binary VLE data for these systems using a modified differential ebulliometer. The fact that this data is not available in the literature at desired pressures justifies the need to generate it at sub-atmospheric pressures. This data is modelled using Margules 3-suffix, Wilson, NRTL and UNIQUAC models. Additionally, to make the functional group analysis method UNIFAC predictive for these systems, the parameters have been regressed using ASPEN PLUS (ver. 10).

d. Objective and Scope of work:

The objective of the present works includes:

1. To summarize the VLE data available in the open literature with respect to pressure
2. To determine pure component boiling points for C2-C6 alcohols and esters at six different pressures (101.3 to 53 kPa) and to regress the parameters of Antoine equation.
3. To generate partial VLE data (P-T-x) at six pressures using a modified differential ebulliometer for C2-C6 alcohol-ester systems. (Data has not been generated for C1 based system because sufficient data in the given pressure range is available)
4. To determine the model parameters of Margules 3-suffix, Wilson, NRTL, UNIQUAC based on the generated experimental data.
5. To determine Bubble point temperature and vapour mole fraction using modified Raoult's law
6. To regress UNIFAC parameters for C1-C6 alcohol-ester family and in the process make the model predictive.

e. Original Contribution by thesis:

1."Modeling Vapour Liquid Equilibrium of Alcohol-Ester Systems using UNIFAC"

This paper was presented and published in International Conference on Futuristic Trends in Engineering, Science, Pharmacy and Management in 2015.

This paper emphasized on UNIFAC as a group contribution method which is commonly employed to model VLE of binary and multi-component systems. The fact that it is based on functional group analysis and does not require experimental data for modeling, makes it non-predictive at times. Synthesis of esters using reactive distillation technique requires knowledge of kinetics as well as phase equilibrium. The latter requires the use of activity models like UNIFAC. Modeling using UNIFAC was done for alcohol-ester systems for C1 to C6 and the predictions were compared with the conventional models. It was observed that UNIFAC predicts the systems reasonably well till C2 and from C3 onwards it shows a large deviation.

2.Comparison of The VLE Data Based on UNIFAC Parameters Obtained by Regression And Conventional Approach For C1 – C6 Alcohol-Ester Systems

This paper was published in "Design Engineering (Toronto)" which present that UNIFAC is a predictive method based on functional group contributions for determining the activity coefficients. With reference to binary C1 – C6 alcohol-ester systems the conventional UNIFAC approach may or may not be able to predict the experimental data. Regression of the model parameters for a family of alcohol-ester systems can make the predictive method more promising. UNIFAC parameters for methanol – methyl acetate to hexanol – hexyl acetate systems at around 101.33 kPa were regressed using GAMS. These were compared with those obtained using the conventional approach. The VLE data obtained based on these two approaches was compared with the literature data. The VLE data based on regressed UNIFAC parameters shows a good match with the literature data

f. Methodology of Research:

The present work is based on generating pure component vapour pressure data for C2-C6 alcohol-ester systems i.e., ethanol-ethylacetate,1-propanol-1-propyl acetate,1-butanol-1-butyl acetate,1-pentanol-1-pentyl acetate and 1-hexanol-1-hexyl acetate and partial VLE data for the binary mixture. The details of the equipment used, and the procedure followed are discussed in this section. Modified differential ebulliometer is used to generate vapour liquid equilibrium data For the VLE data generation chemicals are fed to the modified ebulliometer. Ebulliometer has a provision of drop counter to ensure equilibrium condition and to generate data with minimum quantity of chemicals. The drop counter facility is unique and provides additional resource to ensure equilibrium condition along with the temperature. The details of the set-up used are given in Table 2.

Table 2: Details of the Experimental Set-up

Temperature Measurement	Mercury Thermometer (0-150 °C), Accuracy 0.1/0.1°C
Pressure Measurement	Mercury Manometer (400 to 760 mmHg) Accuracy 1mmHg
Vacuum Pump	Belt Driven Oil Ring Vacuum Pump
Cooling Media	Cooling water (30-33°C)
Condenser	24-inch Jacketed internal coil type
Ballast	10lit. SS.-316 setup
Heater	0.5 KW External belt heater

Chemicals

C2 to C6 based alcohols and corresponding esters were used for the experimental study. The details of the chemicals used for the experimentation as well as standardization and analysis are given in Table 3.

Table 3 Details of the chemicals used for the experimentation

Chemical	Source	Purity	Analysis method
1-Propanol	LOBA chemical Ltd.	99%	GC
n-Propyl Acetate	LOBA chemical Ltd.	99%	GC
Isopropyl Alcohol	LOBA chemical Ltd.	99%	GC
1-Butanol	SDFCL	99.5%	GC
n-Butyl Acetate	SDFCL	99.5%	GC
1-Pentanol	SDFCL	98	GC
n-Pentyl Acetate	Sigma Aldrich	99%	GC
1-hexanol	LOBA chemical Ltd.	99.4%	GC
n-Hexyl Acetate	Sigma Aldrich	99%	GC

Analysis:

The VLE data generated was using an ebulliometer wherein only liquid composition is obtained along with the temperature. Hence, to ensure that there is no change in the composition during experimentation due to losses, the sample of the mixture which was charged in the VLE still and the one withdrawn after the end of the experiment were analysed. Chemito -1000 Gas Chromatograph (GC) with 1.8 m Chromosorb column was used for the analysis. The composition of the binary mixtures was determined based on the calibration plot obtained using synthetic mixtures using isopropyl alcohol as an external standard. The GC parameters and the temperature programming used for various systems is given in Tables 4 and 5 respectively.

Table 4: GC Conditions

GC Parameters	Conditions
Column	Packed
Column Diameter	3.175 mm
Column Length	1.8 m
Carrier Gas(N2) Pressure	0.8 bar
Injector Temperature	200 ^{o} C
Detector Temperature	220 ^{o} C
Injection Quantity	0.1 µL
Method	8

Table 5: Temperature Programming for various systems

SYSTEM	**Oven Temperature(^{0}C)**	**Rate(^{0}C/min)**
Ethanol -Ethyl Acetate	60-190	6
1-Propanol-n-Propyl acetate	80-190	9
1-Butanol-n-Butyl acetate	70-190	9
1-Pentanol-n-Pentyl acetate	100-190	6
1-Hexanol-n-Hexyl acetate	100-190	6

Results /Comparison:

The P-T data generated for C2 to C6 alcohols and esters is shown in Figures 1 and 2 respectively.

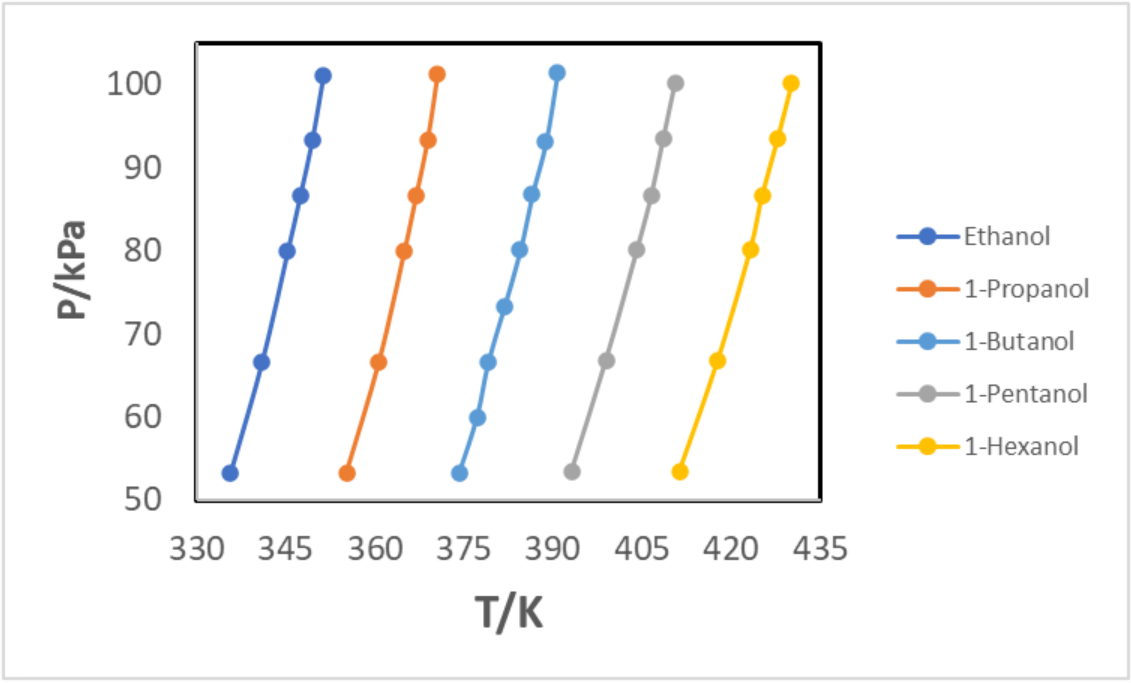

Figure 1: P-T data for C2 to C6 alcohols

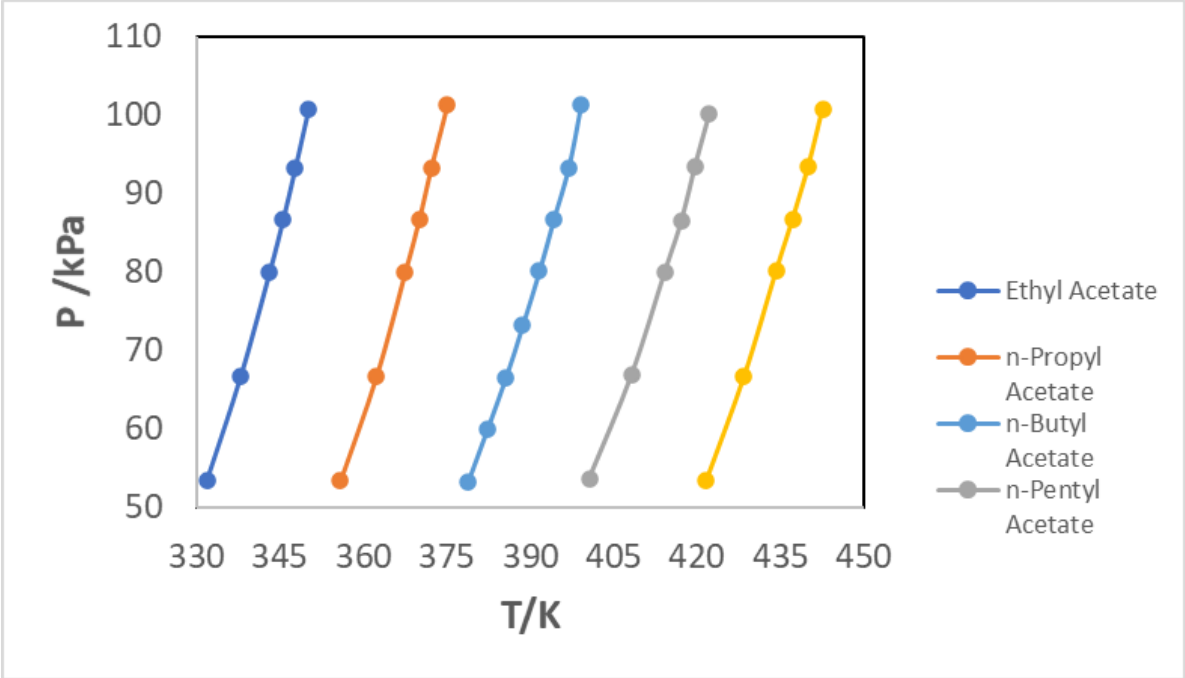

Figure 2: P-T data for C2 to C6 esters

The parameters of the Antoine equation were determined based on the generated experimental data with regression analysis using SOLVER feature of MS Excel. The parameters are tabulated in Table 6.

Table 6: Regressed Antoine Parameters

Species	A	B	C	RMSD
Ethanol	16.60	3758.30	-37.80	0.09
Ethyl Acetate	14.11	2799.35	55.36	0.09
1-Propanol	16.19	3415.75	-75.63	0.15
n-Propyl Acetate	16.85	4691.06	8.74	0.13
1-Butanol	15.89	3499.99	-80.27	0.26
n-Butyl Acetate	15.78	4216.18	-21.49	0.14
1-Pentanol	13.32	2277.52	-149.32	0.1
n-Pentyl Acetate	13.96	3215.11	-78.46	0.14
1-Hexanol	14.37	3015.96	-120.96	0.15
n-Hexyl Acetate	14.42	3422.81	-93.35	0.2

P = (101.4 - 53.33) kPa, ln (P/kPa) = A - B/ (C + (T/K));

The experimental data for the pure species has been compared with the literature data. The RMSD based on temperature is reported in Table 7. It is pictorially represented as a deviation plot of experimental temperature with literature based on the minimum and maximum deviations observed in Figure 3 and Figure 4 for alcohols and esters respectively.

Table 7 Comparison of experimental PT data with literature

Component	RMSD	Reference
Ethanol	0.34	(Gomes et al. 2014)
	0.50	(Susial et al. 2011)
	0.28	(Ortega and Susial 1990)
	0.33	(Riddick et al. 1986)
	0.37	(Orchillés et al. 2007)
	0.13	(Yaws, L 2015)
Ethyl Acetate	0.19	(Gomes et al. 2014)
	1.02	(Susial et al. 2011)
	0.16	(Ortega and Susial 1990)
	0.22	(Riddick et al. 1986)
	0.23	(Orchillés et al. 2007)
	0.13	(Yaws, L 2015)
1-Propanol	0.64	(Kemme and Kreps 1969)
	1.10	(Dejoz et al. 1997)
	0.81	(Brown and F 1959)
	0.75	(Ngema et al. 2012)
	0.75	(Prasad, A and Rao, K 1986)
	0.85	(Siimer et al. 1989)
	1.09	(Yaws, L 2015)
	0.75	(Sapei et al. 2011)
n-Propyl Acetate	0.17	(Yaws, L 2015)
	0.52	(Sapei et al. 2011)
	0.19	(Ambrose et al. 1981)
	0.50	(Fernández et al. 2013)
	0.23	(Polák and Mertl 1965)

	0.53	(Meyer et al. 1980)
	0.86	(Ortega et al. 2006)
	0.78	(Fárková and Wichterle 1993)
	0.38	(González et al. 1999)
	0.19	(Riddick et al. 1986)
	0.24	(Texas Engineering Experiment Station. Thermodynamics Research Center. 1996)
1-Butanol	0.80	(Susial et al. 2015)
	0.44	(Yaws, L 2015)
	0.61	(Reddy et al. 2013)
	0.39	(Dejoz et al. 1997)
	0.27	(david and Henry 1994)
n-Butyl Acetate	0.30	(Meyer et al. 1980)
	0.51	(Yaws, L 2015)
	0.41	(Lladosa et al. 2008)
	0.27	(Riddick et al. 1986)
	0.94	(Sheehan and Langer 1969)
	0.34	(Laavi et al. 2013)
	0.47	(Ortega et al. 2005)
	0.25	(Kirss et al. 1992)
	0.30	(Kuus et al. 1991)
	0.42	(Li and Li 2012)

	0.48	(Aucejo et al. 1995)
1-Pentanol	0.15	(Cepeda 2010)
	0.28	(Kirss et al. 2011)
	0.33	(Yaws, L 2015)
n-Pentyl Acetate	0.99	(Cepeda 2010)
	0.18	(Kirss et al. 2011)
	2.00	(Yaws, L 2015)
1-Hexanol	0.18	(Schmitt and Hasse 2005)
		(Yaws, L 2015)
1-Hexanol	Minimum:0.18 Maximum:0.85	Minimum: Schmitt et al. (2005) Maximum: Yaws (2015)
n-Hexyl Acetate	Minimum:0.49 Maximum:1.34	Minimum: Yaws (2015) Maximum: Schmitt et al. (2005)

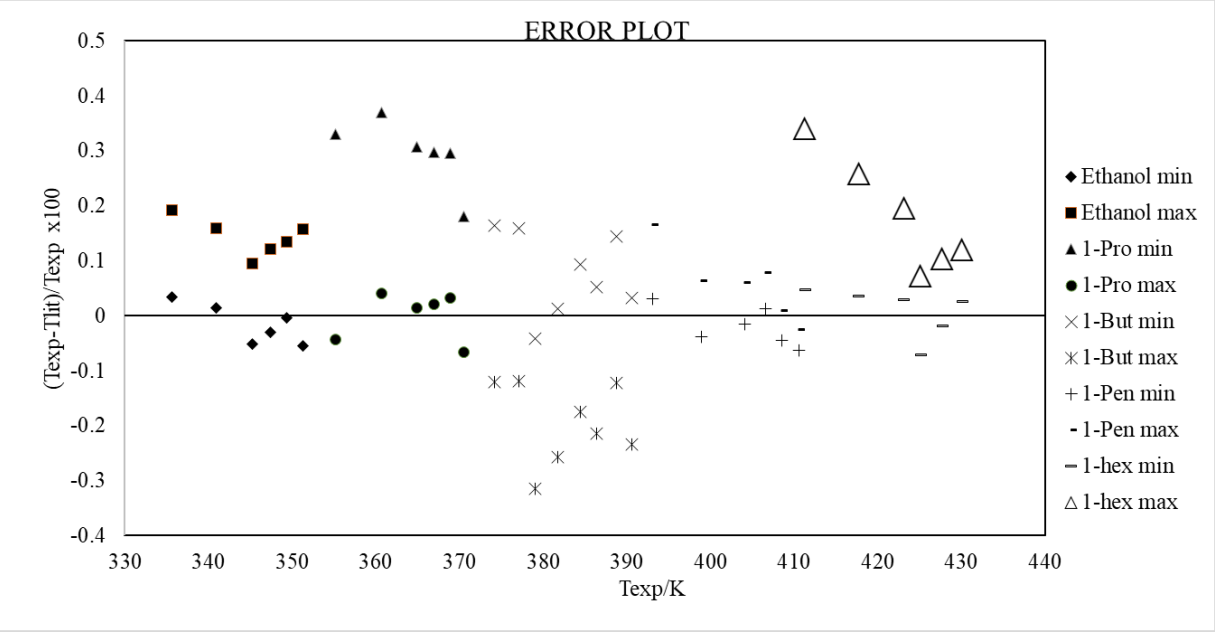

Figure 3 Relative difference of the experimental and literature boiling points for alcohols

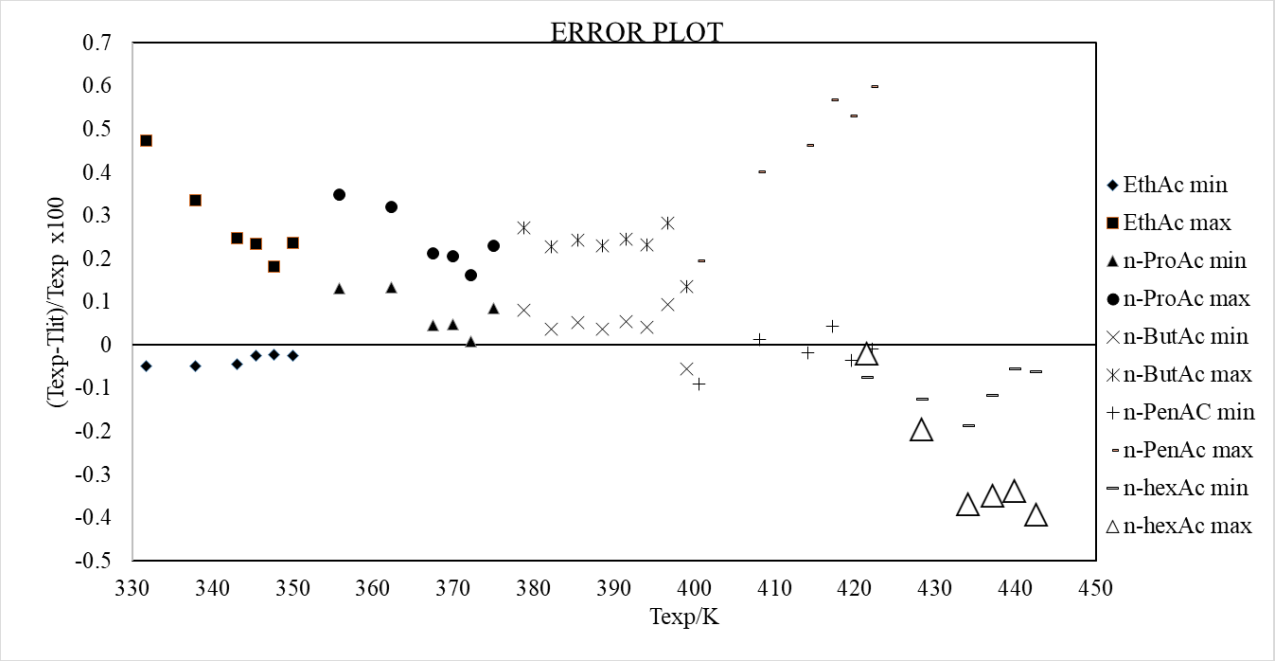

Figure 4 Relative difference of the experimental and literature boiling points for esters

The T-x data for binary systems was generated at 6 different pressures for C2 to C6 alcohol-ester systems. The vapour composition was determined based on the combination of BUBL P and BUBL T calculations. Margules model predicts the experimental data well for C2 and C6 systems, NRTL for C4 and C5 systems and the experimental data for C3 system is validated much better by Wilson model. The T-x-y data for the model which gives the best fit is shown in Figures 6 to 10. The fact that sufficient data for C1 based system is available the experimental data was not generated and the literature T-x-y data is shown in Figure 5

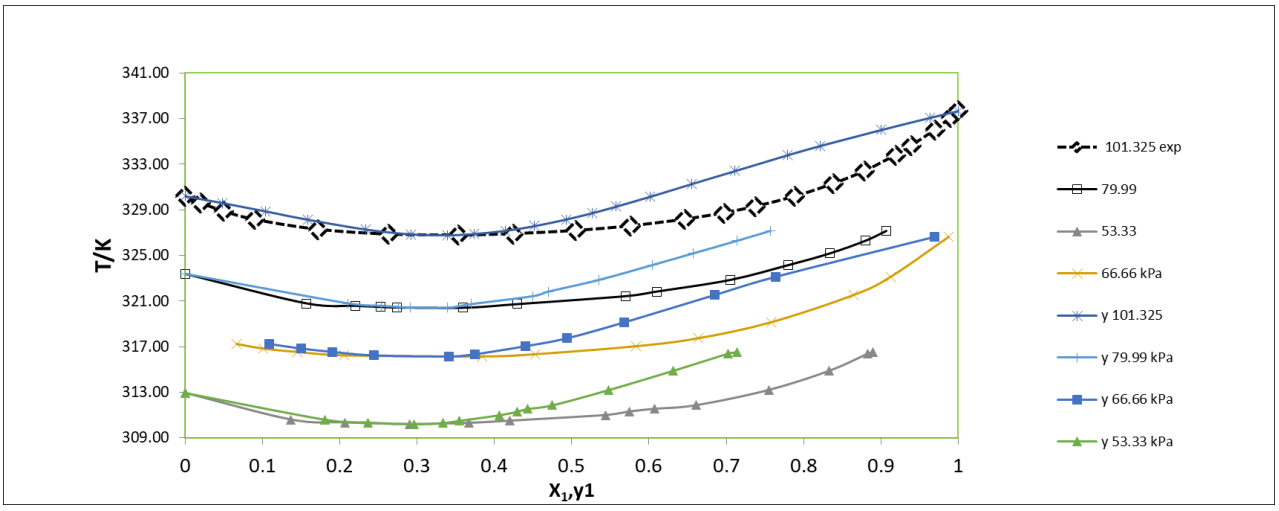

Figure 5 T-x-y data based on the literature for Methanol-Methyl acetate system at different pressures

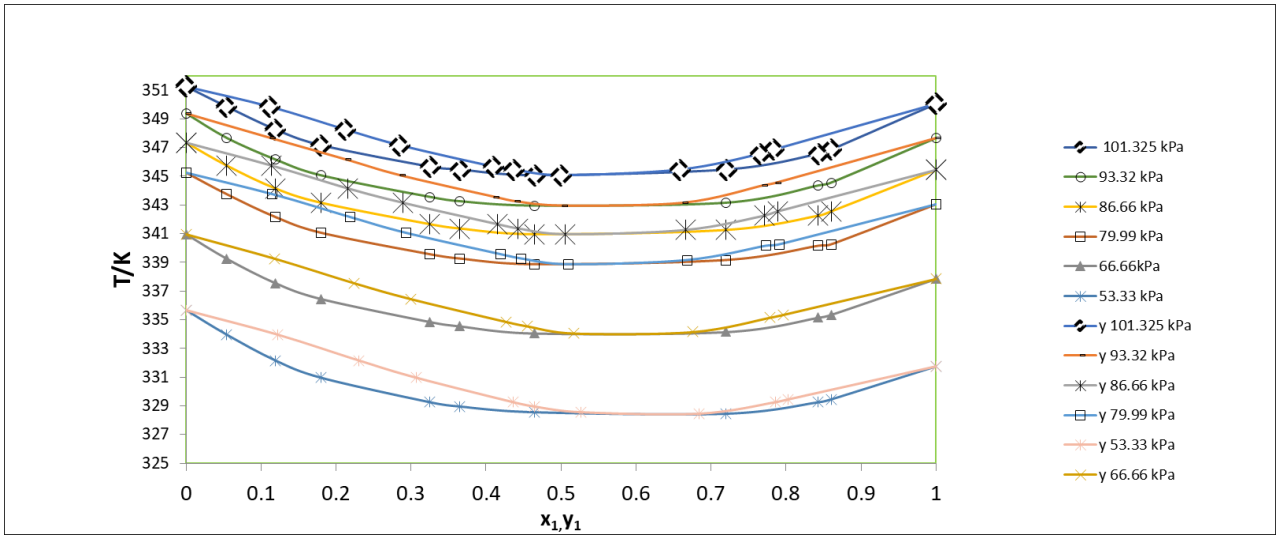

Figure 6 T-x-y data based on the experiment for Ethanol-Ethyl acetate system at different pressures

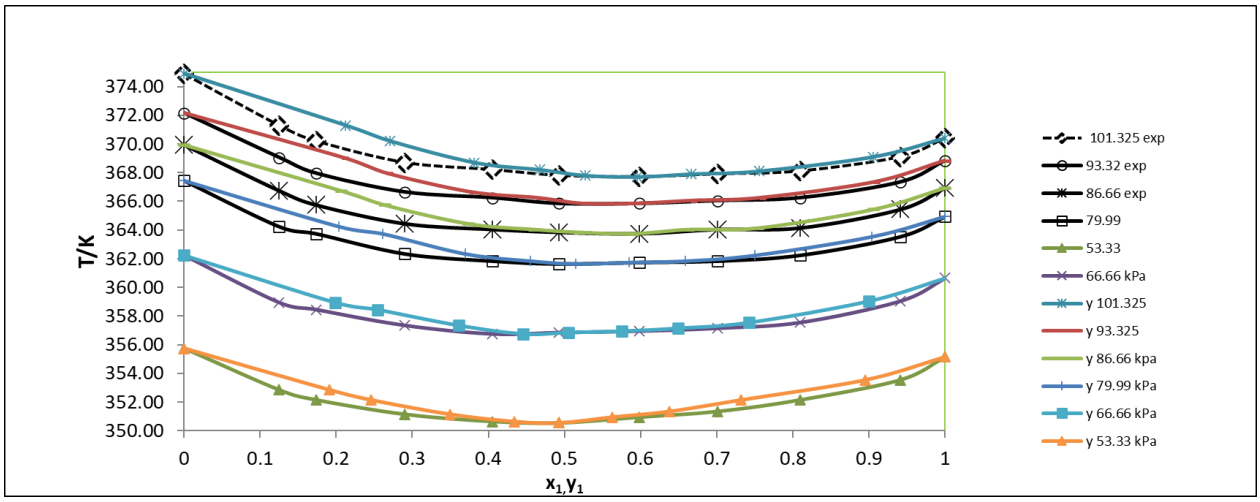

Figure 7 T-x-y data based on the experiment for Propanol-Propyl acetate system at different pressures

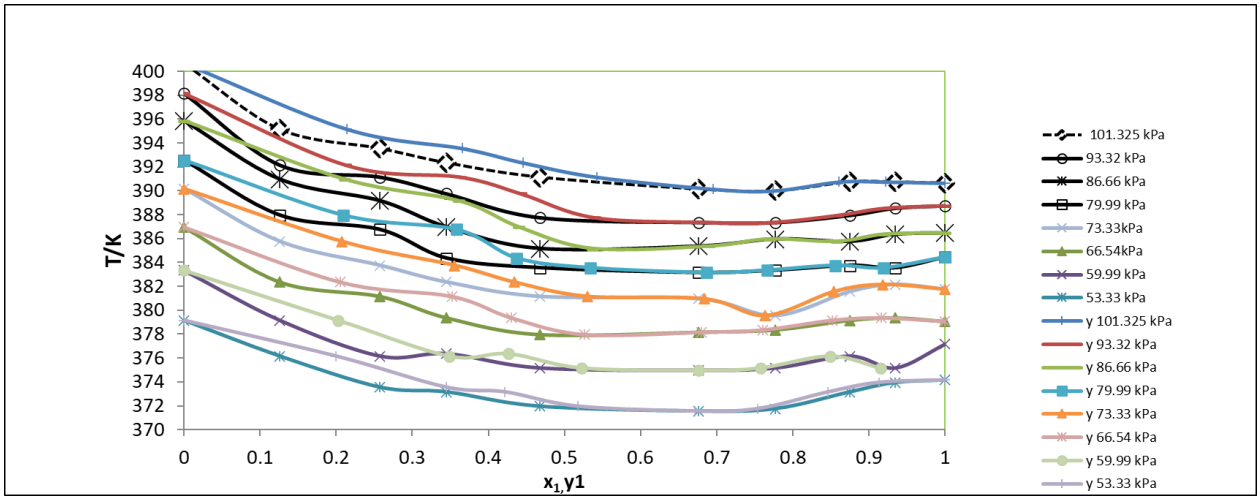

Figure 8 T-x-y data based on the experiment for Butanol-Butyl acetate system at different pressures

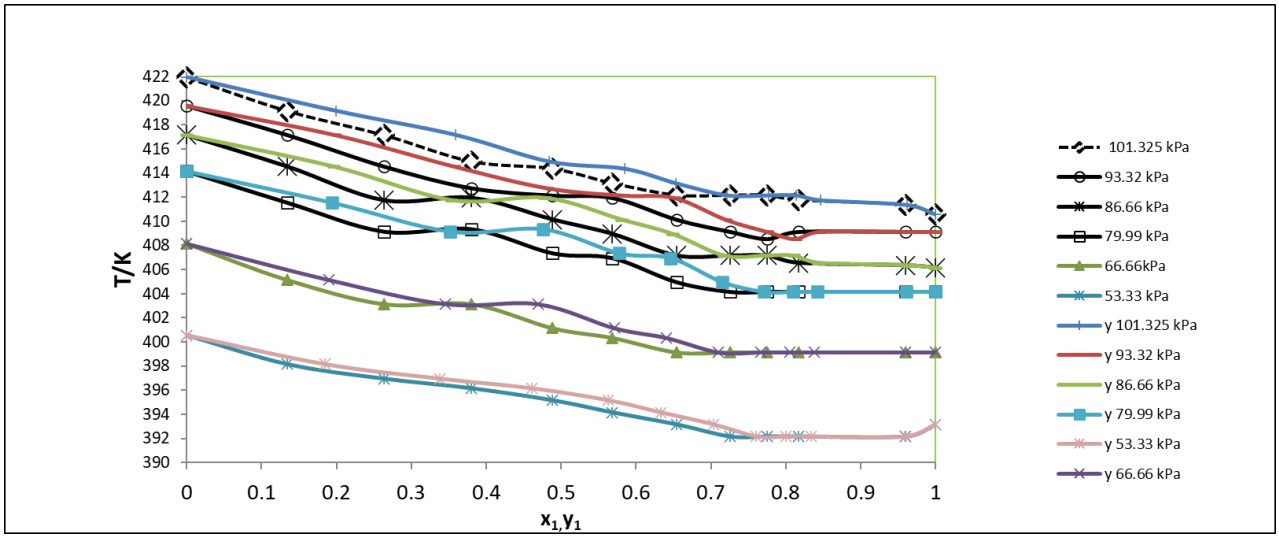

Figure 9 T-x-y data based on the experiment for Pentanol-Pentyl acetate system at different pressures

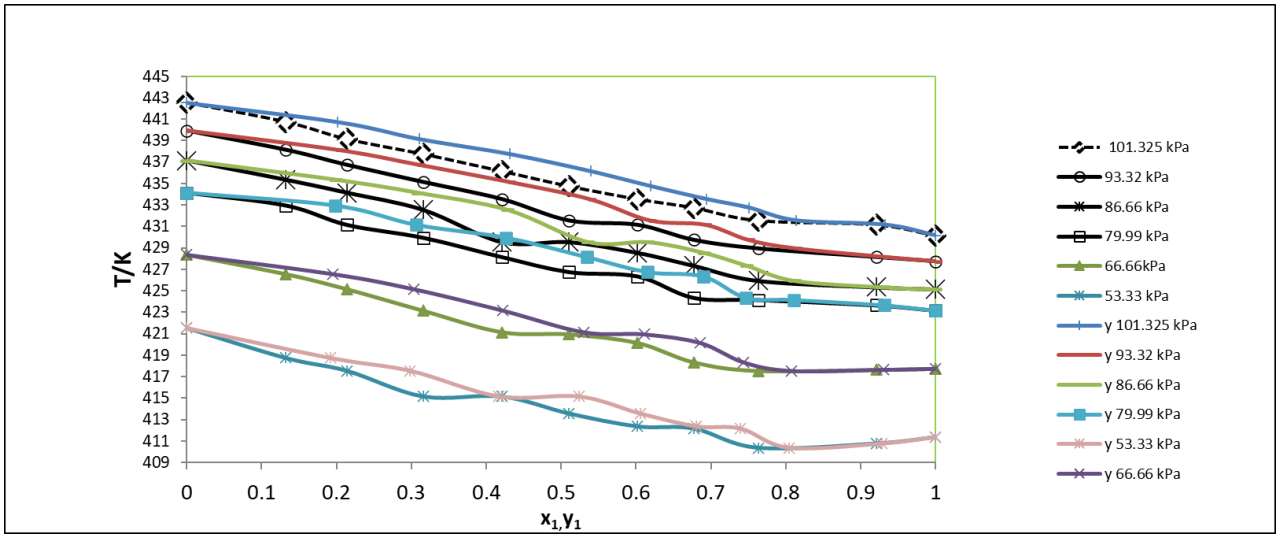

Figure 10 T-x-y data based on the experiment for Hexanol-Hexyl acetate system at different pressures

One of the objectives of the present work was to make the conventional UNIFAC method predictive by regressing the parameters. The comparison of the RMSD based on T based on conventional and regressed UNIFAC parameters is given in Table 8. It is evident from the table that the regressed parameters show a good match with the experimental data relative to the conventional method.

Table 8: Comparison of conventional UNIFAC predictions with the Regressed values for different C2-C6 alcohol-ester systems

Ethanol-Ethyl Acetate			**1-Propanol-n-Propyl Acetate**		
P/kPa	**Conventional UNIFAC Parameters**	**Regressed UNIFAC Parameters**	**P/kPa**	**Conventional UNIFAC Parameters**	**Regressed UNIFAC Parameters**
	RMSD (T)	RMSD (T)		RMSD (T)	RMSD (T)
101.1	0.996	0.361	101.1	0.885	0.223
93.33	1.006	0.393	93.33	1.131	0.448

86.62	1.014	0.400	86.62	1.076	0.155
79.99	1.100	0.354	79.99	1.211	0.154
66.46	1.083	0.456	66.46	1.295	0.204
53.32	1.087	0.671	53.32	1.202	0.202
Average	**1.048**	**0.439**	**Average**	**1.133**	**0.231**

1-Butanol-n-Butyl Acetate			**1-Pentanol-n-Pentyl Acetate**		
P/kPa	**Conventional UNIFAC Parameters**	**Regressed UNIFAC Parameters**	**P/kPa**	**Conventional UNIFAC Parameters**	**Regressed UNIFAC Parameters**
	RMSD (T)	RMSD (T)		RMSD (T)	RMSD (T)
101.1	0.817	0.455	101.1	1.699	0.587
93.33	0.857	0.248	93.33	2.214	0.670
86.62	0.916	0.357	86.62	2.399	0.765
79.99	0.857	0.183	79.99	2.413	0.774
66.46	1.130	0.390	66.46	2.293	0.376
53.32	1.227	0.065	53.32	2.466	0.359
Average	0.982	0.321	**Average**	2.247	0.589

1-Hexanol-n-Hexyl Acetate		
P/kPa	**Conventional UNIFAC Parameters**	**Regressed UNIFAC Parameters**
	RMSD (T)	RMSD (T)
101.1	1.849	0.844
93.33	1.886	0.747

86.62	1.775	0.842
79.99	1.975	0.690
66.46	1.621	0.540
53.32	1.409	0.215
Average	1.752	0.647

g. Achievements with respect to objectives:

The VLE data generated for five alcohol-ester systems at six different pressures and processed for C1 based system using different Excess Gibbs energy models. UNIFAC parameters regressed on the basis of experimental data compare much better with the experimental data relative to the conventional model.

h. Conclusion

i. Paper Published:

1)Title of the paper: Modeling Vapour Liquid Equilibrium of Alcohol-Ester Systems using UNIFAC

International Conference on Futuristic Trends in Engineering, Science, Pharmacy and Management

ISBN: 978-81-933386-0-5

Authors: Upasana Singh, Dr. Nitin Bhate

2) Title of the paper: Comparison Of The Vle Data Based On Unifac Parameters Obtained By Regression And Conventional Approach For C1 – C6 Alcohol-Ester Systems

Design Engineering (Toronto) ISSN: 0011-9342

Authors: Upasana Singh, Rajesh Shah, Vaibhavi Vaghela. Nitin Bhate

j. Patents:

NIL

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