Isobaric Vapor-Liquid Equilibrium Studies for Separation of Acetic Acid from Aqueous Solutions

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1. Abstract

The popularity of acetic acid (AA) has risen due to its versatility in various chemical applications since its discovery. Its low cost and minimal toxicity make it a popular choice as a solvent or raw material in the production of terephthalic acid, cellulose acetate, and other products. Currently, there are two primary methods of manufacturing: chemical and fermentative. While fermentative production has gained traction recently, commercial production has not yet been established. The need for sustainable manufacturing processes that reduce environmental burdens is becoming increasingly important in current trends. All these methods to produce acetic acid (AA) involves the generation of large amounts of dilute aqueous solutions, typically with concentrations between 10-30%. To prevent environmental harm and reduce costs, it is necessary to develop effective methods for recovering acetic acid from diluted aqueous solutions. Conventional distillation techniques are often costly and require large trays and high reflux ratios to separate acetic acid from water, making it difficult to do so. In the industry, adding an entrainer/solvent is a common method to overcome this difficulty and use heterogeneous azeotropic distillation or liquid-liquid extraction. Choosing a right solvent is the critical step for solvent extraction efficiency and overall economy of operation. The most promising solvents for separating acetic acid (AA) from an aqueous solution are methyl tert-butyl ether (MTBE), cyclopentyl methyl ether (CPME) and 2-methyl tetrahydrofuran (2-MeTHF). However, isobaric VLE data for MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) in the wide range of low pressure is not available in literature. In designing the separation system, isobaric VLE data of these systems are essential for separation of pure acetic acid (AA) from aqueous solutions.

In this work, the isobaric VLE data for the binary mixtures of the MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) systems were experimentally measured at the pressure ranges from 60-101.325 kPa using an ebulliometer. The excess Gibbs energy models Wilson, NRTL, and UNIQUAC were used to correlate activity coefficients. Antoine constant was calculated using experimental data and compared with literature data. All modes were fitted satisfactory with experimental data. This work reported the average absolute deviations between the experimental values and calculated values for the pressure and temperature. The experimental data were verified using R-K and L-W tests of thermodynamic consistency. The presented data can be utilized for designing extractive or azeotropic distillation columns for the separation of acetic acid from the solvent MTBE, CPME, and 2-MeTHF.

2. Brief description of the state of the art of the research topic

In the chemical industry, acetic acid ranks among the top 50 chemicals. It is utilized in the manufacturing of various products such as vinyl acetate, acetic anhydride, acetate esters, monochloroacetic acid, and as a solvent in the production of dimethyl terephthalate and terephthalic acid [1]. Traditionally, acetic acid has been used for food preservation, solvent production, and intermediate chemical production. Vinegar, a 4-6% acetic acid solution, serves as both a preservative and flavoring agent [2] . The principal method of producing acetic acid on an industrial scale is via the petrochemical route, which involves carbonylation of methanol, liquid-phase oxidation of hydrocarbons, and oxidation of acetaldehyde. By 2012, approximately 90% of acetic acid production utilized low-pressure methanol carbonylation technologies [3]. Fermentation-derived acetic acid is typically found in dilute aqueous solutions, usually less than 10 wt. %. Consequently, all these processes require separation of acetic acid from aqueous solution.

Acetic acid recovery can be achieved economically using various separation processes such as conventional distillation, azeotropic distillation, extraction, and hybrid processes. Distillation, which requires a large number of plates and a high reflux ratio, is often used to separate water and acetic acid due to their close relative volatility [4]. Among these methods, liquid-liquid extraction followed by heteroazeotropic distillation is considered the most energy-efficient process [5]. Choosing the right solvent is crucial for the process, as it affect plant economy. Solvent recovery is necessary for economic viability, and distillation separates solute and solvent. Solvents are chosen according to many factors, including selectivity, distribution coefficient, recoverability, chemical reactivity, viscosity, vapor pressure, freezing point, density, toxicity, cost, and many others.

Acetic acid (AA) can be separated from an aqueous solution using solvent such as methyl tert-butyl ether (MTBE), cyclopentyl methyl ether (CPME) and 2-methyl tetrahydrofuran (2-MeTHF) through extraction [6] [7] [8]. According to Parsana et al., isobaric VLE data have been measured for binary systems, including CPME (1) -AA (2) [9], 2-MeTHF (1) -AA(2) [10], at atmospheric pressure. Moreover, they measured isobaric VLE data of Tetrahydrofuran (THF) (1)-AA (2) [11] at low pressures as well. Peng et al. measured VLE data for Dimethyl sulfoxide (DMSO)(1)-AA (2) [12] and Dimethylformamide (DMF) (1)-AA (2) [12] at low pressure. However, Isobaric VLE data of MTBE (1)-AA (2), CPME (1)-AA (2), and 2-MeTHF (1)-AA (2) are not reported in the literature in a wide range of low pressures. Furthermore, low-pressure VLE is critical as lower pressure heating duties are reduced. In this work, we measured isobaric VLE data at low pressures for binary mixtures of MTBE (1)-AA (2), CPME (1)-AA (2), and 2-MeTHF (1)-AA (2) for the separation of acetic acid (AA) from aqueous solutions.

3. Definition of the Problem

Acetic acid can be produced through various methods, including chemical processes, enzymatic fermentation, biomass hydrolysis, electrochemical reduction, and CO_2 or CO. AA produced through these processes requires separation from aqueous solation. Due to the presence of a pinch point at the pure end of water, conventional distillation cannot be used to separate AA from water. Acetic acid separation from aqueous solutions is a vital industrial process that has a significant impact on product economics, environmental conservation, and resource management. Various methods have been used to remove water from acetic acid, including conventional distillation, azeotropic distillation, extraction, and hybrid processes. Although distillation has advantages, it is not a viable option due to its high energy cost, multiple stages in the column, and high reflux ratio. Among these methods, liquid-liquid extraction followed by heteroazeotropic distillation is considered the most energy-efficient process. This is a solvent-based separation process, where the choice of solvent and recovery of solvent are the most crucial design parameter. In the solvent recovery step, isobaric VLE data is required for the the design of separation column for separation of solvent and acetic acid from the aqueous solution.

4. Objectives and scope of work

- To measure isobaric VLE data of MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) in the pressure range of 60-101.325 kPa by modified ebulliometer. Isobaric VLE data are essential to a design of distillation column in the solvent recovery step for separation acetic acid.
- To verify experimental VLE data using R-K test and Wisniak's L-W Test of thermodynamic consistency.
- To determine binary interaction parameter of experimental binary data using various activity coefficient models such as Wilson, NRTL, UNIQUAC, etc.
- To predict VLE data of data using UNIFAC methods and compared with experimental data.
- Isobaric VLE data are essential to a design of distillation column in the solvent recovery step for separation acetic acid from aqueous solution.

5. Original Contribution of the research

There is no literature available on isobaric VLE data MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) at low pressure. Experimental vapor-liquid equilibrium (VLE) data is crucial for designing separation processes like distillation, which accounts for a large proportion of energy usage in chemical plants and industrial separation processes. Experimental isobaric VLE data of MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) are invaluable for designing separation column for the recovery of solvent from acetic acid for acetic acid aqueous solutions.

6. Methodology of research

6.1 Experimentation Producers

A modified ebulliometer was utilized to measure the boiling points of MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) binary mixtures at various pressures ranging from 60.0 to 101.3 kPa. A total of fifteen data sets of each system encompassing the full range of compositions were examined. The pressure was measured with a mercury-filled U-tube manometer, which had a precision of 0.133 kPa (1 mmHg). The equilibrium temperature was measured using a calibrated Pt-100 temperature sensor with a precision of 0.1 K. Prior to the experiments, the setup was cleaned with acetone to remove any potential impurities in the ebulliometer and condenser. The setup was then kept under vacuum for several minutes to eliminate any traces of residual chemicals and avoid contamination of the samples. The setup's reliability was validated by checking the boiling points of the pure components. The experiments began with the charging of an approximately 60 mL sample into the ebulliometer. The equilibrium chamber's contents were heated using a belt heater, with the heating rate gradually increasing to avoid bumping and superheating of the liquid. The heating rate was precisely regulated by a voltage controller. To prevent any material loss, cooling water flow was initiated before the heater. The temperature and drop rate were closely monitored to determine the equilibrium state. The system was considered in equilibrium when the temperature and drop rate stabilized. The time taken to reach equilibrium was around 30-40 minutes. The modified ebulliometer was equipped with a vacuum pump and a ballast tank to maintain a lower pressure in the system. A manually operated valve was used to adjust the pressure to the desired level. The first set of data was obtained at atmospheric pressure, and subsequent experiments were conducted by changing the pressure and adjusting the heating rate accordingly. PTx diagrams were generated by repeating this procedure at different pressures and compositions. However, it's important to note that gas-phase composition cannot be obtained using ebulliometer.

6.2. Sample Analysis using Refractometer

To ensure the accuracy of the experiment, the samples were collected in separate vials and analyzed using a refractometer. The liquid sample composition was analyzed using a five-digit automatic digital refractometer (RFM-950 supplied by LABMAN), with a measurement range of 1.30000-1.70000 and an accuracy of ±0.00002, as per the supplier's specifications. The refractometer was properly cleaned before and after analyzing each sample. The calibration curve was prepared by calculating the mole fraction from the refractive index values of samples with known compositions.

6.3. The Experimental Vapor-Liquid Equilibrium data

The measurement of vapor-liquid equilibrium data was conducted for three binary systems, MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2). Temperature, pressure, and the compositions of the liquid phases were measured using a modified ebulliometer. The pressure was maintained within the range of 60 to 101.325 KPa. The T-x data recorded for all 15 measurement points and are presented in the table below

Table 1 Experimental isobaric VLE data of the binary system MTBE (1)-AA (2)

101.325 kPa		**90.0 kPa**		**80.0 kPa**		**70.0 kPa**		**60.0 kPa**	
x_1	**T/K**	**x_1**	**T/K**	**x_1**	**T/K**	**x_1**	**T/K**	**x_1**	**T/K**
0.000	391.05	0.000	387.35	0.000	384.05	0.000	380.75	0.000	375.25
0.069	380.75	0.069	377.85	0.069	370.75	0.069	366.70	0.069	363.25
0.127	373.75	0.127	369.65	0.127	362.25	0.127	359.30	0.127	355.75
0.193	367.25	0.193	361.55	0.193	352.85	0.193	350.35	0.193	347.45
0.255	361.05	0.255	355.35	0.255	347.55	0.255	345.05	0.255	343.15
0.324	354.75	0.324	348.55	0.324	343.85	0.324	339.65	0.324	335.95
0.385	350.75	0.385	343.85	0.385	340.45	0.385	337.15	0.385	332.65
0.453	346.25	0.453	340.45	0.453	336.78	0.453	332.02	0.453	329.65
0.528	342.45	0.528	338.25	0.528	335.15	0.528	330.95	0.528	327.25
0.590	339.85	0.590	337.15	0.590	333.45	0.590	328.85	0.590	324.45
0.657	337.05	0.657	334.25	0.657	331.25	0.657	327.05	0.657	322.95
0.757	334.85	0.757	331.45	0.757	327.52	0.757	322.98	0.757	319.15
0.841	331.65	0.841	328.45	0.841	324.35	0.841	320.75	0.841	317.55
0.933	329.95	0.933	326.05	0.933	321.85	0.933	317.65	0.933	313.65
1.000	328.25	1.000	324.65	1.000	320.65	1.000	316.10	1.000	312.05

Table 2 Experimental isobaric VLE data of the binary system CPME (1)-AA (2)

101.325 kPa		92 kPa		84.0 kPa		76.0 kPa		68.0 kPa		60.0 kPa	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0.0000	391.15	0.0000	387.95	0.0000	385.05	0.0000	381.95	0.0000	378.55	0.0000	374.75
0.0710	388.55	0.0710	385.45	0.0710	382.15	0.0710	379.15	0.0710	375.65	0.0710	371.95
0.1430	386.75	0.1430	383.55	0.1430	380.25	0.1430	377.15	0.1430	373.85	0.1430	370.05
0.2140	385.15	0.2140	382.05	0.2140	378.55	0.2140	375.35	0.2140	372.15	0.2140	368.45
0.2860	384.15	0.2860	381.05	0.2860	377.45	0.2860	374.25	0.2860	371.05	0.2860	367.45
0.3570	383.35	0.3570	380.05	0.3570	376.45	0.3570	373.55	0.3570	370	0.3570	366.25
0.4290	382.65	0.4290	379.15	0.4290	375.75	0.4290	372.55	0.4290	369.05	0.4290	365.25
0.5000	381.85	0.5000	378.65	0.5000	375.05	0.5000	371.85	0.5000	368.45	0.5000	364.65
0.5710	381.35	0.5710	378.05	0.5710	374.55	0.5710	371.25	0.5710	367.55	0.5710	363.85
0.6430	380.65	0.6430	377.55	0.6430	374.05	0.6430	370.85	0.6430	367.15	0.6430	363.25
0.7130	380.35	0.7130	377.05	0.7130	373.65	0.7130	370.35	0.7130	366.65	0.7130	362.75
0.7860	380.25	0.7860	376.55	0.7860	373.25	0.7860	370.05	0.7860	366.15	0.7860	362.35
0.8570	379.75	0.8570	376.55	0.8570	373.05	0.8570	369.75	0.8570	366.25	0.8570	362.35
0.9280	379.45	0.9280	376.25	0.9280	372.95	0.9280	369.75	0.9280	366.05	0.9280	362.05
1.0000	379.25	1.0000	375.95	1.0000	372.75	1.0000	369.45	1.0000	365.75	1.0000	361.75

Table 3 Experimental isobaric VLE data of the binary system 2-METHF (1)-AA (2)

101.325 kPa		90.0 kPa		80.0 kPa		70.0 kPa		60.0 kPa	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
0	391.1	0	387.3	0	383.6	0	379.5	0	374.8
0.0841	384.5	0.0841	380.5	0.0841	377.5	0.0841	373.8	0.0841	369.5
0.1520	378.9	0.1520	376.5	0.1520	373.1	0.1520	368.7	0.1520	365.1
0.2218	374.9	0.2218	372.4	0.2218	368.3	0.2218	365.1	0.2218	361.8
0.2978	371.1	0.2978	369.1	0.2978	365.6	0.2978	361.7	0.2978	358.9
0.3657	367.9	0.3657	365.6	0.3657	361.7	0.3657	359.1	0.3657	355.9
0.4215	365.7	0.4215	362.8	0.4215	359.9	0.4215	356.4	0.4215	352.9
0.4972	363.2	0.4972	360.3	0.4972	357.8	0.4972	354.6	0.4972	351.1
0.5792	361.1	0.5792	358.1	0.5792	355.6	0.5792	352.2	0.5792	349.9
0.6310	359.8	0.6310	356.9	0.6310	354.6	0.6310	351.3	0.6310	347.1
0.6927	358.3	0.6927	355.3	0.6927	351.8	0.6927	349.0	0.6927	345.2
0.7819	357.2	0.7819	353.6	0.7819	349.6	0.7819	347.0	0.7819	343.2
0.8639	356.1	0.8639	352.6	0.8639	348.8	0.8639	345.5	0.8639	340.8
0.9394	354.5	0.9394	350.7	0.9394	346.6	0.9394	343.1	0.9394	338.9
1.0000	353.2	1.0000	349.5	1.0000	345.8	1.0000	341.7	1.0000	337.1

7. Results and Discussion

7.1. Vapor-liquid Equilibrium Data of MTBE (1)-AA (2)

Table 4 Antoine constants for MTBE and AA

Component	A	B	C	Temperature range (K)	Reference
MTBE	5.896	708.69	179.9	275.15 – 353.15	[13]
AA	7.2996	147902	216.82	290.15 – 430.15	

Table 5 Comparison in measured and literature vapor pressure data for MTBE and AA

T/K	P_{exp}/kPa	P_{lit}/kPa	$\left(\frac{P_{exp}-P_{lit}}{P_{exp}}\right)$/%
MTBE			
328.3	101.325	101.2	0.12
324.7	90.0	90.8	-0.93
320.7	80.0	80.2	-0.30
316.1	70.0	69.3	0.99
312.1	60.0	60.5	-0.87
AA			
391.1	101.325	101.1	0.23
387.4	90.0	90.2	-0.21
384.1	80.0	81.3	-1.61
379.5	70.0	70.2	-0.28
375.3	60.0	61.0	-1.64

Table 5 compares the measured vapor pressures with those calculated from the literature using the Antoine parameters (reported in Table 4). According to the comparison, the variation in the vapor pressure deviations ranging from -0.93 % to 0.99 % of MTBE and -1.64 % to 0.23 of AA, so the modified ebulliometer is suitable for measuring the boiling temperatures of binary systems experimentally.

Table 6 Optimized binary interaction parameters and average absolute deviation of the binary system MTBE (1)-AA (2) for various models

P/kPa	**BIP**		**AAD(P)**	**AAD(T)**
Wilson				
	$\Delta\lambda_{12}$/(J/mol)	**$\Delta\lambda_{21}$/(J/mol)**		
101.325	-4060.05	8203.04	0.82	0.29
90	-3056.02	5209.38	2.07	0.81
80	-903.44	2810.71	1.56	0.66
70	-1109.16	2643.62	1.32	0.62
60	-1410.02	2376.81	1.13	0.61
NRTL				
	Δg_{12}/(J/mol)	**Δg_{21}/(J/mol)**		
101.33	5547.34	-2521.77	0.78	0.28
90	4045.63	-1740.15	1.85	0.72
80	675.66	1158.48	1.56	0.66
70	694.43	783.95	1.32	1.09
60	224.10	732.20	1.15	0.62
UNIQUAC				
	Δu_{12}/(J/mol)	**Δu_{21}/(J/mol)**		
101.33	3922.32	-1903.32	0.85	0.30
90	3371.82	-1658.11	1.74	0.68
80	1807.64	-699.69	1.56	0.66
70	1657.67	-700.75	1.32	0.62
60	1379.80	-672.50	1.14	0.61

BIPs of models with average deviation (AAD) in pressure and temperature are reported in Table 6. UNIQUAC model was found to have the least $\mathrm{AAD(P)}$ with range of $0.85 - 1.74\ \mathrm{kPa}$, while the Wilson model had the highest $\mathrm{AAD(P)}$ range of $0.82 - 2.07\ \mathrm{kPa}$. A different kind of nature was observed in $\mathrm{AAD(T)}$, Wilson with $0.29 - 0.66\ \mathrm{K}$ being the lowest and NRTL with $0.28 - 1.09\ \mathrm{K}$ being the highest. All three models performed satisfactory in terms of fitting VLE data.

Table 7 Thermodynamic consistency tests of the binary system MTBE (1)-AA (2)

P (kPa)	Redlich-Kister Area Test		L-W Wisniak	
	D	Result	$D\times10^{10}$	Result
101.325	1.9584	pass	0.0009	pass
90.0	0.5867	pass	0.0032	pass
80.0	4.8976	pass	0.0002	pass
70.0	5.0894	pass	0.0005	pass
60.0	5.2647	pass	0.0003	pass

Consistency test results are reported in Table 7, which indicates that all four isobaric VLE data sets are consistent and fulfill criteria of R-K area test and L-W test of Wisniak satisfactorily.

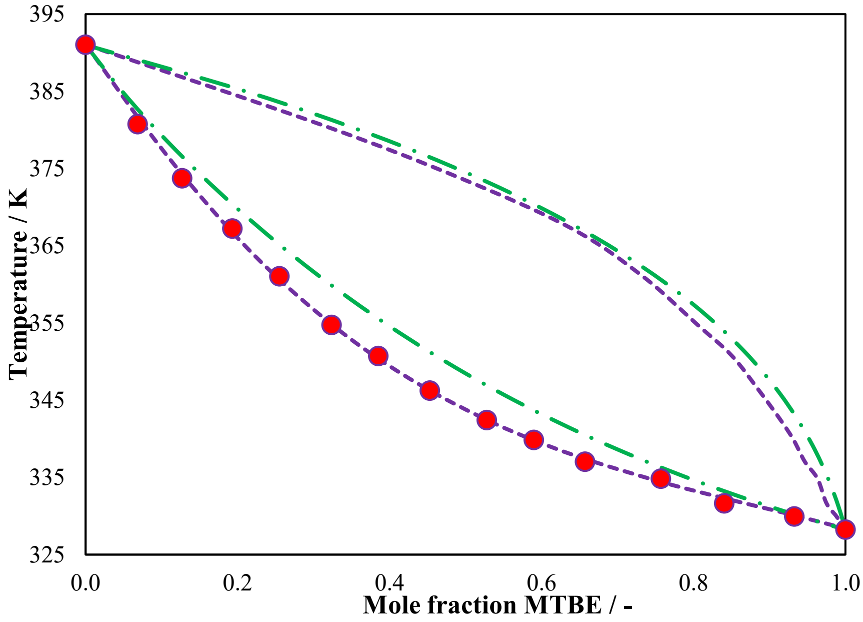

Figure 1 T –x–y diagram for experimental data (circle) , predicted by UNIFAC method (long dash line) and UNIQUAC modeling data (square dot line)

A comparison between the predicted data obtained using the UNIFAC group contribution method and the experimental data generated in this study is provided in the form of T-x-y diagrams, as shown in Figure 1. The T-x-y plots clearly demonstrate that the experimental data closely resembles the data predicted by the UNIFAC method. The deviation between the experimental data and the predicted data from the modified UNIFAC method is reasonably small, suggesting that the UNIFAC model is quite accurate. Both data sets are in good agreement except near the mole fraction of MTBE between 0.2 to 0.7, where minor deviations are observed.

7.2. Vapor-liquid Equilibrium Data of CPME (1)-AA (2)

Table 8 Antoine constants for CPME and AA

Component	A	B	C	Temperature range (K)	Reference
CPME	15.0255	3798.52	-14.2	357-395	[14]
AA	7.2996	147902	216.82	290.15 – 430.15	[13]

Table 9 Comparison in measured and literature vapor pressure data for CPME and AA

T/K	P_{exp}/kPa	P_{lit}/kPa	$\left(\frac{P_{exp}-P_{lit}}{P_{exp}}\right)$/%
CPME			
379.25	101.325	101.5	-0.17
376.0	92.0	92.3	-0.33
372.75	84.0	84.0	-0.06
369.5	76.0	76.2	-0.22
365.75	68.0	68.1	-0.09
361.8	60.0	60.1	-0.17
AA			
391.05	101.325	101.1	0.23
388.0	92.0	91.9	0.12
385.1	84.0	83.9	0.11
382.0	76.0	76.0	-0.01
378.6	68.0	68.0	-0.07
374.8	60.0	60.0	0.05

Table 9 compares the measured vapor pressures with those calculated from the literature using the Antoine parameters (reported in Table 4.9). According to the comparison, the variation in the vapor pressure deviations ranging from -0.06 % to -0.33 % of CPME and -0.07 % to 0.23 of AA, so the modified ebulliometer is suitable for measuring the boiling temperatures of binary systems experimentally.

Table 10 Optimized binary interaction parameters and average absolute deviation of the binary system CPME (1)-AA (2) for various models

P/kPa	BIP		AAD(P)	AAD(T)
Wilson				
	$\Delta\lambda_{12}$/(J/mol)	$\Delta\lambda_{21}$/(J/mol)		
101.325	589.27	1293.54	0.22	0.07
92	406.46	1400.00	0.21	0.08
84	499.56	1538.09	0.10	0.04
76	143.36	1720.40	0.18	0.08
68	-618.63	2205.04	0.21	0.10
60	-533.49	2120.09	0.18	0.09

NRTL				
	Δg_{12}/(J/mol)	Δg_{21}/(J/mol)		
101.325	-1712.05	3681.62	0.21	0.07
92	-1527.27	3390.62	0.83	0.07
84	-1312.13	3369.87	0.12	0.04
76	-1024.28	2885.59	0.19	0.07
68	-352.36	1932.82	0.24	0.10
60	-477.01	2070.00	0.19	0.09
UNIQUAC				
	Δu_{12}/(J/mol)	Δu_{21}/(J/mol)		
101.325	201.96	364.83	0.22	0.07
92	333.16	235.56	0.20	0.07
84	449.38	208.68	0.10	0.04
76	739.79	-72.10	0.18	0.07
68	1275.88	-521.27	0.21	0.10
60	1188.57	-460.76	0.18	0.09

BIPs of models with average deviation (AAD) in pressure and temperature are reported in Table 10. Both, UNIQUAC model and the Wilson model were found to have the least $\mathrm{AAD(P)}$ with range of $0.18 - 0.22$ kPa, while the NRTL model had the highest $\mathrm{AAD(P)}$ range of $0.12 - 0.83$ kPa. A different kind of nature was observed in $\mathrm{AAD(T)}$ of all three models in the range of $0.04 - 0.10$ K. All three models performed satisfactory in terms of fitting VLE data.

Table 11 Thermodynamic consistency tests of the binary system CPME (1)-AA (2)

P (kPa)	Redlich-Kister Area Test		L-W Wisniak	
	D	Result	$D\times10^{10}$	Result
101.325	0.1415	Pass	0.0007	Pass
92	0.5103	Pass	0.0003	Pass
84	1.0852	Pass	0.0011	Pass
76	0.7218	Pass	0.0009	Pass
68	0.7045	Pass	0.0008	Pass

Consistency test results are reported in Table 11, which indicates that all five isobaric VLE data sets are consistent and fulfill criteria of R-K area test and L-W test of Wisniak satisfactorily.

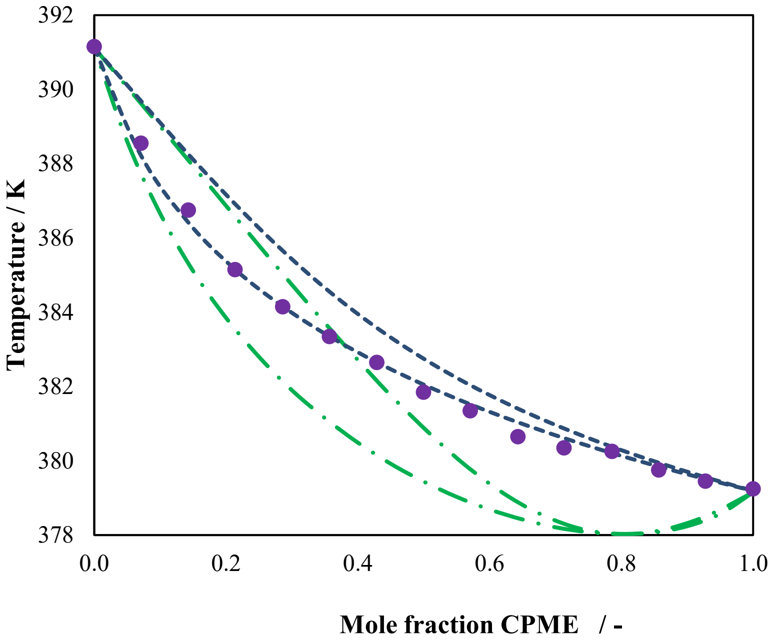

Figure 2 T –x–y diagram for experimental data (circle), predicted by UNIFAC method (long dash line) and UNIQUAC modeling data (square dot line)

In Figure 2, a comparison of reported experimental data in this work with predicted data by UNIFAC method at 101.3 kPa is presented. These results indicate that our experimental data observed pitch points on the pure end of acetic acid. However, the data predicted by the UNIFAC method deviated significantly from the experimental data. This experimental VLE data are observed at pitch point at composition of 80 %.

7.3. Vapor-liquid Equilibrium Data of 2-MeTHF (1)-AA (2)

Table 12 Antoine constants for 2-MeTHF and AA

Component	A	B	C	Temperature range (K)	Reference
2-MeTHF	13.7005	2706.71	-55.3	353–393	[13]
AA	7.2996	1479.02	216.82	290.15 – 430.15	

Table 13 Comparison in measured and literature vapor pressure data for 2-MeTHF and AA

T/K	P_{exp}/kPa	P_{lit}/kPa	$\left(\frac{P_{exp}-P_{lit}}{P_{exp}}\right)$/%
2-MeTHF			
353.2	101.325	100.9	0.38
349.5	90.0	90.0	-0.05
345.8	80.0	80.1	-0.11

341.7	70.0	70.1	-0.12
337.1	60.0	60.1	-0.11
AA			
391.1	101.325	101.1	0.23
387.3	90.0	90.0	-0.06
383.6	80.0	80.1	-0.16
379.5	70.0	70.2	-0.28
374.8	60.0	60.1	-0.11

Table 13 compares the measured vapor pressures with those calculated from the literature using the Antoine parameters (reported in Table 12). According to the comparison, the variation in the vapor pressure is less than 0.38 % of 2-MeTHF and -0.28 % of AA, so the modified ebulliometer is suitable for measuring the boiling temperatures of binary systems experimentally.

Table 14 Optimized binary interaction parameters and average absolute deviation of the binary system 2-MeTHF (1)-AA (2) for various models

P/kPa	**BIP**		**AAD(P)**	**AAD(T)**
Wilson				
	$\Delta\lambda_{12}$/(J/mol)	**$\Delta\lambda_{21}$/(J/mol)**		
101.325	-6.47	1819.76	1.99	0.26
90	-3132.32	5263.50	0.69	0.29
80	-3195.06	4978.98	0.91	0.42
70	546.99	587.13	0.58	0.29
60	2400.57	-523.50	0.78	0.45
NRTL				
	Δg_{12}/(J/mol)	**Δg_{21}/(J/mol)**		
101.325	4407.75	-1877.67	0.61	0.23
90	4253.48	-2152.14	0.63	0.26
80	3265.78	-1808.74	0.89	0.41
70	130.59	452.51	0.74	0.38
60	90.19	-4.57	0.92	0.53
UNIQUAC				
	Δu_{12}/(J/mol)	**Δu_{21}/(J/mol)**		
101.325	3300.14	-1623.43	0.38	0.12
90	3220.10	-1708.17	0.09	0.01
80	2405.48	-1386.50	0.14	0.03
70	-63.23	458.20	0.09	0.04
60	-1268.93	1920.61	0.07	0.03

BIPs of models with average deviation (AAD) in pressure and temperature are reported in Table 14. UNIQUAC model was found to have the least AAD(P) with range of $0.07 - 0.38$, while the WILSON model had the highest AAD(P) range of $0.58 - 1.99$. A different kind of nature was observed in AAD(T), UNIQUAC with $0.01 - 0.12$ being the lowest and NRTL with $0.23 - 0.53$ being the highest.

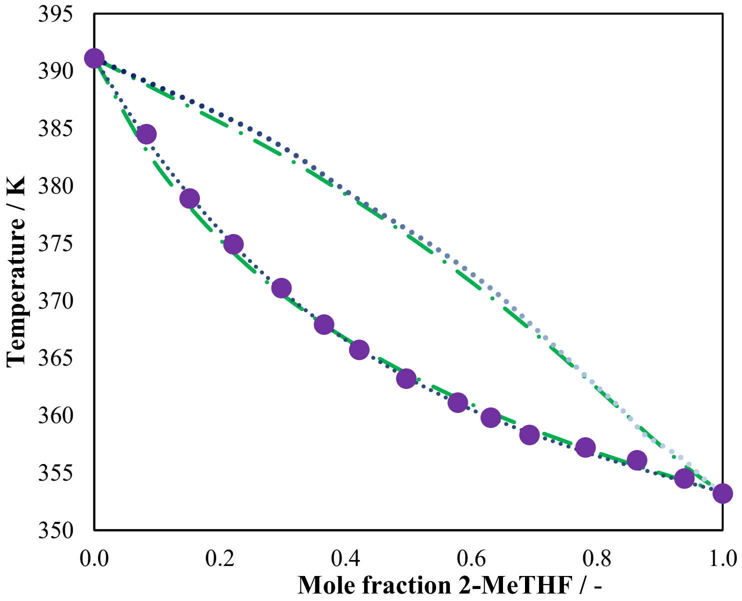

Figure 3 T –x–y diagram for experimental data (circle), predicted by UNIFAC method (long dash line) and UNIQUAC modeling data (square dot line)

A comparison between the predicted data obtained using the UNIFAC group contribution method with the experimental data generated in this study is provided in the form of T-x-y diagrams, as depicted in Figure 3. The T-x-y plots clearly indicate that the experimental data generated in this study closely aligns with the data predicted by the UNIFAC method. The discrepancies between the experimental data and the predicted data from the modified UNIFAC method are very small, suggesting that the UNIFAC model is quite accurate.

8. Achievements with respect to objectives

To measure isobaric VLE data of MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) in the pressure range of 60-101.325 kPa by modified ebulliometer.	The measurement of vapor-liquid equilibrium data was conducted for three binary systems, MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2). This was done using a modified ebulliometer, in

	which temperature, pressure, and the compositions of the liquid phases were all measured. The T-x data recorded for all 15 measurement points.
To verify experimental VLE data using R-K test and Wisniak's L-W Test of thermodynamic consistency.	Consistency test results are reported which indicates that isobaric VLE data sets of MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) are consistent and fulfill criteria of R-K area test and L-W test of Wisniak satisfactorily.
To determine binary interaction parameter of experimental binary data using various activity coefficient models such as Wilson, NRTL, UNIQUAC, etc.	Binary interaction parameters (BIPs) of models with average deviation (AAD) in pressure and temperature were reported.
To predict VLE data of data using UNIFAC methods and compared with experimental data.	The T-x-y plots clearly demonstrate that the experimental data closely resembles the data predicted by the UNIFAC method for MTBE (1)-AA (2) and 2-MeTHF (1)-AA (2). However, the data predicted by the UNIFAC method deviated significantly from the experimental data for CPME (1)-AA (2).

9. Conclusion

- In this work, measurement of vapor−liquid equilibrium (VLE) for MTBE (1)-AA (2), CPME (1)-AA (2) and 2-MeTHF (1)-AA (2) binary systems were carried out using modified ebulliometer under isobaric conditions.
- The VLE data were regressed using NRTL, Wilson and UNIQUAC models in which their corresponding binary interaction parameters (BIPs) were obtained. All three models fitted satisfactorily with the experimental data.
- The average absolute deviations between experimental values and calculated values for pressure and temperature were reported at different pressures which ranged from 60 to 101.325 kPa.

- The experimental and modeling findings show that MTBE (1)-AA (2) and 2-MeTHF (1)-AA (2) system shows a simple phase behavior with no azeotrope formation, while the CPME (1)-AA (2) system shows a pinch point to the pure acetic acid end.
- The deviation between the UNIFAC method's predicted data and the experimental data is reasonably small for MTBE (1)-AA (2) and 2-MeTHF (1)-AA (2) binary systems. However, the data predicted by the UNIFAC method deviated significantly from the experimental data for CPME (1)-AA (2).
- The data presented in this work can be utilize for designing distillation columns for the solvent recovery step in the acetic acid separation from aqueous solution.

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List of Publication:

Journal:

1. **Vapor-Liquid Equilibrium of System Comprising Green Solvents: Holistic Review,** Current Green Chemistry,11.3(2024),229–235. doi: 10.2174/0122133461272026231101094324. **(Scopus)**
2. **Computation of Isobaric Vapor-Liquid Equilibrium (VLE) Data of Methyl Tert-Butyl Ether (MTBE)+ Acetic Acid (AA) System.** Physical Chemistry Research 12.3 (2024): 745-752. doi: 10.22036/pcr.2024.411606.2396. **(Scopus)**
3. **Measurement & Correlation of Isobaric Vapor-Liquid Equilibrium (VLE) Data of Methyl Tert-butyl Ether (MTBE) + Acetic Acid (AA) System**, Chemical Data Collections, 51 (2024), 101134. https://doi.org/10.1016/j.cdc.2024.101134. **(Scopus)**

Conference Proceedings:

1. **A comparative Vapor – Liquid Equilibrium data for ethyl lactate-lactic acid system using Group contribution methods and simulator**, under the Green Energy theme presented in 74th Annual Session of Indian institute of chemical engineers (CHEMCON-2021) organized by CSIR-Institute of Minerals and Materials technology, Bhubaneswar from 26th December -30th December 2021.
2. **Review on Modeling and Experimental Measurement of Vapour-Liquid Equilibrium data of System Comprising Green Solvents,** presented in a national conference (ARTCHEM 2022) organized by Chemical Engineering Department, SCET,Surat on 22-23 December 2022.