Experimental Binary Vapor Liquid Equilibrium Data of Morpholine with Methanol, 1–Propanol and 2–Ethoxyethanol

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ABSTRACT:

Experimental PTx data have been measured and reported for three binary mixtures containing morpholine at 18 conditions by using Sweitoslawski–type ebulliometer. The measured Pressure (P), Temperature (T) and Liquid(x) composition (PTx) data were correlated by five activity coefficients models using Gauss-Newton (GN) two parameter optimization procedures to obtain the vapor composition and optimized parameters. The predicted results suggested that the Margules model had the best prediction. UNIFAC predictions were also conducted for each data set at 18 conditions for analysing the structure of the mixture properties. The binary mixtures have shown negative deviations from Raoult's law. A Comparison made between available literature values and present experimental PTx data. Comparison also made with published data. All correlations and predictions were in satisfactory agreement with new experimental data.

1. INTRODUCTION

"Distillation is a process in which a liquid or vapor mixture of two or more substances is separated into its component fractions of desired purity, by the application and removal of heat. Distillation is based on the fact that the vapor of a boiling mixture will be richer in the components that have lower boiling points. Therefore, when this vapor is cooled and condensed, the condensate will contain more volatile components. At the same time, the original mixture will contain more of the less volatile material. Distillation columns are designed to achieve this separation efficiently" [18] and also designed based on the boiling point properties of the components in the mixture being separated. Distillation is the most common separation technique. Thus the sizes, particularly the height, of distillation columns are determined by the vapour liquid equilibrium (VLE) data for the mixtures. In this work, new experimental data have been measured under 18 conditions in Sweitoslawski–type ebulliometer and the selected systems have been studied are presented in **Table 1**. The study of morpholine with methanol, 1-propanol and 2-ethoxyethanol are interesting because, this mixture have amine and ethoxy groups. So the studies of mixture properties especially in amine and ethoxy groups are necessary for many industrial processes.

2. EXPERIMENTAL WORK

2.1. Chemical analysis.

The chemicals methanol, 1-propanol, 2-ethoxyethanol and morpholine have purchased analytical grade and purified by laboratory distillation and the "fraction collected at the boiling point for each chemical was used in the experimental runs. The purities of the each chemical used were determined by refractive index(RI) at 293.15K using a Abbe Refractometer with an accuracy of ±0.0002 using a sodium vapor lamp that gives monochromatic emission of 589.3nm and accuracy of the these components were confirmed by Gas chromatographic technique using a Chemito 3865 Gas Chromatograph with flame ionization detector. For morpholine with column TM-1701(30m X 0.32mm ID, 0.5 micron thickness and helium as carrier gas with constant flow rate of 2ml per min), for methanol column DB-624(30m X 0.53mm ID, 3.0micron thickness and nitrogen as carrier gas with constant flow rate of 2ml per min), for 1-propanol and 2–ethoxyethanol columnZB-624(60m X 0.32mm ID, 1.8 micron thickness and helium as carrier gas with constant flow rate of 5.0ml per min)and also the normal boiling point(NBP) temperature, which are given in **Table 2a** and **2b** together with literature values Weissberger et al.[38]. There is good agreement between the experimental and literature values"[23].

2.2 Ebulliometric Measurements.

The Sweitoslawski–type ebulliometer experimental setup and procedure have been described elsewhere by Prasad and Rao[22]. The Experimental PTx data obtained from the above experimental procedure are presented in **Table 3a** to **3b.**

2.3. Uncertainties.

The details of the ebulliometer procedure were described elsewhere by Prasad and Rao[22]. The pressure was measured with the mercury manometer, and it was controlled within ± 0.1333 kPa. The height of the mercury column was measured accurately to the nearest millimeter with the help of a cathetometer. The equilibrium temperature was measured with a standard mercury-in-glass thermometer having an accuracy of ± 0.1K. The thermometer was inserted in a thermowell filled with pure glycerol and was calibrated against a certified thermometer of the National Physical Laboratory, New Delhi. A solution of known composition prepared by weighing 120ml of the solution on a precision electrical balance with an accuracy of ± 0.0001g was charged into the boiling chamber to take the experimental data and the estimated uncertainty in the liquid composition was 0.001 mole fraction.

3. DATA CORRELATION

Correlation of the each experimental data set using Gauss-Newton[4] optimization procedure with five popular two-parameter activity coefficient models Margules[16], Van Laar[13, 14], Wilson[39], NRTL[29] and UNIQUAC[1] to obtain vapor compositions and optimized parameters at 18 conditions and using two versions of the UNIFAC[5, 7, 10] group contribution methods to analyse the structure of the mixture properties.

3.1. Gauss-Newton (GN) Method.

The GN Gauss–Newton method is used to solve a non-linear least squares method based on well-known Gaussian technique problems. It is a modification of Newton's method for finding a minimum of a function. Unlike Newton's method, the Gauss–Newton algorithm can only be used to minimize a sum of squared function values. Non-linear least squares problems arise, for instance, in non-linear regression, where parameters in a model are sought such that the model is in good agreement with available observations. In this work, the VLE data of a binary system is fitted to an active coefficient model (Margules/Van Laar/Wilson/ NRTL/ UNIQUAC) to obtain model parameters, by using the Gauss- Newton method. "An in-house computer package for the GN method developed by Rajendra Prasad[24, 25] to minimizing the objective function defined by Eq. (1), was used for the calculation of the parameters for all the PTx data of the binary sets.

$$F = \sum_{1}^{n}\left[1 - \left(y_{1,cal} + y_{2,cal}\right)\right]^2 \tag{1}$$

The vapor compositions were calculated using the expressions

$$y_i = \frac{x_i \gamma_i \phi_i^s P_i^s}{\phi_i^v P} \exp\left[\frac{V_i\left(P - P_i^s\right)}{RT}\right] \tag{2}$$

The values of ϕ_i^v and ϕ_i^s were calculated using the virial equation of state truncated to the second virial coefficient predicted from the Tsonopoulos[37] correlation. Molar liquid volumes were calculated using the modified Rackett[31] equation. Pure-component critical and other properties were taken from Reid et al.[28] The Poynting correction factors were neglected in the calculations. The optimized parameters of each model for the 18 sets of experimental data are correlated, along with the values of the Average Absolute Deviations (AAD) in pressure and temperature but not presented in this article. The pair of parameters A_{12}& A_{21}, which are known as energy parameters and have dimensions of cal/mole, are equal to $\lambda_{12} - \lambda_{11}$& $\lambda_{21} - \lambda_{22}$ for the Wilson, $g_{12} - g_{22}$& $g_{21} - g_{11}$ for the NRTL and $u_{12} - u_{22}$& $u_{21} - u_{11}$ for the UNIQUAC models respectively; they are dimensionless for the Margules and van Laar models"[23].

4. PREDICTION OF ACTIVITY COEFFICIENTS AND VAPOR COMPOSITION USING UNIFAC MODELS

"The UNIFAC group contribution model was developed by Fredenslund et al.[5]. It is energy interaction among the groups present in the mixture. The parameters required for the use of the UNIFAC model are the group volume, R_k, group surface area, Q_k, and group interaction parameters, $a_{m,n}$ and $a_{n,m}$. The parameters published by Hansen et al.[10] for the UNIFAC model are termed as UNIFAC (O). In addition to this model, another modified version of Gmehling et al.[7, 8], termed as UNIFAC (D), has also been considered for correlating the experimental data in the present investigation. In the latter version, a modified combinatorial term and temperature-dependent interaction parameters were introduced to allow a more reliable description of the liquid phase non-ideality (γ_i). The relevant modified equations for the combinatorial term and the interaction parameters for UNIFAC (D) are given below. The residual terms are the same for the two versions of UNIFAC used here.

$$\ln \gamma_i^C = 1 - V_i' + \ln V_i' - 5q_i\left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \tag{3}$$

$$V_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{4}$$

The interaction parameters for the different version of the UNIFAC model are

UNIFAC (O): $\Psi_{nm} = \exp\left[-\left(a_{nm}/T\right)\right]$ (5)

UNIFAC (Dortmund): $\Psi_{nm} = \exp\left[-\left(a_{nm} + b_{nm}T + C_{nm}T^2/T\right)\right]$ (6)

The classification of groups for the prediction of the activity coefficient using the two versions is presented in **Table 4.** In the context of the classification of groups in the UNIFAC(O) models, it may be mentioned that the cyclic ether group is not separately defined, while in the UNIFAC(D) model, all of the groups for morpholine are available. The AAD values in Pressure (AADP) and Temperature (AADT) obtained from the predictions using the above versions of the UNIFAC model"[23] for both present experimental data and available published data are given in **Table 6**.

5. RESULTS AND DISCUSSION

5.1. Classification of the Experimental PTx Data.

The experimental PTx data at 18 conditions for methanol, 1-propanoland 2-ethoxyethanol with morpholine binary mixtures was presented in **Table 3a** to **3b**. **Figures 1** to **8** present the P-x-y/ T-x-y equilibrium diagrams for Margules model**.** From diagrams **Figures 1** to **8** can been seen, the experimental data are very smooth and well correlated except for the data of morpholine–2–ethoxyethanol at 353.15K.

5.2. Results of Correlations by the Five Two-Parameter Models.

Methanol(1)-Morpholine(2) mixtures: The Margules model best fitted the two sets of isobaric data with GN optimization method except for the set of isothermal data for which the best model has turned out to be the NRTL model at 337.15K. The pair of parameters of the Van Laar and Margules models and deviations in Pressure and Temperature are almost same obtained by GN method.

1-Propanol(1)–Morpholine(2) mixtures: The Margules model is the best model for correlating the three sets of data except two sets of data at 363.15K and 79.99kPa which the best model has Van Laar. It is quite interesting to observe all the models best correlated the data at 34315K giving identical values of AADT and AAΔP.

Morpholine(1)–2-Ethoxyethanol(2) mixtures: All the models best fitted the data, the Margules model provided best correlation for the data at four conditions and the NRTL model for the data at three conditions. At 39.99kPa the UNIQUAC model has best fitted the data and Van Laar for two conditions at 363.15K and 100.92kPa.

5.3. Results with UNIFAC Models.

Table 6 gives the results of the two versions of the UNIFAC predictions in terms of the AAD values in Pressure and Temperature for the present PTx data and available published data. As seen from the tables the AAD values of UNIFAC(O) and UNIFAC(D) models for the parameters reported in this investigation. The worst predictions were obtained for the methanol–morpholine mixtures using the UNIFAC(O) with morpholine assumed to be made of non –cyclic groups. Surprisingly, the UNIFAC(D) did not fare well because of using non –cyclic secondary amines group. Comparatively, better predictions by model with morpholine as a single group for the system have been obtained.

But, the predictions of the UNIFAC(O) model with the three group classification of morpholine are better for the mixtures of morpholine with 1–propanol and 2–ethoxyethanol than the predictions of the UNIFAC(D) model. The UNIFAC(D) has emerged in the case, as the better model to provide the VLE predictions. In general, predictions from two versions of UNIFAC models are disheartening. Definitely, the cyclic secondary amine group in morpholine has to be considered as a different functional group from the non–cyclic secondary amine group in future improvements of the UNIFAC model**.**

5.4. Activity Coefficients.

Comparison of the activity coefficients predicted by the Margules and UNIFAC(O) models were taken place. In general the values of γ of UNIFAC model are not in agreement with the values of $\gamma$of Margules. All the models have predicted the values of γ_i less than one for the mixtures containing morpholine with the following exceptions and the predicted values are not presented in this article. The UNIFAC predictions for the values of γ_i more than one for the methanol–morpholine system at 74.26kPa. The Margules predictions for the values of γ_i more than one for 1–propanol–morpholine system at 39.99kPa.The values of γ_i by the Margules model more than one and maxima and minima behavior in γ–x curves for the system morpholine–2–ethoxyethanol at 343.15K & 353.15K and the γ_i values less than one by the UNIFAC model. The values of γ_i by the Margules models less than one with maxima–minima behavior for the system morpholine–2–ethoxyethanol at other isobaric and isothermal conditions.

5.5. Reliability of the Measured PTx Data.

"The experiments that produce VLE data and the vapor compositions were not measured in the present work, only PTx data measured; it is possible to test the experimental PTx data of the mixtures at the 18 conditions for thermodynamic consistency using calculated values of vapor compositions and activity coefficients.

The integrity of the "experimental P-T-x data can be established by showing the experimental uncertainty is same as the uncertainty expected from the random errors in the absence systematic errors. In the present experimental work, the ebulliometer used was standardized previously"[26]. The deviations in the values of pressure ranges from 0.01 to 0.1 kPa and the deviations in temperature did not exceed 0.1 K. The pressure-residual and temperature–residual plots for the PTx of the systems shown in **Figures 9(a)** to **9(f)** indicate that the residuals are free from systematic errors. It may be noted that the calculated values of P_{cal} and temperatures T_{cal} in the above plots are from the regressed data by Margules model. When the experimental observations are subject to random errors only, the values of the mean deviations between the measured and calculated variables obtained by Margules may be indicative of the quality of each experimental data set. Indeed, the correlation of PTx data with any activity coefficient model is known as Barker[2] method. Though the accurate measurements of vapor composition are needed to compare with the values obtained by the Barker method to demonstrate the consistency of data, the deviations between the measured and calculated values in P and T by the PTx correlation may be considered to show the reliability of the measured data”[23].

In the “present experimental runs, the largest sources of experimental uncertainty come from pressure and temperature measurements. The pressure could be measured to 0.1333 kPa and the temperature to one tenth of a degree Celsius. An experimental uncertainty 0.001 mole fraction in liquid composition was employed in the calculations”[27]. These observations show that the PTx measurements of the present work are reliable. Methanol–morpholine at 101.32 kPa where ΔT is slightly higher in case of Van Laar, Wilson, NRTL and UNIQUAC models. Morpholine–2–ethoxyethanol at 343.15K in case of NRTL &UNIQUAC, at 383.15K UNIQUAC and Wilson, at 66.66 kPa in case of Van Laar, NRTL & UNIQUAC, at 79.99 kPa in case of Van Laar, Wilson and UNIQUAC, the values of ΔP are found to be higher than the experimental uncertainties.

5.6. Comparison of Pure Component Vapor Pressures.

“Comparison of the experimental vapor pressure data of the pure components with those found in the literature is important to obtain a more reliable evaluation of the actual accuracy in the pressure measurement. For this reason, the vapor pressure data measured for the components morpholine, methanol, 1-propanol and 2-ethoxyethanol have been compared with several data reported in the literature. The present work is shown in **Figures 10(A)** to **10(C)**. It is observed that the slope of the linear relation between lnP and 1/T is same for each component at the literature values and the values of the present work. Moreover, the vapor pressures were calculated at the present experimental temperatures using the vapor pressure equations proposed by the above mentioned authors, and the results of this analysis are given in **Table 5**. As observed from the above figures and table, there is a strong consistency between the vapor pressure data of the present work and the data in the literature”[23].

5.7. Comparisons of the VLE Data.

The published VLE data is limited to methanol–morpholine [Pettinati et al.[20]; Palczewska et al.[19]; Savescu et al.[30]] mixtures to compare with the corresponding data of the present work. The published data on the above, out of three binary systems two of the systems[19, 20] were reprocessed to obtain the AAD values in Pressure and Temperature are given in **Table 6** and the same parameter optimizing procedure that has been described. If the AAD values obtained for the present data of methanol–morpholine system at 74.26kPa[20] & 101.32kPa[19] are examined with those given in **Table 6**, it is observed that the present data are comparable with that of published data and also shown in **Figures 11(a)** to **11(b)**.

5.8. Infinite Dilution Activity Coefficients (IDACs).

“The values of the activity coefficients at infinite dilution, γ_1^∞ and γ_2^∞, of a binary mixture are in general more accurate, easier to obtain and more meaningful in their applications. They can be integrated into various activity coefficient models without limiting assumptions, and an entire binary VLE curve can be constructed accurately from these values only. A number of experimental methods have been reviewed for the direct measurement of γ^∞ by Eckert and Sherman[3] and Kojima et al.[11]. The ASOG[12, 36] and UNIFAC[6, 10] models can be used to predict γ^∞ for several mixtures. These models will give poor results for activity coefficients at infinite dilution and for systems whose components differ greatly in size. These short comings can be attributed to the fact that the interaction parameters are obtained for these models from the VLE data in the concentration range of 5–95 mole percent, and the database includes mostly compounds of similar size. A model similar to SPACE based on the data bank of Poe et al.[21] developed by Sherman et al.[32] is superior to the group contribution models and MOSCED[34] model as it treats strong interactions such as hydrogen bonding accurately for non-ideal systems. Tochigi et al.[36] and Gmehling et al.[7] improved both the ASOG and UNIFAC models to handle molecules that differ greatly in size. Tiegs et al.[35] and Gmehling et al.[9] compiled data on infinite dilution activity coefficients (IDAC).

The values of IDAC predicted by using the two versions of the UNIFAC model have been compared with those values calculated from the Margules model. The group classifications for the components in the mixture are given in **Table 4.** As there is no cyclic group defined by Hansen et al. there are two options for handling morpholine: as a single group of C_4H_9NO or using three different groups $2CH_2$, CH_2O and CH_2NH. The predicted IDAC values obtained in both cases for each mixture are given in **Table 7** for comparison with the values of IDAC obtained using the Margules model in conjunction with the Gauss-Newton (GN) method. It may be noted that the energy interaction parameters for the group pair C_4H_9NO-CH_2O are not available”[23] and hence the VLE as well as IDAC value for the mixture containing alkoxy ethanols with morpholine as single group could not be predicted.

The groups for the morpholine in the UNIFAC (D) model are CH_2NH, cCH_2OCH_2 and $2cCH_2$ in one option, and in the second option, non–cyclic groups of 2CH2 and 2CH2O are signed and the required calculations have been performed. The predicted values of $\gamma^\infty$from the UNIFAC (D) model are also presented in **Table 7.**

CONCLUSIONS

New experimental PTx data for binary mixture of morpholine with methanol, 1-propanol and 2-ethoxyethanol measured at 18 conditions in an ebulliometer and reported. The data were correlated using five activity coefficients models with GN optimization procedure and UNIFAC group contribution methods. The binary mixtures have shown negative deviations from Raoult's law. The energy interaction parameters for the group pair C4H9NO-CH2O are not available and hence the VLE as well as IDAC value for the mixture containing alkoxy ethanols with morpholine as single group could not be predicted. The values of infinite dilution activity coefficients (IDAC) at γ^{∞} calculated from the Margules(GN) and UNIFAC models are compared. The values of IDAC of the UNIFAC models for each mixture at the each condition studied do not match the values of IDAC calculated from the Margules model. Methanol–morpholine system at 74.26kPa & 101.32kPa are examined and it is observed that the present data are comparable with that of published data and also with available literature data. The reliability and accuracy of the PTx data at 18 conditions are established by the pressure residual and temperature residual plots which indicate the absence of systematic errors and may be considered to show the reliability of the measured data.

LIST OF SYMBOLS

"A12, A21	adjustable model parameters
F	objective function
n	number of data points
P	total pressure
R	universal gas constant
T	equilibrium temperature
V	Volume of a gas or vapor
ν	molar volume
x	liquid mole fraction
y	vapor mole fraction
Greek letters	
γ	activity coefficient
ϕ	fugacity coefficient
Subscripts	
1	more volatile component
2	less volatile component
cal	calculated
exp	experimental, exponential
I	any component
lit	literature
Super scripts	
s	saturated
v	vapor state"[23]

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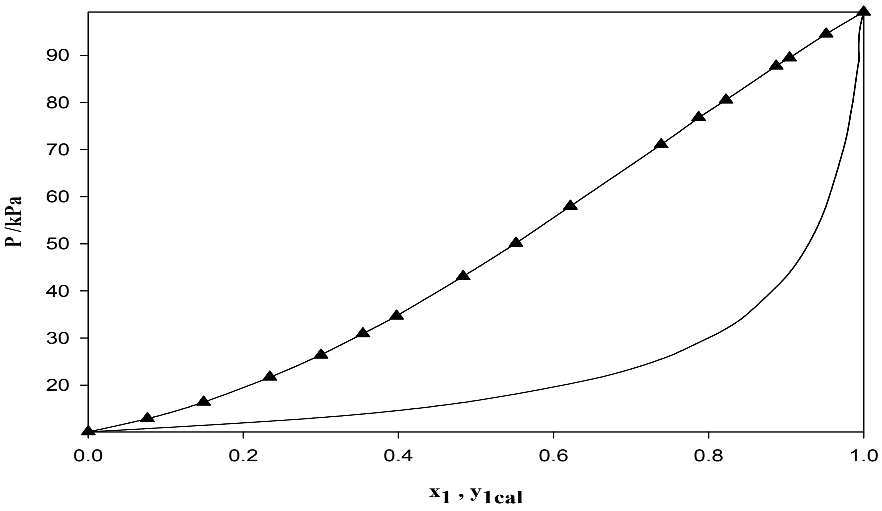


Figure 1. Pressure-composition diagram for the methanol(1)-morpholine(2) system at 337.15K. The points are experimental data, and the lines are correlations result from the Margules model.

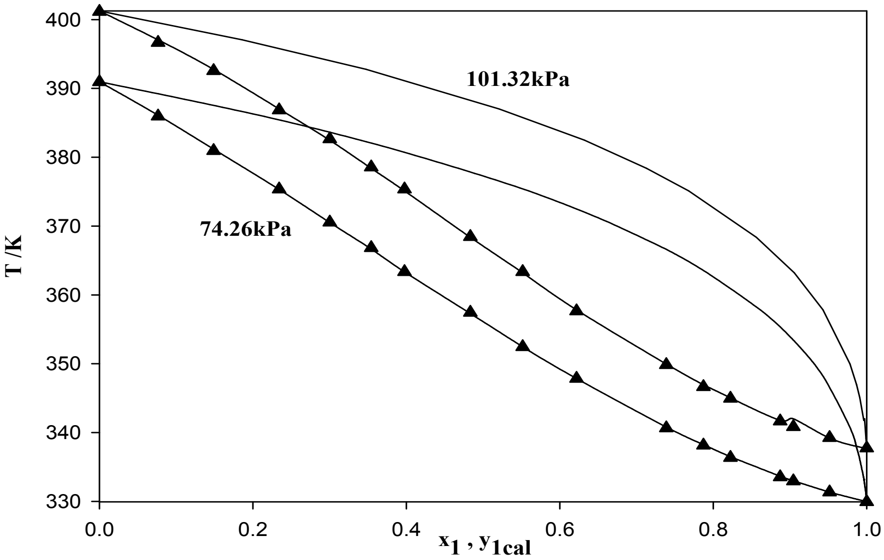


Figure 2. Temperature-composition diagram for the methanol(1)-morpholine(2) system at different pressures. The points are experimental data, and the lines are correlations result from the Margules model.

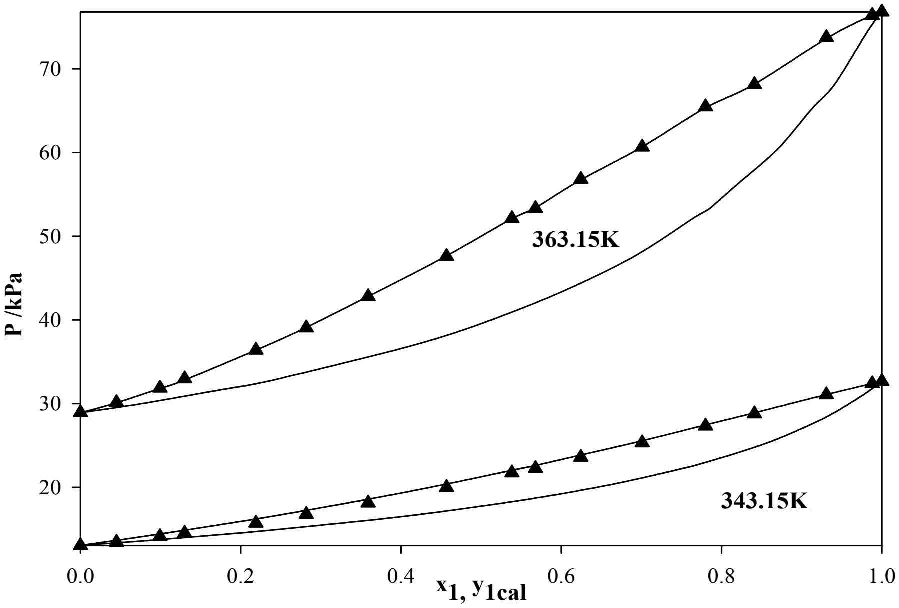


Figure 3. Pressure-composition diagram for the1-propanol(1)-morpholine(2) system at different temperatures. The points are experimental data, and the lines are correlations result from the Margules model.

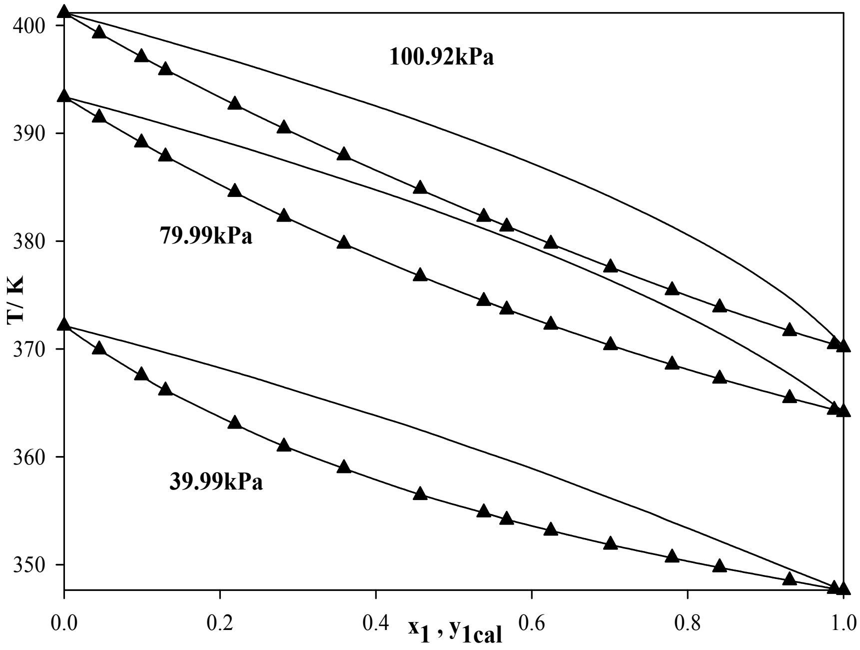


Figure 4. Temperature-composition diagram for the 1-propanol(1)-morpholine(2) system at different pressures.The points are experimental data, and the lines are correlations result from the Margules model.

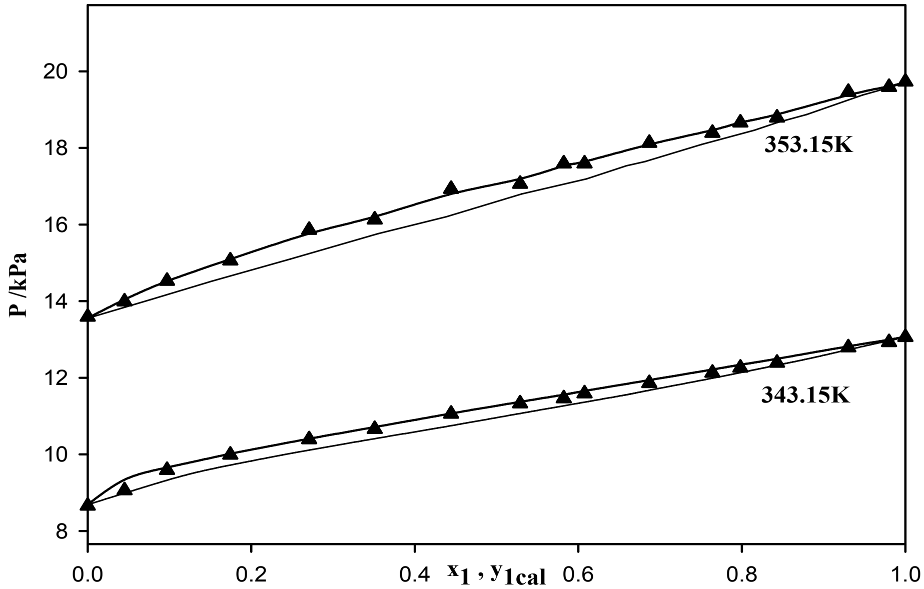


Figure 5. Experimental P-x data and P-x-y behavior diagram for the morpholine(1)-2-ethoxyethanol(2) system at different temperatures. The points are experimental data, and the lines are correlations result from the Margules model.

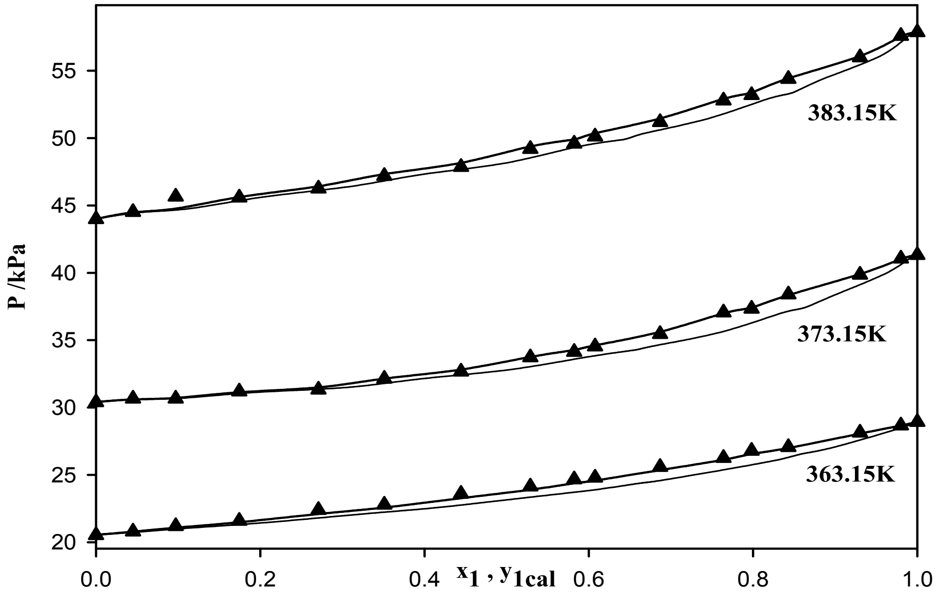


Figure 6. Experimental P-x data and P-x-y behavior diagram for the morpholine(1)-2-ethoxyethanol(2) system at different temperatures. The points are experimental data, and the lines are correlations result from the Margules model.

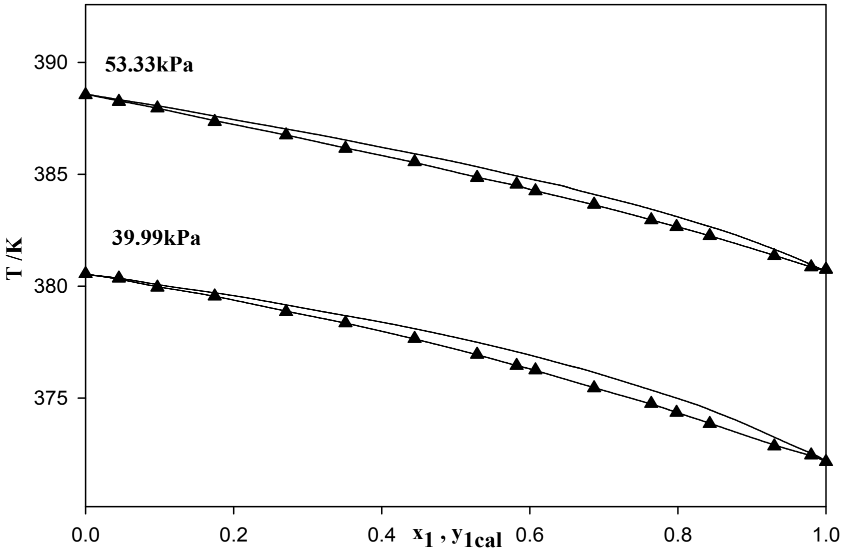


Figure 7. Experimental T-x data and T-x-y behavior diagram for the morpholine(1)-2-ethoxyethanol(2) system at different temperatures. The points are experimental data, and the lines are correlations result from the Margules model.

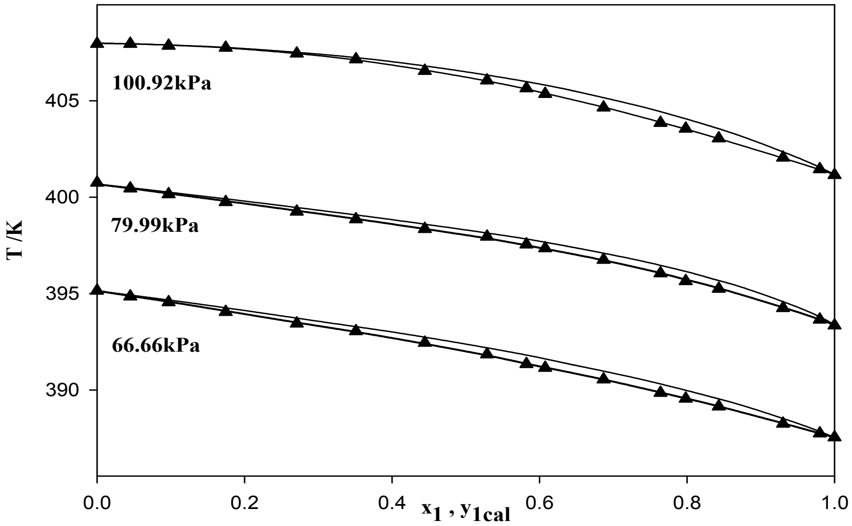
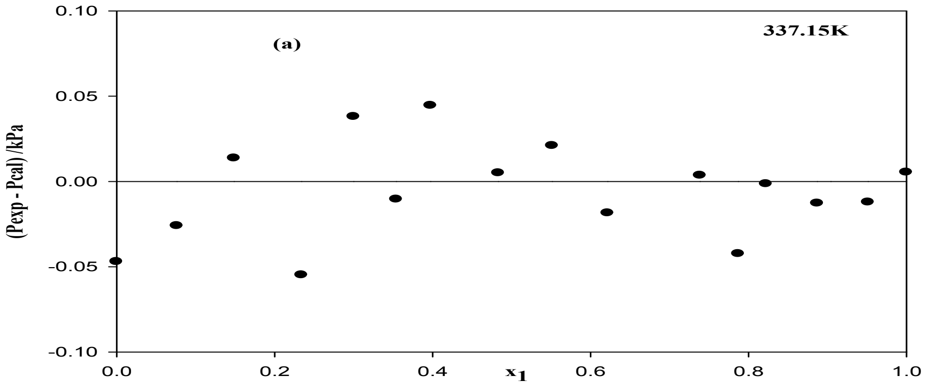
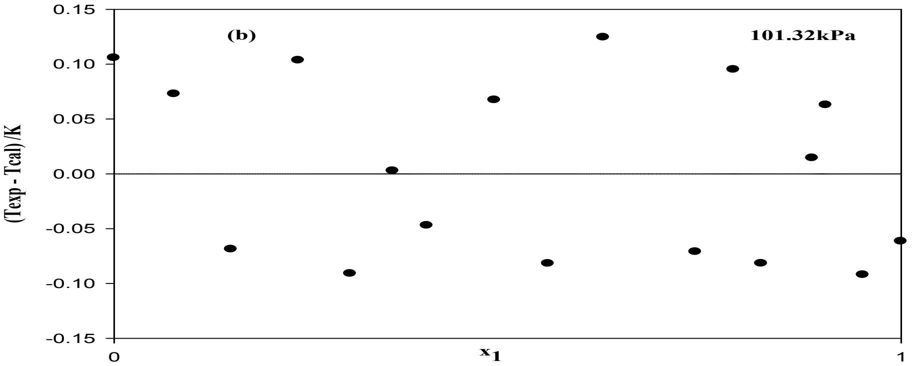
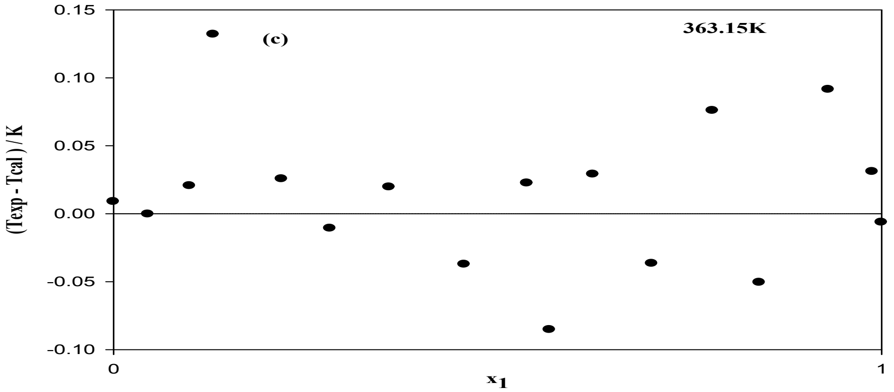


Figure 8. Experimental T-x data and T-x-y behavior diagram for the morpholine(1)-2-ethoxyethanol(2) system at different temperatures. The points are experimental data, and the lines are correlations result from the Margules model.


(a)
337.15K
(Pexp - Pcal) /kPa
0.10
0.05
0.00
-0.05
-0.10
0.0
0.2
0.4
0.6
0.8
1.0
x_1


(b)
101.32kPa
(Texp - Tcal) /K
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
0
1
x_1


(c)
363.15K
(Texp - Tcal) / K
0.15
0.10
0.05
0.00
-0.05
-0.10
0
1
x_1

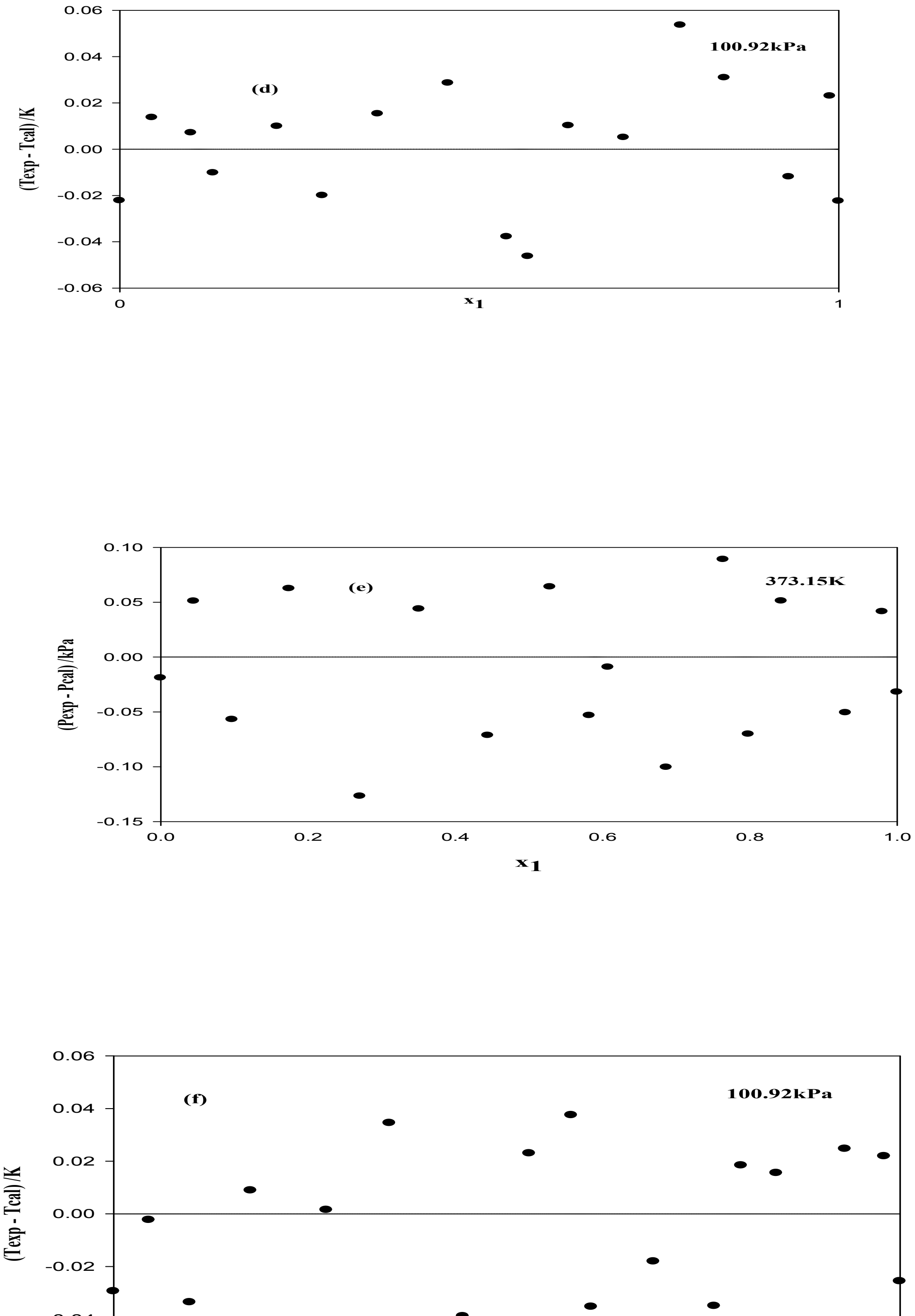
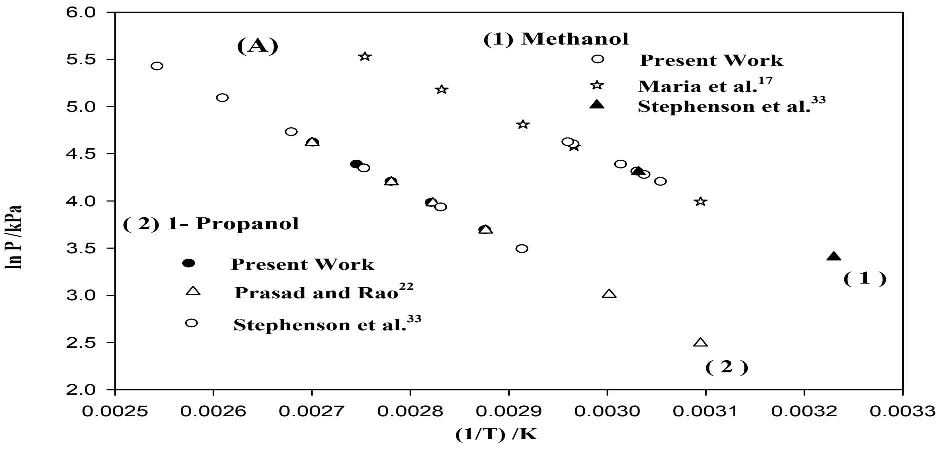
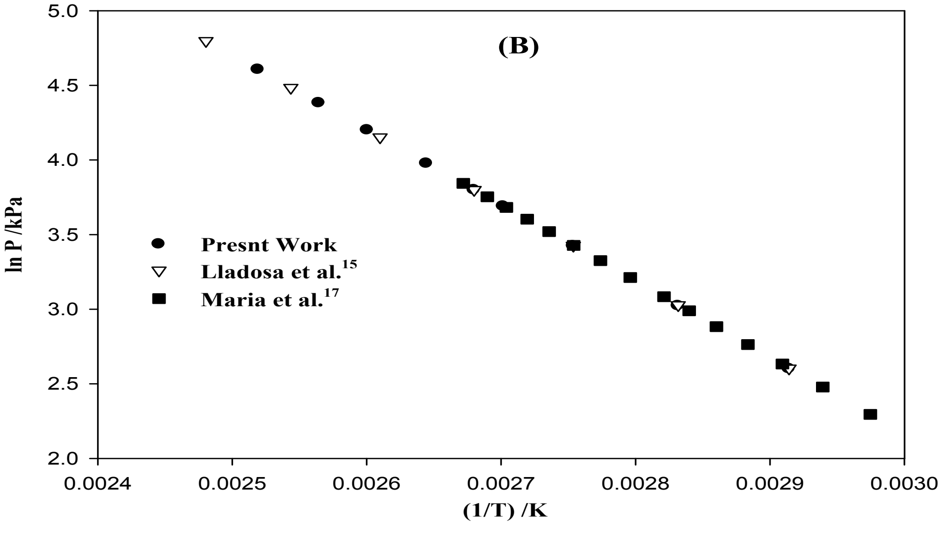


Figure 9. Pressure and temperature residuals vs liquid composition diagrams.
(a) methanol(1)-morpholine(2) at 337.15K, **(b)** methanol(1)-morpholine(2) at 101.32kPa,
(c) 1-propanol(1)-morpholine(2) at 363.15K, **(d)** 1-propanol(1)-morpholine(2) at 100.92kPa,
(e) morpholine(1)-2-ethoxyethanol(2) at 373.15K,
(f) morpholine(1)-2-ethoxyethanol(2) at 100.92kPa.



(A)
(1) Methanol
○ Present Work
☆ Maria et al.17
▲ Stephenson et al.33
(2) 1- Propanol
● Present Work
△ Prasad and Rao22
○ Stephenson et al.33
(1)
(2)
ln P /kPa
(1/T) /K
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
0.0025
0.0026
0.0027
0.0028
0.0029
0.0030
0.0031
0.0032
0.0033



(B)
● Presnt Work
▽ Lladosa et al.15
■ Maria et al.17
ln P /kPa
(1/T) /K
5.0
4.5
4.0
3.5
3.0
2.5
2.0
0.0024
0.0025
0.0026
0.0027
0.0028
0.0029
0.0030

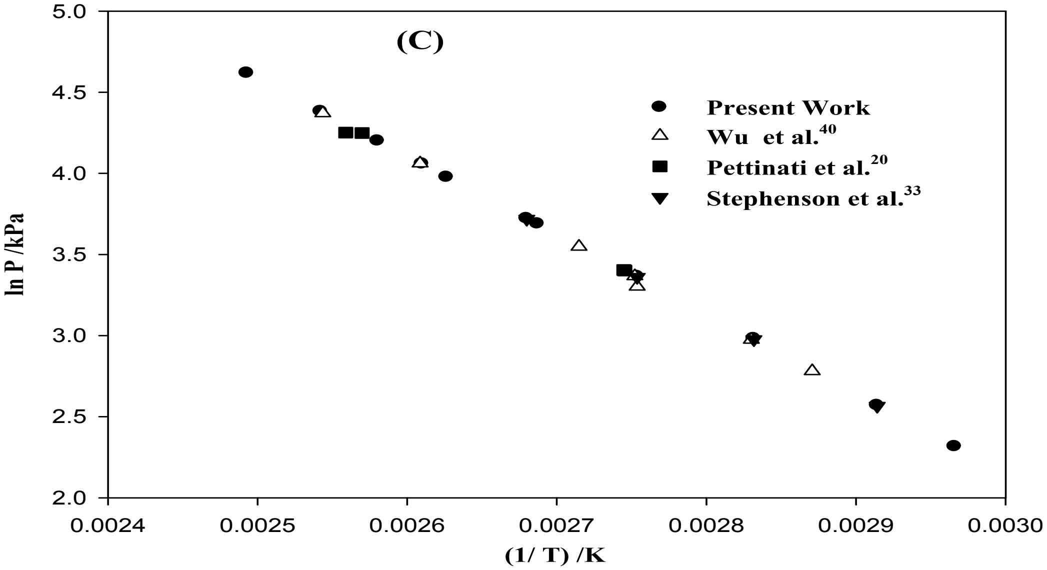
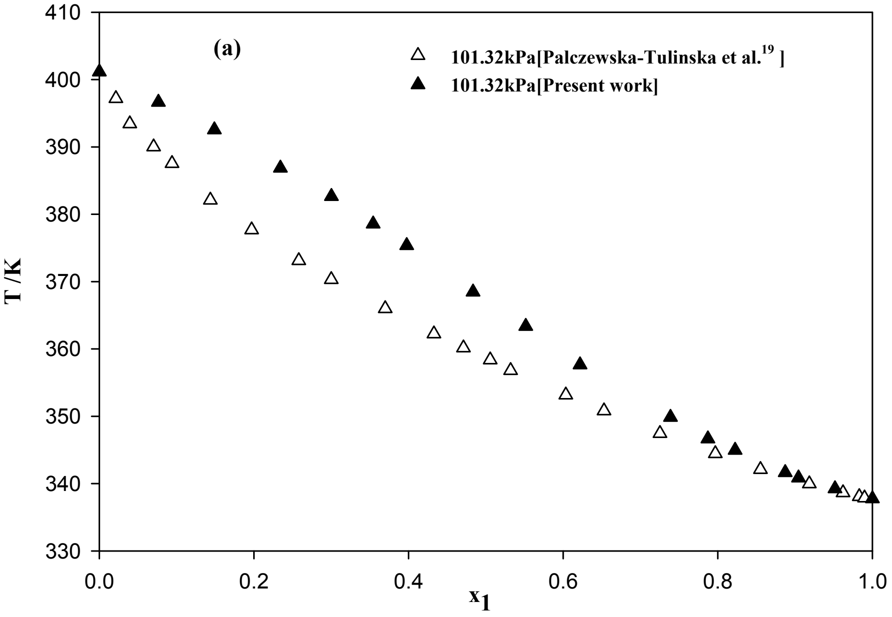


Figure 10. Comparison of vapor pressure data with available published data.
Daigrams **(A)**methanol[17, 33] and 1-propanol[22, 33]**(B)**2-ethoxyethanol[15, 17]**(C)**morpholine[33, 40]



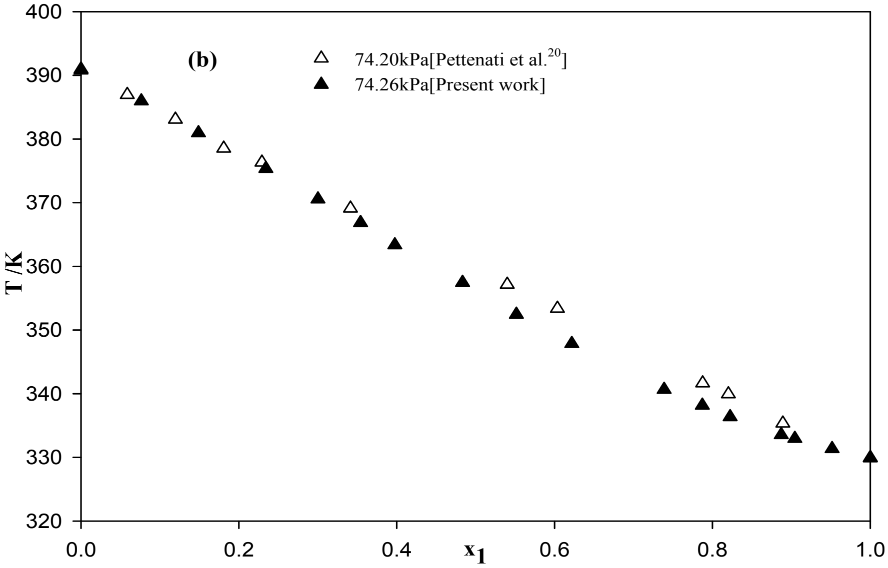


Figure 11. Temperature-composition diagram for methanol(1)-morpholine(2) system. Comparison with published data, and the lines are correlations result from Margules model. Diagrams **(a)** at 101.32kPa[19] and **(b)** at 74.26kPa[20]

Table 1. List of 18 Sets of PTx Data of Methanol, 1-Propanol and 2–Ethoxyethanol with Morpholine

system	isothermal T /K	isobaric P/ kPa
methanol(1)-morpholine(2)	337.15	74.26, 101.32
1-propanol(1)-morpholine(2)	343.15, 363.15	39.99,79.99,100.92
morpholine(1)–2–ethoxyethanol(2)	343.15, 353.15, 363.15, 373.15, 383.15	39.99, 53.33, 66.66, 79.99, 100.92

Table 2a. CAS Registry Number, Mole Fraction Purity and Boiling Temperature(T_b) of the Chemicals with Corresponding Literature Values[38]

chemical name	CAS RN	source	purification method	Final Purity mole fraction	boiling point (T_b)/K[b]		analysis method
					Exp.	Lit.	
methanol	67-56-1	Emerck, India	distillation	0.996	337.75	337.65	GC[a]
1-propanol	71-23-8	Emerck, India	distillation	0.998	370.30	370.30	GC[a]
2–ethoxyethanol	110-80-5	Aldrich, Germany	distillation	0.999	408.15	407.95	GC[a]
morpholine	110-91-8	S D Fine chem, India	distillation	0.993	401.15	401.45	GC[a]

[a]Gas-chromatography Analysis, [b]The pressure for the measurement of T_b was 101.3 kPa, Standard Uncertainties u, u(T) = 0.1K; u(P)=0.1333kPa

Table 2b. Measured Physical Properties of Chemicals with Corresponding Literature Values[38]

chemical name	RI at 293.15K and 101.32kPa[a]		Antoine constants[b]		
	Exp.	Lit.	A	B	C
methanol	1.3282	1.3286	16.5951	3643.97	-33.420
1-propanol	1.3850	1.3855	15.8195	3310.99	-74.687
2–ethoxyethanol	1.4075	1.4075	16.1196	4245.48	-38.980
morpholine	1.4542	1.4545	14.4748	3333.13	-163.15

[b] $\ln P_i / \text{kPa} = A_i - B_i / [t/\text{K} + C_i]$,

[a]Standard Uncertainties u, u(RI)=0.002; u(T) = 0.1K; u(P)=0.1333kPa

Table 3a. List of Experimental PTx Data[a]

	methanol(1)-morpholine(2)		
	337.15K	74.26kPa	101.32kPa
$x_{1,exp}$	P_{exp}/kPa	T_{exp}/K	T_{exp}/K
0.0000	10.13	390.95	401.15
0.0764	12.93	385.95	396.65
0.1488	16.39	380.95	392.55
0.2343	21.73	375.35	386.85
0.3002	26.39	370.55	382.65
0.3543	30.93	366.85	378.55
0.3977	34.66	363.35	375.35
0.4834	43.06	357.45	368.45
0.5517	50.12	352.45	363.35
0.6218	57.99	347.85	357.65
0.7388	71.05	340.65	349.85
0.7873	76.79	338.15	346.65
0.8224	80.52	336.35	344.95
0.8872	87.72	333.55	341.65
0.9044	89.45	332.95	340.85
0.9517	94.52	331.35	339.25
1.0000	99.19	329.95	337.75

	1-propanol(1)-morpholine(2)				
	343.15K	363.15K	39.99kPa	79.99kPa	100.92kPa
$x_{1,exp}$	P_{exp}/kPa	P_{exp}/kPa	T_{exp}/K	T_{exp}/K	T_{exp}/K
0.0000	13.06	28.93	372.15	393.35	401.15
0.0450	13.46	30.13	369.95	391.45	399.25
0.0993	14.13	31.86	367.55	389.15	397.05
0.1300	14.53	32.97	366.15	387.85	395.85
0.2190	15.73	36.39	363.05	384.55	392.65
0.2820	16.79	39.06	360.95	382.25	390.45
0.3590	18.13	42.79	358.95	379.75	387.95
0.4568	19.99	47.59	356.45	376.75	384.85
0.5385	21.73	52.12	354.85	374.45	382.25
0.5680	22.26	53.32	354.15	373.65	381.35
0.6244	23.59	56.79	353.15	372.25	379.75
0.7010	25.33	60.66	351.85	370.35	377.55
0.7801	27.33	65.46	350.65	368.55	375.45
0.8410	28.79	68.12	349.75	367.25	373.85
0.9309	31.06	73.72	348.55	365.45	371.65
0.9880	32.39	76.39	347.75	364.35	370.45
1.0000	32.66	76.79	347.65	364.15	370.15

[a]Standard Uncertainties u, u(T) = 0.1K; u(P)=0.1333kPa; u(x1) = 0.001

Table 3b. List of Experimental PTx Data[a] for Morpholine(1)–2–Ethoxyethanol(2)

$x_{1,exp}$	Pressure(P_{exp}/kPa)					Temperature(T_{exp}/K)				
	343.15K	353.15K	363.15K	373.15K	383.15K	39.99kPa	53.33kPa	66.66kPa	79.99kPa	100.92kPa
0.0000	08.66	13.59	20.53	30.39	43.99	380.55	388.55	395.15	400.75	407.95
0.0450	09.06	13.99	20.79	30.66	44.52	380.35	388.25	394.85	400.45	407.95
0.0970	09.59	14.53	21.19	30.66	45.66	379.95	387.95	394.55	400.15	407.85
0.1745	09.99	15.06	21.59	31.19	45.59	379.55	387.35	394.05	399.75	407.75
0.2708	10.39	15.86	22.39	31.33	46.26	378.85	386.75	393.45	399.25	407.45
0.3511	10.66	16.13	22.79	32.13	47.19	378.35	386.15	393.05	398.85	407.15
0.4445	11.06	16.93	23.59	32.66	47.86	377.65	385.55	392.45	398.35	406.55
0.5289	11.33	17.06	24.13	33.73	49.19	376.95	384.85	391.85	397.95	406.05
0.5823	11.46	17.59	24.66	34.13	49.59	376.45	384.55	391.35	397.55	405.65
0.6076	11.59	17.59	24.79	34.53	50.12	376.25	384.25	391.15	397.35	405.35
0.6868	11.86	18.13	25.59	35.46	51.19	375.45	383.65	390.55	396.75	404.65
0.7641	12.13	18.39	26.26	37.06	52.79	374.75	382.95	389.85	396.05	403.85
0.7982	12.26	18.66	26.79	37.33	53.19	374.35	382.65	389.55	395.65	403.55
0.8430	12.39	18.79	27.06	38.39	54.39	373.85	382.25	389.15	395.25	403.05
0.9302	12.79	19.46	28.13	39.86	55.99	372.85	381.35	388.25	394.25	402.05
0.9800	12.93	19.59	28.66	41.06	57.59	372.45	380.85	387.75	393.65	401.45
1.000	13.06	19.73	28.93	41.32	57.86	372.15	380.75	387.55	393.35	401.15

[a]Standard uncertainties, u are u(T)=0.1K, u(P)=0.1333kPa, u(x)=0.001

Table 4. Group Classification for the UNIFAC Model

component	formula	groups	
		UNIFAC (O)	UNIFAC (D)
methanol	CH_3OH	CH_3OH(single)	CH_3OH
1-propanol	C_3H_8O	CH_3 , $2CH_2$, OH	CH_3 , $2CH_2$, OH (p)
2-ethoxyethanol	$C_4H_{10}O_2$	CH_3 , $2CH_2$, CH_2O, OH	CH_3 , $2CH_2$, CH_2O, OH(p)
morpholine	C_4H_9NO	C_4H_9NO(single) or $2CH_2$, CH_2O, CH_2NH	CH_2NH, cCH_2, cCH_2OCH_2

Table 5.Experimental Vapor Pressure Data and Comparison to the Literature[a] [33]

T/K	exptl P/kPa	Stephenson et al.[33] P/kPa	other data P/kPa
Methanol			Maria et al.[17]
329.95	74.26	70.08	75.00
337.15	99.19	97.09	99.41
337.75	101.32	99.43	101.58
1-Propanol			Prasad and Rao[22]
343.15	32.66	32.65	32.63
347.65	39.99	40.00	39.99
363.15	76.79	76.74	78.75
364.15	79.99	79.84	81.25
370.15	100.9	100.7	100.83
2–Ethoxyethanol		Maria et al.[17]	Lladosa et al.[15]
343.15	08.66	08.60	08.65
353.15	13.59	13.62	13.54
363.15	20.53	20.74	20.60
373.15	30.39	30.45	30.57
383.15	43.99	44.11	44.33
Morpholine			Wu et al.[40]
343.15	13.06	13.02	12.97
353.15	19.73	19.63	19.60
363.15	28.93	28.80	28.78
373.15	41.32	41.22	41.22

[a]Standard uncertainties, u are u(T)=0.1K, u(P)=0.1333kPa

Table 6. Comparison of AAD Values in Temperature and Pressure for Both the UNIFAC Models with Methanol(1)-Morpholine(2)[19, 20] Published Data

details of the system	UNIFAC(O) single morpholine group (C_4H_9NO)				UNIFAC(O) morpholine groups ($2CH_2$, CH_2O, CH_2NH)				UNIFAC(D) morpholine groups (CH_2NH, cCH_2, cCH_2OCH_2)			
	present work		published data[19,20]		present work		published data[19,20]		present work		published data[19,20]	
	AADT	AADP	AADT	AADP	AADT	AADP	AADT	AADP	AADT	AADP	AADT	AADP
74.26kPa[20]	1.620	4.336	3.163	9.012	7.620	25.512	9.216	30.99	2.114	5.746	3.537	9.958
101.32kPa[19]	2.870	10.268	2.924	9.025	9.085	40.330	4.041	15.575	3.394	12.371	2.529	8.079

$\text{AADT} = \text{Average Absolute Deviation in Temperature} = \left(\sum \text{Abs}\left(T_{exp} - T_{cal}\right)\right)/(n)$ $\text{AADP} = \text{Average Absolute Deviation in Pressure} = \left(\sum \text{Abs}\left(P_{exp} - P_{cal}\right)\right)/(n)$

Table 7.Comparisons of Infinite Dilution Activity Coefficients for Calculated Values from G N and UNIFAC Models.

system	temp. / pressure	MARGULES (Gauss-Newton)		UNIFAC(O) morpholine single group (C_4H_9NO)		UNIFAC(O) morpholine groups ($2CH_2$, CH_2O,CH_2NH)		UNIFAC(D) morpholine groups (CH_2NH, cCH_2, cCH_2OCH_2)	
		γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞
methanol(1)-morpholine(2)	337.15K	0.4313	0.4790	0.4513	0.2179	1.1159	1.2787	0.4494	0.1283
methanol(1)-morpholine(2)	74.26kPa	0.4079	0.1973	0.4953	0.2111	1.1505	1.2690	0.5918	0.1099
methanol(1)-morpholine(2)	101.32kPa	0.3751	0.1488	0.5027	0.2185	1.1557	1.2795	0.6078	0.1299
1–propanol(1)–morpholine(2)	343.15K	0.7000	0.7016	0.7916	0.4478	0.8827	0.8122	0.5567	0.4784
1–propanol(1)–morpholine(2)	363.15K	0.7123	0.8519	0.7905	0.4578	0.8869	0.8196	0.5859	0.5223
1–propanol(1)–morpholine(2)	39.99kPa	1.0552	1.1377	0.7904	0.4499	0.8946	0.8155	0.6114	0.4750
1–propanol(1)–morpholine(2)	79.99kPa	0.8525	0.8326	0.7908	0.4583	0.9030	0.8274	0.6716	0.5254
1–propanol(1)–morpholine(2)	100.92kPa	0.8143	0.6662	0.7912	0.4615	0.9060	0.8315	0.6933	0.5436
morpholine(1)–2–ethoxyethanol(2)	343.15 K	1.4326	0.9681	--	--	0.7899	0.8060	0.5194	0.4994
morpholine(1)–2–ethoxyethanol(2)	353.15 K	1.2305	1.0361	--	--	0.8008	0.8151	0.5658	0.5416
morpholine(1)–2–ethoxyethanol(2)	363.15 K	0.9350	0.8418	--	--	0.8111	0.8238	0.6121	0.5850
morpholine(1)–2–ethoxyethanol(2)	373.15 K	0.8102	0.6931	--	--	0.8209	0.8321	0.6581	0.6293
morpholine(1)–2–ethoxyethanol(2)	383.15 K	0.9235	0.7671	--	--	0.8301	0.8402	0.7038	0.6746
morpholine(1)–2–ethoxyethanol(2)	39.99 kPa	0.8979	0.8464	--	--	0.8278	0.8313	0.6920	0.6249
morpholine(1)–2–ethoxyethanol(2)	53.33 kPa	0.9762	0.8768	--	--	0.8350	0.8383	0.7282	0.6637
morpholine(1)–2–ethoxyethanol(2)	66.66 kPa	0.9588	0.8692	--	--	0.8407	0.8436	0.7577	0.6948
morpholine(1)–2–ethoxyethanol(2)	79.99 kPa	0.9683	0.8023	--	--	0.8454	0.8480	0.7824	0.7215
morpholine(1)–2–ethoxyethanol(2)	100.92 kPa	0.8393	0.9999	--	--	0.8512	0.8538	0.8137	0.7578

Table of Content

S.No.	Table	Content
1	1	List of 18 sets of PTx data of morpholine with methanol, 1-propanol and 2-ethoxyethanol
2	2a	CAS Registry Number, Mass Fraction Purity and Boiling Temperature of the Chemicals with Corresponding Literature Values
3	2b	Measured Physical Properties of Chemicals with Corresponding Literature values
4	3a	List of experimental PTx data for morpholine with methanol and 1-propanol
5	3b	List of experimental PTx data for morpholine with 2-ethoxyethanol
6	4	Group classification for the UNIFAC model
7	5	Experimental Vapor pressure data and Comparison to Literature
8	6	Comparison of AAD Values in Temperature and Pressure for both UNIFAC models
9	7	Comparisons of Infinite Dilution Activity Coefficients for calculated values from G N and UNIFAC