VAPOR-LIQUID EQUILIBRIA OF 2-PROPANOL - 1,4-DIOXANE MIXTURES

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ABSTRACT

Eight sets of experimental P-T-x data were determined for 2-propanol-1,4 -dioxane mixtures ebulliometrically. Five popular activity coefficient models and coexistence equation have been used to correlate each set of data through different optimization methods to obtain the values of vapor phase compositions and excess Gibbs free energy. The results of these correlations have been compared. An attempt was made to evaluate the group interaction parameters for alcohol-1,4-dioxane mixtures to improve VLE predictions using the UNIFAC method.

Keywords: Vapor-Liquid Equilibria, 2-Propanol, 1,4-Dioxane, Activity Coefficient Models, Prediction

INTRODUCTION

Reliable and accurate experimental vapor-liquid equilibrium (VLE) data are essential for the design of separation equipment such as distillation columns besides testing for improvement of theoretical models. Moreover, vapor - liquid equilibria of multicomponent mixtures are usually predicted from the constituent binary data through model correlation.

In this article, experimental P-T-x data of 2-Propanol-1,4-dioxane mixtures at isothermal conditions in the temperature range of 323.15 - 353.15K (10K intervals) and at isobaric conditions in the pressure range of 26.66-101.3kPa (26.66kPa intervals) have been reported. The experimental results were correlated using several VLE models. The VLE data for these mixtures at 101.3 kPa were previously reported by Choffe et al. [1]. The UNIFAC group interaction parameters for the functional groups OH/CH_2OCH_2 and CH_2/CH_2OCH_2 were obtained to improve the predictions by the UNIFAC method for alcohol - 1,4-dioxane mixtures.

EXPERIMENTAL

Materials

2-propanol and 1,4-dioxane were of analytical grade, purchased from EMerck (India). Both the chemicals were fractionally distilled in a laboratory glass packed column and the heart cut fractions have been used in the experimental runs. The purity of each chemical had been checked by determining refraction index at 298.15K and boiling point at 101.3kPa which are given in Table 1 together with the literature values [2]. There is a good agreement between experimental and literature values.

Ebulliometric Measurements

The P-T-x data were measured in a Sweitoslawski type ebulliometer of 120 ml. The experimental set up and operating procedure was described elsewhere [3]. Equilibrium pressures, measured with a mercury manometer, were controlled within ± 0.133 kPa (1 mm Hg). Equilibrium temperatures of boiling mixtures were measured with a certified mercury in glass thermometer having an accuracy of 0.1K. Mixtures of known compositions were prepared gravimetrically with in an accuracy of ±0.0001 gm. and charged into the ebulliometer for each experimental run. As the vaporised fraction of the liquid phase being very small, no corrections were made to the liquid composition calculated directly from the weighed amounts. This might have resulted in a maximum error of 0.004 mole fraction in the equilibrium liquid compositions. Prior to the P-T-x measurments, pure component vapor pressure data were obtained and the Antoine constants calculated from the data are given in Table 1.

RESULTS AND DATA REDUCTION

Table 2 presents eight sets of P-T-x data for the 2-propanol-1,4 dioxane mixtures. For each component, i, in the mixture, the equation of equilibrium is

$$y_i = x_i \gamma_i \phi_i^s P_i^s \exp[\frac{v_i (P - P_i^s)}{RT}] / P_i \phi_i^v \qquad (1)$$

The data were regressed by the optimization procedures of Rosenbrock [4], Nelder-Mead [5], and Maximum Likelihood (MLH) [6] to determine binary parameters for the Margules [7], van Laar [7], Wilson [8], NTRL [9] and modified UNIQUAC [10] models for excess free energy. The values of the root mean squared deviations (r.m.s.d.) in pressure and temperature for each set of data are given in Table 3a,3b and 3c.

Vapor phase fugacities were calculated from the second virial coefficients estimated by the method of Hayden and O'Connell [11] in case of MLH method, where as, in the other two cases by the correlation of Tsonopolous[12]. Liquid molar volumes were estimated by the method of Hankinson and Thomson[13]. Pure component critical and other properties have been taken from Reid et al. [14]. The following objective functions were used in optimising the model parameters.

Methods of Rosenbrock and Nelder-Mead :

$$F = \sum_{1}^{n} \left[\left(\frac{P_{i,exp} - P_{i,cal}}{P_{i,exp}}\right)^2 + \left(\frac{T_{i,exp} - T_{i,cal}}{T_{i,exp}}\right)^2 + \{1 - (y_{1,cal} + y_{2,cal})\}^2 \right] \quad (2)$$

Maximum Likelihood Method :

$$F = \sum_{1}^{n} \left[\frac{(P_{i,exp} - P_{i,cal})^2}{\sigma^2_{P_i}} + \frac{(T_{i,exp} - T_{i,cal})^2}{\sigma^2_{T_i}} + \frac{(x_{i,exp} - x_{i,cal})^2}{\sigma^2_{x_i}} \right] \quad (3)$$

Coexistence equation

Values of G^E, γ_i , and y_i from experimental P-T-x data were obtained by using coexistence equation through the method of Mixon et al. [15]. In the calculations, the total pressure has been expressed as a function of excess Gibbs free energy in a finite difference form. Then, it has been determined at each mesh point using a marching procedure by successive iterations minimizing the following objective function

$$E = \left(\frac{P_{exp} - P_{cal}}{P_{exp}}\right) 100 \quad (4)$$

The details of algorithm were given in the earlier paper [3].

UNIFAC Method

The UNIFAC method [16,17], which is a versatile group contribution method, was chosen to predict γ_i , G^E and y_i from the P-T-x data of the 2-propanol-1,4-dioxane mixtures. Computations were performed in two different ways. The 2-propanol molecule was divided

into two CH_3 groups, one CH group and one OH group in both ways of calculations. In the first case, the 1,4-dioxane molecule was treated as having two CH_2 and two CH_2 O groups. The group interaction parameters and pure component data (R,Q) of the functional groups of the liquid mixture were taken from Hansen et al., [18]. In the second case of calculations, the cyclic ether, 1,4-dioxane was considered to be made of two CH_2OCH_2 groups. As the interaction parameters for this ether group with the other functional groups considered for the alcohol were not defined in the published UNIFAC parameter tables so far, these parameters were determined from the published VLE data on hydrocarbon-1,4-dioxane and alcohol-1,4-dioxane systems by means of the parameter estimation procedure of Fredenslund et al. [17]. The values of the parameters thus determined are given below:

$a_{CH_2/CH_2OCH_2} = 164.81$; $a_{CH_2OCH_2/CH_2} = -7.50$; $a_{OH/CH_2OCH_2} = 116.34$; $a_{CH_2OCH_2/OH} = 251.08$;

To characterize the results of the UNIFAC method in the above two ways, the average absolute deviations in P and T were calculated for each of the P-T-x data set and are given in Table 4.

DISCUSSION

The binary mixtures of 2-propanol-1,4-dioxane have shown positive deviations from Raoult's Law and exhibited azeotropic behaviour in all the eight sets of data. The results of the data, regressed by the three parameter estimation methods and compared in Tables 3a-3c, show that the five activity coefficient models considered in this investigation are suitable for representing the VLE of the above binary mixtures. As is observed from the mean deviations in pressure and temperature given in Tables 3a-3c, the MLH method has correlated each data set with all the five models better than the other two methods of parameter estimation. However, the temperature deviations by this method for the Margules model are found to be

comparatively high. It is interesting to find from the values of model parameters (Table of the model parameters are retained with the authors) obtained by the method of Rosenbrock and Nelder-Mead are more or less identical. Irrespective of the parameter optimization methods, all the five activity coefficient models predicted nearly same vapor phase compositions (maximum difference in mole fraction being 0.006) for each set of data. The UNIQUAC model is chosen as a reference and representive of the two parameter models to compare predictions by the other methods. The azeotropic compositions, temperatures/ pressures as calculated by the UNIQUAC model are listed in Table 5. The vapor phase compositions predicted by the coexistence model through the method of Mixon et al. [15] are in good agreement with those predicted by the two parameter activity coefficient models.

As seen from the comparison of absolute average deviation in P and T given in Table 4, the modified parameters for the alcohol - 1,4-dioxane interactions improved the VLE predictions for the system by UNIFAC method, though the predictions for the data sets at 79.98kPa and 101.3kPa have not been satisfactory. This indicates that further refinement of the parameters to extend their application to cover wide temperature range is in order. Hence, reliable and accurate VLE at higher temperature range are needed for the hydrocarbon-1,4-dioxane and alcohol-1,4-dioxane systems.

The values of G^E calculated from the models of UNIQUAC [10], coexistence, UNIFAC [l8] and UNIFAC (Present work) have been graphed in Fig.1 - 4. The G^E curves obtained from the UNIQUAC and coexistence models are closer and exhibit negative temperature dependence with an exception of the data at 343.15K. The calculations using the modified interaction parameters for the groups,CH_2,CH_2OCH_2, OH also show the negative temperature dependence of G^E. But, the G^E values have been always lower than those calculated by the UNIQUAC and Coexistence models. Contrary to these observations, the

results obtained from the Hansen's UNIFAC parameters show a small positive temperature dependence of G^E for the system.

Fig. 5. shows the comparison of the T-x data of Choffe et al. [1] at 101.3 kPa and that of present work. It may be noted that the equilibrium temperatures of the former data are slightly higher.

It is difficult to evaluate the accuracy of experimental P-T-x measurements in the absence of exactly known reference values. However, an accurate fit by the thermo-dynamically consistent VLE models may be regarded as a sufficient condition to establish reliability of the data. As such all the five activity coefficient models correlated the experimental data to give almost identical results. Computer programs for the parameter estimation methods used in this work were written in Quick BASIC. The algorithms of the unconstrained optimization methods of Rosenbrock and Nelder-Mead have been recently tested and applied to process several data sets of binary VLE [19].

CONCLUSIONS

New experimental P-T-x data for 2-propanol-1,4-dioxane mixtures at different isothermal and isobaric conditions have been determined using an ebulliometer. The data have been correlated with five activity coefficients models and coexistence equation to obtain the values of vapor phase composition and excess free energy for each set of data. The results of these correlations compare well. Further, new group interaction parameters for alcohol-1,4-dioxane mixtures have been evaluated to improve the VLE predictions of the above mixtures by using the UNIFAC method.

LIST OF SYMBOLS

A_{12}, A_{21} = adjustible model parameters

E, F = objective function

G^E = excess Gibbs free energy

n = number of data points

P = total pressure

Q = group surface area

R = group volume

T = equilibrium temperature

v = molar volume

x = liquid phase mole fraction

y = vapor phase mole fraction

Greek letters

γ = activity coefficient

ϕ = fugacity coefficient

σ = standard deviation

Subscipts

1 = more volatile component

2 = less volatile component

cal = calculated

exp = experimental

i = any component

lit = literature

Superscripts

s = standard state

v = vapor phase

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Table 1

Boiling points, Refractive indices and Antoine constants of pure components

Normal Boiling Point, K			Refractive Index (n_D) at 298.15 K		Antoine Constants*		
Chemical	Exp.	Lit [2]	Exp.	Lit [2]	A	B	C
2-Propanol	355.55	355.55	1.3745	1.3745	15.80755	3130.3966	-75.623
1,4-Dioxane	374.45	374.47	1.4205	1.42025	15.09680	3579.7727	-32.813

$$* \ln P_i\,(\text{kPa}) = A_i - \frac{B_i}{T(K) + C_i}$$

Table 2

Equilibrium data of 2-propanol (1) - 1,4-dioxane (2) mixtures

x_1	Equilibrium Temperature, K				Equilibrium Pressure, kPa			
	26.66 kPa	53.32 kPa	79.97 kPa	101.3 kPa	323.15 K	333.15 K	343.15 K	353.15 K
0.0000	335.85	354.65	366.85	374.45	15.99	23.99	35.19	50.52
0.0917	331.75	350.45	361.45	369.45	18.93	28.39	42.12	58.91
0.1375	330.55	348.65	359.45	367.55	19.86	30.26	44.92	63.18
0.1835	329.45	347.25	358.05	365.95	20.79	31.59	47.58	66.91
0.2715	327.85	345.15	355.85	363.35	22.39	33.86	51.45	73.18
0.3518	326.85	343.85	354.25	361.35	23.46	35.72	54.65	77.84
0.4014	326.15	343.05	353.55	360.55	23.86	36.52	55.98	80.11
0.4418	325.75	342.65	353.15	359.95	24.26	37.05	57.18	82.11
0.5271	325.35	341.75	352.35	358.65	24.53	38.25	59.05	85.57
0.6109	324.85	341.05	351.55	357.65	24.79	39.05	60.65	88.24
0.7297	324.75	340.65	350.65	356.55	24.93	39.45	61.85	91.57
0.7699	324.65	340.35	350.25	356.25	24.93	39.72	62.11	91.84
0.8469	324.65	340.15	350.15	355.75	24.66	39.45	62.25	93.17
0.8854	324.75	339.95	349.95	355.65	24.53	39.32	62.11	93.30
0.9245	325.05	340.05	349.75	355.55	24.26	39.05	61.85	93.44
0.9607	325.15	340.15	349.55	355.45	24.13	38.79	61.45	93.17
1.0000	325.65	340.25	349.65	355.35	23.59	38.52	60.65	92.50

Table 3 a

Comparison of predictions in P and T by the two parameter activity coefficient models
Rosenbrock Method

Temperature /	Margules		van Laar		Wilson		NRTL (α=0.3)		UNIQUAC	
Pressure	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)
323.15 K	0.12	0.13	0.12	0.13	0.13	0.14	0.12	0.13	0.12	0.13
333.15 K	0.14	0.11	0.14	0.11	0.14	0.10	0.14	0.11	0.13	0.11
343.15 K	0.09	0.12	0.09	0.11	0.09	0.10	0.09	0.11	0.09	0.11
353.15 K	0.20	0.19	0.15	0.17	0.15	0.17	0.15	0.18	0.16	0.17
26.66 kPa	0.11	0.12	0.11	0.12	0.11	0.12	0.11	0.12	0.11	0.12
53.32 kPa	0.17	0.15	0.18	0.15	0.18	0.15	0.18	0.15	0.18	0.15
79.97 kPa	0.25	0.19	0.25	0.19	0.25	0.19	0.25	0.19	0.25	0.19
101.3 kPa	0.22	0.23	0.15	0.22	0.14	0.22	0.16	0.22	0.13	0.22

D(P) = r.m.s.d. in P; D(T) = r.m.s.d. in T

Table 3 b

Comparison of predictions in P and T by the two parameter activity coefficient models
Nelder-Mead Method

Temperature /	Margules		van Laar		Wilson		NTRL (α=0.3)		UNIQUAC	
Pressure	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)
323.15 K	0.12	0.13	0.12	0.13	0.13	0.14	0.12	0.13	0.12	0.13
333.15 K	0.13	0.10	0.14	0.11	0.14	0.10	0.14	0.10	0.13	0.10
343.15 K	0.09	0.11	0.08	0.11	0.09	0.10	0.09	0.11	0.09	0.11
353.15 K	0.19	0.19	0.15	0.17	0.15	0.17	0.15	0.18	0.15	0.17
26.66 kPa	0.11	0.12	0.11	0.12	0.10	0.12	0.11	0.12	0.11	0.12
53.32 kPa	0.17	0.15	0.18	0.15	0.18	0.14	0.17	0.14	0.18	0.14
79.97 kPa	0.25	0.19	0.25	0.19	0.25	0.19	0.25	0.19	0.25	0.19
101.3 kPa	0.21	0.23	0.14	0.22	0.13	0.22	0.16	0.22	0.13	0.22

D(P) = r.m.s.d. in P; D(T) = r.m.s.d. in T

Table 3 c

Comparison of predictions in P and T by the two parameter activity coefficient models
Maximum Likelihood Method

Temperature /	Margules		van Laar		Wilson		NRTL (α=0.3)		UNIQUAC	
Pressure	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)	D(P)	D(T)
323.15 K	0.05	0.03	0.07	0.05	0.08	0.04	0.07	0.05	0.07	0.04
333.15 K	0.004	0.09	0.003	0.08	0.003	0.08	0.004	0.08	0.003	0.08
343.15 K	0.007	0.20	0.001	0.04	0.001	0.04	0.001	0.04	0.001	0.04
353.15 K	0.008	0.31	0.002	0.05	0.002	0.06	0.002	0.05	0.002	0.06
26.66 kPa	0.01	0.23	0.009	0.16	0.009	0.16	0.009	0.16	0.009	0.16
53.32 kPa	0.008	0.23	0.005	0.15	0.005	0.15	0.005	0.15	0.005	0.15
79.97 kPa	0.003	0.14	0.003	0.14	0.003	0.16	0.003	0.15	0.003	0.16
101.3 kPa	0.10	0.21	0.02	0.03	0.014	0.03	0.017	0.04	0.014	0.03

D(P) = r.m.s.d. in P; D(T) = r.m.s.d. in T

Table 4

Comparision of predictions in P and T by the UNIFAC Method

Temperature / Pressure	UNIFAC [18]		UNIFAC (present work)	
	AADP	AADT	AADP	AADT
323.15 K	1.45	0.34	1.73	0.23
333.15 K	1.34	0.14	1.05	0.09
343.15 K	5.14	0.21	4.58	0.31
353.15 K	9.54	0.45	4.68	0.25
26.66 kPa	2.21	0.26	0.86	0.11
53.32 kPa	9.96	0.61	7.60	0.46
79.97 kPa	15.90	0.69	11.20	0.48
101.3 kPa	28.80	1.03	20.10	0.72

AADP= Absolute average deviation in P = $\mathrm{Abs}\left[\frac{\Sigma(P_{exp} - P_{cal})}{n}\right]$

AADT= Absolute average deviation in T = $\mathrm{Abs}\left[\frac{\Sigma(T_{exp} - T_{cal})}{n}\right]$

Table 5

Azeotropic Data Predicted by UNIQUAC model
2-propanol (1)-1,4-dioxane (2) mixtures

Isothermal data			**Isobaric data**		
Tempertature, K	Mole fraction, 2-propanol	Pressure (kPa)	Pressure (kPa)	Mole fraction, 2-propanol	Temperature, K
323.15	0.742	25.00	26.66	0.772	324.55
333.15	0.844	39.59	53.32	0.885	340.00
343.15	0.848	62.32	79.97	0.959	349.65
353.15	0.921	93.49	101.3	0.995	355.35

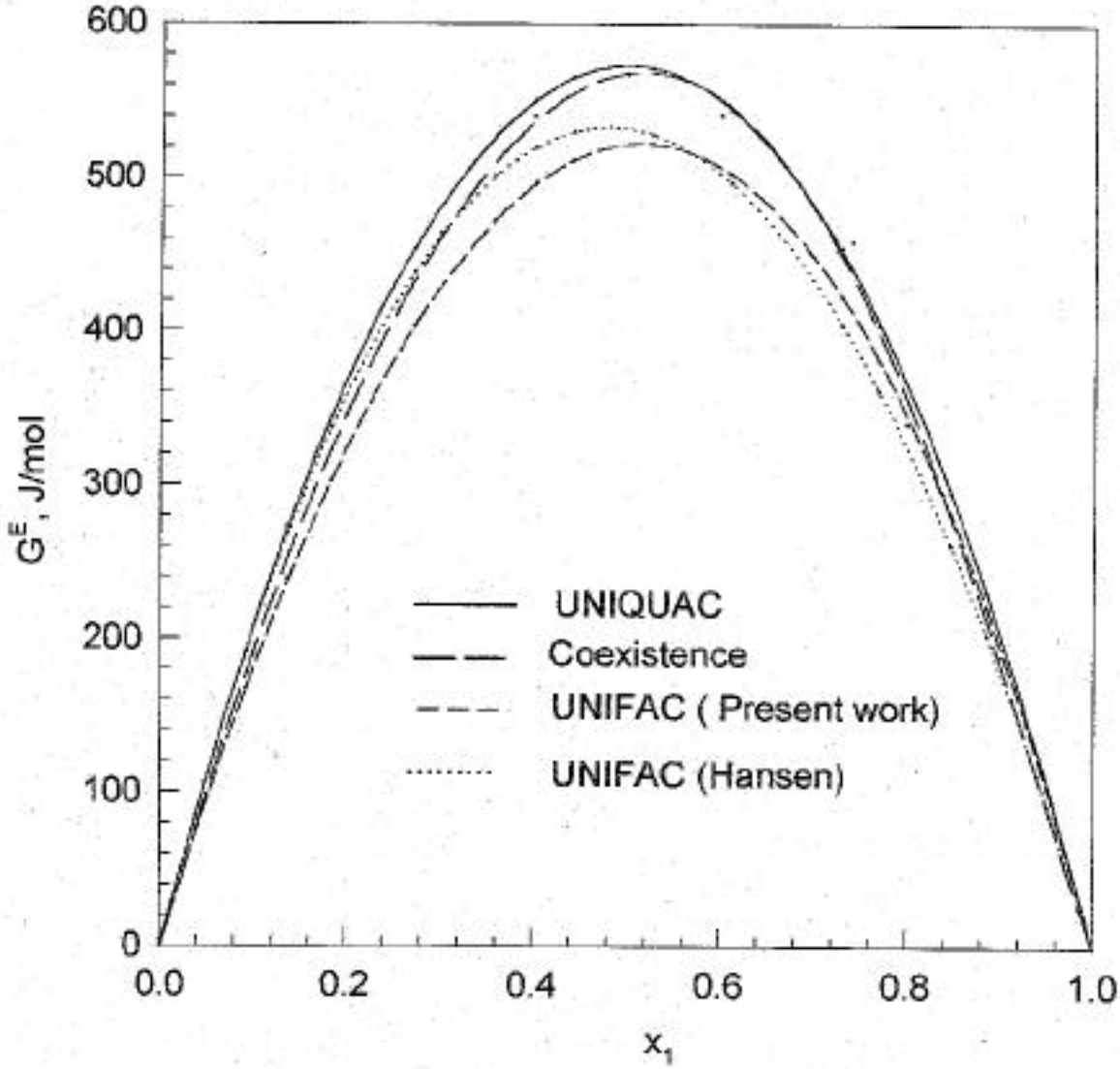

Fig.1. Comparision of G^E values predicted by various models
System : 2- Propanol (1) - 1,4 dioxane (2) at 323.15K

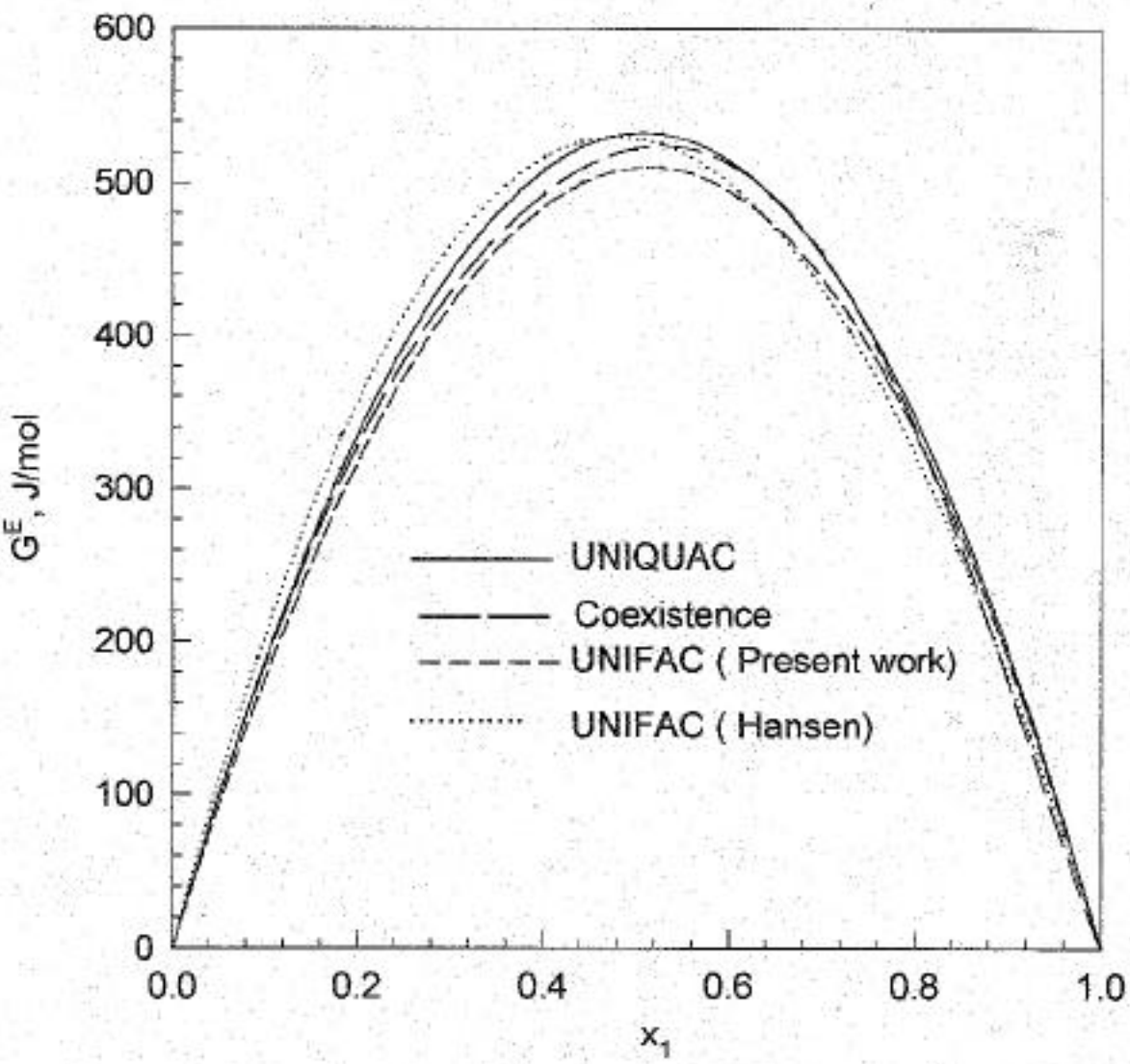

Fig. 2. Comparision of G^E values predicted by various models
System : 2- Propanol (1) - 1,4 dioxane (2) at 333.15 K

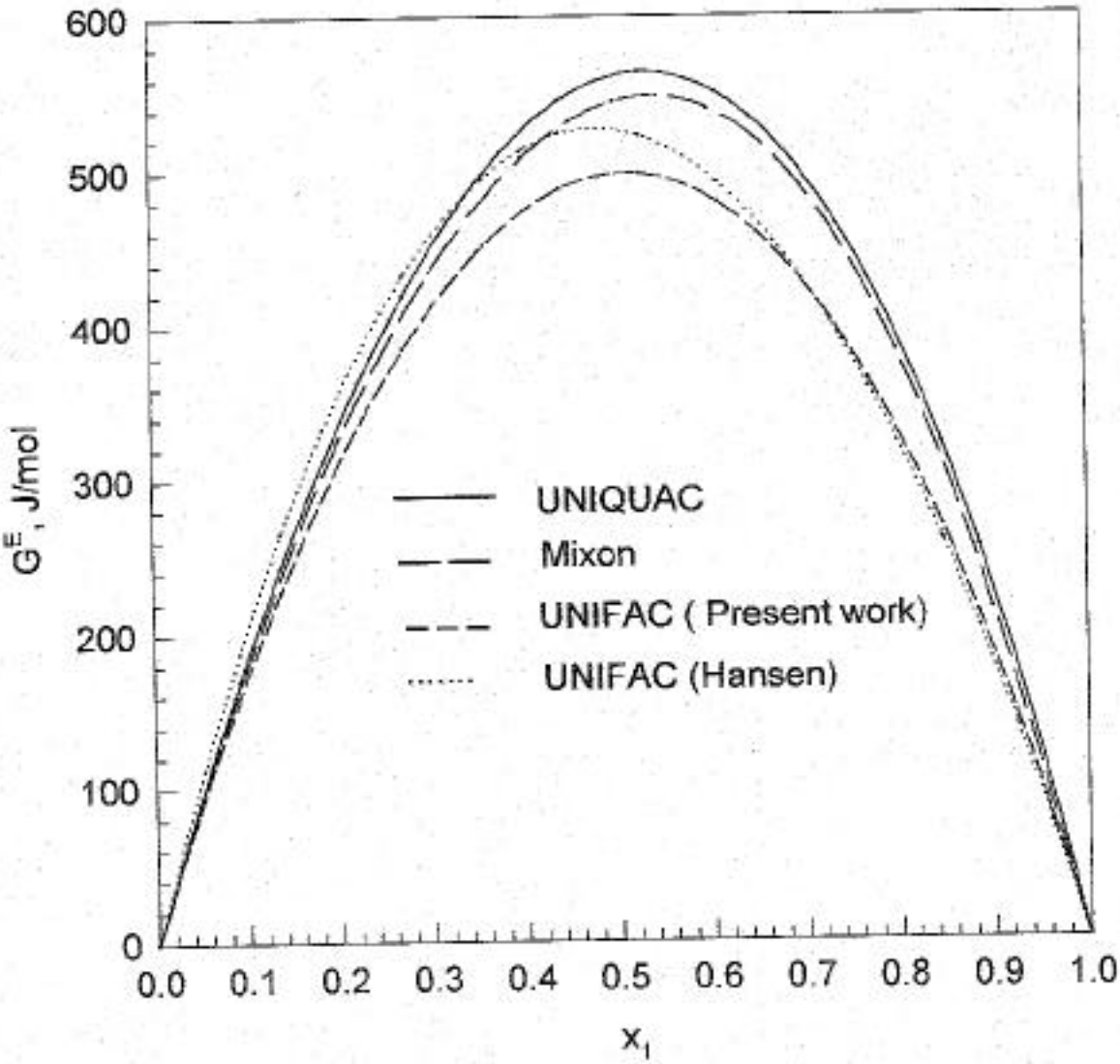

Fig. 3. Comparision of G^E values predicted by various models
System : 2- Propanol (1) - 1,4 dioxane (2) at 333.15 K

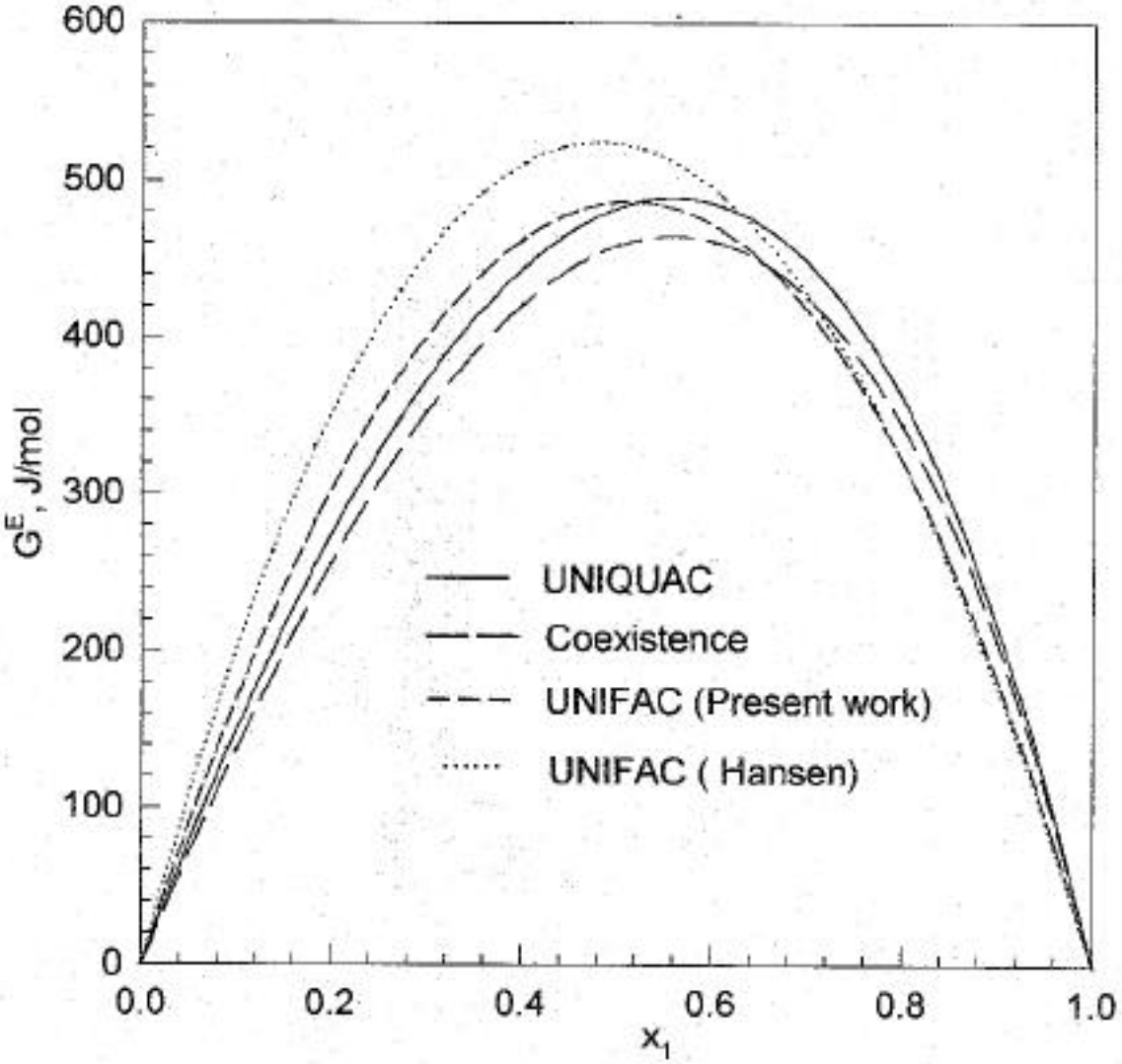

Fig. 4. Comparision of G^E values predicted by various models.
System : 2- Propanol (1) - 1,4 dioxane (2) at 353.15 K

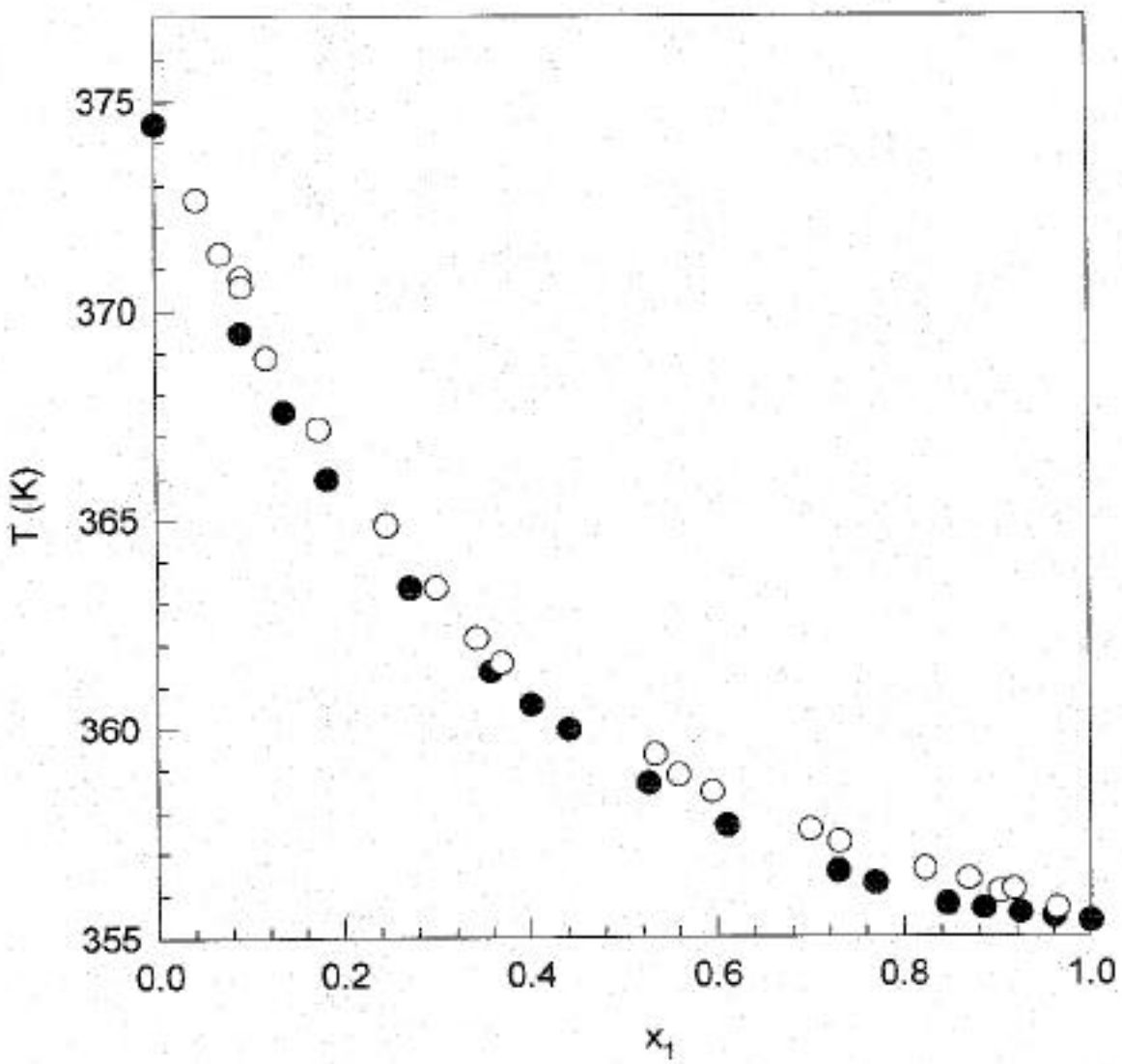

Fig. 5 : T-x diagram

System : 2-Propanol - 1,4 dioxane at 101.3 kPa

● Present work ○ Choffe et al. 1960