



# Phase equilibrium and excess Gibbs energy functions of acetophenone with 1,1,2-trichloroethene and cyclohexane binary mixtures by using NRTL, UNIQUAC, UNIFAC and VANLAAR models at a local atmospheric pressure of 95.3 kPa

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## ARTICLE INFO

### Article history:

Received 23 October 2014

Received in revised form 16 December 2014

Accepted 17 December 2014

Available online 19 December 2014

### Keywords:

Antoine equation

Ebulliometer

Baker method

Gibbs energy

Molecular interactions

## ABSTRACT

Boiling points of pure liquids and their binary mixtures are measured over the entire range of composition at a local atmospheric pressure of 95.3 kPa. The experiments were carried by using a Swietoslawski-type ebulliometer. Vapor pressures of the pure components were computed using Antoine's equation. The activity coefficients and Gibbs energies were calculated for both the binary mixtures under investigation. Excess Gibbs energy values were found to be positive in both the binary systems. Both the binary systems were observed to be positive deviation from Raoult's law due to the dispersal forces acting between the component molecules in the liquid mixture. NRTL, UNIQUAC, UNIFAC and VAN LAAR models have also been applied successfully to both of the binary mixtures presented here. The results are discussed in terms of molecular interactions between the unlike molecules in the binary liquid mixtures.

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## 1. Introduction

Vapor–liquid equilibria (VLE) are fundamental properties, and their knowledge is essential for the design and operation of separation processes. Many experiments are required for obtaining such equilibrium data, at least for binary systems, where non-idealities in both phases must be determined. Knowledge of several properties is required for engineering design and operation of distillation equipment. VLE is also important in the testing and extension of fluid mixture theories. Furthermore, properties of binary mixtures containing components capable of undergoing specific interactions exhibit significant deviations from ideal behavior due to the difference in molecular size, shape and structural changes. To describe the thermodynamic behavior and to study the mechanisms of these processes, physical and phase equilibrium properties of binary liquid mixtures are necessary.

The modeling of a process has received a great deal of attention as a reliable tool to attain efficient, clean and optimal new technologies [1]. The increasing development of process design, under the pressure of growing chemical and related industries, seeks to create environmentally friendly and low energy consuming conditions. To develop such a

modeling it is critically based on the accurate knowledge of the thermodynamic behavior of the chemicals involved; therefore, the availability of the suitable methods and the disposal of reliable physical property data are essential basic requirements to achieve a proper design [2,3].

Acetophenone (CAS Registry No. 98-86-2), an important industrial chemical, is widely used as an ingredient of flavor and fragrance in soaps, detergents, cosmetics, and perfumes. It has also been used as an important intermediate for pharmaceuticals and agrochemicals [4]. The thermodynamic properties of systems containing acetophenone are helpful to better understand molecular interaction and to design and simulate the different processes of separation. Acetophenone, a typical ketone, has been used in perfumery and as a hypnotic under the name “hypnone” [5]. It is also used as a solvent for cellulose ethers.

1,1,2-Trichloroethene is extensively used in industrial, agricultural, and commercial processes as solvents, lubricants, and intermediates in chemical industry, pesticides, pharmaceuticals, and medical equipment. The physical and chemical properties of 1,1,2-trichloroethene differ strikingly from those of saturated aliphatic chlorine compounds. In recent years, the thermodynamic properties of highly polar compounds with chloroethenes have received increasing attention because they serve as model compounds in biochemical considerations [6–8]. 1,1,2-Trichloroethene (CAS Registry No. 79-01-6), a volatile liquid with a pleasant odor, is miscible with other chlorinated solvents. Cyclohexane (CAS Registry No. 110-82-7) is a versatile solvent with good binding

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**Table 1**

Densities of pure components at 303.15 K and boiling points at 95.3 kPa along with the literature values.

Substance	$\rho/\text{kg m}^{-3}$		T/K	
	Exp	Lit	Exp	Lit
Acetophenone	1019.86	1019.9 [16]	472.3 <sup>a</sup>	475.2 <sup>b</sup> [17]
1,1,2-Trichloroethene	1451.32	1451.3 [18]	358.1	358.45 <sup>c</sup> [18]
Cyclohexane	773.85	773.86 [19]	351.6 <sup>a</sup>	353.7 <sup>b</sup> [19]

<sup>a</sup> At a pressure of 95.3 kPa.

<sup>b</sup> At a pressure of 101.3 kPa.

<sup>c</sup> At a pressure of 95.6 kPa.

properties, a blowing agent and dispersion media for broad range of liquids. We could not locate any published experimental vapor–liquid equilibrium data on the systems chosen for the present study. The data presented in this paper were expected to be useful in the design of separation processes (especially by distillation) for mixtures containing the compounds in the selected binary mixtures. The results obtained in this work seem to indicate the molecular interactions of the binary mixture studies.

This paper is a part of our ongoing research effort [9–14] to measure and characterize the VLE and thermodynamic properties of various binary mixtures. It reports the phase equilibrium data of the binary mixtures of acetophenone + 1,1,2-trichloroethene and acetophenone + cyclohexane. No reported mixing properties of these studied systems at a local atmospheric pressure have been found. This work reports measurement of isobaric vapor–liquid equilibria at 95.3 kPa for binary mixtures of acetophenone with 1,1,2-trichloroethene and cyclohexane. The obtained VLE data were correlated by the NRTL, UNIQUAC, UNIFAC and VAN LAAR methods.

## 2. Experimental

### 2.1. Materials

Acetophenone (S. D. Fine Chemicals, India) was dried over anhydrous potassium carbonate for 3 days, filtered, and then distilled. The middle fraction of the distillates is retained [15]. Spectroscopic grade 1,1,2-trichloroethene (S. D. Fine Chemicals, India) was steam-distilled from calcium hydroxide slurry. The organic phase was collected in the temperature (*T*) range of 223 to 243 K, and the ice formed is removed by filtration. The filtrate is subjected to fractional distillation. Cyclohexane (S. D. Fine Chemicals, India) was purified by distillation and stored over activated 4 Å molecular sieves. The final step of the purification of all of the liquids (fractional distillation) was carried out by means of a packed column of height equivalent to 30 theoretical plates, only a few hours prior to the commencement of the phase equilibrium experiment, and enough care was taken to prevent the absorption of moisture, oxidation, and so forth, during the intervening period. On the basis of the lack of the appearance of multiple significant peaks in the gas chromatograms the pure liquids used in the present work were expected to have a mole fraction purity of >0.999.

### 2.2. Methods

#### 2.2.1. Density measurements

Densities ( $\rho$ ) of the pure components were measured at a temperature of 303.15 K and atmospheric pressure using a DSA 4500 density

**Table 2**

Antoine's constants obtained from vapor pressure temperature data.

	A	B	C	$T_{\min}/\text{K}$	$T_{\max}/\text{K}$
Acetophenone	62.688	−8088.8	−5.5434	250	500
1,1,2-Trichloroethene	16.18	3028.13	−43.2	250	500
Cyclohexane	15.75	2766.6	−50.5	250	500

**Table 3**

Binary interaction parameters for both the binary systems using NRTL and UNIQUAC models.

System	NRTL		UNIQUAC	
	$b_{12}$	$b_{21}$	$U_{12}-U_{22}$	$U_{21}-U_{11}$
Acetophenone + 1,1,2-trichloroethene	51.23	49.88	−1586.13	−2255.02
Acetophenone + cyclohexane	333.72	390.89	42.11	−42.15

meter (Anton Paar, Austria) with an accuracy of  $5.10^{-6} \text{ g cm}^{-3}$ . The density determination was based on measuring the period of oscillation of a vibrating U-shaped tube filled with the liquid sample. During the operation, the temperature of the apparatus was maintained constant to within  $\pm 0.01 \text{ K}$ . The densities of the pure components were presented in Table 1 along with the literature data [16–19].

#### 2.2.2. VLE Measurements

Swietoslawski ebulliometer as described by Hala et al. [20] was used to measure the boiling point of the pure components and the binary mixtures. A mixture ( $\sim 40 \text{ cm}^3$ ) with a known composition was charged into the Swietoslawski ebulliometer. It was ensured that the components were adequately mixed before being transferred into the ebulliometer and each binary mixture was used immediately after the preparation. The system pressure was set to the desired value using the pressure controller. Dry nitrogen gas cylinder and a vacuum pump were joined to the ebulliometer with a manometer closed at one end for the maintenance and measurement of the required total pressure of the system. The required pressure was maintained by adjusting the opening of the needle valve of the gas cylinder. In these measurements the total pressure was regulated within  $\pm 0.1 \text{ kPa}$  of the required value, through applying the needed adjustment and often analysis of the mercury columns of the manometer. A glass thermometer with mercury as thermometric fluid, calibrated with a standard platinum resistance thermometer, was used to record the phase equilibrium temperature of the mixture with an accuracy of  $\pm 0.05 \text{ K}$ . The thermometer was placed in a thermo – well filled with mercury to make a note of the steady state temperature of the (vapor + liquid) mixture impinging on the Cottrell tube.

After the binary mixture was introduced into the ebulliometer, the rate of heating was gradually raised with the help of a dimmer stat to

**Table 4**

Temperature, vapor phase composition, activity coefficients and excess Gibbs energy for the binary system, acetophenone + 1,1,2-trichloroethene.

$x_1$	$T_{\text{exp}}$	$T_{\text{cal}}$	$y_1$	$\gamma_1$	$\gamma_2$	$\ln(\gamma_1/\gamma_2)$	$G^E/\text{J mol}^{-1}$
0.0000	358.10	358.10	0.0000	1.1782	1.0000	0.163945	0.00
0.0777	361.46	361.80	0.6950	1.1467	1.0008	0.136089	6.99
0.1441	364.24	364.52	0.8444	1.1232	1.0029	0.113286	12.12
0.2017	366.12	365.27	0.9066	1.1043	1.0057	0.093528	15.90
0.2519	368.42	368.75	0.9356	1.0901	1.0080	0.078301	18.71
0.2963	369.25	369.52	0.9517	1.0783	1.0120	0.063457	20.79
0.3356	370.12	370.05	0.9607	1.0687	1.0154	0.0512	22.32
0.3708	371.10	371.05	0.9634	1.0608	1.0186	0.040604	23.44
0.4025	372.14	372.05	0.9723	1.0543	1.0218	0.031341	24.24
0.4311	374.16	373.61	0.9755	1.0446	1.0248	0.019166	24.80
0.5310	379.16	379.19	0.9843	1.0318	1.0367	−0.004757	25.45
0.5601	380.25	379.91	0.9863	1.0277	1.0407	−0.012532	25.26
0.5927	383.15	383.03	0.9881	1.0234	1.0450	−0.020886	24.84
0.6294	386.54	386.63	0.9900	1.0181	1.0502	−0.031042	24.09
0.6708	389.66	389.65	0.9917	1.0148	1.0564	−0.040175	22.92
0.7181	395.16	396.76	0.9935	1.0106	1.0633	−0.050833	21.13
0.7725	405.16	404.75	0.9951	1.0066	1.0713	−0.062295	18.46
0.8359	420.56	419.09	0.9968	1.0033	1.0799	−0.073574	14.52
0.9106	437.66	437.61	0.9984	1.0009	1.0906	−0.085828	8.69
1.0000	472.30	472.30	1.0000	1.0000	1.1004	−0.095674	0.00

Standard uncertainty in temperature  $u(T) = 0.05 \text{ K}$ , combined standard uncertainty in composition  $u(x) = 0.0001$ , and pressure  $u(P) = 0.05 \text{ kPa}$  at a confidence level of 95%.

**Table 5**

Temperature, vapor phase composition, activity coefficients and excess Gibbs energy for the binary system, acetophenone + cyclohexane.

$x_1$	$T_{\text{exp}}$	$T_{\text{cal}}$	$y_1$	$\gamma_1$	$\gamma_2$	$\ln(\gamma_1/\gamma_2)$	$G^E/\text{J mol}^{-1}$
0.0000	351.60	351.60	0.0000	1.1816	1.0000	0.166869	0.00
0.0777	354.16	354.49	0.4152	1.1492	1.0010	0.138067	8.30
0.1441	355.16	356.97	0.4631	1.1256	1.0036	0.114723	14.22
0.2017	356.16	356.75	0.5449	1.1071	1.0070	0.094768	18.48
0.2519	357.16	357.45	0.6172	1.0924	1.0109	0.077556	21.55
0.2963	358.16	358.75	0.6696	1.0805	1.0149	0.062594	23.75
0.3356	359.16	359.33	0.7101	1.0708	1.0190	0.049573	25.33
0.3708	360.16	360.33	0.7424	1.0684	1.0231	0.043335	26.43
0.4025	362.16	362.45	0.7675	1.0628	1.0258	0.035406	27.18
0.4311	363.16	363.69	0.7881	1.0550	1.0270	0.026928	27.28
0.5310	369.66	369.55	0.8483	1.0418	1.0455	-0.003545	27.85
0.5601	373.16	373.52	0.8630	1.0320	1.0500	-0.017291	27.51
0.5927	376.16	377.63	0.8783	1.0283	1.0554	-0.026032	26.88
0.6294	380.16	384.14	0.8942	1.0239	1.0617	-0.036281	25.91
0.6708	388.16	387.91	0.9107	1.0194	1.0684	-0.046928	24.45
0.7181	421.55	421.65	0.9277	1.0149	1.0764	-0.058852	22.33
0.7725	442.45	442.45	0.9448	1.0105	1.0857	-0.07178	19.31
0.8359	445.45	445.56	0.9625	1.0066	1.0964	-0.085417	15.00
0.9106	460.34	460.15	0.9807	1.0032	1.1080	-0.099362	8.85
1.0000	472.30	472.30	1.0000	1.0000	1.122	-0.115113	0.00

Standard uncertainty in temperature  $u(T) = 0.05$  K, combined standard uncertainty in composition  $u(x) = 0.0001$ , and pressure  $u(P) = 0.05$  kPa at a confidence level of 95%.

achieve the required boil up rate so that a drop count of about 2 drops/s was achieved. After the steady state was achieved, the equilibrium temperature was noted, by confirming the steadiness of the equilibrium temperature and consistency of the drop rate for a minimum of 30 min in any case. The composition of the mixture was verified individually at the commencement and at the closing stages of each experimentation by taking a Gas Chromatograph (GC-17A, Shimadzu), and the analysis was carried out using a thermal conductivity detector fitted with an SE 30 column. The boiling points of the pure liquids were recorded in Table 1 along with the literature data.

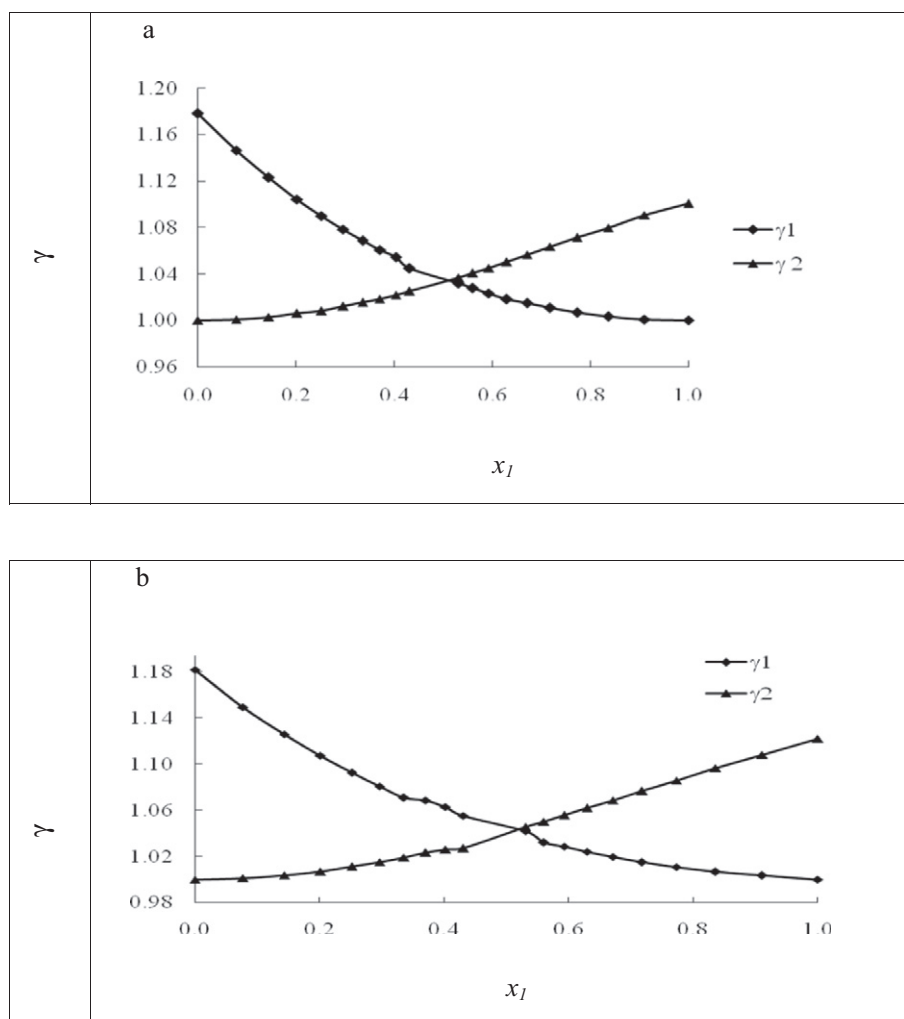
### 3. Results and discussion

#### 3.1. Pure components

The experimental vapor pressures of the pure compounds were measured and the data was fitted to the Antoine equation to check their consistency:

$$\ln[P/(\text{kPa})] = \{A - B/[T/(\text{K}) + C]\} \quad (1)$$

where A, B and C were Antoine coefficients determined from the experimental vapor pressure and boiling point data of the pure liquids over temperature range calculated were presented in Table 2. The



**Fig. 1.** Plot of activity coefficient  $\gamma$  against mole fraction  $x_1$  acetophenone (a)  $\{x_1 \text{ acetophenone} + (1 - x_1) 1,1,2\text{-trichloroethene}\}$ , (b)  $\{x_1 \text{ acetophenone} + (1 - x_1) \text{cyclohexane}\}$ .

objective function  $Q$  was the sum of the squared relative deviations in pressure:

$$Q = \sum \left( \frac{p_{\text{cal}} - p_{\text{exp}}}{p_{\text{exp}}} \right)^2 \quad (2)$$

### 3.2. Binary systems

Regarding the two binary mixtures, the data measure in the experiment consists of the liquid composition and temperature. Reduction of the data for the binary mixtures is done using the method of Barker [21] according to well established procedures [22,23]. The objective function is the sum of the squared absolute deviations in pressure. The non-ideality of the vapor phase is taken into account with the virial equation of state, truncated after the second term. Second virial coefficients are calculated by the Hayden and O'Connell method [24] using the parameters reported by Dymond and Smith [25]. The values of the

molar excess Gibbs free energy  $G^E$  are estimated from a third-order Redlich–Kister equation:

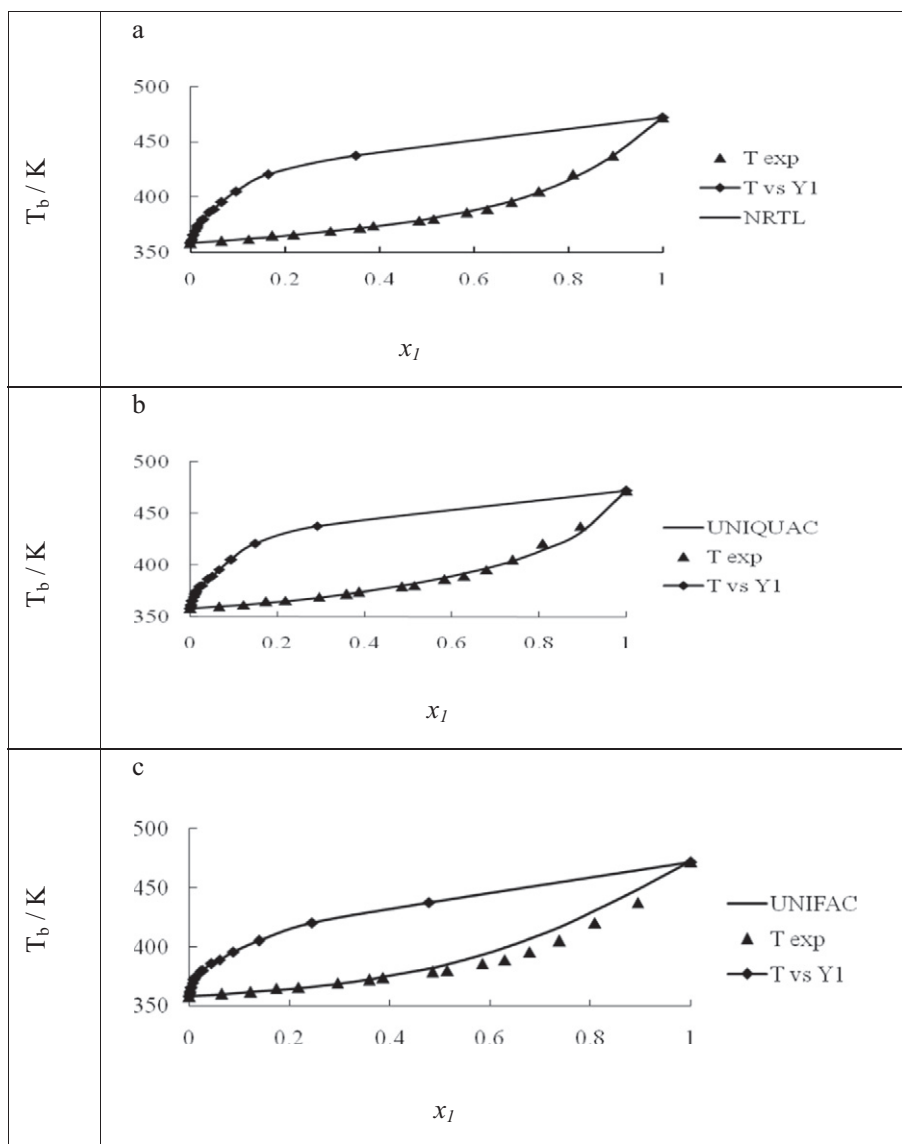
$$G^E = x_1(1-x_1) \sum_{j=1}^m RTG_j(2x_1-1)^{j-1}. \quad (3)$$

The coefficients  $G_j$  are determined by regression through minimization of the sum of deviations in vapor pressures. Vapor phase deviations are accounted for in terms of the second molar virial coefficients, estimated by the method of Tsonopoulos [26,27].

The vapor phase compositions are calculated from:

$$y_i = \frac{x_i \gamma_i P_i}{p} \quad (4)$$

where  $p$  is the total equilibrium pressure,  $P_i$  is the vapor pressure of pure component  $i$ ,  $x_i$  is the mole fraction in the liquid phase of component  $i$ , and  $\gamma_i$  is the activity coefficient of component  $i$  in the liquid mixture.



**Fig. 2.** Plot of boiling point against mole fraction  $x_1$  acetophenone for the binary mixture  $\{x_1 \text{ acetophenone} + (1 - x_1) \text{ 1,1,2-trichloroethene}\}$ , (a) NRTL model, (b) UNIQUAC, and (c) UNIFAC model.

The non-random parameter ( $\alpha$ ) in the NRTL equation has been fixed to 0.3 for all cases. The fitting parameters ( $b_{ij}$  and  $b_{ji}$ ) are given in Table 3 along with the UNIQUAC parameters  $U_{12}$ – $U_{22}$  and  $U_{21}$ – $U_{11}$ .

The liquid and vapor phase compositions  $x_1$ ,  $y_1$  respectively for the mixtures (acetophenone + 1,1,2-trichloroethene), and (acetophenone + cyclohexane), along with the activity coefficients  $\gamma_1$  and  $\gamma_2$ , experimental  $T_{\text{exp}}$  and calculated temperatures  $T_{\text{cal}}$  and the values of the excess Gibbs energies  $G^E$  calculated by Barker's methods are reported in Tables 4 and 5. No literature data was found to be compared with the present study. Both the investigated binary systems do not show azeotropic behavior.

The NRTL [28] and UNIQUAC [29] equations were also used to correlate the experimental VLE data and estimate the liquid phase activity coefficients. The Simulis thermodynamic software developed by Prosim (France) was used to correlate the data and to fit the parameters.

Additionally, prediction of VLE for the systems studied has been carried out by the Modified UNIFAC (Do) group contribution method [30] using the same software. It is observed that the descriptions of the systems by the Modified UNIFAC (Do) method are very high for both the systems under examination.

Furthermore, prediction of VLE for the systems studied has been carried out by the Van laar equation. The data obtained by this model is fairly in good agreement with the other models used for the prediction the VLE data.

The expressions for activity coefficients are given for NRTL by:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} - \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left( \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right) \quad (5)$$

$$\text{where } \tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \quad (6)$$

$$g_{ij} - g_{jj} = C_{ij}^0 + C_{ij}^T (T - 273.15) \quad (7)$$

$$\alpha_{ij} = \alpha_{ij}^0 + \alpha_{ij}^T (T - 273.15) \quad (8)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}). \quad (9)$$

And for UNIQUAC by:

$$\ln \gamma_i = \ln \gamma_{\text{comb}} + \ln \gamma_{\text{res}} \quad (10)$$

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (11)$$

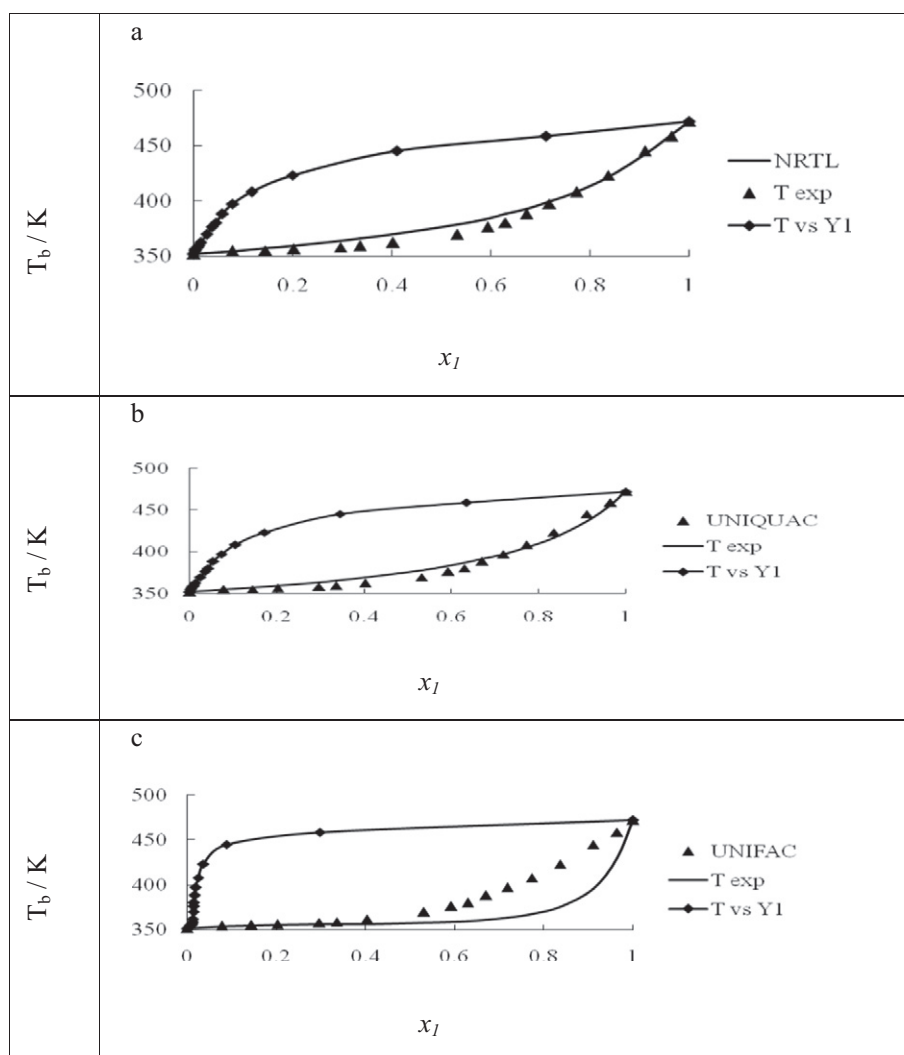


Fig. 3. Plot of boiling point against mole fraction  $x_1$  acetophenone for the binary mixture  $\{x_1 \text{ acetophenone} + (1 - x_1) \text{ cyclohexane}\}$ , (a) NRTL model, (b) UNIQUAC, and (c) UNIFAC model.

$$\ln \gamma_i^{res} = q'_i - q'_i \ln \left( \sum_{j=1}^n \theta_j \tau_{ji} \right) - q'_i \sum_{j=1}^n \frac{\theta'_j \tau_{ij}}{\sum_{k=1}^n \theta'_k \tau_{ik}} \quad (12)$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \quad (13)$$

where  $r_i$  and  $q_i$  are molecular volume and surface area, called van der Waals volume and area, which are estimated using the group contribution values of Bondi. The coordination number  $Z$  is equal to 10. The interaction parameters are as follows:

$$\tau_{ij} = \exp \left( -\frac{U_{ij} - U_{jj}}{RT} \right) \quad (14)$$

$$\Delta U_{ij} = U_{ij} - U_{jj} = (U_{ij} - U_{jj})^0 + (U_{ij} - U_{jj})^T \cdot T. \quad (15)$$

Van laar equation used to find the activity coefficients:

$$RT \ln \gamma_1 = A^1 / \left[ 1 + (A^1 x_1 / B^1 x_2) \right]^2 \quad (16)$$

$$RT \ln \gamma_2 = B^1 / \left[ 1 + (B^1 x_2 / A^1 x_1) \right]^2 \quad (17)$$

$$\text{where } A^1 = \frac{M_1}{\rho_1} \text{ and } B^1 = \frac{M_2}{\rho_2}.$$

For the binary systems under investigation, the Herington method [31] is used to verify the quality of all experimental data. The method suggests that

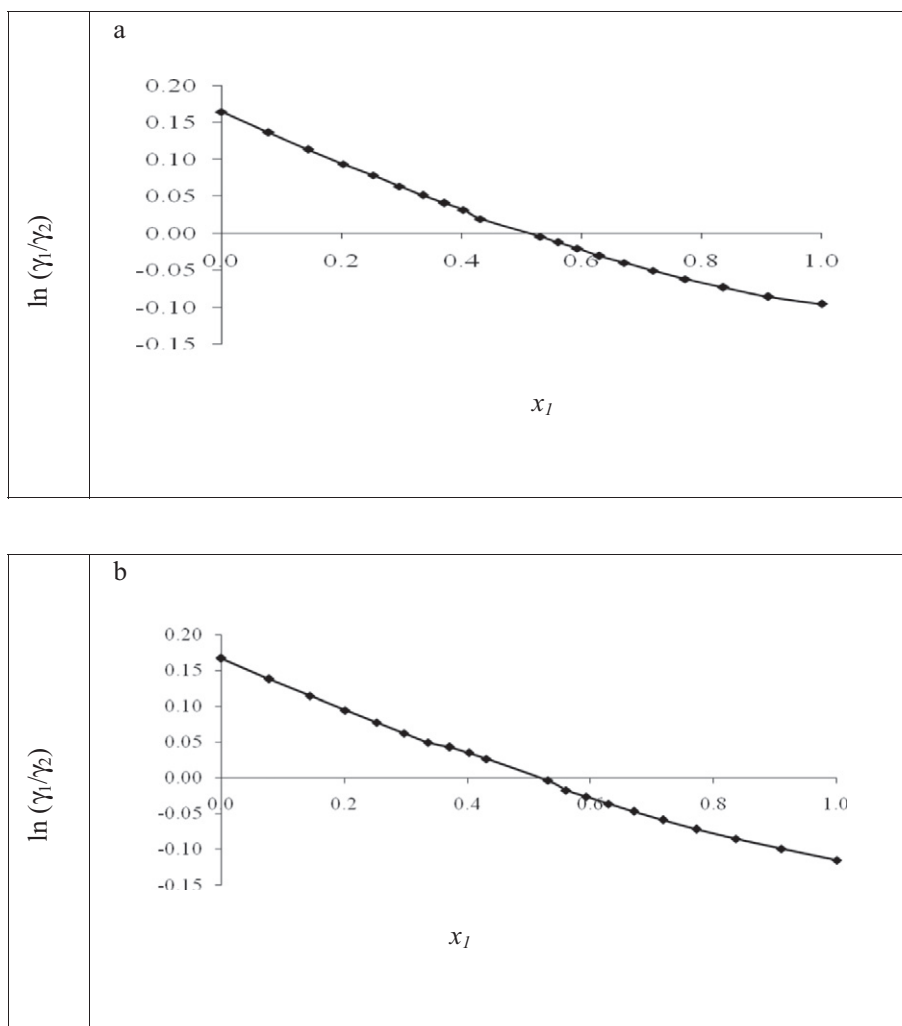
$$D = \left| \frac{S_a - S_b}{S_a + S_b} \right| \times 100 \quad (18)$$

where  $S_a$  is the area of  $\ln(\gamma_1 / \gamma_2) - x_1$  above the x-axis, and  $S_b$  is the area of  $\ln(\gamma_1 / \gamma_2) - x_1$  under the x-axis.

$$J = 150 \times \left| \frac{T_{\max} - T_{\min}}{T_{\min}} \right| \quad (19)$$

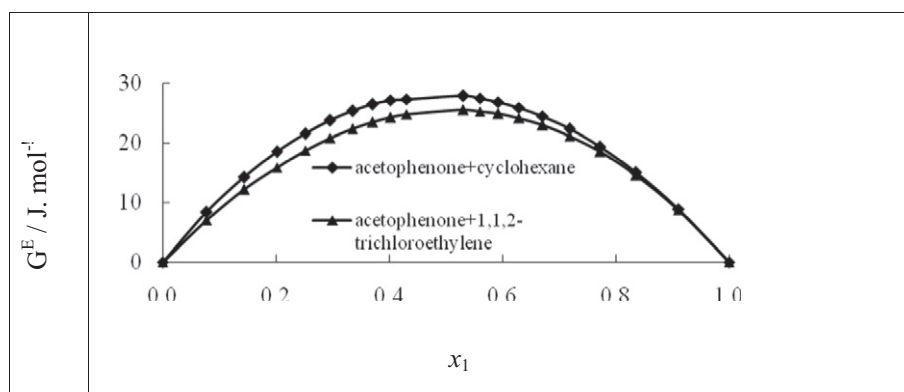
where  $T_{\max}$  and  $T_{\min}$  are the maximum and minimum temperatures of the system, respectively. If  $D < J$ , the isobaric VLE data can be considered to conform to the thermodynamic consistency test. Both the binary systems under investigation passed the thermodynamic consistency test.

Fig. 1 shows the variation of activity coefficients with the liquid mole fraction of acetophenone ( $x_1$ ). From Fig. 1, it is evident that the values of activity coefficients were more than unity for both the binary systems under study indicating the non-ideal behavior due to the molecular interactions between the component molecules in the binary liquid mixtures.



**Fig. 4.** Plot of  $\ln(\gamma_1 / \gamma_2)$  against mole fraction  $x_1$  acetophenone for the binary system (a)  $\{x_1 \text{ acetophenone} + (1 - x_1) \text{ 1,1,2-trichloroethene}\}$ , (b)  $\{x_1 \text{ acetophenone} + (1 - x_1) \text{ cyclohexane}\}$ .





**Fig. 5.** Plot of the change in Gibbs energy  $G^E$  against mole fraction  $x_1$  acetophenone for the binary systems  $\{x_1 \text{ acetophenone} + (1 - x_1) \text{ 1,1,2-trichloroethene}\}$  and  $\{x_1 \text{ acetophenone} + (1 - x_1) \text{ cyclohexane}\}$ .

Furthermore it can be discussed that the molecular interactions are repulsive in both the binary systems under investigation. Both the curves meet up almost at mid composition range of acetophenone, where high repulsions are expected. The boiling point ( $T$ ) versus mole fraction curves in both liquid phase ( $x_1$ ) and vapor phases ( $y_1$ ) are presented in Figs. 2 and 3. The plots showed the results of correlation using NRTL, UNIQUAC and UNIFAC models for the two investigated mixtures. The NRTL, UNIQUAC and UNIFAC models fit the experimental results of the systems very well except in cyclohexane system in which UNIFAC model temperature deviations are more. Also, it is observed that no azeotropic mixtures are formed in both the binary mixtures. The positive deviations from Raoult's law observed in the systems perhaps due to the presence of dispersal forces over the whole composition range at a constant pressure of 95.3 kPa. The positive and negative deviations for non-ideal solutions from vapor–liquid studies are well described by Carlson et al. [32].

A plot representing variation in  $\ln(\gamma_1/\gamma_2)$  versus mole fraction of acetophenone ( $x_1$ ) for both the binary systems is presented in Fig. 4. From the figure it is observed that a curve represents positive and negative values, from which the area above and below the axis is calculated to check the thermodynamic consistency test. It is found that both the binary mixtures under the present investigation passed the Herington's thermodynamic consistency test.

A plot representing the variation in Gibbs energy with the mole fraction of acetophenone ( $x_1$ ) is presented in Fig. 5. Both the systems under examination have positive values. From the Gibbs energy values, it can be inferred that the molecular interactions are weak due to the dispersal forces between the dissimilar molecules on mixing. Garcia-Mardones et al. [33] observed positive excess Gibbs energies and interpreted that the positive nature is due to the rupture of bonds between the unlike molecules of the binary liquid mixtures. In the binary system of acetophenone with cyclohexane the excess Gibbs energy values are higher than that of the 1,1,2-trichloroethene system. Acetophenone, 1,1,2-trichloroethene, and cyclohexane are self associated liquids due to the presence of dipole–dipole interactions in their pure state. When 1,1,2-trichloroethene or cyclohexane is added to acetophenone, the compact molecular structure is formed as the dispersion forces are operating between the dissimilar molecules. Also, it was observed from the figure that the Gibbs energy values are more for the binary system cyclohexane with acetophenone than the other binary system probably due to the geometrical mismatching of the sutures besides the dispersal forces acting between the unlike molecules in the binary system. In the present investigated binary systems it is observed that, both the binary systems exhibit positive deviation from Raoult's law.

#### 4. Conclusions

VLE data for the binary mixtures of acetophenone with 1,1,2-trichloroethene and cyclohexane were measured at 95.3 kPa using a

Swietoslawski ebulliometer. The VLE data of acetophenone with both the binary systems under study showed no azeotropic point at the pressure of 95.3 over the entire composition range. The experimental VLE data for both the binary mixtures were correlated by the NRTL, UNIQUAC, UNIFAC and VAN LAAR models. Thermodynamic consistencies of both the binary mixtures were checked by using Herington's test. Our results indicate that both the binary systems were non-ideal liquid mixtures deviating from Raoult's law. Also, observed results suggest that both the binary systems exhibit positive values of excess Gibbs energy due to dispersion forces and geometrical mismatching between the unlike molecules.

#### Acknowledgments

One of the authors, K. Rayapa Reddy wishes to thank Latifa Negadi, for her help in calculations and suggestions.

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