



# ISOBARIC VAPOUR-LIQUID EQUILIBRIUM DATA OF THE SYSTEM ISOPROPANOL-METHYL ISOBUTYL KETONE AT (101.32, 66.67, AND 40.00 ± 0.02) KPa

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## ABSTRACT

Isobaric vapour-liquid equilibrium (VLE) data for the isopropanol - methyl isobutyl ketone system has been measured experimentally at (101.32, 66.67, and 40.00 ± 0.02) kPa. Consistency of the experimental results has been checked by Redlich-Kister, Broughton-Brearley, Black and Herington test methods. The equilibrium data was compared with UNIFAC and Margules models, two classical methods which have different calculation mechanism and which are methods widely used in this field. The results were illustrated as diagrams and tables, and the experimental data were contrasted with the calculated by evaluating the deviations. It was seen that the models exhibited an ineligibility with the experimental data, especially at low pressures, probably because of the insufficient pressure sensivity of the used model equations.

**Key Words** : Vapour-Liquid Equilibrium, UNIFAC, Margules, Activity Coefficient

## İZOPROPANOL-METİL İZOBUTİL KETON SİSTEMİNİN (101.32, 66.67 VE 40.00 ± 0.02) KPa BASINÇLARDAKİ İZOBARİK SIVI-BUHAR DENGE VERİLERİ

## ÖZET

Izopropanol - metilsikloheksan sistemine ait izobarik sıvı-buhar denge verileri (101.32, 66.67 ve 40.00 ± 0.02) kPa basınçlarda deneysel olarak elde edilmiştir. Deneysel verilerin tutarlılığı Redlich-Kister, Broughton-Brearley, Black and Herington test yöntemleriyle sınanmıştır. Denge verileri, bu alanda sıkça kullanılan ve farklı hesaplama yollarına sahip iki klasik metod olan UNIFAC ve Margules yöntemlerinden elde edilen verilerle karşılaştırılmıştır. Sonuçlar tablolar ve grafikler halinde sunulmuş, sapmalar değerlendirilmek suretiyle deneysel ve hesaplama sonuçları arasındaki farklar vurgulanmıştır. Muhtemelen model denklemlerin yetersiz basınç hassasiyeti dolayısıyla, elde edilen verilerin özellikle düşük basınçlarda, deneysel verilerden sapma gösterdiği görülmüştür.

**Anahtar Kelimeler** : Sıvı-Buhar dengesi, UNIFAC, Margules, Aktivite katsayısı

## 1. INTRODUCTION

Models to estimating activity coefficients provide the process engineer for predicting equilibrium conditions required in distillation column design. For cost-effective and energy efficient distillation columns, the VLE data must be achieved accurately and rapidly for different material combinations and at different operating conditions (isobaric or

isothermal). It is sophisticated and time consuming to get these data in experimental ways. Therefore, many calculation methods have been improved by different scientist to describe the mechanism of phase equilibrium. There are two types of prediction methods used in this field. The first group are the group contribution methods based on local compositions, such as Wilson, NRTL, UNIQUAC, UNIFAC, ASOG. Some of them such as UNIFAC-

Lyngby (Larsen et al., 1987), UNIFAC-Dortmund (Gmehling et al., 1993) and UNIQUAC-A (Fu et al., 1995) models were modified for special cases. The second group of estimation methods are the Margules and van Laar type equations which are empirical models of solution behaviour derived from the extrapolation of Gibbs Energy function (Smith and Van Ness, 1988; Kyle, 1992). These models stated above represent the excess Gibbs energy function in different type of mathematical expressions and were used both in vapour-liquid and liquid-liquid equilibrium calculations.

The aim of this work is to show the behaviour of the UNIFAC (Fredenslund, 1977a) and Margules (Kyle, 1992) models at low pressures for the system isopropanol - methyl isobutyl ketone. The activity coefficients ( $\gamma_1, \gamma_2$ ), vapour phase compositions ( $y_1$ ) and equilibrium temperatures (T) for each system were determined in isobaric conditions experimentally at (101.32, 66.67, and  $40.00 \pm 0.02$ ) kPa and furthermore predicted by models. The main occasion for selecting this models was the difference of the calculation mechanisms. The UNIFAC model is a group contribution method based on local compositions and Margules model is an empirical model of solution behaviour derived from the extrapolation of Gibbs Energy function, and both represents the two type of calculation methods, as mentioned above.

## 2. THERMODYNAMIC BASIS

For any vapour-liquid system in equilibrium we write from the equality of fugacities of pure components

$$y_i \cdot \hat{\phi}_i \cdot P = x_i \cdot \gamma_i \cdot f_i^0 \quad (1)$$

Where  $y_i$  is the mol fraction of component  $i$  in vapour phase,  $x_i$  is the mol fraction in liquid phase,  $\hat{\phi}_i$  is the fugacity coefficient of  $i$  in the vapour phase,  $P$  is the total pressure,  $\gamma_i$  is the activity coefficient of  $i$  in the liquid phase and  $f_i^0$  is the standard-state fugacity of the pure  $i$  component. The standard-state fugacity is here taken as the fugacity of pure liquid  $i$  ( $f_i$ ) at system temperature and pressure and is given by

$$f_i = P_i^S \hat{\phi}_i^S \exp\left(\frac{V_i^L(P - P_i^S)}{RT}\right) \quad (2)$$

Where, for pure liquid,  $P_i^S$  is the saturation (vapour) pressure,  $\hat{\phi}_i^S$  is the fugacity coefficient at saturation

and  $V_i^L$  is the molar liquid volume, all at temperature  $T$ . The exponential is known as the Poynting factor. Substituting the Eq. (1) for  $f_i$  by Eq. (2) and solving for  $\gamma_i$  gives

$$\gamma_i = \frac{y_i \cdot \hat{\phi}_i \cdot P}{x_i \cdot P_i^S} \quad (3)$$

where

$$\hat{\phi}_i = \frac{\hat{\phi}_i^A}{\hat{\phi}_i^S} \cdot \exp\left[-\frac{V_i^L(P - P_i^S)}{RT}\right] \quad (4)$$

At low pressures, vapour phases usually approximate ideal gases, for which  $\hat{\phi}_i^A = \hat{\phi}_i^S = 1$  and the Poynting factor, represented by the exponential, differs from unity by only a few parts per thousand and their influence in Eq. (4) tends to cancel. Thus the assumption that  $\hat{\phi}_i = 1$  introduces little error for low-pressure VLE data and the Eq. (3) reduces to:

$$\gamma_i = \frac{y_i \cdot P}{x_i \cdot P_i^S} \quad (5)$$

## 3. EXPERIMENTAL

Isopropanol and methyl isobutyl ketone were used in Merck quality. An all-glass dynamic recirculating vapour-liquid equilibrium apparatus developed by Fischer Scientific Co. equipped with temperature and pressure controllers were used in the equilibrium determinations. The still allows good mixing and flowing of both vapour and liquid phases through an extended contact line, which guaranties an intense phase exchange and their separation once the equilibrium is reached. The equilibrium temperature was measured using a mercury glass thermometer (Fischer certificated) within an accuracy of  $\pm 0.05$  K. The temperature control of heating was achieved by a digital thermometer provided with a Pt-100 sensor. The total pressure of the system was controlled by an electronic manometer. The VLE tests were run at 101.32, 66.67 and  $40.00 \pm 0.02$  kPa pressures. The equilibrium conditions were checked by the reproducibility of the results of GC analysis of liquid samples taken from two phases.

The experimental procedure on the equilibrium apparatus, was performed as follows: Approximately 100 mL isopropanol was put in the boiler of the apparatus. The pressure was set for a defined value via a controller and the heaters were then actuated. Reaching to the boiling point, the

equilibrium temperature of the pure isopropanol was determined. After that, 2-2.5 mL methyl isobutyl ketone was added to the boiler and waited for the equilibrium conditions. The attainment of a constant temperature for about 1 h was the sign of equilibrium reached. In equilibrium, samples were taken from liquid and condensed vapour phases for analysing with GC. Thus in a known pressure (P), the liquid and vapour phase compositions ( $x_1$ ,  $x_2$ ,  $y_1$ ,  $y_2$ ) of a mixture at the equilibrium temperature (T) were determined experimentally. By adding a few mL methyl isobutyl ketone in each time and continuing this procedure, the equilibrium data of the methyl isobutyl ketone enriched mixtures were determined as well. Finally, the boiling point for pure methyl isobutyl ketone was determined.

Samples withdrawn from the liquid and condensed vapour phases were analysed with a Hewlett-Packard GC Analyser, model HP-6890, equipped with FI detector and coupled with HP Chem-Station software. An innowax (PEG) capillary column, 30m

x 320  $\mu\text{m}$  x 0.5  $\mu\text{m}$  in size was used to separate the compounds at tailorized oven programs available for each binary system studied. Nitrogen was used as carrier gas at a flow rate of 0.8  $\text{mL}\cdot\text{min}^{-1}$ . All injections were performed on the split rate of 5/1. The GC was calibrated with gravimetrically prepared standard solutions to convert the peak area to the mole fraction composition. Mole fractions were accurate to better than  $\pm 0.002$ .

## 4. RESULTS AND DISCUSSION

Table 1 presents the experimental T-  $x_1$  -  $y_1$  vapour-liquid equilibrium values and the activity coefficients,  $\gamma_1$  and  $\gamma_2$ , calculated using the Eq. (5) in which the vapour phase is assumed as ideal gas, at (40, 66.67 and 101.32  $\pm$  0.02) kPa. The pure component vapour pressures,  $P_i^S$ , were estimated through the Antoine equation using the constants  $A_i$ ,  $B_i$ , and  $C_i$  given in Table 2.

Table 1. Experimental Vapour-Liquid Equilibrium Data. Boiling Temperature T, Liquid Phase Mole Fraction x, Vapour Phase Mole Fraction y and Activity Coefficient  $\gamma$

T (K)	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	T (K)	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
Isopropanol (1) - Methyl isobutyl ketone (2) at (101.32 $\pm$ 0.02) kPa									
355.55	0.9564	0.9726	1.0107	1.7800	368.55	0.2810	0.6081	1.3331	1.0021
356.05	0.9151	0.9488	1.0108	1.6753	370.95	0.2107	0.5395	1.4504	0.9952
357.25	0.8191	0.9050	1.0289	1.3993	374.05	0.1720	0.4750	1.4076	0.9836
358.35	0.7369	0.8718	1.0566	1.2504	375.75	0.1402	0.4002	1.3748	1.0280
359.65	0.6691	0.8349	1.0612	1.2256	377.85	0.1084	0.3621	1.5011	0.9904
361.85	0.5237	0.7778	1.1639	1.0650	379.15	0.0913	0.3053	1.4399	1.0187
362.15	0.5017	0.7690	1.1882	1.0477	382.95	0.0461	0.1827	1.5099	1.0233
364.95	0.3776	0.6916	1.2823	1.0217	384.35	0.0333	0.1340	1.4696	1.0282
Isopropanol (1) - Methyl isobutyl ketone (2) at (66.67 $\pm$ 0.02) kPa									
346.70	0.9333	0.9568	0.9658	1.6887	355.95	0.3003	0.6277	1.3613	0.9946
347.00	0.8863	0.9365	0.9832	1.4394	357.35	0.2424	0.5770	1.4695	0.9944
347.30	0.8611	0.9208	0.9829	1.4522	360.15	0.1805	0.5115	1.5742	0.9652
347.90	0.7967	0.8915	1.0036	1.3294	364.25	0.1181	0.4048	1.6369	0.9541
348.70	0.7277	0.8656	1.0325	1.1943	365.15	0.1050	0.3683	1.6210	0.9690
349.55	0.6263	0.8240	1.1033	1.1047	368.05	0.0646	0.2713	1.7499	0.9745
350.75	0.5581	0.7878	1.1278	1.0789	371.65	0.0283	0.1463	1.9030	0.9817
351.65	0.5089	0.7551	1.1438	1.0846	372.15	0.0192	0.1288	2.4249	0.9774
352.85	0.4316	0.7253	1.2351	1.0073	373.15	0.0110	0.0729	2.3074	1.0003
354.05	0.3550	0.6779	1.3388	0.9976					
Isopropanol (1) - Methyl isobutyl ketone (2) at (40.00 $\pm$ 0.02) kPa									
335.50	0.8985	0.9314	0.9594	1.6619	344.50	0.1989	0.5978	1.8811	0.8669
336.00	0.8270	0.8945	0.9789	1.4689	346.15	0.1739	0.5630	1.8914	0.8583
336.45	0.7892	0.8791	0.9879	1.3572	347.15	0.1372	0.5323	2.1738	0.8475
337.45	0.6583	0.8265	1.0651	1.1539	348.05	0.1101	0.4859	2.3828	0.8736
338.45	0.5941	0.7937	1.0845	1.1098	349.25	0.1031	0.4673	2.3311	0.8593
338.60	0.5038	0.7689	1.2306	1.0111	349.65	0.0833	0.3868	2.3503	0.9537
340.35	0.3906	0.7236	1.3839	0.9190	351.65	0.0726	0.3655	2.3493	0.9075
339.85	0.4824	0.7721	1.2219	0.9099	351.85	0.0698	0.3299	2.1901	0.9485
340.50	0.3803	0.7127	1.3913	0.9336	353.25	0.0568	0.2792	2.1536	0.9572
342.25	0.3523	0.7005	1.3688	0.8702	355.50	0.0362	0.1869	2.0744	0.9762
342.45	0.3299	0.6669	1.3799	0.9283	356.65	0.0203	0.1308	2.4698	0.9865
344.25	0.2698	0.6264	1.4683	0.8918	357.70	0.0153	0.0877	2.1149	0.9935

Table 2. The Constants of the Antoine Equation for Pure Component Vapour Pressure<sup>a</sup>

Compound	A <sub>i</sub>	B <sub>i</sub>	C <sub>i</sub>
Isopropanol	18.6929	3640.20	-53.54
Methyl isobutyl ketone	15.7165	2893.66	-70.75

<sup>a</sup> : (Reid et. al., 1987);  $\ln(P_i^S / \text{mmHg}) = A_i - B_i / (C_i + T / K)$

Table 3. Results of Consistency Tests Applied to Binary Mixture

System Pressure (kPa)	Redlich-Kister test <sup>a</sup> (area)	Broughton-Brearely test <sup>b</sup> (area)   A-B	Black test <sup>c</sup> (R <sup>2</sup> )	Herington test <sup>d</sup>   D-J
101.32	0.0045	2.81	0.9058	8.02
66.67	0.0406	15.82	0.8744	16.59
40.00	0.0776	27.47	0.7706	31.03

<sup>a</sup> : Consistency criterion is  $\int_0^1 \log(\gamma_1 / \gamma_2) dx_1 = 0$  (Redlich and Kister, 1948)

<sup>b</sup> : A and B are the areas above and below the x-axis of the plot T-log( $\gamma_1/\gamma_2$ ) versus  $x_1$ , respectively

<sup>c</sup> : Consistency criterion is a straight line of the plot  $(\log \gamma_1)^{0.5}$  versus  $(\log \gamma_2)^{0.5}$ ; R = regression coefficient (Van Winkle, 1967)

<sup>d</sup> :  $D=100 |A-B| / (A+B)$ ;  $J=150 |T_{\max}-T_{\min}| / T_{\min}$ ; A and B are the areas above and below the x-axis of the plot  $\log(\gamma_1/\gamma_2)$  versus  $x_1$ , respectively;  $|D-J| < 10$  is the criterion for consistency (Herington, 1951).

Table 4. Mean Deviations Between Experimental and Calculated VLE Data For Isopropanol – Methyl isobutyl ketone System

System Pressure (kPa)	$\overline{\Delta Y_i}$ , Margules			$\overline{\Delta Y_i}$ , UNIFAC		
	$\gamma_1$	$\gamma_2$	$y_1$	$\gamma_1$	$\gamma_2$	$y_1$
101.32	0.0388	0.0389	0.0069	0.1243	0.1076	0.0232
66.67	0.1993	0.0740	0.0243	0.0935	0.1439	0.0104
40.00	0.5767	0.1097	0.0844	0.2020	0.1541	0.0406

The thermodynamic consistency of the data was evaluated in terms of the area tests of Redlich-Kister, Broughton-Brearely, and Herington test methods, as well as with Black test, assuming the excess enthalpy term turned out to be virtually negligible. The consistency tests of various versions give similar results. All the mixtures in vacuum proved to be more inconsistent than the mixtures in atmospheric pressure. The results of the test methods are reported in Table 3.

The observed values of activity coefficients,  $\gamma_i$  and the vapour phase composition,  $y_i$ , were compared with estimates obtained from the group contribution method UNIFAC and the Margules method. Table 4 presents a quantitative assessment of the predictions achieved for each method with respect to mean deviation of the activity coefficients and vapour phase compositions. Mean deviation taken as described elsewhere (Fredenslund, et al., 1977b), is shown in Eq. 6.

$$\text{Mean deviation} = \overline{\Delta Y_i} = \sum_{k=1}^n |Y_{i,k}(\text{exptl}) - Y_{i,k}(\text{calcd})| / n \quad (6)$$

The convenience of the calculation methods were also studied through a plot of observed  $\gamma_i$ , and  $y_i$  values against the estimates (Figures 1, 2, 3, 4, 5, and 6).

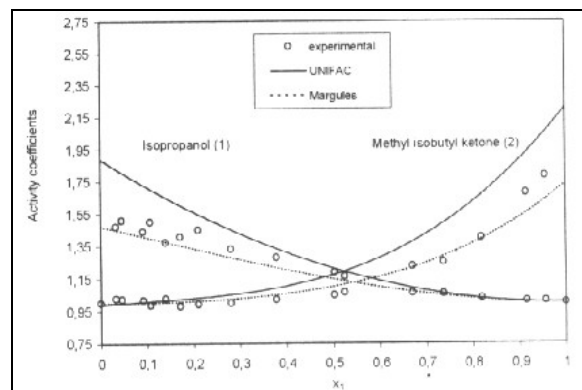


Figure 1. Comparison of Calculated and Experimental Activity Coefficients at 101.32 kPa, Isopropanol + Methyl isobutyl ketone

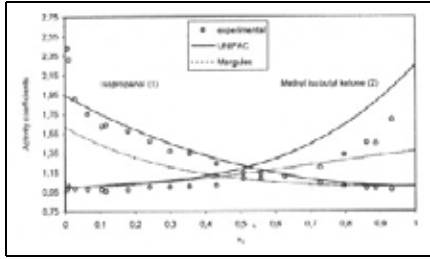


Figure 2. Comparison of Calculated and Experimental Activity Coefficients at 66.67 kPa, Isopropanol + Methyl isobutyl ketone

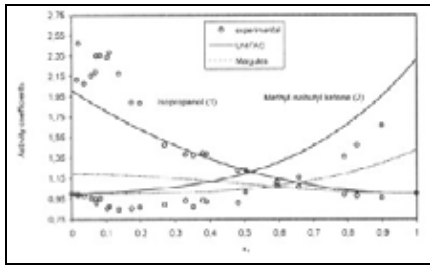


Figure 3. Comparison of Calculated and Experimental Activity Coefficients at 40.00 kPa, Isopropanol + Methyl isobutyl ketone

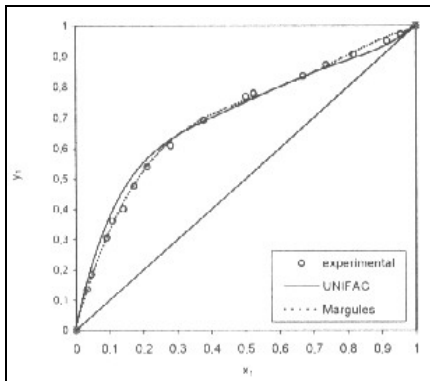


Figure 4. Comparison of Calculated and Experimental Vapour Phase Compositions at 101.32 kPa, Isopropanol + Methyl isobutyl ketone

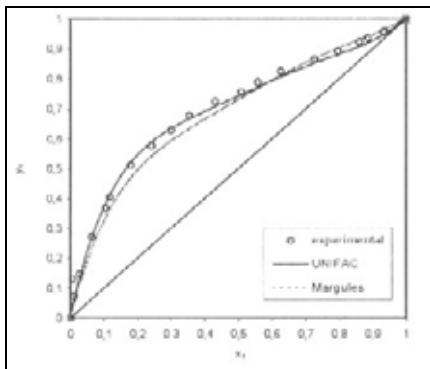


Figure 5. Comparison of Calculated and Experimental Vapour Phase Compositions at 66.67 kPa, Isopropanol + Methyl isobutyl ketone

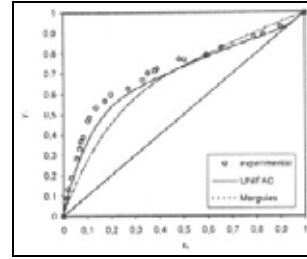


Figure 6. Comparison of Calculated and Experimental Vapour Phase Compositions at 40.00 kPa, Isopropanol + Methyl isobutyl ketone.

It was seen that at low pressures, the activity coefficients show an irregularity in limit compositions, especially by the isopropanol, probably because of the limiting activity coefficient effect. The limiting activity coefficient characterises the behaviour of a single solute molecule completely surrounded by solvent. As such, it generally indicates a maximum nonideality since the order-disorder effect disappears (Eckert et al., 1981).

Consequently, the Margules model indicated a good agreement with the observed data at atmospheric pressure (101.32 kPa). Decreasing the pressure, the Margules model do not track well the observed values with high deviations. In UNIFAC method, despite the pressure is taken care indirectly through the temperature, it is seem to be insufficient. A general method, that have a potent means to deal with pressure, must be studied.

## 5. NOMENCLATURE

- $f_i$  : Fugacity of pure liquid  $i$  at system temperature and pressure
- $f_i^0$  : Standard-state fugacity of the pure component  $i$
- $P$  : Pressure (kPa)
- $P_i^S$  : Saturation (vapour) pressure of pure liquid  $i$
- $T$  : Temperature (K)
- $V_i^L$  : Molar liquid volume of pure component  $i$
- $x_i$  : Molar fraction of component  $i$  in liquid phase
- $Y_i$  : Mol fraction of component  $i$  in vapour phase
- $\overline{\Delta Y_i}$  : Mean deviation
- $\phi_i^S$  : Fugacity coefficient of pure component  $i$  at saturation
- $\hat{\phi}_i$  : Fugacity coefficient of component  $i$  in the vapour phase
- $\gamma_i$  : Activity coefficient of  $i$  in the fluid phase

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