

Developing a Thermodynamical Method for Prediction of Activity Coefficient of TBP Dissolved in Kerosene

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ABSTRACT

Results of the experimental measurements on the partial molar volume of kerosene used as a medium for dissolving TBP are utilized to determine the activity of TBP in the binary kerosene-TBP solution through the application of Gibbs-Duhem equation. The treatment is based on combination of the experimental data with the thermodynamic values available on the compressibility factor of pure kerosene at room temperature. It is shown that the activity of TBP in kerosene has a positive deviation from ideality with an activity coefficient derived as follows: 1) at $X_{\text{TBP}} \leq 0.01$:

$$\gamma_{\text{TBP}} = 42.530, \quad 2) \text{ at the } 0.01 < X_{\text{TBP}} < 0.2 : \ln \gamma_{\text{TBP}} = \frac{0.2913 - 0.2843 X_{\text{kerosene}}}{1 - 1.8674 X_{\text{kerosene}} + 0.8687 X_{\text{kerosene}}^2} \quad 3) \text{ at higher TBP concen-}$$

$$\text{trations } 0.2 < X_{\text{TBP}} < 0.97 : \ln \gamma_{\text{TBP}} = \frac{-0.0146 + 1.2826 X_{\text{kerosene}}}{1 + 1.5595 X_{\text{kerosene}} - 1.9594 X_{\text{kerosene}}^2} \quad \text{and 4) at TBP Raoultian concentrations}$$

$0.97 \leq X_{\text{TBP}} : \gamma_{\text{TBP}} = 1$. These quantities can be utilized at temperature closed to 298 K.

Keywords: Thermodynamics; Activity; Activity Coefficient; Kerosene; TBP; Organic Solution

1. Introduction

Activities of the species dissolved in organic aromatic solutions are of the important information required for understanding of the thermodynamics of the solvent extraction regimes usually utilized in production of the nonferrous metals. It has been reported that the activity coefficients of involved components in the extraction reaction of metals during extraction processes are usually equal to one [1-10]. However, the activities in the real component values are significantly different from the ideal state. The activity coefficient of components (especially components in aqueous media) was estimated by using some conventional thermodynamic models such as Debye-Hückel or Pitzer Equation [11]. On the other hand, due to the physicochemical interaction of organic components, the mathematical models could be used in some special cases. By applying the correct value of the activity coefficients in the extraction equations, a correct mathematical model can predict an acceptable value for extracted metals.

The thermodynamic evaluation of the distribution ratio of metals, for instance, becomes much easier if the activity of coefficient tri-n-butyl phosphate (TBP) dissolved in kerosene becomes precisely known. There is, however, no data available in the literature on the activity coefficient of different species dissolved in such aromatic or aliphatic solutions as kerosene.

TBP is a common organic material which uses as extractant and/or modifier in the presence of some aliphatic diluents such as kerosene. Therefore, developing an analytical method for the prediction of the activity coefficients of organic component could be useful for future investigations. In this paper, an analytical method for determination of the activity and the activity coefficient of TBP dissolved in kerosene is developed and presented.

2. Thermodynamical Parameters and Prediction of the Activity and the Activity Coefficients

It is shown that the excess partial molar Gibbs free

energy of the species i depends on the composition of the solution. The difference between the partial molar Gibbs free energy of the species i and the molar Gibbs free energy of pure i is the change in the Gibbs free energy accompanying the formation of one mole of i dissolved in the solution; $\Delta\bar{G}_i^S$ [12-15]. Thus:

$$\Delta\bar{G}_i^S = RT \ln a_i = RT \ln(\gamma_i X_i) = RT (\ln \gamma_i + \ln X_i) \quad (1)$$

on the other hand:

$$d(\Delta\bar{G}_i^S) = -\Delta\bar{S}_i^S dT + \Delta\bar{V}_i^S dP \quad (2)$$

where $\Delta\bar{S}_i^S$ and $\Delta\bar{V}_i^S$ are the partial molar entropy and the partial volume change of the dissolution reaction, respectively. In the isothermal condition, Equation (2) is rewritten as:

$$d(\Delta\bar{G}_i^S) = \Delta\bar{V}_i^S dP \quad (3)$$

The molar volume of a multi component solution is defined by:

$$\bar{V}^S = \sum_{i=1}^n X_i \bar{V}_i^S \quad (4)$$

The molar volume of the mechanical mixture can similarly be defined by:

$$V^\circ = \sum_{i=1}^n X_i V_i^\circ \quad (5)$$

The volume change due to the formation of the solution is, thus, given by:

$$\Delta\bar{V}^S = \bar{V}^S - V^\circ = \sum_{i=1}^n X_i (\bar{V}_i^S - V_i^\circ) \quad (6)$$

The value of ΔV^S for a binary solution, which exhibits negative deviation from ideality, is less than zero. Based on known thermodynamic relationships available [12-15], the volume change of the species A in a binary A-B system can be obtained from:

$$\Delta\bar{V}_A^S = \Delta\bar{V}^S + \left[\frac{\partial(\Delta\bar{V}^S)}{\partial X_A} \right]_{T,P} X_B \quad (7)$$

Also, the isothermal compressibility of a substance, or a system, is defined as:

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (8)$$

This is the fractional decrease in the volume of the system for unit increase in pressure at constant temperature. For pure A, the isothermal compressibility is defined as:

$$\beta_{A^\circ} = -\frac{1}{V_A^\circ} \left(\frac{\partial V_A^\circ}{\partial P} \right)_T \quad (9)$$

and for species A of the binary solution:

$$\beta_A = -\frac{1}{\bar{V}_A} \left(\frac{\partial \bar{V}_A}{\partial P} \right)_T \quad (10)$$

if we assume that:

$$\beta_{A^\circ} = \beta_A \quad (11)$$

then from Equations (9) and (10):

$$-\frac{1}{V_A^\circ} \left(\frac{\partial V_A^\circ}{\partial P} \right)_T = -\frac{1}{\bar{V}_A} \left(\frac{\partial \bar{V}_A}{\partial P} \right)_T \quad (12)$$

hence at a constant temperature, we have:

$$\frac{\partial V_A^\circ}{V_A^\circ} = \frac{\partial \bar{V}_A}{\bar{V}_A} \quad (13)$$

or:

$$\frac{\partial V_A^\circ}{\partial \bar{V}_A} = \frac{V_A^\circ}{\bar{V}_A} \quad (14)$$

and also:

$$\frac{\partial V_A^\circ}{\partial \bar{V}_A - \partial V_A^\circ} = \frac{V_A^\circ}{\bar{V}_A - V_A^\circ} \quad (15)$$

or:

$$\frac{\partial V_A^\circ}{\partial(\Delta\bar{V}_A^S)} = \frac{V_A^\circ}{\Delta\bar{V}_A^S} \quad (16)$$

then:

$$-\frac{1}{V_A^\circ} \left(\frac{\partial V_A^\circ}{\partial P} \right)_T = -\frac{1}{\Delta\bar{V}_A^S} \left(\frac{\partial(\Delta\bar{V}_A^S)}{\partial P} \right)_T \quad (17)$$

hence:

$$\beta_A = -\frac{1}{\Delta\bar{V}_A^S} \left[\frac{\partial(\Delta\bar{V}_A^S)}{\partial P} \right]_T \quad (18)$$

At a constant temperature, Equation (18) can be rearranged as:

$$dP = -\frac{d(\Delta\bar{V}_A^S)}{\beta_A \Delta\bar{V}_A^S} \quad (19)$$

by substituting the value of (dP) from Equation (19) into Equation (3), we have:

$$d(\Delta\bar{G}_A^S) = -\frac{d(\Delta\bar{V}_A^S)}{\beta_A} \quad (20)$$

and from Equation (1), we obtain:

$$d(\ln a_A) = -\frac{d(\Delta\bar{V}_A^S)}{RT \beta_A} \quad (21)$$

Integrating Equation (21) from the initial condition where $X_A = 1$ and $\Delta\bar{V}_A^S = 0$, one can write:

$$\int_{\ln a_A \text{ at } X_A=1}^{\ln a_A \text{ at } X_A} d(\ln a_A) = \int_{\Delta \bar{V}_A^S \text{ at } X_A=1}^{\Delta \bar{V}_A^S \text{ at } X_A} -\frac{d(\Delta \bar{V}_A^S)}{RT\beta_A} \quad (22)$$

or:

$$\ln a_A = \int_0^{\Delta \bar{V}_A^S} -\frac{d(\Delta \bar{V}_A^S)}{RT\beta_A} \quad (23)$$

The value of the right hand side at Equation (23) can graphically be obtained by plotting the quantity of

$\frac{1}{RT\beta_A}$ vs $\Delta \bar{V}_A^S$, and determining the area under the curve. The activity coefficient of the species A of binary solution can thus be obtained from:

$$\gamma_A = \frac{a_A}{X_A} \quad (24)$$

The activity coefficient of the second component of the solution can be determined by integration the Gibbs-Duhem equation [12-15]:

$$\int_{\ln \gamma_B \text{ at } X_B=1}^{\ln \gamma_B \text{ at } X_B} d(\ln \gamma_B) = \int_{\ln \gamma_A \text{ at } X_B=1}^{\ln \gamma_A \text{ at } X_B} -\frac{X_A}{X_B} d(\ln \gamma_A) \quad (25)$$

At the boundary condition where X_B and γ_B are equal to one, γ_A equals to γ_A° , thus:

$$\ln \gamma_B = \int_{\ln \gamma_A}^{\ln \gamma_A^\circ} -\frac{X_A}{X_B} d(\ln \gamma_A) \quad (26)$$

The activity of species B is, thus, determined from:

$$a_B = X_B \gamma_B \quad (27)$$

3. Material and Methods

Both TBP and kerosene, which were used, were of analytical grade from Fluka AB., Switzerland. Small quantity of TBP weighted with a mettler 240 balance system was added to a calibrated 100-ml. Kerosene was instilled to the 100-ml flask and the solution was mixed thoroughly. The solution was then retained for five to ten minutes to absorb the required heat for reaching to chemical equilibrium. The total weight of the solution was then measured.

The experiments were carried out at constant room temperature (298 K). The molecular weight of the pure TBP was equal to 263.32 gr/mole. The molecular weight of the used kerosene was determined by the gas chromatography and the change of the melting point methods. In the latter, the melting temperature change was measured by analytical grade phenol with a molecular weight of 94.11 gr/mole. The molecular weight of kerosene was the determined from [16,17]:

$$\ln X_{\text{phenol}} = -\frac{1000\Delta H_{f,\text{phenol}}^\circ \Delta T}{M_{\text{phenol}} RT_{m,\text{phenol}} m} \quad (28)$$

where X_{phenol} is mole fraction of phenol in dilute phenol-kerosene solution, $\Delta H_{f,\text{phenol}}^\circ$ is the latent heat of melting of phenol in its melting point $T_{m,\text{phenol}}$, ΔT is the change of melting point of solution when the molality of kerosene in dilute solution is m and M_{phenol} is the molecular weight of phenol. The result was equal to 173.3 gr/mole.

With the experimental data, the integral molar volume of the solution (\bar{V}^S) and the integral molar volume change of the solution ($\Delta \bar{V}^S$) were determined from Equations (4) and (6). a_{kerosene} (Equation (23)), γ_{kerosene} (Equation (24)), γ_{TBP} (Equation (26)) and a_{TBP} (Equation (27)) were then evaluated.

4. Results and Discussion

There is not much known of the physical properties of TBP. Determination of the activity and the activity coefficient of TBP is, therefore, derived from the corresponding quantities for kerosene. The isothermal compressibility of kerosene at 298 K and 1 atm pressure is known to be $1.45 \times 10^{-4} \text{ atm}^{-1}$ [18]. Applying this value to Equation (23), the activity of kerosene is, therefore, being determined.

Figure 1 shows the integral molar volume of the binary kerosene-TBP solution as a function of the kerosene mole fraction; X_{kerosene} . As shown in this figure, the integral molar volume of the solution has a positive deviation from the ideal behavior (dashed line). This quantity is defined by Equation (4). **Figure 2** illustrates the relative molar volume of the binary solution ($\Delta \bar{V}^S$) versus kerosene mole fraction. It is seen from this figure that, the molar volume of the formation of the binary solution has a positive deviation from ideality and has a maximum near $X_{\text{kerosene}} = 0.45$. The predicted value of the

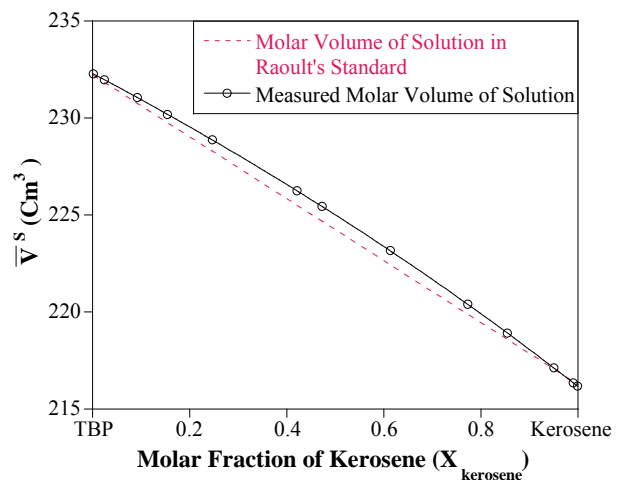


Figure 1. The integral molar volume of TBP-kerosene binary solution as a function of measured X_{kerosene} at room temperature.

volume change has a correlation with the experimental data:

$$\Delta \bar{V}^S = 1.75X_{\text{kerosene}} - 3.49X_{\text{kerosene}}^{2.5} + 1.24X_{\text{kerosene}}^3 + 0.46X_{\text{kerosene}}^{0.5} \tag{29}$$

The molar volume change of the kerosene dissolved in the binary solution is determined from Equation (7) as a function of X_{kerosene} . **Figure 3** illustrated the partial molar volume change of kerosene ($\Delta \bar{V}_{\text{kerosene}}^S$) as a function of X_{kerosene} . The partial molar volume changes of the kerosene in the pure TBP ($X_{\text{kerosene}} = 0$) and in the pure kerosene ($X_{\text{kerosene}} = 1$) are equal to infinity and zero, respectively.

Based on Equation (14), the activity of kerosene can be determined by using a graphical method. **Figure 4**

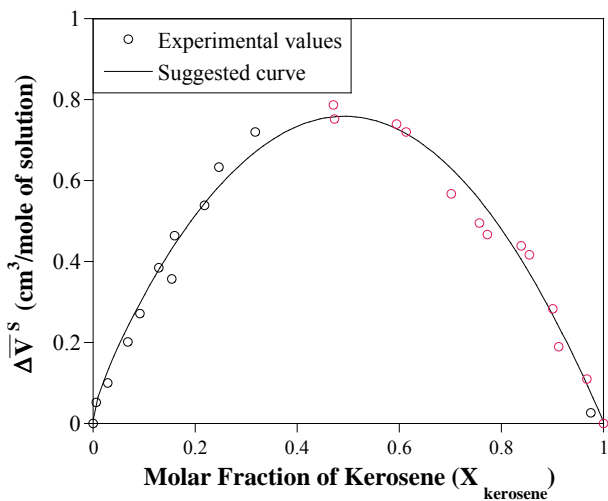


Figure 2. The relative integral molar volume of the kerosene-TBP solution versus the solution composition.

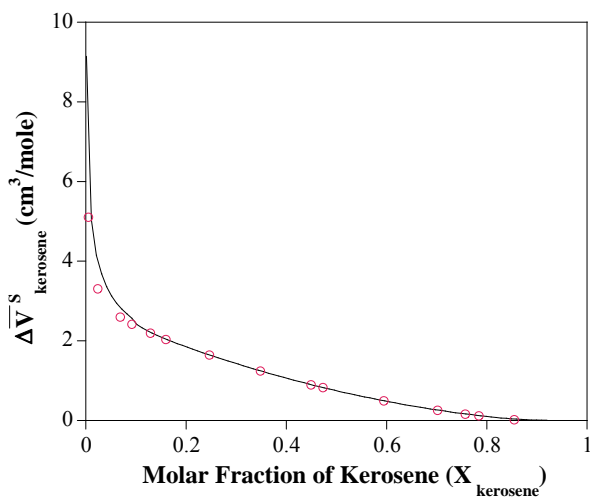


Figure 3. The relative partial molar volume of kerosene as a function of composition.

illustrates that the change of $-1/RT\beta_{\text{kerosene}}$ vs $\Delta \bar{V}_{\text{kerosene}}^M$ at the constant temperature 298°K. We have assumed that the isothermal compressibility constant of the kerosene at every composition of binary solution is constant and that the compositional change has no significant effect on its value. So the activity of the kerosene is determined from the area under the curve plotted in **Figure 4**, as was stated by Equation (23). The results are given in **Figure 5** (solid line). As shown in this figure, the activity of the kerosene indicates a very positive deviation from ideality, especially at low concentrations. A curve fitting method can be used to determine the activity of the kerosene at

$$X_{\text{kerosene}} < 0.03$$

$$a_{\text{kerosene}} = 213.045 - 213.045X_{\text{TBP}} = 213.045X_{\text{kerosene}} \tag{30}$$

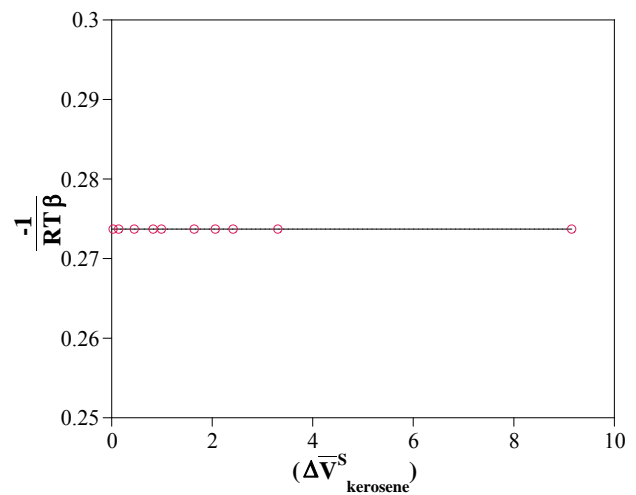


Figure 4. The value of $-1/RT\beta_{\text{kerosene}}$ vs molar volume change of kerosene in binary kerosene-TBP solution.

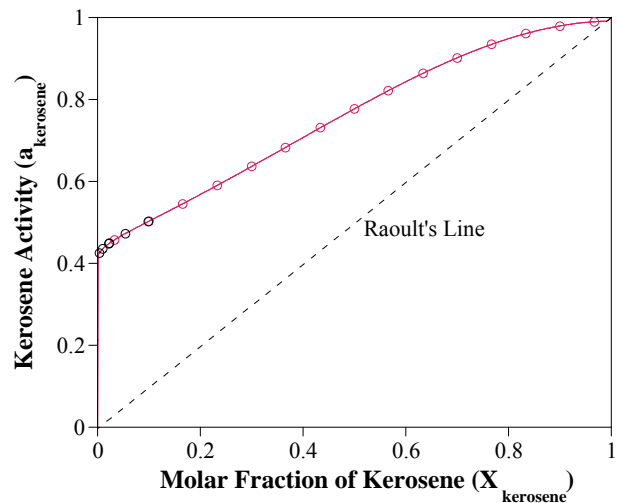


Figure 5. Activity of kerosene as a function of composition of the solution.

and at the higher kerosene concentration, the activity of kerosene is determined by:

$$a_{\text{kerosene}} = \frac{0.993 - 1.210X_{\text{TBP}} + 0.23087X_{\text{TBP}}^2 - 0.002X_{\text{TBP}}^3}{1 - 1.169X_{\text{TBP}} + 1.068X_{\text{TBP}}^2 - 0.870X_{\text{TBP}}^3} \quad (31)$$

The activity coefficient of kerosene is determined from Equation (24). **Figure 6** shows the change of γ_{kerosene} as a function of X_{kerosene} . With the method of curve fitting, the activity coefficient of the kerosene at $0.03 < X_{\text{kerosene}} < 0.2$ is determined by:

$$\ln \gamma_{\text{kerosene}} = \frac{0.2796 - 0.5576X_{\text{TBP}} + 0.2784X_{\text{TBP}}^2}{1 - 2.9145X_{\text{TBP}} + 2.8292X_{\text{TBP}}^2 - 0.9146X_{\text{TBP}}^2} \quad (32)$$

at the higher kerosene concentrations ($0.2 < X_{\text{kerosene}} < 0.99$), the activity coefficient of kerosene is determined by:

$$\ln \gamma_{\text{kerosene}} = \frac{-0.0006 - 0.1858X_{\text{TBP}}}{1 - 1.8296X_{\text{TBP}} + 1.1551X_{\text{TBP}}^2} \quad (33)$$

The Henry's constant for the kerosene ($\gamma_{\text{kerosene}}^\circ$) is determined by:

$$\gamma_{\text{kerosene}}^\circ = \lim_{X_{\text{kerosene}} \rightarrow 0} \gamma_{\text{kerosene}} = \lim_{X_{\text{kerosene}} \rightarrow 0} \frac{a_{\text{kerosene}}}{X_{\text{kerosene}}} = 214.35 \quad (34)$$

The Gibbs-Duhem Equation and its results (Equations (23) and (26)) help to determine the activity coefficient of the TBP with a graphical method. **Figure 7** shows the value of $\frac{X_{\text{kerosene}}}{X_{\text{TBP}}}$ vs $\ln \gamma_{\text{kerosene}}$. The results of the

calculations are shown in **Figure 8**. With the curve fitting method, the activity coefficient of the TBP at

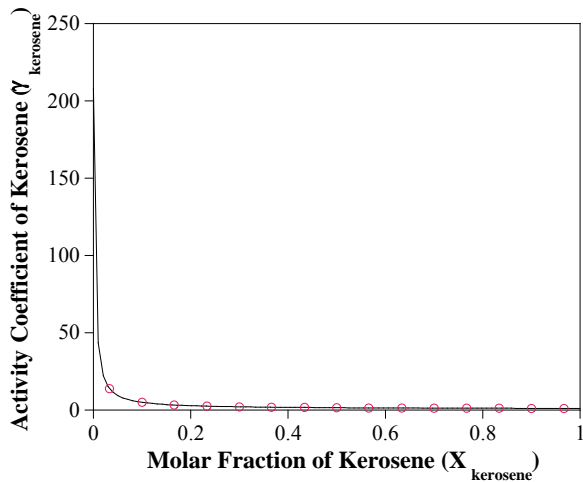


Figure 6. Activity coefficient of kerosene as a function of concentration.

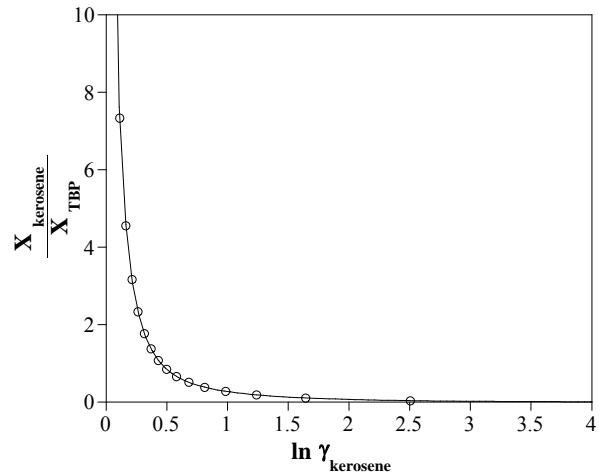


Figure 7. The value of $\frac{X_{\text{kerosene}}}{X_{\text{TBP}}}$ vs $\ln \gamma_{\text{kerosene}}$.

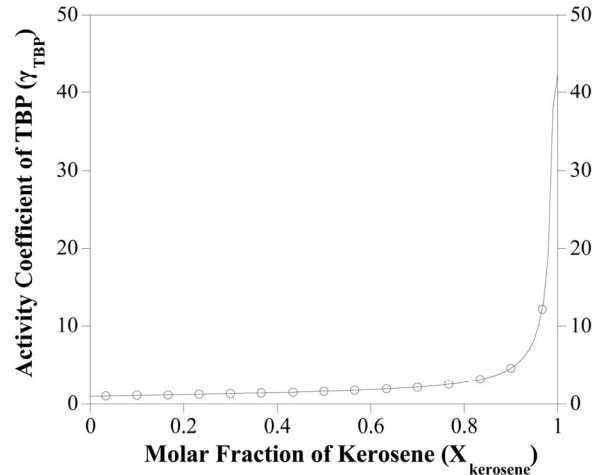


Figure 8. The activity coefficient of TBP as a function of the molar fraction of the kerosene.

$X_{\text{TBP}} < 0.01$ is determined by:

$$\gamma_{\text{TBP}} = 42.530, \quad (35)$$

at $0.01 < X_{\text{TBP}} < 0.2$ is given by:

$$\ln \gamma_{\text{TBP}} = \frac{0.2913 - 0.2843X_{\text{kerosene}}}{1 - 1.8674X_{\text{kerosene}} + 0.8687X_{\text{kerosene}}^2} \quad (36)$$

and at the higher TBP concentrations

($0.2 < X_{\text{TBP}} < 0.97$), the activity coefficient of TBP is evaluated by:

$$\ln \gamma_{\text{TBP}} = \frac{-0.0146 + 1.2826X_{\text{kerosene}}}{1 + 1.5595X_{\text{kerosene}} - 1.9594X_{\text{kerosene}}^2} \quad (37)$$

So the Henry's constant for the TBP is equal to 42.530. The values of the activity of the TBP evaluated from an equation similar to Equation (24) are shown in **Figure 9**. The activity of the TBP has a very positive deviation

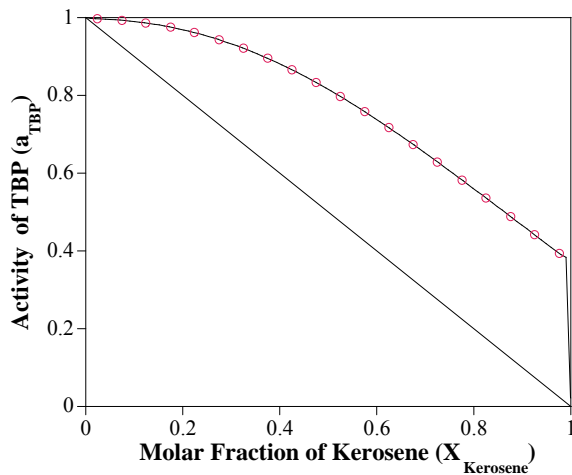


Figure 9. The activity of TBP vs X_{kerosene} .

from ideality. With the curve fitting method, the activity of the TBP at $X_{\text{TBP}} < 0.01$ is determined by:

$$a_{\text{TBP}} = 42.35 - 42.35X_{\text{kerosene}} = 42.35X_{\text{TBP}}, \quad (38)$$

at $0.01 < X_{\text{TBP}} < 0.2$. It is evaluated by:

$$\ln a_{\text{TBP}} = \frac{-0.1013 - 0.0134X_{\text{kerosene}}}{1 - 1.5101X_{\text{kerosene}} + 0.6266X_{\text{kerosene}}^2} \quad (39)$$

at the higher TBP concentration ($0.2 < X_{\text{TBP}} < 0.97$), the activity of TBP is determined by:

$$\ln a_{\text{TBP}} = \frac{0.0031 - 0.1264X_{\text{kerosene}}}{1 - 2.0240X_{\text{kerosene}} + 1.2479X_{\text{kerosene}}^2} \quad (40)$$

and at Raoultian range ($0.97 \leq X_{\text{TBP}}$): $a_{\text{TBP}} = X_{\text{TBP}}$.

5. Summary

An analytical method is presented in this paper for determination of the activity of the TBP dissolved in the kerosene through a simple physical property measurement. The results show that the binary solution of the kerosene with the TBP has a positive deviation from the Raoult's law behavior. The Henry's constant of very dilute TBP in kerosene is equal to 42.350. This constant for very dilute kerosene in TBP is equal to 214.35. The activity coefficient of the TBP at $X_{\text{TBP}} < 0.01$ is determined by: $\gamma_{\text{TBP}} = 42.530$, at $0.01 < X_{\text{TBP}} < 0.2$ is given by:

$$\ln \gamma_{\text{TBP}} = \frac{0.2913 - 0.2843X_{\text{kerosene}}}{1 - 1.8674X_{\text{kerosene}} + 0.8687X_{\text{kerosene}}^2}$$

and at the higher TBP concentrations the activity coefficient of the TBP is determined by:

$$\ln \gamma_{\text{TBP}} = \frac{-0.0146 + 1.2826X_{\text{kerosene}}}{1 + 1.5595X_{\text{kerosene}} - 1.9594X_{\text{kerosene}}^2}$$

Also the activity of TBP at $X_{\text{TBP}} < 0.05$ is deter-

mined by:

$$a_{\text{TBP}} = 42.35 - 42.35X_{\text{kerosene}} = 42.35X_{\text{TBP}}$$

at $0.01 < X_{\text{TBP}} < 0.2$ is given by:

$$\ln a_{\text{TBP}} = \frac{-0.1013 - 0.0134X_{\text{kerosene}}}{1 - 1.5101X_{\text{kerosene}} + 0.6266X_{\text{kerosene}}^2}$$

and at the higher TBP concentrations the activity of TBP is determined by:

$$\ln a_{\text{TBP}} = \frac{0.0031 - 0.1264X_{\text{kerosene}}}{1 - 2.0240X_{\text{kerosene}} + 1.2479X_{\text{kerosene}}^2}$$

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