

# Prediction of Vapor Pressure of Edible Vegetable Oils with Solvents at Temperature 348.15 K to 373.15 K from Activation Energy

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## Abstract

Edible vegetable oil is a food product extracted from plant seeds and is one of the key ingredients in global cuisine. It plays a vital role in enhancing the flavor, texture, and color of food. Additionally, vegetable oils contain natural antioxidants such as tocopherols, phenolic compounds, and phytosterols, which have health benefits. Vegetable oils play a crucial role in various industries, including food, chemicals, pharmaceuticals, cosmetics, and fuels. Predicting the vapor pressure of vegetable oils and solvents in a two-component phase equilibrium system is essential for solvent extraction processes and their subsequent reuse. This study presents a predictive equation for vapor pressure derived from Gibbs free energy, accounting for the influence of molecular interactions in the two-component phase equilibrium system. The research focuses on three types of vegetable oils: soybean oil, sunflower oil, and canola oil, along with three solvents: methanol, ethanol, and hexane, evaluated at temperatures of 348.15 K to 373.15 K across a molar concentration range of solvent  $x_1 = 0.2$ –1.0. The proposed equation is  $\ln p_{\text{blend}} = A_1 + A_2x_1 + A_3x_1^2 + (A_4 + A_5x_1 + A_6x_1^2) / T$  demonstrates high accuracy, with an average bias of -0.01 and an average absolute deviation (AAD) of 1.030.

**Keywords:** Prediction, Vapor Pressure, Activation Energy, Edible Vegetable Oils

## 1. Introduction

Edible vegetable oils are food products extracted from plant seeds cultivated across various regions of the world and constitute an essential component of global cuisine. These oils enhance both the flavor and visual appeal of consumed foods while containing hydrophilic antioxidants (such as tocopherols, phenolic compounds, and phytosterols) that facilitate the metabolism of fat-soluble vitamins [1], including vitamins A, D, E, and K. Furthermore, vegetable oils contain essential fatty acids, notably polyunsaturated fatty acids (PUFAs) and monounsaturated fatty acids (MUFAs).

The production and application of edible oils are heavily influenced by geographical, cultural, and technological factors. Advances in extraction methods and analytical techniques have enabled the development of high-quality oils with improved stability and enhanced nutritional profiles. Furthermore, increasing awareness of the health benefits associated with plant-based diets has spurred interest in functional edible oils enriched with antioxidants and other health-promoting components.

The unsaturated fatty acids are categorized into omega groups, specifically omega-3 and omega-6, which the

human body cannot synthesize independently and must obtain through dietary consumption of vegetable oils [2]. These fatty acids play a crucial role in reducing cardiovascular disease risk. Common edible vegetable oils include soybean oil, palm oil, coconut oil, sunflower seed oil, olive oil, and rice bran oil, each possessing distinct properties and nutritional benefits based on their fatty acid composition and nutrient content. The selection of specific vegetable oils for culinary applications depends on multiple factors, including boiling point, flavor profile, and health properties, all of which influence both food quality and nutritional value [3].

Naturally occurring vegetable oils primarily consist of triglycerides, which are esters composed of one glycerol molecule and three fatty acids molecules. Different vegetable oils contain varying compositions, as illustrated in **Table 1**, [4] typically featuring carbon chains of 12–20 atoms that may be saturated, monounsaturated, or polyunsaturated shown in **Table 2**, [3]. Consequently, the triglyceride composition in vegetable oils represents a highly complex mixture. Additionally, vegetable oils serve as crucial raw materials across various industries, including food, chemical, pharmaceutical, cosmetic, and fuel sectors [5].

**Table 1** Composition of triglycerides and fatty acids in vegetable oils (Percent by Mole).\*

Composition	Brazil nut	Buriti oil	Grapeseed oil	Soybean/Buriti mixture (1:1)	Soybean/Buriti mixture (2:1)	Soybean/Buriti mixture (3:1)	Cocoa butter
PPS	0	0	0	0	0	0	0.6
PSS	0	0	0	0	0	0	2.3
SSS	0	0	0	0	0	0	0
POP	3.56	7.08	0	4.02	3	2.49	15.8
POS	4.12	0.95	0	0.47	0.31	0.24	40.1
SOS	1.36	0	0	0	0	0	27.5
PLiP	3.5	0.73	1	1.59	1.88	2.02	1.6
PLiS	0	0	0	0	0	0	2.3
POO	12	35.7	1.8	19.4	14	11.3	2.7
SOO	6.03	2.53	0.63	1.63	1.33	1.18	2.6
SLiS	0	0	0	0	0	0	2.2
SLiO	0	0	0	0	0	0	0.7
PLiO	15.31	2.07	6.64	6.35	7.77	8.47	0
OOO	13.55	45.01	3.69	24.23	17.35	13.92	0.4
SOA	0	0	0	0	0	0	1.1
PLiLi	7.31	1.2	11.41	7.64	9.77	10.84	0
PLiLn	0	0	0	1.4	1.86	2.09	0
OOLi	17.22	2.5	13.24	7.16	8.71	9.48	0
OLiLi	12.22	2.23	28.75	12.41	15.78	17.46	0
LiLiLi	3.82	0	32.84	10.87	14.47	16.27	0
LiLiLn	0	0	0	2.83	3.77	4.24	0

Note: \*Data according to [4]

**Table 2** Chemical composition of edible vegetable oils.

Cz:y	MW	Soybean oil *	Sunflower oil *	Canola oil *
C12:0	200.32	0.05	0.07	0.06
C14:0	228.38	0.10	0.11	0.09
C15:0	242.40	0.04	0.05	0.04
C16:0	256.43	11.46	6.94	4.89
C16:1	254.42	0.11	0.13	0.22
C17:0	270.45	0.09	0.04	0.06
C17:1	268.43	0.06	0.04	0.07
C18:0	284.49	3.40	3.02	1.78
C18:1	282.47	28.90	25.52	62.98
C18:2	280.45	48.73	62.47	18.64
C18:2T	280.45	0.19	0.40	0.10
C18:3	278.44	5.20	0.09	7.47
C18:3T	278.44	0.57	-	1.14
C20:0	312.54	0.32	0.21	0.51
C20:1	310.52	0.27	0.20	1.27
C22:0	340.59	0.38	0.52	0.25
C22:1	338.57	-	-	0.34
C24:0	368.65	0.12	0.18	0.10
C24:1	366.63	-	-	0.10

Note: MW is molecular weight, \*Data according to [3]

In developing countries, vegetable oil production often employs mechanical crushing equipment similar to mortars and pestles, powered by cattle or horses, though yielding relatively low output. Health-conscious consumers in America and Europe prefer mechanically extracted oils obtained through pressing or grinding. However, both methods produce lower percentage yields compared to solvent extraction, which is the prevalent industrial production method due to its superior yield, faster processing time, and cost-effectiveness. The

increasing demand for vegetable oils has driven industrial efforts to develop various solvent extraction processes and technologies to enhance efficiency. The final processing stage involves oil purification through distillation and solvent recovery from the oil-solvent mixture, which directly correlates with Vapor-Liquid Equilibrium (VLE) data.

Therefore, knowledge of phase equilibrium data and thermophysical properties is essential for designing machinery operations and related equipment [4]. This

data remains relatively understudied, and obtaining accurate values requires experimental work using sophisticated instrumentation and specialized expertise to ensure data accuracy. Research has presented numerous methods for predicting liquid vapor pressure, with the Antoine equation being widely utilized. The Antoine equation represents a class of semi-empirical correlations that describe the relationship between vapor pressure and temperature of pure substances, derived from the Clausius-Clapeyron Eq. [5], as shown in Eq. (1):

$$\ln(p) = A + \frac{B}{C+(T)} \quad (1)$$

Where:

$P$  = saturated vapor pressure (Pa)  
 $A, B,$  and  $C$  = specific constants  
 $T$  = absolute temperature (K)

Ndiaye et al. [5] investigated the vapor pressure of soybean oil, castor oil, soybean biodiesel, and castor biodiesel at temperatures ranging from 290–355 K. Their findings revealed that vegetable oils exhibited vapor pressures between 0.19–2.16 kPa, significantly lower than both biodiesel types, which reached maximum vapor pressures of 4.85 kPa. They reported the determination of constants in Eq. (1), with test results showing high accuracy and a correlation coefficient ( $R$ ) of 0.999.

Murata & Tanaka [6] examined the vapor pressure of six cooking vegetable oils: soybean oil, rapeseed oil, cottonseed oil, safflower oil, rice wax, and sesame oil at temperatures between 250–330°C. The Riedel Equation was employed for approximation, as shown in Eq. (2):

$$\ln P_{vp} = A + B \cdot T^{-1} + C \cdot \ln T + D \cdot T^6 \quad (2)$$

Where:

$P_{vp}$  = vapor pressure (Pa)  
 $T$  = absolute temperature (K)  
 $A, B, C,$  and  $D$  = specific constants

Srisaipet et al. [7] presented an equation relating vapor pressure to Gibbs free energy for predicting properties of alkyl chlorides, alkyl bromides, alkyl aldehydes, fatty acid methyl esters, and alkyl acetates with carbon chain lengths of 5–14 atoms, as shown in Eq. (3):

$$\ln\left(\frac{p}{p_{ref}}\right) = -\frac{\Delta G}{RT} \quad (3)$$

Where:

$P$  = saturated vapor pressure (Pa)  
 $P_{ref}$  = saturated vapor pressure at standard reference conditions (Pa)  
 $R$  = gas constant ( $\text{JK}^{-1}\text{mol}^{-1}$ )  
 $T$  = absolute temperature (K)  
 $\Delta G$  = Gibbs free energy (J)

Kay's Mixing Rule was commonly employed to calculate various properties of mixtures containing

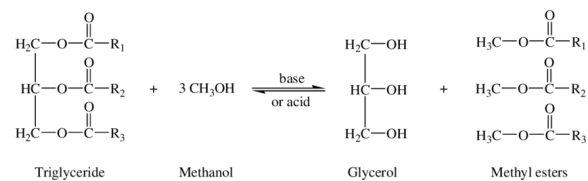
two or more components [8],[9], including mixture vapor pressure, as shown in Eq. (4):

$$\ln(p_{mix}) = \sum_{i=1}^n x_i p_i \quad (4)$$

Where:

$p_{mix}$  = saturated vapor pressure of mixture (Pa)  
 $x_i$  = molar or volumetric fraction  
 $p_i$  = saturated vapor pressure of component (Pa)

Based on the above information, Srisaipet et al. [7] approach established a theoretical connection between compound vapor pressure and Gibbs free energy according to thermodynamic principles derived from molecular structure, enabling clear relationship analysis. Consequently, this research applied Srisaipet et al. [7] methodology to investigate vapor pressure relationships of vegetable oils and their solvent mixtures at various temperatures. This approach was particularly relevant as vegetable oils possessed carbon chain structures similar to fatty acid methyl esters, which were triglyceride derivatives produced through transesterification reactions with alcohols, as illustrated in **Figure 1**, [10].



**Figure 1** The transesterification reaction of vegetable oil with methanol.

## 2. Theory

In industrial vegetable oil production, solvents such as hexane are commonly employed to maximize yield. Hexane facilitates efficient oil extraction, with the final stage involving distillation to purify the oil and recover hexane for reuse, thereby reducing new solvent requirements and production costs. The vapor pressure behavior in pure substances and mixtures may exhibit non-linear characteristics due to intermolecular force interactions, which correlate with activation energy, as shown in Eq. (5) [9].

$$\Delta G_{blend} = \sum_{i=1}^n x_i \Delta G_i \quad (5)$$

For binary mixtures, Eq. (5) can be expanded as shown in Eq. (6):

$$\Delta G_{blend} = x_i \Delta G_i + x_j \Delta G_j + x_i x_j \Delta G_{ij} \quad (6)$$

Where:

$\Delta G_{blend}$  = total activation energy of mixture  
 $\Delta G_i$  = activation energy of molecules  $i$   
 $\Delta G_{ij}$  = interaction activation energy between molecules  $i$  and  $j$  where  $i \neq j$   
 $x_i$  = molar fraction of molecule  $i$   
 $x_j$  = molar fraction of molecule  $j$

Dividing Eq. (6) by  $RT$ :

$$-\frac{\Delta G_{blend}}{RT} = -\frac{\Delta G_1}{RT}x_1 - \frac{\Delta G_2}{RT}x_2 - \frac{\Delta G_{12}}{RT}x_1x_2 \quad (7)$$

Substituting Eq. (7) into Eq. (3) yields Eq. (8):

$$\ln\left(\frac{p}{p_{ref}}\right) = -\frac{\Delta G_1}{RT}x_1 - \frac{\Delta G_2}{RT}x_2 - \frac{\Delta G_{12}}{RT}x_1x_2 \quad (8)$$

Expanding Eq. (8) using enthalpy (H) and entropy (S) according to the relationship  $G = H - ST$ :

$$\ln(p)_{blend} = \ln(p_{ref})_{blend} - \left(\frac{H_1 - S_1T}{RT}\right)x_1 - \left(\frac{H_2 - S_2T}{RT}\right)(1 - x_1) - \left(\frac{H_{12} - S_{12}T}{RT}\right)x_1(1 - x_1) \quad (9)$$

Following the derivation process from Eq. (5) to (9), the structured relationship is formulated as Eq. (10), where the thermodynamic variables are consolidated into constants  $A_1$  to  $A_5$  as shown in Eq. (11).

$$\ln(p)_{blend} = A_1 + A_2x_1 + A_3x_1^2 + \frac{A_4 + A_5x_1 + A_6x_1^2}{T} \quad (10)$$

Where:

$$\begin{aligned} A_1 &= \ln(p_{ref})_{blend} + \frac{\Delta S_2}{R} \\ A_2 &= \frac{\Delta S_1 - \Delta S_2 + \Delta S_{12}}{R} \\ A_3 &= -\frac{\Delta H_2}{R} \\ A_4 &= -\frac{\Delta S_{12}}{R} \\ A_5 &= \frac{\Delta H_2 - \Delta H_1 + \Delta S_{H12}}{R} \\ A_6 &= -\frac{\Delta H_{12}}{R} \end{aligned} \quad (11)$$

Where:

$$\begin{aligned} x_1 &= \text{molar fraction of component 1} \\ T &= \text{absolute temperature (K)} \\ R &= \text{gas constant (J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \end{aligned}$$

### 3. Research Methodology

The study investigated vapor pressure prediction for three types of edible vegetable oils: soybean oil, sunflower oil, and canola oil, utilizing data from Belting et al.'s (2015) literature review. The vapor pressure measured using a computer-driven static apparatus with a resolution of approximately 0.0005% of the maximum pressure (0.35 MPa) [3]. The chemical composition of these edible vegetable oils is presented in Table 2.

#### 3.1 Determination of Constants in Eq. (10)

The constants  $A_1$ – $A_6$  in Eq. (10) were determined using multiple linear regression analysis, following the methodology of Phankosol et al. [9] and utilizing experiment data from Belting et al. [3].

### 3.2 Statistical Analysis

Deviation ( $D(\%)$ )

$$D(\%) = \frac{P_{exp} - P_{cal}}{P_{exp}} \times 100 \quad (12)$$

Where  $P_{exp}$  and  $P_{cal}$  represent experimental and predicted vapor pressure, respectively.

Absolute Deviation ( $AD(\%)$ )

$$AD(\%) = \left| \frac{P_{exp} - P_{cal}}{P_{exp}} \right| \times 100 \quad (13)$$

Where  $P_{exp}$  and  $P_{cal}$  represent experimental and predicted vapor pressure, respectively.

Average Absolute Deviation ( $AAD(\%)$ )

$$AAD(\%) = \sum_{i=1}^n \left| \frac{P_{exp,i} - P_{cal,i}}{P_{exp,i}} \right| \times 100 \quad (14)$$

Where  $P_{exp}$ ,  $P_{cal}$  and  $n$  represent experimental vapor pressure, predicted vapor pressure, and number of data points, respectively.

Bias (%)

$$Bias(\%) = \sum_{i=1}^n \frac{P_{exp,i} - P_{cal,i}}{P_{exp,i}} \times 100 \quad (15)$$

Where  $P_{exp}$ ,  $P_{cal}$  and  $n$  represent experimental vapor pressure, predicted vapor pressure, and number of data points, respectively.

Coefficient of Determination ( $R^2$ )

$$R^2 = \left[ \frac{\sum_{i=1}^n P_{exp} P_{cal} - (\sum_{i=1}^n P_{exp})(\sum_{i=1}^n P_{cal})}{\left[ \sum_{i=1}^n P_{exp}^2 - (\sum_{i=1}^n P_{exp})^2 \right] \left[ \sum_{i=1}^n P_{cal}^2 - (\sum_{i=1}^n P_{cal})^2 \right]} \right]^{1/2} \quad (16)$$

Where  $P_{exp}$ ,  $P_{cal}$  and  $n$  represent experimental vapor pressure, predicted vapor pressure, and number of data points, respectively.

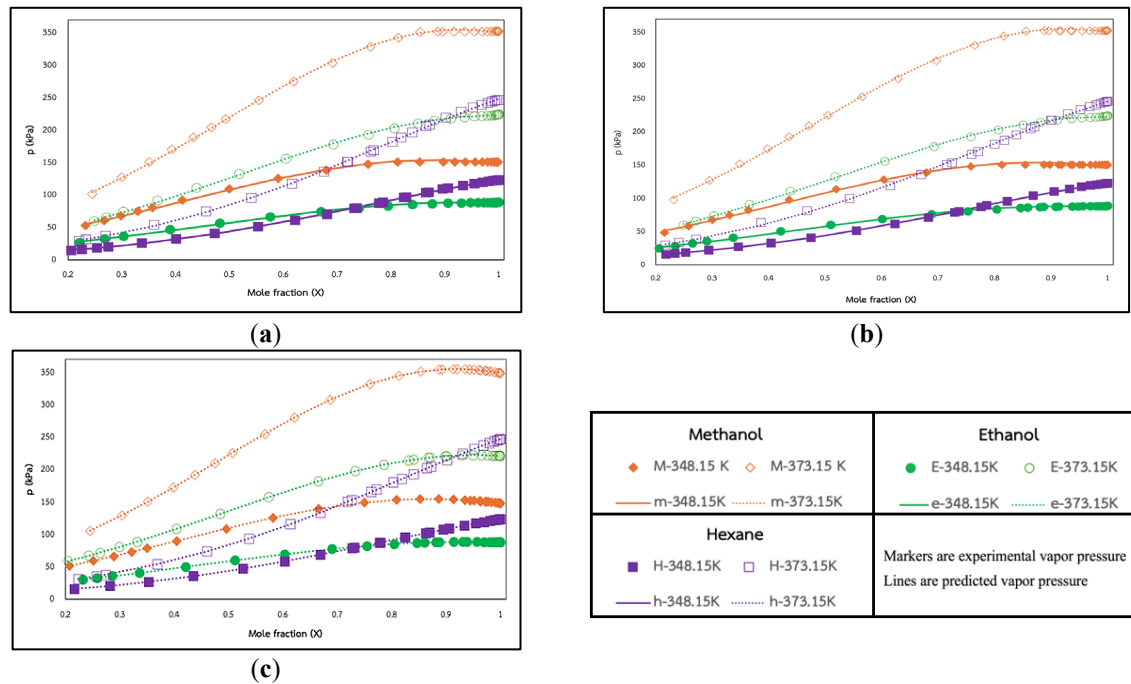
### 4. Results

The fatty acid composition analysis of the three vegetable oils began with the conversion to fatty acid methyl esters through the transesterification reaction, as shown in Figure 1, followed by gas chromatography analysis. The study analyzed data from three vegetable oils (soybean oil, sunflower oil, and canola oil) and three solvents (methanol, ethanol, and hexane), comprising 493 experimental data sets at temperatures of 348.15 K pressure graphs comparing experimental results to 373.15 K. The temperature range is limited by the boiling point of the solvent. The derived constants for mixture vapor pressure prediction are presented in Table 3, and the vapor predictions from Eq. (10) at various concentrations are shown in Figure 2(a)–(c).

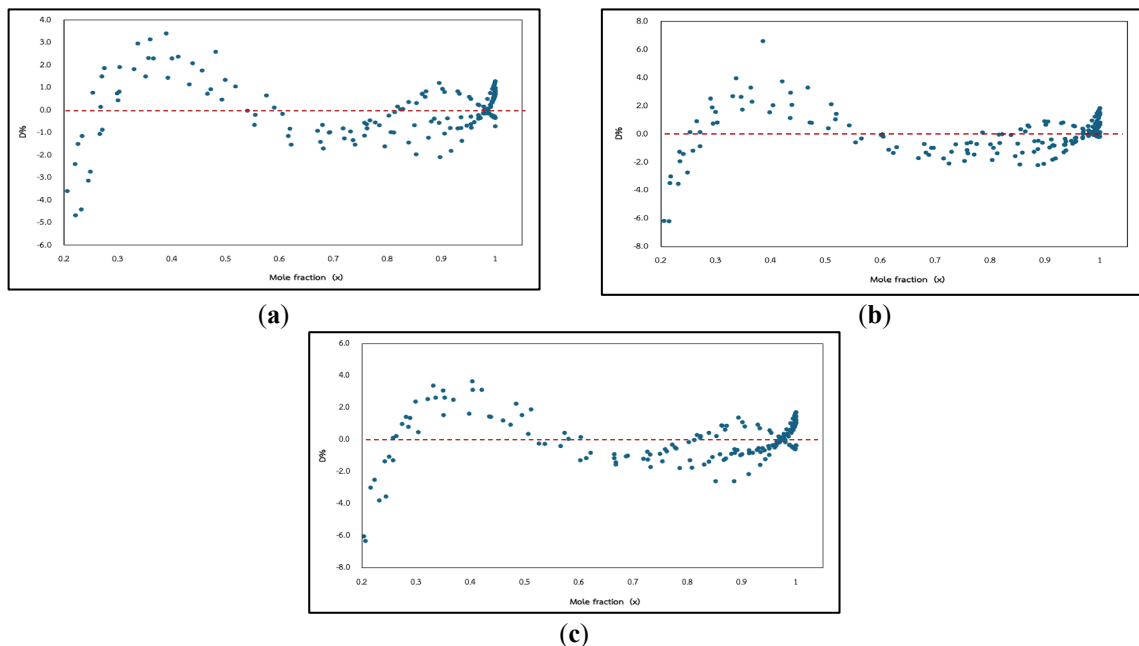
The results demonstrated that vapor pressure increased correspondingly with solvent concentration ( $x_1$ ), which was attributable to the lower boiling points of solvents compared to vegetable oils. As solvent concentration increased, the vapor pressure from solvent evaporation also rose. When examining the effect of increasing carbon atoms in solvent molecules, a notable decrease in vapor pressure was observed, corresponding to increased molecular mass [3]. Furthermore, vapor pressure values at 374.15 K were consistently higher than those at 348.15 K. The predicted and experimental vapor pressure curves

showed precise overlaps at all data points, indicating strong agreement between theoretical predictions and experimental measurements.

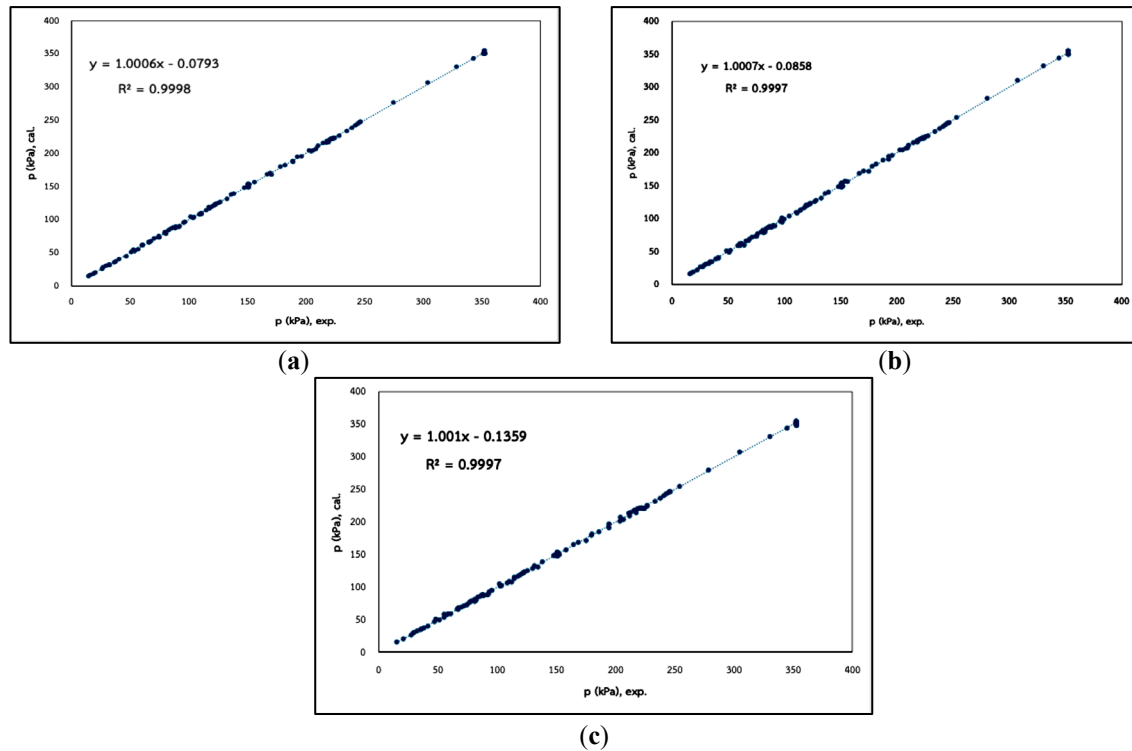
Statistical analysis of vapor pressure predictions using Eq. (10) compared to experimental data calculated from Eq. (12)–(16), as compiled in **Table 4**, revealed that soybean oil exhibited the lowest AAD, followed by canola oil and sunflower oil, with values of 0.937, 1.041, and 1.109, respectively. The calculated Bias and AAD for all vegetable oils combined were -0.01 and 1.030, respectively (**Table 4**).



**Figure 2** Comparison of experimental vapor pressure [3] and predicted vapor pressure using Eq. (10) at various concentrations. (a) Soybean Oil (b) Sunflower Oil (c) Canola Oil



**Figure 3** Distribution of percent deviation predicted by Eq. (10) compared to experimental data [3]. (a) Soybean Oil (b) Sunflower Oil (c) Canola Oil



**Figure 4** Relationship between experimental vapor pressure [3] and predicted vapor pressure using Eq. (10).  
(a) Soybean Oil (b) Sunflower Oil (c) Canola Oil

**Table 3** Constants for Eq. (10).

Oil	Solvent ( $x_1$ )	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$
Soybean	Methanol	10.2179	-2,463.1688	12.8096	-2,965.1107	-5.2465	979.3580
	Ethanol	11.6717	-3,189.2684	9.9728	-2,017.2285	-3.2743	368.5779
	Hexane	10.9617	-3,207.7358	6.1742	-387.9949	-1.9019	-31.4464
Sunflower	Methanol	11.0530	-2,767.3106	10.5936	-2,147.5921	-3.8037	442.4368
	Ethanol	11.9604	-3,296.9753	8.4884	-1,463.3101	-2.0028	-105.8557
	Hexane	11.5717	-3,410.5607	5.6959	-236.8034	-2.1409	57.0535
Canola	Methanol	10.2394	-2,471.3512	12.5021	-2,831.2379	-4.9504	848.5700
	Ethanol	12.4802	-3,444.5102	11.1044	-2,461.5012	-5.2799	1,090.0575
	Hexane	11.2837	-3,310.8931	5.1362	-68.7099	-1.2357	-230.2572

**Table 4** Statistical values from predictions using Eq. (10) compared to experimental data [3].

Oil	Solvent ( $x_1$ )	Bias	AAD	Number of experiments	Figure 4		
					intercept	Slope	R <sup>2</sup>
Soybean	Methanol	-0.008	0.960	53	-0.0793	1.0006	0.9998
	Ethanol	-0.008	0.951	51			
	Hexane	-0.007	0.904	55			
	Overall average	-0.008	0.937	159			
Sunflower	Methanol	-0.012	1.182	59	-0.0858	1.0007	0.9997
	Ethanol	-0.013	1.160	53			
	Hexane	-0.012	0.979	54			
	Overall average	-0.012	1.109	166			
Rapeseed	Methanol	-0.012	1.131	60	-0.1359	1.0010	0.9997
	Ethanol	-0.013	1.160	55			
	Hexane	-0.006	0.815	53			
	Overall average	-0.010	1.041	168			
Overall		-0.010	1.030	493			

The percentage deviation (D) distribution patterns for various vegetable oils with all three solvents at different concentrations (**Figure 3(a)–(c)**), showed similar dispersion characteristics. Higher deviations were observed as concentrations approached  $x_1 = 0.2$ , while maximum accuracy was achieved as concentrations approached  $x_1 = 1.0$ . This enhanced accuracy at higher concentrations could be attributed to the minimal presence of vegetable oil vapor, resulting from two factors:

- 1) Low compositional quantity in the mixture and
- 2) Inherently low vapor pressure of vegetable oils.

The graphical comparison between experimental vapor pressure ( $p_{exp}$ ) and predicted vapor pressure ( $p_{cal}$ ) using Eq. (10) (**Figure 4(a)–(c)**), demonstrated a strong linear relationship across all data points. The slope values ranged between 1.0006–1.0010, with coefficient of determination ( $R^2$ ) values ranging from 0.9997–0.9998 (Eq. (16)). These statistical parameters indicated an exceptionally high correlation and close agreement between predicted and experimental values.

## 5. Discussion

Vapor pressure is an intensive property wherein solutions with stronger intermolecular forces exhibit lower vapor pressure, while those with weaker intermolecular forces demonstrate higher vapor pressure. For binary solutions, vapor pressure can be calculated using Raoult's law, while Henry's law applies to highly dilute solutions. This study focused on vapor pressure behavior conforming to Raoult's law at solvent concentrations above 20% ( $x_1 = 0.2$ ), yielding constants for Eq. (10) as shown in **Table 3**.

Belting et al. [3] (2015) expanded the Clausius-Clapeyron relationship using the UNIQUAC (Universal Quasi-Chemical) statistical modeling method to calculate activity in equilibrium systems where solution components have different molecular sizes and shapes. Their complex calculations predicted vapor pressure behavior of binary systems comprising edible vegetable oils (soybean, sunflower, and canola) with solvents (methanol, ethanol, and hexane) at temperatures of 348.15 K and 373.15 K. The results showed an AAD of 4.46%, which is higher than the 1.030% AAD achieved using Eq. (10).

Eq. (6) extended the vapor pressure relationship for binary phase equilibrium systems by incorporating Gibbs free energy in terms of intermolecular interaction forces ( $x_1 x_2 \Delta G_{12}$ ). These interactions were particularly significant due to the large molecular structure of vegetable oils, which feature bending at double bond positions and coiling in longer carbon chains. This resulted in considerable molecular disorder and significant differences from solvent molecules. When studying physical phenomena in binary phase equilibrium systems, it is essential to first verify the influence of intermolecular interaction forces to determine if their impact is negligible and can be excluded, which may occur in components with similar molecular structures and sizes.

## 6. Conclusions

This study presented vapor pressure estimation for binary phase equilibrium systems comprising three vegetable oils (soybean, sunflower, and canola) and three solvents (methanol, ethanol, and hexane), utilizing Gibbs free energy in terms of intermolecular interaction forces. The resulting equation employed simple parameters of molar fraction ( $x_1$ ) and absolute temperature (T/K), effectively covering concentrations between  $x_1 = 0.2$ –1.0. Applications outside this range may result in increased deviations. For predictions involving other components, all six constants in Eq. (6) had to be recalculated due to their specific nature. Even for identical vegetable oil types from different sources, minor deviations occurred due to variations in fatty acid composition resulting from different origins and extraction processes. For vapor pressure predictions in binary phase equilibrium systems of vegetable oils and solvents at concentrations between  $x_1 = 0.0$ –0.2, separate consideration was required due to distinct slope characteristics. Additional theoretical development may be necessary to achieve comprehensive coverage while maintaining practical applicability.

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