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Research Article

Reformulated Mathematical Models for Correlating the Solubility of Solid Drugs in Supercritical Carbon Dioxide

Vikram Ramalingam, Amrithaa Raghavan, Chandrasekhar Garlapati*

Department of Chemical Engineering, Puducherry Technological University, Puducherry 605014, India
E-mail: chandrasekhar@ptuniv.edu.in

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Abstract: Solubility is the fundamental thermodynamic key parameter influencing supercritical technology in practice. In the literature, several solubility models are available to represent the solubility data. They are classified into several categories based on their origin and the background on which they were developed. Some important categories of solubility models are solvate complex models, mathematical models, and phase equilibrium models. Among them, mathematical models have shown good correlation efficiency for several solute-solvent systems. However, some do not comply with the fundamental phase rule in their functional form, which can cause them to be termed redundant models. Therefore, the current investigation aims to address the redundant nature of some mathematical models. Models considered in the work relate solubility as a function of temperature, pressure, and density in a nonlinear relationship (i.e., $y_2 = f(T, P, \rho_1)$). Reformulation was aimed at converting solubility models to a dimensionally consistent form in which the mole fraction of the solute is represented as a function of the reduced density of the solvent and the reduced temperature. Thus, all solubility models considered in the work are converted to $y_2 = f(T_r, \rho_r)$. Further, existing models and reformulation models were tested with four standard solute-solvent systems namely, naphthalene-$SCCO_2$, anthracene-$SCCO_2$, phenanthrene-$SCCO_2$, and salicylic acid-$SCCO_2$. Finally, the comparison between the existing and the reformulated models was done in terms of global values of AARD%, R^2, R^2_{adj}, and ΔAIC. From the results, it is quite clear that reformulated models are showing better results than the existing models.

***Keywords*:** correlations, evaluation, solubility models, reformulated solubility models, supercritical carbon dioxide

Nomenclature

a and b	Adjustable constants in Chrastil model
a_0-a_4	Model parameters of Mitra Wilson model
b_0-b_5	Model parameters of Gordillo et al.
c_0-c_5	Model parameters of Jouyban et al.
d_0-d_3	Model parameters of Jafari Nejad et al.
e_0-e_4	Model parameters of Keshmiri et al.
f_0-f_3	Model parameters of Hozhabr et al.
g_0-g_4	Model parameters of Khansary et al.

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h_0-h_5	Model parameters of Sodeifian et al. model
a'_0-a'_4	Reformulated Model parameters of Mitra Wilson model
b'_0-b'_5	Reformulated Model parameters of Gordillo et al.
c'_0-c'_5	Reformulated Model parameters of Jouyban et al.
d'_0-d'_3	Reformulated Model parameters of Jafari Nejad et al.
e'_0-e'_4	Reformulated Model parameters of Keshmiri et al.
f'_0 - f'_3	Reformulated Model parameters of Hozhabr et al.
g'_0-g'_4	Reformulated Model parameters of Khansary et al.
h'_0-h'_5	Reformulated Model parameters of Sodeifian et al. model
M	Molecular mass
P	Pressure, MPa
P_c	Pressure, bar
T	Temperature of the system, K
T_c	Critical temperature, K
T_r	Reduced temperature of the system
y_2	Solubility of compounds in mole fraction
$AARD\%$	Average absolute relative deviation Percentage
AIC	Akaike information criterion
R	Gas constant/(mol·K)
R^2	Square of coefficient of regression
R^2_{adj}	Statistical parameter Adjusted R^2
$RMSD$	Root Mean Square Deviation
SSE	Sum of Squares due to Error

Subscripts

c	Critical
r	Reduced
1	Solvent
2	Solute

1. Introduction

The supercritical condition is attained by any fluid when it is subjected to a temperature and pressure greater than its critical point [1], [2]. At temperatures and pressures surpassing critical conditions (31.1 °C and 73.8 bar), CO_2 enters a fluid condition displaying exceptional solubility traits, and it is known as supercritical CO_2 [1], [2]. Around the critical conditions, minor changes in temperature or pressure radically alter the physical properties of the supercritical CO_2 [1], [2]. Supercritical fluid processes such as food processing, extraction, pharmaceutical processing, dyeing, polymer processing, and nuclear fuel reprocessing leverage the distinctive characteristics of carbon dioxide's supercritical state to deal with specific components of liquids and solids [1]-[4].

Supercritical fluid usage in several processes is extremely beneficial, but their initial installation cost is high [5]. The success of all these supercritical processes greatly depends on the exact solubility information [6]. However, the required solubility data is limited for several solute-solvent systems [4], [7]. Although it is good to have exact experimental data, conducting experiments and obtaining solubility information at all desired conditions is time-consuming and expensive; thus, its modelling is essential [8]. Several modelling techniques are presented in the

literature to describe solubility phenomena [4], [9]. They are classified into several categories based on their origin and the background on which they were developed [4]. Some important categories of solubility models are solvate complex models, mathematical models, CFD models, solution theory models, EoS models, and phase equilibrium models [3], [4], [6]-[8], [10]-[11]. The correlating ability of the solubility model greatly depends on the number of adjustable parameters in the model [4], [12], [13]. Mathematical models have shown good correlation efficiency, but they don't comply with the fundamental phase rule in their functional form, due to which they may be termed redundant models and this fact was reported in the year 2017 by Si-Moussa et al. [14]. Therefore, the present study aims to address the redundant nature of the mathematical solubility models via the reformulation technique. In the process of reformulation existing mathematical solubility models are transformed into a functional form in which solubility is expressed as a function of density and temperature [12], [15]. For dimensional consistency, solubility is expressed as mole fraction, solvent density is expressed as reduced density, and temperature is expressed as reduced temperature [4], [14]-[16]. The proposed models are validated with four standard solute-$SCCO_2$ systems along with recently published eight drug solutes-$SCCO_2$ systems. The standard solutes considered in the work are naphthalene [17], [18], anthracene [19], phenanthrene [19], and salicylic acid [20]. These are the compounds vividly used for the testing of newly established solubility measuring devices; thus, they are known as standard solutes [19], [21], [22], hence their solubility data modelling is meaningful. Further, recently published eight drugs considered for the work are fexofenadine hydrochloride [23], tramadol hydrochloride [24], paracetamol [25], gefitinib hydrochloride [26], digitoxin [27], alprazolam [28], phenytoin [29], and raloxifene [29].

2. Existing mathematical solubility models

Mitra and Wilson (1991) proposed an empirical model based on the dependency of solubility on the pressure and temperature of the system [30]:

$$\ln y_2 = a_0 \ln P + a_1 T + a_2 PT + \frac{a_3 P}{T} + a_4 \tag{1}$$

where model constants are a_0; a_1; a_2; a_3; a_4.

Gordillo et al. (1999) proposed a solubility model that correlates mole fraction with pressure (P, bar) and temperature (T, °C) [31]:

$$\ln y_2 = b_0 + b_1 P + b_2 P^2 + b_3 PT + b_4 T + b_5 T^2 \tag{2}$$

where model constants are b_0; b_1; b_2; b_3; b_4; b_5.

Jouyban et al. (2002) developed an empirical equation to calculate solute solubility based on the following observations [32]:

(a) Non-linear relationship between y_2 and pressure at isothermal conditions.

(b) Non-linear relationship between y_2 and temperature at isobaric conditions.

(c) Linear relationship between y_2 and ρ_1 in certain ranges of pressure and temperature.

$$\ln y_2 = c_0 + c_1 P + c_2 P^2 + c_3 PT + \frac{c_4 T}{P} + c_5 \ln \rho_1 \tag{3}$$

where model constants are c_0; c_1; c_2; c_3; c_4; c_5.

Jafari Nejad et al. (2010) proposed an equation based on the following observations [33]:

(a) Non-linear relationship between y_2 and pressure at isothermal conditions.

(b) Nonlinear relationship between y_2 and temperature at isobaric conditions.

(c) Linear relationship between y_2 and ρ_1 in certain ranges of pressure and temperature.

$$\ln y_2 = d_0 + d_1 P^2 + d_2 T^2 + d_3 \ln \rho_1 \tag{4}$$

where model constants are d_0; d_1; d_2; d_3.

Keshmiri et al. (2014) proposed a solubility equation based on the following observations [34]:

(a) Nonlinear behaviour between y_2 and T at isobaric conditions.

(b) Nonlinear behaviour between y_2 and P at isothermal conditions

(c) Linear relationship between y_2 and ρ_1 in certain ranges of pressure and temperature

$$\ln y_2 = e_0 + e_1/T + e_2 P^2 + \left(e_3 + e_4/T\right) \ln \rho_1 \tag{5}$$

where model constants are e_0; e_1; e_2; e_3; e_4.

Hozhabr et al. (2015) proposed a 4-parameter empirical correlation taking into account the following observations [35]:

(a) Nonlinear behaviour between y_2 and T at isobaric conditions.

(b) Nonlinear behaviour between y_2 and P at isothermal conditions.

(c) Linear relationship between y_2 and ρ_1 in certain ranges of pressure and temperature.

$$\ln y_2 = f_0 + f_1/T + f_2 \rho_1/T - f_3 \ln P \tag{6}$$

where model constants are f_0; f_1; f_2; f_3; f_4; f_5.

Khansary et al. (2015) proposed an empirical correlation based on the following observations [36]:

(a) A non-linear relationship between pressures at isothermal conditions with $\ln y_2$.

(b) A non-linear relationship between temperatures at isobaric conditions with $\ln y_2$.

(c) When density is constant, y_2 and temperature show nonlinear behaviour.

(d) A non-linear relationship between densities at isothermal conditions with $\ln y_2$.

(e) Linearity between $\ln y_2$ and $\ln \rho_1$.

$$\ln y_2 = g_0/T + g_1 P + g_2 P^2/T + \left(g_3 + g_4 P\right) \ln \rho_1 \tag{7}$$

where model constants are g_0; g_1; g_2; g_3; g_4.

Sodeifian et al. (2019) proposed an empirical solubility model based on the following observations [37]:

(a) A non-linearity between $\ln y_2$ and ρ, when T is constant (isothermal conditions).

(b) A non-linearity between $\ln y_2$ and T, when pressure is constant.

(c) A Linearity between $\ln y_2$ and $(\rho_1 T)$ within a certain range of density and temperature.

(d) A non-linearity between $\ln y_2$ and P at isothermal conditions.

$$\ln y_2 = h_0 + \frac{h_1 P^2}{T} + h_2 \ln\left(\rho_1 T\right) + h_3 \rho_1 \ln \rho_1 + h_4 P \ln T + \frac{h_5 \ln \rho_1}{T} \tag{8}$$

where model constants are h_0; h_1; h_2; h_3; h_4; h_5.

Where P, T, and ρ_1 are the pressure, temperature of the system, and density of $SCCO_2$, respectively.

It is important to note that except for two models, Mitra and Wilson and Gordillo et al., all other models considered in the work are inconsistent with the Gibbs phase rule in their functional form.

3. Reformulated mathematical solubility models

Solubility is a physical phenomenon, and the number of independent parameters that influence the solubility phenomenon is given by the Gibbs phase rule [3], [4], [14], [15], [38], [39]. According to Gibb's rule, the independent variables that affect the solubility are pressure and temperature, however, Si-Moussa et al. suggested that the solubility is best represented in the function of density and temperature [14]. Therefore, in this work, the redundant nature of the mathematical solubility models is addressed by transforming them into models that are functional forms of density and temperature. The transformation is done with the help of the equation of state $\left(P = \frac{ZRT\rho}{M}\right)$ [38]. Thus, the final functional form of the solubility model is

$$y_2 = f\left(\rho_1, T\right) \tag{9}$$

(or) in terms of reduced density ($\rho_r = \rho_1/\rho_{c1}$) and temperature ($T_r = T/T_{c1}$) as

$$y_2 = f\left(\rho_r, T_r\right) \tag{10}$$

To exemplify the proposed reformulation, Mitra and Wilson model is considered in more detail as follows:

$$\ln y_2 = a_0 \ln P + a_1 T + a_2 PT + a_3 P/T + a_4 \tag{11}$$

Substituting the real gas equation $P = Z\rho RT/M$ into Eq. (11) gives Eq. (12):

$$\ln y_2 = a_0 \ln\left(Z\,\rho\, RT/M\right) + a_1 T + a_2\left(Z\,\rho\, RT/M\right)T + a_3\left(Z\,\rho\, RT/M\right)/T + a_4 \tag{12}$$

The Eq. (12) is manipulated to Eqs. (13)-(15) by introducing reduced variables

$$\ln y_2 = a_0 \ln\left(Z\,\rho_r RT_r \rho_{c1} T_{c1}/M\right) + a_1 T_r T_{c1} + a_2\left(Z\,\rho_r RT_r \rho_{c1} T_{c1}/M\right)\left(T_r T_{c1}\right)$$

$$+a_3 (Z\,\rho_r RT_r \rho_{c1} T_{c1}/M)/T_r T_{c1} + a_4 \tag{13}$$

$$\ln y_2 = a_0 \ln\left(\rho_r T_r\right) + a_0 \ln\left(Z\,R\rho_{c1} T_{c1}/M\right) + a_1 T_r T_{c1} + a_2\left(Z\,\rho_r RT_r \rho_{c1} T_{c1}/M\right)\left(T_r T_{c1}\right)$$

$$+a_3\left(Z\,\rho_r RT_r \rho_{c1} T_{c1}/M\right)/T_r T_{c1} + a_4 \tag{14}$$

$$\ln y_2 = a_0' \ln\left(\rho_r T_r\right) + a_1' T_r + a_2' \rho_r T_r^2 + a_3' \rho_r + a_4' \tag{15}$$

where $a_0' = a_0$; $a_1' = a_1 T_{c1}$; $a_2' = a_2 ZR\rho_{c1} T_{c1}^2/M$; $a_3' = a_3 ZR\rho_{c1}/M$; $a_4' = a_4 + a_0 \ln\left(ZR\rho_{c1} T_{c1}/M\right)$.

Thus, Eq. (15) is a reformulated Mitra and Wilson model.

4. Results and discussions

The solute-solvent systems used in the study are Naphthalene-$SCCO_2$ [17], [18], Anthracene-$SCCO_2$ [19], Phenanthrene-$SCCO_2$ [19], Salicylic acid-$SCCO_2$ [20], Fexofenadine hydrochloride-$SCCO_2$ [23], Tramadol hydrochloride-$SCCO_2$ [24], Paracetamol-$SCCO_2$ [25], Gefitinib hydrochloride-$SCCO_2$ [26], Digitoxin-$SCCO_2$ [27],

Alprazolam-$SCCO_2$ [28], Phenytoin-$SCCO_2$ [29], Raloxifene-$SCCO_2$ [29]. Table 1 shows the solubility information of standard compounds. Table 2 shows the existing and reformulated equations.

Table 1. Solubility information's of the systems considered the work

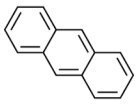
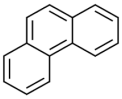
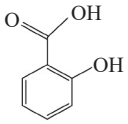
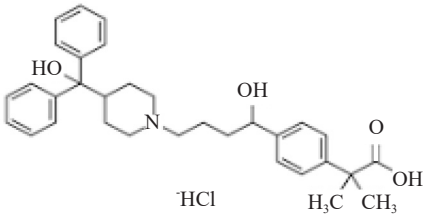
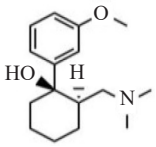
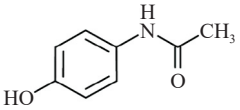
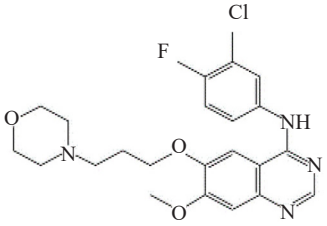
S.No	System	Structure	Molecular weight (g/mol)	Solubility range in mole fraction, y_2	Range of T (K); P (bar); ρ (Kg/m^3)	Ref.
1	Naphthalene-$SCCO_2$		128.17	8.74×10^{-4} to 1.02×10^{-2}	308-328; 60-340; 150-950	[17], [18]
2	Anthracene-$SCCO_2$		178.23	9.2×10^{-5} to 1.02×10^{-4}	313-333; 11-35; 132-355	[19]
3	Phenanthrene-$SCCO_2$		178.23	9.19×10^{-4} to 1.02×10^{-3}	313-333; 10-35; 370-940	[19]
4	Salicylic acid-$SCCO_2$		138.122	1.23×10^{-4} to 7.30×10^{-5}	308-328; 81-202; 250-870	[20]
5	Fexofenadine hydrochloride-$SCCO_2$		538.1	7.3×10^{-6} to 8.54×10^{-5}	308.2-338.2 388-914; 120-270	[23]
6	Tramadol hydrochloride-$SCCO_2$		263.38	2.46×10^{-5} to 13.84×10^{-4}	308-338; 266-914; 100-270	[24]
7	Paracetamol-$SCCO_2$		151.16	3.1×10^{-7} to 1.636×10^{-4}	311-358; 196.2-898.9; 95-265	[25]
8	Gefitinib hydrochloride-$SCCO_2$		483.4	9.84×10^{-5} to 1.06×10^{-4}	308-338; 914-388; 120-270	[26]

Table 1. (cont.)

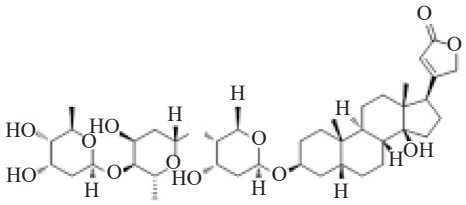
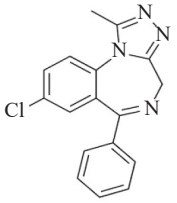
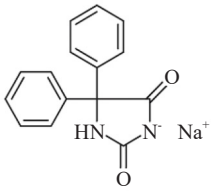
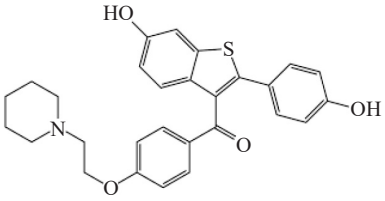
S.No	System	Structure	Molecular weight (g/mol)	Solubility range in mole fraction, y_2	Range of T (K); P (bar); ρ (Kg/m^3)	Ref.
9	Digitoxin-SCCO$_2$		764.93	9.5×10^{-7} to 1.12×10^{-5}	311-343; 349.0-918.8; 120-200	[27]
10	Alprazolam-SCCO$_2$		308.76	2.7×10^{-6} to 6.32×10^{-5}	308-338; 384.1-929.6; 120-200;	[28]
11	Phenytoin-SCCO$_2$		252.26	6.8×10^{-7} to 1.57×10^{-4}	313-345; 222.2-880.7; 95-250	[29]
12	Raloxifene-SCCO$_2$		473.58	7.9×10^{-6} to 8.09×10^{-4}	313-343; 247.9-873.7; 100-240;	[29]

Table 2. Summary of existing and reformulated solubility model used in the study

S.No	Model Name (Year of Publication)	Existing Solubility Models: $y_2 = f(T, P, \rho)$	Reformulated Solubility Models: $y_2 = f'(T_r, \rho_r)$
1	Mitra-Wilson (1991) [30]	$\ln y_2 = a_0 \ln P + a_1 T + a_2 PT + a_3 P/T + a_4$	$\ln y_2 = a_0' \ln(\rho_r T_r) + a_1' T_r + a_2' \rho_r T_r^2 + a_3' \rho_r + a_4'$
2	Gordillo et al. (1999) [31]	$\ln y_2 = b_0 + b_1 P + b_2 P^2 + b_3 PT + b_4 T + b_5 T^2$	$\ln y_2 = b_0' + b_1' \rho_r T_r + b_2' \rho_r^2 T_r^2 + b_3' \rho_r T_r^2 + b_4' T_r + b_5' T_r^2$
3	Jouyban et al. (2002) [32]	$\ln y_2 = c_0 + c_1 P + c_2 P^2 + c_3 PT + c_4 T/P + c_5 \ln \rho$	$\ln y_2 = c_0' + c_1' \rho_r T_r + c_2' \rho_r^2 T_r^2 + c_3' \rho_r T_r^2 + c_4'/\rho_r + c_5' \ln \rho_r$
4	Jafari Nejad et al. (2010) [33]	$\ln y_2 = d_0 + d_1 P^2 + d_2 T^2 + d_3 \ln \rho_1$	$\ln y_2 = d_0' + d_1' \rho_r^2 T_r^2 + d_2' T_r^2 + d_3' \ln \rho_r$
5	Keshmiri et al. (2014) [34]	$\ln y_2 = e_0 + e_1/T + e_2 P^2 + (e_3 + e_4/T) \ln \rho_1$	$\ln y_2 = e_0' + e_1'/T_r + e_2' \rho_r T_r + (e_3' + e_4'/T_r) \ln \rho_r$
6	Hozhabr et al. (2014) [35]	$\ln y_2 = f_0 + f_1/T + f_2 \rho_1/T - f_3 \ln P$	$\ln y_2 = f_0' + f_1'/T_r + f_2' \rho_r/T_r - f_3' \ln(\rho_r T_r)$
7	Khansary et al. (2015) [36]	$\ln y_2 = g_0/T + g_1 P + g_2 P^2/T + (g_3 + g_4 P) \ln \rho_1$	$\ln y_2 = g_0'/T_r + g_1' T_r \rho_r + g_2' \rho_r^2 T_r + (g_3' + g_4' \rho_r T_r) \ln \rho_r$
8	Sodeifian et al. (2019) [37]	$\ln y_2 = h_0 + h_1 P^2/T + h_2 \ln(\rho_1 T) + h_3 \rho_1 \ln \rho_1 + h_4 P \ln T + h_5 \ln \rho_1/T$	$\ln y_2 = h_0' + h_1' \rho_r^2 T_r + h_2' \ln(\rho_r T_r) + h_3' \rho_r \ln \rho_r + h_4' \rho_r T_r \ln T_r + h_5' \ln \rho_r/T_r$

To compute the model parameter, the following objective function is used [40]:

$$OF = \sum_{i=1}^{N} \frac{\left| y_{2i}^{\exp} - y_{2i}^{cal} \right|}{y_{2i}^{\exp}} \tag{16}$$

where N is the number of experimental solubility data points, y_2 represents the solute mole fraction in $SCCO_2$, and the superscripts '*cal*' and '*exp*' denote the calculated and experimental values, respectively. The *fminsearch* library function of MATLAB 2022b is used for the data fit.

The accuracy of the models was reported in terms of percentage average absolute relative deviation percentage (*AARD*%), error sum of squares (*SSE*), and root mean square error (*RMSE*) [4], [12].

$$AARD\% = \frac{100}{N_i} \sum_{i=1}^{N} \frac{\left| y_{2i}^{\exp} - y_{2i}^{cal} \right|}{y_{2i}^{\exp}} \tag{17}$$

$$SSE = \left[\sum_{i=1}^{N_i} \left(y_{2i}^{\exp} - y_{2i}^{cal} \right)^2 \right] \tag{18}$$

$$RMSE = \left[\frac{1}{N_i} \sum_{i=1}^{N_i} \left(y_{2i}^{\exp} - y_{2i}^{cal} \right)^2 \right]^{1/2} \tag{19}$$

The correlating ability of the eight reformulated models and existing models is reported in terms of global *AARD*%, global R^2, and global *AIC*. It is interesting to note that both models have a similar number of adjustable variables in their models. Tables 3-18 show model parameters, statistical parameters (*SSE*, *RMSE*, R^2, R^2_{adj}, and *AARD*%), and their global values for existing and reformulated models. From the global R^2 and R^2_{adj} values, it is observed that the six reformulated models proposed by Mitra-Wilson, Gordillo et al., Jouyban et al., Hozhabr et al., Khansary et al., and Sodeifian et al. show better correlating results in comparison with their existing counterpart. The remaining two reformulated models of Jafari Nejad et al. and Keshmiri et al. have shown the same correlation ability as that of their existing counterparts.

Table 3. Model parameters and statistical parameters of Mitra-Wilson model

S.No	Model parameters					Statistical parameters				
	a_0	a_1	a_2	a_3	a_4	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD*%
1	9.3687	-3.978×10^{-2}	1.2397×10^{-4}	-26.144	-31.895	1.273×10^{-3}	4.531×10^{-3}	0.871	0.869	29.477
2	3.4541	8.951×10^{-3}	2.462×10^{-5}	-5.7522	-28.658	3.798×10^{-9}	6.607×10^{-6}	0.975	0.974	8.436
3	5.0862	-0.04486	9.4555×10^{-5}	-14.912	-15.718	1.272×10^{-6}	1.231×10^{-4}	0.986	0.986	7.224
4	14.757	-0.12403	3.0166×10^{-4}	56.376	-30.368	7.278×10^{-8}	3.935×10^{-5}	0.941	0.940	20.296
5	2.2976	-7.979×10^{-2}	1.6836×10^{-4}	-17.586	3.4210	1.087×10^{-9}	7.030×10^{-6}	0.904	0.904	10.59
6	0.11814	-3.505×10^{-2}	1.1216×10^{-4}	-10.116	0.14702	8.749×10^{-10}	5.801×10^{-6}	0.948	0.946	6.90

Table 3. (cont.)

S.No	Model parameters					Statistical parameters				
	a_0	a_1	a_2	a_3	a_4	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
7	2.7264	-4.571×10^{-2}	1.9665×10^{-4}	-21.673	-12.047	1.559×10^{-10}	2.025×10^{-6}	0.848	0.844	21.65
8	1.5965	-9.697×10^{-2}	2.1344×10^{-4}	-21.960	12.820	3.326×10^{-9}	1.229×10^{-5}	0.779	0.769	13.827
9	22.681	-15.008	0.61464	-11.766	9.4674	2.532×10^{-11}	9.869×10^{-7}	0.919	0.916	22.015
10	5.0395	-4.366×10^{-2}	8.4261×10^{-5}	-13.615	-20.076	2.268×10^{-10}	2.953×10^{-6}	0.967	0.966	13.447
11	3.1867	1.7548×10^{-2}	7.7846×10^{-5}	-10.840	-33.235	4.344×10^{-11}	1.203×10^{-6}	0.930	0.928	10.532
12	3.2816	2.9173×10^{-3}	7.5911×10^{-5}	-11.687	-26.115	2.244×10^{-9}	9.290×10^{-6}	0.867	0.861	15.08
Global values								0.911	0.908	14.95

Table 4. Model parameters and statistical parameters of reformulated Mitra-Wilson model

S.No	Model parameters					Statistical parameters				
	a'_0	a'_1	a'_2	a'_3	a'_4	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	3.6057	5.777	2.6753	-3.4263	-10.962	7.959×10^{-5}	1.133×10^{-3}	0.992	0.991	10.897
2	10.598	31.321	-15.094	8.0290	-33.490	2.627×10^{-9}	5.495×10^{-6}	0.985	0.985	4.0447
3	-0.46708	6.1041	5.7973	0.84895	-18.467	7.867×10^{-7}	9.677×10^{-5}	0.992	0.992	4.044
4	2.2057	7.4836	6.5086	-4.1988	-17.287	7.093×10^{-9}	1.228×10^{-5}	0.993	0.993	6.5273
5	-10.048	-8.6458	8.6392	0.48326	-12.287	1.118×10^{-9}	7.129×10^{-6}	0.904	0.900	10.722
6	-2.0513	-11.889	6.1040	-4.2850	-0.0381	7.303×10^{-10}	5.300×10^{-6}	0.943	0.941	7.15
7	1.7968	14.586	1.9635	-0.95500	-31.632	2.696×10^{-11}	8.424×10^{-7}	0.964	0.963	18.252
8	0.45347	0.84382	2.4755	-0.74913	-14.271	9.444×10^{-10}	6.551×10^{-6}	0.924	0.920	13.354
9	1.8027	21.408	-4.3835	6.4190	-38.332	1.266×10^{-11}	6.978×10^{-7}	0.933	0.931	8.64
10	0.61944	0.57943	3.0582	-0.78912	-15.865	8.472×10^{-11}	1.805×10^{-6}	0.987	0.986	5.34
11	-0.64059	27.244	-0.37744	3.1232	-4.5459	3.003×10^{-11}	1.000×10^{-6}	0.947	0.945	9.5856
12	0.26777	29.884	-3.9324	5.7643	-44.395	1.009×10^{-9}	6.232×10^{-6}	0.904	0.901	13.061
Global values								0.955	0.954	9.301

Table 5. Model parameters and statistical parameters of Gordillo et al. model

S. No	Model parameters						Statistical parameters				
	b_0	b_1	b_2	b_3	b_4	b_5	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	1.2615	-0.020331	-3.2440×10^{-3}	4.3527×10^{-4}	-0.05462	1.7697×10^{-5}	4.095×10^{-3}	8.127×10^{-3}	0.381	0.371	35.639
2	-1.0657	-0.044299	-4.2348×10^{-4}	2.1696×10^{-4}	-0.049	3.7854×10^{-5}	1.108×10^{-7}	1.129×10^{-5}	0.938	0.937	10.435
3	-1.5259	-0.05406	-5.1575×10^{-4}	2.6559×10^{-4}	-0.00525	-76.109	2.277×10^{-6}	1.647×10^{-4}	0.975	0.975	9.852
4	0.46775	-0.096742	-4.004×10^{-4}	7.456×10^{-4}	-0.02685	-1.1913×10^{-4}	1.372×10^{-7}	5.403×10^{-3}	0.885	0.883	25.37
5	5.393×10^{-3}	-0.03755	-6.9313×10^{-5}	2.3872×10^{-4}	-0.039616	2.282×10^{-5}	6.187×10^{-9}	5.303×10^{-6}	0.947	0.945	13.02
6	-12.348	2.436×10^{-4}	-2.9682×10^{-5}	5.1489×10^{-5}	0.0071317	1.6094×10^{-5}	1.889×10^{-9}	8.525×10^{-6}	0.849	0.843	13.25
7	-22.287	-8.610×10^{-4}	-1.2392×10^{-4}	1.8713×10^{-4}	0.012997	1.7238×10^{-5}	1.272×10^{-11}	5.787×10^{-7}	0.982	0.92	22.501
8	-12.203	3.072×10^{-5}	-1.1219×10^{-4}	1.7304×10^{-4}	0.008729	6.6601×10^{-5}	2.225×10^{-9}	1.005×10^{-5}	0.877	0.872	18.175
9	-9.2863	-0.03786	-5.0664×10^{-5}	2.076×10^{-4}	0.008328	8.8548×10^{-5}	5.500×10^{-12}	4.599×10^{-7}	0.975	0.972	6.2459
10	-0.57887	-0.039363	-4.7633×10^{-5}	2.1310×10^{-4}	-0.042714	$1.3318 \times 10^{-6.}$	1.897×10^{-10}	2.701×10^{-6}	0.968	0.963	14.727
11	3.5702	-0.14070	-1.1548×10^{-4}	5.9322×10^{-4}	-0.079589	4.1146×10^{-5}	2.905×10^{-10}	3.112×10^{-6}	0.817	0.810	19.417
12	18.849	0.040028	-8.7760×10^{-5}	-7.2502×10^{-6}	-0.23621	41475×10^{-4}	1.339×10^{-9}	7.177×10^{-6}	0.887	0.883	13.336
Global values									0.873	0.864	16.83

Table 6. Model parameters and statistical parameters of reformulated Gordillo et al. model

S. No	Model parameters						Statistical parameters				
	b'_0	b'_1	b'_2	b'_3	b'_4	b'_5	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-14.668	4.4856	-6.0538	7.7688	-0.65951	5.024	3.828×10^{-5}	7.858×10^{-4}	0.996	0.996	7.541
2	-55.157	34.502	-6.7358	-17.469	42.613	-7.0093	2.670×10^{-9}	5.539×10^{-6}	0.984	0.984	4.2994
3	3.7116	14.910	-1.1373	-6.4400	-45.229	28.599	5.969×10^{-7}	8.430×10^{-5}	0.993	0.993	3.666
4	-21.411	12.911	-3.9016	-1.3385	-2.6854	8.9212	6.413×10^{-4}	1.168×10^{-5}	0.993	0.993	5.9437
5	3.8539	-19.39	2.9007	12.418	-6.2567	-4.8843	1.4728×10^{-9}	8.1819×10^{-6}	0.874	0.868	10.537

Table 6. (cont.)

S. No	Model parameters						Statistical parameters				
	b'_0	b'_1	b'_2	b'_3	b'_4	b'_5	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
6	4.6261	-18.78	1.1506	15.498	-4.0658	-8.2539	1.0817×10^{-9}	6.4501×10^{-6}	0.935	0.933	6.53
7	-55.180	8.5767	-1.2332	-2.2925	42.830	-9.1492	1.4558×10^{-11}	6.1896×10^{-7}	0.980	0.976	18.358
8	27.490	-21.11	1.3338	17.794	-43.654	7.8309	1.7461×10^{-9}	8.9089×10^{-6}	0.854	0.848	12.557
9	-15.462	-1.224	0.38954	2.2153	-0.6091	0.7331	2.0969×10^{-11}	8.9805×10^{-7}	0.927	0.921	5.9895
10	-16.854	0.6793	-0.24202	2.8266	-1.0671	1.5628	8.4144×10^{-11}	1.7990×10^{-6}	0.987	0.986	5.1741
11	-44.782	-9.888	1.0714	8.3812	46.844	-16.718	1.010×10^{-10}	1.835×10^{-6}	0.893	0.889	9.482
12	-14.421	7.9801	0.17882	-6.7259	-21.870	22.429	1.285×10^{-9}	7.031×10^{-6}	0.883	0.879	22.429
Global values									0.941	0.938	9.375

Table 7. Model parameters and statistical parameters of Jouyban et al. model

S. No	Model parameters						Statistical parameters				
	c_0	c_1	c_2	c_3	c_4	c_5	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-21.385	-0.085992	-2.9513×10^{-5}	3.0859×10^{-4}	-0.0315	2.475	3.283×10^{-4}	2.301×10^{-3}	0.971	0.971	14.937
2	-2.5504	-0.06551	2.4840×10^{-4}	1.4500×10^{-4}	-1.9585	-0.14522	9.808×10^{-9}	1.062×10^{-5}	0.952	0.951	8.552
3	-17.655	-0.034329	-9.4621×10^{-6}	1.1915×10^{-4}	-0.6691	1.7865	3.460×10^{-7}	6.418×10^{-5}	0.996	0.996	2.983
4	-26.921	-0.094565	-1.4697×10^{-5}	3.0979×10^{-4}	-0.30805	2.9022	7.883×10^{-9}	1.295×10^{-5}	0.993	0.992	6.467
5	-5.2332	-0.071325	1.0286×10^{-4}	5.6598×10^{-5}	-2.3375	0.8009	1.728×10^{-9}	8.863×10^{-6}	0.848	0.841	17.944
6	0.58025	-0.12466	1.4720×10^{-4}	1.4533×10^{-4}	-2.5130	0.52783	3.273×10^{-9}	1.122×10^{-5}	0.877	0.873	14.542
7	-12.190	-0.079625	6.1196×10^{-6}	2.2817×10^{-4}	-1.2683	0.32805	4.116×10^{-11}	1.040×10^{-6}	0.950	0.948	18.46
8	-12.559	-0.047770	1.7407×10^{-5}	1.0196×10^{-4}	-1.5829	1.1591	1.305×10^{-9}	7.703×10^{-6}	0.914	0.910	15.402
9	-5.6531	-0.068153	8.0467×10^{-5}	5.7858×10^{-5}	-2.6396	0.67789	1.170×10^{-11}	6.708×10^{-7}	0.947	0.945	7.9972
10	-12.778	-0.10164	9.2319×10^{-5}	1.4290×10^{-4}	-2.6306	2.0913	3.409×10^{-10}	3.621×10^{-6}	0.958	0.957	6.4563
11	-18.953	-0.081700	-5.8706×10^{-5}	3.4271×10^{-4}	-0.043885	0.48686	1.751×10^{-10}	2.416×10^{-6}	0.862	0.858	13.97
12	1.3585	-0.14489	9.7985×10^{-5}	2.7699×10^{-4}	-2.4812	-0.050868	5.030×10^{-9}	1.391×10^{-5}	0.786	0.788	18.814
Global values									0.921	0.919	12.210

Table 8. Model parameters and statistical parameters of reformulated Jouyban et al. model

S. No	Model parameters						Statistical parameters				
	c'_0	c'_1	c'_2	c'_3	c'_4	c'_5	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-19.135	12.338	-11.867	14.971	-0.7896	-6.3835	5.767×10^{-5}	9.645×10^{-4}	0.994	0.994	9.9214
2	-26.400	18.166	-6.8453	7.6843	-1.9486	-10.379	8.549×10^{-9}	9.913×10^{-6}	0.960	0.960	2.7740
3	-21.685	11.074	-7.9256	10.140	2.4434	0.92243	4.893×10^{-7}	7.632×10^{-5}	0.995	0.995	3.0562
4	-17.358	-2.0724	-5.2957	17.473	-0.5434	-2.8571	8.437×10^{-9}	1.339×10^{-5}	0.995	0.995	7.3753
5	11.494	-41.246	6.7405	11.479	0.24345	16.471	1.725×10^{-9}	8.856×10^{-6}	0.844	0.834	11.673
6	8.1438	-52.768	5.3111	18.708	10.639	34.329	7.505×10^{-10}	5.372×10^{-6}	0.959	0.957	5.9647
7	-31.467	55.734	-4.4437	-11.745	-23.768	-58.581	1.065×10^{-11}	5.295×10^{-7}	0.98	0.98	15.632
8	-13.201	-0.6462	0.0051465	3.0718	-0.8665	-1.2545	9.886×10^{-10}	6.703×10^{-6}	0.920	0.988	13.36
9	-16.394	-0.2548	0.14479	2.3683	0.1923	6.0882	1.882×10^{-11}	8.509×10^{-7}	0.932	0.929	6.0882
10	-12.898	-0.8877	0.27006	3.3803	-2.7638	-3.0246	7.798×10^{-11}	1.731×10^{-6}	0.98	0.98	5.3342
11	-18.807	-6.7556	0.053815	12.077	-1.4675	-6.836	1.801×10^{-10}	2.450×10^{-6}	0.849	0.844	11.778
12	-20.259	4.2313	-1.1558	5.8634	-0.8259	-8.3866	2.905×10^{-9}	1.057×10^{-5}	0.814	0.807	14.906
Global values									0.935	0.938	8.988

Table 9. Model parameters and statistical parameters of Jafari Nejad et al. model

S.No	Model parameters				Statistical parameters				
	d_0	d_1	d_2	d_3	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-33.013	-2.131×10^{-6}	9.1964×10^{-4}	2.9987	7.914×10^{-5}	1.130×10^{-3}	0.99	0.99	11.119
2	-48.696	3.243×10^{-8}	9.3188×10^{-5}	4.4286	7.252×10^{-9}	9.130×10^{-6}	0.967	0.966	5.606
3	-45.015	4.176×10^{-7}	7.3559×10^{-5}	4.6397	3.712×10^{-7}	6.648×10^{-5}	0.996	0.996	5.158
4	-40.182	6.058×10^{-6}	8.6466×10^{-5}	3.5039	7.287×10^{-9}	1.245×10^{-5}	0.993	0.993	6.635
5	-12.059	-2.975×10^{-6}	-7.414×10^{-6}	3.4112	2.546×10^{-9}	1.075×10^{-5}	0.462	0.438	27.889
6	-9.7694	1.4366×10^{-5}	-4.625×10^{-6}	1.9528×10^{-4}	4.547×10^{-9}	1.322×10^{-5}	0.608	0.593	17.519
7	-39.476	1.1690×10^{-5}	9.1820×10^{-5}	2.4558	2.742×10^{-11}	8.494×10^{-7}	0.964	0.963	18.166
8	-36.510	6.555×10^{-7}	5.016×10^{-5}	3.2401	9.463×10^{-10}	6.558×10^{-6}	0.926	0.922	14.116
9	-35.778	4.2448×10^{-6}	3.1587×10^{-5}	3.0403	9.935×10^{-12}	6.181×10^{-7}	0.960	0.959	7.771
10	-27.084	1.0771×10^{-5}	2.7342×10^{-5}	1.9876	2.337×10^{-10}	2.998×10^{-6}	0.962	0.960	13.466
11	-33.115	1.7828×10^{-5}	1.0138×10^{-6}	1.4141	6.475×10^{-11}	1.469×10^{-6}	0.914	0.912	10.7
12	-25.185	8.7706×10^{-6}	7.3601×10^{-5}	1.0417	1.622×10^{-9}	7.899×10^{-6}	0.879	0.875	16.186
Global values							0.885	0.880	12.860

Table 10. Model parameters and statistical parameters of reformulated Jafari Nejad et al. model

S.No	Model parameters				Statistical parameters				
	d'_0	d'_1	d'_2	d'_3	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-11.455	-0.57244	8.2165	3.2786	1.018×10^{-5}	1.281×10^{-3}	0.988	0.988	11.869
2	-17.638	-0.39100	8.7948	4.9349	7.145×10^{-9}	9.062×10^{-5}	0.967	0.967	5.6363
3	-13.631	1.9972	5.9751	2.4957	6.566×10^{-7}	8.841×10^{-5}	0.993	0.993	4.1061
4	-17.301	1.4180	8.6149	2.8152	6.713×10^{-9}	1.195×10^{-5}	0.993	0.993	6.1288
5	-31.331	1.5053×10^{-5}	1.6252×10^{-5}	2.8255	2.194×10^{-9}	9.988×10^{-6}	0.816	0.807	17.42
6	-14.022	0.031702	2.8716	0.46897	1.464×10^{-9}	7.503×10^{-6}	0.892	0.888	10.043
7	-26.207	0.16649	9.9093	2.9116	1.9719×10^{-11}	7.203×10^{-7}	0.976	0.975	17.491
8	-16.456	0.18055	4.3166	2.5928	9.132×10^{-10}	6.443×10^{-6}	0.928	0.925	13.753
9	-17.361	0.54892	2.6865	1.0676	1.816×10^{-11}	8.359×10^{-7}	0.935	0.933	6.0517
10	-18.540	0.31215	4.9004	3.0285	7.754×10^{-11}	1.727×10^{-6}	0.987	0.987	4.7403
11	-26.566	0.63099	10.651	0.31478	3.965×10^{-11}	1.149×10^{-6}	0.934	0.931	9.0717
12	-20.842	0.61613	7.9235	-0.36750	2.274×10^{-9}	9.352×10^{-6}	0.866	0.861	13.859
Global values							0.939	0.937	10.01

Table 11. Model parameters and statistical parameters of Keshmiri et al. model

S.No	Model parameters					Statistical parameters				
	e_0	e_1	e_2	e_3	e_4	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-0.58905	-11,966	-2.0416×10^{-6}	14.72	943.16	1.242×10^{-4}	1.415×10^{-3}	0.984	0.983	12.423
2	2.7037	-16,219	-4.6567×10^{-7}	7.6723	1474.3	4.921×10^{-9}	7.521×10^{-6}	0.976	0.976	4.805
3	2.1648	-15,973	-4.0858×10^{-7}	7.6836	1610.7	1.673×10^{-7}	4.463×10^{-5}	0.998	0.998	4.669
4	-0.17756	-12,930	5.8443×10^{-6}	9.6069	1105	8.711×10^{-9}	1.361×10^{-5}	0.992	0.992	6.811
5	-128.23	28,050	6.6354×10^{-6}	19.227	-4703.7	1.014×10^{-9}	6.791×10^{-6}	0.922	0.918	16.611
6	-19.100	5.9874×10^{-6}	2.3494×10^{-5}	1.0278	10018	1.529×10^{-9}	7.669×10^{-6}	0.880	0.766	10.231
7	-38.142	2,722.3	6.9069×10^{-6}	7.2363	-1540.3	2.668×10^{-11}	8.380×10^{-7}	0.965	0.964	18.474
8	-35.106	1,714.2	2.2220×10^{-6}	5.2034	-709.68	9.518×10^{-10}	6.577×10^{-6}	0.921	0.917	14.568
9	-117.07	28,210	7.4441×10^{-6}	17.118	-4611.3	9.392×10^{-11}	1.900×10^{-6}	0.985	0.984	6.724
10	-117.86	30,496	8.1322×10^{-6}	16.465	-47815	1.274×10^{-11}	7.000×10^{-7}	0.947	0.945	8.435
11	-102.72	26,075	1.6270×10^{-5}	17.366	-5173.1	1.036×10^{-10}	1.858×10^{-6}	0.891	0.887	18.189
12	-17.783	-0.86108	9.1635×10^{-5}	3.6014	-810.46	1.860×10^{-9}	8.459×10^{-6}	0.877	0.873	16.098
Global values								0.944	0.933	11.50

Table 12. Model parameters and statistical parameters of reformulated Keshmiri et al. model

S.No	Model parameters					Statistical parameters				
	e'_0	e'_1	e'_2	e'_3	e'_4	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-23.768	20.739	-0.79551	9.5110	-6.3355	18.677×10^{-5}	1.183×10^{-3}	0.980	0.980	11.026
2	-18.533	17.395	-8.0205	-11.470	23.080	2.976×10^{-9}	5.848×10^{-6}	0.980	0.980	4.356
3	-20.854	9.4528	5.7922	-4.5736	5.3825	5.898×10^{-7}	8.379×10^{-5}	0.994	0.994	3.5866
4	-28.029	17.324	3.3895	2.1514	-2.3450	7.266×10^{-9}	1.243×10^{-5}	0.993	0.993	6.1318
5	-12.276	-8.843	9.2817	-5.2560	-10.233	1.347×10^{-9}	7.826×10^{-6}	0.872	0.866	11.308
6	-13.596	1.0053	2.0786	5.9428	-7.6921	1.167×10^{-9}	6.700×10^{-6}	0.915	0.912	8.3774
7	-39.124	22.496	0.36791	1.4686	1.6964	1.641×10^{-11}	6.573×10^{-7}	0.976	0.978	17.172
8	-16.318	3.0065	1.8085	7.5904	-7.5657	9.326×10^{-10}	6.510×10^{-6}	0.921	0.918	13.637
9	-24.249	8.9199	1.9876	1.3140	0.24427	8.166×10^{-11}	1.772×10^{-6}	0.987	0.986	5.0258
10	-21.068	3.7421	3.1625	-0.7044	-0.43128	1.723×10^{-11}	8.141×10^{-7}	0.938	0.935	5.9913
11	-36.754	17.893	3.7666	5.9572	-8.8556	5.9509×10^{-11}	1.408×10^{-6}	0.920	0.918	8.9951
12	-30.035	15.037	2.7159	0.03392	-1.9124	2.1619×10^{-9}	9.118×10^{-6}	0.871	0.866	13.482
Global values								0.945	0.943	9.090

Table 13. Model parameters and statistical parameters of Hozhabr et al. model

S.No	Model parameters				Statistical parameters				
	f_0	f_1	f_2	f_3	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	29.462	-10,809	5.6105	1.0228	0.001582	1.107×10^{-3}	0.992	0.992	13.466
2	16.127	-9379.6	5.6372	0.48446	6.384×10^{-5}	8.127×10^{-6}	0.972	0.972	5.2975
3	13.862	-7,907.7	5.6261	0.33977	2.991×10^{-7}	5.967×10^{-5}	0.996	0.996	3.1564
4	21.857	-10,222	6.0328	0.80579	8.523×10^{-9}	1.346×10^{-5}	0.991	0.991	6.6514
5	-6.0697	-7.8202	-0.082429	6.1725	6.763×10^{-10}	5.544×10^{-6}	0.945	0.942	16.171
6	-2.0906	-9.9192	1.0944	0.34321	1.753×10^{-9}	8.211×10^{-6}	0.866	0.861	11.012
7	24.823	-13,075	3.1780	0.95025	2.640×10^{-11}	8.335×10^{-7}	0.963	0.962	24.676
8	10.062	-7071.2	2.4496	0.71186	8.224×10^{-10}	6.114×10^{-6}	0.936	0.933	13.609
9	-2.9111	-4,405.6	1.8656	0.002075	1.246×10^{-11}	6.923×10^{-7}	0.949	0.947	6.6871
10	7.8850	-7,340.5	2.6605	0.39032	9.954×10^{-11}	1.956×10^{-6}	0.984	0.984	6.2898
11	15.852	-34.384	2.8561	-0.58074	2.067×10^{-11}	8.300×10^{-7}	0.960	0.958	8.6928
12	-21.597	-0.28587	-0.9727	-2.6080	1.502×10^{-9}	7.601×10^{-6}	0.835	0.829	21.646
Global values							0.949	0.949	11.297

Table 14. Model parameters and statistical parameters of reformulated Hozhabr et al. model

S.No	Model parameters				Statistical parameters				
	f'_0	f'_1	f'_2	f'_3	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	11.913	-15.217	-0.45251	3.1346	1.281×10^{-9}	8.196×10^{-6}	0.972	0.971	12.064
2	6.0722	-15.188	-0.15603	4.5640	5.845×10^{-9}	8.196×10^{-6}	0.972	0.971	5.1384
3	8.9324	-20.297	5.7567	0.97298	4.750×10^{-7}	7.520×10^{-5}	0.995	0.995	3.6653
4	11.007	-21.912	3.6458	1.9545	8.923×10^{-9}	1.377×10^{-5}	0.991	0.991	6.1115
5	-18.963	0.13679	0.73130	-1.3152	2.9922×10^{-9}	1.166×10^{-5}	0.665	0.650	18.349
6	-1.9640	-10.097	1.1329	0.31295	1.7712×10^{-9}	8.253×10^{-6}	0.867	0.862	10.996
7	8.3870	-25.660	0.80806	2.6435	1.7995×10^{-11}	6.881×10^{-7}	0.977	0.974	17.463
8	-2.3679	-10.582	0.83584	2.3376	9.1545×10^{-10}	6.450×10^{-6}	0.927	0.924	14.015
9	-2.9996	-14.369	2.8371	0.02782	1.2311×10^{-11}	6.881×10^{-7}	0.948	0.947	6.6831
10	-0.74047	-14.733	1.8541	2.1529	9.2272×10^{-11}	1.883×10^{-6}	0.985	0.984	5.4164
11	7.8413	-8457.4	1.0220	-66.395	2.077×10^{-11}	8.321×10^{-7}	0.961	0.960	7.8759
12	11.091	-25.884	2.2407	-0.74323	1.2622×10^{-9}	6.967×10^{-6}	0.906	0.902	12.453
Global values							0.930	0.927	10.019

Table 15. Model parameters and statistical parameters of Khansary et al. model

S.No	Model parameters					Statistical parameters				
	g_0	g_1	g_2	g_3	g_4	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-6,409.3	-0.04629	-0.00134	2.4935	0.006857	1.018×10^{-4}	0.012815	0.987	0.987	10.391
2	-8,258.8	-0.1557	-3.9929×10^{-3}	2.4776	0.023467	3.822×10^{-9}	6.628×10^{-6}	0.981	0.981	4.450
3	-5,494.8	-0.12425	-7.5067×10^{-3}	1.457	0.020018	1.592×10^{-7}	4.353×10^{-5}	0.998	0.998	3.557
4	-7,031.7	-0.11195	-0.00257	2.1194	0.0171	1.008×10^{-8}	1.464×10^{-5}	0.991	0.990	6.886
5	-6,443.3	-0.26574	-9.6223×10^{-3}	1.4877	0.040798	-1.206×10^{-8}	6.839×10^{-6}	0.905	0.901	16.373
6	-2,828.4	-0.095155	-4.0973×10^{-3}	-0.16837	0.014923	1.656×10^{-9}	7.981×10^{-6}	0.858	0.853	10.469
7	-8,847.8	-0.080274	-7.9240×10^{-3}	2.0650	0.013322	2.190×10^{-11}	7.591×10^{-7}	0.968	0.967	18.524
8	-4,412.6	-0.15585	-1.0705×10^{-2}	0.48022	0.025018	1.035×10^{-9}	6.860×10^{-6}	0.916	0.916	14.279
9	-3,825.3	-0.17332	-5.1781×10^{-3}	-0.07491	0.026722	2.680×10^{-11}	1.015×10^{-6}	0.893	0.896	7.8721
10	-6,651.6	-0.19557	1.2525×10^{-3}	1.6737	0.028442	1.544×10^{-10}	2.437×10^{-6}	0.976	0.975	7.2533
11	-6,116.3	0.002690	-1.4193×10^{-2}	0.57029	0.0030214	1.819×10^{-11}	7.788×10^{-7}	0.964	0.963	7.8974
12	-2,572.3	5.0796×10^{-4}	-3.2396×10^{-2}	-1.0093	0.006.091	8.323×10^{-10}	5.657×10^{-6}	0.928	0.925	12.42
Global values								0.947	0.946	10.03

Table 16. Model parameters and statistical parameters of reformulated Khansary et al. model

S.No	Model parameters					Statistical parameters				
	g'_0	g'_1	g'_2	g'_3	g'_4	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-11.958	14.478	-6.7084	-0.61023	-0.78591	5.033×10^{-5}	9.010×10^{-4}	0.995	0.995	7.6467
2	-14.686	3.6907	1.7109	2.3543	-5.0911	6.294×10^{-9}	8.506×10^{-6}	0.970	0.969	5.3294
3	-11.903	11.589	-5.4643	-1.0102	6.0126	6.025×10^{-7}	8.469×10^{-5}	0.994	0.993	3.4013
4	-14.771	10.801	-3.6059	0.15196	-0.079187	8.209×10^{-9}	1.321×10^{-5}	0.992	0.992	6.4239
5	-10.195	2.8933	-5.2939	-6.9393	14.931	1.100×10^{-9}	7.072×10^{-7}	0.899	0.894	11.41
6	-9.4220	0.075132	-1.5872	0.18512	4.2265	1.613×10^{-9}	7.878×10^{-6}	0.888	0.884	9.9417
7	-20.756	1.2331	3.4937	2.4246	-7.9631	9.132×10^{-12}	4.902×10^{-7}	0.987	0.986	15.179
8	-9.3640	3.1664	-5.6034	-2.8672	12.764	1.021×10^{-9}	6.814×10^{-6}	0.917	0.913	12.818
9	-12.123	-1.8177	-0.38669	2.1662	2.8882	1.334×10^{-11}	7.165×10^{-7}	0.947	0.945	6.2346
10	-13.507	-0.35173	0.38523	3.0825	0.17518	8.715×10^{-11}	1.830×10^{-6}	0.987	0.986	5.263
11	-21.695	4.7204	1.5020	-2.0828	-4.0046	3.674×10^{-11}	1.106×10^{-6}	0.944	0.942	7.7736
12	-2620.6	0.0010814	-0.032148	-0.98255	0.0062798	8.569×10^{-10}	5.741×10^{-6}	0.928	0.928	12.421
Global values								0.954	0.952	8.653

Table 17. Model parameters and statistical parameters of Sodeifian et al. model

S. No	Model parameters						Statistical parameters				
	h_0	h_1	h_2	h_3	h_4	h_5	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD%*
1	-20.842	-0.02988	1.1659	0.001292	0.008014	4.7748	0.001429	0.004801	0.846	0.842	24.127
2	-142.86	1.9844×10^{-4}	11.187	4.5834×10^{-4}	-1.6711×10^{-4}	-9.0384	5.615×10^{-9}	8.034×10^{-6}	0.972	0.972	5.333
3	-2.733	-0.01975	-0.5642	-0.00192	0.007002	8.7101	3.467×10^{-6}	2.031×10^{-4}	0.958	0.958	9.406
4	-146.94	2.6204×10^{-4}	11.711	4.9409×10^{-4}	-2.6467×10^{-4}	-9.7801	7.217×10^{-9}	1.239×10^{-5}	0.993	0.993	5.80
5	-0.037507	-0.012612	-1.2532	2.1359×10^{-4}	4.0256×10^{-2}	1.5167	1.601×10^{-9}	8.531×10^{-6}	0.831	0.823	16.449
6	-0.19861	-7.5814×10^{-3}	-0.9217	-4.1046×10^{-4}	2.6089×10^{-3}	2.4418	2.094×10^{-9}	8.975×10^{-6}	0.767	0.758	12.761
7	-0.49578	-4.647×10^{-2}	-1.5521	-1.1190×10^{-3}	1.3022×10^{-2}	3.8618	1.043×10^{-11}	5.239×10^{-7}	0.984	0.984	19.07
8	1.3851	-2.493×10^{-2}	-1.2779	-1.1528×10^{-3}	7.2616×10^{-3}	6.3333	1.418×10^{-9}	8.030×10^{-6}	0.902	0.898	15.262
9	1.6352	-1.196×10^{-2}	-1.4024	-8.4550×10^{-4}	4.3317×10^{-3}	5.2601	9.811×10^{-12}	6.142×10^{-7}	0.950	0.948	7.6193
10	-22.276	-1.309×10^{-2}	0.86157	-2.1669×10^{-3}	5.2660×10^{-3}	8.9169	1.388×10^{-10}	2.311×10^{-6}	0.977	0.976	8.0036
11	1.0837	-5.716×10^{-2}	-1.7222	-6.8510×10^{-4}	1.4395×10^{-2}	2.5177	1.896×10^{-11}	7.951×10^{-7}	0.956	0.955	16.431
12	-0.65952	-4.423×10^{-2}	-1.249	-1.7825×10^{-4}	1.0465×10^{-2}	0.50381	9.188×10^{-10}	5.944×10^{-6}	0.913	0.909	14.499
Global values									0.920	0.918	12.89

Table 18. Model parameters and statistical parameters of reformulated Sodeifian et al. model.

S. No	Model parameters						Statistical parameters				
	h'_0	h'_1	h'_2	h'_3	h'_4	h'_5	*SSE*	*RMSE*	R^2	R^2_{adj}	*AARD*%
1	-3.2407	-0.7306	6.7338	-0.096924	11.600	-3.9336	6.746×10^{-5}	1.043×10^{-3}	0.993	0.993	10.523
2	-2.6221	-6.5896	27.314	7.5969	-27.313	-18.256	2.210×10^{-9}	5.040×10^{-6}	0.998	0.998	3.7621
3	-5.0462	-0.59341	10.189	4.3265	-0.53937	-6.7337	4.742×10^{-7}	7.514×10^{-5}	0.995	0.995	3.8363
4	-7.6576	0.41000	10.621	1.9518	2.8032	-7.5704	8.165×10^{-9}	1.318×10^{-5}	0.992	0.992	6.2247
5	-13.450	1.1174	-0.88933	0.28785	5.6184	-0.6475	8.341×10^{-10}	6.157×10^{-6}	0.926	0.922	13.038
6	-11.214	1.4410	-13.660	-2.1559	16.278	11.884	9.750×10^{-5}	6.123×10^{-6}	0.941	0.939	6.4306
7	-19.853	3.2204	22.046	-6.9818	-12.656	-17.665	7.876×10^{-12}	4.552×10^{-7}	0.988	0.988	14.932
8	-12.122	0.22113	4.728	3.4983×10^{-3}	1.6508	-2.4657	9.249×10^{-10}	6.484×10^{-6}	0.926	0.923	13.744
9	-14.794	0.52224	4.8102	1.2502×10^{-3}	9.3805×10^{-3}	-3.454	1.536×10^{-11}	7.687×10^{-7}	0.942	0.940	6.2284
10	-13.769	0.28192	8.0750	0.19243	-0.31047	-5.0639	8.289×10^{-11}	1.785×10^{-6}	0.987	0.986	5.0434
11	-16.114	0.60335	13.845	-1.1649×10^{-2}	9.1439×10^{-2}	-13.162	3.4781×10^{-11}	1.076×10^{-6}	0.946	0.944	8.3206
12	-0.6595	-0.0442	-1.2490	-1.7825×10^{-4}	1.0465×10^{-2}	0.50381	9.188×10^{-10}	5.944×10^{-6}	0.913	0.909	14.499
Global values									0.962	0.960	8.881

The Akaike Information Criterion (*AIC*) is used to assess the relative goodness of the models depending on the number of data points and number of model constants, and it is defined as follows [41]:

$$AIC = N \ln\left(\frac{SSE}{N}\right) + 2K \tag{20}$$

$$AIC_c = AIC + \frac{2K(K+1)}{N-K-1} \tag{21}$$

Where K represents the number of parameters and N represents the number of data points. Tables 19-20 indicate values for the existing and reformulated mathematical solubility models. When the solubility data point for a system is greater than 40, the global values for existing mathematical models are observed to be as follows, Mitra-Wilson model (-1,331.12), Gordillo et al. (-1,266.31), Jouyban et al. (-1,384.92), Jafari Nejad et al. (1,417.92), Keshmiri et al. (1,432.22), Hozhabr et al. (-1,426.37), Khansary et al. (1,440.3), and Sodeifian et al. (1,325.32), whereas the global values for the reformulated models are Mitra-Wilson model (-1,243.34), Gordillo et al. (-1,438.78), Jouyban et al. (-1,410.84), Jafari Nejad et al. (-1,399.07), Keshmiri et al. (1,424.26), Hozhabr et al. (-1,407.14), Khansary et al. (1,414.36), and Sodeifian et al. (1,436.17). When the solubility data point for a system is lesser than 40, the global values for existing mathematical models are observed to be as follows, Mitra-Wilson model (-720.95), Gordillo et al. (-721.49), Jouyban et al. (-724.26), Jafari Nejad et al. (-734.45), Keshmiri et al. (-734.45), Hozhabr et al. (-738.29),

Khansary et al. (-740.29), and Sodeifian et al. (-742.00), whereas the global values for the reformulated models are Mitra-Wilson model (-744.19), Gordillo et al. (-723.93), Jouyban et al. (-742.14), Jafari Nejad et al. (-738.16), Keshmiri et al. (-738.46), Hozhabr et al. (-745.46), Khansary et al. (-750.25), and Sodeifian et al. (-746.69). For standard compounds, the global is lowest for the reformulated models when compared with their existing counterparts. For drug compounds, the global AIC_c is lowest for the reformulated models when compared with their existing counterparts In terms of global $AARD\%$, global R^2, and global R^2_{adj}, all the proposed reformulated models are observed to be superior to their existing counterparts. All these observations are indicated in Tables 3-20. The global values of existing and reformulated mathematical solubility models are shown in Tables 19-20. The global difference value [42], [43] is used to compare existing and reformulated mathematical solubility models, and it is quantified as global .

$$Global\Delta AIC = GlobalAIC_{Existing} - GlobalAIC_{Reformulated} \tag{22}$$

$$Global\Delta AIC_c = GlobalAIC_{c_{Existing}} - GlobalAIC_{c_{Reformulated}} \tag{23}$$

If the absolute value ofis greater than 10, then the models considered for the comparison are significantly different [42], [43]. Tables 21-22 indicates the AIC_c values of existing and reformulated models.

The summary of global differences for existing and reformulated models are as follows: Mitra-Wilson model (87.78), Gordillo et al. (172.47), Jouyban et al. (25.92), Jafari Nejad et al. (18.77), Keshmiri et al. (7.95), Hozhabr et al. (19.23), Khansary et al. (25.93), and Sodeifian et al. (110.84). For the case of drug compounds considered in the work, the global AIC_c differences for existing and reformulated models are: Mitra-Wilson model (23.24), Gordillo et al. (2.43), Jouyban et al. (17.87), Jafari Nejad et al. (3.70), Keshmiri et al. (3.70), Hozhabr et al. (7.16), Khansary et al. (9.96), and Sodeifian et al. (4.69). The study indicates that reformulated models show better correlation for standard compounds, which are well-known polycyclic aromatic hydrocarbons (PAHs), and their dissolution pattern is understood at the molecular level [44], and it is found to be consistent with the solubility data present in the literature; thus, their solubility data is reliable. However, such molecular-level information is unavailable for the drug compounds considered in the study, which limits our understanding of the literature-reported data. Figures 1-8 show the parity plot of existing and reformulated models.

Table 19. AIC values of existing models

S.No	Mitra and Wilson model (1991) [30]	Gordillo et al. (1999) [31]	Jouyban et al. (2002) [32]	Jafari Nejad et al. (2010) [33]	Keshmiri et al. (2014) [34]	Hozhabr et al. (2014) [35]	Khansary et al. (2015) [36]	Sodeifian et al. (2019) [37]
1	-682.83	-606.04	-767.56	-862.6	-831.77	-865.12	-844.48	-673.4
2	-2,115.09	-2,017.79	-2,028.65	-2,059.52	-2,092.04	-2,080.23	-2,114.52	-2,078.29
3	-1,540.5	-1,488.44	-1,650.48	-1,648.43	-1,714.98	-1,666.99	-1,719.25	-1,452.3
4	-986.06	-952.98	-1,092.97	-1,100.82	-1,090.08	-1,093.13	-1,082.93	-1,097.3
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
Global values	-1,331.12	-1,266.31	-1,384.92	-1,417.92	-1,432.22	-1,426.37	-1,440.3	-1,325.32

Table 20. AIC values of reformulated models

S.No	Mitra and Wilson model (1991) [30]	Gordillo et al. (1999) [31]	Jouyban et al. (2002) [32]	Jafari Nejad et al. (2010) [33]	Keshmiri et al. (2014) [34]	Hozhabr et al. (2014) [35]	Khansary et al. (2015) [36]	Sodeifian et al. (2019) [37]
1	-860.23	-907.07	-878.84	-846.43	-854.70	-831.73	-889.56	-868.81
2	-2,147.87	-2,143.42	-2,040.8	-2,060.84	-2,136.79	-2,078.71	-2,070.12	-2,161.27
3	-1,100.14	-1,603.57	-1,620.66	-1,599.38	-1,606.61	-1,627.22	-1,604.77	-1,623.36
4	-865.12	-1,101.07	-1,103.07	-1,089.63	-1,098.95	-1,090.89	-1,092.98	-1,091.24
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
Global values	-1,243.34	-1,438.78	-1,410.84	-1,399.07	-1,424.26	-1,407.14	-1,414.36	-1,436.17

Table 21. AIC_c values of reformulated model

S.No	Mitra and Wilson model (1991) [30]	Gordillo et al. (1999) [31]	Jouyban et al. (2002) [32]	Jafari Nejad et al. (2010) [33]	Keshmiri et al. (2014) [34]	Hozhabr et al. (2014) [35]	Khansary et al. (2015) [36]	Sodeifian et al. (2019) [37]
1	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-558.84	-550.23	-644.53	-554.36	-640.22	-570.91	-559.22	-563.87
6	-670.61	-657.61	-667.85	-657.48	-852.85	-645.807	-648.41	-660.52
7	-1109.86	-1132.52	-1145.00	-1129.71	-731.95	-1126.04	-1153.18	-1157.09
8	-562.89	-548.14	-559.80	-563.20	-775.51	-563.64	-561.011	-561.39
9	-784.15	-681.17	-771.04	-775.51	-563.20	-784.93	-782.67	-776.73
10	-730.92	-731.12	-703.58	-731.95	-1129.71	-730.53	-763.15	-729.54
11	-874.74	-835.91	-815.41	-852.85	-657.48	-886.53	-868.28	-868.04
12	-661.54	-654.77	-629.95	-640.22	-554.36	-655.29	-666.13	-656.39
Global values	-744.194	-723.934	-742.145	-738.16	-738.16	-745.46	-750.256	-746.696

Table 22. AIC_c values of existing model

S.No	Mitra and Wilson model (1991) [30]	Gordillo et al. (1999) [31]	Jouyban et al. (2002) [32]	Jafari Nejad et al. (2010) [33]	Keshmiri et al. (2014) [34]	Hozhabr et al. (2014) [35]	Khansary et al. (2015) [36]	Sodeifian et al. (2019) [37]
1	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-559.51	-571.04	-644.49	-561.17	-561.17	-535.22	-560.83	-548.22
6	-665.55	-641.99	-626.60	-649.91	-649.91	-646.09	-647.68	-639.11
7	-1,039.68	-1,137.90	-1,090.95	-1,110.28	-1,110.28	-1,110.71	-1,118.19	-1,145.85
8	-532.67	-542.33	-553.12	-562.71	-562.71	-566.21	-560.68	-551.13
9	-764.74	-714.62	-784.36	-783.97	-783.97	-784.59	-763.15	-789.29
10	-703.35	-708.35	-663.75	-728.04	-728.04	-726.41	-714.11	-715.09
11	-862.92	-802.12	-816.30	-835.11	-835.11	-886.69	-890.77	-887.44
12	-639.18	-653.62	-614.57	-644.42	-644.427	-650.41	-666.95	-659.92
Global values	-720.95	-721.496	-724.268	-734.451	-734.452	-738.291	-740.295	-742.006

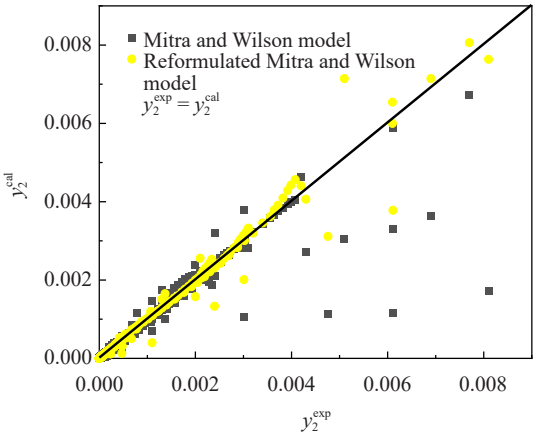


Figure 1. Parity plot of Mitra-Wilson model and reformulated Mitra-Wilson model

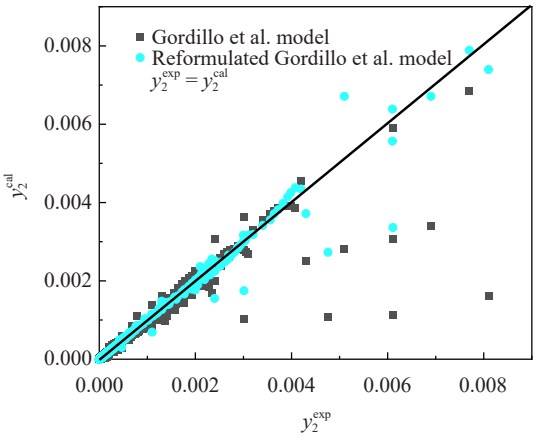


Figure 2. Parity plot of Gordillo et al. model and reformulated Gordillo et al. model

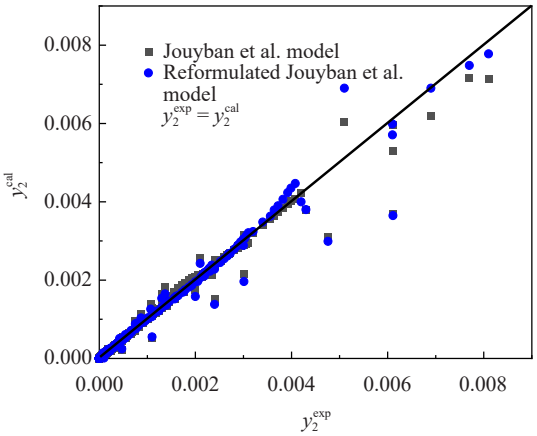


Figure 3. Parity plot of Jouyban et al. model and reformulated Jouyban et al. model

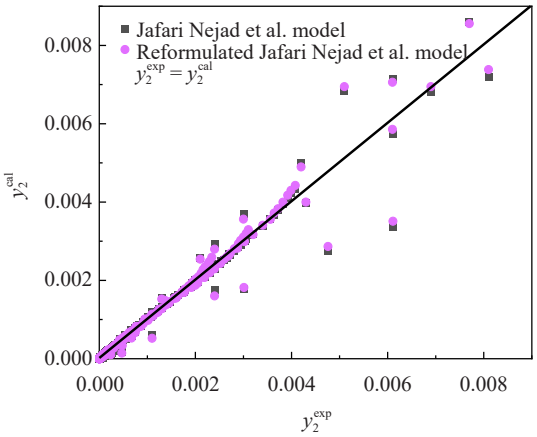


Figure 4. Parity plot of Jafari Nejad et al. model and reformulated Jafari Nejad et al. model

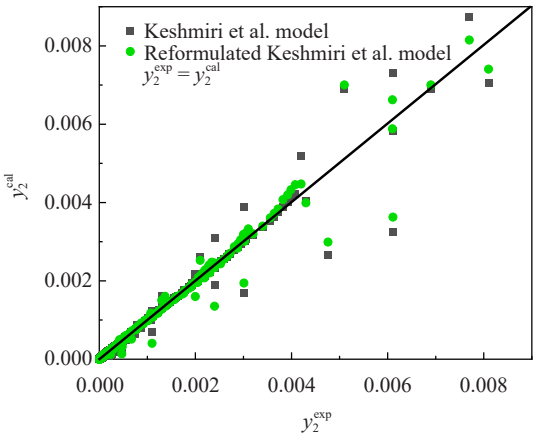


Figure 5. Parity plot of Keshmiri et al. model and reformulated Keshmiri et al. model

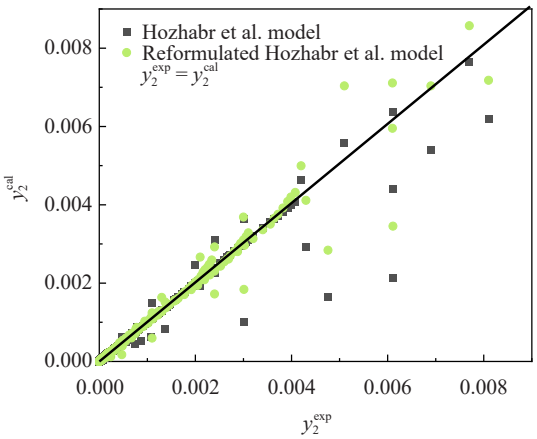


Figure 6. Parity plot of Hozhabr et al. model and reformulated Hozhabr et al. model

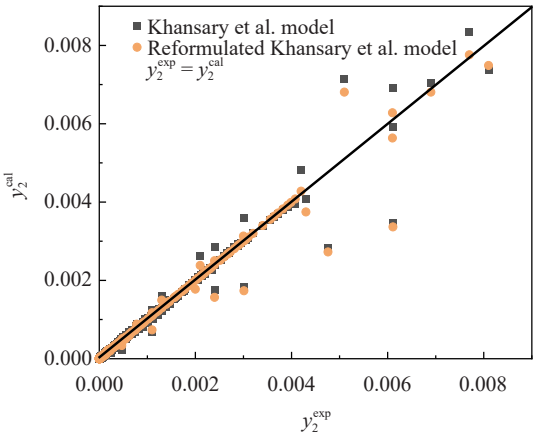


Figure 7. Parity plot of Khansary et al. model and reformulated Khansary et al. model

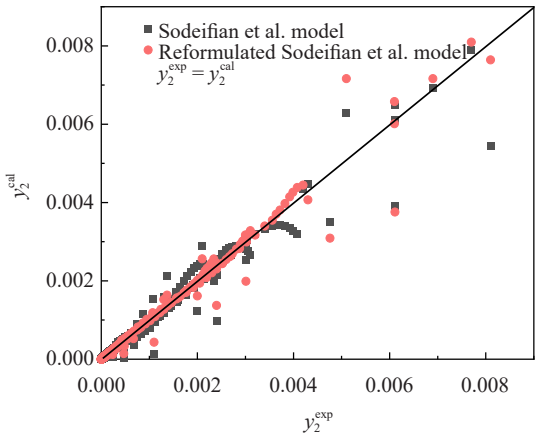


Figure 8. Parity plot of Sodeifian et al. model and reformulated Sodeifian et al. model

5. Conclusion

In this work, eight widely used mathematical solubility models used in supercritical fluid-based solubility studies are reformulated with the help of the equation of state. Existing and reformulated mathematical solubility models are evaluated with twelve compounds' solubility data in $SCCO_2$. The reformulated mathematical solubility models are found to be better than the existing mathematical solubility models, in terms of global *AARD*%, global R^2, and global R^2_{adj} value of Mitra-Wilson model (9.301, 0.955, 0.954), Gordillo et al. (9.375, 0.941, 0.938), Jouyban et al. (8.988, 0.935, 0.938), Jafari Nejad et al. (10.01, 0.939, 0.937), Keshmiri et al. (9.090, 0.945, 0.943), Hozhabr et al. (10.01, 0.932, 0.927), Khansary et al. (8.653, 0.954, 0.952), and Sodeifian et al. (8.881, 0.962, 0.960). Global ΔAIC analysis for standard compounds indicates that existing mathematical solubility models and reformulated mathematical solubility models are distinctly different except Keshmiri et al. model.

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Conflict of interest

The authors declare no competing financial interest.

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Appendix A

MATLAB CODING

MAIN FUNCTION

```
% %% declaring variables and reading data from file
clc ;
clear all;
global k m a AARD b2 AARD2 AAR2 cca mm AAR;
i=1;
%% A contains input data 1 molefraction, density, temperature and pressure
%Napthalene data
a=[
2.40E-04    162.65  308     60.795
7.50E-04    291.47  308     75.99375
8.70E-04    311.74  308     77.007
1.07E-03    338.17  308     78.02025
1.37E-03    375.46  308     79.0335
3.01E-03    400.55  308     79.540125
4.76E-03    464.12  308     80.553375
6.11E-03    496.14  308     81.06
8.10E-03    638.58  308     87.1395
9.20E-03    677.69  308     92.20575
1.10E-02    735.55  308     106.39125
1.17E-02    749.31  308     111.4575
1.25E-02    771.83  308     121.59
1.32E-02    790.02  308     131.7225
1.39E-02    805.40  308     141.855
1.46E-02    818.79  308     151.9875
1.51E-02    830.69  308     162.12
1.63E-02    860.27  308     192.5175
1.74E-02    883.89  308     222.915
1.77E-02    897.46  308     243.18
1.84E-02    926.22  308     293.8425
1.87E-02    945.51  308     334.3725
4.70E-04    152.12  318     62.8215
4.80E-04    198.01  318     72.954
6.70E-04    227.89  318     78.02025
7.80E-04    257.42  318     82.07325
1.10E-03    289.51  318     85.619625
1.30E-03    317.49  318     88.15275
2.10E-03    373.66  318     92.20575
4.30E-03    432.50  318     95.752125
5.10E-03    519.01  318     97.778625
6.10E-03    490.27  318     99.2985
6.90E-03    519.01  318     101.325
9.70E-03    574.96  318     106.39125
1.13E-02    599.90  318     109.431
1.42E-02    657.09  318     119.5635
1.54E-02    684.26  318     126.65625
1.83E-02    726.07  318     141.855
1.97E-02    752.56  318     155.02725
```

```
2.45E-02    816.25  318     202.65
2.85E-02    877.46  318     278.64375
2.94E-02    898.59  318     314.1075
1.10E-03    190.28  328     77.007
2.40E-03    269.63  328     92.20575
2.00E-03    283.21  328     94.23225
2.40E-03    321.28  328     99.2985
3.00E-03    347.04  328     102.33825
4.20E-03    384.22  328     106.39125
6.10E-03    432.62  328     111.4575
7.70E-03    460.85  328     114.49725
9.20E-03    478.77  328     116.52375
1.08E-02    503.90  328     119.5635
1.27E-02    526.73  328     122.60325
1.42E-02    547.30  328     125.643
1.81E-02    582.35  328     131.7225
2.34E-02    630.92  328     142.86825
2.64E-02    660.78  328     151.9875
3.00E-02    687.42  328     162.12
3.24E-02    709.42  328     172.2525
3.56E-02    728.15  328     182.385
3.99E-02    751.90  328     197.58375
4.59E-02    794.62  328     233.0475
4.85E-02    814.00  328     253.3125
5.50E-02    866.11  328     324.24
];
format short e
% warning( 'off','MATLAB:xlswrite1:AddSheet' );
k =  [9.3687 -3.978e-2          1.2397e-4          -26.144  -31.895];
b=( fminsearch('function1',k));
a1=AARD;
a2=0;
while   a1~=a2
   xx=(fminsearch('function1',b));
a3=AARD;
   a1=a2;
   a2=a3;
   b=xx;
end
[~,g]= createFit(a(:,1),m(:,1)) % Analyse the input moles with output moles
mol=[a(:,1),m(:,1)];
b                   % computed constants for minimal AARD
AARD                    % AARD
m(:,1)

                                %%%%%%%function1 file%%%%%%%%%%%%
function [ aard ] = function(k)
global m a yy AARD AAR;
aard=0.00;
yy=length (a);
```

```
m=[];
for i=1:yy;
m(i,1) = exp(k(1)*log (a(i,4))+ k(2)*(a(i,3))+(k(3)*a(i,4)*a(i,3))+(k(4)*((a(i,4))/(a(i,3))))+k(5));  %%%%Mitra wilson
reldev=abs(a(i,1)-m(i,1))/a(i,1);
aard=aard+reldev;
ya=aard;
end
AARD=aard*100/yy;
AAR=aard*100/(yy-length(k));
end
```

CREAT FIT

```
function [fitresult, g] = createFit(a,b)
%% Fit: 'untitled fit 1'.
[xData, yData] = prepareCurveData( a, b );

% Set up fittype and options.
ft = fittype( 'poly1' );

% Fit model to data.
[fitresult, g] = fit( xData, yData, ft, 'Normalize', 'on' );
end
```

OUTPUT

```
sse: 1.2728e-03
rsquare: 8.7126e-01
dfe: 62
   adjrsquare: 8.6918e-01
         rmse: 4.5309e-03

b =

  9.3686e+00-3.9781e-02   1.2397e-04-2.6143e+01-3.1895e+01

AARD =

  2.9477e+01

ans =

  2.0255e-04
  8.0572e-04
  8.7002e-04
  9.3792e-04
  1.0095e-03
  1.0467e-03
  1.1241e-03
  1.1642e-03
  1.7258e-03
```

2.3129e-03
4.5572e-03
5.5620e-03
7.8299e-03
1.0326e-02
1.2881e-02
1.5317e-02
1.7468e-02
2.1133e-02
2.0181e-02
1.7700e-02
9.7822e-03
4.9449e-03
2.1514e-04
5.6601e-04
8.5477e-04
1.1550e-03
1.4750e-03
1.7392e-03
2.2281e-03
2.7263e-03
3.0418e-03
3.2934e-03
3.6491e-03
4.6403e-03
5.3049e-03
7.8827e-03
9.9849e-03
1.5066e-02
1.9701e-02
3.1580e-02
2.4147e-02
1.6265e-02
7.0796e-04
2.1143e-03
2.3948e-03
3.2094e-03
3.7807e-03
4.6438e-03
5.8917e-03
6.7325e-03
7.3316e-03
8.2877e-03
9.3119e-03
1.0403e-02
1.2774e-02
1.7693e-02
2.2127e-02
2.7270e-02
3.2400e-02

3.7264e-02
4.3575e-02
5.1233e-02
5.0719e-02
3.2127e-02