Correlation and prediction of solubility of hydrogen in alkenes and its dissolution properties

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Abstract

In this work, solubility of hydrogen in some alkenes was investigated at different temperatures and pressures. Solubility values were calculated using the Peng–Robinson equation of state. Binary interaction parameters were calculated using fitting the equation of state on experimental data, Group contribution method and Moysan correlations and total average absolute deviation for these methods was 3.90, 17.60 and 13.62, respectively. Because hydrogen solubility in Alkenes is low, Henry's law for these solutions were investigated, too. Results of calculation showed with increasing temperature, Henry's constant was decreased. The temperature dependency of Henry's constants of hydrogen in ethylene and propylene was higher than to other alkenes. In addition, using Van't Hoff equation, the thermodynamic parameters for dissolution of hydrogen in various alkenes were calculated. Results indicated that the dissolution of hydrogen was spontaneous and endothermic. The total average of dissolution enthalpy (ΔH°) and Gibbs free energy (ΔG°) for these systems was 3.867 kJ/mol and 6.361 kJ/mol, respectively. But dissolution of hydrogen in almost of alkenes was not an entropy-driven process.

Keywords PR EoS · Solubility · Henry's constant · Thermodynamic properties · Hydrogen · Alkene

Introduction

Study on the solubility of gases in a variety of hydrocarbons and their dissolution properties is important. Hydrogen is one of these gases which its solubility in hydrocarbons is one of the important parameters in designing, optimizing and interpreting kinetic reactions that are needed in various industrial processes and the commissioning of related equipment. Hydrogenation reactors in petrochemical complexes, are one of the equipment that hydrogen solubility in the input feed can affect the quality of products. Therefore, reliable estimation of hydrogen solubility in alkenes is needed, which results in more precise information gained for designing and optimizing hydrogenation reactors and amount of hydrogen consumed in a unit. Sagara et al. [21, 22], Vasileva

et al. [32], Sokolov and Polyakov [28], and Xie et al. [33] experimentally investigated the hydrogen-olefin systems. Baird et al. [5] studied the solubility of hydrogen in shale oil experimentally. The results showed that the solubility of hydrogen is very small due to phenolic polar compounds in shale oil. Given that prediction and calculation of solubility and phase equilibrium with cubic equations of state for hydrogen-hydrocarbon systems is good, these systems are modeled more with cubic equations of state. Ferrando and Ungerer [7] modeled phase equilibria of hydrogen-1-hexene and hydrogen-1-octene systems by PR [20] equation of state using interaction parameter that presented by Moysan et al. [12]. Also Qian et al. [19] studied the phase equilibria of hydrogen-ethylene, hydrogen-propylene and hydrogen-1-hexene systems using the PR equation with binary interaction parameter obtained by group contribution method [10]. Aguilar-Cisneros et al. [1, 2] investigated the solubility of hydrogen in heavy oil cuts by combining the PR and UNI-FAC model (Universal Quasi-Chemical Functional Group Activity Coefficients), with an overall error near to 15%. Torres et al. [30] presented augmented Grayson-Streed model for predicting hydrogen solubility in normal alkanes and aromatics by studying the hydrogen solubility in these hydrocarbons using the Grayson-Streed [29] model. The

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proposed model improves the predicted values of hydrogen solubility in normal alkanes and aromatics. Also, Nasery et al. [14] developed a model based on adaptive neuro fuzzy inference system (ANFIS) to predict hydrogen solubility in oil cut, based on available data from open literature. The average absolute deviation and coefficient of determination (R^2) of model were 3.4% and 0.99, respectively, which indicates good accuracy and correlation of the model. The results showed that the model could predict experimental data with acceptable accuracy.

Solubility of gases in a solution decreases significantly by increasing or decreasing pressure that applied on the solution and according Henry's law, the amount of gas that is dissolved at a constant temperature in a certain amount of liquid is directly proportional to the partial pressure of the gas above the solution. Due to the fact that dilute solutions follow the Henry's law, usually the Henry's constant of these systems is calculated. Nakahara and Hirata [13], Orentlicher and Prausnitz [15] studied Henry's constant of hydrogen in alkenes such as ethylene and propylene, Angelo and Francesco [6] studied Henry's constant of hydrogen in alcohols and Park et al. [17] studied Henry's constant of hydrogen in heavy paraffins. Recently, Trinh et al. [31] have studied Henry's constant of hydrogen in compounds containing alkanes, alcohols, aldehydes, carboxylic acids, esters and ethers.

The thermodynamic properties of dissolution, such as enthalpy, entropy, and Gibbs free energy, are important in terms of theoretically and practically. Using these quantities, one can predict and calculate behavior of the system at different conditions without laboratory data. The calculation of thermodynamic dissolution properties is carried out using the Van't Hoff equation. Anthony et al. [4] calculated enthalpy and entropy of dissolved various gases (hydrogen, nitrogen, argon, etc.) in ionic liquid [bmim] [PF6] using the Van't Hoff equation. In other work, they examined the enthalpy and entropy of water dissolution in a variety of ionic liquids by this equation [3]. Recently, Liu et al. [11] investigated the thermodynamic properties of the dissolution of various types of gases, including hydrogen, in the ionic liquid [emim] [Tf2N] using the Van't Hoff equation. Also Shakeel et al. [23–26] using the Van't Hoff equation, calculated the thermodynamic properties of dissolved solids in liquids.

In this work, the solubility of hydrogen in olefins that exist in a variety of petrochemical streams is considered and will be investigated. The studied olefins in this work are ethylene, propylene, 1-butene, 1-hexene, 1-heptene and 1-octene. A thermodynamic model was developed for investigating the solubility of hydrogen in these olefins. In this model, the PR equation of state is used, and the interaction parameter between hydrogen and olefins is obtained by fitting the experimental data of hydrogen solubility in olefins. Interaction parameters are also calculated using methods

such as Moysan and GCM and are compared with the interaction parameter obtained by fitting. Using methods such as Moysan and GCM to calculate the interaction parameter in equation of state, it is possible to predict the hydrogen solubility in olefins. Henry's constant of hydrogen is also rarely investigated in the previous work. In this work, Henry's constant of hydrogen is calculated and evaluated in all systems studied with the PR equation of state. Finally, the thermodynamic properties of dissolution such as enthalpy (heat of solution), entropy and Gibbs free energy of dissolution are calculated for these systems because these properties are necessary to describe these solution and design of processes. These properties are also obtained for the first time and are not observed in previous work.

Thermodynamic modeling

The Peng–Robinson equation of state is written as follows [20]:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}. \quad (1)$$

With

$$a = a_c \alpha(T), \quad (2)$$

$$b = 0.0777960739 \frac{RT_c}{P_c}, \quad (3)$$

$$a_c = 0.457235529 \frac{R^2 T_c^2}{P_c}, \quad (4)$$

$$\alpha(T) = \left[1 + m \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2, \quad (5)$$

where P , R , T , v , T_c , P_c and ω are pressure, universal gas constant, temperature, molar volume, critical temperature, critical pressure and acentric factor, respectively. The parameter m is calculated according the value of the acentric factor:

$$\omega < 0.49 : m = 0.37464 + 1.54226\omega - 0.426992\omega^2, \quad (6)$$

$$\omega > 0.49 : m = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3. \quad (7)$$

a and b for the mixtures are:

$$a = \sum_{i=1}^N \sum_{j=1}^N z_i z_j \sqrt{a_i a_j} [1 - k_{ij}(T)], \quad (8)$$

$$b = \sum_{i=1}^N z_i b_i, \quad (9)$$

where in Eqs. (8) and (9), z_i , z_j and k_{ij} are mole fraction of component i and j in mixture and binary interaction parameter, respectively. Binary interaction parameters were calculated using three methods:

- Fitting
- Group contribution method
- Moysan correlation

In the first method, binary interaction parameter was obtained by fitting experimental hydrogen solubility by equation of state. The binary interaction parameter between hydrogen and the alkenes has been evaluated by minimizing the following objective function:

$$\text{O.F.} = \left(\frac{1}{N}\right) \sum_{i=1}^N \text{Abs} \left(\frac{P_{\text{exp}_i} - P_{\text{cal}_i}}{P_{\text{exp}_i}} \right), \quad (10)$$

where N is the number of points used, P_{exp} is the experimental pressure from literatures and P_{cal} is the calculated pressure with the PR78 equation of state that Binary interaction parameters were calculated using fitting the equation of state on experimental data, group contribution method and Moysan correlation. Bubble point calculations have been used to calculate the total pressure in these systems.

In the second method, the GCM [10] was used to calculate the binary interaction parameter:

$$k_{ij}(T) = \frac{-\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T} \right)^{\left(\frac{B_{kl}}{A_{kl}} - 1 \right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)}{2 \frac{\sqrt{a_i(T)a_j(T)}}{b_i b_j}}, \quad (11)$$

where in Eq. (11), N_g is the number of different groups defined by the method and a_{ik} is the fraction of molecule i occupied by group k . $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups) are constant parameters that were determined by Qian et al. [19].

The third method for calculating the binary interaction parameter between hydrogen and alkenes for this equation of state is the proposed equation by Moysan et al. [12]:

$$k_{H_2,j} = 1 + \frac{0.0417(T_{r,H_2} - 1) - 1}{\sqrt{\alpha_{H_2}}}. \quad (12)$$

In Eq. (12), T_{r,H_2} is reduced temperature of hydrogen and α_{H_2} is defined by Eq. (5).

Thermodynamic parameters for dissolution of hydrogen

The thermodynamic parameters for dissolution of hydrogen in various alkenes were expressed (or measured) in terms of dissolution enthalpy (ΔH°), Gibbs free energy (ΔG°), and dissolution entropy (ΔS°). The ΔH° values for dissolution behavior of hydrogen in each alkene were determined using Van't Hoff equation [23–26]. The ΔH° was calculated using Eq. (13):

$$\Delta H^\circ = -R \frac{\partial \ln(x)}{\partial \left(\frac{1}{T} - \frac{1}{T_{\text{mean}}} \right)}. \quad (13)$$

where R is the universal gas constant (8.314 J/mol K), and T_{mean} , is the mean of the experimental temperatures. The ΔH° values were obtained from the slope of the plot of $\ln(x)$ versus $\left(\frac{1}{T} - \frac{1}{T_{\text{mean}}} \right)$. The ΔG° for the dissolution of hydrogen can be calculated as:

$$\Delta G^\circ = -RT * \text{intercept}. \quad (14)$$

In which the intercept was obtained from the plot of $\ln(x)$ versus $\left(\frac{1}{T} - \frac{1}{T_{\text{mean}}} \right)$. Finally, from these evaluated ΔH° and ΔG° values, the ΔS° of dissolution were obtained using Eq. (15):

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T_{\text{mean}}}. \quad (15)$$

Results and discussion

Correlation and prediction of hydrogen solubility

Table 1 presents the critical properties of the compounds used. The Binary interaction parameter is obtained at each temperature by fitting the equation of state on experimental data, group contribution method (GCM) and Moysan correlation. The binary interaction parameters are given in Table 2.

The average absolute deviation (AAD) between experimental data and correlation/prediction of H_2 solubility in the different alkenes is given in Table 3. The results show that using the PR equation with k_{ij} obtained from the fitting of data, has lower average error in comparison with the k_{ij}

Table 1 Critical properties and acentric factors

	Hydrogen	Ethylene	Propylene	1-Butene	1-Heptene	1-Hexene	1-Octene
T _c (K)	33.19	282.3	365.6	420.0	537.29	504.0	567.0
P _c (bar)	13.13	50.40	46.65	40.43	28.30	31.40	26.80
ω	−0.216	0.087	0.140	0.191	0.331	0.280	0.393
Ref.	Smith et al. [27]	Smith et al. [27]	Smith et al. [27]	Smith et al. [27]	Smith et al. [27]	Smith et al. [27]	Poling et al. [18]

Table 2 Binary interaction parameter and calculated Henry's constant values

Systems	Temp (K)	x (H ₂ molar fraction)	Pressure (bar)	k_{ij}			$H_{1,2}$ (bar)*	Ref.**
				Fitting	Moysan	GCM		
Hydrogen/ethylene	123.15	0.0053–0.0146	20.3–81.1	0.1010	0.0886	−0.0218	3769.0	Sagara et al. [21]
	148.15	0.0074–0.0266	20.3–81.1	0.1265	0.1160	0.0059	2641.6	Sagara et al. [21]
	173.15	0.0087–0.0361	20.3–81.1	0.1690	0.1441	0.0322	1989.6	Sagara et al. [21]
	198.15	0.0100–0.0489	20.3–81.1	0.1898	0.1727	0.0573	1431.1	Sagara et al. [21]
	223.15	0.0084–0.0603	20.3–81.1	0.2315	0.2019	0.0816	913.95	Sagara et al. [21]
Hydrogen/propylene	173.20	0.0054–0.0200	20.3–81.1	0.2200	0.1441	0.2078	3775.0	Sagara et al. [22]
	198.20	0.0060–0.0239	20.3–81.1	0.3200	0.1728	0.1824	3331.5	Sagara et al. [22]
	223.20	0.0086–0.0275	20.3–81.1	0.3649	0.2019	0.1695	2534.0	Sagara et al. [22]
	248.20	0.0098–0.0499	20.3–81.1	0.3220	0.2316	0.1588	1763.5	Sagara et al. [22]
Hydrogen/1-butene	253.20	0.0390–0.2100	50.0–300.0	0.0055	0.2376	0.1482	1137.3	Vasileva et al. [32]
	314.69	0.0420–0.2360	50.0–300.0	0.2341	0.3123	0.1519	964.18	Vasileva et al. [32]
	356.78	0.0470–0.1980	50.0–200.0	0.3877	0.3647	0.1591	727.95	Vasileva et al. [32]
Hydrogen/1-hexene	333.20	0.0400–0.2280	39.2–294.2	0.2003	0.3352	0.2033	940.95	Sokolov and Polyakov [28]
	393.20	0.1090–0.2490	100.0–250.7	0.3557	0.4107	0.2247	719.13	Sokolov and Polyakov [28]
	403.20	0.0410–0.3030	39.2–294.2	0.3552	0.4234	0.2285	681.69	Sokolov and Polyakov [28]
	453.20	0.1400–0.3460	100.0–250.7	0.5084	0.4878	0.2479	487.28	Sokolov and Polyakov [28]
Hydrogen/1-heptene	333.20	0.0280–0.2010	39.2–294.2	0.3444	0.3352	0.2230	1152.7	Sokolov and Polyakov [28]
	403.20	0.0401–0.2650	39.2–294.2	0.3907	0.4234	0.2521	747.88	Sokolov and Polyakov [28]
Hydrogen/1-octene	313.15	0.0080–0.0600	9.3–73.6	0.1471	0.3104	0.2092	1142.6	Xie et al. [33]
	328.20	0.0240–0.1860	39.2–294.2	0.3095	0.3290	0.2193	1248.9	Sokolov and Polyakov [28]
	333.15	0.0080–0.0590	9.4–70.0	0.2227	0.3422	0.2226	1123.1	Xie et al. [33]
	393.20	0.0380–0.2430	40.5–304.0	0.3505	0.4107	0.2617	873.42	Sokolov and Polyakov [28]
	463.20	0.0490–0.3180	40.5–304.0	0.4827	0.5008	0.3057	591.36	Sokolov and Polyakov [28]

*Calculated Henry's constant by fugacity coefficients using PR equation of state with fitting binary interaction coefficient

**References of experimental data (P–T–x)

obtained from the Moysan and GCM method, which was predictable.

Comparison of the modeling results using the k_{ij} obtained from the Moysan and GCM method shows that the average error associated with the Moysan method is less than the GCM. Of course, this result was unexpected because the GCM method is a newer method than Moysan and is expected to have better results. The reason for the weak results of the GCM method may be the optimal parameters of the model (A_{kl} and B_{kl}) and the components used to optimize the parameters of the GCM model. For example, optimization of the parameters of the GCM model was done with cyclic and high-carbon number hydrocarbons. But in

the present work, hydrocarbons with a low carbon number are modeled. So that average error between experimental hydrogen solubility and modeling results by GCM method for systems hydrogen + ethylene or propylene was high.

Another reason that could lead to errors in the results of the prediction of general models such as GCM and Moysan is the temperature range in which the parameters of these models is fitted in this range. If the fitting of the parameters was performed at high temperature and these parameters used at low temperatures, this can be caused the high error and the weakness of the model results (for example, the prediction results of the hydrogen + 1-butene system at 253.2 K using the Moysan k_{ij}).

Table 3 Average absolute deviation (AAD) for solubility of hydrogen in alkenes

Systems	<i>T</i> (K)	<i>x</i> (H ₂ molar fraction)	Pressure (bar)	(AAD)%		
				PR78 + <i>k_{ij}</i> fitting	PR78 + <i>k_{ij}</i> Moysan	PR78 + <i>k_{ij}</i> GCM
Hydrogen/ethylene	123.15	0.0053–0.0146	20.3–81.1	7.86	10.24	43.39
	148.15	0.0074–0.0266	20.3–81.1	5.34	7.28	35.71
	173.15	0.0087–0.0361	20.3–81.1	5.22	9.97	32.01
	198.15	0.0100–0.0489	20.3–81.1	4.98	7.44	24.76
	223.15	0.0084–0.0603	20.3–81.1	1.09	3.53	15.65
Hydrogen/propylene	173.20	0.0054–0.0200	20.3–81.1	4.71	20.69	4.90
	198.20	0.0060–0.0239	20.3–81.1	5.12	28.62	26.51
	223.20	0.0086–0.0275	20.3–81.1	5.08	24.03	28.55
	248.20	0.0098–0.0499	20.3–81.1	4.17	24.39	16.18
Hydrogen/1-butene	253.20	0.0390–0.2100	50.0–300.0	1.62	62.38	33.24
	314.69	0.0420–0.2360	50.0–300.0	2.41	11.23	10.44
	356.78	0.0470–0.1980	50.0–200.0	1.44	2.71	17.83
Hydrogen/1-hexene	333.20	0.0400–0.2280	39.2–294.2	3.92	18.45	3.94
	393.20	0.0280–0.2010	100.0–250.7	1.82	4.90	12.45
	403.20	0.0410–0.3030	39.2–294.2	3.81	12.01	7.19
	453.20	0.0410–0.2650	100.0–250.7	4.31	7.26	18.67
Hydrogen/1-heptene	333.20	0.0280–0.2010	39.2–294.2	6.34	6.60	15.34
	403.20	0.0410–0.2650	39.2–294.2	2.69	3.15	13.86
Hydrogen/1-octene	313.15	0.0080–0.0600	9.3–73.6	1.38	17.50	6.69
	328.20	0.0240–0.1860	39.2–294.2	8.67	9.05	15.36
	333.15	0.0080–0.0590	9.4–70.0	1.41	12.57	1.42
	393.20	0.0380–0.2430	40.5–304.0	3.57	4.88	11.45
	463.20	0.0490–0.3180	40.5–304.0	4.68	5.17	12.02
Total AAD%				3.98	13.65	17.72

Figure 1 shows solubility of hydrogen in alkenes using PR EoS with k_{ij} by Fitting, GCM and Moysan correlations.

Henry's law

Henry's law is used to describe the low solubility of hydrogen in a variety of alkene solvents. Based on definition, the Henry's constant of a solute in a solvent, $H_{1,2}$ is given as:

$$H_{1,2} = \lim_{x_1 \rightarrow 0} \left(\frac{f_1^l}{x_1} \right) = \lim_{x_1 \rightarrow 0} (\varphi_1 P), \quad (16)$$

where f_1^l , x_1 , and φ_1 are the fugacity, mole fraction and fugacity coefficient of hydrogen in the liquid phase, respectively. The Henry's constant was calculated using the PR equation and binary interaction parameter derived from the fitting of experimental solubility data. Accordingly, at each temperature, pressure and mole fraction of hydrogen in liquid phase, fugacity coefficient of hydrogen in liquid phase was calculated. The calculated fugacity coefficient was multiplied by system pressure. The obtained values were plotted in terms of hydrogen mole fraction in the liquid phase. Draw

the best passing line through the points, and the intersection of this line with the vertical axis gives the Henry's constant at that temperature. Figure 2 shows how to use this method to calculate the Henry's constant of hydrogen in ethylene at 123.15 K. The Henry's constant of hydrogen in some alkenes are given in Table 2. Also, Fig. 3 presents the temperature dependency of these Henry's constants.

According to Fig. 3, Henry's constant of hydrogen decrease with increasing temperature, which show that with increasing temperature, the solubility of hydrogen in alkenes increases (see Fig. 1; Tables 2, 3, columns 2, 3). Temperature dependency of Henry's constant of hydrogen in ethylene and propylene is higher than that of other alkenes, which indicates that the temperature has a greater effect on the solubility of hydrogen in ethylene and propylene.

The calculated Henry's constant values of hydrogen in ethylene in this work and the values calculated by Nakahara and Hirata (BWR equation of state, [13], were compared to experimental data [13], and Orentlicher and Prausnitz [15] at temperature 173 and 199 K. also, that comparison was made for calculated Henry's constant of hydrogen in propylene at temperature 200 K. The Comparison showed that average

Fig. 1 Correlation and prediction of solubility of hydrogen in alkenes using PR EoS with k_{ij} by fitting, GCM and Moysan correlations. Solid points (●): experimental data. Solid line (—): solubility correlation using PR EoS with k_{ij} by fitting, dashed line (---): solubility prediction using PR EoS with k_{ij} by GCM, dotted line (.....):

solubility prediction using PR EoS with k_{ij} by Moysan correlation. Systems: **a** hydrogen+ethylene, **b** hydrogen+propylene, **c** hydrogen+1-butene, **d** hydrogen+1-hexene, **e** hydrogen+1-heptene, **f** hydrogen+1-octene

Fig. 2 Evaluation of Henry's constant of hydrogen in ethylene at $T = 123.15$ K

absolute deviation (AAD%) between experimental data and calculated Henry's constant in this work was 9.80% and AAD% between experimental data and calculated Henry's constant by BWR equation of state [13], was 8.85%. These comparisons show that the equation of state and method used in this work to obtain the Henry's constant of hydrogen in the alkenes is reliable and the errors associated to this model are in the level and size of previous work. These results were shown in Table 4.

Thermodynamic parameters for dissolution of hydrogen in Alkenes

The values of thermodynamic parameters for dissolution of hydrogen in Alkenes are listed in Table 4. The ΔH° values for the dissolution of hydrogen were positive for all solvents studied. The positive values of ΔH° indicated endothermic dissolution of hydrogen. The ΔG° values for the dissolution of hydrogen were also observed to be positive for all the solvents studied. Positive values of ΔG° indicating that the dissolution of hydrogen was spontaneous and the positive values of ΔG° in Alkene solvents were possible due to strong molecular interactions between hydrogen-solvent molecules in comparison with weak molecular interactions between hydrogen-hydrogen and solvent-solvent molecules. As can be seen from Table 5, all dissolution entropy of hydrogen in ethylene, propylene, 1-butene, and 1-hexene at 100 bar, and 1-octene at 45.5 and 101.3 bar are negative that indicate the dissolution of hydrogen are not an entropy-driven process. Other value of ΔS° of hydrogen in alkene (1-hexene at $P = 150$ bar, $P = 200$ bar, $P = 250$ bar and 1-octene at

$P = 202.7$ bar, $P = 304.0$ bar) are positive, that indicate the dissolution of hydrogen are an entropy-driven process.

Also according to Table 5 (4) the values of ΔH° and ΔG° for the dissolution of hydrogen in alkenes were very low, which indicated that relatively low energy is required for the solubilization of hydrogen in alkenes.

In this work, the thermodynamic properties for dissolution of nitrogen, helium, argon and methane in alkenes have been studied, too (Table 6). Comparison of the values of the thermodynamic properties of hydrogen, nitrogen, helium, argon and methane shows that the enthalpy of light gases in alkenes is very low. Also, the positive values of enthalpy of hydrogen and helium in alkenes indicates an increase solubility by increasing the temperature and negative values of enthalpy of nitrogen, argon and methane in alkenes indicates a decrease in solubility with increasing temperature.

Conclusion

The solubility of hydrogen in ethylene, propylene, 1-butene, 1-hexene, 1-heptene and 1-octene was investigated. The PR equation was used to correlate and predict the hydrogen solubility in alkenes. Binary interaction parameter was obtained by fitting the equation of state on experimental data, group contribution method and Moysan correlations. The results showed PR EoS with fitting binary interaction parameter had lowest absolute average error than Moysan and group contribution method, respectively. Because most dilute solutions follow Henry's law, Henry's constant was calculated for all studying systems using PR equations of state with fitting binary interaction parameter. With increasing temperature, Henry's constant of hydrogen in alkenes decreased and hydrogen solubility increased in these systems. Also Henry's constants of hydrogen in ethylene and propylene were more than in other alkenes. These binary interaction parameters and Henry's constant can be used in simulation software to simulate industrial processes containing hydrogen and alkenes (petrochemical industries). In addition, Thermodynamic analysis indicated endothermic and spontaneous dissolution behavior of hydrogen in the studied alkene solvents. But results show the dissolution of hydrogen in some of alkenes is an entropy-driven process, such as 1-hexene and 1-octene. Also some recommendations for future work are: (a) using statistical associating fluid theory (SAFT) family equation of state to model system containing hydrogen, (b) ternary systems and mixtures containing hydrogen will be investigated, (c) another olefin such as branched and cyclo-olefin will be investigated.

Fig. 3 Experimental and calculated Henry's constant of hydrogen in some alkenes studied in this work vs. temperature

Table 4 Experimental Henry's constant data and calculated by equation of states

	T (K)	Experimental Henry's constant by Nakahara and Hirata	Experimental Henry's constant by Orentlicher and Prausnitz	Calculated Henry's constant by BWR* EOS	Calculated Henry's constant by PR EOS	AAD%	
		Nakahara and Hirata [13]	Orentlicher and Prausnitz [15]	Nakahara and Hirata [13]	This work	This work and experimental Henry's constant data	BWR and experimental Henry's constant data
Hydrogen/ethylene	173	2037	2070	1824	1990	9.80	8.85
	199	1449	1419	1358	1431		
Hydrogen/propylene	200	2685	2634	2391	3331		

*Benedict–Webb–Rubin equation of state

Table 5 Thermodynamic parameters of hydrogen dissolution at different pressures and the mean of the experimental temperatures (T_{mean})

Solvent	T_{mean} (K)	P (bar)	ΔH° (KJ/mol)	ΔG° (KJ/mol)	ΔS° (J/mol K)
Ethylene	173.15	20.27	1.229	6.933	− 32.94
		40.53	2.314	5.836	− 20.34
		60.80	2.950	5.145	− 12.68
		81.06	3.202	4.751	− 8.947
Propylene	210.70	20.27	3.998	8.660	− 22.13
		40.53	3.208	7.570	− 20.70
		60.80	3.356	6.664	− 15.70
		81.06	3.170	6.265	− 14.68
1-Butene	308.20	50.00	1.270	8.065	− 22.04
		100.0	1.652	6.228	− 14.85
		150.0	1.979	5.226	− 10.54
		200.00	2.120	4.534	− 7.834
1-Hexene	395.70	100.0	4.951	7.175	− 5.623
		150.0	5.997	5.982	0.040
		200.0	5.670	5.060	1.542
		250.0	6.198	4.455	4.405
1-Octene	394.87	40.50	5.583	10.72	− 13.01
		101.3	6.841	7.700	− 2.176
		202.7	6.715	5.528	3.005
		304.0	4.938	4.538	1.013

Table 6 Thermodynamic dissolution parameters of nitrogen, helium, argon and methane in some alkenes at different pressures, and the mean of the experimental temperatures (T_{mean})

Solute	Solvent	T_{mean} (K)	P (bar)	ΔH° (KJ/mol)	ΔG° (KJ/mol)	ΔS° (J/mol K)	Ref.*
N ₂	Ethylene	153.09	26.00	− 3.013	2.784	− 37.87	Gasem et al. [9]
		154.50	16.00	− 2.963	3.627	− 42.66	Gasem et al. [9]
		128.43	10.00	− 2.888	3.039	− 46.15	Gasem et al. [9]
He	Ethylene	178.67	60.00	6.839	7.819	− 5.482	Garber and Ziegler [8]
He	Propylene	213.56	60.00	7.658	9.136	− 6.922	Garber and Ziegler [8]
Ar	Propylene	135.00	12.00	− 13.78	2.214	− 118.5	Orobinsky et al. [16]
CH ₄	Ethylene	223.20	40.53	− 11.80	1.947	− 61.57	Sagara et al. [21]

*References of experimental data (P–T–x data)

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