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Original Paper

Hydrogen solubility prediction for diesel molecules based on a modified Henry equation

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ABSTRACT

Diesel hydrotreatment removes heteroatoms and polycyclic aromatics in diesel in the presence of high-pressure hydrogen gas. The hydrogen solubility is the basis for hydrogen consumption prediction and process design/optimization. In the presented study, we established a method to predict the hydrogen solubility of diesel molecules and mixture. A modified Henry equation was proposed to illustrate the hydrogen solubility variation among the temperature and pressure. The parameters of the modified Henry equation for typical molecules were regressed from literature data. Then we established an empirical correlation between the parameter and the structure and property of molecules. The method was then combined with a molecular-level compositional model to accurately predict the hydrogen solubility in diesel, illustrating the validity of the method.

1. Introduction

The content of sulfur in diesel is one of the important indicators for diesel quality. The combustion of sulfur compounds in diesel has a significant negative impact on the environment and human health (Ma et al., 1994; Fujikawa et al., 2006). The cetane number of diesel depends on the content of polycyclic aromatic hydrocarbons, which undergo saturation during the hydrotreating process. The kinetic modeling of the hydrotreating process requires hydrogen solubility information. As the capacity of hydrotreating equipment increases, the chemical hydrogen consumption of the refinery also increases sharply (Alves and Towler, 2002; Ahmad et al., 2010). The hydrogen solubility is the basis for calculating the hydrogen consumption of the hydrogenation process. Therefore, it is of great significance to develop a simple and accurate hydrogen solubility prediction model.

In the past few decades, many researchers have studied the solubility of hydrogen in organic solvents and oils. Brunner (1985) measured the solubility of hydrogen in ten organic solvents such as n-octane and toluene at different temperatures. Park et al. (1995, 1996) measured the solubility of hydrogen in heavy n-alkanes such as decane, eicosane, and aromatic hydrocarbons such as benzene, naphthalene, and phenanthrene. It is known through experiments that the solubility of hydrogen in paraffin is higher than that of aromatics. For paraffins, as the carbon number increases, the solubility of hydrogen increases. And for aromatics, the number of aromatic rings increases, and the solubility of hydrogen decreases. Sebastian et al. (1978), Peter et al. (1960) and Berty et al. (1966) have studied the gas-liquid equilibrium of hydrogen in cyclohexane and its homologues. Tsuji et al. (2005) measured the solubility of hydrogen in binary systems of benzene and cyclohexane, methylcyclohexane and toluene, and calculated the solubility of hydrogen in binary mixed systems using the Peng-Robinson equation-of-state and mixing rules. Trinh et al. (2015) collected or calculated the Henry coefficient from different sources, and used the Monte Carlo molecular simulation method to obtain the Henry coefficient. The simulation results showed that the Henry coefficient decreased with increasing temperature, which was consistent with the experimental value. Florusse et al. (2003) measured the solubility of hydrogen in heavy n-alkanes and performed correlation calculations through molecular state equations based on statistical association theory (SAFT). Ronze et al. (2002) used chromatography to measure the solubility of hydrogen in an organic solvent (cyclohexane) and applied this method to measure the solubility of hydrogen in straight-run gasoil. Lal et al. (1999) used a batch autoclave to measure the solubility of hydrogen in

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Athabasca bitumen. The correlated and predicted the hydrogen solubility using the Peng-Robinson equation, the Soave–Redlich–Kwong equation, and the Grayson–Streed method. Other researchers (Cai et al., 2001; Baird et al., 2017) also developed a method for hydrogen solubility measurement in low-volatile liquid media such as shale oil and asphalt.

The abundant open-reported experimental data leads to more efforts in the hydrogen solubility prediction. Hydrogen solubility refers to the content of hydrogen in the liquid phase, which is a typical gas-liquid equilibrium problem (Chao and Seader, 1961; Streed, 1963; Sebastian et al., 1981; Torres et al., 2013). For the prediction of hydrogen solubility of oil fractions under high temperature and high-pressure system, the equation of state method has good applicability. The equation of the state method calculates the solubility of hydrogen depending on modification parameters. For calculation of hydrogen solubility, modification parameters are often obtained experimentally (Moysan et al., 1983; Ding et al., 1985; Lin et al., 1985a,b; Lin et al., 1985a,b, 1985a,b; Wiegand et al., 1989; Lal et al., 1999; Gross and Sadowski, 2001; Ronze et al., 2002; Saajanlehto et al., 2014). To overcome such disadvantages, other models, such as the UNIFAC solution model, group contributions, molecular dynamics simulations, to predict the solubility of hydrogen are reported in the open literature (Hartounian and Allen, 1988; Fahim and Elkilani, 1992; Yuan et al., 2010; Safamirzaei and Modarress, 2011; Qian et al., 2013; Xu et al., 2015; Uribe-Vargas et al., 2016; Aguilar-Cisneros et al. 2017, 2018). Riazi et al. (2005, 2007) proposed a method to calculate the hydrogen solubility parameter based on the type of solvent or its molecular weight, to predict the solubility of hydrogen in solvents with different contents of alkanes, naphthenes, and aromatics. Shaw et al. (1987) proposed a correlation for hydrogen solubility in aromatic, alicyclic, and heterocyclic hydrocarbon solvents. Deshmukh and Mather (1981) proposed a mathematical model for equilibrium solubility of hydrogen sulfide and carbon dioxide in aqueous alkanolamine solutions. There are also some other methods used in predicting gas solubility prediction models (Khamehchi et al., 2009; Bastami et al., 2014; Nasery et al., 2016; Tatar et al. 2016a,b; Tatar et al. 2016a,b, 2016a,b; Yang et al., 2019).

Diesel hydrogen solubility refers to the liquid phase concentration of hydrogen when it reaches the vapor-liquid equilibrium in diesel. Temperature, pressure, and the composition of the solvent have a significant effect on the solubility of hydrogen. Generally speaking, the methods for calculating the solubility of hydrogen are based on experimental data, exploring the dissolution rule of hydrogen in the solvent, and correlation calculations on the solubility of hydrogen.

In this paper, the modified Henry equation is established by the hydrogen solubility of alkanes, naphthenes, and aromatics, which obtained from the above-mentioned literature are close to 300 data points. Correlating the Henry coefficient with the bulk properties or structural parameters of hydrocarbons, an easy-to-measure or easy-to-calculate hydrogen solubility prediction method is proposed. Finally, molecular management techniques were used to predict the hydrogen solubility of diesel.

2. Establishment of a modified Henry equation

Henry law means that the amount of gas dissolved in a liquid at a certain temperature is proportional to the partial pressure of the gas in equilibrium with the solution. Henry law often applies to gases with very low solubility in solvents, that is, the solution formed is in the range of a dilute solution. However, in the process of diesel hydrotreating, often under high-temperature and high-pressure conditions, Henry law no longer applies. Therefore, we have to modify the Henry model to meet the calculation requirements. Luo et al. (2010) proposed a mathematical model based on the Pierotti method and Henry law to calculate the solubility of hydrogen in coal tar at saturation. Carroll et al. (1991) proposed a model based on the Herry model to calculate the solubility of carbon dioxide in water at low pressure. Murad and Gupta (2000) used the simple molecular dynamics simulation to calculate the Henry constant and solubility of gases in liquids. Yaws et al. (1997) used the fugacity coefficient of a cubic equation of state, Henry law constant of a solute in a solvent is incorporated into binary interaction parameter of the classical attractive parameter mixing rule. The developed model accurately describes the solubility of gases including methane, ethane, nitrogen, carbon dioxide and hydrogen sulphide in heavy n-alkanes from low to high pressure for wide range of temperature.

Through the analysis of the experimental data of hydrogen solubility, it is found that under low-pressure conditions, the hydrogen solubility and pressure show a linear relationship, but with the increase of pressure, the hydrogen solubility and pressure will appear non-linear. To apply to high-temperature and high-pressure systems, the modified Henry equation is established in this paper. The Henry coefficient is related to the hydrogen concentration in the liquid phase, and the Henry coefficient itself is also related to the temperature, so the following formula is established to calculate the Henry coefficient using the liquid hydrogen concentration and temperature. Fig. 1 shows the change of the solubility of hydrogen in m-xylene with pressure at 139.85 °C. In the figure, the blue line is Henry law to calculate the hydrogen solubility, and the red line is the calculation result of the modified Henry equation. It can be seen that it is necessary to modify the Henry equation.

$$P^* = Hx \tag{1}$$

$$H = a + bx + cT \tag{2}$$

In the formula, H is the Henry coefficient. T is the temperature °C. P^* is the partial pressure of the gas in equilibrium, MPa. Considering that the solvent is less volatile and the gas phase is mostly hydrogen, this article uses the total pressure. a, b, c are Henry coefficient parameters to be obtained by regression. The parameter regression method in the article uses the multiple nonlinear regression method, ensure that the error obtained by the optimization algorithm is within an acceptable range.

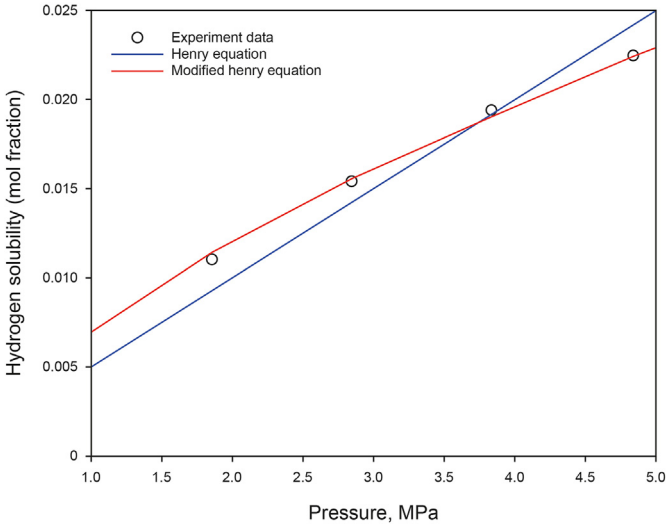

Fig. 1. Calculating the solubility of hydrogen in m-xylene before and after modification of Henry equation.

To better establish a model for predicting the hydrogen solubility of diesel, parameter regression was performed according to the typical hydrocarbon compounds in diesel. As we all know, diesel is mainly composed of alkanes, naphthenes, and aromatic hydrocarbons. Polycyclic naphthenes and aromatic hydrocarbons are mainly bicyclic and tricyclic. To this end, by investigating hydrogen solubility data in the literature, C_7-C_{28} 15 model compounds were selected, and a total of nearly 300 data points were used to regress Henry coefficient parameters, thereby calculating the Henry coefficient of each hydrocarbon compound. By regressing the hydrogen solubility data, it was found that the parameter *c* in the temperature term in the calculation of the Henry coefficient is all negative, indicating that the Henry coefficient decreases with increasing temperature. Fig. 2 shows the hydrogen solubility calculated by the modified Henry equation compared with experimental data in the literature. It can be seen from the figure that most of the calculated results are in good agreement with the experimental data by the modified Henry equation, except for individual hydrocarbons that differ greatly from the experimental results under certain conditions. Considering that there are certain errors in the measurement of the hydrogen solubility experiment itself and the model, it is feasible to use the liquid phase hydrogen concentration and temperature to calculate the Henry coefficient, thereby calculating the hydrogen solubility at different pressures and temperatures. See the regression parameters *a*, *b*, and *c* in supporting information.

3. Henry coefficient parameters correlation

The modified Henry equation was used to calculate the hydrogen solubility of 15 model compounds, and the feasibility of the equation was verified. It can better represent the relationship between the amount of hydrogen dissolved in the solvent at a certain temperature and the pressure at that time. Based on the experimental data of hydrogen solubility, the Henry coefficient parameters of each model compound are obtained. However, in the calculation of diesel hydrotreating, the system involves hundreds of compounds, and there is no way to measure the hydrogen solubility

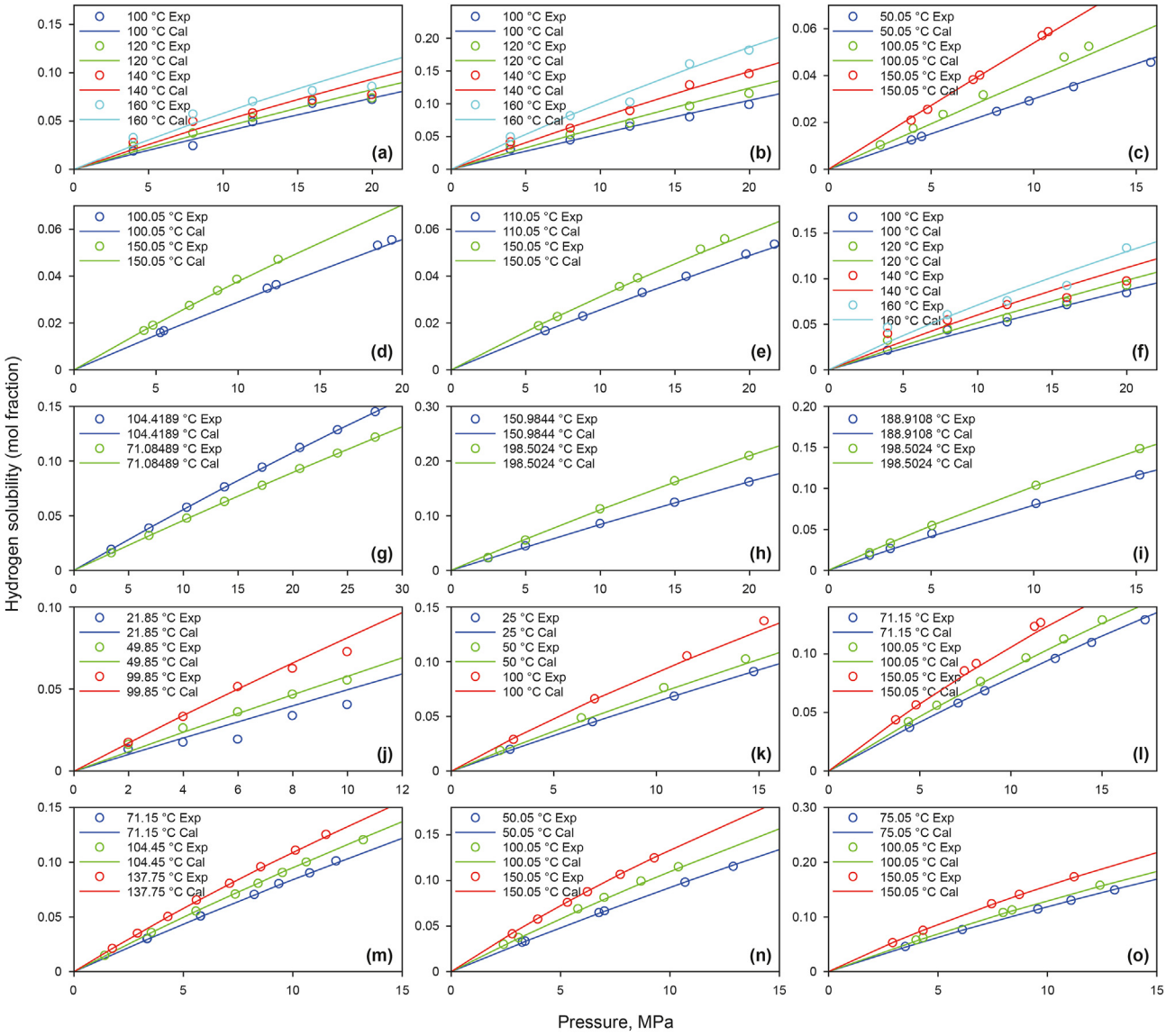

Fig. 2. Calculation of solubility of hydrogen and pure solvent system by modified Henry equation. Tetrahydronaphthalene, Toluene, Benzene, Naphthalene, Phenanthrene(a-e). Decahydronaphthalene, Cyclohexane, Methylcyclohexane, Bicyclohexane(f-i). Heptane, Octane, Decane, Dodecane, Eicosane, Octadecane(j-o).

of these compounds one by one, and the Henry coefficient parameters of each compound cannot be obtained by regression. Therefore, based on the bulk properties or structure of the compound, it is necessary to predict the relationship between its Henry coefficient and the liquid phase hydrogen concentration and temperature and then predict the hydrogen solubility. To this end, in this paper, through the regression of the Henry coefficient parameters obtained from the experimental data of the typical hydrocarbon compounds in the diesel, the relationship between the basic bulk properties and chemical structure of the hydrocarbon compounds and the Henry coefficient parameters is sought. In this section, two types of correlation models for Henry coefficient parameters are constructed: correlation calculation is performed based on the easy-to-measure bulk properties of hydrocarbons; correlation calculation is performed based on the easy-to-calculate structural parameters of hydrocarbons.

3.1. Bulk properties correlation Henry coefficient parameters

In the petroleum processing process, it is often necessary to measure the general bulk properties of hydrocarbons (such as relative molecular mass, boiling point, specific gravity, etc.). These bulk properties are also the basis for defining virtual components. The research literature found that the solubility of hydrogen in alkanes is higher than that of aromatics. Hydrogen solubility increases with the number of alkane carbons and decreases with the number of aromatic rings (Park et al. 1995, 1996). It can be seen that the structure of a compound determines its hydrogen solubility and also causes changes in bulk properties. Therefore, a correlation between bulk properties and hydrogen solubility can be established. This method can predict the hydrogen solubility of pure compounds and can also help predict the hydrogen solubility of virtual components. Generally, the measurement of the relative molecular mass, boiling point, and specific gravity of hydrocarbons are easy to obtain and the measurement accuracy is high. Therefore, in this section, the above three parameters are selected to establish the correlation between them and the Henry coefficient parameters, so that the Henry coefficient under different temperature and composition conditions can be calculated, and then the solubility of the liquid phase hydrogen in the saturated state is obtained. After that, we tested several association methods. First, we performed multiple linear regression, but due to the existence of nonlinear terms, the calculation results were not good. Therefore, we added a quadratic term and obtained the parameters using multiple nonlinear regression. By comparing with the experimental value, we believe that this equation form is satisfactory in terms of accuracy and applicability, so we choose the following form:

$$a = k_{11}*T_b^{0.6} + k_{12}*S_g^{0.6} + k_{13}*M^{0.6} + k_{14}*T_b*M + k_{15}*T_b*S_g + k_{16}*S_g*M + k_{17}*T_b*M*S_g + k_{18} \tag{3}$$

$$b = k_{21}*T_b^{1.5} + k_{22}*S_g^{1.5} + k_{23}*M^{1.6} + k_{24}*T_b*M + k_{25}*T_b*S_g + k_{26}*S_g*M + k_{27}*T_b*M*S_g + k_{28} \tag{4}$$

$$c = k_{31}*T_b^{0.6} + k_{32}*S_g^{0.6} + k_{33}*M^{0.6} + k_{34}*T_b*M + k_{35}*T_b*S_g + k_{36}*S_g*M + k_{37}*T_b*M*S_g + k_{38} \tag{5}$$

In the formula, T_b is the boiling point of the hydrocarbons, °C. S_g is the specific gravity of the hydrocarbons. $M$is the relative molecular mass of the hydrocarbons. Bulk properties of model compounds were obtained in Aspen Plus. k is the parameter that needs regression. See supporting information for regression results.

Therefore, this paper establishes a model for predicting the solubility of hydrogen based on the bulk properties of hydrocarbons. As shown in Fig. 3, comparisons of the Henry coefficient parameters were calculated based on the bulk properties of hydrocarbons with the parameters of experimental data regression. It can be seen from the figure that the use of the bulk properties of the compound to calculate the Henry coefficient parameters through the correlation equation is in good agreement with the experimental data regression Henry coefficient parameters, and meets the law that the Henry coefficient decreases with increasing temperature. Fig. 4 shows the comparison of the calculated hydrogen solubility of typical hydrocarbon compounds in diesel based on bulk properties with experimental data. It can be seen from the figure that using the bulk properties of the compound to calculate the solubility of hydrogen is in good agreement with the experimental data, and the error is within the acceptable range. It is proved that there is a functional relationship between the bulk properties of the compound and its Henry coefficient. The above-mentioned correlation formula can be used to calculate the Henry coefficient using its bulk properties, and then the hydrogen solubility at different temperatures and pressures can be obtained. From this, the Henry coefficient can be obtained from the easy-to-measure bulk properties of compounds, and then the solubility of hydrogen at different temperatures and pressures can be calculated.

3.2. Structural parameter correlation Henry coefficient parameters

Another way to predict the Henry coefficient parameters is to directly establish the relationship between the structure of the hydrocarbon compound and the Henry coefficient. According to the concept of the hydrocarbon structure group composition, no matter how complicated the structure of hydrocarbons in petroleum, they are composed of three structural units: alkyl, naphthenic and aromatic. Therefore, the hydrocarbon compound is regarded as composed of three structural units of the aromatic ring, naphthenic ring, and alkyl side chain. And in this section, the ratio of carbon atoms on the aromatic ring to the total carbon atoms of the molecule (f_A), the ratio of carbon atoms on the naphthenic ring to the total carbon atoms of the molecule (f_N) and the carbon atoms on the alkyl side chain account for the total ratio of carbon atoms (f_P) represents the proportion of three structural units in the molecule. Through the different solubility of hydrogen in different hydrocarbons and the variation of hydrogen solubility with carbon number, it can be seen that the structure of hydrocarbon compounds affects the solubility of hydrogen. Therefore, in this section, the aromatic carbon ratio, naphthenic carbon ratio, alkyl carbon ratio, and relative molecular mass of 15 typical hydrocarbon compounds in diesel are related to the Henry coefficient parameters, and the following correlation formula is established according to the bulk properties correlation Henry coefficient parameters method.

$$a = k_{11}*f_A + k_{12}*f_N + k_{13}*f_P + k_{14}*M + k_{15}*f_A*f_N*f_P*M + k_{16} \tag{6}$$

$$b = k_{21}*f_A + k_{22}*f_N + k_{23}*f_P + k_{24}*M + k_{25}*f_A*f_N*f_P*M + k_{26} \tag{7}$$

$$c = k_{31}*f_A + k_{32}*f_N + k_{33}*f_P + k_{34}*M + k_{35}*f_A*f_N*f_P*M + k_{36} \tag{8}$$

In the formula, f_A is the aromatic carbon ratio. f_N is the

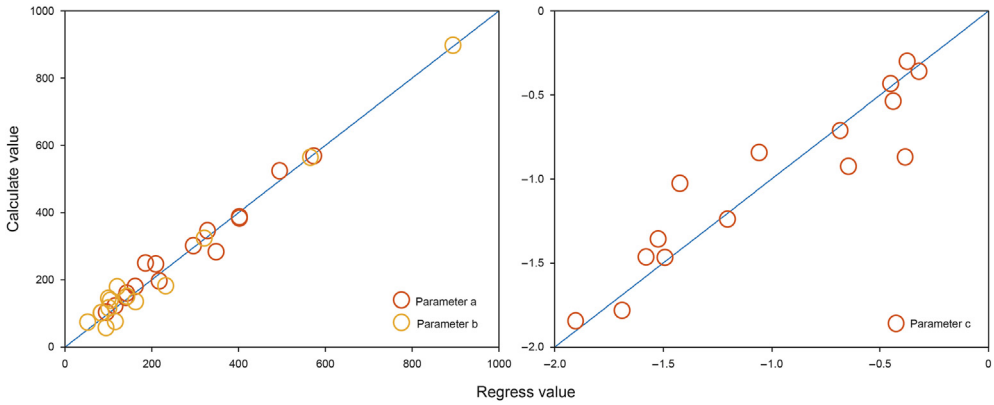

Fig. 3. Parity plots of the bulk property calculation modified Henry equation parameters.

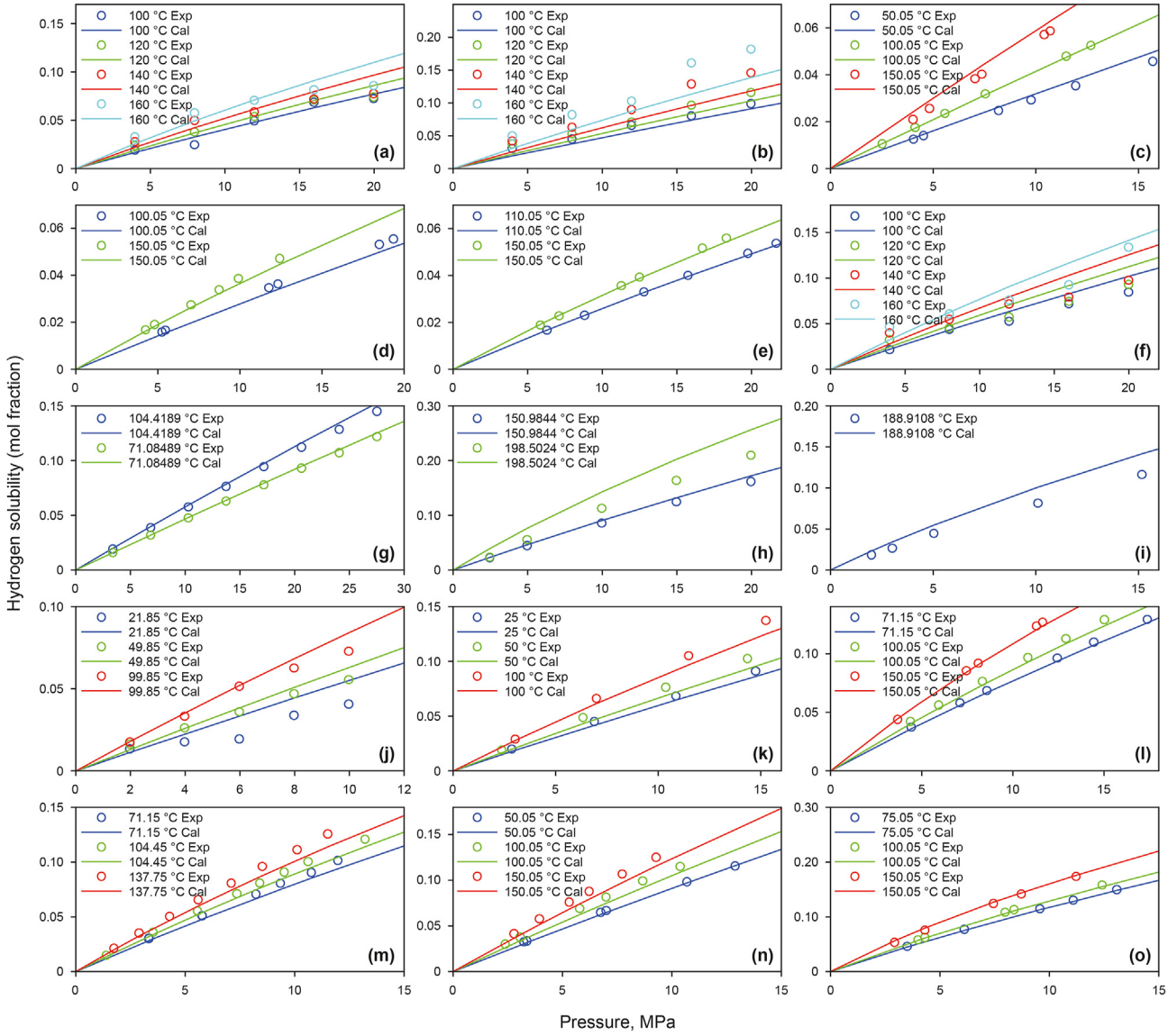

Fig. 4. Bulk properties correction Henry equation parameters to calculate the solubility of hydrogen and pure solvent system. Tetrahydronaphthalene, Toluene, Benzene, Naphthalene, Phenanthrene(a-e). Decahydronaphthalene, Cyclohexane, Methylcyclohexane, Bicyclohexane(f-i). Heptane, Octane, Decane, Dodecane, Eicosane, Octadecane(j-o).

naphthenic carbon ratio. f_P is the alkyl carbon ratio. M is the relative molecular mass. k is the parameter that needs regression. See supporting information for regression results.

Therefore, this paper establishes a second Henry coefficient parameters correlation method, and calculates the Henry coefficient through the correlation of structural parameters of hydrocarbon compounds, thereby calculating the solubility of hydrogen in the saturated state. Fig. 5 shows the comparison of the calculated Henry coefficient parameters using the molecular structure parameters with the regression of experimental data. The feasibility of correlating the Henry coefficient parameters with the structural parameters is proved from the figure. Fig. 6 shows the calculation of hydrogen solubility in a solvent system based on molecular structure parameters. It can be seen from the figure that the Henry coefficient is calculated by the structural parameters of the hydrocarbon compound, and then the solubility of hydrogen at different temperatures and pressures can be calculated to meet the subsequent processing calculations, and the error is within the acceptable range.

Under the same carbon number, the hydrogen solubility of different hydrocarbons is different, and with the increase of the side chain carbon number, the hydrogen solubility of hydrocarbons has a certain change law. To verify the accuracy of calculating the solubility of hydrogen by the structural parameters of hydrocarbon compounds, extrapolation of paraffin, naphthenes, and aromatics in the same carbon number range as the side chain carbon number increases to verify that the hydrogen solubility increases with the side chain carbon number change trend. Fig. 7 shows the trend of hydrogen solubility changes of different homologues with an increase in side-chain carbon number at a temperature of 100 °C and a pressure of 8 MPa. It can be seen from the figure that the prediction of the hydrogen solubility of different homologues by structural parameters agree well with experimental laws in the literature (Park et al. 1995, 1996). Hydrogen has the highest solubility in alkanes, followed by naphthenes and aromatics. The solubility of hydrogen increases as the number of carbons in the side chain increases between homologues. For naphthenes and aromatics, as the number of rings increases, the solubility of hydrogen decreases. And it can also be seen in the figure that when the carbon number of the side chain increases to a certain carbon number, the hydrogen solubility of different homologues will converge at one point. Because when the side chain carbon number increases to a certain level, the side chain carbon number contributes the most to the solubility of hydrogen, the number of aromatic rings and naphthenic rings can be neglected, that is, the alkyl carbon rate is much greater than the aromatic carbon rate and naphthenic Carbon rate. Therefore, it is feasible to calculate the solubility of hydrogen based on the structural parameters of hydrocarbon compounds.

According to the macroscopic properties and structural parameters of the model compound, the average relative error of hydrogen solubility is within 10%, which is similar to the correlation proposed in the open literature. However, the advantage of the method developed in this paper is that the calculation is simple and fast, it can predict the hydrogen solubility based on the information of the molecular level.

3.3. Predicting the solubility of hydrogen in binary systems

Based on the above work, this paper constructs a modified Henry equation, and uses the bulk properties and structural parameters of hydrocarbon compounds to calculate the Henry coefficient parameters, and calculates the solubility of hydrogen in different temperatures and pressures has achieved good results. To prove that the method can be applied to mixed systems, this paper selects benzene/cyclohexane and methylcyclohexane/toluene binary systems and uses two correlation methods to predict the solubility of hydrogen in the binary mixed system. For the binary mixed system to predict the solubility of hydrogen, since the types of its molecules have been confirmed, two methods are used to predict the solubility of hydrogen. The solubility of hydrogen in the binary system is regarded as the solubility of hydrogen in each pure solvent system, and then linear addition is performed in proportion; The binary mixed system is defined as a pseudo-component, whose bulk properties and structural parameters are calculated in proportion, and then the bulk properties and average structural parameters of the pseudo-component are used to predict the hydrogen solubility respectively.

(a) and (b) in Fig. 8 correspond to the bulk properties and the average structural parameters of the mixture to predict the solubility of hydrogen in the binary mix system. The left side of (a) and (b) is used to calculate the hydrogen solubility of each compound separately, and then the linear summation method is used, and the right side is used to calculate the hydrogen solubility using the method of defining pseudo-components. Among them, I and II are hydrogen in a toluene + methylcyclohexane binary mix system, III and IV are hydrogen in a benzene + cyclohexane binary mix system. It can be seen from the figure that predicting the hydrogen solubility of a binary mixed system based on bulk properties is better than predicting the hydrogen solubility of a mixed system based on average structural parameters, and both related methods can better predict the hydrogen solubility of a mixed system. For the two methods of linear addition and defined as a pseudo-component treatment of binary system, the difference in hydrogen solubility prediction effect is not much, and both can

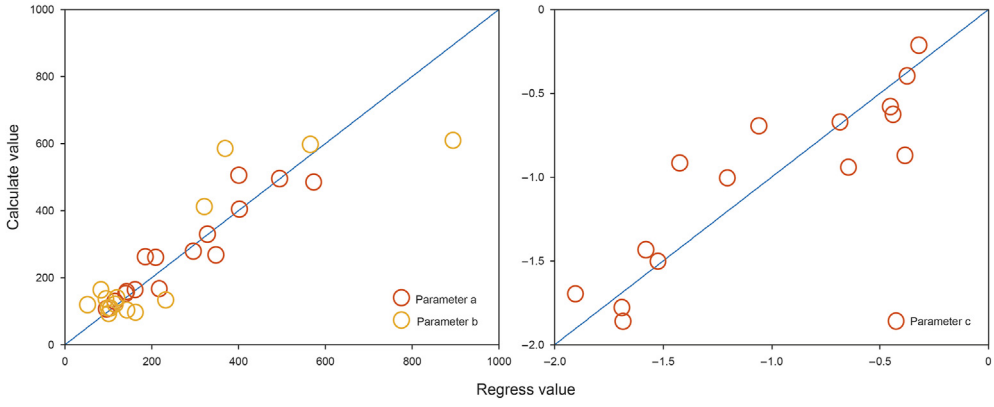

Fig. 5. Parity plots of the structural parameter calculation modified Henry equation parameters.

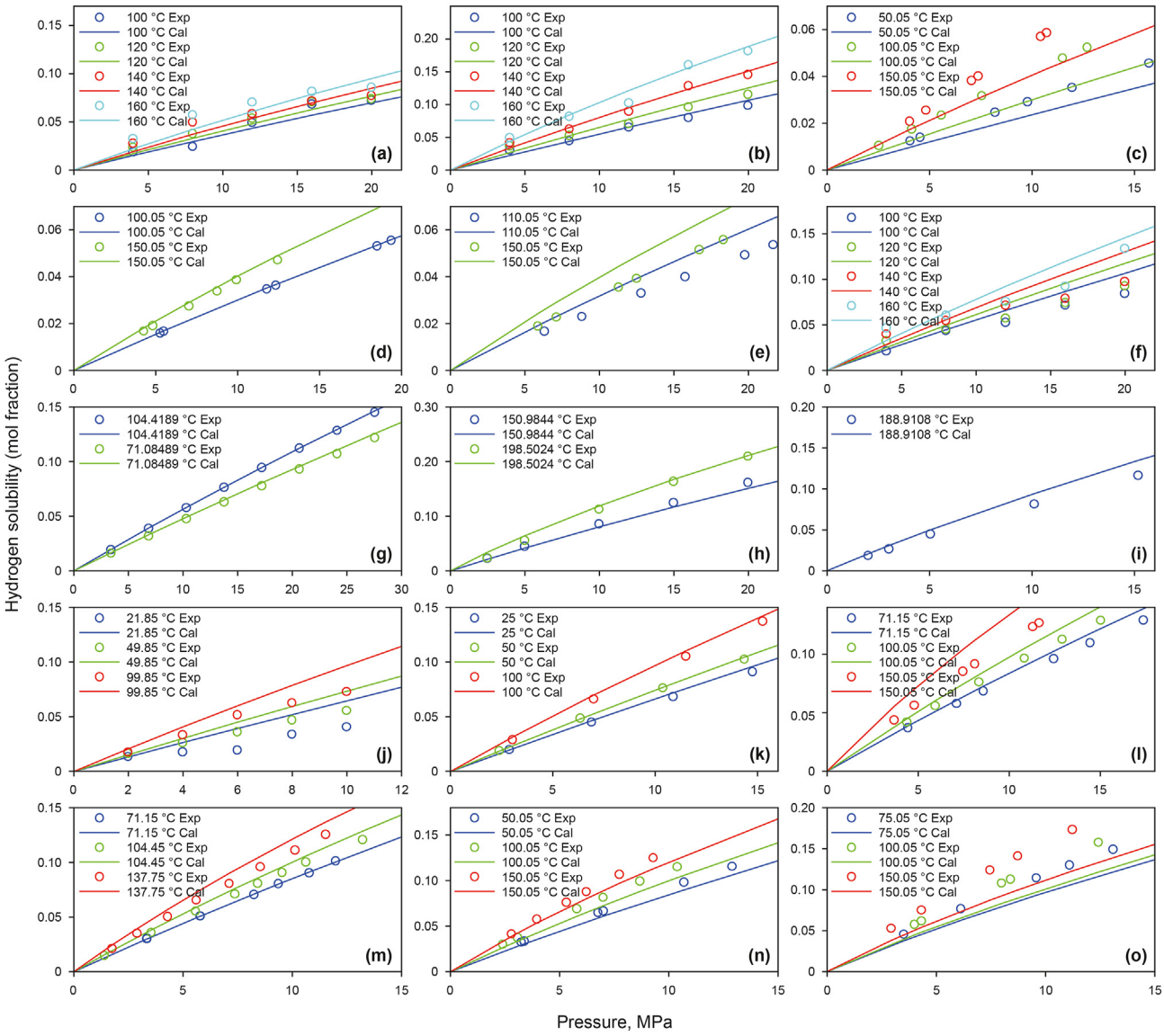

Fig. 6. Structural parameter correlation modified Henry equation parameter to calculate the solubility of hydrogen and pure solvent system. Tetrahydronaphthalene, Toluene, Benzene, Naphthalene, Phenanthrene(a-e). Decahydronaphthalene, Cyclohexane, Methylcyclohexane, Bicyclohexane(f-i). Heptane, Octane, Decane, Dodecane, Eicosane, Octadecane(j-o).

meet the subsequent calculation needs of the hydrogenation process. Therefore, it is possible to further predict the hydrogen solubility of a complex mixed system such as diesel.

4. Model application

After constructing a model for predicting hydrogen solubility based on the modified Henry equation, we hope to apply this model to diesel hydrotreating to provide gas-liquid phase equilibrium data for subsequent calculations. For a binary mix system of known molecular species, this article predicts hydrogen solubility based on linear addition and uses the bulk properties and average structure parameters that define virtual components to predict the hydrogen solubility of the mixed system. So for diesel, a highly complex mixed system composed of multiple hydrocarbons, if the molecular information of diesel can be accurately known, the hydrogen solubility of diesel can be predicted according to the type and content of the molecule. At present, various molecular-level models are used in various petroleum processing processes and have achieved good simulation results (Ahmad et al., 2011; Chen et al., 2019). Therefore, a diesel composition model is constructed based on the molecular level, and the molecular information is used to predict the hydrogen solubility of the diesel.

4.1. Construction of diesel molecular composition model

To predict the hydrogen solubility of diesel based on the modified Henry equation, the molecular level information of diesel must be obtained. Therefore, molecular management technology was used to construct a molecular composition model for diesel. The composition of petroleum molecules is complex, but not irregular. Flory, Shibata, et al. (1936;1987) found that petroleum is "continuous" and the carbon number of the side chain of petroleum molecules can satisfy the Gamma distribution. In this paper, the Structural Unit and Bond-Electron Matrix(SU-BEM) method are used to digitize the expression of oil molecules, and the molecular

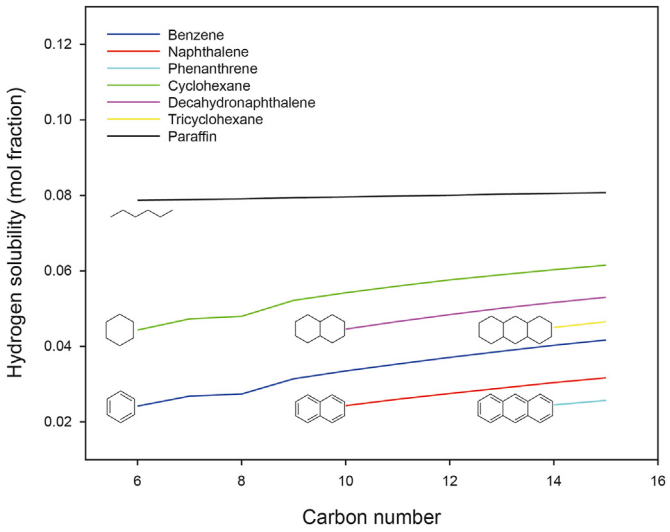

Fig. 7. Prediction of hydrogen solubility of various homologues by molecular structural parameters at a temperature of 100 °C and a pressure of 8 MPa.

composition is constructed based on the molecular properties predicted by the group contribution method. First, Elementary analysis, GC-MS, and other analytical methods were used to obtain different side information of the two FCC diesel. After that, the representative core molecules in diesel were selected, and 320 diesel molecules were generated. See supporting information for diesel molecular composition. Then, select the appropriate probability density function, and use the software developed by the research group to complete the adjustment and optimization of the molecular composition, so that it can accurately represent the real diesel molecular composition. Please refer to the work of this research group for the method of constructing the molecular composition model (Feng et al., 2019).

Fig. 9 shows the distribution of the total carbon number of two diesel molecules. It can be seen from the figure that the distribution of the total carbon number of the diesel molecules satisfies the Gramma distribution. The construction results of the two types of diesel are shown in Tables 1 and 2. From the data in the table, it can be seen that the predicted values of density and element content are consistent with the experimental values. Besides, the group composition results representing the diesel structure distribution also corresponded to the experimental values one by one. This shows that the composition model can represent the structure and properties of real diesel, and the group composition distribution is consistent with the real diesel, and its accuracy can meet the needs of subsequent hydrogen solubility prediction.

4.2. Diesel hydrogen solubility

This paper builds a molecular-level diesel composition model based on the molecular management platform developed by this research group. In this model, the bulk properties and structural parameters of diesel can be obtained, and the hydrogen solubility of diesel can be predicted based on the modified Henry equation. Fig. 10 shows the overall operation flow from the input of the model to the output of the model. From the measurement of the bulk and chemical properties and structural distribution of diesel by analytical methods to the construction of a molecular-level diesel composition model, the bulk properties and average structural parameters are obtained. Finally, the hydrogen solubility of diesel is predicted.

Firstly, the bulk properties are obtained by the diesel composition model, and the bulk properties correlation Henry coefficient parameters method is used to predict the diesel hydrogen solubility. Fig. 11 shows the prediction of the hydrogen solubility of diesel by bulk properties correlation Henry coefficient parameters method. It can be seen from the figure that the prediction of hydrogen solubility using bulk properties calculated by diesel molecular composition model correlation Henry coefficient parameters differed greatly from the experimental data. This is because the bulk properties obtained by the diesel molecular composition model are a mapping relationship between the SU-BEM structural unit and the group, which is automatically converted into a group by entering the structural unit and calculating common bulk and chemical properties. Then, a large number of empirical correlation equations are used when calculating the bulk properties using the group contribution method, and the parameters in the empirical correlation equations require a large amount of experimental data for fitting regression. In the process of fitting the regression of data, there will be errors. Then, the bulk properties calculated by the diesel molecular composition model are brought into the Henry coefficient parameters correlation equation, and there will be transmission errors. And the Henry coefficient parameters correlation equation in the modified Henry equation is obtained by regression of a large amount of hydrogen solubility experimental data, and there will also be model errors. The error of the bulk properties of the diesel molecular composition model calculation will be passed down, which will cause this error to become bigger. To this end, we should eliminate the errors caused by the diesel molecular composition model and make the calculation of diesel hydrogen solubility more accurate.

To this end, this section starts from the molecular chemical structure in diesel and uses average structure parameters obtained from the diesel molecular composition model to correlate Henry coefficient parameters to calculate the hydrogen solubility of diesel. Because the diesel molecular composition model is constructed, the molecular composition and content of the diesel can be accurately known, and the accurate average structural parameters of the diesel can be obtained. (a) and (b) in Fig. 12 show the diesel molecular composition model to calculate average structure parameters correlation Henry coefficient parameters method to predict the hydrogen solubility results. As can be seen from the figure, the prediction of diesel hydrogen solubility based on average structural parameters is in good agreement with experimental data. Figs. 12 (a) and Fig. 10 are the same FCC diesel using the bulk properties and average structural parameters to correlate the Henry coefficient parameters method to predict hydrogen solubility. It can be seen that the hydrogen solubility results predicted by average structural parameters are better than the bulk properties predicted hydrogen solubility results. It shows that after eliminating the error caused by the diesel molecular composition model, the error produced by the diesel hydrogen solubility model is within the acceptable range, and there is no transmission error. Therefore, by comparing the prediction results of the binary mix system hydrogen solubility and diesel hydrogen solubility using bulk properties and structural parameters, respectively, the two related methods can predict the hydrogen solubility to meet the calculation needs of subsequent hydrogenation processes. However, based on the molecular-level diesel composition model, the use of diesel bulk properties correlation Henry coefficient parameters method to calculate diesel hydrogen solubility will produce a transmission error, the error is larger, and the use of diesel average structure parameters correlation Henry coefficient parameters method to calculate diesel hydrogen solubility will not produce the transmission error and the calculation result is more accurate. Therefore, for the case where diesel molecular information can be obtained by

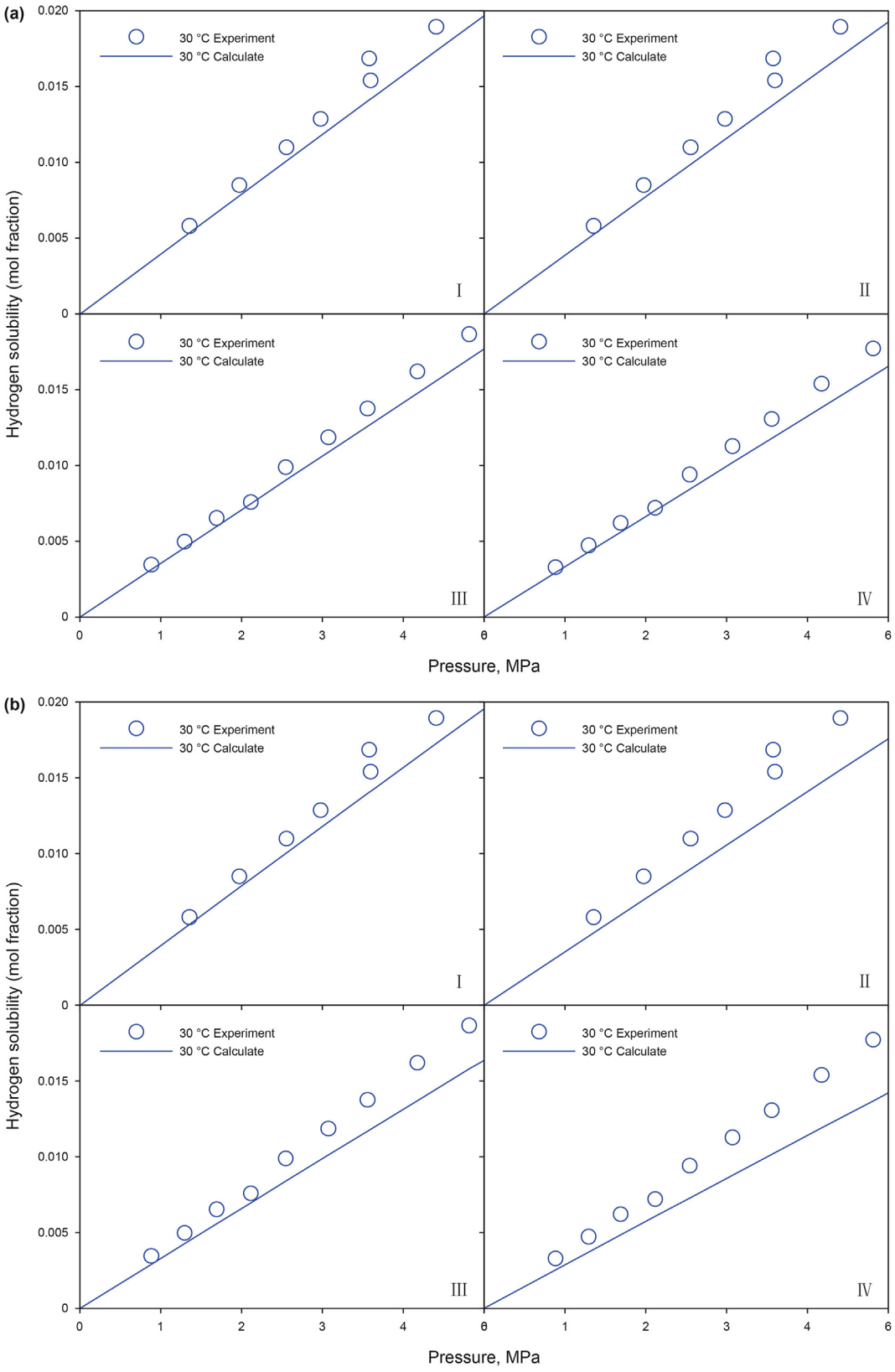

Fig. 8. (a) Bulk properties and (b) Structural parameters correlate with modified Henry equation parameters to predict the solubility of hydrogen in binary systems. Toluene + Methylcyclohexane(I, II), Benzene + Cyclohexane(III, IV).

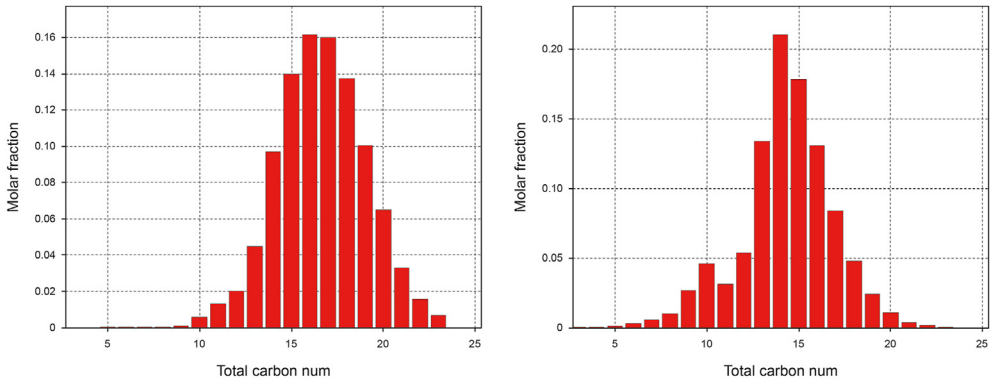

Fig. 9. Total carbon number distribution of two diesel molecules.

Table 1
Experimental and predicted bulk properties of diesel 1.

	Experimental value	Predicted value
Density (20°C), g/cm^3	0.9518	0.9131
Alkanes, wt%	11.1	11.1
Monocyclic, wt%	4.1	3.6
Bicycloalkanes, wt%	0.7	0.6
Tricycloalkanes, wt%	0.1	0.0
Monocyclic aromatic, wt%	27.4	27.3
Bicyclic aromatic, wt%	48.7	48.7
Tricyclic aromatic, wt%	7.9	3.7

Table 2
Experimental and predicted bulk properties of diesel 2.

	Experimental value	Predicted value
Density (20°C), g/cm^3	0.9535	0.9572
	Elemental, wt%	
S, wt%	0.4432	0.3825
C, wt%	90.20	90.20
H, wt%	9.44	9.44

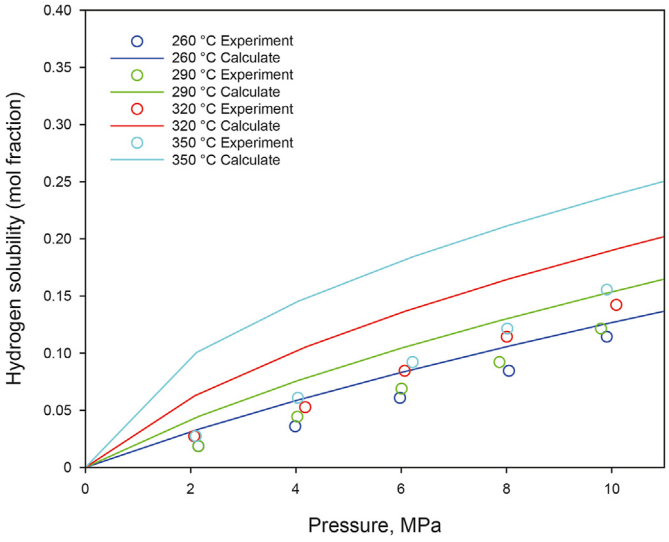

Fig. 11. Prediction of hydrogen solubility based on bulk properties of diesel.

constructing a diesel molecular composition model through experimental data, the diesel hydrogen solubility is calculated based on the correlation of average structural parameters; if the molecular information in diesel is not known, the bulk properties correlation based on experimental measurements can be used to calculate the hydrogen solubility of diesel.

5. Conclusion

The Henry coefficient is related to the temperature and the hydrogen liquid concentration. In the presented paper, a modified Henry equation is proposed. Two correlation methods for Henry coefficient parameters are developed, which are based on easy-to-measure bulk properties and structural parameters of

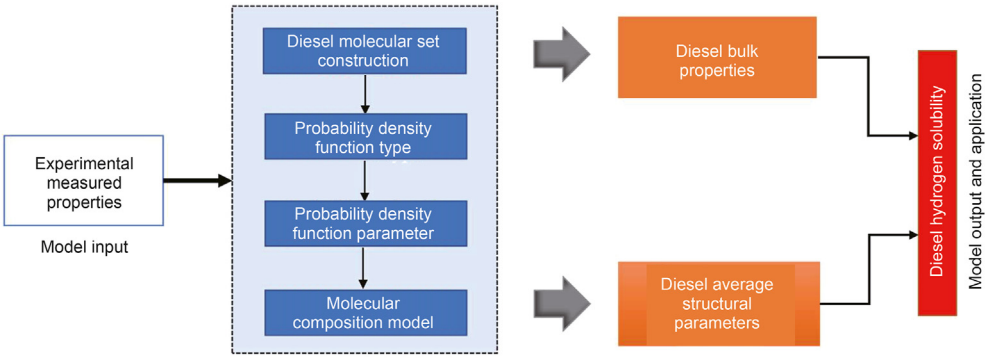

Fig. 10. Flow chart for predicting diesel hydrogen solubility based on modified Henry equation.

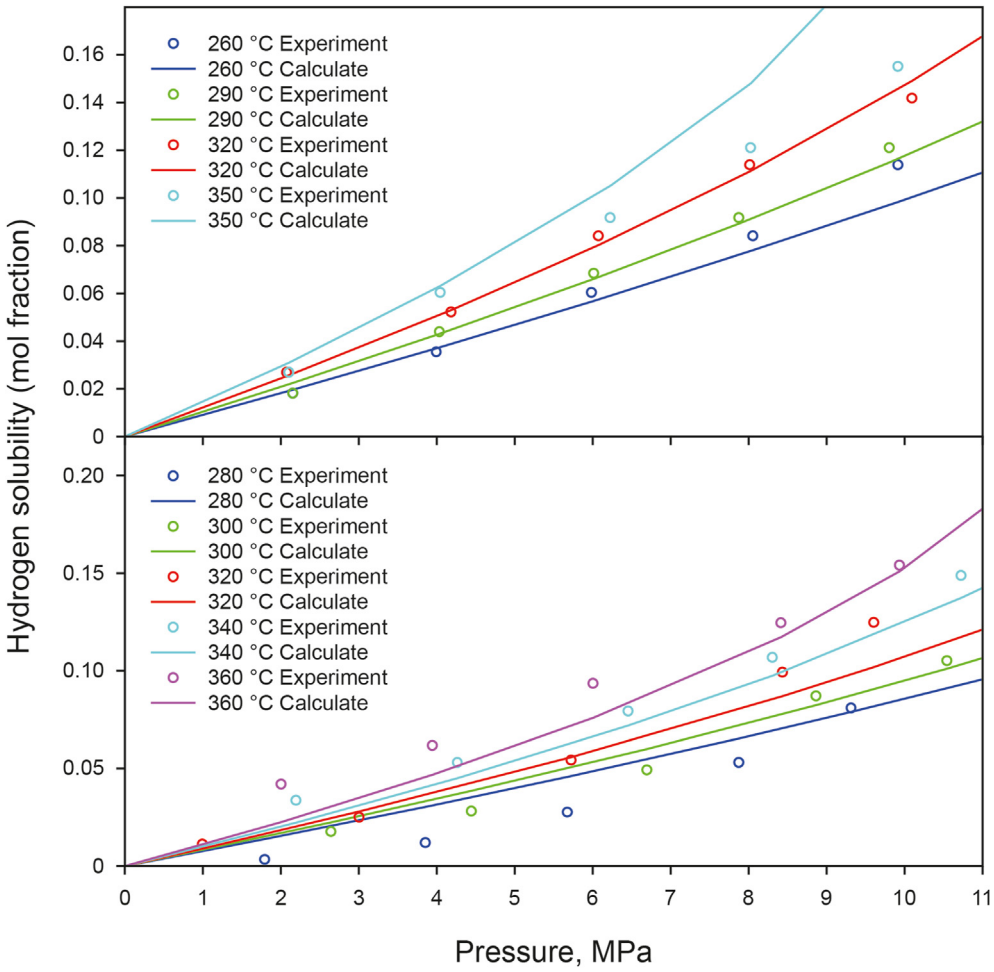

Fig. 12. Prediction of hydrogen solubility based on average structure parameters of diesel.

hydrocarbons, respectively. The two correlation methods were applied to the binary mixed system, proving that the method can be applied to the mixture. A molecular-level diesel composition model was constructed to obtain the bulk properties and average structure parameters of diesel. The hydrogen solubility of diesel was calculated based on the two proposed hydrogen solubility prediction methods. The diesel hydrogen solubility prediction based on the average structure parameter is more accurate than that based on bulk properties due to the existence of compositional model property prediction error. For the case where diesel molecular model can be constructed to obtain molecular information, the average structural parameter correlation is used to calculate the hydrogen solubility. If the molecular composition in diesel is not known, the measured bulk properties can be used to calculate hydrogen solubility.

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