Prediction of Surface Tension of Heavy Oil Based on Principle of Corresponding States Combined with Detailed Composition and Molecular Structure Analysis

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In this work, a new method of predicting the surface tension of heavy oils and its temperature dependence was developed. The surface tensions of five fractions and residue fractionated by the vacuum distillation of atmospheric residue (AR), and AR itself were predicted, based on a detailed composition and molecular structure analysis, i.e., “petroleomics”. In this method, the chemical compositions and molecular structures of compounds included in the fractions and residue were identified by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and then the critical pressure, critical temperature and boiling point of each compound were calculated by the group contribution method. Next, using the calculated properties, the surface tension of each compound was predicted by the principle of corresponding states. Finally, a mixing rule, in which the surface tension of mixtures was expressed as a linear function of mole fraction of each compound, was used to predict the surface tensions of the five fractions and residue of AR and AR itself. By comparing the predicted and experimental values of the surface tensions and their temperature dependence, it was found that the present method is useful for predicting the surface tension of heavy oils.

Key Words
Petroleomics, Surface tension, Heavy oil, Principle of corresponding states

1. Introduction
With the increasing demand for petrochemical feedstock and middle distillates, seldom used heavy oils, such as atmospheric and vacuum residues of crude oils, have recently attracted attention as new petroleum resources. Also, the recovery of unconventional crude oils such as bitumen from oil sands has begun. Since the quality of such heavy oils whose viscosity is very high is relatively poor, however, technical developments to advance the upgrading process of heavy oils are necessary for effective utilization of the oils. Therefore, it is desirable to acquire knowledge of the flow, thermal and diffusion fields in the upgrading reactors, such as residuum desulfurization (RDS) reactors, as well as to clarify the reaction kinetics of the upgrading process and to develop new catalysts to accelerate the reactions.

Knowledge of the physical properties of heavy oils,
particular at high temperatures and high pressures, is indispensable for the analysis of flow and thermal fields in the upgrading reactors of heavy oils. Surface tension is one of the most important properties affecting the flow behavior of heavy oils in multiphase reactors, such as the trickle-bed reactor used for the RDS process, and the wetting tendency of catalysts by heavy oils in the reactors. Therefore, it is important to establish a method for precisely measuring the surface tension of heavy oils at high temperatures and high pressures, and to develop a method for accurately predicting the surface tension.

The surface tension of heavy oils and the interfacial tension between water and heavy oils, including crude oils, have been measured by the Wilhelmy plate method, the pendant drop method, and so on. The temperature dependence of the surface and interfacial tensions, and the relation between the density and surface tension of crude oils, or between the interfacial tension of crude oil/sea water and their chemical compositions have been reported, although the number of reports are limited. Recently, we have measured the surface tensions of five fractions and residue fractionated by the vacuum distillation of atmospheric residue (AR) and AR itself at temperatures up to 250°C under atmospheric pressure using the pendant drop method, and we investigated the relation between the surface tensions of the five fractions and residue and the compositions of their sub-fractions fractionated by column chromatography. As a result, it was revealed that the fractions rich in saturated hydrocarbon sub-fraction have lower surface tension, and that the surface tension of the residue containing the sub-fraction with the highest molecular weight is the highest.

In addition, the surface tensions of pure hydrocarbons and their mixtures have been predicted on the basis of the parachor method, the principle of corresponding states and density gradient theory. There are also a few reports on the prediction of surface tensions of crude oils, heavy oils, and biodiesel fuels. In the previous work, we predicted the surface tension of the five fractions and residue of AR using the predictive equation of Brock and Bird based on the principle of corresponding states, where the critical temperature, critical pressure and boiling point of each fraction were determined using the method proposed by Nji et al. who estimated the thermodynamic properties of heavy hydrocarbons on the basis of perturbation theory using n-paraffins as a reference. Although the surface tensions of the fractions were predicted with reasonable accuracy, that of the residue was considerably underestimated. This is because the previous predictive equation of surface tension is not applicable to heavy hydrocarbons, and in addition, it is considered that each fraction of AR is the fundamental compound of AR. Therefore, to accurately predict the thermodynamic properties such as critical constants and the boiling point, and also the surface tension of heavy oils, it is desirable that the compositions and molecular structures of all compounds included in heavy oils are analyzed in detail, the properties of each compound are estimated precisely, and then the surface tension of heavy oils is predicted as mixtures of their compounds following a mixing rule.

Recently, ultrahigh-resolution mass spectrometry (MS), namely, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), has been developed, and using this technique, the detailed chemical compositions and molecular structures of crude oils have been analyzed at the molecular level. This technique is called “petroleomics”, which can link the molecular structures of compounds in crude oils to their properties. In Japan, a platform for coupling petroleomics with molecule-based kinetic modeling and informatics is being constructed to analyze the chemical compositions and molecular structures of the hundreds of thousands of compounds in heavy oils, and finally to develop new petroleum-upgrading processes.

In this work, a new method for accurately predicting the surface tension of heavy oils was developed on the basis of detailed composition and molecular structure analysis by FT-ICR MS, and petroleomics. Here, the thermodynamic properties of compounds in the five fractions and residue fractionated by the vacuum distillation of AR were calculated by the group contribution (GC) method, and then the surface tension of each compound was predicted by the principle of corresponding states. The surface tensions of the fractions and residue of AR and AR itself, which were measured using a mixing rule, were compared with those predicted by the pendant drop method.

2. Prediction of surface tension

In this work, the surface tensions of five fractions (hereinafter called Fr.1-Fr.5) and a residue (hereinafter called BTM), which were fractionated by the vacuum distillation of atmospheric residue (AR) according to ASTM D1160 and whose mass fractions and atmospheric equivalent temperatures (AET) are shown in Table 1, and AR itself were predicted, based on the principle of corresponding states, i.e., the following equation proposed by Brock and Bird:

$$
\frac{\gamma}{P^* T^*} = \phi \left[ 1 - \frac{T}{T_c} \right]^{11/9},
$$

where $P^*$, $T$, $T_c$ and $\gamma$ are the critical pressure, temperature,
Table 1  Mass fractions and atmospheric equivalent temperatures of five fractions and residue fractionated by vacuum distillation of AR

|                  | Fr.1  | Fr.2  | Fr.3  | Fr.4  | Fr.5  | BTM   |
|------------------|-------|-------|-------|-------|-------|-------|
| Mass fraction    | 0.092 | 0.096 | 0.096 | 0.099 | 0.038 | 0.579 |
| Atmospheric      |       |       |       |       |       |       |
| equivalent       | 391.2 | 431.6 | 464.5 | 496.3 | 503.2 |       |
| temperature (°C) |       |       |       |       |       |       |

Table 2  Mole fractions of each component in Fr.1 to Fr.5 and BTM fractionated by column chromatography

|          | Sa    | 1A    | 2A    | 3A+   | Po    | PA    | As    |
|----------|-------|-------|-------|-------|-------|-------|-------|
| Fr.1     | 0.5952| 0.1845| 0.0477| 0.1392| 0.0311| 0.0023| 0.0000|
| Fr.2     | 0.4980| 0.1885| 0.0851| 0.1698| 0.0586| 0.0000| 0.0000|
| Fr.3     | 0.4741| 0.1971| 0.0926| 0.1945| 0.0409| 0.0007| 0.0000|
| Fr.4     | 0.4152| 0.1804| 0.0903| 0.2256| 0.0883| 0.0003| 0.0000|
| Fr.5     | 0.3553| 0.2087| 0.1043| 0.2646| 0.0655| 0.0066| 0.0000|
| BTM      | 0.0977| 0.0935| 0.0578| 0.3046| 0.1565| 0.2143| 0.0756|

critical temperature and surface tension, respectively. Although the equation proposed by Miller has been commonly used to estimate \( Q \) in Eq. (1), a new equation for \( Q \), which can be applied to heavy hydrocarbons, is proposed here. The procedure to predict the surface tension of heavy oils is described below.

### 2.1 Determination of compositions and molecular structures of compounds in heavy oils

Firstly, the five fractions (Fr.1 to Fr.5) and residue (BTM) of AR fractionated by the vacuum distillation were respectively separated into the following sub-fractions by column chromatography: saturate fraction (Sa), one-ring aromatic fraction (1A), two-ring aromatic fraction (2A), three or more- ring aromatic fraction (3A+), polar resin fraction (Po), polyaromatic resin fraction (PA) and asphaltene fraction (As). The structures of the top five compounds were used even for BTM, where As fraction was only contained in BTM.

Next, the chemical compositions and molecular structures of all compounds included in each of Sa, 1A, 2A, 3A+, Po, PA and As fractions in Fr.1 to Fr.5 and BTM were identified by FT-ICR MS, where the atmospheric pressure photoionization (APPI) was used as an ionization method for analyses of 1A, 2A, 3A+ and Po fractions, the laser desorption ionization (LDI) for PA and As fractions, and the laser desorption combined with silver cationization (LDI-Ag) for Sa fraction, respectively. To predict the surface tension of heavy oils in this work, however, the chemical compositions and molecular structures of the top five compounds with relatively high contents were used as those of the representative compounds in each fraction because the analysis by FT-ICR MS indicated the existence of more than 100,000 compounds in heavy oils. In addition, it was assumed that the molecular structure of each compound is composed of a core structure and a side chain according to the carbon number of the compound. The details of the above analyses, i.e., the determination of the core structures of all compounds in each fraction and the molecular structures of top five compounds, have been reported in refs. 46 and 50. Although the top 10 compounds were considered for the fractions in BTM in ref. 46, the molecular structures of the top 5 compounds were used even for BTM in this work. We have confirmed that the predicted values of surface tension are the same when the molecular structures of top 8 compounds are used instead of top 5 compounds. Therefore, the selection of top 5 compounds is sufficient to predict the surface tension.

### 2.2 Prediction of critical constants by GC method

The critical pressure \( P_c \), critical temperature \( T_c \) and boiling point \( T_b \) of the top five compounds with the molecular structures determined in Sec. 2.1 for each of Sa, 1A, 2A, 3A+, Po, PA and As fractions in Fr.1 to Fr.5 and BTM were predicted using the group contribution (GC) method of Marrero and Gani, who proposed equations to estimate the normal boiling point, critical temperature, critical pressure, critical volume, standard enthalpy of formation, standard enthalpy of vaporization, standard Gibbs energy, normal melting point and standard enthalpy of fusion of pure organic compounds. Among them, the equations for \( P_c \), \( T_c \) and \( T_b \) are given as follows:

\[
\exp \left( \frac{T_b}{231.239} \right) = \sum N_i T_{si} + \sum J_i T_{si} + \sum K_i T_{si},
\]

\[
(P_c - 5.9827)^{-0.108998} = \sum N_i P_{si} + \sum J_i P_{si} + \sum K_i P_{si},
\]

\[
\exp \left( \frac{T_c}{222.543} \right) = \sum N_i T_{si} + \sum J_i T_{si} + \sum K_i T_{si},
\]

where \( N_i, J_i, K_i, P_{si}, P_{si}, T_{si}, T_{si}, T_{si} \) are the group parameters for

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2.3 Prediction of parameter $Q$

Although $Q$ in Eq. (1) is commonly estimated using the equation proposed by Miller, it is not appropriate for predicting the surface tension of heavy hydrocarbons such as the compounds in this work. Therefore, new equations for estimating $Q$ are proposed here. Firstly, 62 pure compounds whose properties are already known were divided into two groups, i.e., paraffins and non-paraffins, then the following equations for $Q$ were obtained by regression using the data set of $P_c$, $T_c$ and $T_b$ and the surface tensions of the 62 pure compounds, as shown in Fig. 1.

\[
\begin{align*}
Q_{\text{paraffins}} &= 16.8 \left( \frac{T_b}{T_c} \right)^2 - 21.4 \left( \frac{T_b}{T_c} \right) + 7.45 \\
Q_{\text{non-paraffins}} &= 6.16 \left( \frac{T_b}{T_c} \right)^2 - 6.62 \left( \frac{T_b}{T_c} \right) + 2.35
\end{align*}
\]

Fig. 2 shows a comparison between the surface tensions estimated by Eqs. (1), (5) and (6) and the measured values in previous works for 62 pure compounds. The measured surface tensions of the compounds were estimated within an accuracy of 10%, although the surface tension prediction of relatively higher polar compounds, such as phenol, pyrrolidine, and N,N-dimethylaniline, was not quite well.

2.4 Prediction of surface tension of heavy oils

Using the critical pressure, critical temperature and boiling point of the top five compounds in each of Sa, 1A, 2A, 3A+, Po, Pa and As fractions obtained in Sec. 2.2, the surface tension of the compounds was predicted by Eqs. (1), (5) and (6). Then, the surface tensions of Sa, 1A, 2A, 3A+, Po, Pa and As fractions in Fr.1 to Fr.5 and BTM of AR were estimated by the following equation based on the mixing rule.

\[ \gamma = \sum x_i \gamma_i \]

where $x_i$ is the mole fraction of the ith compound obtained in Sec. 2.2 and $\gamma_i$ is the predicted surface tension. In a similar manner, the surface tensions of Fr.1 to Fr.5 and BTM of AR and AR itself were predicted. For the prediction of the surface tension of AR itself by the mixing rule, the weight fraction in Table 1 was used instead of the mole fraction.

3. Results and discussion

Fig. 3 shows a comparison between the predicted surface tensions and the measured values for Fr.1 to Fr.5 and BTM of AR. Also, Fig. 4 shows a comparison for the surface tension of AR. In these figures, the surface tensions predicted using $Q$ by Miller instead of $Q$ in Eqs. (5) and (6) are also shown, where the predictive method of surface tension was the same, namely, based on the detailed composition and molecular structure analysis, the GC method and the principle of corresponding states. Although it seems that the present method cannot predict well the surface tensions of Fr.1 to Fr.3, particularly at higher temperature, the prediction accuracy is improved at least compared with the prediction by Miller’s method. One of the possible reasons why the present method cannot predict well for Fr.1 to Fr.3 particularly at higher temperature is as follows. As mentioned in our previous study on the surface tension measurement of heavy oils, the density of each sample is necessary to estimate the surface tension by the pendant drop method. The temperature range of the oscillating U tube method used in the previous study to measure the density was 15 to 105 °C. Therefore,
the density at higher temperature beyond the above temperature range was determined by extrapolation of that at lower temperature.

Since the surface tension prediction with Miller’s $Q$ is not appropriate for heavy hydrocarbons, it could not predict well the measured surface tensions of Fr. 4, Fr. 5 and BTM containing the compounds with relatively high molecular weight. In addition, our previous prediction method, which was based on the idea that Fr.1 to Fr.5 and BTM fractionated by the vacuum distillation of AR are the fundamental compounds of AR, underestimated considerably the surface tension of BTM. One possible reason for this is that the perturbation theory using...
n-paraffins as a reference system was applied to estimate the critical properties and boiling point of BTM as well as Fr.1 to Fr.5, even though BTM contains a lot of saturated hydrocarbons, aromatic hydrocarbons, and resins with relatively high-molecular weights.

The present prediction method based on the detailed composition and molecular structure analysis of heavy oil overcomes all of the problems in the previous works. The relative deviations between the predicted and measured values for all the temperature conditions were calculated. Table 3 shows the relative deviations for Fr. 1 to Fr. 5, BTM, and AR itself. As shown in Table 3, the present prediction method enables to predict the surface tension of heavy oil within an accuracy of 10%.

4. Conclusions

In this work, a new method of predicting the surface tension of heavy oils was proposed, in which a detailed composition and molecular structure analysis by petroleomics, a group contribution method and the principle of corresponding states were coupled. Firstly, the chemical compositions and molecular structures of compounds in the five fractions and residue of AR were identified using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and then the critical pressure, critical temperature and boiling point of each compound were predicted by the group contribution method. Next, using the predicted properties, the surface tension of each compound was predicted by the principle of corresponding states, then the surface tensions of five fractions and residue of AR and AR itself were predicted by a mixing rule. By comparing the predicted and experimental values of surface tension and their temperature dependence, it was found that the present method can predict the surface tension of heavy oils within an accuracy of 10%.

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| Fr. | RD [%] |
|-----|-------|
| Fr. 1 | 7.16 |
| Fr. 2 | 4.99 |
| Fr. 3 | 4.19 |
| Fr. 4 | 1.79 |
| Fr. 5 | 3.90 |
| BTM  | 5.86 |
| AR   | 3.81 |
