

Surface Tension of Toluene-Extracted Bitumens from Utah Oil Sands As Determined by Wilhelmy Plate and Contact Angle Techniques

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The surface tension values for toluene-extracted bitumens from Whiterocks, Sunnyside, PR Spring, Asphalt Ridge, and Circle Cliffs oil sands were measured with the Wilhelmy plate technique and found to vary from 20.6 to 31.2 mN m⁻¹ at 333 K. A linear relationship between the bitumen surface tension and temperature was observed in the temperature range 310-356 K, which allowed for the calculation of the temperature coefficients of surface tension. The temperature coefficients were found to vary among the bitumens from -0.063 mN m⁻¹ deg⁻¹ to -0.097 mN m⁻¹ deg⁻¹. Also, the surface tensions of these bitumens at room temperature were calculated from contact angle measurements using Neumann's equation-of-state. Satisfactory agreement between the results for bitumen surface tensions as determined from contact angle data and direct surface tension measurements with the Wilhelmy plate technique were obtained for the Whiterocks, Sunnyside, and PR Spring bitumens. However, large discrepancies, 6.4-9.4 mN m⁻¹, were observed between the bitumen surface tension data obtained from Neumann's equation-of-state and the bitumen surface tensions determined by direct Wilhelmy plate measurements for the Asphalt Ridge and Circle Cliffs bitumens.

Introduction

As the conventional crude oil deposits are rapidly being depleted, there is a greater need to develop other petroleum resources. One such resource is oil sand, a bitumen-impregnated sandy material, which is successfully mined and processed in Canada. The bitumen is separated from sand using the hot-water process and further upgraded to synthetic crude oil. At the University of Utah, researchers have developed both water-based separation processes and several thermal processing approaches for bitumen recovery from the Utah oil sand deposits, however, these technologies have not yet been commercialized.¹

Processing of oil sands involves several steps in which the physicochemical properties of the bitumen may be of particular significance in bitumen recovery and upgrading. Particularly, properties such as surface tension, interfacial tension, and electrical charge at the bitumen/air and bitumen/water interfaces may affect the efficiency of bitumen separation from oil sands using the hot-water process.²⁻⁴ Also, bitumen surface tension may be an important property in upgrading processes such as hydrotreating and hydrocracking when three-phase ebulliated bed reactors are used.⁵ In this regard, there is a need for basic research leading to specification of the physical and chemical properties of bitumen. This task

has received more attention at the University of Utah in recent years, and the surface properties of Utah oil sand bitumens have been studied. Electrophoretic properties of bitumen emulsions were reported for Asphalt Ridge,⁶ Sunnyside,⁶ and Whiterocks⁴ bitumens. The bitumen/air surface tension and the bitumen/aqueous phase interfacial tension for Whiterocks bitumen were also examined.^{3,4} In this contribution, the surface tension of toluene-extracted bitumens from the Whiterocks, Asphalt Ridge, Sunnyside, PR Spring, and Circle Cliffs oil sands were measured and the results are presented herein.

Literature Survey of Surface Tension Data. Only a limited amount of experimental data is reported in the literature on the surface tension of bitumens, and most of these measurements were carried out for Canadian bitumens.^{2-4,7-9} Bowman² and Isaacs and Smolek⁷ measured the surface tension of bitumen recovered from the Athabasca oil sand. Results presented by Bowman² have only limited practical significance as they were obtained for nonequilibrated systems and the procedure used was not well-defined. Isaacs and Smolek⁷ reported the surface tension value of the bitumen, which was obtained from the commercial hot-water processing of Athabasca oil sand, using du Nouy ring tensiometry. The bitumen surface tension was reported to be 29.6 mN m⁻¹ at 64 °C which decreased to 25 mN m⁻¹ at 112 °C. Potoczny et al.⁸ measured the surface tension of several Canadian bitumen samples from different sites using the Wilhelmy plate technique. The surface tension values of these samples varied from about 23 to 32 mN m⁻¹ at 40 °C, depending

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on the location of oil sand sample and solvent type used for bitumen extraction. Vargha-Butler et al.⁹ proposed that the surface tension of bitumen at room temperature can be determined from contact angle measurements using Neumann's equation-of-state for surface tension.¹⁰ The surface tension of bitumens, as determined from contact angle measurements was reported to be in the range of 24.4 to 33.8 mN m⁻¹ at 23 °C, depending on the sample origin and the experimental procedure used in bitumen preparation. This new technique for the bitumen surface tension determination based on contact angle measurements was examined for five different Utah oil sand bitumens and the results are presented in this paper. The theoretical background for the relationship between the bitumen surface tension and contact angle data is briefly reviewed in the following section.

Equation-of-State for Interfacial Tensions. The force balance at a solid surface involving a three-phase system in which the equilibrium contact angle is established can be resolved in terms of the interfacial free energies by using the Young equation:¹¹

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

$$\gamma_{SV} - \gamma_S = \pi \quad (1a)$$

where γ_S , γ_{SV} , γ_{SL} , and γ_{LV} are the surface free energy of solid in contact with vacuum, surface free energy of solid in contact with saturated liquid vapor, interfacial free energy of the solid/liquid interface, and liquid/vapor surface tension, respectively; θ is the contact angle; π is the equilibrium film pressure of the adsorbate (adsorbed liquid vapors), which is assumed to be zero for low-energy solid surfaces.

A difficulty in the application of the Young equation (1) is that there are two parameters, γ_{SV} and γ_{SL} , which cannot be measured directly. In this regard, several researchers have tried to estimate the surface free energy of solids based on contact angle data for various liquids, and calculation methods based on the dispersive and nondispersive theory of interaction between phases have been proposed,¹² including Neumann's equation-of-state.¹⁰

Girifalco and Good¹³ suggested that if two phases are immiscible and interact only through additive dispersion forces the interfacial free energy can be expressed by the following equation:

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 2\phi(\gamma_S\gamma_{LV})^{1/2} \quad (2)$$

where ϕ is the correction factor called the interaction parameter.

According to Neumann et al.,¹⁰ there is a relationship between the surface free energy of the solid, γ_S , of the liquid, γ_{LV} , and the solid/liquid interfacial free energy, γ_{SL} :

$$\gamma_{SL} = f(\gamma_S, \gamma_{LV})$$

It was assumed that the interaction parameter, ϕ , is a function of the interfacial free energy of solid/liquid interface, γ_{SL} :

$$\phi = \alpha\gamma_{SL} + 1 \quad (3)$$

where α is a constant with a value of 0.0075 m²/mJ, as determined from contact angle data for hydrophobic surfaces.

Substituting the value of ϕ and the Young equation (1) into eq 2, and neglecting the contribution of π , Neumann et al.¹⁰ obtained the following equation-of-state in terms of the appropriate interfacial tensions:

$$\cos \theta = \frac{2(\alpha\gamma_S - 1)(\gamma_S\gamma_{LV})^{1/2} + \gamma_{LV}}{\gamma_{LV}[2\alpha(\gamma_S\gamma_{LV})^{1/2} - 1]} \quad (4)$$

Vargha-Butler and others⁹ have proposed that the equation-of-state (4) can be used for determination of the surface tension of bitumens at room temperature. Advancing contact angles for water and glycerol drops placed on Canadian bitumen films were measured. They found that for most bitumens the surface tension data calculated from eq 4 were in good agreement with surface tension data obtained from direct measurements using the Wilhelmy plate technique. However, in a few cases the difference in the surface tension values by these two methods exceeded 2 mN m⁻¹.

A disadvantage of the equation-of-state (4) lies in the discontinuity of the dependence of $\cos \theta = f(\gamma_S)$ when $2\alpha(\gamma_S\gamma_{LV})^{1/2}$ approaches 1. In order to overcome this disadvantage, the above equation-of-state was revised and a new equation was derived by Li and Neumann:^{14,15}

$$\cos \theta = 2\left(\frac{\gamma_S}{\gamma_{LV}}\right)^{1/2} e^{-\beta(\gamma_{LV}-\gamma_S)^2} - 1 \quad (5)$$

where β is a constant with a value of 0.000 124 7 (m²/mJ)², which was determined from contact angle data for low-energy solids.¹⁵

The principal advantage of the equation-of-state for interfacial tension is that it allows for the determination of γ_S (the surface tension of bitumen in our case) from a measurement of the contact angle using only one liquid. The applicability of the equation-of-state for bitumen surface characterization was examined in this study. The surface tension values calculated from eq 5 using contact angle measurements for water drops placed on bitumen films are compared with the surface tension data obtained from direct tensiometric measurements.

Experimental Procedure

Bitumen Samples. Oil sand samples used in this investigation were obtained from the Whiterocks, Sunnyside, PR Spring, Asphalt Ridge, and Circle Cliffs deposits of Utah. The bitumen was extracted from the oil sand samples using spectrograde toluene (EM Science, U.S.A.). The extractions were carried out for 24 h at 385–390 K in a Dean-Stark apparatus with Whatman cellulose thimbles, as described in a previous contribution.¹⁶ Shark skin filter paper was wrapped around the thimble to retain fine mineral particles which penetrated through the thimble wall. The toluene/bitumen solutions were subjected to 12–14 h vacuum distillation on the rotary evaporator, 20 Torr and 358 K. The residual toluene in the bitumen was less than 0.2 wt %, as determined by gas chromatography. The bitumen samples were stored in dark place in air-tight glass containers to avoid bitumen oxidation before use.

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Table 1. Physical Properties of Extracted Bitumens from Utah Oil Sands (Data from Refs 1 and 17–19)

| property | Whiterocks | Sunnyside | PR Spring | Asphalt Ridge | Circle Cliffs |
|--------------------------|------------|-----------|-----------|-----------------|------------------|
| bitumen content, wt % | 7.1–8.3 | 8.5–10 | 5–14 | 10.9–13.1 | 2.8 ^a |
| specific gravity | 0.981 | 1.033 | 1.016 | 0.970 | ND |
| gravity, °API | 12.7 | 5.5 | 7.8 | 14.4 | 14.3 |
| Conradson carbon, wt % | 8.8 | 14.8 | 14.0 | ND ^b | 23.3 |
| ash, wt % | 0.24 | 2.4 | 3.3 | 0.04 | 0.06 |
| viscosity at 323 K, Pa·s | 32 | 1500 | 280 | 80 | 258 ^a |

^a Bukka, K., unpublished data. ^b ND = not determined.**Table 2. Fractional Composition (wt %) of the Utah Oil Sand Bitumens (Data from Refs 17, 20, and 21)**

| bitumen fraction | Whiterocks | Sunnyside | PR Spring | Asphalt Ridge | Circle Cliffs ^a |
|------------------|------------|-----------|-----------|---------------|----------------------------|
| saturates | 29.5 | 24.9 | 26.6 | 32.4 | 23.8 |
| aromatics | 22.2 | 18.1 | 25.7 | 22.4 | 19.2 |
| resins | 42.4 | 30.0 | 31.7 | 37.6 | 28.8 |
| asphaltenes | 3.3 | 23.7 | 16.0 | 7.3 | 28.1 |
| atomic H/C ratio | 1.60 | 1.45 | 1.57 | 1.56 | 1.37 |
| molecular weight | 500 | 588 | 820 | 490 | 744 |

^a Bukka, K., unpublished data.

The physical and chemical characteristics of toluene-extracted bitumens from the Whiterocks, Sunnyside, PR Spring, Asphalt Ridge, and Circle Cliffs deposits, as reported in the literature, are shown in Tables 1 and 2, respectively.

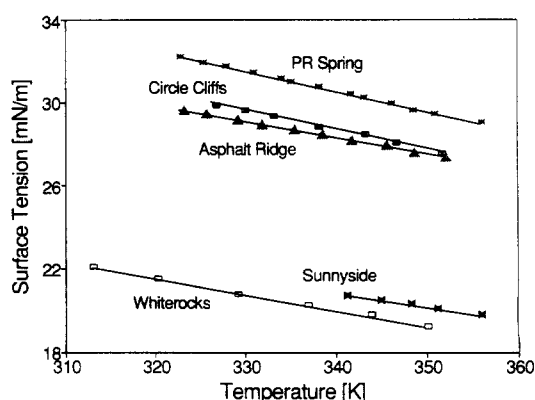
Wilhelmy Plate Technique. The surface tension of bitumen was measured on a Digital-Tensiometer K10T (KRÜSS, GmbH, Germany) with a fine platinum roughened plate. The tensiometer was connected to a constant temperature water bath to maintain the desired temperature. A 10-mL bitumen sample was placed in the sample container, which was installed in the tensiometer. The sample was allowed to reach thermal equilibrium. The instrument with the attached platinum plate was calibrated before being brought in contact with the bitumen sample. The sample container was raised against the bottom edge of the platinum plate until the plate became moistened by the sample. The resulting force, due to the wetting, was then measured. The accuracy of the measurement was within 0.2 mN m⁻¹ of the reported value. The results were recorded when no change in the surface tension was observed, typically after 20–30 min.

Contact Angle Measurements. A film of bitumen was spread mechanically on a clean and warm (323–333 K) glass slide to form a thickness of less than 5–6 μm, as was estimated from the difference in the weight of a clean glass slide and that covered by the bitumen film. The glass slide with the bitumen film was cooled to room temperature (294 ± 1 K). The bitumen films, as prepared, were uniform and smooth. Importantly, viscous bitumens, in particular Sunnyside bitumen, could only be uniformly deposited on the glass slide at elevated temperature.

A 4–6 mm diameter water drop was placed on the bitumen film and the contact angle was measured on both sides of the drop with the NRL goniometer (Rame-Hart Inc., U.S.A.) with an accuracy of 2°. In all experiments, distilled water with specific conductivity less than 10⁻⁶ S/cm, pH = 5.8 ± 0.1, and surface tension of 72.6 ± 0.1 mN m⁻¹, was used. In each case 5–10 water drops were placed on 2–3 slides each covered with freshly prepared bitumen films and then the contact angles were measured. Only the average value of contact angle and confidence intervals for the experimental data are reported. In selected experiments with the Whiterocks and Circle Cliffs bitumens, the contact angle variation with time was recorded, whereas in other experiments the contact angle was measured immediately, 15–20 s, after the water drop had been placed on the bitumen film.

Results and Discussion

Direct Measurement of Surface Tensions. Results from the temperature dependence of surface tension for the Whiterocks, Sunnyside, PR Spring, Asphalt Ridge, and Circle Cliffs bitumens, using the Wilhelmy plate technique, are presented in Figure 1. Surface tension measurements were carried out in the temperature range

**Figure 1.** Effect of temperature on the surface tension of bitumens separated from the Utah oil sands.

310–356 K. It was found that the surface tension values were reproducible in this temperature range. Further, in no case was hysteresis observed during temperature cycling. Always, for a given bitumen, the same linear relationship between surface tension and temperature was observed regardless of whether the temperature was increased or decreased during the experiments. Reproducibility of the results suggests that such phenomena as evaporation of light bitumen fractions, oxidation of asphaltenes, or chemical reactions at the platinum/bitumen interface, if such reactions could be significant, did not affect the surface tension during the time of these measurements.

For each bitumen at a certain low temperature, the measured surface tension value was found not to be reproducible, and the recorded values were always higher than expected from the linear relationship of $\gamma_B = f(T)$. This limiting low temperature was observed to vary with bitumen source. The low-temperature limits for the bitumens under study were as follows: $T < 310$ K for Whiterocks bitumen, $T < 320$ K for PR Spring and Asphalt Ridge bitumens, $T < 325$ K for Circle Cliffs bitumen, and $T < 340$ K for Sunnyside bitumen. The higher viscosity of bitumen at low temperature could contribute to the experimental error in the surface tension measurements with the Wilhelmy plate, as was suggested in the literature.⁸

Linear relationships between surface tension of bitumen and temperature were obtained for bitumen samples in the range of temperatures examined, 310–356 K (Figure 1) and were in general agreement with surface tension

Table 3. Measured Surface Tension Values for the Utah Oil Sand Bitumens

| bitumen | surface tension at 333 K (60 °C), mN m ⁻¹ | temp coeff of surface tension, mN m ⁻¹ deg ⁻¹ | literature |
|-------------------|---|--|------------|
| Utah Bitumens | | | |
| Whiterocks | 20.6 ± 0.2 | -0.077 ± 0.002 (313–350 K) | this work |
| Sunnyside | 21.3 ± 0.2 | -0.063 ± 0.001 (341–356 K) | this work |
| PR Spring | 31.2 ± 0.2 | -0.097 ± 0.001 (322–356 K) | this work |
| Asphalt Ridge | 28.9 ± 0.2 | -0.078 ± 0.001 (323–352 K) | this work |
| Circle Cliffs | 29.3 ± 0.2 | -0.093 ± 0.002 (325–325 K) | this work |
| Canadian Bitumens | | | |
| Athabasca | ~27.2 | ~-0.19 (313–368 K) | ref 2 |
| | 29.6 (64 °C) | -0.095 (337–385 K) | ref 7 |
| Peace River | 22.0–29.2 | -(0.048–0.072) (313–363 K) | ref 8 |
| Pelican Lake | 24.0–30.9 | -(0.044–0.078) (313–363 K) | ref 8 |
| Fort McMurray | 22.2–30.6 | -(0.050–0.082) (313–363 K) | ref 8 |

Table 4. Comparison of Bitumen Surface Tension Values Calculated from Contact Angle Measurements with Bitumen Surface Tension Determined by Wilhelmy Plate Measurements (21 °C)

| | bitumen | | | | |
|---|------------------------|------------------------|------------------------|------------------------|------------------------|
| | Whiterocks | Sunnyside | PR Spring | Asphalt Ridge | Circle Cliffs |
| contact angle for water drop at bitumen film at 294 K, deg | 98.3 ± 1.8 | 93.8 ± 2.2 | 85.1 ± 2.9 | 98.0 ± 2.4 | 95.8 ± 1.2 |
| calculated bitumen surface tension, mN m ⁻¹ | 23.9 ± 1.2 | 26.7 ± 1.5 | 32.2 ± 1.9 | 24.2 ± 1.5 | 25.5 ± 0.8 |
| bitumen surface tension after extrapolation of experimental data in Figure 1 to 294 K, mN m ⁻¹ | 23.5 ± 0.2 | 23.7 ± 0.2 | 35.0 ± 0.2 | 31.9 ± 0.2 | 33.0 ± 0.2 |
| difference in determination of the bitumen surface tension by both methods, direct measurement and using contact angle data, mN m ⁻¹ | +0.4 (-1.0 to +1.8) | +3.0 (+1.7 to +4.7) | -2.8 (-4.9 to -0.7) | -6.9 (-9.4 to -6.4) | -7.5 (-8.5 to -6.9) |

data reported in the literature for Canadian bitumens.⁸ The surface tensions of toluene-extracted bitumen samples from Utah oil sands were found to vary from 20.6 to 31.2 mN m⁻¹ at 333 K and are comparable to values reported for Canadian bitumens, 22.0–30.9 mN m⁻¹ at 333 K (see Table 3).

The results presented in Figure 1 can be described by the following equation:

$$\gamma_B(T) = \frac{d\gamma_B}{dT}T + \gamma_B(T=0) \quad (6)$$

For each bitumen the temperature coefficient of the surface tension, $d\gamma_B/dT$, was calculated from the linear relationship (Figure 1) and is presented in Table 3. The temperature coefficient values varied from -0.063 to -0.097 mN m⁻¹ deg⁻¹, depending on the bitumen sample. Similar values of the temperature coefficient for the bitumen surface tensions were reported for Canadian bitumens (-0.044 to -0.095 mN m⁻¹ deg⁻¹) (Table 3).

There was no apparent relationship between the bitumen surface tension (Table 3) and fractional composition of bitumen examined (Table 2). Also, there seems to be no correlation of the bitumen surface tension and average molecular weight of bitumen when data from Table 3 are compared with data from Table 2.

Bitumen Surface Tension from Contact Angle Measurements. The applicability of the equation-of-state (5) for bitumen surface tension determination was examined, and the advancing contact angle was measured for water drops resting on a bitumen film. The contact angle was measured immediately (15–20 s) after placement of water drops at the bitumen film surface. Rapid measurement of contact angle was required in order to minimize the effect of liquid penetration and chemical interaction between the two phases on the contact angle measurement.⁹ Interactions at the interphase cause a decrease in the contact angle value with time as shown in Figure 2 for the Whiterocks and Circle Cliffs bitumens.

The results of contact angle measurements and the

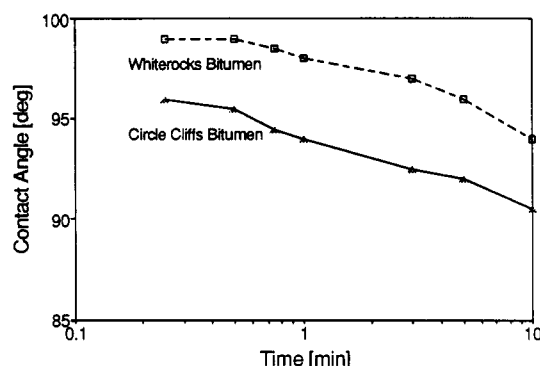


Figure 2. Variation of contact angle with respect to contact time for a water drop placed on the surface of the bitumen film.

bitumen surface tension values calculated from eq 5 are presented in Table 4. The surface tension of bitumen was found to vary in a narrow range of values from 23.9 mN m⁻¹ for Whiterocks bitumen to 26.7 mN m⁻¹ for Sunnyside bitumen. Only for the PR Spring bitumen the surface tension was found to be significantly greater, 32.2 mN m⁻¹, than the other Utah bitumens. As shown in Table 4, the average values for the surface tension calculated from contact angle data using equation-of-state (5) are close to the extrapolated values at 294 K from direct measurements using the Wilhelmy plate technique, for Whiterocks, Sunnyside, and PR Spring bitumens. Significant discrepancies between the two different techniques were observed for the Asphalt Ridge and Circle Cliffs bitumens. Vargha-Butler et al.⁹ noted similar discrepancies for Canadian bitumens which were found to differ from 0.4 to 5.3 mN m⁻¹; but there was no systematic trend in this difference.

There is no reason to assume that the linear surface tension/temperature relationship, which is a characteristic property of liquids¹¹ and also melted polymers,²² does not

exist for bitumens. The high bitumen viscosity in the 294–310 K temperature region makes surface tension measurements difficult with the Wilhelmy plate technique; nevertheless, the bitumens still exhibit liquid properties for this temperature range. In this regard, it is believed that the extrapolation procedure used for determination of the bitumen surface tension at room temperature could not account for such large discrepancies between surface tension values obtained with the two different techniques, Wilhelmy plate tensiometry and contact angle measurements.

It should be noted that a special precaution was taken to avoid overheating the bitumen during film preparation. The bitumen was spread on a warm glass slide and immediately cooled to room temperature to minimize the destructive effect of the thermal energy on the bitumen composition. In our preliminary experiments, Whiterocks and Asphalt Ridge bitumens were deposited on a glass slide at room temperature. For such bitumen films, as prepared, the advancing contact angle as measured for a water drop was found to be in close agreement with that measured for a water drop placed on the bitumen film prepared at elevated temperature. These experiments suggest that annealing of the bitumen films, during the time of the experiment, has no significant effect on the surface properties of the bitumen films. The bitumen samples used in the tensiometric measurements were also subjected to elevated temperatures. In this regard, in both techniques the thermal energy could affect the bitumen samples in a similar way.

Vargha-Butler et al.⁹ suggested that the presence of clay particles in bitumen can affect the energetic state of the bitumen surface, and thus, may be responsible for the difference in the surface tension as measured directly and as calculated from contact angle data. The procedure for bitumen extraction from oil sand samples and bitumen purification from solvent, as used in these studies, suggests that clay particles are probably not responsible for the observed difference.

Some interaction between molecules of water and bitumen occurred rapidly during the contact angle measurements as presented in Figure 2. This may involve reorientation of molecules or some groups of bitumen molecules at the bitumen/water interface which affect the contact angle. Also, factors such as solubility of bitumen compounds in water and/or water in bitumen, deformation of bitumen film at the three-phase contact line, and spreading of bitumen or bitumen constituents at the water drop surface could affect the contact angle measurements. These effects caused difficulties in the selection of an appropriate time for contact angle measurements, and thus, thermodynamic equilibrium for the three-phase system could not be defined. In this regard, the contact angle measurements for liquid drops at a bitumen film surface may involve some uncertainty. Also, it was recently pointed out that the equation-of-state has several limitations, such as for example, applicability to apolar systems involving only physisorption.²³ Apolar liquids such as hydrocarbons cannot be used in the characterization of the bitumen surface due to the mutual solubility of the phases.⁴ In this regard, the bitumen surface tension determination based on contact angle measurements using polar liquids, such as water in our studies or water and

glycerol in the studies of Vargha-Butler et al.,⁹ may account for some inaccuracy in the surface tension determination of the bitumens. Also, inaccuracy in the bitumen surface characterization using the equation-of-state may point to the weakness of the theoretical considerations used in the derivation of eq 5. (Note that additional proofs on the weakness of Neumann's approach for the surface tension determination of low-energy surfaces based on contact angle measurements were recently recognized in our laboratory during surface tension measurements of polymers.²⁴)

Finally, another disadvantage of the contact angle technique is its limitation in the determination of the bitumen surface tension at room or lower temperatures when the bitumen becomes a semisolid. In practice, oil sands are processed at elevated temperatures, mostly from 323 to 358 K, and thus, the bitumen surface tension at higher temperatures is of more practical importance.

Summary and Conclusions

The surface tension of toluene-extracted bitumens from the Whiterocks, Sunnyside, PR Spring, Asphalt Ridge, and Circle Cliffs oil sands was determined by the Wilhelmy plate technique and found to be 20.6, 21.3, 31.2, 28.9, and 29.3 mN m⁻¹ at 333 K, respectively. No apparent correlation between the bitumen surface tension and fractional composition of bitumen was observed.

A linear relationship between the bitumen surface tension and temperature was found for Utah bitumens examined in the temperature range 310–356 K (depending on bitumen sample). The temperature coefficient for surface tension was calculated to be -0.077, -0.063, -0.097, -0.078, and -0.093 mN m⁻¹ deg⁻¹ for the Whiterocks, Sunnyside, PR Spring, Asphalt Ridge, and Circle Cliffs bitumen, respectively.

The contact angles for water drops at the surface of bitumen films were measured, and the bitumen surface tension at 294 K was calculated from Neumann's equation-of-state. The contact angle technique provided comparable values for the bitumen surface tension at room temperature for the Whiterocks, Sunnyside, and PR Spring samples. Significant discrepancies between the bitumen surface tension values as calculated from contact angle measurements and as obtained from direct surface tension measurements with the Wilhelmy plate technique were found for the Asphalt Ridge and Circle Cliffs bitumens. In this regard, the contact angle technique, which is based on Neumann's equation-of-state and contact angle measurements, may not be valid and, in any event, is limited to a small temperature range. Several possible reasons for the discrepancies between surface tension values determined by direct measurements and those calculated based on contact angle data were discussed in this contribution; however, the weakness of the theory, expressed by eq 5, especially its limitations to apolar systems involving only physisorption, seems to be the most reasonable explanation to account for such discrepancies.

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