Application of Taylor Dispersion Technique to Measure Mutual Diffusion Coefficient in Hexane + Bitumen System

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A novel approach with fewer technical and analytic limitations in liquid solvent-bitumen diffusion studies is used in this article. The Taylor dispersion technique was selected for its convenient short run time experiments and reliable data analysis to find mutual diffusion coefficients in a hexane + bitumen mixture. For the first time, the infinite-dilution molecular diffusion coefficients of bitumen in hexane were measured in both the presence and relative absence of asphaltene particles in the solution at atmospheric pressure and temperatures of 303.15, 310.15, and 317.15 K. The polydisperse nature of bitumen was clearly revealed. Results were compared with common predictive tools. Also, the asphaltene surface charge in the hexane precipitating solvent was demonstrated. Through concentration dependency investigations at atmospheric pressure and 303.15 K, it was determined that the mutual diffusion coefficients monotonically decrease as the viscosity of mixture increases within the studied 0–34% volumetric concentration of bitumen. The Taylor dispersion technique shows great potential for diffusion studies of liquid solvent-bitumen systems. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2670–2682, 2014
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Introduction

Steam injection for the mobilization of bitumen through viscosity reduction is the current general practice that yields a high rate of oil recovery. However, it consumes a great deal of energy and water to produce steam, produces very large amounts of carbon dioxide (CO_2), and involves water-related issues, such as limited supply and expensive post-water treatment. Therefore, investigators are continually pursuing modifications to thermal recovery techniques. The addition of a light solvent to steam is one such adaptation that seems very promising. Solvents have long been used to dilute the produced bitumen for transportation to an upgrader or refinery. The novel idea is to inject a proper solvent with steam to enhance viscosity reduction by dissolution in bitumen and, consequently causing *in situ* asphaltenes precipitation and resulting in *in situ* upgraded bitumen.

The steady demand for petroleum products combined with increasing concern about greenhouse gas emissions have prompted numerous studies of solvent-assisted recovery of bitumen or heavy oil in recent years. Thus, the solvent-bitumen mass-transfer phenomenon has been investigated more thoroughly in modeling and experimental studies. A critical review of available literature in liquid solvent + bitumen/heavy oil systems has been presented by Ghanavati et al.[1] The limited mutual diffusion coefficient data of liquid solvent + bitumen/heavy oil systems reported in the literature suffer from experimental limitations and analysis procedure difficulties that make their interpretation puzzling. Moreover, when solvent is placed on top of bitumen/heavy oil in a stagnant diffusion cell, asphaltene precipitates at the interface, forming a barrier that hinders the diffusion process. All these shortcomings emphasize the necessity of using a new measurement technique that would not be limited by practical restrictions and, more importantly, by sensitivity to calculation procedures.

The first objective of this work was the determination of the infinite-dilution mutual diffusion coefficient of bitumen in *n*-hexane, as a typical *n*-alkane solvent, at several temperatures, which to the best of our knowledge is not available in the literature. Knowledge of infinite-dilution molecular diffusion coefficients is crucial in qualitative description of the solute structure and quantitative description of the diffusion process. For instance, knowing the infinite-dilution diffusion coefficients of solute in solvent and solvent in solute and taking advantage of the thermodynamic behavior of the solution under study, models can be used to find concentration-dependent mutual molecular diffusion coefficients.[2] The Taylor dispersion technique has been selected to achieve this objective, due to its convenience and short run times.

The second objective was the evaluation of some common predictive methods on the basis of the generated data. Finally, the feasibility of the application of the Taylor dispersion technique to measure concentration dependency of the molecular diffusion coefficient in our hexane-bitumen system was targeted as the third objective.

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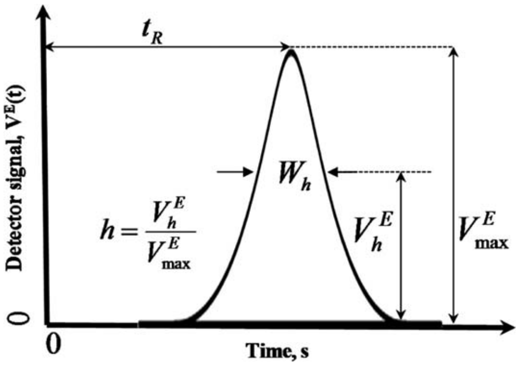

Figure 1. Schematic of Taylor dispersion peak-width analysis (after Callender and Leaist).

Theory of the Experiments

In a Taylor dispersion experiment, a minute amount of solute, called a pulse, is injected into a laminar carrier stream of a slightly different composition of solvent flowing in a long capillary tube. As the pulse travels through the tube, it spreads out into a nearly Gaussian profile under the combined actions of molecular diffusion and convection.[3] The shape of the dispersed peak measured by an appropriate detector, commonly at the end of the tube, is used to determine the molecular diffusion coefficient D from the dispersion coefficient K[4]

$$K=D+\frac{R^2\bar{u}^2}{48D} \tag{1}$$

where R is the tube internal radius and $\bar{u}$ is the average velocity of the laminar flow in the tube. It is noteworthy that experimental conditions are usually designed such that the first term in comparison to the second term in Eq. 1 can be safely ignored (Taylor formulation for dispersion[2]).

The acquired dispersion profiles (refractometer voltages in our work) can be analyzed using the nonlinear least-square method based on the normal distribution equation, assuming that the concentration and voltage are linearly correlated as

$$V^E(t)=V_{0}^E+V_{\max}^E\exp\left(-0.5\left(\frac{t-t_R}{\sigma_t}\right)^2\right) \tag{2}$$

where $V_{\max}^E$ is the peak height relative to the baseline voltage V_0^E, t_R is the residence time, and σ_t is the peak variance in time unit. In ideal Taylor experiments, the volumes of the pulse and detector should be zero, and the mean and the standard values obtained from the fitting procedure are corrected for unwanted errors introduced by practically finite volumes.[5]

Dispersion coefficient K is correlated to t_R and σ_t through $\sigma_t^2=2\frac{Kt_R}{\bar{u}^2}$, provided that the distribution is spatially Gaussian in the detector.[6] Finally, the molecular diffusion coefficient is calculated from the following simple, yet accurate equation (tolerance error of ~1%)[7]

$$D=\frac{R^2}{24}\frac{t_R}{\sigma_t^2} \tag{3}$$

The dispersion profiles can also be analyzed using the peak-width technique[8] to investigate the polydisperse nature of the bitumen. In this technique, the molecular diffusion coefficients are calculated according to[8]

$$D_h=-\frac{\ln h}{3}\frac{R^2 t_R}{W_h^2} \tag{4}$$

where h is any arbitrary fractional peak height and W_h is the subsequent peak width at h (see Figure 1).

In a monodisperse solution, D_h does not vary with the fractional height; however, it does vary in polydisperse solutions. The maximum at the uppermost of the peak and the minimum at the bottommost of the peak correspond to the lightest and heaviest solutes in the injected sample, respectively.

Since its introduction in 1953, the Taylor dispersion technique has become increasingly popular for measuring diffusion coefficients in liquids, mainly due to its moderate accuracy (~1%) convenient and short run times[9] and its applicability in a wide range of temperature and pressure conditions.[10] Moreover, it conveniently recognizes concentration dependency, due to the small concentration difference between the pulse and its carrier, so that the molecular diffusion coefficient can be considered constant in each experiment. Finally, secondary effects caused by the heat of mixing and molal volume changes are negligible; hence, the diffusion coefficients measured via the Taylor dispersion technique are the true constant Fickian diffusion coefficients.[11]

Experimental

The apparatus

Essential elements of a setup operating on the principle of the Taylor dispersion theory are a steady laminar carrier stream flow, a noninterrupted solute pulse injection, a constant temperature and pressure in the dispersion tube, and detection of the dispersion profile (see Figure 2). A Quizix double-cylinder pulse-free (QX-6000, Chandler Engineering) pump assured a steady continuous flow within ±0.1% of the set flow rate. The pump rate accuracy and consistency were checked through the measurement of pump effluent weights at different time intervals and conversion of the mass values into subsequent volumes through pertinent densities.

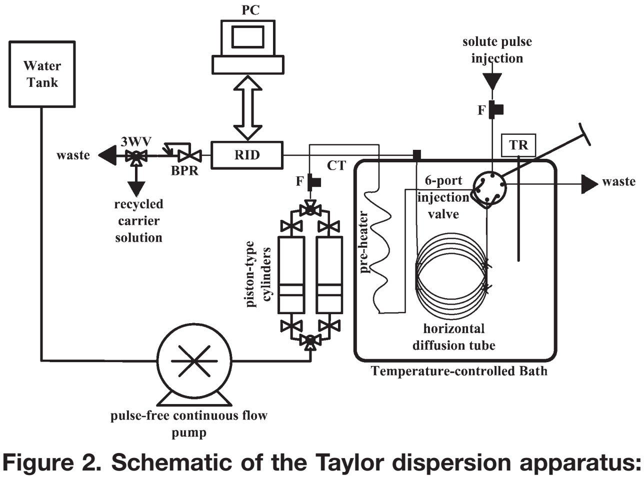

Figure 2. Schematic of the Taylor dispersion apparatus: BPR, back-pressure regulator; CT, connecting tube; F, 0.5 micron in-line filter; PC, National LabVIEW data acquisition system; RID, differential refractive index detector; TR, thermoregulator; 3WV, 3-way valve.

As the solvents and solutions used were not compatible with the pump sealings and valves, they were not injected directly through the pump, as is the common practice in high-performance liquid chromatography (HPLC). Instead, solutions were injected through piston-type cylinders, with water as the pushing fluid flowing through the pump. Of the two cylinders, one was used as the backup or, in some runs, as the container for the washing fluid (toluene and acetone). In the injection system, two in-line 0.5 micron filters (TF series, Swagelock) were used to avoid particle plugging in the fine-bore capillary tubes, injection valve, and refractive index detector. The in-line filters were periodically washed using toluene and acetone to retain their performance.

In this work, natural polyether ether ketone (PEEK) tubing was used as the diffusion tube (~9 m in length). Due to the profound importance of the internal radius on the accuracy of the diffusion measurement (note that the molecular diffusion coefficient correlates with the second power of the internal radius, as demonstrated in Eq. 3), the internal volume of the tube was found through the measurement of the weight of the tube when empty and when filled with distilled water of a known density. The required tube length was measured accurately with a ruler with an accuracy of 0.05 cm.

Knowing the internal volume and length, the internal radius could be determined accurately: it had a difference of almost 7% from the nominal factory reported value. The diffusion tube was wound in a smooth helical coil on an aluminum ring and placed horizontally to avoid any unwanted convection into the temperature-controlled water bath (Techne calibration), the temperature stability and uniformity (<0.01 K) of which was precisely controlled through a thermoregulator.

The diffusion tube was directly connected to a six-port rotary liquid chromatography injection valve (Valco, C6-1006) at its upstream end. The injection valve used continuous flow technology, so that steady flow of the carrier fluid was not interrupted when the flow path was changed at the moment of the solute pulse injection. The injection valve was dipped into the bath so that the solute slug and its carrier solution were at the same temperature when injected. It was fitted with a sample loop of a nominal volume of 0.020 cm^3, which was loaded via a syringe pump (Teledyne Isco, 500 D) and manually controlled through a custom-built handle.

One meter of stainless steel capillary tube (0.158 cm or commercially 1/16″) was used at the upstream end of the injection valve as a preheater. The preheater quickly increased the temperature of the carrier solution from the laboratory condition to that of the experimental setup. This allowed the temperatures of the solute already residing in the dipped injection valve and its carrier solution to be equal at the moment of injection. The equality in temperature was important, as a temperature difference may have introduced thermal expansion and thermal diffusion.

The diffusion tube was connected to the detector through a connecting tube. The connecting tube length and inner radius were carefully minimized to reduce unwanted dispersion as a result of the difference between the ambient and experimental setup temperatures. This was particularly important when the carrier stream exited the diffusion tube at the experimental setup temperature and encountered ambient temperature before entering the detector at the setup temperature again. The very low thermal diffusivity of PEEK (typically 0.19×10^{-2} cm^2/s),[12] which hindered carrier stream heat dissipation before entering the detector, also helped minimize the unwanted dispersion.

Table 1. Physical Specifications of the Taylor Dispersion Apparatus

Diffusion tube length	914.00 ± 0.05 cm
Diffusion tube radius	0.0537 ± 0.0001 cm
Connecting tube length	32.00 ± 0.05 cm
Connecting tube radius	0.0277 ± 0.0001 cm
Coiling ratio	492
Injection volume	0.020 ± 0.001 cm^3
Detector cell volume	0.008 cm^3

The time evolution of the concentration at the end of the diffusion tube (connecting tube influence was negligible, as previously discussed) was detected through a differential refractive index detector (BI-DNC, Brookhaven Instruments Cooperation). Both the sample and reference cells were initially flushed with the carrier phase. The reference cell was then closed, and the carrier stream flowed only through the sample cell.

The refractive index at a fixed wavelength depends only on the density of the medium. This density is influenced by temperature, pressure, and composition, all of which are constant. Thus, the detector produced a constant zero voltage, which served as the baseline voltage. When the injection was made and the dispersed slug finally entered the sample cell, the composition and, consequently, refractive index of the sample cell content changed, generating a corresponding voltage. The detector voltages were recorded by National Instruments LabVIEW data acquisition system. The LabVIEW software also documented the injection rate and pressure of the Quzix pump and the temperature of the bath.

A 0.2 MPa (30 psi) back-pressure regulator (BPR) was used downstream of the detector to avoid outgassing of the solutions passing through it; otherwise, the baseline stability of the detector was strictly violated. The common more efficient techniques to avoid outgassing in HPLC included either sparging of the solvent container continuously with helium, as the solvent is withdrawn through the pump, or using an in-line degasser before the pump. These methods were not applicable in our setup because the solvent was not injected directly through the pump, but through piston cylinders.

Finally, a three-way valve was used to recycle the carrier stream when the detector signal was not yet stable and, hence the system was not ready for solute injection. Depending on the solution type, 300–500 cm^3 of the carrier stream was injected prior to baseline stability. At the moment of injection, the carrier stream was diverted into a waste container. The physical specifications of the setup (see Table 1) were selected so that the flow rates, anticipated molecular diffusion coefficients, and conditions for the utilization of simple Eqs. 3 and 4 were easily met.[5]

The following inequality for the Peclet number Pe had to be met with each run[5]

$$700 \leq Pe = \frac{\bar{u}R}{D} \leq \left(5\frac{\upsilon R_C}{DR}\right)^{0.5} \tag{5}$$

where υ is the kinematic viscosity and R_c is the coil radius. The Pe lower bound avoided axial diffusion influence (Taylor dispersion formulation), while the upper bound avoided secondary coil flow by manipulating the criterion $De^2Sc < 20$,[5] where De and Sc are the Dean and Schmit numbers, respectively. In practice, the experiments were repeated for each molecular diffusion coefficient measurement at several rates (starting from the rate obtained from Eq. 5) to find the diffusion coefficient that was independent of velocity and, hence, free from coil flow.

Another upper limit for the Peclet number ensured that the skewness parameter of the normal distribution curve was negligible,[6] as the mixing zone passed through the recording point, regarding the strict criterion proposed by Erkey and Akgerman[7]

$$Pe=\frac{\bar{u}R}{D}\leq 0.048\left(\frac{L}{R}\right) \tag{6}$$

where L is the length of the diffusion tube. Of the two upper limits for the Peclet number, the more stringent one was utilized.

For the solute, the first condition was a δ-pulse injection, so that the volume ratio of the pulse to the diffusion tube was less than 0.01.[13] The solute slug composition was also slightly different from the carrier composition, for example, 0.5 g/dm^3.[14] This condition assured the recorded voltage and concentration were linearly related, allowing for the analysis of the detected dispersion profile to be practical and convenient.

To test the reliability of our Taylor dispersion apparatus, molecular diffusion coefficients of urea in an aqueous urea solution of 0.248 molar were measured at several flow rates and a temperature T of 298.15 K; and the results were compared with accurate values from the literature.[15] The mean and standard values obtained from the fitting procedure were corrected for unwanted errors introduced by the finite volume of the pulse and detector, so that the corrected molecular diffusion coefficients could be determined.[5]

The corrected molecular diffusion coefficients differed from the uncorrected ones by no more than 0.7%, assuring that the volume of the pulse and detector were reasonably negligible. Considering this small error found in reliability runs, the correction procedure did not seem necessary for the hexane-bitumen systems, particularly given that the molecular diffusion coefficients necessary for correction terms were also unknown. This check showed that our setup measurements were accurate within 1–2%, provided the more conservative criterion of $De^2Sc<10.52$[7] was met, which ensured that the diffusion coefficients in the hexane-bitumen systems were not influenced by the coil flow.

With confirmation of the reliability of the setup, the Taylor dispersion technique was applied to measure the molecular diffusion coefficients of the hexane-bitumen systems in three different sets of experiments:

- Type A experiments investigated the infinite-dilution mutual diffusion coefficient (D^0_{12}) of the unfiltered bitumen solution in hexane.
- Type B experiments examined the concentration dependency of the mutual diffusion coefficient for unfiltered hexane-bitumen mixtures.
- Type C experiments investigated the infinite-dilution mutual diffusion coefficient of the filtered bitumen solution in hexane as a function of temperature.

A pure solvent like hexane was selected because of its potential application in solvent-bitumen/heavy oil recovery processes, its known structure, its reasonable price, and its relatively high boiling point temperature at near the atmospheric pressure. The hexane used in experiments was 99.5% HPLC grade from a Merck KGaA provider. The solute selected was MacKay River bitumen, with an estimated molecular weight of 512.5 ± 6.9 g/gmol. The density and viscosity properties of pure bitumen and hexane-bitumen mixtures are reported in the Appendix.

Experimental procedure

To prepare infinite-dilution solutions with bitumen as the solute, a tiny amount of bitumen ($\sim$0.05 g) was added to a 77 cm^3 container of hexane to give a solute concentration of about 0.001 mol/dm^3. Upon mixing, large asphaltene particles were formed and precipitated (note that hexane, as are other *n*-alkanes, is a bad precipitating solvent that cannot suspend asphaltene particles). In the Type C experiments, homogeneous solutions were required; therefore, the mixture was filtered through a Millipore GSWP filter with a nominal pore size of 0.22 μm to remove the suspended particles sized more than 0.22 μm. No filtration was used in the Type A and B experiments.

In the concentration dependency experiments (Type B), different concentrations of hexane-bitumen solutions were prepared gravimetrically. The maximum volumetric concentration of bitumen tested was around 34%, above which the solutions were too opaque for the detector. The concentration difference between the carrier stream and the solute was minimized to values distinguishable with the detector, so that a reliable dispersion profile was measured.

In all three types of experiments, the sample loop (0.020 cm^3) of the injection valve was rinsed several times with the prepared solutes. The loaded solute was injected into the carrier stream of the solvent only when the temperatures of detector and the bath enclosing the diffusion tube, the injection pressure and rate were stable and the baseline had been constant within a ±4 mV tolerance during the 2-h period prior to the injection. All experiments were carried out at BPR's set pressure of 0.2 MPa.

To start the experiments and set the injection rate for the first series of experiments (Type A, infinite-dilution case), an estimate of the mutual diffusion coefficient was required to determine the proper Peclet number. Due to the absence of infinite-dilution diffusion coefficient data for bitumen solute in the literature, the Stokes-Einstein equation[16] was used to find an estimate of the diffusion coefficient, from which the initial set rate was selected. The experiment was repeated at several rates to investigate the secondary coil flow effect. For each single flow rate, four slugs were usually injected.

Results and Discussions

Infinite-dilution mutual diffusion coefficient of unfiltered bitumen solution in hexane (type A experiments)

Following the procedure described previously, the diffusion coefficient of the infinite dilution of an unfiltered bitumen solution in hexane at 303.15 ± 0.01 K was measured. The initial rate of 0.035 cm^3/min estimated from the Stokes-Einstein equation[16] was lowered by almost 30% to ensure the coefficients were not under the centrifugal effect of coil flow.

A typical fitting analysis is demonstrated in Figure 3. For the sake of brevity, analyses of other dispersion profiles are not shown, but the results are summarized in Table 2. It

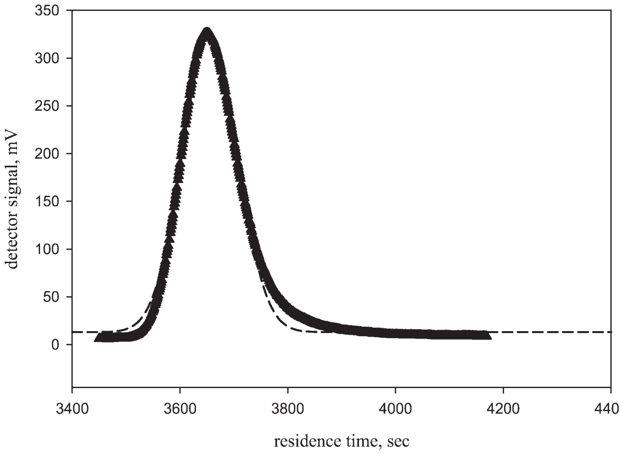

Figure 3. Typical dispersion profile for diffusion of infinite dilution of unfiltered bitumen solution in hexane ($T = 303.15$ K): experimental data (▲) fitted with Eq. 2 (---).

should be noted that some of the dispersion profiles (6 out of 30) were very thin, resulting in surprisingly high diffusion coefficients, even greater than the molecular self-diffusion coefficient of the solvent hexane. However, as those thin dispersion profiles could not be justified with any theory, they were considered to be caused by a band of suspended particles that were pumped through the diffusion tube like a wad.* Hence, they were not considered as Taylor dispersion profiles and are not reported here.

As can be seen from Table 2, while the correlation fitness parameter assured a normal distribution for all the dispersion profiles, the molecular diffusion coefficients covered a wide range. This was most likely due to random forming and deforming of asphaltene clusters, resulting in different aggregate sizes and, hence, different mutual diffusion coefficients. To recognize this size dependency of the molecular diffusion coefficient, the measured diffusion coefficients were considered as apparent values. The average of the apparent infinite-dilution diffusion coefficients of bitumen in hexane was $1.59 \pm 0.14 \times 10^{-5}$ cm^2/s, where 0.14 was the standard deviation of the data.

In addition, the peaks were analyzed through the peak-width analysis procedure.[8] The analysis for the data shown in Figure 3 is demonstrated in Figure 4, where h is the fractional peak height and D_h is the corresponding diffusion coefficient. Considering the graph in Figure 4, one can see that the diffusion coefficient ranged from 1.21×10^{-5} to 1.56×10^{-5} cm^2/s (~30% difference). For some other peaks, this difference was as high as 50%. This wide range of diffusion coefficients emphasizes the polydisperse nature of bitumen solute, where species with completely different sizes and shapes participate in the diffusion process through the solvent. Hence, as stated previously, the reported value for the diffusion coefficient should be considered as an apparent value.

Concentration dependency of molecular diffusion coefficient for unfiltered hexane-bitumen mixtures (type B experiments)

The first concentration-dependent experiment (7.5% by volume of bitumen in the solution) did not involve any challenges, and the peaks showed a Gaussian distribution, as presented in Table 3. Consequently, the calculated molecular diffusion coefficients were close to each other. However, as the bitumen concentration increased the peaks departed from a Gaussian distribution at the trailing edge, most probably due to higher suspended asphaltene particles (Figure 5). As the colloidal solution entered the flow cell of the detector, it faced less shear stress due to the cell's larger cross section than that of the capillary tube; hence, the suspended asphaltene particles settled down while the colloidal solution left the flow cell. As the particles settled down, the refractive index of the colloid passing through the cell changed sharply due to density changes, resulting in the peak's nonuniform trailing edge.

Table 2. Summary of Runs for Measuring Mutual Diffusion Coefficients of Infinite-Dilution of Unfiltered Bitumen Solution (1) in Hexane (2) at 303.15 K

Q (cm^3/min)	Correlation Fitness Parameters (R^2)	$D^0_{12} \times 10^5$ (cm^2/s)
0.035	0.9944	1.37
	0.9966	1.63
0.025	0.9905	1.55
	0.9906	1.56
	0.9876	1.69
	0.9990	1.76

Another challenge of the more concentrated solutions was that the analysis of their pertinent dispersion profiles yielded different mutual diffusion coefficients depending on the content of suspended particles in the colloidal solution. For instance, with a bitumen concentration of 18.2% in hexane, the mutual diffusion coefficient of 1.40×10^{-5} cm^2/s was approximately as high as the infinite-dilution diffusion coefficient of 1.59×10^{-5} cm^2/s (see Table 2).

At higher concentrations of bitumen, the asphaltene particles had more opportunities to collide and form bigger clusters, which presumably settled down into the path. This assertion can be justified by the lower pressure drops for the higher concentrated solutions than the less concentrated solutions, proving that the solution being pumped was less viscous due to the lower content of suspended particles. It should be noted that this settling process continued until the

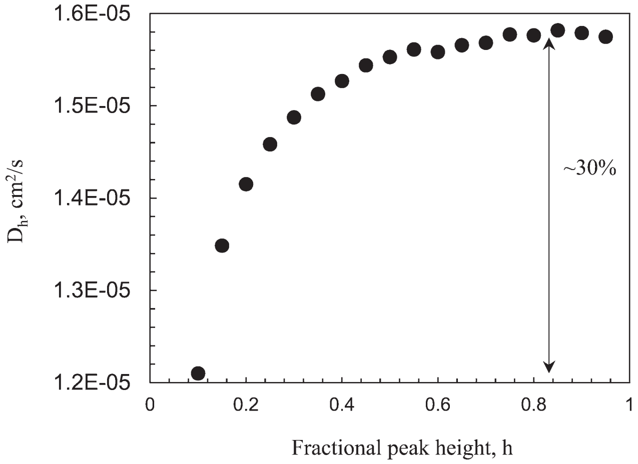

Figure 4. Typical molecular diffusion coefficients against the fractional peak height for diffusion of infinite dilution of unfiltered bitumen solution in hexane ($T = 303.15$ K).

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*Leaist DG, private communications, 2012.

Table 3. Summary of Runs for Measuring Apparent Molecular Diffusion Coefficient of Unfiltered Hexane-Bitumen Mixtures at 303.15 K

Bitumen Volume in Mixture (%)	Q (Flow Rate) (cm^3/min)	Correlation Fitness Parameters (R^2)	$D \times 10^5$ (cm^2/s)
7.5	0.035	0.9966	1.23
		0.9974	1.23
	0.050	0.9966	1.18
		0.9968	1.20
18.2	0.025	0.9789	1.4
		0.9774	1.21
		0.9774	0.999
		0.9767	0.970
	0.035	0.9718	1.07
		0.9822	0.882
	0.025$^{\text{(repeated)}}$	0.9766	0.876
		0.9764	0.904
33.6	0.025	0.9540	0.472
		0.9780	0.373
		0.9545	0.466
		0.9783	0.397

Table 4. Average of Apparent Molecular Diffusion Coefficient for Unfiltered Hexane-Bitumen Mixtures at 303.15 K

Bitumen Volume in Mixture (%)	Standard Deviation of Data	Average $D \times 10^5$ (cm^2/s)
0 (infinite dilution)	0.14	1.59 ± 0.14
7.5	0.02	1.21 ± 0.02
18.2	0.015	0.933 ± 0.092
33.6	0.050	0.427 ± 0.050

path was completely blocked by the settled particles and the pressure built up sharply. The more concentrated solutions often encountered a plugging problem, as one would expect. The plugging problem changed the pressure abruptly, resulting in sharp changes in the refractive index of the medium and, hence, the unreliability of the measured dispersion profile. This condition created a risk of detector failure, as the detector flow cell could withstand a pressure of no more than 0.7 MPa.

With all these difficulties, only the more reliable peaks were considered for the analysis reported in Table 3. Their average of the apparent mutual diffusion coefficients (D) are reported in Table 4. It is worth noting that, for the bitumen volume concentration of 18.2%, only four mutual diffusion coefficients of 1.07, 0.882, 0.876, and 0.904 ($\times 10^5$ cm^2/s) were considered as the injection pressure in their relevant experiments were more stable compared to the initial experiment with flow rate of 0.025 cm^3/min.

The concentration dependency of the molecular diffusion coefficient could not be investigated for more than almost one third of the whole concentration range, due to the opacity of the solutions at higher bitumen concentrations. However, one can see from Table 4 that there was a clear remarkable declining trend for the apparent molecular diffusion coefficients as the bitumen concentration and subsequently mixture viscosity increased. This observed trend clearly contradicts the counterintuitive trends found by some researchers, such as Oballa and Butler,[17] and the absence of concentration dependency by Zhang and Shaw[18] as discussed in Ghanavati et al.[1]

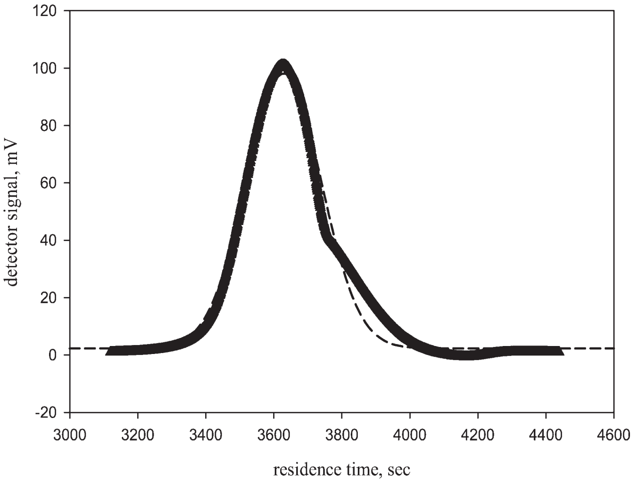

Figure 5. Typical dispersion profile for an 18.2% volumetric concentration of unfiltered bitumen-hexane mixture ($T = 303.15$ K): experimental data (▲) fitted with Eq. 2 (---).

In the Taylor dispersion analysis used in this work, the molecular diffusion coefficients at different concentrations were readily obtained from Eq. 3. However, in other techniques, the molecular diffusion coefficient cannot be considered as a constant for the designed experiments and, thus, the analysis would be more complex and demanding, introducing unwanted errors in the concentration dependency trends.[1,19] Therefore, the results demonstrated here are free from inherent analysis error involved in other analysis techniques and can be considered as the actual physical behavior of the system.

The molecular diffusion coefficients as a function of the volumetric concentration of bitumen are plotted in Figure 6 without any data smoothing, which is a routine procedure in *in situ* concentration measurement techniques.[17,18] It can be seen that the apparent hexane-bitumen mutual diffusion coefficients were neatly correlated to the volumetric concentration of the bitumen through an exponential decay relationship, as given by

$$D(C)=2\times10^{-5}\exp\left(-0.04\times C_{B,V}\%\right) \quad (7)$$

where D is the molecular diffusion coefficient in cm^2/s and $C_{B,V}\%$ is the volumetric concentration of bitumen in the mixture as a percentage. It is worth noting that the measured

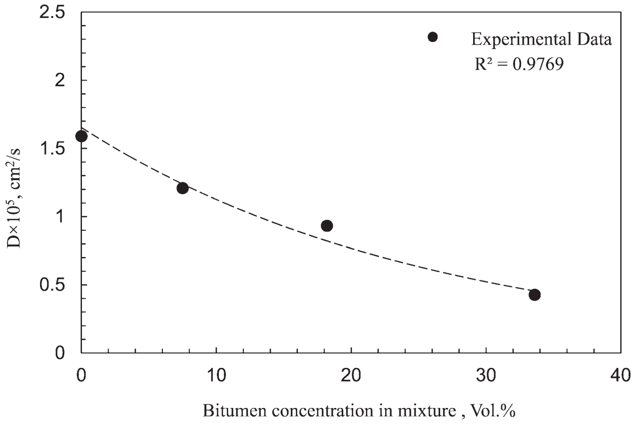

Figure 6. Concentration dependency of the mutual diffusion coefficient for unfiltered hexane-bitumen mixtures at 303.15 K.

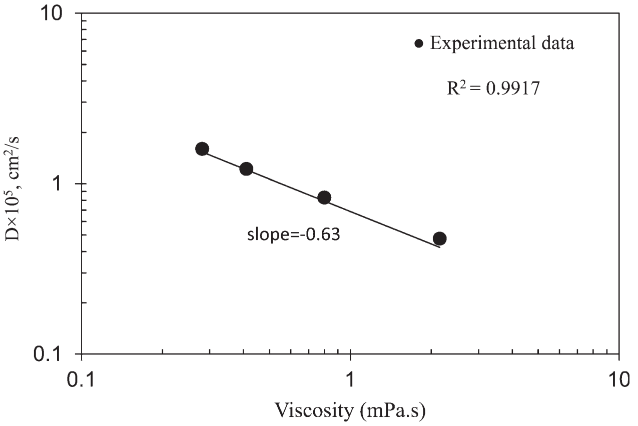

Figure 7. Relationship between the mutual diffusion coefficient and the viscosity in an unfiltered hexane-bitumen system at 303.15 K when plotted in a log-log scale.

diffusion coefficients could have also been correlated to the volumetric concentration of bitumen through a linear relationship with slightly better correlation fitness parameter of $R^2 = 0.9877$. However, such a linear relationship underestimates the mutual diffusion coefficients at higher bitumen concentrations such that the diffusion coefficient will be negative after volumetric bitumen concentration of around 67%, which is unrealistic.

Although it cannot be guaranteed that the same correlation found for only one third of the concentration range can be used to the whole range, one can get an indication of the diffusion coefficients at higher concentrations, using extrapolation of the experimental data. For instance, one can find an estimated value of 4.5×10^{-7} cm^2/s for the infinite dilution of hexane in bitumen when the bitumen concentration is 100%, which is in the same order of 7.81×10^{-7} cm^2/s reported by Guerrero-Anoncha et al.[19] for a hexane-heavy oil system at 298.15 K. It is stressed that the contribution of this part of our work is not the values themselves, but the obvious decreasing trend of the diffusion coefficient with increased bitumen concentration. This trend is in line with the theory, as well with the experimental observations reported by Guerrero-Anoncha et al.[19] for the heavy oil concentration range of 20–100%, where they used an X-ray computed tomography *in situ* measurement technique and analyzed the measured concentration profiles through the slope-intercept approach.[20,21]

To find a relationship between the diffusion coefficient and the viscosity (μ), mutual diffusion coefficients were also plotted in a log-log scale vs. the experimentally measured viscosities of the solutions (Figure 7 and reported in the Appendix). Within the concentration range studied, a clear exponential trend is observed as given by

$$D\mu^{0.63} = \text{cons} \tag{8}$$

Fascinatingly, Hiss and Cussler[22] found the viscosity power as 2/3 (0.6667) for infinite-dilution molecular diffusion coefficients of hexane and naphthalene in a series of hydrocarbons with a viscosity range of 0.5–5000 mPa s.

Once again it is emphasized that the correlation obtained over a limited concentration range, corresponding to a viscosity range of almost one order of magnitude (0.281–2.15 mPa s), cannot be extrapolated over the whole viscosity range of 0.281–71912 mPa s. Moreover, the impeding effect of viscosity on diffusion used through its power is reduced at higher viscosities, such that, according to Cussler,[16] in extremely high-viscosity materials, diffusion becomes almost independent of viscosity like the diffusion of sugar in jelly, which is very nearly equal to the diffusion of sugar in water. Thus, the obtained power of 0.63 would be lower at higher concentrations of bitumen. It would be challenging, yet fascinating, if the viscosity dependency of molecular diffusion coefficients over almost five orders of magnitude of viscosity change (0.281–71,912 mPa s) could be determined.

The consideration of thermodynamic concentration dependency models was intended for the prediction of the obtained values. However, to do so, infinite-dilution molecular diffusion coefficients at two concentration extremes are required. In our case, only the infinite-dilution mutual diffusion coefficient of bitumen in hexane was measured; and the value for the infinite-dilution molecular coefficient of hexane in bitumen was not available. Moreover, for the determination of the thermodynamic correction factor, either the activity coefficient or the fugacity is required, both of which require some accurate input data; however, these data are unfortunately not available for a complex system like bitumen. Although estimations are available in the literature for the determination of some of the input data, such as critical properties in the tuning of an equation of state, accurate characterization of the bitumen is necessary, which was not available in our case.

It should be noted that the experimental conditions of 303.15 K and 0.2 MPa (almost atmospheric conditions) were selected, so that measured data could be compared with data reported in the literature. Otherwise, the experiments could have been carried out at higher temperatures and/or pressures. The limited concentration range in our work (almost one third of the whole range) can be eliminated by the selection of a more suitable and, of course, more expensive detector than the refractive index detector. For instance, detectors using infrared light can penetrate through opaque solutions, such as those in our experiments, and provide the capability of scanning the whole concentration range.

It is worth noting that higher bitumen concentrations and, hence, higher viscosities caused higher pressure drops in the tiny capillary tubes, which can be easily overcome by running the experiments at the high temperatures that are common in the thermal recovery of bitumen. An extremely high viscosity of 71912 mPa s at 303.15 K is reduced by four orders of magnitude to 7.2 mPa s at 465.15 K (see Eq. A1 in the Appendix).

Infinite-dilution molecular diffusion coefficient of filtered bitumen solution in hexane as a function of temperature (type C experiments)

The mutual diffusion coefficients of the infinite dilution of bitumen in hexane were also measured when the solutes were filtered (homogeneous mixture). Experiments were conducted at three temperatures, and the results are summarized in Table 5; and the average values of the apparent diffusion coefficients, along with their standard deviations, are reported in Table 6. A comparison between these results and those obtained from unfiltered mixtures shows that there was a better correlation when the mixtures were filtered: a lower degree of variation from the mean exists among these data, compared to the standard deviation of ±0.14 reported in Table 4 for unfiltered solutions.

The apparent diffusion coefficients (average values) are plotted vs. the absolute temperature in Figure 8,

Table 5. Summary of Runs for Measuring the Infinite-Dilution Molecular Diffusion Coefficient of Filtered Bitumen Solution (1) in Hexane (2) at Three Temperatures

Temperature (K)	Q (cm^3/min)	Correlation Fitness Parameters (R^2)	$D^0_{12}\times10^5$ (cm^2/s)
303.15 ± 0.01	0.018	0.9989	2.09
		0.9991	2.08
		0.9997	2.16
		0.9995	2.13
310.15 ± 0.01	0.018	0.9995	2.55
		0.9991	2.57
		0.9997	2.52
317.15 ± 0.01	0.018	0.9993	2.95
		0.9979	2.84
		0.9989	2.79
		0.9953	2.93

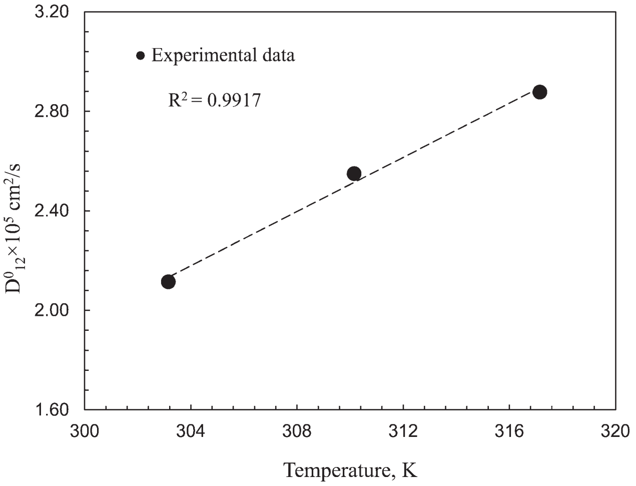

Figure 8. **Apparent diffusion coefficient (average values) of the infinite dilution of filtered bitumen solution in hexane vs. temperature.**

demonstrating a linear trend as expected from the Stokes-Einstein equation.[16] However, with this limited temperature range, our intention was not the generalization of the temperature dependency, but the practical demonstration of the flexibility of the Taylor dispersion technique to run the experiments at different temperatures.

As before, the peaks were analyzed through the peak-width analysis procedure,[8] as shown in Figure 9. In the figure, one can see the diffusion coefficient variation of around 12%, which is not surprising for a solute like bitumen, which consists of components with different sizes and molecular weights. The ranges varied between 10 and 15% for all other peaks at different injections and temperatures. This range was narrower than the 30–50% obtained for the unfiltered solutions, due to filtration of larger particles. The narrower range implies that the remaining suspended asphaltene particles of less than 0.22 μm (the filter size used to filter the solution) after filtration did not aggregate to form larger asphaltene clusters, as either they were not thermodynamically forced to or they did not have enough time (kinetics issue). Otherwise, the range would have been wider, due to the clusters' larger size and molecular mass.

To analyze the measured data quantitatively, the most common predictive tools according to Poling et al.[23] along with the less common predictive tool of Fedors[24] were tabulated and are presented in Table 7, so that they could be readily compared. It should be recalled that in formulations, index 1 refers to solute while index 2 refers to the solvent. Before proceeding with calculations, it is necessary to discuss how the required parameters of the correlations were found.

As it can be seen in Table 7, the very first parameter required in almost all formulas is the molar volume V_M, defined as $V_M = M/\rho$ where M is the molecular mass and ρ is the density. The molar volume usually needs to be calculated at the normal boiling point of the substance, as in the Wilke–Chang,[25] Tyn–Calus,[26] and Hayduk–Minhas[27] correlations. The normal boiling point of a pure substance like hexane is a readily available fixed value, however, it is neither readily available nor a constant value for bitumen, due to its composition of different components. For instance, four boiling cuts of 798.15, 848.15, 898.15, and 948.15 K have been reported for Athabasca bitumen.[28] In the absence of data for Mackay River bitumen and due to its molecular mass similarity to Athabasca bitumen, the same boiling points as Athabasca bitumen were considered for Mackay bitumen.

The densities at the required temperatures were evaluated through the obtained temperature-dependency correlation of the available measured densities in the temperature range of 303.15–333.15 K (see Eq. A2 in the Appendix). For the molecular mass of bitumen, the reported yet uncertain value of 512.5 g/gmol was used in the molar volume formula. If one asserts molecules are spherical and uniformly packed beside each other, a good estimate of the molecular size can readily be found as $V_M = 4/3\ \pi R^3 N_A$, where R is the radius of the molecule and N_A is the Avogadro's constant. With the application of this procedure, the average radii (with respect to the three temperatures) of 3.75×10^{-10} m and 6.24 ×

Table 6. Average of the Apparent Molecular Diffusion Coefficients for the Infinite Dilution of the Filtered Bitumen Solution (1) in Hexane (2) at Several Temperatures

Temperature (K)	Standard Deviation of Data	Average $D^0_{12}\times10^5$ (cm^2/s)
303.15 ± 0.01	0.04	2.12 ± 0.04
310.15 ± 0.01	0.03	2.55 ± 0.03
317.15 ± 0.01	0.08	2.88 ± 0.08

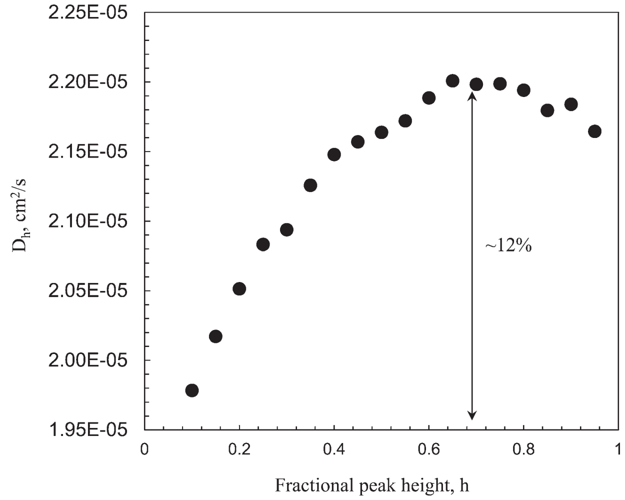

Figure 9. **Typical molecular diffusion coefficients vs. the fractional peak height for diffusion of infinite dilution of filtered bitumen solution in hexane (T = 303.15 K).**

Table 7. Predictive Tools Used to Evaluate the Measured Diffusion Coefficients of Infinite Dilution of Bitumen in Hexane

Predictive Tool	Formula	Remarks and Required Data
Stokes-Einstein[16]	$D^0_{12}=\frac{k_BT}{\beta\pi\mu_2R_1}$	$\beta=6$ if solute size is far bigger than solvent size, otherwise either 4 or 2
Wilke and Chang[25]	$D^0_{12}=7.4\times10^{-8}\,\frac{(\phi MW_2)^{1/2}T}{V^{0.6}_{M,1}\mu_2}$	Molar volume of solute evaluated at its normal boiling point
Tyn and Calus[26]	$D^0_{12}=8.93\times10^{-8}\,\frac{V^{0.267}_{M,1}}{V^{0.433}_{M,2}}\frac{T}{\mu_2}\left(\frac{\gamma_2}{\gamma_1}\right)^{0.15}$	Molar volumes of both solute and solvent and their surface tensions evaluated at their normal boiling points
Hayduk and Minhas[27]	$D^0_{12}=13.3\times10^{-8}V^{-0.71}_{M,1}\mu_2^{(10.2/V_{M,1}-0.791)}T^{1.47}$	Molar volume of solute evaluated at its normal boiling point
Fedors[24]	$D^0_{12}\left(V^C_{M,1}-\bar{\upsilon}^0_1\right)^{1/2}=D_{22}\left(V^C_{M,2}-V_{M,2}\right)^{1/2}$	Critical volumes of both solute and solvent, molar volume of solvent, and molar volume of solute in solution at infinite dilution and molecular selfdiffusion coefficient of solvent all evaluated at experiment temperature

10^{-10} m were obtained for hexane (R_2) and bitumen (R_1) molecules, respectively. It is worth mentioning that the calculated value for the bitumen molecules is basically an apparent radius, due to the various molecules present in bitumen structure. The reported sphere-equivalent diameter for asphaltene monomers is approximately 1.5×10^{-9} m and around 6×10^{-9} m for small asphaltene clusters.[29] For hexane, the calculated radius matches well with the result of the empirical correlation that Robinson and Stokes[30] proposed for paraffins (3.67×10^{-10} m).

The other requirements are the surface tensions of the solute and solvent for the Tyn–Calus correlation.[26] To the best of our knowledge, such data do not exist for the bitumen. Moreover, given the small power of 0.15 for the surface tension ratio, it can be safely ignored. This assumption can be further justified, as most organic liquids at normal boiling point have similar surface tensions, according to Poling et al.[23]

Except for the molecular self diffusion coefficient of the hexane solvent, which is readily available,[31,32] the other requirements for the Fedors correlation[24] are demanding. Finding the critical volume for a multicomponent solute like bitumen is difficult. This is especially challenging when the concentration distribution of the bitumen components upon mixing with solvent changes, due to asphaltene precipitation. We used the rough value of 1543 cm^3/mol, as reported by Johnson for Athabasca bitumen.[33]

No data are available for the molar volume of bitumen in a hexane solution at infinite dilution or the bitumen partial molar volume in hexane, $\bar{\upsilon}^0_1$. In the absence of data, Fedors[24] suggested using the molar volume of the pure solute itself when it is not mixed with solvent. In our case, this value for bitumen solute was approximately 512.5 cm^3/mol. Nikooyeh et al.[34] recently reported the partial volume of Athabasca *n*-pentane asphaltenes in hexane as 0.84 cm^3/g. However, due to the wide range of asphaltene molecular weight reported in the literature and also large uncertainty involved in relating the partial volume of Athabasca asphaltene to the partial molar volume of the MacKay bitumen, Fedors'[24] recommendation was considered to be more reasonable.

All the input parameters for the predictive tools were prepared; however, the normal boiling point of MacKay bitumen was uncertain. The molecular diffusion coefficients at different values of molar volumes corresponding to different normal boiling points (798.15, 848.15, 898.15, and 948.15 K) were calculated and compared to experimental measurement data. The normal boiling point of 798.15 K was selected as the proper normal boiling point as it produced the least prediction error for the diffusion coefficient.

The ultimate estimated values of all predictive tools were compared with the measured data in our work, as depicted in Figure 10. The single measured data of the unfiltered solution are also included in the figure. The error analysis of predictive tools is shown in Table 8. Before the performance assessment of the used predictive tools, it is worth noting that solutes, even in the second case of prefiltration, are not actually homogeneous. The used filter was very fine (0.22 μm = 2200×10^{-10} m); however, it could not filter all the suspended asphaltene monomers and clusters in the solution, as some were in the range of 1.5–6×10^{-9} m,[29] which was far finer than the filter pore size. Therefore, strictly speaking, the diffusion process in our study was diffusion in a colloidal medium. In this case, depending on the conditions, the diffusing particles may interact with each other and the solvent, which is very challenging. The interaction of the diffusing particles with the solvent and not with each other can be modeled in current predictive tools. The hint stated here is to rationalize our expectation from the predictive tools, which are basically developed for homogenous solutions.

A general overview of the results for the filtered bitumen solution shown in Figure 10 and Table 8 reveals the very poor prediction of the Tyn–Calus' correlation[26] and the Stokes-Einstein equation ($\beta=2$).[16] The standard Stokes-Einstein equation ($\beta=6$),[16] and Hayduk–Minhas[27] and Wilke–Chang[25] correlations had similar prediction performances. In terms of accuracy of the predictive tools, surprisingly the commonly recommended Tyn–Calus' correlation,[26] as in Poling et al.,[23] appeared to be the least successful,

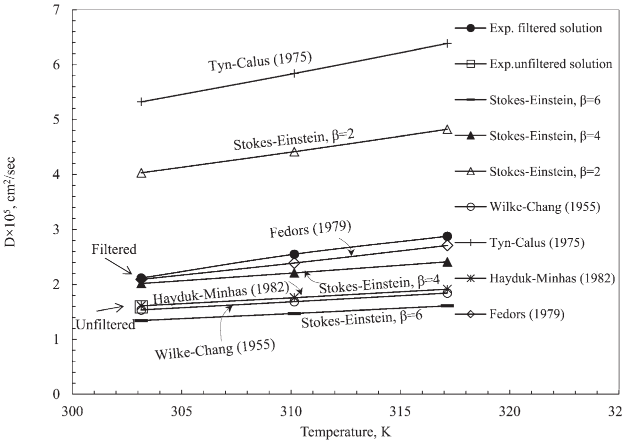

Figure 10. Measured mutual diffusion coefficient of the infinite dilution of bitumen solution in hexane compared with common correlations.

Table 8. Error Analysis of the Used Predictive Tools in the Evaluation of the Measured D_{12}^0

	Error of Prediction (%)						
	Stokes-Einstein[16]						
Temperature (K)	$\beta = 6$	$\beta = 4$	$\beta = 2$	Wilke–Chang[25]	Tyn–Calus[26]	Hayduk–Minhas[27]	Fedors[24]
Filtered bitumen solution							
303.15	−36.5	−4.7	+90.6	−27.4	+151.6	−23.9	−1.1
310.15	−42.3	−13.4	+73.2	−34.0	+129.00	−31.1	−6.3
317.15	−44.1	−16.2	+67.6	−36.0	+121.9	−33.5	−5.8
Average error (%)							
310.15	−41.0	−11.4	+77.1	−32.5	+134.2	−29.5	−4.4
Unfiltered bitumen solution							
303.15	−15.5	+26.8	+153.5	−3.5	+234.7	+1.2	+31.5

while the least-recognized Fedors' correlation[24] seemed to be more accurate for our particular colloidal system, followed by the Stokes-Einstein equation[16] with $\beta = 4$.

For the unfiltered bitumen solution, the Hayduk–Minhas correlation[27] had far better prediction results than the Fedors' correlation.[24] However, the satisfactory prediction of the simple homogeneous-based Hayduk–Minhas correlation[27] for the unfiltered solution, which was rich in suspended particles, appears to have just been accidental. Therefore, our discussion is focused on the performance of the predictive tools for the more homogeneous filtered solution.

The very important point that can be ascertained from the results for the filtered bitumen solution shown in Figure 10 and Table 8 is that all correlations, excluding the very poor predictive tools of the Tyn–Calus' correlation[26] and the Stokes-Einstein equation ($\beta = 2$),[16] underestimated the molecular diffusion coefficient. This appears unusual, as one would expect overestimation of values predicted by correlations that were developed on the basis of diffusion in homogeneous solutions, but were used for colloidal solutions full of suspended particles.

Scalettar et al.[35] modeled experimental data of protein diffusion and showed that mutual diffusion in such colloidal systems was inhibited by attractions, but enhanced by repulsions. This is even more fascinating if one considers that asphaltene particles have been found to be positively charged in polar and nonpolar solvents, such as nitromethane[36,37] and toluene,[38–40] respectively. The stability of asphaltene particles in polar solvents has also been correlated reasonably to the electrostatic repulsion between such particles in these low dielectric constant media.[38]

Asphaltene particles have been recognized to have surface charges.[41–43] Although hexane is a nonpolar solvent, our measured molecular diffusion coefficients were higher than the predictions, which could have been due to some kind of electrostatic repulsion between asphaltene particles. If so, our results provide new experimental evidence of the surface charge of asphaltene particles in a bad precipitating solvent like hexane. It is worth noting that the presumably electrostatic repulsion between charged asphaltene particles could not have influenced diffusion considerably when there were substantial collisions amid large asphaltene particles in the unfiltered solution.

To analyze the predictive behavior of the Stokes-Einstein equation,[16] the investigation of the molecular size and shape of the solute and solvent is crucial. First of all, the assumption of a spherical shape for complex bitumen molecules, which is the principal basis for derivation of this equation, is very simplistic. Also, except for large asphaltene monomers and clusters, the molecular size difference between the bitumen solute and the hexane solvent (6.24×10^{-10} m vs. 3.75×10^{-10} m) is not considerable. According to Chen et al.,[44] solute molecules should be five times larger than solvent molecules for the application of the standard Stokes-Einstein equation.[16]

Finally, bitumen as a polydisperse solute is composed of different molecules with different sizes and shapes. This variety causes a wide range of diffusion coefficients, as clearly demonstrated with the peak-width analysis shown in Figures 4 and 9. It seems reasonable to assume that, among the many constituent particles in bitumen, some molecules are big and spherical enough so that their diffusion can be modeled via the Stokes-Einstein equation.[16]

In fact, through the comparison of the performance of the standard Stokes-Einstein equation ($\beta = 6$)[16] for the measured data of the unfiltered and filtered solutions at 303.15 K (i.e., the average error of −15.5% vs. −41.0%, respectively, in Table 8), a better prediction was provided when more suspensions were present in the system. This was likely due to presence of bigger particles when the solution was not filtered and, hence, met more appropriately the assumption behind the standard Stokes-Einstein equation.[16] Electrostatic repulsion forces are also weaker in the presence of bigger particles. With the filtered solution, the large particles were filtered out and smaller molecules diffused into the solvent, the assumption of $R_1/R_2 > 5$ was violated; hence, the standard Stokes-

Table 9. Sensitivity Analysis of the Bitumen Critical Molar Volume in the Fedors' Correlation[24]

	Sensitive Parameter Basis		Prediction Error (%)	
Temperature (K)	V_M^C (cm^3/mol)	Probable Error in Sensitive Parameter (%)	Individual	Average
303.15	1543	−25	25.0	+20.9
310.15			18.5	
317.15			19.2	
303.15		+25	−15.7	−18.5
310.15			−20.1	
317.15			−19.7	

Table 10. Sensitivity Analysis of the Bitumen Partial Molar Volume in Hexane in the Fedors' Correlation[24]

Temperature (K)	Sensitive Parameter Basis $\bar{v}_1^0$ (cm^3/mol)	Probable Error in Sensitive Parameter (%)	Prediction Error (%) Individual	Prediction Error (%) Average
303.15	512.2	−25	−6.8	−9.9
310.15	514.6		−11.7	
317.15	517.0		−11.3	
303.15	512.2	+25	+5.6	+2.2
310.15	514.6		+0.2	
317.15	517.0		+0.7	

Table 11. Sensitivity Analysis of Both the Bitumen Critical Molar Volume and the Bitumen Partial Molar Volume in Hexane in the Fedors' Correlation[24]

Temperature (K)	Sensitive Parameter Basis V_c	Sensitive Parameter Basis $\bar{v}_1^0$	Probable Error in Sensitive Parameter (%)	Prediction Error (%) Individual	Prediction Error (%) Average
	(cm^3/mol^{-1})				
303.15	512.2	1543	−25	+14.1	+10.3
310.15	514.6			+8.2	
317.15	517.0			+8.7	
303.15	512.2		+25	−11.6	−14.5
310.15	514.6			−16.2	
317.15	517.0			−15.8	

Einstein equation needed to be modified by reducing the friction force. This was evidently the case, since Stokes-Einstein equation[16] with $\beta = 4$ resulted in a better prediction.

The Fedors' correlation[24] is distinguishable from other predictive tools, as it considers the molar volume of the solute in the solution at infinite dilution. This is probably the reason behind its better prediction. However, in the application of the Fedors' correlation for bitumen solute, the critical molar volume and its molar volume at infinite dilution in hexane were uncertain. Sensitivity analyses on these two parameters are shown in Tables 9–11.

It is clear from the comparison of the calculated errors shown in Tables 9 and 10 that the Fedors' correlation[24] was more sensitive to the bitumen critical volume. Sensitivity analyses assured a far better performance of the Fedors' correlation[24] for the filtered hexane-bitumen system. Unfortunately, there is no background information on this predictive tool. Even in his own articles,[24,45] Fedors only stated successful testing of his correlation with the extensive data in the literature. However, as postulated previously, the inclusion of the molar volume of the solute in the solution at infinite dilution is conceivably the key factor in this success.

It is worth noting that the comparison of our measured infinite-dilution molecular diffusion coefficients with values from the literature was not straightforward, as there is no experimental value for the infinite-dilution diffusion coefficient of bitumen in hexane. Nortz et al.[46] applied the Taylor dispersion technique at two typical elevated temperatures for the infinite dilution of heavy fractions of Athabasca bitumen and Western Canadian crude in 1-methyl-naphthalene (which is a good solvent for these systems, as the asphaltene particles are dispersed in the solvent). They presented two correlations at the two temperatures to predict the infinite-dilution molecular diffusion coefficients on the basis of molecular weight. If it is assumed that those correlations can be used in our bitumen + precipitating hexane solvent, a diffusion coefficient can be calculated based on the estimated molecular weight of 512.5 g/gmol, albeit at a higher temperature. To compare this calculated value with our measured diffusion coefficient, the viscosity of the solvent into which the bitumen molecules diffuse should be adjusted. With the Stokes-Einstein equation,[16] one may intuitively assume the molecular diffusion coefficient is a direct function of the absolute temperature and an inverse function of the viscosity. Following this presumption, the adjustment yielded a value of 1.26×10^{-5} cm^2/s, which was in the range of our measured diffusion coefficients. Guerrero-Aconcha et al.[19] extrapolated their measured diffusion coefficients over the hexane concentration range of 0–80% for heavy oil with a viscosity of 6000 mPa s and found an infinite-dilution diffusion coefficient of 1.71×10^{-5} cm^2/s at 298.15 K. Although it was not measured directly, the extrapolated value was not significantly different from our measured value of 1.59×10^{-5} cm^2/s for the unfiltered bitumen solution, considering a much higher bitumen viscosity and a slightly higher experimental temperature in our case.

Conclusions

The work reported here demonstrates that the reliable and convenient Taylor dispersion technique can be used for measuring molecular diffusion coefficients in liquid solvent-bitumen systems in a time efficient way at desired temperatures. The results of this study led to the following conclusions.

1. Mutual diffusion coefficients are strongly concentration dependent within the concentration range studied (volumetric bitumen concentrations of 0–34%). Thus, the assumption of a constant molecular diffusion coefficient, at least for the liquid solvent-bitumen system tested, would cause considerable errors in designing solvent-assisted recovery processes.
2. Mutual diffusion coefficients monotonically follow the viscosity-concentration trend within the concentration range studied: as the mixture viscosity increased with increased concentrations of bitumen, the molecular diffusion coefficient decreased.

3. In the course of the peak-width analysis, it was discovered that bitumen has a highly polydisperse solute, which means that there is a wide contrast in the molecular diffusion coefficients of its different components. Thus, the reported values at each concentration should be considered as apparent molecular diffusion coefficients, to recognize the polydisperse nature of bitumen.
4. Fedors' correlation in our experiments estimated the infinite-dilution molecular diffusion coefficient of a filtered bitumen solution in hexane significantly better than other common predictive tools. More experimental data are required to generalize the finding reliably.
5. The selection of an appropriate detector to overcome the opacity issue of bitumen concentrated solutions is highly recommended, so that molecular diffusion coefficient dependency for the whole concentration range can be determined; therefore, the Taylor dispersion technique could be viewed as an innovative diffusion coefficient measurement technique in solvent-bitumen/heavy oil systems, due to its convenience, rapidness, accuracy, flexibility of measurements at any temperature and/or pressure condition and, more significantly, reliable data analysis.

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Appendix

Viscosity measurements

The viscosities of the hexane-bitumen solutions at the experimental temperature condition of 303.15 K were measured with a Cambridge Viscometer model SLC 372 (Table A1). The viscosities of pure bitumen were also measured at several temperatures (Table A2) to find its relationship with temperature as

Table A1. Viscosities of Hexane-MacKay Bitumen Mixtures at 303.15 K

Bitumen volumetric concentration (%)	0	7.5	18.2	33.6
Viscosity (mPa s)	0.281	0.41	0.80	2.15

Table A2. Viscosities of MacKay Bitumen at Several Temperatures

Temperature (K)	315.05	321.56	343.17
Viscosity (mPa s)	20168	8714	1433

$$\mu[\text{mPa s}]=\exp(\exp(-0.0108T[\text{K}]+5.7023)) \tag{A1}$$

Density measurements

The densities of the hexane-bitumen solutions at the experimental temperature condition of 303.15 K were measured with an Anton Paar DMA 512 HPHT (Table A3). The densities of pure bitumen were also measured at several temperatures (Table A4) to find its relationship with temperature as

Table A3. Densities of Hexane-MacKay Bitumen Mixtures at 303.15 K

Bitumen volumetric concentration (%)	0	7.5	18.2	33.6
Density (g/cm^3)	0.650	0.674	0.733	0.833

Table A4. Densities of Mackay Bitumen at Several Temperatures

Temperature (K)	308.26	313.86	332.48
Density (g/cm^3)	0.9979	0.9936	0.9823

$$\rho[\text{g/cm}^3]=3.247T^{-0.206}[\text{K}] \tag{A2}$$

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