



Full Length Article

Diffusion of sulfur-containing compounds in petroleum residue fractions I. Hindered diffusion through polycarbonate membranes at ambient conditions



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ABSTRACT

Hindered diffusion of sulfur-containing compounds in Venezuela atmospheric residue fractions through pore of polycarbonate membranes was investigated by using a diaphragm cell at 298 K. The results confirmed that residue fractions are all polydisperse mixtures. The sizes of membrane pore and fractions are the principal factors to diffusivities. In contrast to four fractions obtained by SFEF (supercritical fluid extraction and fraction) technique, there is a significant decrease in diffusion coefficients of maltenes and asphaltenes with increase of concentrations. Combining diffusivity variation of sulfur compounds in maltenes and asphaltenes with the study in literature, different aggregate degree was deduced for them over concentrations of 0.1–40 g/L. The influence of aggregation on diffusion coefficients enlarged as fractions become heavier and membrane pores become narrower. Hindered diffusion shows significant effect on transfer of residue fractions across membrane pores, especially for heavier fractions with higher concentrations diffusing through 15 nm membrane. Therefore, a number of large pores are required to provide sufficient channels for easy access of heavy components into active sites of catalyst. Comparisons between experimental results and theoretical prediction revealed that the actual hindered degree of sulfur-containing compounds in Venezuela residue fractions is more severe than that of predicted by the Renkin equation, which is due to the nonspherical structure of sulfide or thiophene derivatives.

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1. Introduction

With the depletion of conventional crude oil and increasing demand of energy resources, effective conversion of heavier crude oils to clean fuels has become one of the most critical issues in the petroleum processing industry [1,2]. Residue hydrotreating (HDT) is expected to contribute in a decisive way to worldwide demands for fuels with improved quality. It is well-known that the rate of HDT reactions is influenced by diffusion of reactant molecules into the interior of catalyst pores due to the large size of residue species. Resistance to diffusion would significantly reduce the effectiveness of the catalysts and the overall reaction rate. Large pores can provide better access to active sites within the catalyst. However, the reaction rate decreases with increasing pore diameter because the area of the reacting surface decreases. Optimum conversion of low-value petroleum heavy residues to high-value products requires knowledge of mass transfer of the reactants along limited pores.

Motivated by solving the problems encountered in residue hydrotreating, hindered diffusion of heavy oils through porous materials has been extensively studied during the past several decades. Three primary methods have been used to investigate hindered diffusivity of residue and asphaltenes, which are diaphragm diffusion cell [3–5], adsorptive uptake [6–8] and reactive kinetic methods [9–11]. The former two methods were performed under unreactive conditions, whereas the last one was carried out under reactive conditions. Although less important effects of hindered diffusion under reaction conditions have been postulated [12,13], most experimental results to date confirmed that the hindered effect is significant for residue diffusing through pores with typical HDT catalyst size. It should be meaningful to perform diffusion experiments both under nonreactive and reactive conditions with the same feedstock. The debate can be settled by relating diffusivities estimated at these two different conditions.

Theoretical and experimental studies on hindered diffusion of large molecules in liquid-filled pores attributed hindrance to two factors: steric restriction and hydrodynamic drag resistance. The hindrance factor, the ratio of effective to bulk diffusivity, has been commonly used to quantitatively describe the hindered degree of

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Nomenclature

C	concentration of solution (g/L)
d	diameter of solute (nm)
d_p	diameter of pore (nm)
D	diffusion coefficient of solute (cm ² /s)
F	hindered factor of diffusion
l	effective diffusion path length (cm)
m	the amount of the solute (g)
S	effective diffusion area of the membrane pores (cm ²)
t	time of sampling (s)
V	volume of chamber of diaphragm cell (mL)

Greek letters

β	constant of the diaphragm cell (cm ⁻²)
λ	ration of molecule diameter to pore diameter, d/d_p

Subscript

b	bulk diffusion
e	effective diffusion
j	sampling number
L	lower chamber
U	upper chamber

diffusion. Numerous theoretical correlations have been proposed to relate hindrance factor to λ , which is the ratio of solute size d to pore size d_p . Combining equilibrium partition coefficient from Ferry and centerline drag coefficients from Lane allowed Renkin to obtain the relationship [14]:

$$D_e/D_\infty = F(\lambda) = (1 - \lambda)^2(1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5), \quad (1)$$

where D_e is the effective diffusion coefficient of solute in the small pore, D_∞ is the bulk diffusion coefficient of solute and $F(\lambda)$ is the hindrance factor of diffusion. Good agreement between the Renkin equation and experimental data has been observed [10,15]. However, there are also some results which were not in accordance with the Renkin equation [9,16]. Several alternative empirical expressions have been subsequently developed. The following power-law relationship used to correlate hindered diffusion [9,17]:

$$F(\lambda) = (1 - \lambda)^n. \quad (2)$$

The parameter n indicates the hindered magnitude of diffusion. A value of $n = 4.4$ approaches the predicted result of the Renkin equation.

In spite of significant efforts on diffusion behavior of petroleum molecules, most of previous studies have been done using the whole residue or asphaltene as feedstocks. The size of molecules comprising these feedstocks can range from less than 1 nm to 3 nm in diameter. The hindered magnitude of diffusion for these feedstocks varies across the investigations due to the high complicated composition of the residues and apt aggregation of asphaltene molecules [3,6,9,18]. With regard to the effect of aggregation on hindered diffusion of residue, there is little published information.

In our previous study, hindered diffusivities of residue fractions through polycarbonate membranes have been investigated at concentration of 10 g/L [19]. More significant restrictive effect has been found for fractions of Athabasca oil sand bitumen vacuum residue as compared to model prediction for a hard spherical solute molecule diffusing through a cylindrical pore. However, our recent study indicates that aggregation of heavy fractions can occur at concentration lower than 0.1 g/L [20]. As a result, additional research is still required to investigate the effect of molecular aggregation on diffusion of residue fractions.

In this series of two articles, a comparative study on diffusion behavior of residue molecules in pores of membranes and catalysts was conducted under nonreactive and reactive conditions, respectively. This is the first paper in a series on hindered diffusivities of residue fractions through membranes and the effect of aggregation on diffusion. Model membranes, which have ideal pore geometry, can provide a significant insight into the fundamental nature of the transport processes. Highly dilute solutions were used in diffusion experiments to avoid interference from molecular aggregation. The aggregation behavior of residue fractions was further

investigated by increasing the concentrations. To our knowledge, the existence of aggregation and its effect on diffusion behavior of residue fractions in porous materials has not been reported by previous investigations.

2. Experimental

2.1. Feedstock preparation

Atmospheric residue derived from Venezuela Orinoco heavy crude oil (VAR) was separated into 15 extractable fractions and an unextractable end-cut by the supercritical fluid extraction and fractionation (SFEF) technique. The separation process and operating procedure have been reported elsewhere [21,22]. Normal pentane was used as the solvent and operated in programming pressure with an increasing gradient of 1.0 MPa/h. A major advantage of SFEF technology is that it can obtain sufficient quantities of narrow fractions of residue for further in-depth studies.

It is known that properties of SFEF fractions vary gradually with increased SFEF yield. Hence, four extractable SFEF fractions (SFEF-4, SFEF-8, SFEF-12 and SFEF-15) of the residue were chosen as feedstocks for the diffusion experiments. Furthermore, our previous study show the end-cut has large polydispersity and asphaltenes are enriched in it [23]. Therefore, maltenes and asphaltenes were further separated from the end-cut using *n*-heptane following the procedure of ASTM D6560 and were also performed to diffusion experiments. The SFEF fractions and the further separated maltenes and asphaltenes are all called VAR fractions herein. The residues and the corresponding fractions were subjected to various analyses, which have been described elsewhere [20].

Each fraction (~20 g) was diluted with 0.5 L of toluene to make a stock solution (40 g/L) that was further diluted by using toluene to yield a series of solutions with required concentrations. The solutions were sonicated 1 h prior to diffusion experiment to ensure complete dissolution and mixture homogeneity. HPLC-grade toluene (Sigma-Aldrich Chemical) was used as solvent.

2.2. Diaphragm diffusion cell

The diffusion experiments were carried out using a diaphragm diffusion cell described in detail elsewhere [19,20]. A brief summary of the diffusion cell is given below. The apparatus illustrated in Fig. 1 contains two glass chambers clamped together with a membrane between them. Teflon-coated magnetic stirring bars are mounted in the chambers and are driven by the rotation of an external magnet. To maintain a constant temperature of 298 ± 0.1 K, the cell was placed in a thermostatic bath (Labline 1286Q, USA) during experiments.

The lower and upper chamber holds a volume of 45.9 and 55.6 mL, respectively. Track-etched Nuclepore polycarbonate

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