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DEC 19 1990 DOE/PC/90504--T17

DOE/PC/90504--T17

DE91 005031

QUARTERLY PROGRESS REPORT

ON

CONFIGURATIONAL DIFFUSION OF COAL MACROMOLECULES

Grant No. DEFG2286PC90504

September 15, 1990 to December 15, 1990

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Acknowledgements

The work reported herein was made possible by the efforts of the following personnel of the Auburn Coal Conversion Laboratory. Their contributions to this report and to the progress of this work are hereby gratefully acknowledged.

Seonjae Kim

Frank Bowers

Objective and Task Outline

Objective

To investigate the phenomenon of hindered diffusion of coal macromolecules in idealized porous media.

Task Outline

- Task 1. Construct a diffusion cell with ideal pore structure for determination of diffusion coefficients.
- Task 2. Prepare and characterize ideal porous membranes.
- Task 3. Perform model compound experiments to calibrate and test diffusion apparatus and methodology.
- Task 4. Prepare and characterize coal macromolecules.
- Task 5. Analyze data to evaluate the diffusional behavior of coal macromolecules.

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SUMMARY OF PROGRESS

As shown in last quarter's report (see Figures 1 and 2 in this report), the hindered diffusion data for both TPP and coal macromolecules were significantly different from the theoretical correlations. In order to evaluate the factors which could lead to this difference an error analysis was conducted, and the detailed results reported herein. Generally, we did not find any errors which could account for the deviation from the theory, and thus we conclude that this deviation is real and can be ascribed to some factor not considered by the hindered diffusion theory, i.e., attractive or repulsive forces.

Detailed Progress

An evaluation of experimental factors influencing the uncertainty of diffusivity data obtained in the current research has been made. In general, for a variable Y which may be expressed as a function of n variables, $x_1, x_2, \dots, x_n$, the uncertainty in Y was obtained by: Here, S stands for

$$S^2(Y) = \sum_{i=1}^n \left(\frac{\partial Y}{\partial x_i} \right)^2 S^2(x_i) + \dots \quad (F.1)$$

the standard deviation of each variable.

The uncertainty of diffusivity data obtained in the current research is dependent on many experimental variables. Basically, all experimental variables were subjected to error analysis in order to evaluate the uncertainty of diffusivity data. However, in the present error analysis, special interest was given to the variables associated with the properties of track-etched membranes and the concentration analysis, since these were the major sources of error in the current research.

Effect of Errors in Pore Length

In the analyses of experimental data used in the current study, nominal values of membrane thicknesses supplied by the manufacturer were used for actual pore lengths. However, the maximum deviation of the actual pore lengths from the nominal membrane thicknesses reported in the literature was 6.8 %. Since this type of error is not

random, all error analyses conducted in this section were based on this maximum value.

The errors in pore length affect the errors in pore size determination from permeability tests and diffusivity measurements of n-octane and, consequently, influence the errors in diffusivity data. In Table F.1, results of error analyses in the pore size determination methods are summarized, and in Table F.2, the effects of errors in pore lengths on the diffusivity data of TPP and coal macromolecules are summarized. In the same table, relative errors in the ratios of effective to bulk diffusivities and in the ratios of Stokes-Einstein radii to pore radii affected by the errors in pore length are also summarized. As shown in these tables, the relative errors in these ratios are not significant. Thus, it appears that the errors in pore length do not seriously affect the positions of experimental data presented in the previous quarterly report. In other words, errors in pore lengths are not primarily responsible for the differences between experimental data and theoretical curves presented in Figures 1 and 2.

Errors in Pore densities of Membranes

Errors in pore densities affect the errors in measured pore size data and diffusivity data in a manner similar to the errors in pore length. In this analysis, the tolerance limit of rated pore densities specified in Nuclepore

Table F.1

Effects of Errors in Pore Length on Uncertainties
of Pore Sizes Determined from the
Various Methods

Item	Pore size Det. Methods		
	Liq. Per. Test	Gas Per. Test	Diffusion
Equations Used in the Analyses	Eqn. 3.1	Eqn 3.2 3.3 3.4	Eqn 3.5
Error Analysis Methods	Use Eqn. F.1	Use Eqn. F.1	Direct ^a Calculation
$\Delta(r_o)^b$			
----- r_o	1.7 %	1.7-2.3 % avg. 2.1% ^c	3.2 % ^d

- a. Pore sizes were recalculated with actual pore length, and differences were analyzed.
 b. $\Delta(r_o)$ = absolute difference between the pore size calculated from using a actual pore length and the one from a nominal membrane thickness
 c. basis: 0.05 μm nominal pore size NucleporeTM membrane
 d. basis: 200 Å pore size membrane

Note: Equation numbers in this Table refer to those in reference (1).

Table F.2

Relative Errors in Diffusivity Data of TPP and
Coal Macromolecules Affected By the
Errors in Pore Length

Molecules	$\Delta(D_e)^a$	$\Delta(r_s)$	$\Delta(r_o)$	$\Delta(D_e)$	$\Delta(D_e/D_o)$	$\Delta(r_s/r_o)$
	D_e	r_s	r_o	D_e	D_e/D_o	r_s/r_o
TPP	1.6 %	1.6 %	3.2 %	0.3 %	1.6 %	3.6 %
Equations Used in Anal.	Eqn. 6.1	c	Eqn. 3.5	Eqn. ^b 2.2	-	-
Error Analysis Methods	d	d	d	d	Eqn. F.1	Eqn. F.1
Coal Macro- molecules	0.5 %	0.5 %	3.2 %	0.3 %	0.3 %	3.2 %
Equations Used in Anal.	Eqn. 6.2	c	Eqn. 3.5	Eqn. ^b 2.2	-	-
Error Analysis Methods	d	d	d	d	Eqn. F.1	Eqn. F.1

a. $\Delta(D_e)$ = absolute difference between a diffusivity calculated from using actual pore length and one calculated from using nominal pore thickness
b. Boundary layer resistances and entrance-exit effects were neglected.
c. Stokes-Einstein equation d. Direct calculations were used, see Table F.1

Note: Equation numbers refer to equations in reference (1).

membrane product catalog ($\pm 15\%$) was used as a calculation basis. In Tables F.3 and F.4, the results of error analysis related to the errors in pore densities are summarized. As shown in these tables, 15% error in the pore density also does not significantly affect the relative errors in diffusivity data or those in measured pore radii.

Since the errors in pore densities of membranes were random type errors, the results presented in Tables F.3 and F.4 did not give a clear explanation about how the experimental data points presented in the previous report were affected by these relative errors. Thus, sensitivity analyses were conducted to examine the effect of errors in pore density on the movements of such experimental data points. In Figure F.1, results from the sensitivity analysis of TPP experimental data are presented. As shown in this figure, the changes in TPP experimental data points in this figure are not significantly affected by the changes in pore densities of membranes. Also these experimental data points move along the theoretical curve as the pore densities are changed. Accordingly, it was concluded that the differences between the experimental data and the theoretical curves shown in Figures 1 and 2 were not attributed to the errors caused by using the nominal values of pore densities in the analyses of experimental data. A similar conclusion can also be drawn from the sensitivity analysis of coal experimental data shown in Figure F.2.

Table F.3

Effects of Errors in Pore Density on Uncertainties
of Pore Sizes Determined from the
Various Methods

Item	Pore size Det. Methods		
	Liq. Per. Test	Gas Per. Test	Diffusion
Equations Used in the Analyses	Eqn. 3.1	Eqn 3.2 3.3 3.4	Eqn 3.5
Error Analysis Methods	Use Eqn. F.1	Use Eqn. F.1	Direct ^a Calculation
$\Delta(r_o)^b$			
----- r_o	3.8 %	3.8-5.0 % avg. 4.4% ^c	5.1 % ^d

- a. Pore sizes were recalculated with a increased pore density and differences were analized.
- b. $\Delta(r_o)$ = absolute difference between the pore size calculated from using a increased pore density and the one from a nominal pore density
- c. basis: 0.05 μm nominal pore size NucleporeTM membrane
- d. basis: 200 Å pore size membrane

Note: Equation numbers refer to the equations in reference (1).

Table F.4

Relative Errors in Diffusivity Data of TPP and
Coal Macromolecules Affected By the
Errors in Pore Density

Molecules	$\Delta(D_o)^a$	$\Delta(r_s)$	$\Delta(r_o)$	$\Delta(D_e)$	$\Delta(D_e/D_o)$	$\Delta(r_s/r_o)$
	D_o	r_s	r_o	D_e	D_e/D_o	r_s/r_o
TPP	3.2 %	3.2 %	5.1 %	3.5 %	4.7 %	6.0 %
Equations Used in Anal.	Eqn. 6.1	c	Eqn. 3.5	Eqn. ^b 2.2	-	-
Error Analysis Methods	d	d	d	d	Eqn. F.1	Eqn. F.1
Coal Macro- molecules	0.5 %	0.5 %	5.1 %	3.5 %	3.5 %	5.1 %
Equations Used in Anal.	Eqn. 6.2	c	Eqn. 3.5	Eqn. ^b 2.2	-	-
Error Analysis Methods	d	d	d	d	Eqn. F.1	Eqn. F.1

a. $\Delta(D_o)$ = absolute difference between a diffusivity calculated from using
a increased pore density and one calculated from using nominal pore density
b. Boundary layer resistances and entrance-exit effects were neglected.
c. Stokes-Einstein equation d. Direct calculations were used, see Table F.1

Note: Equation numbers refer to equations in reference (1).

Effects of Errors in Concentration Measurements

The accuracy of diffusivity data or calculated pore sizes were not limited by the accuracies of concentration measurements where gas chromatography or UV spectrometry was adopted as an analytical technique, since the measurement errors in these instruments are very low (usually less than ± 1 % in the current research). However, the average relative measurement error in GPC analysis was found to be around ± 2 % in the current research. In the diffusion experiments using coal macromolecules, concentration measurements of samples taken from both compartments of the diffusion cell were conducted independently. Thus, a maximum uncertainty in measured diffusivity data of coal macromolecules occurred when the errors in concentration measurements of samples had opposite signs.

The average error in the bulk diffusivity of coal fractions calculated on the basis of this maximum error in the measurements using GPC was found to be 8.3%, while the average error in the effective diffusivity data was 7.6%.

References

1. Kim, S.J., Ph.D. Thesis, Auburn University, Auburn, AL (1990).
2. Quarterly Report for June 15 to September 15, 1990.
Grant No. DEFG2286PC90504.

Figure 1 Dependence of D_{eff}/D_{∞} on λ in Hindered Diffusion of TPP

Figure 2 Dependence of D_{eff}/D_{∞} on λ in Hindered Diffusion of Coal Asphaltene

Figure F.1 Sensitivity Analysis of TPP Diffusion Data

Figure F.2 Sensitivity Analysis of Coal Diffusion Data

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