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International Journal of Coal Geology 42 (2000) 241–271

International Journal of

coal
geology

www.elsevier.nl/locate/ijcoalgeo

Binary gas adsorption/desorption isotherms: effect of moisture and coal composition upon carbon dioxide selectivity over methane

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Received 10 October 1998; accepted 30 June 1999

Abstract

The effect of coal moisture content and composition upon methane/carbon dioxide mixed gas adsorption characteristics is investigated. Separation factors are used to quantify the relative adsorption of carbon dioxide and methane. Experimental data indicate that carbon dioxide separation factors vary slightly between coal lithotypes, but the effects of variable coal composition and moisture upon selective adsorption are difficult to isolate. Model predictions based upon single-component isotherms show that although some variability in carbon dioxide selectivity exists for different coal types, there is no clear relationship between coal composition and carbon dioxide selectivity. Model predictions also indicate that coal moisture decreases carbon dioxide selectivity. The ideal adsorbed solution (IAS) theory and the extended Langmuir model differ substantially in their ability to predict binary gas adsorption behaviour. Comparison of model predictions to experimental data demonstrates that IAS theory, in conjunction with the Dubinin–Astakhov single-component isotherm equations are more accurate for the prediction of mixed gas desorption isotherms collected in this study than the extended Langmuir. IAS predictions, however, are strongly dependent upon the choice of pure gas isotherm equation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: binary gas adsorption; methane; carbon dioxide; coal composition

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1. Introduction

Coalbed gas generally consists of mixtures of methane, carbon dioxide, nitrogen, and heavier hydrocarbons ($> C_2$), although methane is often the primary component. Because gas adsorption is the primary mechanism of gas storage in most economic coalbed gas reservoirs, accurate modeling of adsorption behaviour is necessary for economic forecasting of coalbed gas production. Further, the effect of coal properties, such as composition and moisture content, upon adsorbent selectivity for component gases is important for the proper economic evaluation of heterogeneous coal reservoirs. Of considerable theoretical and practical interest is the study of mixed gas adsorption/desorption in coal.

The composition of coalbed gas, and hence, the commercial value of the gas, changes during production. For example, coalbed gas from the San Juan Basin has increased in carbon dioxide concentration (Deo et al., 1993) during gas well production. Accurate economic forecasts must account for evolving gas compositions through time during the production life of a coalbed gas reservoir.

Laboratory measurements of coalbed gas adsorption isotherms are commonly used for the prediction of desorbed gas volumes as reservoir pressure decreases during production (Mavor et al., 1990). Adsorption isotherms are often determined using pure methane as an analysis gas and are inaccurate for predicting multicomponent gas desorption volumes. The composition of adsorbate gas significantly affects the total and single-component adsorbed gas volumes in coal systems (Stevenson et al., 1991; Arri et al., 1992; Greaves et al., 1993; Harpalani and Pariti, 1993; Hall et al., 1994). Multicomponent desorption isotherms, determined using realistic initial reservoir gas compositions, are required for accurate predictions of adsorbed gas content during production.

Nonmethane gas injection may be used to increase methane gas recovery during production, either by lowering the methane partial pressure in the free gas, or by competitive adsorption (Zuber et al., 1996). Reznik et al. (1984) demonstrated that carbon dioxide injection increases the recovery of in situ methane in coalbeds. Puri and Yee (1990) showed that nitrogen flooding also increases methane recovery. Enhanced recovery principles may also be used to reduce greenhouse gas emissions through the disposal of anthropogenic carbon dioxide into coal seams (Gunter et al., 1997). Knowledge of multicomponent adsorption characteristics of coal is therefore necessary for the accurate assessment of enhanced recovery operations.

Most studies of multicomponent adsorption on coal have focused on the accurate modeling of equilibrium gas adsorption with little consideration of coal compositional effects. To the authors' knowledge, no systematic study has been performed to assess the effect of coal properties such as moisture content and composition (organic and mineral) upon the selective adsorption of carbon dioxide in carbon dioxide–methane–water–coal adsorption systems. Because pure gas adsorption has been shown to be a function of water content (Joubert et al., 1973, 1974; Levy et al., 1997) and coal composition (Lamberson and Bustin, 1993), it is reasonable to anticipate that binary gas adsorption is also a function of these properties.

The current study examines the effect of coal moisture and composition upon binary gas adsorption using experimental data as well as model predictions of binary adsorption

from pure component isotherm data. The commonly applied extended Langmuir equation (Ruthven, 1984; Yang, 1987), as well as the ideal adsorbed solution (IAS) theory (Myers and Prausnitz, 1965), are used to predict binary gas adsorption. First, to examine differences in the performance of the models, predictions of binary gas equilibrium, over a broad range of pressures and gas compositions, are made. A variety of commonly used pure gas isotherm models are used in conjunction with IAS theory in order to assess the effect of isotherm curve-fit error upon IAS theory predictions. The effect of gas pressure and composition upon predicted carbon dioxide selectivities over methane is examined. Model predictions using pure gas isotherm data for dry and moisture-equilibrated coal are also used to determine the effect of moisture and coal composition upon binary gas adsorption. Binary gas experimental data are examined to determine the effect of gas composition, pressure, and coal lithotype upon the desorption characteristics of moisture-equilibrated coals. Finally, the results of model predictions are used to interpret binary gas experimental data, and the model fits are assessed using the current experimental data, as well as that of Hall et al. (1994).

1.1. Previous studies

Few experimental studies have examined the adsorption/desorption behaviour of mixed gases in coal under reservoir conditions. Stevenson et al. (1991) measured and examined adsorption of binary and ternary mixtures of CH₄, CO₂, and N₂ on dry Australian Westcliff Bulli seam coals at 30°C and pressures up to 5.2 MPa. Greaves et al. (1993) studied mixed gas (CH₄, CO₂) adsorption/desorption isotherms on dry Sewickley seam coal at 23°C. The Greaves et al. (1993) study demonstrates the importance of adsorption/desorption isotherm hysteresis in predicting adsorbed phase compositions.

The presence of moisture in the coal matrix significantly changes the adsorption equilibrium characteristics of mixed gases. Arri et al. (1992) collected binary (methane–nitrogen and methane–carbon dioxide) gas isotherm (46°C) data at various pressures for a moisture-equilibrated coal system. Arri et al. (1992) showed that each component gas does not adsorb independently, but competes for adsorption space. The extended Langmuir isotherm (Ruthven, 1984; Yang, 1987) provided a reasonable fit to the Arri et al. (1992) data. Harpalani and Pariti (1993) obtained ternary gas (methane–carbon dioxide–nitrogen) adsorption/desorption data for a moisture-equilibrated coal system at 44°C. The methane concentration in the free-gas (nonadsorbed) phase was shown to decrease with pressure during desorption. A reasonable fit to the Harpalani and Pariti (1993) data was also obtained using the extended Langmuir isotherm.

There have been several attempts to apply thermodynamically rigorous mixed gas adsorption models to moisture-equilibrated and dry coal/mixed gas adsorption systems (Stevenson et al., 1991; DeGance, 1992; Hall et al., 1994). Hall et al. (1994) applied a variety of models to pure and mixed gas Fruitland coal isotherm data and quantitatively assessed model predictions using an extensive data set. Hall et al. (1994) found that although all models used for pure gas adsorption performed comparably, the IAS theory of Myers and Prausnitz (1965) and 2-D equation-of-state (EOS) models were more accurate than the extended Langmuir model for mixed gas adsorption. In the study of

Stevenson et al. (1991), IAS theory was found to be adequate for predicting binary and ternary mixed gas adsorption on dry coal.

1.2. Theory

The extended Langmuir model (Ruthven, 1984; Yang, 1987) and IAS theory (Myers and Prausnitz, 1965) are most commonly used for the prediction of mixed gas adsorption on coal. Both the extended Langmuir model and IAS theory require pure component isotherm data for multicomponent predictions. The simplest model used for prediction of multicomponent adsorption isotherms is the extended Langmuir equation:

$$V_i = \frac{(V_L)_i b_i P_i}{1 + \sum_j b_j P_j}, \quad (1)$$

where $(V_L)_i$ and b_i are the pure gas isotherm Langmuir constants. Partial pressures of the component gases in the free-gas phase are determined using the following equation:

$$P_i = Py_i. \quad (2)$$

Langmuir parameters for pure component isotherms are used to predict component adsorbed volumes for gas mixtures at any total gas pressure and free-gas composition.

A convenient method for expressing the relative adsorption of components in an adsorption system is through the calculation of a separation factor. The separation factor, or selectivity ratio, for a binary gas adsorption system may be defined as (Ruthven, 1984):

$$\alpha_{ij} = \frac{(x/y)_i}{(x/y)_j}. \quad (3)$$

For the extended Langmuir isotherm, the separation factor is simply the ratio of the adsorption equilibrium constants for the pure component isotherms (Ruthven, 1984) and is independent of concentration and total pressure. The assumption of a constant separation factor is not, however, necessarily accurate for all systems (Ruthven, 1984). An increasing selectivity for the most strongly adsorbed component with decreasing concentration of that component is generally observed (Myers, 1968).

The IAS theory (Myers and Prausnitz, 1965) is based upon the assumption that the adsorbed mixture behaves like an ideal, adsorbed solution, and hence, is analogous to Raoult's law for bulk solutions. Activity coefficients of the adsorbed solution are therefore assumed to be unity and the equilibrium between the gas phase mole fraction of a component and the adsorbed phase mole fraction is given by:

$$Py_i = P_i^\circ(\pi) x_i, \quad (4)$$

where P_i° is the gas (vapour) pressure of the pure component adsorbed at the same temperature and spreading pressure as the solution. Fugacities may be substituted for pressures in Eq. (4) to account for gas phase nonidealities. The spreading pressure for

the pure components may be determined through integration of the Gibbs adsorption isotherm to the vapour pressure of the pure component, P_i° :

$$\pi_i^* = \frac{\pi_i A}{RT} = \int_0^{P_i^\circ} \frac{n(P)}{P} dP, \quad (5)$$

where $n(P)$ is the pure component adsorption isotherm. The spreading pressure (π) may be defined as the reduction in surface tension of a surface due to the spreading of the adsorbate over the surface (Ruthven, 1984). Any pure component isotherm equation may be used to evaluate Eq. (5).

Mole fraction constraints include:

$$\sum_{i=1}^{n_c} x_i = 1; \quad \sum_{i=1}^{n_c} y_i = 1. \quad (6)$$

The total amount of adsorbed gas in the mixture (for an ideal solution) is given by:

$$\frac{1}{n_t} = \sum_{i=1}^{n_c} \frac{x_i}{n_i^\circ}. \quad (7)$$

The actual amount of each component adsorbed in the mixture is given by:

$$n_i = n_t x_i. \quad (8)$$

Eq. (5) may be evaluated for each component using an isotherm equation, such as the Langmuir single-component isotherm equation, or may be determined graphically. Richter et al. (1989) demonstrated the effect of fitting pure component isotherm data with different isotherm equations upon the prediction of multicomponent adsorption equilibria using the IAS method. The calculations of mixed gas equilibria were shown to be very sensitive to curve-fit error of the pure gas isotherm equation.

Although the Dubinin–Radushkevich (D–R) and Dubinin–Astakhov (D–A) equations have been shown to be more accurate for the modeling of coal/pure gas isotherms (Clarkson et al., 1997), the incorrect low-pressure limit of these isotherm equations may affect spreading pressure calculations for IAS theory. The correct low-pressure limit of any adsorption isotherm equation should be (Richter et al., 1989):

$$\lim_{p \rightarrow 0} n/p = H. \quad (9)$$

Although the Langmuir equation has the correct low-pressure limit, the D–R/D–A equation low-pressure limit is zero (Talu and Myers, 1988). The effects of the incorrect low-pressure limits of the D–R and D–A equations upon spreading pressure calculations are examined in a later section.

2. Methods

2.1. Sample preparation

Four medium-volatile bituminous coal lithotype samples from the Lower Cretaceous Gates Formation of northeastern British Columbia were used in this study. The coals

were chosen for their variable organic contents and compositions. The samples were crushed by hand (stage crushed) to pass through a 4 mesh (4.75 mm) sieve and four subsamples were obtained. A –4 mesh fraction was retained and the other subsamples were crushed to pass through an 8 (2.38 mm), 20 (0.841 mm), and 60 (0.250 mm) mesh sieve. Only the –4 and –60 mesh fractions were used for isotherm analysis. Proximate analysis (ash and moisture) was performed for each of the subsamples used for isotherm analysis. Petrographic analysis was performed on –60 mesh splits using manual point counts on polished pellets (Bustin et al., 1985). Coals were stored in vacuum desiccators or refrigerated sealed containers between isotherm runs to prevent oxidation. Periodic free-swelling index tests (American Society for Testing Materials, 1980) of bright coals demonstrated that the coals were not oxidized appreciably.

The –4 Mesh coal samples were dried in an oven at 110°C overnight and then evacuated at isotherm temperature for 24 h prior to “dry” isotherm analysis. The –60 mesh coals were equilibrated with moisture at 30°C prior to desorption isotherm analysis. Equilibrium moisture was achieved using a procedure similar to that described by Levy et al. (1997).

2.2. Experimental procedure

High-pressure (up to ~8 MPa) 303.15 K isotherms were obtained using a volumetric adsorption apparatus similar to that described by Mavor et al. (1990) and Levy et al. (1992). Sample void volume calibrations were performed using helium expansion as described elsewhere (Mavor et al., 1990). Pure gas adsorption isotherm data collection for the –4 mesh coals is also described elsewhere (Clarkson, 1998).

Methane and carbon dioxide desorption isotherms were collected for the –60 mesh, moisture-equilibrated coal using the following procedure. The reference cell was charged with gas to a pressure greater than the anticipated sample cell starting pressure and allowed to thermally equilibrate with the thermostated water bath. Gas was then dosed from the reference cell to the sample cell for a few seconds and then the valve between the two cells closed. Pressure in the sample cell dropped as gas was adsorbed to the equilibrium value. Equilibrium was considered reached when the pressure in the sample cell remained constant ($\Delta P = 0.000$ MPa) over a period of 2 h. Twelve hours total was generally sufficient to reach equilibrium. Desorption isotherm steps were then collected by reversing the adsorption step procedure: gas was dosed to the (evacuated) reference cell from the sample cell and the sample cell was isolated from the reference cell until equilibrium was achieved. The following mass balance calculation was used in conjunction with the real-gas law to calculate pure gas adsorbed volumes isotherms at STP ($T = 273.15$ K, $P = 0.101325$ MPa) at each isotherm step:

$$V_{\text{ads}} = \left[\frac{T_{\text{STD}}}{TP_{\text{STD}} m_c} \right] \times \left[V_{\text{ref}} \left(\frac{P_{\text{ref}}^{I-1}}{z} - \frac{P_{\text{ref}}^I}{z} \right) - (V_v - V_s) \left(\frac{P_{\text{sc}}^I}{z} - \frac{P_{\text{sc}}^{I-1}}{z} \right) \right]. \quad (10)$$

The sample void volume (V_v), which is the volume in the sample cell not occupied by solid coal, may be corrected for the volume occupied by the adsorbate (V_s) if a molar density of the adsorbate is assumed. In the current study, the adsorbate density was

taken as that at normal boiling for methane (0.423 g/cm³) and at the triple point for carbon dioxide (1.18 g/cm³). If the adsorbate volume is neglected, the Gibbs isotherm is obtained.

For mixed gas studies, a similar procedure to the pure gas isotherms was used, except that small gas samples were taken during a desorption step for gas chromatographic (GC) analysis. Sample cells were used to extract small (~ 3 ml) gas samples with a syringe following pressure stabilization in the sample cell during a sorption step. The pressure drop after extraction was usually small ($\ll 0.01$ MPa), and the pressure was again allowed to stabilize for several hours prior to the next desorption step. As with the study of Greaves et al. (1993), the pressure drop accompanying extraction was assumed to have a negligible effect on adsorbed gas composition. The reference cell was then dosed with a small amount of mixed gas from the sample cell to initiate the next desorption step. A gas sample was extracted from the reference cell for GC analysis to determine the composition of the gas in the reference cell.

Compositional (mole fraction) equilibrium as well as mechanical (pressure) is required for an equilibrium multicomponent isotherm. Compositional equilibrium was tested for periodically during desorption steps by gas compositional analyses. Equilibrium times for mixed gas adsorption were generally much longer than for pure gas adsorption. For example, for the 75% CH₄/25% CO₂ binary gas desorption isotherm, 5–7 days were allowed for equilibration at each step.

For binary gas isotherms, mass balance was performed for each component using Eq. (11):

$$V_{\text{ads}}^j = \left[\frac{T_{\text{STD}}}{TP_{\text{STD}} m_c} \right] \times \left[V_{\text{ref}} \left(\frac{(y_{\text{ref}}^j P_{\text{ref}})^{I-1}}{z} - \frac{(y_{\text{ref}}^j P_{\text{ref}})^I}{z} \right) - (V_v - V_s) \left(\frac{(y_{\text{sc}}^j P_{\text{sc}})^I}{z} - \frac{(y_{\text{sc}}^j P_{\text{sc}})^{I-1}}{z} \right) \right], \quad (11)$$

where V_{ads}^j is the volume of component j adsorbed from the mixture at each adsorption step, and y^j is the free-gas (unadsorbed) mole fraction of component j . The volume of the adsorbed phase, assuming the adsorbed gas behaves like an ideal solution, was calculated using the following equation:

$$V_s = \sum_{i=1}^{n_c} x_i V_{mi}, \quad (12)$$

where V_{mi} is the molar volume of the liquid adsorbate. Eqs. (10) and (11) must be solved iteratively at each sorption step, with the Gibbs adsorption volumes used as the initial guess for Eq. (10). Gas compressibility factors for pure and mixed gases were determined using the Peng–Robinson EOS (Peng and Robinson, 1976).

Replicate runs performed for methane adsorption isotherms on the dried –4 mesh coals and methane desorption isotherms for moisture-equilibrated –60 mesh coals were within 6% and 10% relative, respectively. The estimated uncertainties determined from replicate analysis vary with coal type. For example, for the dry, –4 mesh coals methane

adsorption isotherm, the relative errors are around 2% for the banded bright and bright coals (B2-11 and C3-2), but around 4% and 6% for the two dull coals (B2-10 and D3-3, respectively). Similarly, for the moist – 60 mesh coals, the desorption isotherm errors are around 5% for the bright coals, but about 10% for the dull coals. The dull coals have

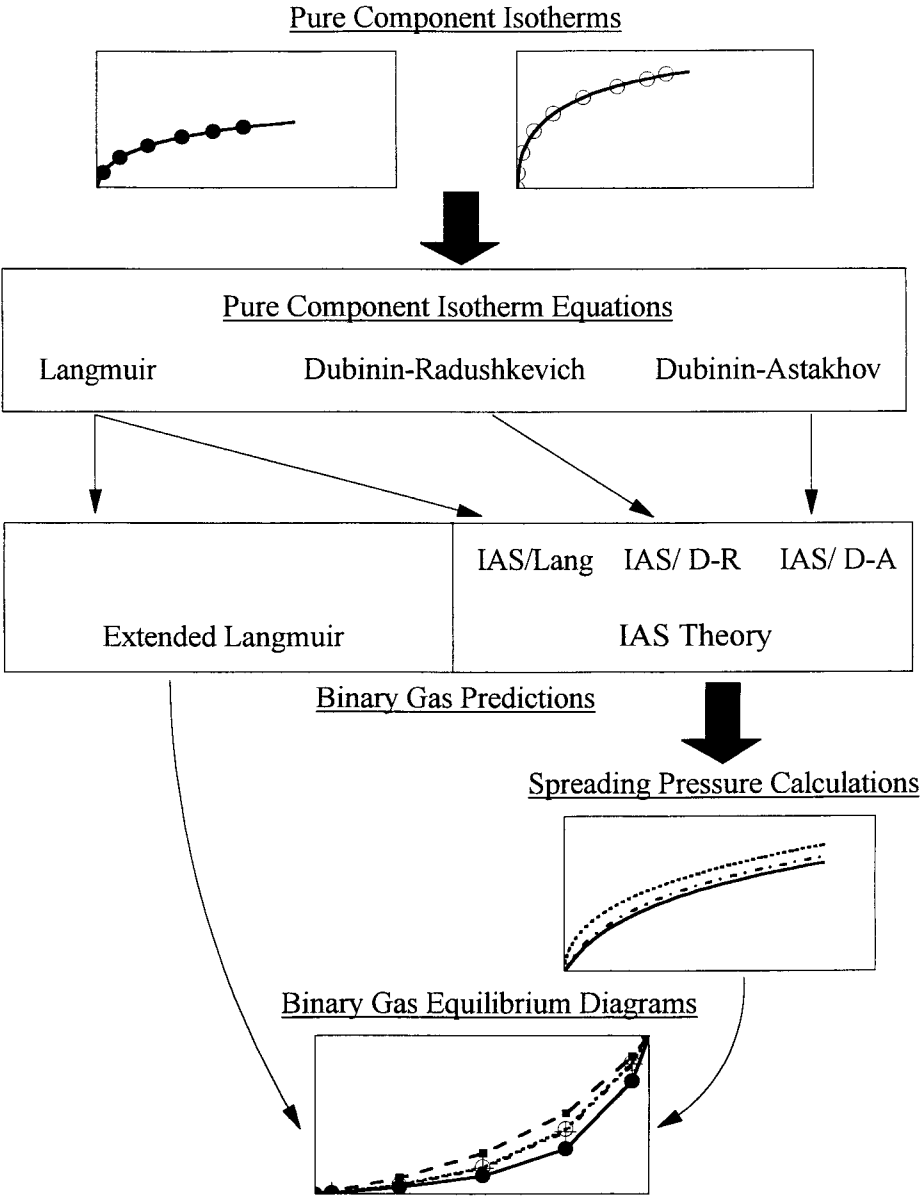


Fig. 1. Diagram illustrating protocol for binary gas adsorption predictions.

a higher ash content, and adsorb much less gas and thus have greater measurement errors than the bright and banded bright coals. The moist coal desorption isotherms have a greater uncertainty than the dry adsorption isotherms possibly due to slight variations in moisture content between replicate analyses. The estimated uncertainty in methane adsorption isotherms on moist coals, however, is generally less than 3%, for a variety of coals analyzed by the authors.

Gas mixture compositions are known within 0.002 mole fraction based upon replicate analysis of calibration standards and analysis gas.

2.3. Isotherm regression analysis

The Langmuir, D–R, and D–A isotherm equations were fitted to single-component isotherm data. The relevant equations are (Langmuir, 1918; Dubinin and Astakhov, 1971; Yang, 1987):

$$\text{Langmuir: } V = \frac{V_L bP}{1 + bP} \quad (13)$$

$$\text{Dubinin–Radushkevich (D–R): } \frac{V}{V_o} = \exp\{-D[\ln P_o/P]^2\} \quad (14)$$

$$\text{Dubinin–Astakhov (D–A): } \frac{V}{V_o} = \exp\{-D[\ln P_o/P]^n\}. \quad (15)$$

Application of the Langmuir, D–R, and D–A equations to adsorption isotherm data has been discussed previously (Clarkson et al., 1997). The parameters b and V_L in the Langmuir equation, and V_o , D , and n were optimized using a least-squares routine coupled with a multiparameter optimization algorithm in MATLAB[®].

Application of IAS theory for multicomponent adsorption isotherm predictions requires integration of the pure component isotherms in the spreading pressure equation (Eq. (5)). For the Langmuir isotherm, the spreading pressure equation was calculated using an analytical equation, whereas for the D–A and D–R equations, the spreading pressure was calculated by numerical integration. A diagram summarizing the analytical protocol is given in Fig. 1.

3. Results and discussion

3.1. Coal petrographic data

The selected Gates coals represent a wide range in maceral and ash contents (Table 1). Two coals (C3-2 and B2-11) have high vitrinite (> 50 vol.%, mineral matter-free) and low ash (< 20 wt.%) contents, whereas B2-10 and D3-3 have low vitrinite (< 50 vol.%) and high ash (> 20 wt.%) contents.

Table 1

Maceral composition (vol.%, mineral matter-free), equilibrium moisture (wt.%, 30°C), and ash yields (wt.%, dry-basis)

Sample	Structured vitrinite ^a	Desmocollinite	Semifusinite	Fusinite	Other inertinite ^b	Liptinite	Equilibrium moisture (%)	Ash (%)
C3-2	75	23	1	1	–	–	2.4	13.0
B2-11	29	30	33	5	3	–	2.7	3.7
D3-3	20	30	23	–	27	–	1.4	46.1
B2-10	13	28	49	3	6	1	1.6	30.3

^aIncludes telocollinite and telinite.

^bIncludes macrinite and inertodetrinite.

3.2. Pure gas isotherms

High-pressure methane and carbon dioxide isotherms (303 K) (Fig. 2) exhibit the expected trend of increasing gas adsorption with a decrease in ash content. If the results are plotted on an ash-free basis (Fig. 3), which assumes that mineral matter adsorbs negligible amounts of gas, there is still a significant difference in the amount adsorbed between the coals. Maceral composition thus exhibits some control upon gas adsorption. The trend of increasing gas adsorption with total vitrinite content, as demonstrated in previous studies (Lamberson and Bustin, 1993), is not strictly obeyed here. The highest adsorbing coal (B2-11) does not have the highest vitrinite content. Lamberson and Bustin (1993) also found that although methane gas adsorption generally increased with vitrinite content, the highest adsorbing coals did not have the highest vitrinite content, but had a mixture of vitrinite and inertinite. The amount of adsorption is related to the microporous structure of the coal, as discussed in a previous study (Clarkson and Bustin, 1996).

Moisture has the effect of decreasing the amount of gas adsorbed (Fig. 4), as observed in previous studies (Joubert et al., 1973, 1974; Levy et al., 1997). For example, at 3 MPa, the ratio of the volume adsorbed on the dry coal (B2-11) to the volume adsorbed on the moisture-equilibrated coal ($V_{\text{dry}}/V_{\text{wet}}$) is ~ 1.28 for methane adsorption and ~ 1.25 for carbon dioxide adsorption for sample B2-11.

The D–R, D–A, and Langmuir equations were applied to pure gas isotherm data and an estimate of curve-fit error is given in Table 2. The D–A equation fits the moisture-equilibrated and dry coal isotherm data within experimental error, whereas the Langmuir equation does not in all cases. The D–R equation, which is a two-parameter equation like the Langmuir equation, provides a fit intermediate to the D–A and Langmuir equations. The curve-fits for all equations are generally better for methane isotherms than for carbon dioxide. The Langmuir curve-fits are much better for the moisture-equilibrated coal data than for the dry coal. The effect of curve-fit error upon IAS predictions will be examined in Section 3.3.

The D–R, D–A, and Langmuir equations were also applied to the pure gas adsorption isotherm data of Hall et al. (1994), to facilitate comparison with their 2-D EOS models. The pressure ranges and objective functions for least-squares fitting

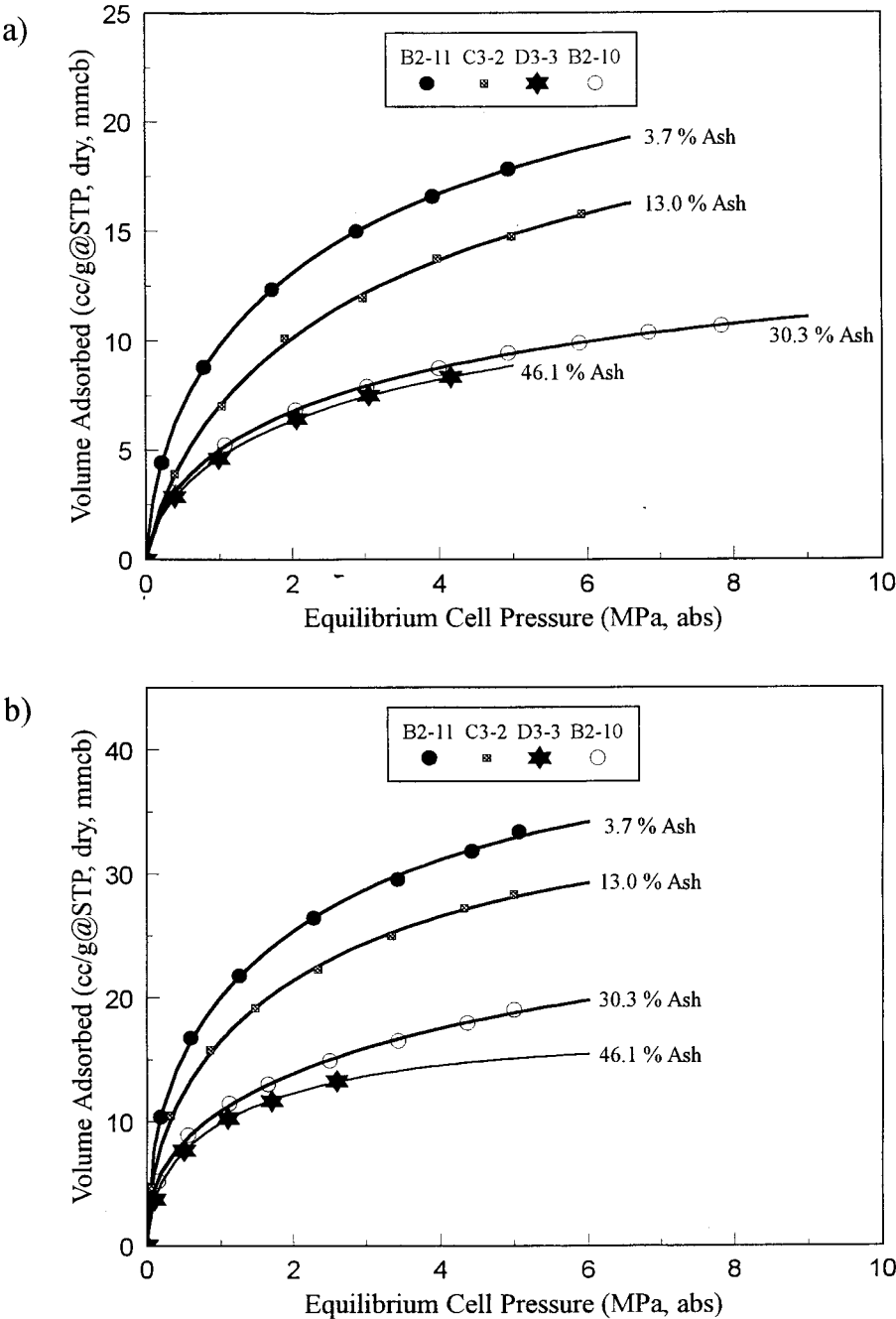


Fig. 2. Methane (a) and carbon dioxide (b) adsorption isotherm data for dry –4 mesh coals. Results are plotted on a dry, mineral matter-containing basis (mmcb). Ash contents (dry) are indicated. Lines are D–A fit to data.

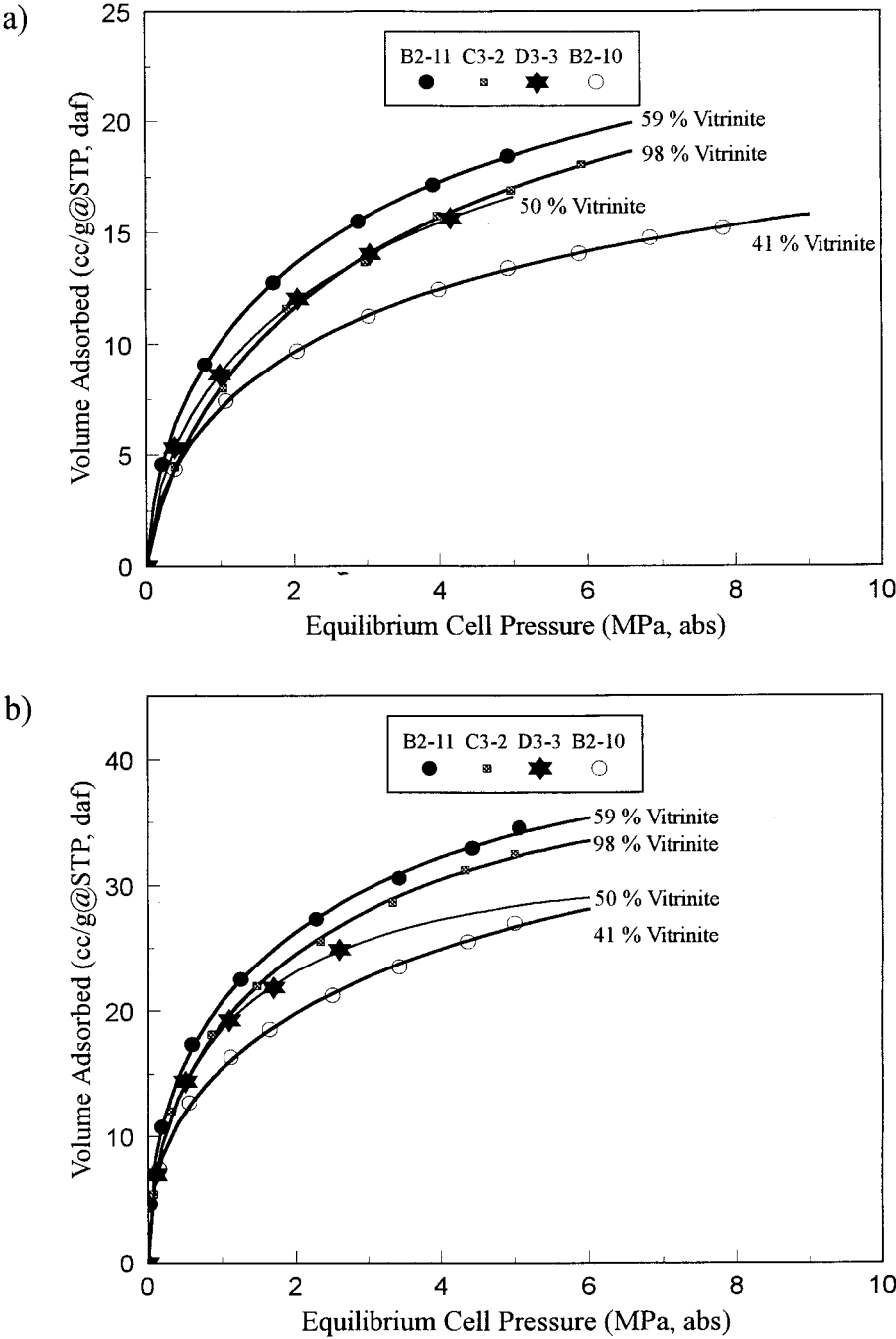


Fig. 3. Methane (a) and carbon dioxide (b) adsorption isotherm data for dry –4 mesh coals. Results are plotted on a dry, ash-free basis (daf). Total vitrinite contents are indicated. Lines are D–A fit to data.

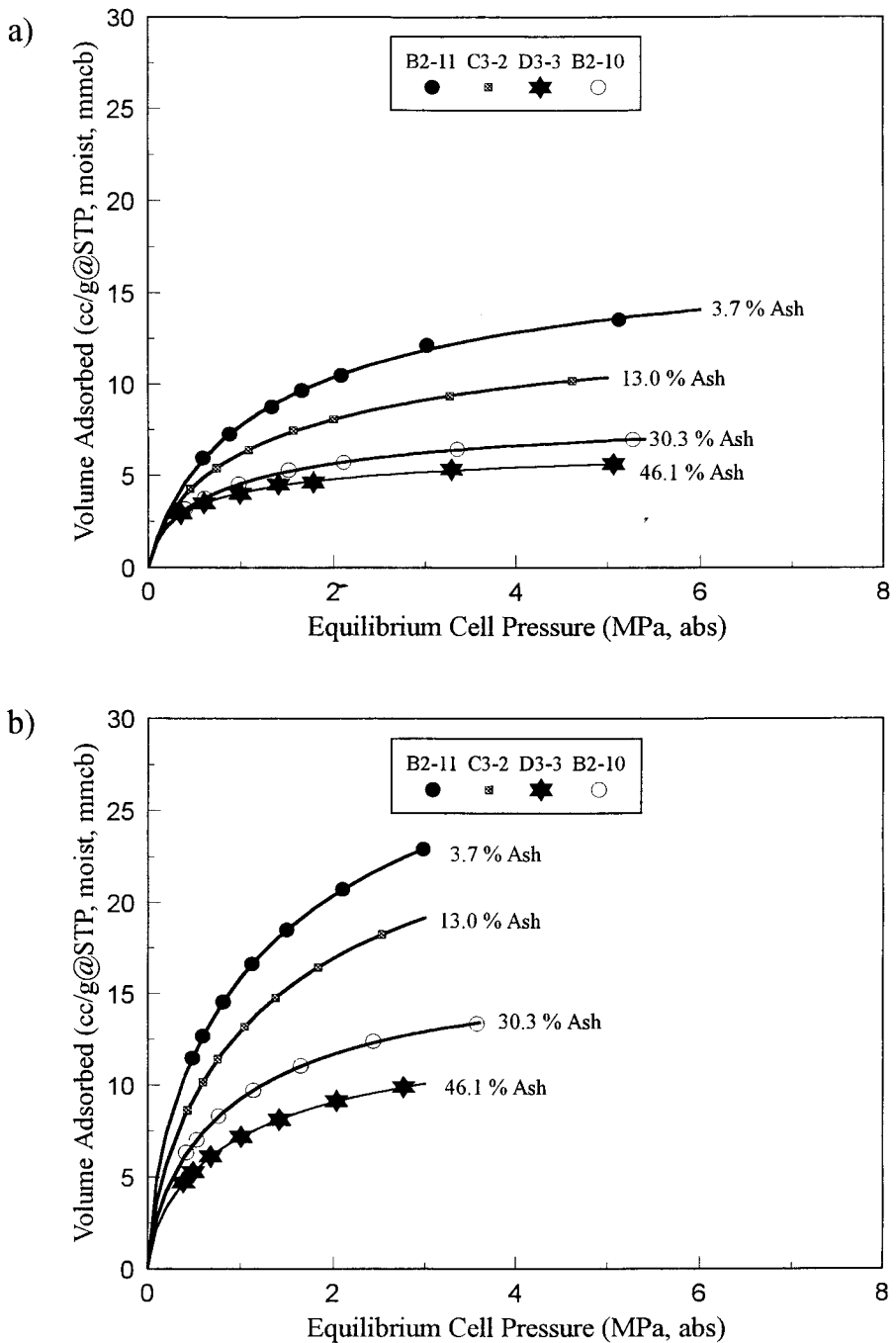


Fig. 4. Methane (a) and carbon dioxide (b) desorption isotherm data for moisture-equilibrated -60 mesh coals. Results are presented on a moisture-equilibrated, mmcb coal basis. Ash contents (dry) are indicated. Lines are D-A fit to data.

Table 2

Relative error^a calculations for isotherm fits

Sample	Dry coal						Moisture-equilibrated coal					
	CH ₄ isotherm			CO ₂ isotherm			CH ₄ isotherm			CO ₂ isotherm		
	Langmuir	D–R	D–A	Langmuir	D–R	D–A	Langmuir	D–R	D–A	Langmuir	D–R	D–A
B2-11	5.16%	1.29%	0.18%	13.6%	12.0%	1.25%	1.79%	0.98%	0.83%	1.71%	1.47%	0.05%
C3-2	2.91%	1.76%	1.29%	9.76%	9.10%	2.05%	2.19%	0.44%	0.37%	1.48%	1.26%	0.00%
D3-3	3.78%	1.16%	0.19%	6.97%	4.00%	0.56%	2.89%	0.89%	0.81%	1.67%	1.13%	0.11%
B2-10	4.74%	1.63%	0.53%	8.41%	7.73%	1.23%	2.43%	0.72%	0.54%	1.63%	1.21%	0.39%

^a Average relative error = $(100/N) \sum_{j=1}^N \text{abs}(V_{\text{calc}} - V_{\text{exp}})_j / V_{\text{exp}}$, where N = number of data points.

specified by Hall et al. (1994) were used for comparison. The D–A isotherm equation provided as good a fit to the data as the 2-D EOS models used by Hall et al. (1994). The average relative error or, average percentage deviation, for the D–A equation is about 0.7 for methane and 1.8 for carbon dioxide compared to about 0.7 and 1.7 for the EOS models, respectively. Both the D–A and 2-D EOS equations have three adjustable parameters. The D–R equation generally provides better fits than the Langmuir equation for pure component isotherm correlation, despite having the same number of adjustable parameters.

3.3. Binary gas isotherm predictions: effect of pure gas isotherm equation

The extended Langmuir (Eq. (1)) and IAS theory (Eqs. (4)–(7)), using the Langmuir, D–R, and D–A equations for spreading pressure calculation, were applied to the pure gas isotherm data for prediction of binary gas adsorption behaviour. Prior to assessing the results of the model predictions, however, the issue of the incorrect zero-pressure limit of n/P for the D–R and D–A isotherms, and hence, the suitability of these equations for spreading pressure calculation, is addressed.

The function n/P , calculated using the Langmuir, D–R, and D–A equations, is plotted vs. pressure for dry sample B2-11 in Fig. 5. All models provide excellent fits to the data for pressures greater than 0.5 MPa for methane and carbon dioxide, but the Langmuir model deviates substantially from the D–A/D–R at $P < 0.5$ MPa. Because significant deviation occurs only at very low pressures, the incorrect limit of the D–A/D–R isotherm is unlikely to substantially affect spreading pressure calculations in the range of pressures used in the current study. A similar conclusion was reached by Richter et al. (1989), who used the D–R equation for spreading pressure calculations for methane and ethane adsorption on activated carbon. Reduced spreading pressure plots (Fig. 5) show that all models predict similar spreading pressures for methane, but are substantially different for carbon dioxide. The difference in spreading pressure plots likely reflects the difference in the curve-fits for the isotherm equations.

Calculated equilibrium adsorption data plots (Figs. 6 and 7) for the methane/carbon dioxide binary system illustrate the differences in predictions of the extended Langmuir model and IAS theory (with different pure gas adsorption isotherm equations). At a constant pressure of 2.5 MPa and a given gas concentration, the extended Langmuir

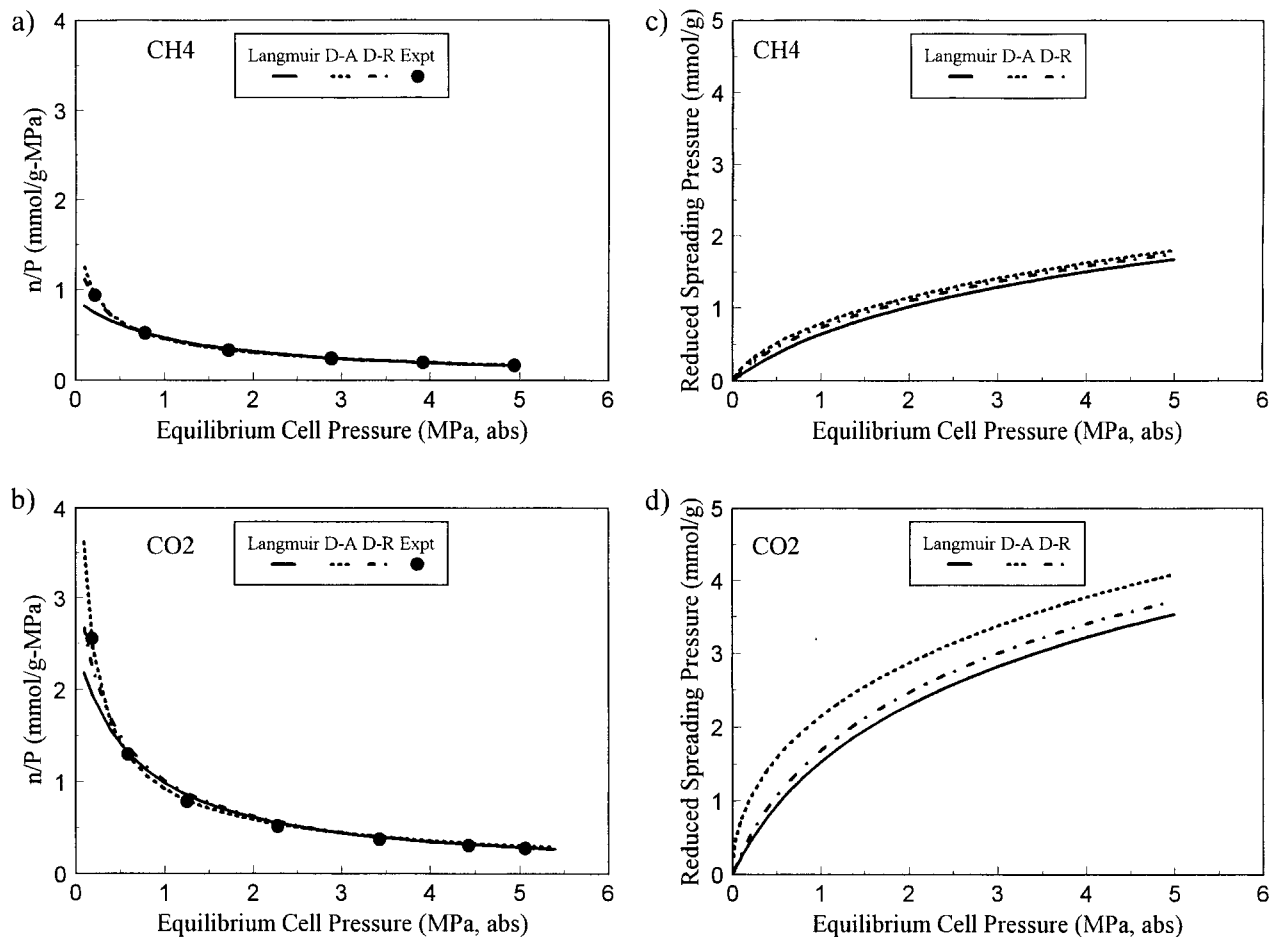


Fig. 5. n/p (a and b) and reduced spreading pressure plots (c and d) for methane and carbon dioxide B2-11 (dry) isotherm data.

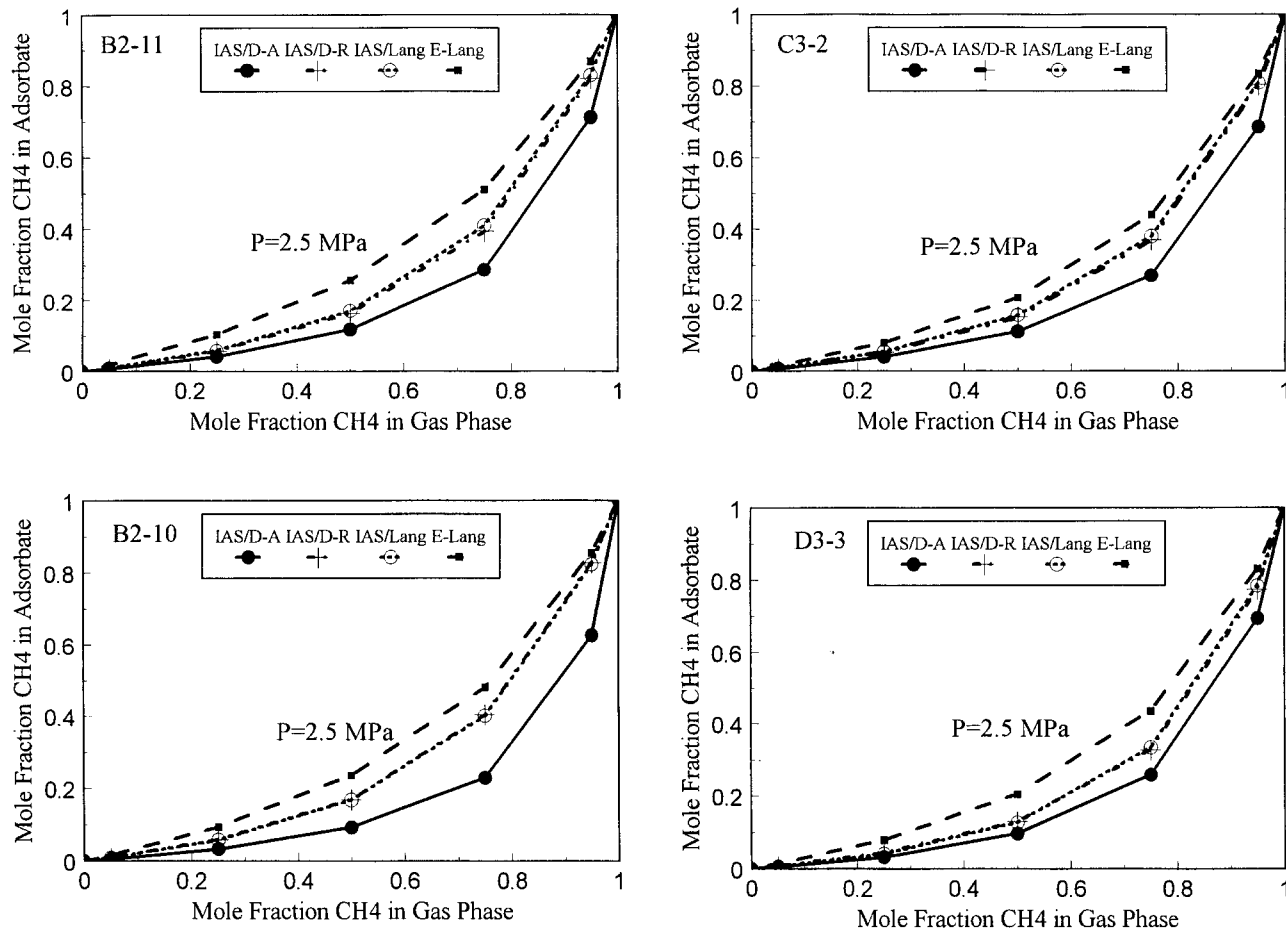


Fig. 6. Predicted equilibrium compositions for dry -4 mesh coal binary gas adsorption isotherm data.

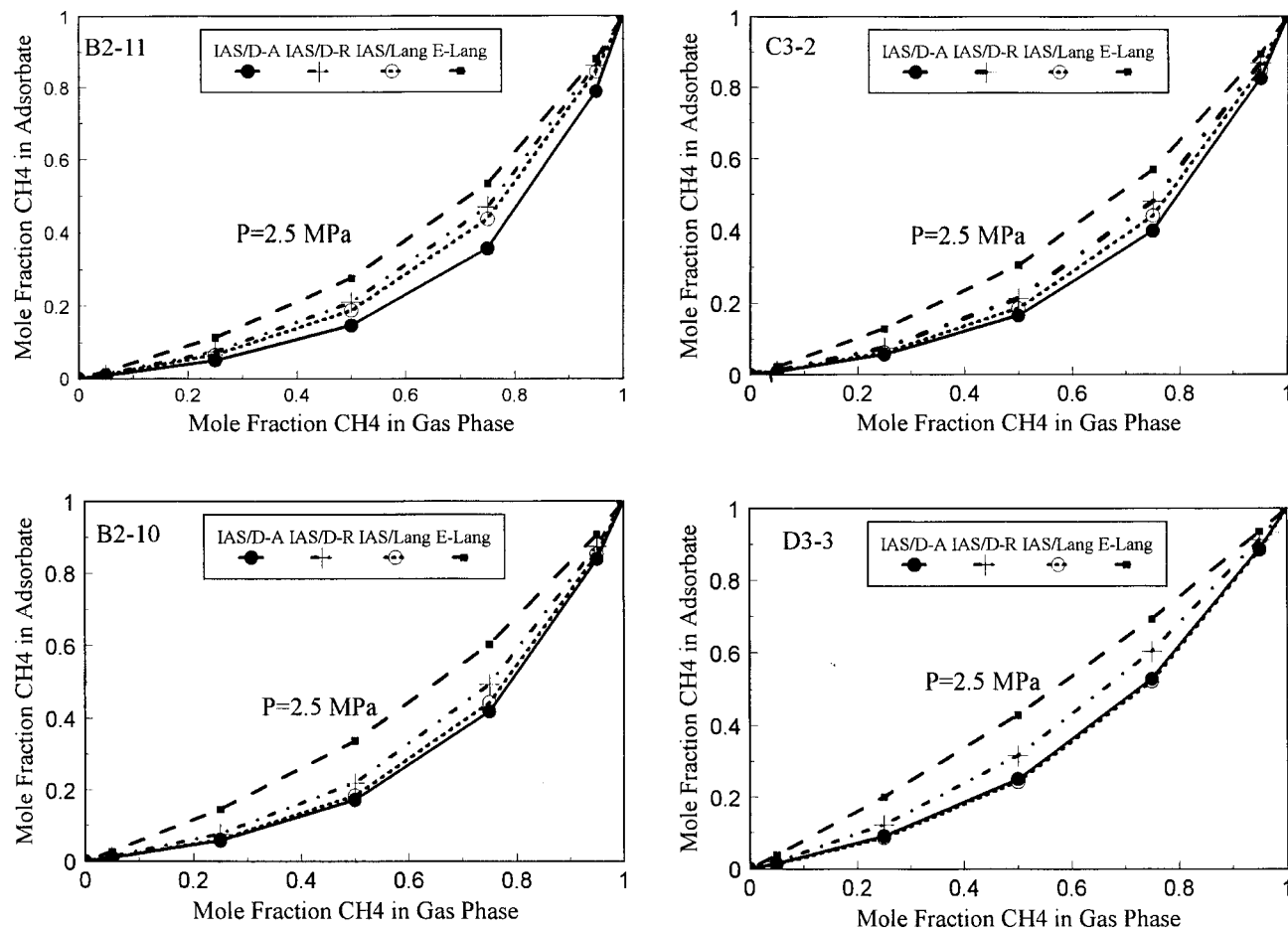


Fig. 7. Predicted equilibrium compositions for moisture-equilibrated – 60 mesh coal binary gas desorption isotherm data.

model consistently predicts a greater adsorbed methane mole fraction than the IAS predictions using the Langmuir (IAS/Langmuir), D–R (IAS/D–R), and D–A equations (IAS/D–A). The IAS/D–R and IAS/Langmuir yield comparable predictions, whereas the IAS/D–A predicts lower adsorbed methane mole fractions. Differences in IAS predictions are likely due to a difference in pure component isotherm curve-fits.

The effect of total gas pressure, moisture content, and coal composition upon binary gas adsorption, as predicted from single-component isotherms, can be illustrated using separation factor (Eq. (3)) plots (Figs. 8 and 9). For purposes of clarity, only three model predictions are shown: the extended Langmuir, IAS/Langmuir, and IAS/D–A. For dry coal, the carbon dioxide separation factor, as determined from IAS theory, is a function of pressure (Fig. 8). The IAS/D–A theory predicts a decrease in carbon dioxide separation factor with an increase in pressure and with carbon dioxide concentration, with the exception of sample D3-3. The trend of decreasing selectivity with an increase in concentration of the more strongly adsorbed component is consistent with previous findings (Myers, 1968). The IAS/Langmuir theory predicts the opposite: carbon dioxide selectivity increases with pressure and gas phase concentration. The extended Langmuir equation gives a constant separation factor, which is independent of total gas pressure and concentration. For moisture-equilibrated coal data (Fig. 9), IAS/D–A, and IAS/Langmuir predictions are similar and separation factors increase with an increase in total pressure, and with an increase in carbon dioxide gas concentration. The carbon dioxide separation factors for moisture-equilibrated coal data are generally smaller than for dry coal data.

Model predictions indicate that the presence of moisture in coal decreases the selectivity for carbon dioxide. Water competes with both gases for adsorption sites, and apparently occupies the higher energy sites that would otherwise be occupied by carbon dioxide if the coal was dry.

The effect of coal composition upon carbon dioxide selectivity, as determined from model predictions, is not as clear. Although some variability between coals exists, there is no clear relationship between coal composition and carbon dioxide selectivity, particularly for dry coal (Fig. 8). For the wet coals (Fig. 9), the bright (C3-2) and banded bright (B2-11) coals have higher carbon dioxide selectivities than the dull coals (B2-10 and D3-3), despite having a higher moisture content (Table 1). The difference in selectivities is minor, however.

3.4. Experimental binary gas desorption isotherms

Binary gas desorption (303 K) isotherms for two feed gas compositions (90% CH₄/10% CO₂ and 75% CH₄/25% CO₂) illustrate similar trends with coal composition as found with pure gas isotherms (Fig. 10). The total adsorbed gas volumes are greater for the bright and banded bright coals than for the two dull coals. If the results are plotted on a daf basis (Fig. 11), there is less of a discrepancy between isotherms (as was observed for pure component isotherm data). Although a relationship between coal maceral composition and gas adsorption appears to exist, this relationship is not simply one of increasing gas adsorption with increasing total vitrinite content. Inertinite macerals such as semifusinite may also contribute greatly to the adsorption capacity of

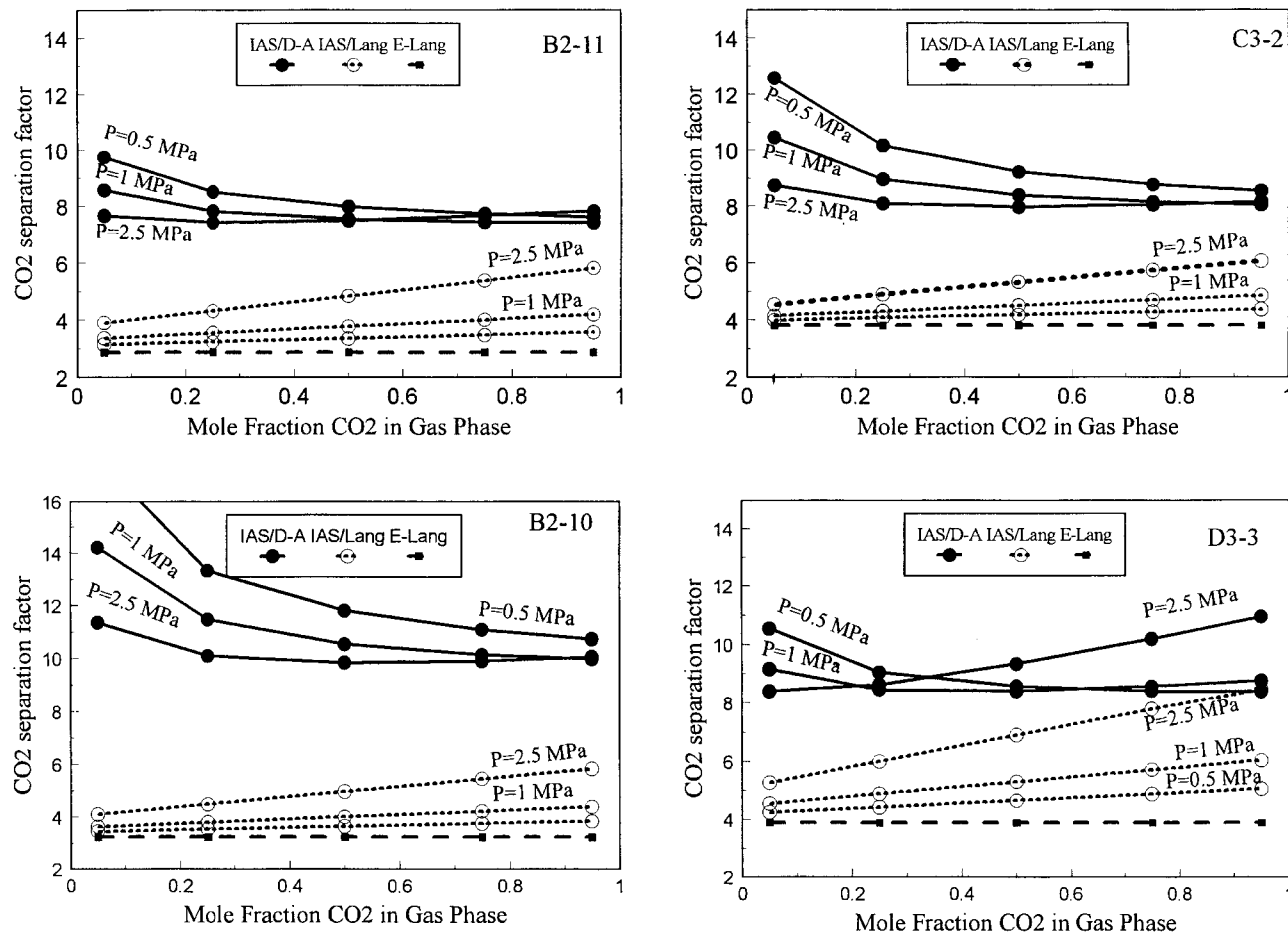


Fig. 8. Predicted carbon dioxide separation factors for dry – 4 mesh coal binary gas adsorption isotherm data.

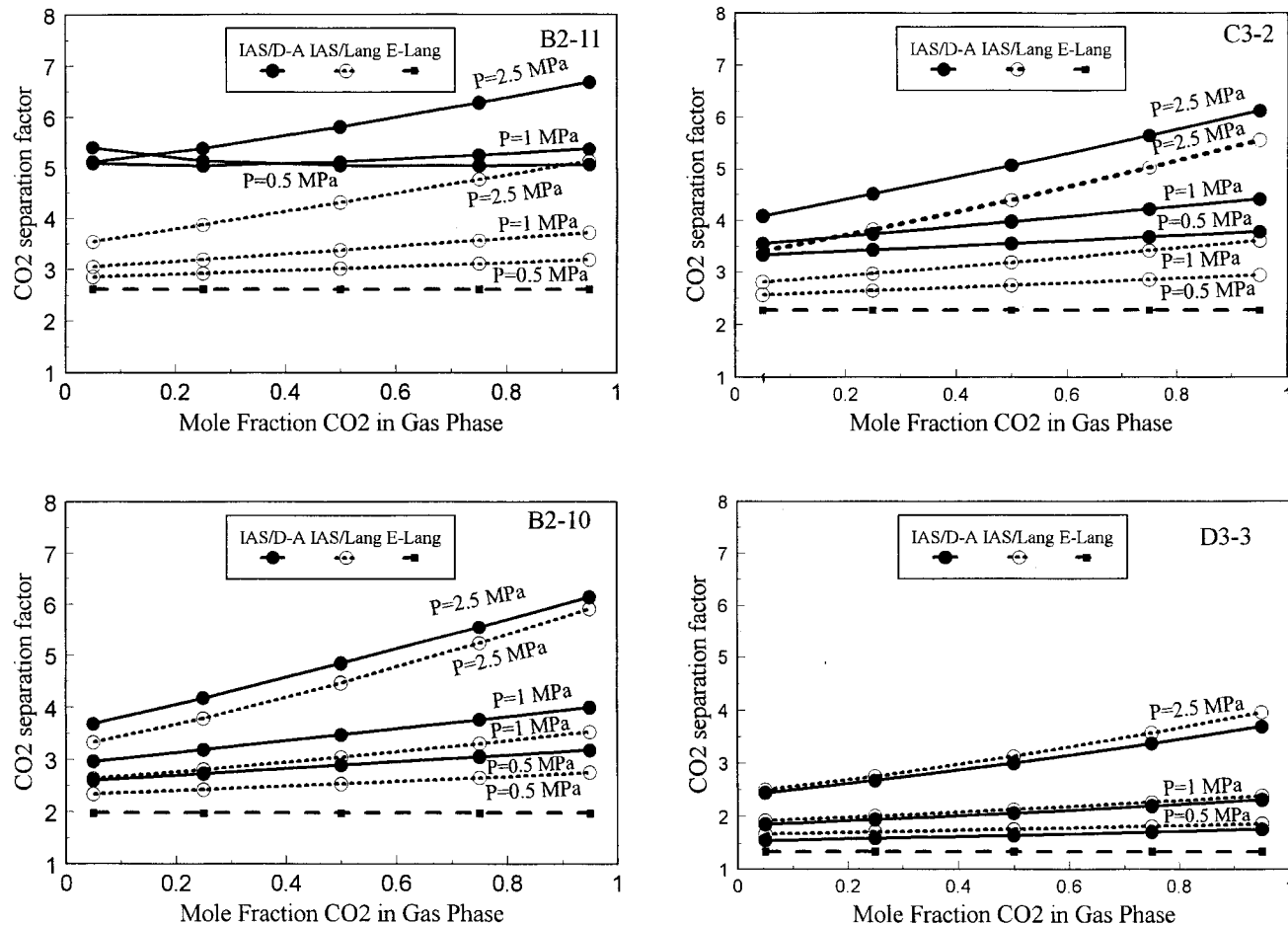


Fig. 9. Predicted carbon dioxide separation factors for moisture-equilibrated –60 mesh coal binary gas desorption isotherm data. Note scale change from Fig. 8.

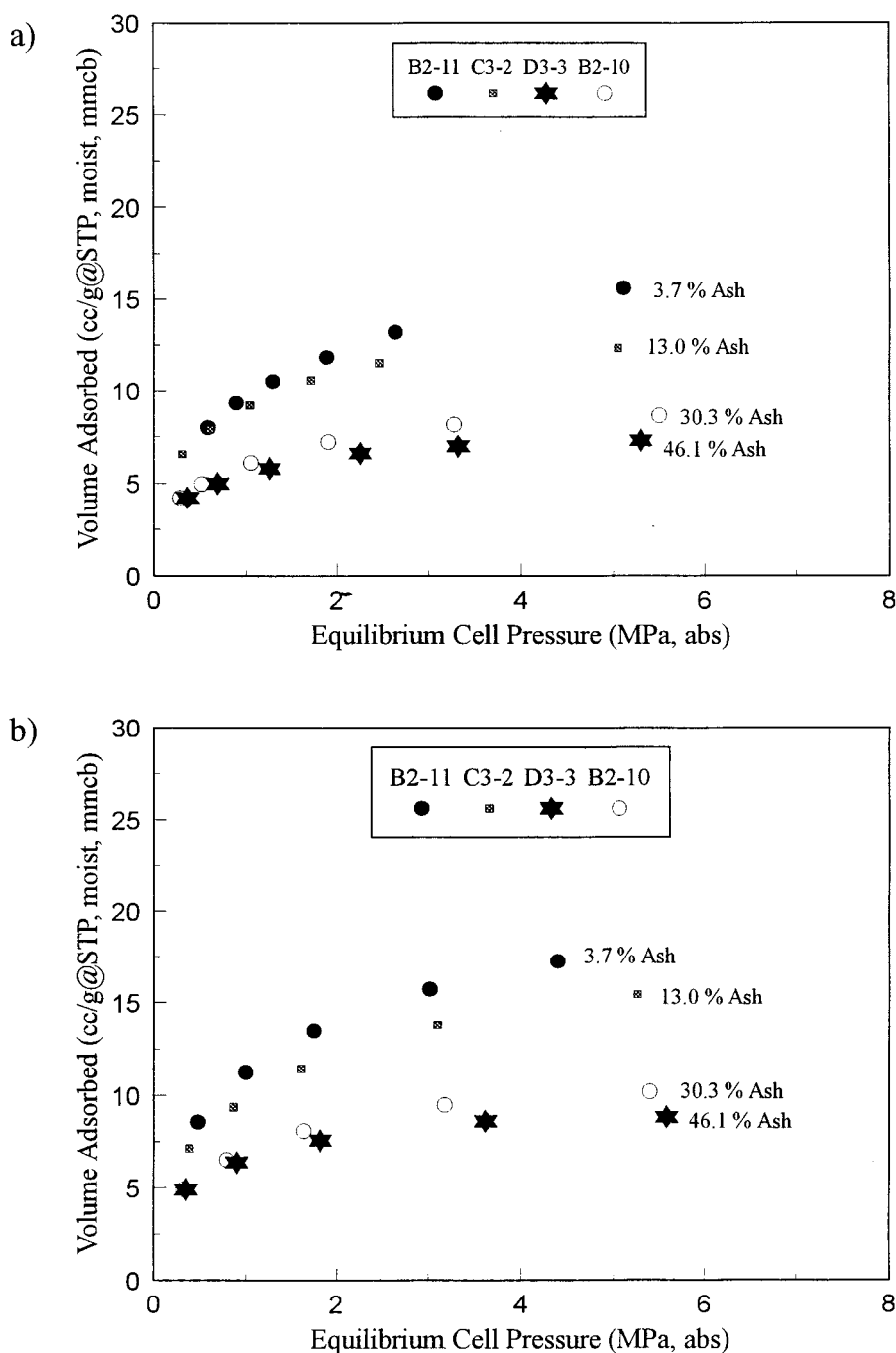
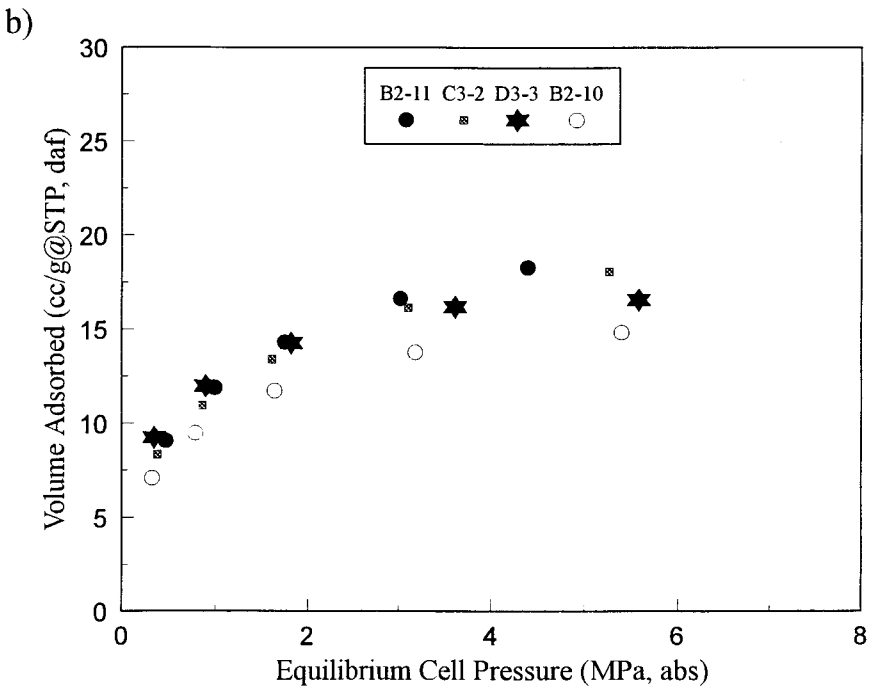
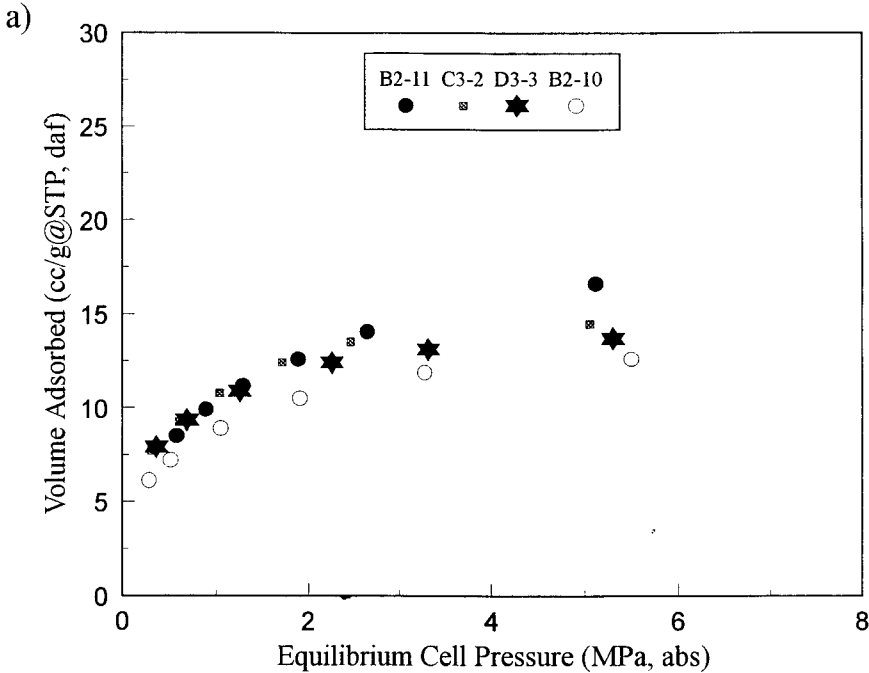


Fig. 10. (a) 90% Methane/10% carbon dioxide and (b) 75% methane/25% carbon dioxide total desorption isotherms for moisture-equilibrated – 60 mesh coals. Results presented on a moisture-equilibrated, mmcb coal basis. Ash contents (dry) are indicated.



coals (Lamberson and Bustin, 1993); the highest-adsorbing coal in this study (B2-11) contains a mixture of vitrinite and semifusinite macerals. This coal also has the greatest amount of microporosity (Clarkson, 1998).

Component adsorption isotherms (Fig. 12) demonstrate that methane is preferentially released at higher pressures during desorption; thus, the methane-adsorbed phase mole fraction decreases with a decrease in total gas pressure. For the 90% CH₄/10% CO₂ (feedgas) isotherm, significant carbon dioxide desorption occurs only at relatively low pressure. Greaves et al. (1993), who studied binary gas adsorption/desorption on dry coal, observed a similar retention of carbon dioxide until low pressures. As suggested by those authors, economic assessments must take into consideration the relative adsorption of component gases for the accurate prediction of economic gas (methane) reserves.

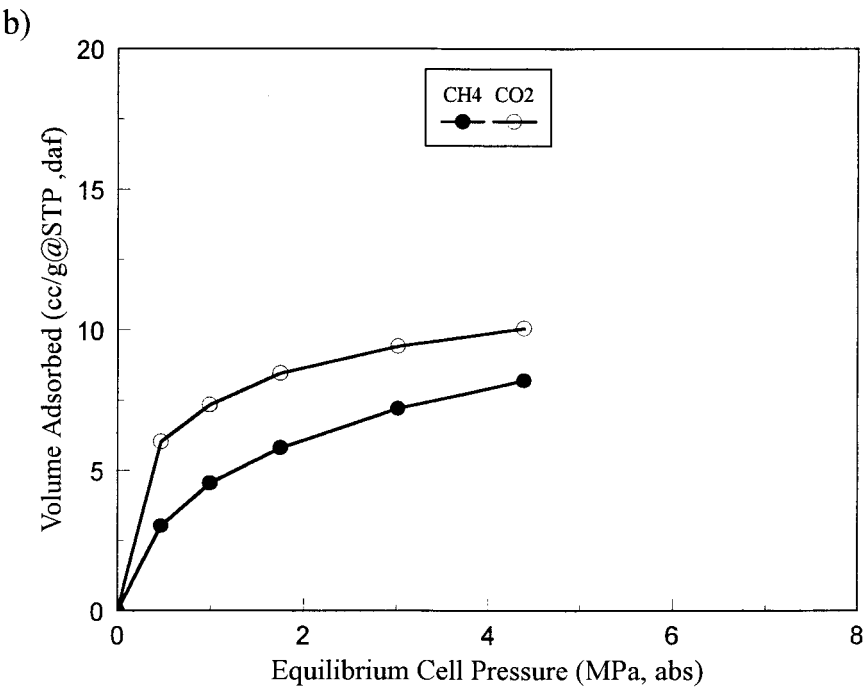
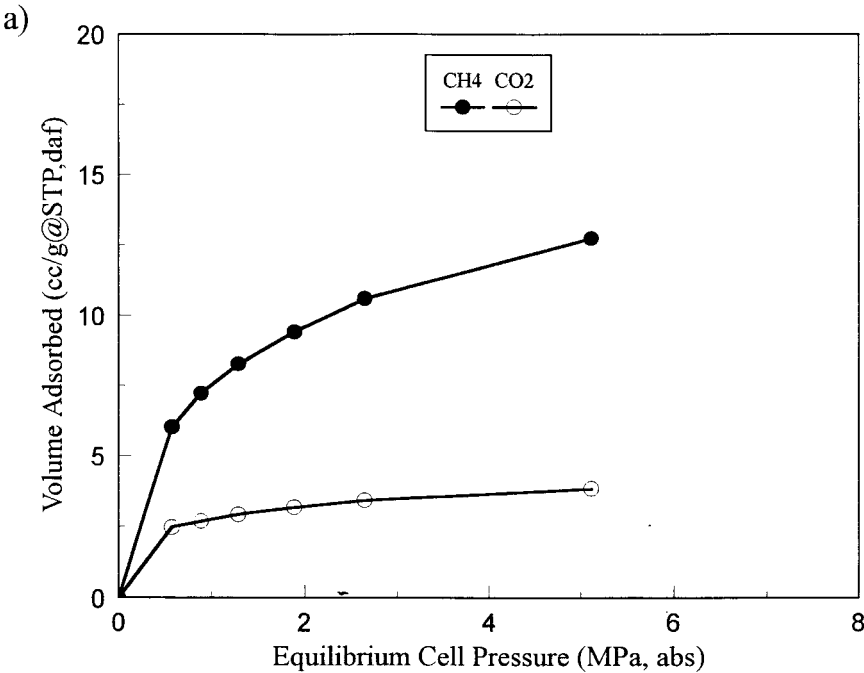
CO₂ separation factors for the 75% CH₄/25% CO₂ (feedgas) desorption isotherm are plotted against gas composition in Fig. 13. The separation factors decrease with an increase in the CO₂ gas phase mole fraction. Separation factors determined from 90% CH₄/10% CO₂ (feedgas) desorption isotherm also generally decrease with CO₂ gas phase mole fraction (not shown). Although there is some variability between coals, the difference in carbon dioxide selectivities is probably not significant based upon a 10% experimental error in each component. Model predictions from pure component data suggest that coal moisture content is a control upon carbon dioxide selectivity. Because the coals studied vary in moisture content as well as organic composition and mineral content, the control of these factors upon gas selectivity is difficult to isolate with the current binary gas data set. It appears, however, that although coal bulk composition and organic matter composition are important controls upon the adsorbed volume of each component, the selectivity of carbon dioxide over methane is not significantly affected.

3.5. Binary gas model fits to experimental data

The extended Langmuir model and IAS theory were used to predict the binary gas adsorption data of sample B2-11, the purest (lowest ash) coal in the current data set. In addition, the data of Hall et al. (1994) were used for model comparison, as the Hall et al. (1994) data span a much greater range of gas compositions than the current data set. Only the binary gas data at total pressures less than ~ 5.5 MPa of Hall et al. (1994) were used to facilitate comparison with the current data set.

Table 3 contains the relative error estimates of each model for sample B2-11 total gas, methane, and carbon dioxide adsorption. For total gas adsorption, the IAS models are slightly more accurate than the extended Langmuir equation. The IAS models are also generally superior for component adsorption, particularly for the 75% CH₄ isotherm. Of the IAS models, the IAS/D–A provides a better fit than all other models for the 75% isotherm.

Relative error estimates for the binary gas data of Hall et al. (1994) (Table 4) are quite variable, and depend upon the feed gas composition. Relative errors for total gas



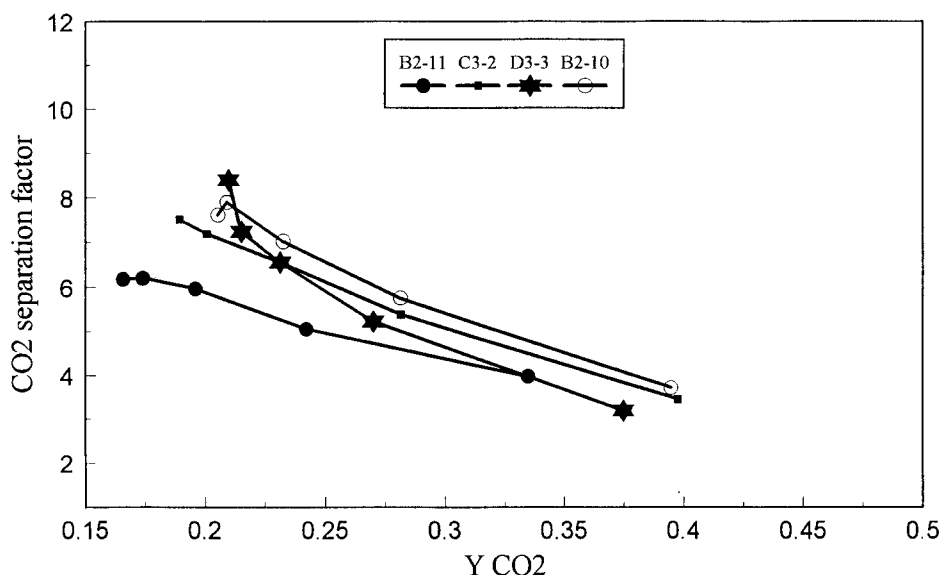


Fig. 13. Experimental carbon dioxide separation factors for moisture-equilibrated –60 mesh coal 75% methane/25% carbon dioxide desorption isotherm data. Note system is not at constant pressure.

adsorption are comparable for the extended Langmuir and IAS models, but are variable for the single-component adsorption. Surprisingly, the extended Langmuir and the IAS/Langmuir models provide, on average, a better fit to component data than the IAS/D–R and IAS/D–A models. This is despite the fact that the D–A and D–R equations fit the pure component isotherms better than the Langmuir equation. A possible cause of the poorer curve fits of the IAS/D–A and IAS/D–R for component adsorption is the error introduced in the spreading pressure calculation due to the incorrect limit expressed by Eq. (9). This potential source of error could be tested by the application of modifications of the Dubinin equations, as proposed by Kapoor et al. (1989), to give the correct Henry's law limit. The modification suggested by Kapoor et al. (1989), however, involves the addition of two extra parameters for each Dubinin equation, giving a total of four and five adjustable parameters for the D–R and D–A equations, respectively.

Model predictions for the variation of carbon dioxide selectivity with gas concentration also differ (Fig. 14). The experimental results of Hall et al. (1994) show that the carbon dioxide selectivity for each isotherm slightly decreases with an increase in carbon dioxide gas phase mole fraction or partial pressure. The IAS/D–A model is the only model to at least qualitatively predict the experimental trend in carbon dioxide selectivity, despite predicting a higher selectivity than the other models. The extended Langmuir model predicts a constant carbon dioxide separation factor, which is not

Fig. 12. Sample B2-11 component desorption isotherms for (a) 90% methane/10% carbon dioxide and (b) 75% methane/25% carbon dioxide gas mixtures. Results presented on a daf basis.

Table 3

Relative error^a calculations for binary gas isotherm fits

Sample	Extended Langmuir			IAS/Langmuir			IAS/D–R			IAS/D–A		
	V_{total}	V_{CH_4}	V_{CO_2}	V_{total}	V_{CH_4}	V_{CO_2}	V_{total}	V_{CH_4}	V_{CO_2}	V_{total}	V_{CH_4}	V_{CO_2}
<i>90% CH₄ / 10% CO₂ (feedgas) isotherm (six data points)</i>												
B2-11	9%	5%	30%	8%	6%	13%	8%	2%	24%	7%	16%	19%
<i>75% CH₄ / 25% CO₂ (feedgas) isotherm (five data points)</i>												
B2-11	11%	28%	38%	9%	14%	25%	9%	25%	32%	7%	7%	8%

^aAverage relative error = $(100/N) \sum_{j=1}^N \text{abs}(V_{\text{calc}} - V_{\text{exp}})_j / V_{\text{exp}}$, where N = number of data points.

consistent with the experimental data. The IAS/D–R and IAS/Langmuir models both predict an increase in CO₂ selectivity with an increase in partial pressure, which is also in disagreement with the experimental data. The variability of carbon dioxide selectivity with gas composition and pressure for the Hall et al. (1994) data set is quite small, but in systems where the selectivity varies greatly, the incorrect selectivity predictions by the IAS and extended Langmuir models could lead to serious errors in predictions of binary gas adsorption/desorption.

3.6. Implications for carbon dioxide sequestering and reservoir characterization

Mixed gas desorption isotherms collected using realistic initial feedgas compositions and pressures are an important tool for the accurate prediction of gas storage capacities, which are in turn used for economic assessment of gas reservoirs. Experimental results for moisture-equilibrated coal in the current study have demonstrated that the adsorbed phase methane mole fraction generally decreases with total gas pressure, which is consistent with previous studies of dry coal/binary gas systems (Greaves et al., 1993).

Table 4

Relative error^a (absolute average percentage deviation) calculations for Hall et al. (1994) binary gas isotherm fits. The terminology of Hall et al. (1994) is retained

Langmuir			IAS/Langmuir			IAS/D–R			IAS/D–A		
ω	ω_1	ω_2	ω	ω_1	ω_2	ω	ω_1	ω_2	ω	ω_1	ω_2
<i>20% CH₄ (1) / 80% CO₂ (2) (feedgas) isotherm (five data points)</i>											
4%	20%	3%	4%	13%	5%	4%	17%	5%	3%	21%	5%
<i>40% CH₄ (1) / 60% CO₂ (2) (feedgas) isotherm (five data points)</i>											
7%	17%	6%	8%	13%	10%	8%	16%	10%	7%	18%	14%
<i>60% CH₄ (1) / 40% CO₂ (2) (feedgas) isotherm (five data points)</i>											
4%	13%	6%	5%	7%	9%	5%	11%	10%	4%	14%	15%
<i>80% CH₄ (1) / 20% CO₂ (2) (feedgas) isotherm (five data points)</i>											
3%	6%	11%	4%	6%	16%	3%	7%	17%	3%	10%	27%

^aAverage relative error = $(100/N) \sum_{j=1}^N \text{abs}(\omega_{\text{calc}} - \omega_{\text{exp}})_j / \omega_{\text{exp}}$, where N = number of data points.

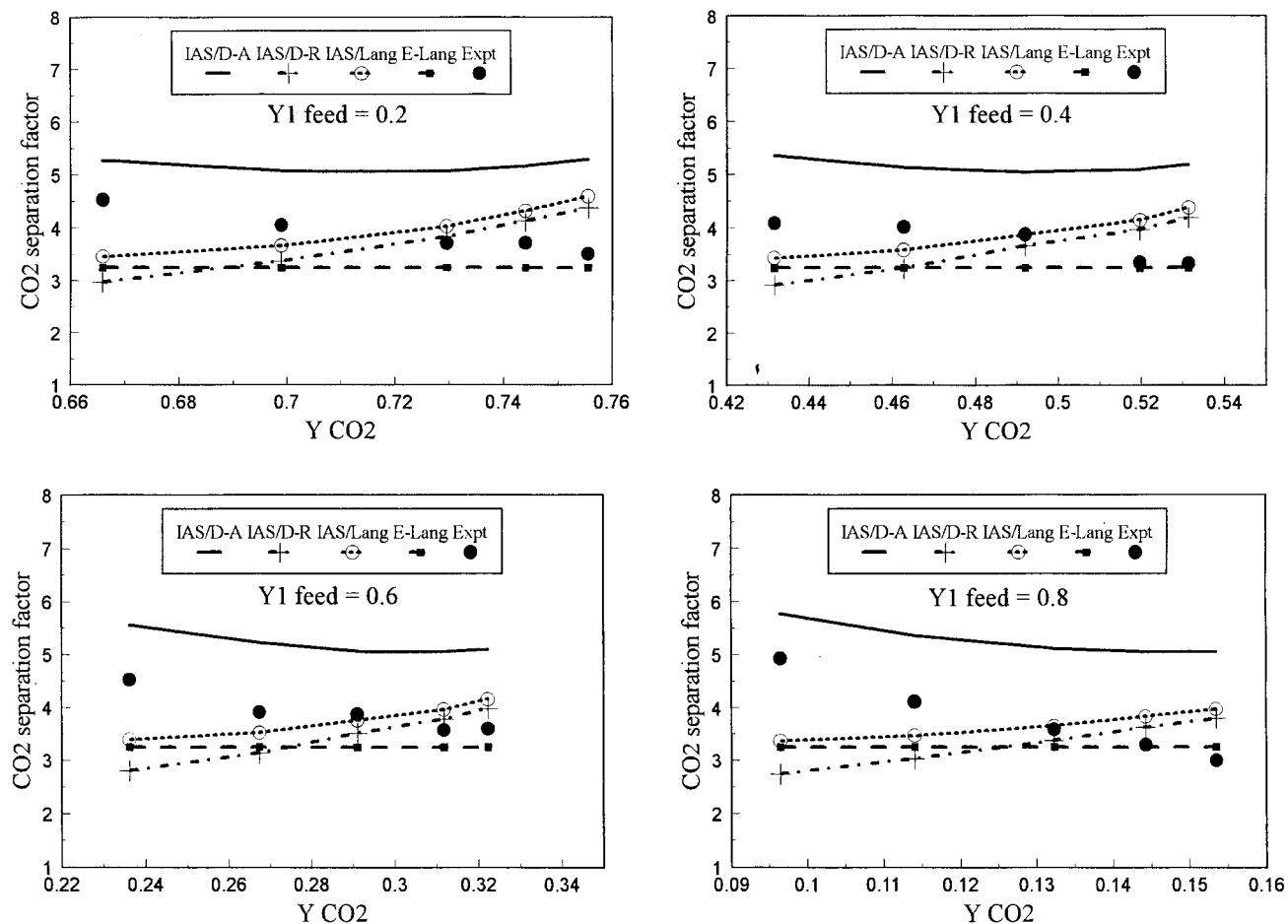


Fig. 14. Experimental and predicted carbon dioxide separation factors for moisture-equilibrated coal adsorption isotherm data. Note system is not at constant pressure. Data from Hall et al. (1994).

Carbon dioxide selective adsorption over methane is an important coal characteristic that will have important implications for the success of any enhanced recovery project involving carbon dioxide injection. The current study has demonstrated that CO₂ selectivity is a function of moisture content and total gas pressure. The relative insensitivity of CO₂ selectivity to coal composition should simplify recovery predictions in regions where coal seams are highly heterogeneous with respect to organic and mineral content. Complicating predictions, however, is the fact that selectivity is a function of carbon dioxide concentration and total gas pressure. In addition, selectivity is a function of coal moisture content, and therefore an accurate estimate of in situ coal matrix water content is required for the accurate prediction of binary gas adsorption.

Models used for binary gas adsorption differ in their ability to predict carbon dioxide selectivity trends with reservoir pressure. If the selectivity varies strongly with pressure for a particular coal composition or rank, the extended Langmuir model may not be adequate for binary gas adsorption predictions. The poor fit of the Langmuir isotherm to pure gas adsorption isotherms for some coal/gas systems, such as for dry coals used in the current study, could lead to inaccurate extended Langmuir predictions for binary gas adsorption.

4. Conclusions

The effect of coal composition and moisture content upon binary gas adsorption, as well as the effect of various single-component isotherm equations upon binary gas predictions, was investigated. The following conclusions are drawn.

(1) The Dubinin–Astakhov and Dubinin–Radushkevich equations are clearly superior to the Langmuir equation for fitting methane and carbon dioxide pure component isotherm data, particularly for dry coals. This conclusion is based on curve-fitting of dry and moisture-equilibrated Gates Formation coal isotherm data, as well as for moisture-equilibrated coal data of Hall et al. (1994). The Langmuir curve-fit errors are much larger for dry coal than for moisture-equilibrated coal data.

(2) IAS and extended Langmuir predictions using pure component isotherm data show that although some variability in carbon dioxide selectivities exists for different coal types, there is no clear relationship between coal composition and carbon dioxide selectivity.

(3) IAS and extended Langmuir predictions using pure component dry coal adsorption isotherm data and moisture-equilibrated coal desorption isotherm data suggest that carbon dioxide selectivity is greater for dry coals than for moisture-equilibrated coals.

(4) Predicted equilibrium compositional diagrams illustrate a large discrepancy between the IAS models and the extended Langmuir model. The IAS models typically predict lower methane-adsorbed phase concentrations at a given pressure than the extended Langmuir model. Only the IAS/D–A predicts a decrease in carbon dioxide selectivity with increasing carbon dioxide concentration for dry coal data, which is in agreement with experimental findings. The IAS/D–R and IAS/Langmuir models both predict an increase in carbon dioxide selectivity with carbon dioxide concentration. The discrepancy between IAS models is likely a result of pure component isotherm curve-fit errors. The extended Langmuir model predicts a constant selectivity.

(5) Experimental binary gas adsorption data demonstrate that total gas adsorption is affected by coal composition. A slight variation in selectivity exists between coal types, but the variation is not large and is difficult to separate from the effect of varying coal moisture content.

(6) Methane-adsorbed phase concentration decreases with pressure for the moisture-equilibrated coal/binary gas desorption isotherms in agreement with previous studies of dry coal.

(7) IAS models are generally more accurate for both total gas adsorption and component adsorption than the extended-Langmuir model for the current experimental binary gas adsorption data set. IAS predictions for the Hall et al. (1994) binary gas adsorption data, however, are generally not superior to the extended Langmuir model.

(8) Carbon dioxide selectivities, obtained from the data of Hall et al. (1994), decrease with an increase in carbon dioxide concentration. All model predictions, with the exception of the IAS/D–A model, fail to qualitatively predict this behaviour.

5. Nomenclature

A	Adsorbent surface area
b	Langmuir model constant
D	Constant of D–A or D–R equation
H	Henry's law coefficient
m	Mass
n	Amount adsorbed [mol/g or mmol/g] or D–A equation exponent
n_c	Number of components
n_i°	Amount of pure component adsorbed from pure gas at the same temperature and spreading pressure as the adsorbed mixture
n_t	Total amount adsorbed
P	Total pressure
P_i	Partial pressure of component i
P_i°	Gas (vapour) pressure of the pure component adsorbed at the same temperature and spreading pressure as the solution
P_o	Adsorbate saturation vapour pressure
R	Gas constant: 8.3145 [J/mol K]
T	Temperature
V	Volume or volume adsorbed at STP
V_L	Langmuir isotherm adsorption constant
V_o	D–A or D–R micropore capacity
x_i	Adsorbed phase mole fraction of component i
y_i	Gas phase mole fraction of component i
<i>Subscripts</i>	
ads	Adsorbed
c	Coal
i	Component i

L	Langmuir
<i>m</i>	Molar quantity
ref	Reference cell
s	Adsorbate
sc	Sample cell
STD	Standard conditions
v	Voids
<i>z</i>	Gas compressibility factor

Superscripts

<i>I</i>	Current pressure step
<i>I</i> – 1	Previous pressure step

Greek symbols

α	Separation factor or selectivity ratio, Eq. (3)
π	Spreading pressure
π^*	Reduced spreading pressure, Eq. (5)

Acknowledgements

Financial support for this study was provided by NSERC grant A-7337 to R.M. Bustin.

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