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# Hydrated Cement Paste – Thermodynamics of Length Change

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# **Hydrated Cement Paste – Thermodynamics of Length Change**

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## **Abstract**

The length change behavior of microporous cement hydrates exposed to both methanol and water vapor is described in thermodynamic terms and is correlated with the elastic and adsorptive properties of the adsorbent. The approach assumes that both the adsorbate and adsorbent can each exist separately in equilibrium with externally applied forces in states that are thermodynamically identical with their states in the combined adsorbate-adsorbent system. Estimates of the compressibility of the solid hydrates using scanning curves obtained from methanol adsorption isotherms are similar to those obtained from reconstructed ‘reversible’ water adsorption isotherms satisfying the requirement for thermodynamic reversibility. Calculations of the modulus of elasticity as a function of the equilibrium partial pressure of both methanol and water adsorbates are in agreement with measured values. Differences in the role of water and methanol in the elastic response of the hydrated cement matrix are discussed.

## **Introduction**

Water adsorption in hydrated cement systems and the resulting dimensional changes have been studied extensively [1]. Observation of large primary and secondary hysteresis in both the weight change and length change adsorption isotherms indicates that processes other than adsorption are operative [2]. Several authors have described the C-S-H products in hydrated cement as poorly crystalline layered silicates [3]. Hysteresis in the

adsorption isotherm is attributable to the irreversible nature of the intercalation effects. It has been shown however that it is possible to separate the 'reversible' and 'irreversible' effects using 'scanning' curves to construct the associated isotherms [2].

There has been limited study of methanol adsorption in hydrated cement systems. The weight change isotherms obtained by Mikhail and Feldman are similar [4,2] and exhibit low pressure hysteresis of the same magnitude. The isotherm is very flat after significant adsorption at very low pressures. The results approximate a Langmuir isotherm. The length change results obtained by Feldman also show marked irreversibility. The length change isotherm for methanol adsorption is very similar to the 'irreversible' construct isotherm for water. Typical weight change and length change isotherms for water and methanol adsorption in cement paste are plotted in Figure 1.

The application of the Flood-Heyding (F-H) thermodynamic approach (utilizing reversibly constructed water adsorption isotherms) to hydrated cement paste has been demonstrated to be an excellent method of predicting length change behavior due to sorption [6]. In addition the elastic sensitivity of the adsorbent (e.g. compressibility, modulus of elasticity, structural factors) predicted by the F-H theory correspond well with experimental measurements. It was of interest to determine if the F-H approach was applicable to adsorption of other adsorbates in hydrated cement systems e.g. methanol. Further insight on the effect of adsorption on the elastic properties of the solid adsorbent was envisaged. An analysis of the data from methanol adsorption isotherms was conducted with a view to providing additional evidence for the role of the intercalate on the dimensional stability of C-S-H. A comparison of the effects of methanol and water adsorption and their interaction with the solid adsorbent was undertaken.

## F-H analysis

The F-H approach was employed to analyze and predict the length change response of hydrated cement paste exposed to methanol vapor at various partial pressures. The elastic sensitivity of the solids to methanol adsorption was compared to that for water adsorption [5]. The basic assumption is that assemblies of volumes of the pure adsorbent can each exist separately in equilibrium with external applied forces in states that are thermodynamically identical with their states in the adsorbent-adsorbate system. It is then theoretically possible to correlate this change in state of stress with the elastic constants of the pure adsorbent and with its dimensional change. The following expression for the pressure of the pure adsorbate,  $p_a$ , in the pore volume,  $V_a$ , is derived from the conditions of reversibility and equilibrium.

$$p_a = \int_0^{p_1} \frac{\rho_a}{\rho_1} dp_1 = \overline{\rho_a / \rho_1} \cdot p_1 = \alpha p_1 \quad (1)$$

where  $\rho_a$  is the mean density of the substance in  $V_a$ , and  $p_1$  and  $\rho_1$  are the gas pressure and density of the gas surrounding the sample. The term,  $\alpha$ , is the mean value of  $\rho_a / \rho_1$  averaged over the pressure interval  $dp_1$ . The pressure on the solid adsorbent in equilibrium with the surrounding gas at pressure  $p_1$  can be expressed as  $p_s = (1 + \phi - \alpha\phi)p_1$ , where  $\phi = V_a / V_s$  and  $V_s$  is the non-porous solid volume.

The length change isotherm (for uniform pressure on the solid adsorbent) can be obtained from the equation:

$$\Delta l/l = \frac{1}{3} \beta (1 + \phi - \phi \alpha) dp_1 \quad (2)$$

where  $\beta$  is the compressibility of the porous body.

A small numerical factor,  $K$ , is introduced into equation (2) when solid pressures are not constant i.e. the term in brackets becomes  $(1 + \phi K - \phi K \alpha)$ .  $K$ , the ratio of the linear average pressures to volumetric average pressures, is a characteristic of the structure of the adsorbent and generally independent of the nature of the adsorbate. Flood and Heyding found that  $K$  varied from 1.0 to 5.6 depending on the nature of the pore system. For large adsorptions  $\alpha \gg 1$  and

$$\delta l/l = \frac{1}{3} \beta \phi K dp_a \quad (3)$$

i.e.  $\delta l/l$  becomes proportional to  $\int_0^{p_1} \rho_a/\rho_1 . dp_1$

### **Application of the F-H procedure to methanol adsorption on cement paste**

The F-H procedure was applied to the methanol adsorption isotherm obtained by

Feldman [2]. It was first necessary to evaluate the integral  $\int_0^{p_1} \rho_a/\rho_1 . dp_1$  in order to apply

equation (3) to the cement paste system. The specimens comprised well hydrated

Portland cement paste (water/cement=0.50) moist cured for several years. The following parameters were utilized in order to determine  $\rho_a$  from the isotherm: porosity of cement paste = 26% ;  $\phi = V_a/V_s = 0.351$ ; C-S-H density = 2.20 g/cc; mass/volume of porous sample =  $2.20 \times 0.74 = 1.63$  g/cc or 1g of porous sample =  $1/1.63 = 0.610$ cc.

It follows that  $V_a/\text{g of sample} = 0.260 \times 0.610 = 0.160$ cc and  $\rho_a = \Delta w/w/V_a = 6.26 \Delta w/w$

Where  $\Delta w/w$  is the weight change per unit weight of sample. The mass of gas in the void volume,  $V_a$ , is negligible in relation to the mass in the adsorbed phase. The density of the gas (methanol vapor),  $\rho_1$ , is  $17.4 \times 10^{-5}$  g/cc at  $21.2^\circ \text{C}$  under saturated conditions.

A plot of  $\rho_a/\rho_1$  versus  $p_1$  is given in Figure 2. Graphical integration of this plot facilitates the calculation of  $\beta K$  and the length change of the cement paste due to the adsorption of methanol. The following section reports the results of the application of the F-H procedure to the methanol adsorption isotherm and addresses the similarities and differences in the length change response due to adsorption of methanol and water.

## **F-H analysis**

The application of the F-H analysis to the methanol-cement paste adsorption isotherm is described in this section. The significance of the  $\beta K$  parameter and the elastic sensitivity of cement paste systems containing methanol and water is also discussed.

It is first necessary to construct the 'reversible' weight and length change isotherms for methanol adsorption utilizing the scanning curves depicted in Figure 1. This procedure was employed by Feldman for the water isotherm which exhibited marked hysteresis [2].



The ‘reversible’ weight change isotherm for methanol adsorption is plotted in Figure 3 and the data for both length and weight change ‘reversible’ isotherms is tabulated in Table 1. Adsorption is reversible in the region of partial pressure up to  $p/p_0 = 0.30$ . Hysteresis occurs at higher partial pressures due to capillary condensation effects. The integral in equation (1) was evaluated by graphically integrating the plot of  $\rho_a/\rho_1$  versus  $p_1$  shown in Figure 2. This provided a means of estimating the adsorbate pressure or  $\alpha p_1$  and the compressibility product  $\beta K$ . Values of these parameters are also given in Table 1.

### **Length change and the compressibility product $\beta K$**

The adsorption branch of the ‘reversible’ length change isotherm is plotted in Figure 4. There is excellent agreement with the calculations resulting from the application of equation (3) when an average value of  $\beta K = 1.81 \times 10^{-4} \text{ MPa}^{-1}$  is used. This is close to the value of  $1.76 \times 10^{-4} \text{ MPa}^{-1}$  obtained with water as an adsorbate. In general,  $K$ , should be more or less independent of the nature of the adsorbate but a characteristic of the structure of the adsorbent and the nature of the surface forces involved in adsorption. This assumption appears to be valid for the cement paste-water and cement paste-methanol systems as evidenced by the similarities in the average value of  $\beta K$ . It is however important to recognize that the ‘reversible’ isotherm is a required construct for the cement paste system.  $K$  is regarded as a structure factor. Recognizing that the slope of the total or primary methanol adsorption curve (in the adsorption region) is relatively small and only slightly greater than the corresponding

slopes of the scanning curves calculations of  $\beta K$  were also performed using data from the ‘total’ adsorption isotherm. The values ranged from  $1.85\text{-}2.00 \times 10^{-4} \text{ MPa}^{-1}$ . It appears that the error in using the adsorption branch of the ‘total’ methanol adsorption isotherm for estimation of the elastic response of the microporous system is relatively small. Equation (3) provides a good fit to the data for an average value of  $\beta K = 1.88 \times 10^{-4} \text{ MPa}^{-1}$ . Changes or perturbations to the solid as a result of methanol adsorption (in this region of the isotherm) are apparently not significant. This is clearly not the case when water is the adsorbate. Analysis of the desorption scanning curves on the adsorption branch of the methanol isotherm result in estimates of  $\beta K$  that range from  $2.03\text{-}2.30 \times 10^{-4} \text{ MPa}^{-1}$ , slightly higher than those values calculated for the primary adsorption curve.

### **Elastic constants**

Values of the compressibility for cement paste,  $\beta$ , can be calculated from the  $\beta K$  values (see Table 1) assuming a value for the structure factor  $K$ . Choice of the value for  $K$  (1.91) gives an initial value of  $\beta$  calculated from the relation  $\beta = 3/E (1-2\nu)$  (where  $\nu$  is Poisson’s ratio = 0.20) as well as  $\beta$  determined by other methods [7].  $E$  is the modulus of elasticity. Values of  $\beta$  and  $E$  are calculated using the values of  $\beta K$  determined from the methanol adsorption isotherm (see Table 2).

Plots of  $\beta K$  and  $E$  versus partial pressure of methanol and water are given in Figure 5.

Values of  $\beta K$  for the water cement-paste system (in the range  $0.10 < p/p_0 < 0.60$ ) decrease

from about  $2.08 \times 10^{-4} \text{MPa}^{-1}$  to  $1.52 \times 10^{-4} \text{MPa}^{-1}$ . Conversely values of  $\beta K$  increase from about 1.65 to  $1.91 \times 10^{-4} \text{MPa}^{-1}$  for the methanol-cement paste system (Figure 5(a)). Two distinct regions separate the curves. These are denoted I and II. The  $\beta K$  values for the system with water as an adsorbate are higher than those for the methanol adsorbate in region I, i.e.  $0.10 < p/p_0 < 0.30$ . This suggests that the water-cement paste system is more compressible at these values of partial pressure. It is further suggested that the lower compressibility for the methanol-cement paste system is a result (at least in part) of intercalation effects, the bulk of which occur at very low values of partial pressure. The intercalation of water into the C-S-H structure is a more gradual and complete process. The compressibility of both cement paste systems is similar at  $p/p_0 = 0.30$  as a sufficient amount of water has entered the interlayer regions resulting in a decrease in compressibility of the water-cement paste system. The  $\beta K$  values for the water and methanol paste systems decrease and increase respectively and monotonically up to this point. Water continues to intercalate into the interlayer regions of cement paste at higher values of partial pressure (region II). Changes in the interlayer penetration of methanol are small in this region although the compressibility of the cement paste continues to increase. The continued increase in compressibility over the entire range of partial pressure may be due (in part) to a chemical interaction of methanol with the cement paste solids [8]. Examination of the weight change isotherms indicates that the volume of methanol adsorbed by the cement paste is significantly less than the volume of water adsorbed. This indicates that the methanol only partially penetrates the interlayer region [2] and that other mechanisms may contribute to increases in compressibility.

The compressibility of the water-cement paste system continues to decrease in region II. This is compatible with results for modulus of elasticity previously reported [6]. Calculated values of modulus of elasticity versus  $p/p_0$  are plotted in Figure 5(b). The trends as expected are the inverse of those for the  $\beta K$  values. Calculated values for the cement-paste water system are in general agreement with those obtained by experiment [2]. Calculated values for the cement-paste-methanol sorption are also similar to that measured by the authors. Values for the latter were determined at partial pressures of methanol equal to 0.11 and 0.98. They were  $1.49$  and  $1.39 \text{ MPa} \times 10^5$  respectively.

## Conclusions

1. The length change behavior of cement paste can be predicted from thermodynamic considerations (Flood-Heyding analysis) of reversible adsorption data for methanol and water adsorbates.
2. ‘Reversible’ isotherms are required for valid length change prediction. These can be constructed using scanning curves on both the adsorption and desorption branches of the isotherm.
3. Estimates of the compressibility,  $\beta$ , and modulus of elasticity,  $E$ , of cement paste and their dependence on the partial pressure of adsorbates can be obtained through application of the Flood-Heyding thermodynamics-based analysis.
4. The assumption that  $K$  (a microstructure descriptor referred to as a structure parameter) should generally be independent of the nature of the adsorbate appears

- to be valid as average values of  $\beta K$  (compressibility product) are similar for both methanol and water adsorbates.
5. Evidence of partial intercalation of methanol into the C-S-H structure in cement paste is provided by the  $\beta K$  versus partial pressure curves. Low compressibility values for cement paste (compared to results for the water adsorbate) at low values of partial pressure are compatible with the rapid adsorption of methanol in this pressure region.
  6. The observation that the compressibility of the methanol-cement paste system increases with partial pressure of the adsorbate is consistent with a chemical interaction mechanism involving methanol and the cement paste solids.

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Table 1: Calculation of the compressibility product,  $\beta K$ , from the ‘reversible’ methanol adsorption isotherm.

$p_1$ (MPa $\times 10^3$ )	$p/p_0$ (%)	$\Delta W/W$ (%)	$\Delta l/l$ (%)	$\alpha p_1 \times 10^{-2}$ (MPa)	$1/3\phi\alpha p_1$ $\times 10^{-2}$ (MPa)	$\beta K \times 10^{-4}$ (MPa $^{-1}$ )
1.30	10	0.35	0.0065	3.34	0.39	1.65
2.60	20	0.38	0.0095	4.55	0.53	1.78
3.90	30	0.46	0.0110	5.28	0.62	1.76
5.20	40	0.45	0.0115	5.89	0.69	1.67
6.50	50	0.50	0.0140	6.39	0.75	1.89
7.80	60	0.65	0.0155	6.90	0.81	1.91

Table 2: Values of  $\beta$  and  $E$  for cement paste calculated from the reversible methanol adsorption isotherm.

$p/p_0$ (%)	$\beta K \times 10^4$ (MPa $^{-1}$ )	$\beta \times 10^{-4}$ (MPa $^{-1}$ )	$E \times 10^{-5}$ (MPa)
10	1.65	0.86	0.209
20	1.78	0.93	0.191
30	1.76	0.92	0.196
40	1.87	0.87	0.206
50	1.89	0.99	0.181
60	1.91	1.00	0.180

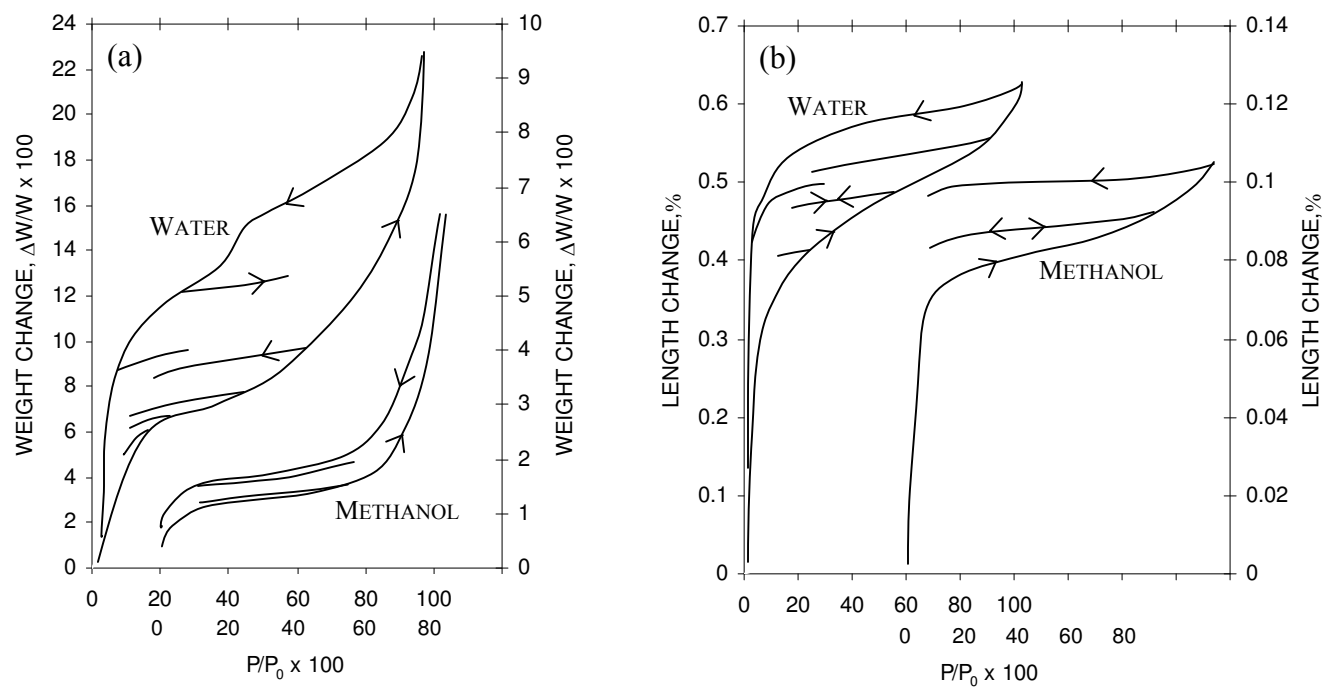


FIG. 1  
Weight change (a) and length change (b) isotherms (with scanning curves) for water and methanol adsorption on cement paste.



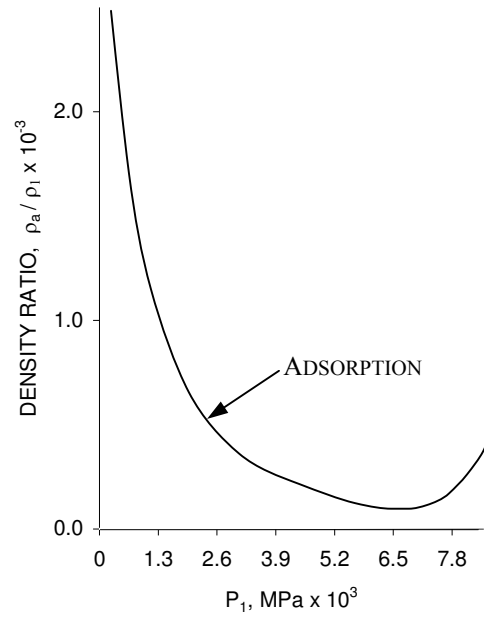


FIG. 2  
Ratio of methanol adsorbate density to gas density versus equilibrium gas pressure – methanol adsorption on cement paste.

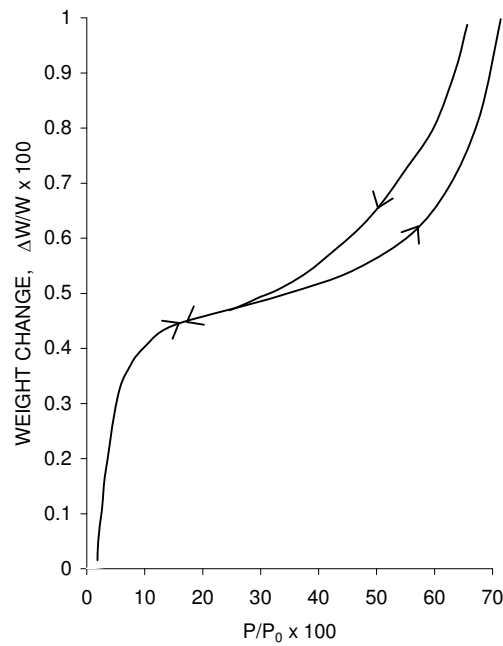


FIG. 3  
The constructed 'reversible' weight change isotherm for methanol adsorption on cement paste.

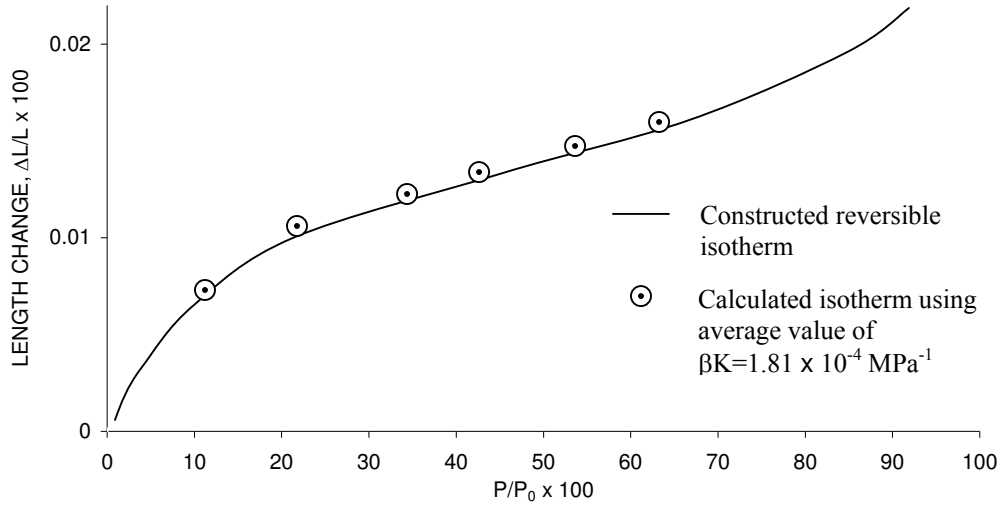


FIG. 4  
Adsorption branch of 'reversible' length change adsorption isotherm for methanol adsorption on cement paste.

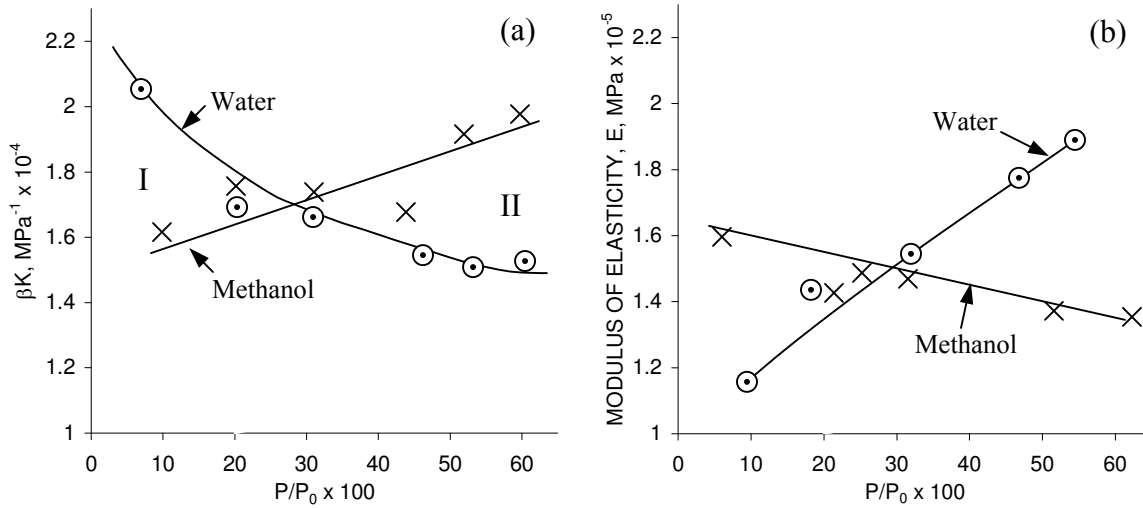


FIG. 5  
The compressibility product,  $\beta K$ , (a) and modulus of elasticity,  $E$ , (b) versus  $P/P_0$  for water and methanol adsorption on cement paste.