Calculation of Osmotic Suctions for Bentonite in Saline Solutions

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Abstract. Bentonites are usually selected as the engineered barrier material of repositories for radioactive waste. The saline solution from surrounding rock fissures can affect the mechanical behaviour of bentonite for the reason that the osmotic suction in pore water can act as an additional total stress component on bentonite. The osmotic coefficient, as the key to calculate the osmotic suction, is usually obtained by measuring the vapor pressure of a solution and that of the pure solvent with a differential manometer in experimental method. Considering that the vapor pressure is affected by many factors such as solute type, concentration, and temperature, it is very complicated to obtain the osmotic coefficient by experimental method. In this paper, the osmotic coefficient is calculated according to the modified Debye-Hückel equations and the calculated results are validated by comparing with the experimental data in other literature. In this way, the osmotic suction for different solutions under different temperatures can be obtained by calculation.

Keywords: Bentonite · Saline solution · Osmotic suction

1 Introduction

Compacted bentonite is widely used as a barrier material for HLW repositories mainly because it has the property of swelling in water to fill the surrounding rock fissures and form an impermeable layer to prevent the emission of nuclear waste into the surrounding environment. The mechanical behaviour may be strongly influenced by physicochemical effects when saline concentrated pore fluids are introduced to clays [1]. The increasing of pore water concentration will weaken the swelling ability of clay [2]. The composition and concentration of the pore water solution can significantly affect the shear strength of bentonite [3]. The influence of pore water on the mechanical behavior of bentonite is mainly due to the reason that osmotic suction from pore water acts as an additional total stress component that favours the reduction in swell potential and the increase in shear strength of the compacted clay specimens [4]. Thus, the quantitative research of the osmotic suctions of different solutions is sig-

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nificant to study the mechanical behavior of bentonite in saline solution. Van't Hoff gives the osmotic suction π related to solution concentration as follows:

$$\pi = \zeta RTm\phi \tag{1}$$

where ζ is the number of ions that the solute can dissociate in solution (e.g., NaCl = 2), R the universal gas constant (8.31 J/mol/K), T the absolute temperature in Kelvin, m the molality of solute (mol/kg) and ϕ the osmotic coefficient given as [5]:

$$\phi = \frac{\rho_{\mathrm{w}}}{\zeta m M_{\mathrm{w}}} \ln\left(\frac{P_w}{P_0}\right) \tag{2}$$

where the M_{w} is the molar mass of water (18.016 g/mol), ρ_{w} the unit weight of water, P_{w} the saturated vapor pressure on the surface of the pore water solution and P_0 the saturated vapor pressure on the surface of the pure water. The osmotic coefficient is usually obtained in experimental method by measuring the vapor pressure of a solution and that of the pure solvent with a differential manometer [6]. Considering that saturated vapor pressure is affected by factors such as solute type, concentration and temperature [5], the experimental method of measuring the saturated vapor pressure to get the osmotic coefficients of different solutions is very complicated and inconvenient for engineering application. In addition, according to the van't Hoff equation, only the osmotic coefficient of a highly diluted solution can be considered as 1. Thus, the difficulty in obtaining osmotic coefficients hinders the calculation of the osmotic suction π. In this paper, a calculation method based on the modified Debye-Hückel equations is found to obtain the osmotic coefficients of different saline solutions, and the calculated results are verified by experimental results from other literature.

2 Calculation of Osmotic Suctions

The osmotic coefficient can be derived by differentiation from the excess free energy theory, which is complicated and inconvenient to calculate [7]. Based on Debye-Hückel equations, Kenneth and Guillermo [8, 9] simplified the determination method of the osmotic coefficients, which is empirically superior to the conventional form. The equation to calculate the osmotic coefficients of single electrolytes MX is as follows:

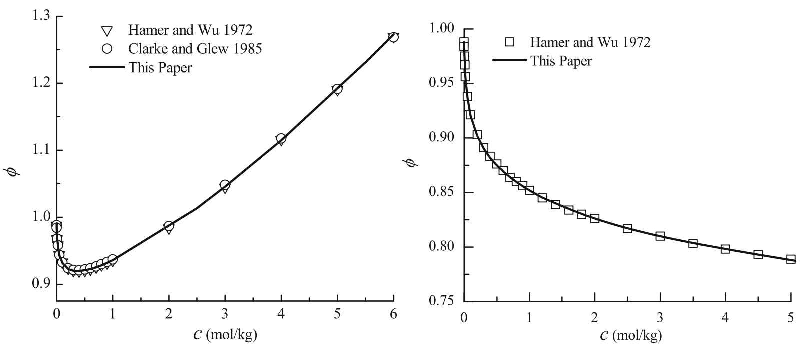
$$\phi = |Z_{\mathrm{M}} Z_{\mathrm{X}}| f^{\phi} + m\left(\frac{2V_{\mathrm{M}} V_{\mathrm{X}}}{V}\right) B_{\mathrm{MX}}^{\phi} + m^2 \frac{2(V_{\mathrm{M}} V_{\mathrm{X}})^{3/2}}{V} C_{\mathrm{MX}}^{\phi} + 1 \tag{3}$$

where V_{M} and V_{X} are the number of M cation and X anion respectively in the chemical formula, $V = V_{\mathrm{M}} + V_{\mathrm{X}}$. Z_{M} and Z_{X} are respective charges, and m is molality. $B_{\mathrm{MX}} = \beta_{\mathrm{MX}}^{(0)} + \beta_{\mathrm{MX}}^{(1)} e^{-\alpha I^{1/2}}$, hereinto, $\beta_{\mathrm{MX}}^{(0)}$, $\beta_{\mathrm{MX}}^{(1)}$ and C_{MX}^{ϕ} are empirical parameters related to the solute type obtained by looking up the table given by Kenneth and Guillermo [9], and α = 2 is found to satisfy most of the common solutes. The f^{ϕ} is given as:

$$f^{\phi} = -A^{\phi}\frac{I^{1/2}}{1 + bI^{1/2}} \tag{4}$$

where I, the ionic strength, equals to $\sum(m_i z_i^2)/2$, b as an empirical parameter is selected 1.2 here and A^{ϕ}, the Debye-Hückel coefficient for the osmotic function has the value of 0.392 for water at 298 K [8]. The osmotic coefficients of $NaNO_3$ and NaCl solute under different concentrations in water are calculated according to the equations above and the results are compared with experimental data from other literature [6, 10] (see Fig. 1). The calculated results are consistent with the experimental results.

For the 2–2 electrolytes solutions, adding a term to B_{MX} would create a better



(a) NaCl solution (b) $NaNO_3$ solution

Fig. 1. Relationship between osmotic coefficient and concentration in water (298 K).

agreement with the experimental results [9]. In this case, B_{MX} has the following form:

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}e^{-\alpha_1 I^{1/2}} + \beta_{MX}^{(2)}e^{-\alpha_2 I^{1/2}} \tag{5}$$

where $\beta_{MX}^{(2)}$ is an empirical parameter related to the solute type, $\alpha_1 = 2$, $\alpha_2 = 1.4$ and other parameters are the same as they are defined in Eq. (3) previously.

The osmotic coefficients of $CaCl_2$ and $Ca(NO_3)_2$ in ethanol at 298 K have also been calculated by using the same method in this paper. Under the same calculation method, the osmotic efficient in ethanol is different from that in the water due to the differences of some parameter values (e.g., $A^{\phi} = 2.006$ for ethanol). The comparison between calculated results and the experimental results from other literature [11, 12] in Fig. 2 indicates that the osmotic coefficients of $CaCl_2$ and Ca $(NO_3)_2$ in ethanol at 298 K calculated from the mentioned method in this paper are in agreement with the experimental ones. Therefore, the calculation method is proved reliable and the osmotic coefficients of other kinds of single electrolytes solutions or double electrolytes in

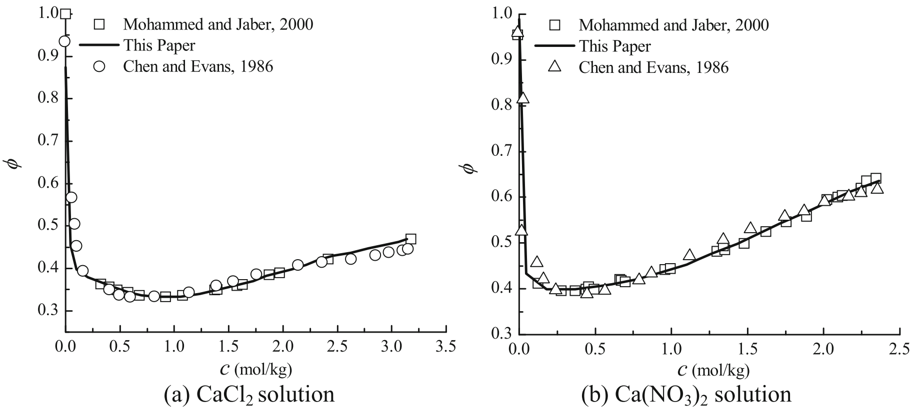


Fig. 2. Relationship between osmotic coefficient and concentration in ethanol (298 K).

different kinds of solutions at different temperatures can be calculated by the modified Debye-Hückel equations.

3 Conclusions

According to the results of this study, the osmotic coefficients that determine the osmotic suction of different solutions are calculated by the modified Debye-Hückel equation, and the correctness of the calculation results has been validated by other literature. Further research about the osmotic suction of mixed saline solution is needed. In addition, some tests, such as obtaining swelling pressure and shear strength for bentonite in saline solution, are still required in order to obtain further calculating of the mechanical behaviour of bentonite in saline solution.

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