An alternative approach to determine suction of aqueous polyethylene glycols for laboratory testing of unsaturated soils

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Determination of suction of Polyethylenglycol (PEG) is vital for unsaturated laboratory testing that use osmotic technique to study the hydro-mechanical behaviour of fine-grained soils. To date, suctions of PEG solutions are either experimentally measured or calculated from established semi-empirical relationships between concentration of PEG and suction. The current paper presents an alternative approach to determine suctions of aqueous PEG solutions based on a modified Flory-Huggins equation. Using the proposed method, suctions of various PEGs can be precisely calculated by knowing the average molar mass, concentration of the solution and an interaction coefficient which represents the quality of PEG-solvent interaction. The suggested method relies on the characteristics and thermodynamical behaviour of PEGs in solution. Experimental data of several PEG-water mixtures reported in the literature were analysed. The superiority of the current approach remains with abilities to verify molar of mass of PEGs and estimate suctions of PEG at high concentrations.

KEYWORDS: Suction, Partial saturation, Laboratory equipment, Laboratory tests

INTRODUCTION

The osmotic technique (Zur, 1966) is commonly used in the laboratory for establishing the water retention curves of fine-grained soils (Williams and Shaykewich, 1969; Fleureau et al., 1993; Delage et al., 1998; Fleureau et al., 2002; Tripathy et al., 2014). The technique has been used to study the hydro-mechanical behaviour of swelling soils by several researchers (Kassiff and Ben Shalom, 1971; Cuisinier and Masrouri, 2005). In an osmotic test, a soil sample is brought in contact with a solution of Polyethylenglycol (PEG) separated by a semipermeable membrane. The suction (osmotic pressure or water potential or osmotic suction) of the polymer in solution, is a measure of the unequal chemical potential between the soil sample and the PEG solution. The chemical potential gradient causes the water to flow through the semipermeable membrane until an equilibrium is reached at which the suction of PEG solution is equal to the suction of the soil sample. During the test soil solids and PEG molecules are retained by the semipermeable membrane. Using the technique, a very high magnitude of suction can be applied within a reasonable time. Studies in the past have shown that suction up to 10 MPa can be applied using the osmotic technique (Delage et al., 1998) that far exceeds the maximum applied suction of 1.5 MPa in pressure plate and pressure membrane tests.

Suctions of PEG solutions can be determined by using various techniques, such as freezing-point depression, membrane osmometry, chilled-mirror dew-point, vapor pressure osmometry, thermocouple psychrometry, vapour equilibrium, osmotic tensiometer, and laser-light scattering (Tripathy and Rees, 2013; Slatter et al., 2000; Delage et al., 1998; Michel and Kaufmann, 1973; Williams and Shaykewich, 1969; Peck and Rabbidge, 1968; Lagerwerff et al., 1961). The measurement accuracies and applicability of some of the techniques have been reported to be poorer at high concentrations and temperatures (Michel and Kaufmann, 1973; Lagerwerff et al., 1961; Hasse et al., 1995).

Michel and Kaufmann (1973), Money (1989), Delage et al. (1998), and Tripathy and Rees (2013) have established relationships between concentration and suction of several PEGs based on the results from various measurement techniques. For quick determination of suctions of PEG solutions, the Brix index values from refractometer measurements have also been used by some researchers (Tripathy and Rees, 2013; Delage et al., 1998). Although much effort has been devoted to measure and predict suctions of PEGs, accuracies of these predictions are limited due to the inadequate consideration of polymer characteristics (i.e. molar mass) (Tripathy et al., 2011; Monroy et al., 2007).

Previous studies have shown very good agreements between results from osmotic, pressure plate, and pressure membrane tests for a variety of soils (Tripathy et al., 2014; Delage and Cui, 2008; Delage et al., 1998; Zur, 1966). Delage et al. (1998) stated that suction measurements in case of PEGs involve vapour phase equilibrium process, whereas the osmotic technique used to impose suction in soils involves the water phase continuity between the soil sample and PEG solution. Therefore, a difference between the imposed and measured suctions in case of soils is related to the osmotic component of the suction. Tripathy et al. (2014) noted that an equilibrium between ion concentration on both sides of the semipermeable membrane may be lacking in case of clays and therefore, the osmotic technique may not always impose the desired matrix suction in soils. The magnitudes of suction imposed in soil samples during osmotic tests and for known applied suctions have been verified by high capacity tensiometer measurements (Delage and Cui, 2008; Monroy et al., 2007; Tarantino and Mongiovi, 2000; Slatter et al., 2000; Dineen and Burland, 1995). These studies have shown that the membrane effect (i.e., interaction between PEG and semi-permeable membrane) generally causes a reduction in suction imposed and it depends

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upon the type of semipermeable membrane and the PEG type used. An assessment of suction imposed in a soil sample requires the suction of the PEG used as a reference and hence correct estimations of suction of PEGs becomes extremely crucial for laboratory testing of unsaturated soils.

The objective of the paper is to introduce an alternative approach for determining suctions of aqueous PEG solutions based on their known properties (molar mass in g/mol and mass ratio of the solution in g PEG/g water) and a single empirical coefficient (Γ). Reported experimental data of several PEG-water mixtures were used to derive Γ and another set of experimental data reported in literature was used to validate the suggested approach.

INTERACTION BETWEEN PEG MOLECULES AND WATER

PEG (HO-$(CH_2CH_2O)_n$-H) (Hasse et al., 1995) is an unbranched and linear polymer made up of repeating units of molecular chain. The molecular chain length of PEG may be varied during the production process, which in turn dictates the molar mass. A representative mean value for chain length is the number average molar mass (M_n). M_n is calculated by dividing the sum of molecular mass of molecules by the number of molecules present in the PEG (Ward, 1981). The molar mass influences the suction and viscosity of PEGs (Gonzalez-Tello et al., 1994; Money, 1989).

The osmotic suctions of salt solutions can be calculated from the simplified van't Hoff's law (Equation (1)). Steuter et al. (1981) stated that the osmotic suction of true solutions is directly a function of the number of molecules in solution and therefore, a linear relationship persists between concentration and osmotic suction for salt solutions based on Equation (1), where π [MPa] is the osmotic pressure, c [g/ml] is the concentration, R [8.314 J/mol K] is the gas constant, and T [K] is the temperature.

$$\pi = RTc \tag{1}$$

PEG solutions exhibit non-linear suction-concentration relationships and hence an application of van't Hoff's law to calculate suctions of PEG-water mixtures is very limited. Some of the factors that have been considered to influence the non-linear relationships between suction and concentration, and the magnitude of suction at any concentration of PEGs are (Orofino and Flory, 1957; Michel and Kaufmann, 1973; Steuter et al., 1981; Ward, 1981; Minagawa et al., 1994): (i) kinetic and thermodynamic effects, (ii) concentration and hydrodynamic size effects, (iii) the molecular mass effect, and (iv) the Tyndall effect which is particular more relevant for PEGs with high molar mass.

In order to include the thermodynamic effects of polymers in solution, the Flory-Huggins virial expression (Equation (2)) has been proposed (Orofino and Flory, 1957). In Equation (2), M_n [g/mol] is the number average molar mass and A_2 [mol cm^3 g^{-2}] and A_3 [mol cm^6 g^{-3}] are virial coefficients. The virial coefficients are a measure of the thermodynamical active volume occupied by a single macromolecule of PEG and the PEG-solvent interaction. In a good solvent, the volume occupied by PEG molecules is higher than that occurs in a poor solvent (Fleer et al., 1988). Theoretical derivations of the virial coefficients are given by Casassa (1972) and Orofino and Flory (1957).

Based on the measured suctions of several PEGs from various experimental techniques, such as laser-light scattering, isopiestic methods, and membrane osmometry, Hasse et al. (1995) proposed Equations (3) and (4) for calculating the virial

coefficients, where T [K] is the actual temperature and T_Θ [K] is a polymer characteristic [$T_{\Theta,PEG}$ = 375.5 K].

$$\left(\frac{\pi}{c}\right)_{c=0} = RT\left(\frac{1}{M_n} + A_2 \cdot c + A_3 \cdot c^2 ...\right) \tag{2}$$

$$A_2 = 2.49\left(\frac{1}{T} - \frac{1}{T_\Theta}\right) \tag{3}$$

$$A_3 = 29.3\left(\frac{1}{T} - \frac{1}{T_\Theta}\right) \tag{4}$$

CURRENT STUDY

The precise calculation of suctions of high concentrated polymer solutions using Equation (2) requires determination of the third virial coefficient. Determination of this virial coefficient requires adopting experimental approaches which is beyond the scope of this study. Therefore, in this paper a simplified approach was adopted that relied on the measured suctions at specified boundary conditions (temperature and origin of suction measurements) relevant to unsaturated soil mechanics. The Flory-Huggins virial expression (Equation (2)) was modified in this study by replacing the virial coefficients in Equation (2) by a single empirical coefficient, Γ [mol cm^{3}g^{-2}], that represents the conjugate effects of PEG-water interaction. Equation (5) presents the modified Flory-Huggins virial expression.

$$\pi = RTc^*\left(\frac{1}{M_n} + \Gamma \cdot c^*\right) \tag{5}$$

Equation (5) provides a linear distribution of the experimental results in a normalized suction (π/c^*)-c^* plot, where c^* is the concentration in g of PEG per ml of water. The interaction coefficient (Γ) can be determined through linear regression. That is, the gradient of π/c^* versus c^* plot yields the value of Γ. The intersection of the linear regression on the π/c^* axis provides RT/M_n. The latter can be used to verify the actual average molar mass of PEGs.

The application of Equation (5) has several advantages over the empirical relationships suggested by various researchers in the past (Michel and Kaufmann, 1973; Money, 1989; Tripathy et al., 2011) in that (i) the method is unit balanced, (ii) enables to verify the actual molar mass, (iii) ensures a precise prediction of suction since polymer properties are taken into account.

Suctions of various PEGs reported by Tripathy and Rees (2013), Monroy et al. (2007) and Michel and Kaufmann (1973), were considered to determine the values of average molecular mass of the PEGs and the associated interaction coefficient Γ (Table 1). The reported suctions by these studies are corresponding to various molar mass of PEGs, measurement techniques, temperatures, and different ranges of PEG concentration.

MOLAR MASS (M_n) AND INTERACTION COEFFICIENT (Γ)

The measured suctions of various PEGs reported by Tripathy and Rees (2013), Monroy et al. (2007), and Michel and Kaufmann (1973) are plotted in π/c^*-c^* space in Fig. 1. Best-fitting of the data presented in Fig. 1 enables determining the values of M_n and Γ. Near linear relationships were noted with very high R^2 values in all cases considered. The values of M_n and Γ obtained from these plots are shown in Table 1.

The calculated values of M_n based on Tripathy and Rees (2013)'s data for PEGs 1500, 4000, and 6000 emphasized the applicability of the suggested procedure in which cases good agreements can be noted between the designated and

Table 1. Designated molar mass and calculated molar mass based on experimental data (shown as measured M_n) and the interaction coefficients for various reported PEGs.

| Designated molar mass	Measurement technique	T [C°]	c* [g$_{PEG}$/ml$_{H_2O}$]	RT·M_n^{-1}	Measured M_n	Γ·10^{-3} [mol cm^3 g^{-2}]	R^2	
1500	Chilled-Mirrow Hygrometer	25	0.096-1.092	1.6041	1544	0.00375	0.9901	Tripathy and Rees (2013)
4000			0.097-1.099	0.6463	3833	0.00378	0.9927	
6000			0.096-1.091	0.4389	5645	0.00380	0.9937	
20000			0.096-1.090	0.1771	13990	0.00390	0.9933	
6000	Psychrometer	25	0.100-0.401	0.6110	4055	0.00391	0.9968	Michel and Kaufmann (1973)
6000	Vapour pressure osmometer	25	0.100-0.401	0.1426	17374	0.00415	0.9993	

calculated molar mass of the PEGs (Table 1). The same trend can be observed for the M_n values calculated based on Monroy et al. (2007)'s data. A significant difference is noted between the calculated and the designated molar mass for PEG 20 000 reported by Tripathy and Rees (2013) in which case, the calculated M_n is found to be smaller than the designated value. Similarly, differences are also noted between the calculated and the designated molar mass for PEG 6000 reported by Michel and Kaufmann (1973). In this case, the calculated M_n based on psychrometer tests is found to be smaller, whereas that calculated based on vapour pressure osmometry is found to be greater than the designated molar mass. Hasse et al. (1995) have also noted deviations from manufacturers specifications of the average molar masses of PEGs.

Examination of the reported data considered in the current study indicated that a strong correlation exists between the calculated M_n and Γ for various PEGs, as shown in Fig. 2 and Equation (6). Equation (6) allows a direct calculation of the interaction coefficient for a known value of M_n.

$$\Gamma = 1.2\,M_n \cdot 10^{-8} + 0.00375 \qquad (6)$$

Application of the suggested method

The proposed modified Flory-Huggins approach introduced in Equation (5) can be used to establish c*-π relationships for any PEG based on the known value of M_n. As seen in Table 1, variations between the designated and actual values of M_n may be expected for specific cases. Therefore, it is advisable to determine the actual values of M_n based on experimental data. For this purpose, some limited experimental data (concentrations and the corresponding suctions) for any PEG may determined using the available technique and the data may be plotted in a π/c*-c* space for determining actual value of M_n (see Fig. 1). In the event of non-availability of experimental data, manufacturer's information on M_n may be considered. The interaction coefficient Γ can be determined from Equation (6). The suction for any concentration can then be calculated from Equation (5).
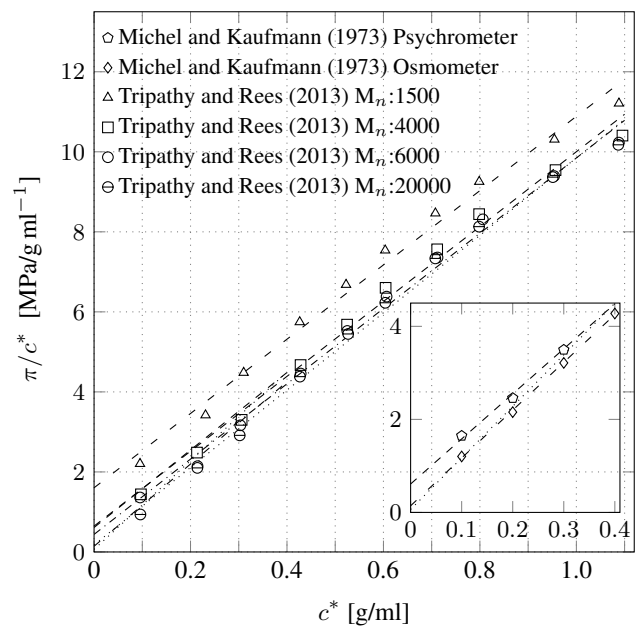
Fig. 1. c* versus π/c* plot based on experimental data reported in the literature

Figures 3 and 4 show comparisons of experimental data and calculated concentration-suction relationships for various PEGs. For the experimental data in Figs. 3 and 4, the concentrations of the PEGs were calculated by converting the actual reported concentration units to the desired unit in this study (Tripathy and Rees, 2013). The calculated concentration-suction relationships presented in Figs. 3 and 4 are based on three different approaches: (i) the approach suggested in this study (Equations (5) and (6)), (ii) Hasse et al. (1995)'s approach using Equations (2) to (4), and (iii) the widely used empirical relationship proposed by Delage et al. (1998) (Equation (7)). The unit of c^* in Equation (7) is in g of PEG per g of water. In all cases the values M_n determined by linear regression were used and the values of Γ were calculated using Equation (6). The values of coefficient of determination based on experimental and calculated suctions are shown in the legends of Figs. 3 and 4 for all the approaches.

$$\pi = 11(c^*)^2 \qquad (7)$$

Figures 3 and 4 show that in general, the calculated concentration-suction relationship based on Equation (7) shows a tendency to remain below the experimental data for low concentrations, whereas it remains above the experimental data for lower M_n PEGs indicating an overestimation of the calculated suctions. For higher M_n PEGs, Equation (7) yields results that are similar to the results from the approach suggested in the paper. In contrast the Flory-Huggins approach using the virial coefficients suggested by Hasse et al. (1995) (Equations (2) to (4)) show poorer agreements with the experimental data sets considered in this study for all cases. The concentration-suction relationship from the suggested approach in this study show very good agreements with the experimental data. The measured suction versus calculated suction (from Equation (5)) for various PEGs are shown in Fig. 5. Figure 5 shows very good agreements between the measured and calculated suctions for a large range of concentration and for various PEGs, in particular the agreements are better at high concentrations or high suctions.

CONCLUSIONS

Determination of suctions of PEGs is commonly required for imposing predetermined values of suction in soil samples in the laboratory. In this paper a new approach is proposed
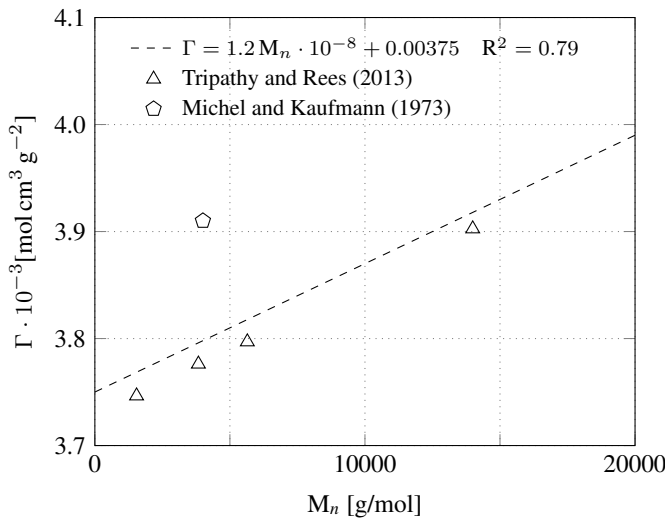
Fig. 2. Interaction coefficient (Γ) as a function of the number average molar mass (M_n)
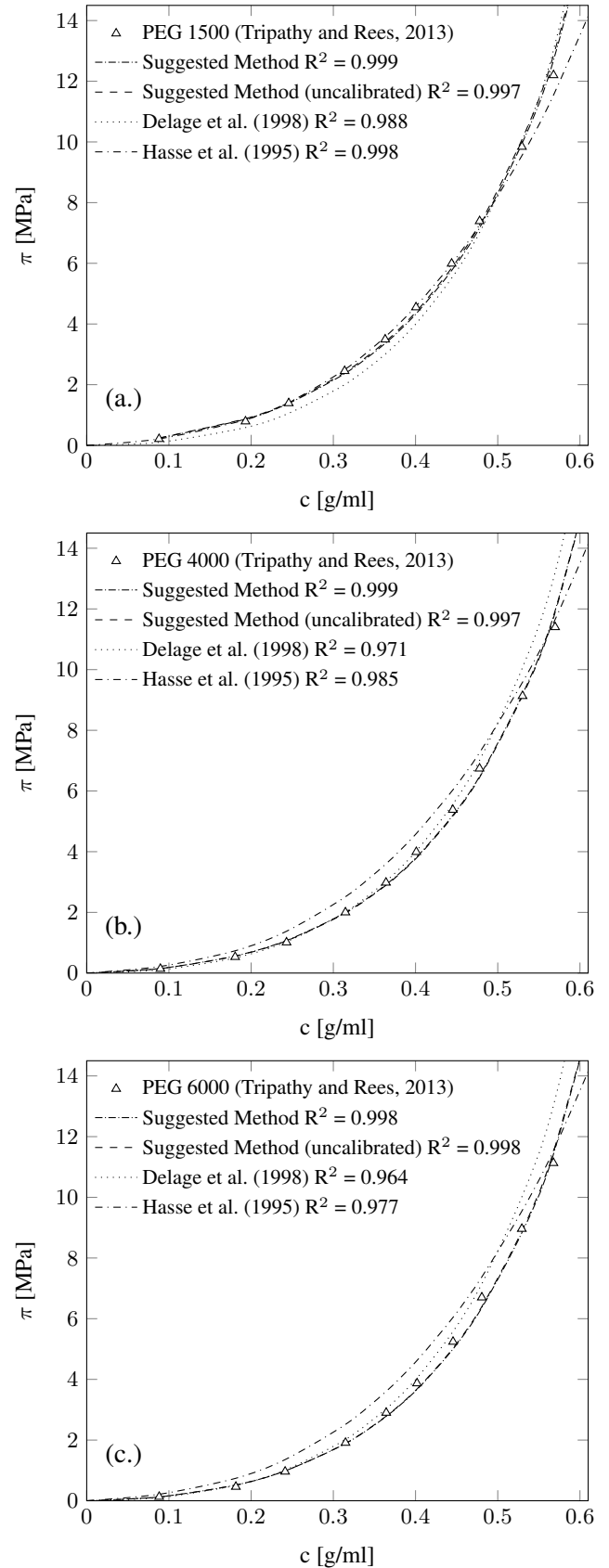
Fig. 3. Comparisons of measured and calculated values of suction for PEGs 1500, 4000, and 6000.

to determine suctions of PEG solutions that considers the combined effects of the hydrodynamic size of PEG molecules in solution and the interactions between PEG molecules and
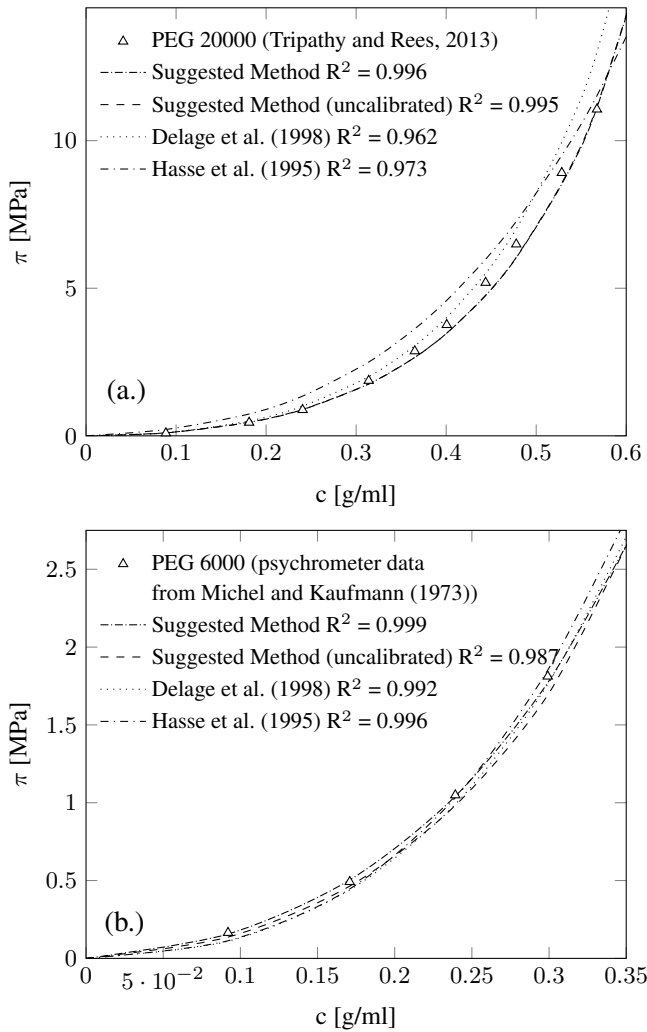
Fig. 4. Comparisons of measured and calculated values of suction for PEGs 6000 and 14000.
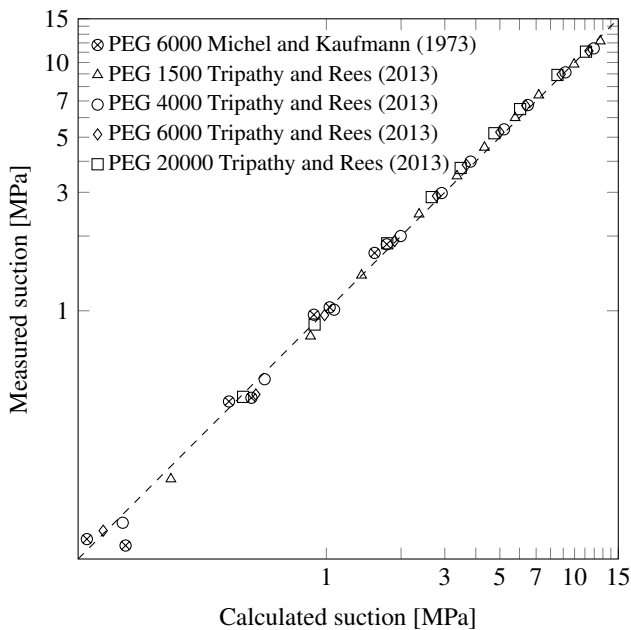

Fig. 5. Comparisons of measured and calculated suctions from the current study

water. The approach requires two important characteristics of PEGs, such as the number average molar mass (M_n) and an interaction coefficient (Γ) for calculating suction. Additionally, the new approach can be used to verify the actual number average molar mass (M_n) of PEGs. A detailed investigation in this study showed that Γ is directly correlated to M_n of PEGS. The suggested approach may be considered as the key reference for assessing suctions imposed during testing of unsaturated soils in the laboratory.

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