Scaling of two-phase capillary pressure-saturation relationships: water-air and oil-air systems

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A b s t r a c t. Solutions of various problems related to soil contamination by non-aqueous phase liquids (NAPL) require a knowledge of capillary pressure-saturation relationships. In soil-water-air systems, this relationship is frequently denoted as the soil water retention curve. Results of measurements of capillary pressure-saturation relationships for two two-phase systems (air-water and air-oil) in two soils (loamy sand and silt loam) are presented. A prediction technique based on a modification of Leverett's concept was applied. The suitability of the method was tested for loamy sand and silt loam by comparison of the scaling factors based on theoretical interfacial tension values with the actual scaling factors between two capillary pressure functions. The data measured shows that the scaling factors for soil-air-water and soil-air-oil consist of the ratios of the interfacial tensions and the wetting angles of both liquids. Both parameters cannot easily be predicted and should be studied in detail.

K e y w o r d s: immiscible phases, capillary pressure-saturation relationship, interfacial tension, scaling

INTRODUCTION

Contamination of soil and ground water by nonaqueous phase liquid (NAPL) due to waste spills is a serious problem. Predictions of NAPL movement require mathematical models describing the movement of immiscible phases in the sub-surface. In order to use those models, relationships between fluid pressure, saturation and hydraulic conductivity must be known. Due to a lack of simple experimental techniques to measure the required relationships directly, prediction techniques are commonly used. Parker *et al.* [12] proposed prediction of a capillary pressure-saturation relationship for different two- and three-phase combinations from the measured capillary pressure-saturation relationship for the air-water system. The method was based on the modified Leverett's scaling relationship [10] for identical porous media. Scaling of capillary pressure-saturation data assumes that only one fluid wets the solid surface and that the intermediate wetting fluid forms a continuous layer. In addition, the scaling factor can be evaluated as the ratio of interfacial tensions [8].

The method by Parker *et al.* [12] was further tested by Lenhard and Parker [9], Demond and Roberts [6], Dane *et al.* [5], Bradford and Leij [2], Hofstee *et al.* [7] and Liu *et al.* [11], among others. The method has not always been successful. Demond and Roberts [6] tested this method for air-water and different organic liquid-water combinations. They showed increasing deviations between measured and predicted values with decreasing interfacial forces. They proposed corrections for interface curvature and roughness. Bradford and Leij [2] presented improvements of the scaling approach by using the contaminated air-water interfacial tension with advancing and receding contact angles. Bradford and Leij [3, 4] studied two- and three-fluid capillary pressure-saturation curves for porous media with a fractional ability to become wet. They proposed a prediction technique involving the percentage of oil-wet fractions. Hofstee *et al.* [7] presented measurements of perchloroethylene (PCE)-air and water-PCE-air capillary pressure-saturation curves. They found that the PCE phase breaks up into micro-lenses for critical PCE saturation. Consequently the assumption that the intermediate wetting fluid spreads over the water-air interface is not fulfilled and Leverett's concept

is not valid. In spite of these problems, the prediction technique based on Leverett's assumptions is frequently applied.

We present here measured capillary pressure-saturation curves for two soils and for two types of two-phase systems. We applied Leverett's concept for a prediction of the capillary pressure functions. The theoretical interfacial tension scaling factor was determined as a ratio of interfacial tensions. The actual scaling factors between two capillary pressure functions were also calculated and compared with the theoretical interfacial tension scaling factors. Scaling factors were then used to predict a function for one two-phase combination from a function for another two-phase combination.

METHODS

Performed tests

Capillary pressure-saturation relationships were measured for two two-phase systems: water-air and oil-air (diesel oil). Tests were carried out for two soils: loamy sand and silt loam. The mean bulk density of the loamy sand (LS) was 1.60 g cm^{-3} and the mean bulk density of the silt loam (SL) was 1.33 g cm^{-3}. The clay contents were 1% (LS) and 12% (SL), the silt contents 10% (LS) and 60% (SL), and the sand contents 71% (LS) and 28% (SL), according to USDA classification. The loamy sand contained 18% of fine gravel (>2 mm). The organic matter content was 2.11% (LS) and 3.15% (SL). Two types of test were performed. Capillary pressure-saturation curves were obtained either in a sand tank and using a pressure plate apparatus (only for the water-air system), or in a Tempe pressure cell. Air-dried and unsieved materials were packed into sampling cylinders of 100 cm^3 in volume for the tests in the sand tank and the pressure plate apparatus, or into polyacrylate cylinders (100 cm^3 in volume) placed in a Tempe pressure cell with a 1/2 bar porous ceramic membrane. Samples were initially slowly saturated with the wetting fluid to reach the maximum saturation levels. However, no special treatment was used to ensure full saturation of the soil samples. Sequential steps of the pressure heads were subsequently applied by either lowering the water container of the sand tank and raising the air overpressure in the pressure plate apparatus, or lowering and raising the burette with the wetting fluid (water or oil) connected to the bottom of the Tempe pressure cell. Equivalent wetting fluid saturations were determined gravimetrically or from outflow/inflow values measured with the burette.

For the loamy sand, the following capillary pressure-saturation curves were obtained: 4 drying water-air capillary pressure-saturation curves using the sand tank and the pressure plate apparatus (w-a A, B, C and D), 2 drying /wetting water-air capillary pressure-saturation curves using the Tempe pressure cell (w-a 1 and 2), and 1 drying/wetting oil-air capillary pressure-saturation curve with the Tempe pressure cell (o-a). For the silt loam, the following capillary

pressure-saturation curves were measured: 1 drying/wetting water-air capillary pressure-saturation curve using the Tempe pressure cell (w-a), and 1 drying/wetting oil-air capillary pressure-saturation curve using the Tempe pressure cell (o-a). The specific gravity of water, ρ_w, was considered 1 g cm^{-3} and the specific gravity of oil, ρ_o, was determined to be 0.87 g cm^{-3}. Specific gravities of both fluids were used to express pressure heads for oil-air capillary pressure-saturation curves in cm of water.

Analytical function

Measured curves were fitted with the van Genuchten equation [13]:

$$S_{eW} = \left(\theta_W - \theta_{Wr}\right) / \left(\theta_{Wr} - \theta_{Ws}\right) = \left[1 + \left(\alpha h_c\right)^n\right]^{-m}, \quad (1)$$

where S_{eW} is the effective wetting fluid saturation, θ_{Wr} and θ_{Ws} are the residual and saturated wetting fluid saturations (L^3/L^3), respectively, α (1/L) and n (-) are fitting parameters, $m = 1 - 1/n$, and h_c (L) is the capillary pressure head. The effective saturation of the non-wetting fluid (S_{eNW}) is defined as:

$$S_{eNW} = 1 - S_{eW}. \quad (2)$$

The nonlinear optimization program RETC [14] was used to fit the $\theta(h)$ data. In cases of multiple measurements, single curves were obtained by fitting the entire data set.

Scaling of the capillary pressure-saturation curves

Leverett's concept for the prediction of capillary pressure functions [10] was applied. The water-air capillary pressure function $h_{c,wa}(S_{eW})$ can be predicted from the oil-air capillary pressure function $h_{c,oa}(S_{eW})$, for both h_c expressed in cm of water, using the following equation:

$$h_{c,wa}\left(S_{eW}\right) = \left(\frac{\sigma_{wa} \cos \gamma_{wa}}{\sigma_{oa} \cos \gamma_{oa}}\right) h_{c,oa}\left(S_{eW}\right), \quad (3)$$

where $(\sigma_{wa} \cos \gamma_{wa}) / (\sigma_{oa} \cos \gamma_{oa})$ is the scaling factor determined as the ratio of the interfacial tensions, σ (F/L), and the ratio of cosines of the contact angles, γ This relationship is frequently simplified assuming that $\cos \gamma_{wa} / \cos \gamma_{oa} = 1$, while the scaling factor is determined as the ratio of the interfacial tensions, $\sigma_{wa} / \sigma_{oa}$. In this study, we first evaluated the theoretical interfacial tension scaling factor as the ratio of the interfacial tensions for water-air ($\sigma_{wa} = 0.07 \text{ N m}^{-1}$) and oil-air ($\sigma_{oa} = 0.0225 \text{ N m}^{-1}$) systems. The value of σ_{wa} was decreased from that of pure water ($\sigma_{wa} = 0.072 \text{ N m}^{-1}$) to account for changes in the surface tension due to the chemical interaction between the soils and the pore water [11]. A value of σ_{oa} was measured with the drop shape analysis method [1].

The actual scaling factors between two capillary pressure functions (oil-air and water-air) were calculated next for each pair of the corresponding capillary pressure functions using linear regression. For loamy sand, the fitted oil-air drying capillary pressure function was paired with the fitted water-air drying capillary pressure function obtained either using the sand tank and the pressure plate apparatus or the Tempe pressure cell. The other pairs were similarly compared as shown further.

The scaling factors evaluated as the ratio of the interfacial tensions and the actual scaling factors were used to predict the water-air capillary pressure curves from the oil-air capillary pressure curves.

RESULTS AND DISCUSSION

The van Genuchten parameters fitted for each curve (marked as described above) are given in Table 1 for loamy sand and in Table 2 for silt loam. In cases of multiple measurements, single curves were also obtained by fitting all the data points. See results in Table 1 marked as w-a A, B, C, D drying and w-a 1, 2 drying/wetting. Values of the parameter n show that the curvatures of the corresponding functions from the tests performed with the Tempe pressure cell are very similar and only slightly different from the curvatures of functions obtained with the sand tank and the pressure plate apparatus.

Fitted curves marked as f(w-a A, B, C, D), f(w-a 1, 2) and f(o-a) for loamy sand are shown in Fig. 1. Fitted curves marked as f(w-a) and f(o-a) for silt loam are presented in Fig. 2. Those functions were used to evaluate the actual scaling factors between water-air and oil-air capillary pressure-saturation curves using linear regression. The theoretical interfacial tension scaling factor (the same for both soils), and the actual scaling factors for the corresponding functions are presented in Table 3. The theoretical interfacial tension scaling factor is approximately the same as the actual scaling factor for conversion of the oil-air drying capillary pressure function to the water-air drying capillary pressure function only in one case for loamy sand. The water-air functions were obtained with the sand tank and pressure plate apparatus in these instances. For the other pairs, the actual scaling factors are either higher (loamy sand) or lower (silt loam) than the theoretical interfacial tension scaling factor. The actual scaling factors for the corresponding drying and wetting curves for silt loam are relatively close. The actual scaling factors for drying curves are smaller than for the wetting curves for loamy sand.

Data points of all capillary pressure functions measured their best fits in the evaluation of the actual scaling factors and predicted water-air curves (marked as ITSF for the theoretical interfacial tension scaling factor and ASF for the actual scaling factor) are shown in Figs 1 and 2. The water-air curve predicted with the theoretical interfacial tension

T a b l e 1. Parameters of van Genuchten functions for loamy sand

Fitted function	θ_{Wr} (cm³ cm⁻³)	θ_{Ws} (cm³ cm⁻³)	α (cm⁻¹)	n
w-a A drying	0.136	0.397	0.060	1.68
w-a B drying	0.121	0.406	0.053	1.70
w-a C drying	0.124	0.380	0.051	1.54
w-a D drying	0.130	0.396	0.055	1.54
w-a 1 drying	0.110	0.366	0.033	1.63
w-a 1 wetting	0.110	0.339	0.030	1.64
w-a 2 drying	0.110	0.362	0.030	1.66
w-a 2 wetting	0.110	0.333	0.024	1.72
o-a drying	0.114	0.400	0.104	1.79
o-a wetting	0.114	0.395	0.138	1.74
w-a A,B,C,D drying	0.129	0.395	0.056	1.61
w-a 1-2 drying	0.110	0.355	0.026	1.72
w-a 1-2 wetting	0.110	0.332	0.024	1.72

T a b l e 2. Parameters of van Genuchten functions for silt loamy

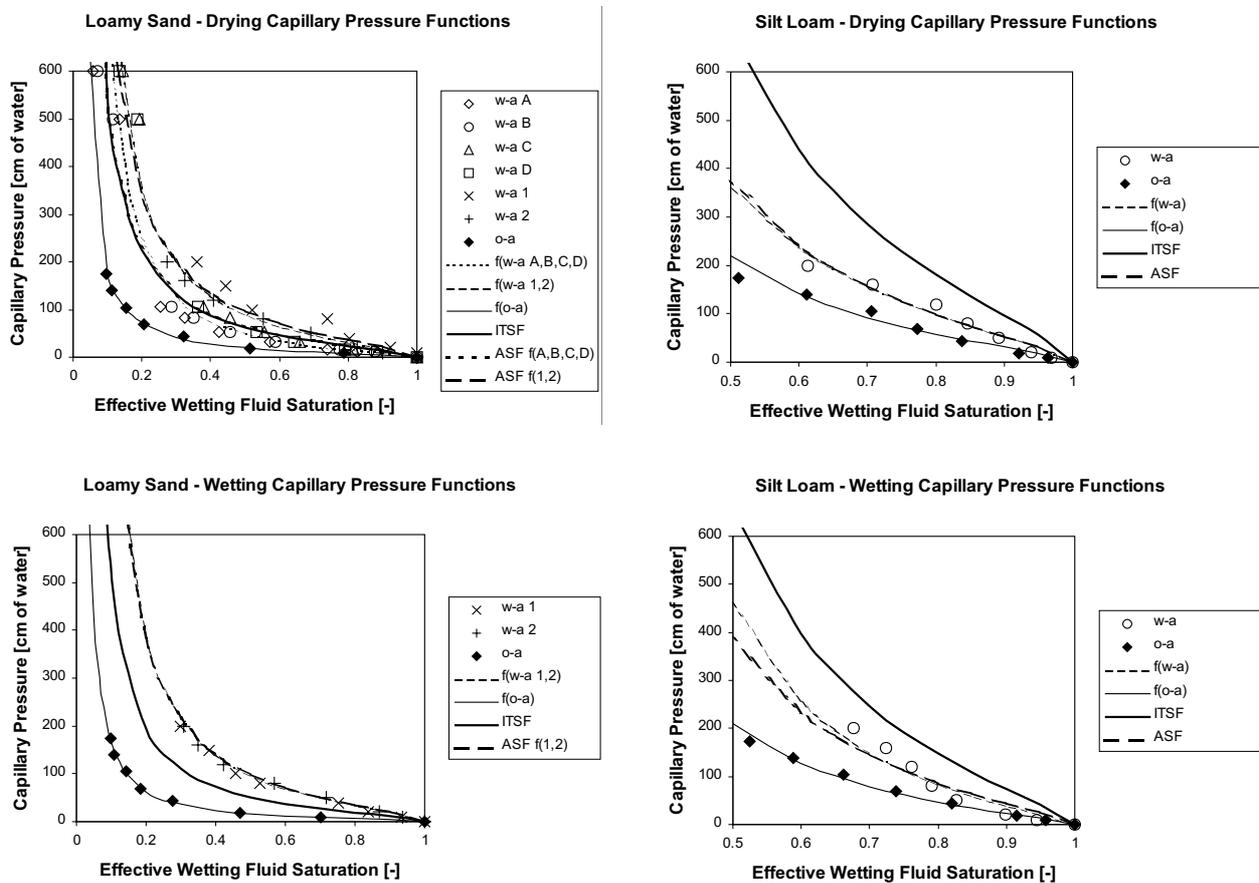| Fitted function	θ_{Wr} (cm³ cm⁻³)	θ_{Ws} (cm³ cm⁻³)	α (cm⁻¹)	n
w-a drying	0.10	0.516	0.0095	1.52
w-a wetting	0.10	0.477	0.0150	1.35
o-a drying	0.10	0.509	0.0167	1.50
o-a wetting	0.10	0.499	0.0230	1.42

Fig. 1. Capillary pressure functions for loamy sand: w-a A, B, C and D are measured data of water-air curves determined using a sand tank and pressure plate apparatus, w-a 1 and 2 are measured data of water-air curves determined using a Tempe pressure cell, o-a are measured data of oil-air curves determined with a Tempe pressure cell, f(w-a A, B, C, D), f(w-a 1, 2) and f(o-a) are the best fits with the van Genuchten function, ITSF are scaled f(o-a) curves with the theoretical interfacial tension scaling factor, ASF f(A, B, C, D) [ASF f(1, 2)] are scaled f(o-a) curves with the actual scaling factor evaluated for f(o-a) and f(w-a A, B, C, D) [f(w-a 1, 2)].

Fig. 2. Capillary pressure functions for silt loam: w-a are measured data of water-air curves determined using a Tempe pressure cell, o-a are measured data of oil-air curves determined with a Tempe pressure cell, f(w-a) and f(o-a) are the best fits with the van Genuchten function, ITSF are scaled f(o-a) curves with the theoretical interfacial tension scaling factors, ASF are scaled f(o-a) curves with the actual scaling factors evaluated for f(o-a) and f(w-a).

T a b l e 3. Scaling factors

Specification method	Scaling factor
Theoretical interfacial tension scaling factor = $_{wa}$ / $_{oa}$	0.07/0.0225 = 3.11
Actual scaling factor – loamy sand, f(o-a) and f(w-a A,B,C,D), drying	3.13
Actual scaling factor – loamy sand, f(o-a) and f(w-a 1,2), drying	4.61
Actual scaling factor – loamy sand, f(o-a) and f(w-a 1,2), wetting	6.01
Actual scaling factor – silt loam, f(o-a) and f(w-a), drying	1.70
Actual scaling factor – silt loam, f(o-a) and f(w-a), wetting	1.80

scaling factor follows the corresponding water-air curve only when the theoretical interfacial scaling factor was approximately the same as the actual scaling factor. Predicted curves are overestimated when the interfacial tension scaling factor was higher than the actual scaling factor. Predicted curves are underestimated for an interfacial tension scaling factor lower than the actual scaling factor. As was expected, the water-air curves predicted with the actual scaling factors follow the corresponding water-air curves in all cases. Predicted and fitted curves for Tempe pressure cell data are almost identical due to similarity in n values. The actual scaling factor can be expressed as a ratio of the α values for curves with the same n value.

The prediction technique with the theoretical interfacial tension scaling factor assumes that the ratio of the cosines of the contact angles is equal to 1. This means that the contact angles for different fluid combinations are the same. If the contact angles are not the same, the ratio is not equal to 1 and knowledge of the contact angles is important for accurate prediction of the curves. The contact angle for the wetting process differs from the contact angle for the drying process; however, the ratio for different fluid combinations may be constant. In our case, the ratio is approximately 1 (1.01) in only one case for loamy sand [drying f(w-a A, B, C, D) and drying f(o-a)]. The ratios for the other loamy sand combinations are: 1.48 for drying f(w-a 1, 2) and drying f(o-a), 1.93 for wetting f(w-a 1, 2) and wetting f(o-a). This means that the ratios are not equal to 1 and vary for wetting and drying processes. The ratios for silt loam are: 0.55 for drying f(w-a) and drying f(o-a), 0.58 for wetting f(w-a) and wetting f(o-a). Those ratios are not equal to 1, however, they are very similar for drying and wetting. The previous discussion is based on the assumption that the ratio of interfacial tensions is a constant value. However, the values of interfacial tensions can vary during the experiments due to contamination of the fluids by soil components. This can be especially important for silt loam that has a higher organic matter content. Since the actual scaling factors for silt loam are substantially lower than the theoretical interfacial tension scaling factor, we have to consider also the hypothesis that the contact angle for water may be greater than the contact angle for oil in those instances. Nevertheless, reasons why we have such low values for the actual scaling factors cannot be deduced from a single type of measurement. In addition to all the factors discussed, the fluid properties may also change due to evaporation of certain fractions of the diesel oil. The most probable is having a combination of several effects. It should be mentioned also that the capillary pressure-saturation curves were not determined on a single soil specimen. Measurements could be influenced somewhat by heterogeneities caused by the packing of the soil samples. This might be another reason why the deviations of the predicted and measured curves for loamy sand are not consistent. Accurate understanding of fluid behavior in contaminated soil porous systems may require more detailed physical modeling.

CONCLUSIONS

Capillary pressure-saturation relationships for two two-phase systems (air-water and air-oil) in two soils (loamy sand and silt loam) were measured. The theoretical interfacial tension and actual scaling factors were evaluated. The theoretical interfacial tension scaling factor was approximately the same as the actual scaling factor only for one set of water-air and oil-air drying capillary pressure functions for loamy sand. All other experimental tests for loamy sand produced actual scaling factors that were higher than the theoretical interfacial scaling factors for both wetting and drying. The value of actual scaling factor was higher for wetting than for drying. We assume that the wetting angle played an important role in this.

For silt loam, the drying and wetting procedures resulted in substantially lower values for the actual scaling factors than the theoretical interfacial scaling factor. We believe that the wetting angle of the liquids played a certain role in this. Unfortunately, the physical nature of the mechanism cannot be deduced from the experiments carried out as part of our study.

The measured data demonstrates that the scaling factors for oil-air, water-air and eventually for oil-water-air systems cannot be estimated from theoretical interfacial tensions only.

REFERENCES

1. **Barták J., Hilar M., Pruška J., Veselá J., and Vrba V., 2001.** Experimental and numerical analysis of flow in soils with multiphase (immiscible) systems: Laboratory determination of saturation-pressure curves for characteristic type of soils. Grant No.103/98/0989 (in Czech), ČVUT FSv, Praque, Czech Republic.

2. **Bradford S.A. and Leij F.J., 1995.** Wettability effects on scaling two- and three-fluid capillary pressure-saturation relations. Environ. Sci. Technol., 29 (6), 1446–1455.

3. **Bradford S.A. and Leij F.J., 1995.** Fractional wettability effects on two- and three-fluid capillary pressure-saturation relationships. J. Contam. Hydrol., 20, 89–109.

4. **Bradford S.A. and Leij F.J., 1996.** Predicting two- and three-fluid capillary pressure-saturation relationships of porous media with fractional wettability. Water Resour. Res., 32, 251–259.

5. **Dane J.H., Oostrom M., and Missildine B.C., 1992.** An improved method for the determination of capillary pressure-saturation curves involving TCE, water and air. J. Contam. Hydrol., 11, 69–81.

6. **Demond A.H. and Roberts P.V., 1991.** Effect of interfacial forces on two-phase capillary pressure-saturation relationship. Water Resour. Res., 27, 423–437.

7. **Hofstee C., Dane J.H., and Hill W.E., 1997.** Three-fluid retention in porous media involving water, PCE and air. J. Contam. Hydrol., 25, 235–247.

8. **Lenhard R.J. and Parker J.C., 1987.** Measurement and prediction of saturation-pressure relationships in three-phase porous media systems. J. Contam. Hydrol., 1, 407–424.

9. **Lenhard R.J. and Parker J.C., 1988.** Experimental validation of the theory of extending two-phase saturation-pressure relations to three-fluid phase systems for monotonic drainage paths. Water Resour. Res., 24, 373–380.

10. **Leverett M.C., 1941.** Capillary behavior in porous solids. Trans. Am. Inst. Min. Met. Pet. Eng., 142, 152–169.

11. **Liu Y.P., Hopmans J.W., Grismer M.E., and Chen J.Y., 1998.** Direct estimation of air-oil and oil-water capillary pressure and permeability relationships from multi-step out-flow experiments. J. Contam. Hydrol., 32, 223–245.

12. **Parker J.C., Lenhard R.J., and Kuppusany T., 1987.** A parametric model for constitutive properties governing multiphase flow in porous media. Water Resour. Res., 23, 618–624.

13. **van Genuchten M.Th., 1980.** A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil. Sci. Soc. Am. J., 44, 892–898.

14. **van Genuchten M.Th., Lei F.J., and Yates S.R., 1991.** The RETC code for quantifying the hydraulic functions of unsaturated soils. EPA/6000/2-91-065, US EPA, Office of Research and Development, Washington.