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Two-Phase Capillary Pressure-Saturation Relationship for Kerosene in Iraqi Sand

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ABSTRACT

Quantitative descriptions of the two-phase flow in the subsurface soil require knowledge of the relative permeability-saturation-capillary pressure Kr-S-Pc relationships. The significance of the present study lies in introducing a physical model that was used to measure the capillary pressure-saturation curve for the two-phase kerosene-water system in Kerbala's sand. The experimental results are fitted with the empirical mathematical function described by (Parker et al., 1987) which is based on (Van Genuchten's model, 1980). This function can be used to specify the residual water saturation, Sr, and Van Genuchten's soil parameters, α and n. The best-fit curve was found by using a nonlinear least squares fitting routine using the SPSS software version 7.5. The fitting parameters Sr, α and n for the best-fit to Van Genuchten's capillary pressure-saturation curve for kerosene-water system have the values of 7%, 0.048 cm^{-1} and 2.7, respectively, for Kerbala's sand.

KEYWORDS: Pressure-saturation relationship, Kerosence, Sand, Iraq.

INTRODUCTION

Two constitutive relationships were often used in the mathematical description of the two-phase liquid flow in porous media. The capillary pressure and the relative permeability of the system are expressed as functions of saturation (Faust, 1985). Unfortunately, there are few data available for these relationships for the liquids and conditions at hazardous waste sites (Lenhard and Parker, 1987). This recognized lack of data (Demond and Roberts, 1991) severely hinders the ability of developing the mathematical models that provide useful insight into the movement of a separate organic liquid phase at spill sites.

Capillary pressure-saturation and relative permeability-saturation relationships have been extensively studied in soil science and petroleum engineering. However, the conditions encountered in contaminated aquifers often differ from those covered by soil science or petroleum engineering studies. While the porous media used in soil science studies span the range of soils occurring at hazardous waste sites, these studies, for the most part, are limited to air-water systems. On the other hand, petroleum engineering studies sometimes use fluid pairs that are similar to those of interest here; however, the measurements are limited to drainage curves, neglecting other important portions of the relationships such as imbibition. Many experimental studies are achieved to measure the capillary pressure-saturation relationship. Roach et al. (2010) measured air-water primary drainage capillary pressure-saturation relationships for medium and fine

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textured sands at three measurement elevations in the same vertical column at a number of different imposed boundary conditions. Bottero et al. (2011) used four different averaging operators to obtain various column-scale average pressures. The average pressure values have been used together with average saturation to construct column-scale capillary pressure–saturation curves.

P_c-S functions are not unique but subject to hysteresis. A non-wetting fluid displacing a wetting fluid has a different P_c-S relationship than a wetting fluid displacing a non-wetting fluid. The first displacement process is referred to as drainage and the latter is referred to as imbibition history. Between these two extremes of P_c-S relationships, other (scanning) curves can be found that depend on the drainage and imbibition history (Wipfler, 2003).

The present study introduces a physical model that was used to measure the capillary pressure-saturation curve for two-phase kerosene-water system in Kerbala's sand. These measurements are fitted with the empirical mathematical function described by (Parker et al., 1987) which is based on (Van Genuchten's model, 1980) to specify the residual water saturation, S_r, and Van Genuchten's soil parameters, α and n.

BACKGROUND

As mentioned above, modeling the immiscible flow of non-aqueous phase liquid in the vadose zone requires the knowledge of the relative permeability-saturation-capillary pressure (K_r-S-P_c) relationships. Currently, the most widely used set of constitutive hydraulic relations, included in multiphase flow models, is a parametric model first derived by Parker et al. (1987) and subsequently expanded by introducing non-wetting fluid entrapment as well as saturation hysteresis by Parker and Lenhard in 1987 as cited by (Kechavarzi, 2005).

For two-phase systems, the capillary pressure-saturation relations are typically experimentally determined and fitted with some empirical mathematical functions originally derived by soil physicists for air-water systems (e.g., Brooks and Corey in 1966 and Van Genuchten in 1980). Van Genuchten (1980) developed a relatively simple equation for soil water content – pressure head curve, $\theta(h)$, which is:

$$\Theta=\frac{\theta-\theta_r}{\theta_s-\theta_r}=\left[1+(\alpha h)^n\right]^{-m} \qquad (1)$$

where *s* and *r* indicate the saturated and residual values of soil water content (θ), respectively, *α, n* and $m(=1-1/n)$ are the Van Genuchten's soil parameters, *h* is the water pressure head and Θ is the degree of water saturation. By substituting eq.(1) into the predictive conductivity model developed by Mualem in 1976, a closed-form analytical expression for the relative hydraulic conductivity, K_r, will be:

$$K_r(\Theta)=\Theta^{1/2}\left[1-\left(1-\Theta^{1/m}\right)^m\right]^2 \quad \text{in terms of saturation} \qquad (2)$$

or,

$$K_r(h)=\frac{\left\{1-(\alpha h)^{n-1}\left[1+(\alpha h)^n\right]^{-m}\right\}^2}{\left[1+(\alpha h)^n\right]^{m/2}}$$

in terms of pressure head (3)

Results obtained with the closed-form analytical expressions based on Mualem theory are compared with observed hydraulic conductivity data for five soils with a wide range of hydraulic properties, and there was a good agreement between them (Van Genuchten, 1980). Parker et al. (1987) proposed a generalized form of the Van Genuchten's model for any two-phase system as follows:

$$\bar{S}_j^{ij}=\frac{S_j^{ij}-S_r}{1-S_r}=\left[1+\left(\alpha_{ij}h_{ij}\right)^n\right]^{-m} \quad \text{for } h_{ij}>0 \qquad (4)$$

$$\bar{S}_j^{ij}=1 \quad \text{for } h_{ij}\le 0$$

where $\bar{S}_j^{ij}$ is the effective saturation of the wetting fluid *j* in a two-phase system composed of two fluids *i* and *j* (*i,j* =a, w, o which stand for air, water and oil (NAPL), respectively). S_j^{ij} is the saturation of the wetting fluid *j*, h_{ij} is the capillary pressure head, S_r is the minimum (also called residual or irreducible) wetting fluid saturation. S_r is assumed to be independent of fluid properties or saturation history. Furthermore, Parker et al. in 1987 and Parker and Lenhard in 1987 as cited by (Kechavarzi, 2005) proposed a scaling procedure allowing the prediction of any two-phase P_c-S relationship from the measurement of a single P_c-S relationship and appropriate interfacial tension data. The scaled two-phase P_c-S relationship can be written as:

$$\bar{S}_j^{ij} = \left[1 + \left(\alpha_{ij}\beta_{ij}h_{ij}\right)^n\right]^{-m} \qquad (5)$$

where β_{ij} is the fluid-dependent scaling coefficient. Lenhard and Parker in 1987 as cited by (Kechavarzi, 2005) proposed the estimation of scaling factor from the ratio of the interfacial tension γ_{ij} ($\beta_{ij} = \gamma_{aw}/\gamma_{ij}$). Hence, the capillary pressure-saturation and relative permeability-saturation relationships for two-phase kerosene-water systems can be written in the following manner:

$$\overline{S_w} = \frac{S_w - S_r}{1 - S_r} \qquad (6)$$

$$\overline{S_w} = \left[1 + \left(\alpha \cdot \beta_{ow} \cdot h_{ow}\right)^n\right]^{-m} \qquad (7)$$

$$k_{rw} = \left(\overline{S_w}\right)^{1/2}\left[1 - \left(1 - \left(\overline{S_w}\right)^{1/m}\right)^m\right]^2 \qquad (8)$$

where h_{ow} is the oil-water capillary pressure head ($=h_o - h_w$), [L], h_w and h_o are the water and oil water equivalent pressure heads, respectively. S_w is the water saturation, $\overline{S_w}$ is the effective water saturation, S_r is the residual or irreducible saturation of water phase, k_{rw} is the relative permeability of water and β_{ow} is the fluid-dependent scaling coefficient.

EXPERIMENTAL WORK

Materials

After considering various organic liquids, kerosene was chosen as the contaminant fluid. The selection was based on the low health hazard of kerosene during experiment, in combination with a number of desirable properties such as specific gravity lower than 1, viscosity comparable to that of water, very low solubility in water and low volatility. The last two properties are necessary to limit the mass transfer between phases during the experiments. Table(1) summaries the pertinent properties of kerosene (Pantazidou and Sitar, 1993). In order to enable visual observations, kerosene was dyed with Sudan III. “Sudan” is a trade mark (or name) for a line of dyestuffs, soluble in hydrocarbons; used for the coloring of fats, oils, waxes,...etc. Sudan III is a powdered, nonvolatile an organic dye of red color which is insoluble in water.

Table1. Kerosene properties (Pantazidou and Sitar, 1993)

Parameter	Value
Specific gravity	0.8 at 15° C
Viscosity	1.152 CP at 21° C
Surface tension: kerosene-air	27.5 dyne/cm at 20° C
Interfacial tension: kerosene-water	48 dyne/cm at 20° C

The porous medium used in the present study was sand. This sand is available in the market and is known as “Kerbala’s sand”. This sand needs an additional sieving to achieve satisfactory uniformity. The sand was clean, well-sorted fine to medium-grained sand. The sand had a particle size distribution ranging from 50 μm to 1 mm (Fig.1) with an effective grain size, d_{10}, of 180 μm, a median grain size, d_{50}, of 370 μm and a uniformity coefficient, $Cu=d_{60}/d_{10}$, of 2.2. The permeability of the sand, measured with a constant head permeability test, was 115 cm/hr.

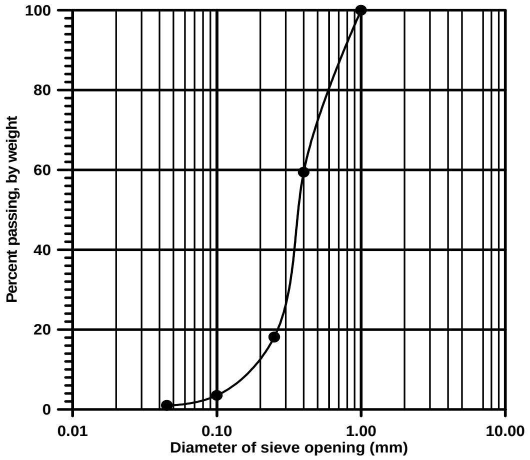

Figure 1: Gradation curve for Kerbala's sand

Equipment

The parts of the experimental apparatus were constructed in the Glass Work Unit/Babylon University and technical workshop in the local market to measure the capillary pressure-saturation curve. The experimental apparatus represents a modification of the one used by Demond and Roberts (1991). This apparatus consists of a pressure cell, effluent collection bottle and tubes with specified lengths. The pressure cell is made-up of stainless steel with Teflon core. Effluent collection bottle and tubes of the apparatus are made-up of Perspex and able to bear values of pressure and temperature up to 3 bar and 600 ° C, respectively.

The pressure cell (Fig.2(a)) represents the middle part of the apparatus. This cell has an inner diameter (ID) of 5.5 cm and a total height of 7 cm. The net inner height of the cell is 4 cm. The upper and lower parts of the cell are supplied with a short tube which has an inner diameter of 15 mm. Kerosene enters the cell by the upper tube and it will be in contact with the sand sample. On the other hand, the lower tube is used to; supply the sand sample with CO_2, saturate the sample with wetting phase (water) and transport the discharged water from the sample under specified oil pressure head to the effluent collection bottle. In the bottom of the pressure cell, there is a ceramic plate as shown in Fig.2(b). This plate (Fig.2(c)) is the filter disk with a certain pressure and mesh size fraction able to separate the oil from the water. The effluent collection bottle represents the lower part of the experimental apparatus with a capacity of 500 ml. It was sealed with a viton


(a)

(b)

(c)

Figure 2: Components of the middle part of experimental apparatus; (a) pressure cell, (b) location of ceramic plate and (c) ceramic plate

stopper, with a 1 mm inner diameter of tube inserted in the stopper to allow pressure equilibration between the ambient atmosphere and the head space in the bottle while minimizing evaporation.

Tubes represent the upper part of the experimental apparatus. They consist of a number of pieces with an inner diameter equal to 15 mm and each piece has a length equal to 0.25 m with a number of side vents. These vents are located at different spaces. The upper part of one of these pieces has a funnel shape and is located at the top of the other pieces. Combination of these pieces of tubes with others will lead to different heads of organic liquid. The specified constant pressure head of organic liquid was achieved by reservoir (1), reservoir (2) and any of the side vents. Fig.3 is a schematic diagram of the experimental apparatus.

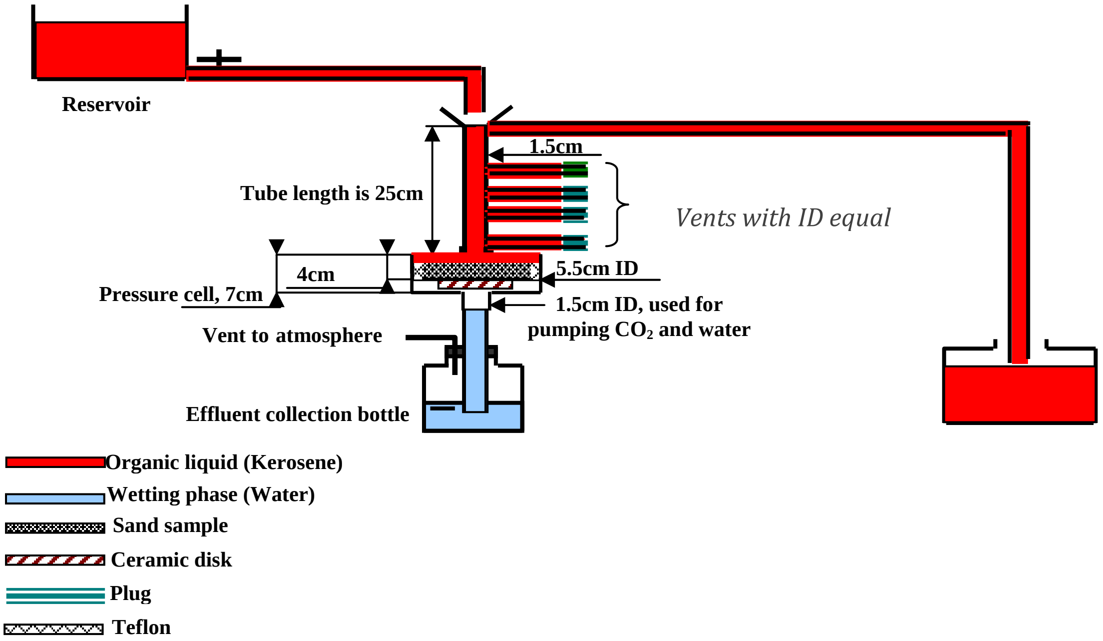

Figure 3: Schematic diagram of the experimental apparatus

Experimental Procedure

A slightly moist sand sample was placed inside the pressure cell directly on the ceramic disk. The sand sample was packed with a height of 3 cm and a diameter of 5.5 cm. Initially, the sample was saturated with carbon dioxide at 15 psi to displace the air in the pore space. After that, the sample was completely wetted with deionized water through slowly flooding upward flow with a degassed aqueous phase at a rate of 2.5 ml/min in order to displace or dissolve as much gas as possible. After the water (or aqueous) phase appeared at the top of the sample, the flow rate was increased 5 times to displace the CO_2-saturated water and to dissolve any residual gas. The system was allowed to equilibrate overnight at about 3 cm of capillary pressure, measured using the bottom of the sand sample as the reference point. This pressure was below the displacement pressure of the system studied and, thus, was considered satisfactory as the starting point of the measurements. All measurements were made in a constant temperature room maintained at $20\pm1^{\circ}$ C.

The capillary pressure was increased by increasing the elevation of organic liquid (kerosene) in the upper tube which was connected with a pressure cell by a suitable fitting. A powdered, nonvolatile red dye (Sudan III) was added to the kerosene at a concentration of 1 mg/l of kerosene in order to enable visual observations. Upon achieving equilibrium after a step increase in capillary pressure, the amount of water discharged from the sample was measured by the weight gain of the effluent collection bottle. Evaporation was negligible. A 10 hour period was allowed to elapse between a change in pressure and the determination of the weight change for that step. The weight stabilization was assumed to indicate the achievement of equilibrium, although it is recognized that this apparent equilibrium is for the bulk liquid only and that discontinuous portions of liquid may take orders of magnitude longer to equilibrate (Demond and Roberts, 1991).

The above procedure was used to measure the primary drainage capillary pressure-saturation curve. The above procedure was repeated until a negligible amount of efflux for an increment in capillary pressure was achieved, suggesting that the aqueous phase had lost its ability to move in response to a hydraulic gradient and that a residual saturation had been achieved (Luchner et al., 1989). In the primary drainage measurements, the aqueous phase content of the porous media was expressed as S_w, the saturation of the aqueous phase. S_w was determined by subtracting the cumulative effluent volume from the total pore volume and dividing that quantity by the total pore volume. The total pore volume was determined from bulk density measurements and the amount of water necessary to flood the sample. The values for saturation, then, are actually those values averaged over the length of the sample. Measurements were not corrected for the saturation distribution within the sample. Bentsen and Anli in 1976 have demonstrated that for a short sample, such as the one employed here, the correction is negligible as cited by (Demond and Roberts, 1991).

RESULTS AND DISCUSSION

The primary drainage relationship for kerosene-water system is shown in Fig.4. This relationship was measured firstly as described previously and, then, it is fitted with Van Genuchten's relationship (eq.(7)) in order to determine the Van Genuchten's parameters (i.e., α and n). The residual saturation of the wetting phase, S_r, represents the major characteristic of the primary drainage curve. S_r is defined as the limiting saturation of the wetting phase, where the wetting phase loses its capacity to move as a linked phase (Luckner et al., 1989). Since the experimentally determined value depend on experimental protocol (such as the highest capillary pressure attained), Brooks and Corey in 1964 and Mualem in 1976 developed extrapolation procedures that Brooks in 1986 claims represent a more objective means of determining the residual saturation. Thus, S_r could be determined in three ways: (1) by the final saturation achieved in the particular experiment, (2) by Brooks and Corey's method in 1964 involving the conformance of the final data point to the straight line on a log-log plot and (3) by the method described by Mualem in 1976, involving the extrapolation of the capillary curve using a variation of a function proposed by Brooks and Corey in 1964. However, the first method was adopted for specifying the residual saturation, S_r, in the present study. The measured residual saturation of water for kerosene-water system from experiments conducted in the present study was 7%. The scaling factors for kerosene-water system used here are β_{ao} =2.75 and β_{ow} =1.57. Fig.4 shows that the P_c-S relation obtained experimentally can be approximated by a scaled Van Genuchten's equation (eq.(7)). The fitting parameters α and n for the best-fit Van Genuchten's capillary pressure-saturation curve for kerosene-water system illustrated in Fig.4 have values of 0.048 cm^{-1} and 2.7, respectively. The best-fit curve was found using a nonlinear least squares fitting routine using SPSS software version 7.5 (Statistical Package for Social Sciences, Version 7.5).

It is clear from Fig.4 that the laboratory-measured values of capillary pressure do not all scale exactly onto the best-fit Van Genuchten's curve, especially, at low saturation. This discrepancy is due to the air-water relation having a residual saturation value greater than the other fluid systems. This discrepancy or variability may indeed have an influence on the results of the numerical simulations incorporating this data set, but it is assumed here that this effect will be negligible with respect to the overall behaviour of the fluids. In order to test the ability of the best-fit equation for representing the experimental measurements in an efficient way, the coefficient of correlation (r) and the coefficient of determination (r^2) were calculated. These coefficients are not enough, but also ANOVA test must be conducted. The correlation coefficient (r) for the best-fit Van Genuchten's curve is equal to 0.925 and the coefficient of determination (r^2) is equal to 0.855. From ANOVA test, $f_{calculated}$ is greater than F_{table} with a confidence interval equal to 0.95. According to these indicators, the best-fit equation gives a good representation for the experimental results.

In a two-phase system, the permeability of both the wetting and nonwetting fluids is a strong function of fluid saturation. At complete saturation with respect to either fluid the permeability of that fluid will equal the saturated permeability, as expressed by a relative permeability as unity. If either fluid is absent, its relative permeability will clearly be zero. At intermediate fluid saturations, the permeability of either phase will be reduced from the saturated value due to the reduction in cross-sectional area available for flow, the increased tortuosity brought about by the presence of the other phase and the decreased hydraulic raduis of the available flow paths. The shape of a relative permeability-saturation curve is therefore governed largely by the pore size distribution of the aquifer material of interest. This pore size distribution governs the nature of the capillary pressure-saturation curve and thereby allows one to have reasonable confidence in using information obtained from the measurement of a capillary pressure-saturation curve in the construction of a relative permeability curve.

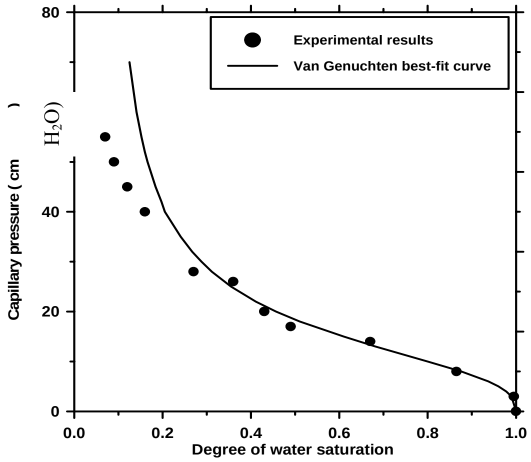

Figure 4: Capillary pressure-water saturation curve for Kerbala's sand

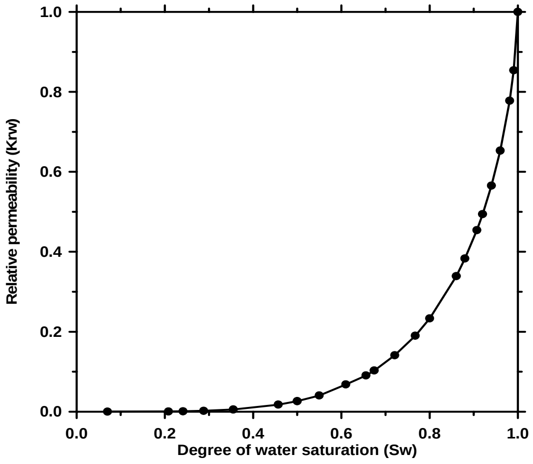

Figure 5: Relative permeability-water saturation curve of Kerbala's sand for kerosene-water system

Several authors have presented empirical relationships allowing for the construction of a drainage relative permeability-saturation function, given the characteristcs of a measured capillary pressure-saturation curve. These include the works of Brooks and Corey (1964), Van Genuchten (1980) and Parker et al. (1987). The expression adopted here is that of Parker et al. (1987), which is consistent with the capillary pressure curves developed by the same authors. The expression of Parker et al. (1987) for the wetting phase relative permeability is given by eq.(8). Fig.5 shows the relative permeability-water saturation curve for the sand used here for kerosene-water system.

CONCLUSIONS

(1) Despite the importance of capillary pressure-saturation relationship to the simulation of organic liquid migration at hazardous waste sites, few measured data are available for the system of interest. Because of the reliance on estimated capillary pressures for the prediction of the subsurface movement of organic liquids, it is important to examine the accuracy of the estimation method by using statistical criteria.

(2) The residual water saturation, S_r, for Kerbala's sand was specified from the direct measurements of the primary drainage capillary pressure-saturation relationship for the kerosene-water system. The set of these measurements was approximated by a scaled Van Genuchten's equation. This set of measurements do not all scale exactly onto the best-fit Van Genuchten's curve, especially, at low saturation. This discrepancy at low saturation occurs because the air-water relation used as reference curve is characterized by a larger residual saturation value than the other fluid systems.

(3) The shape of a relative permeability-saturation curve is governed largely by the pore size distribution of the aquifer material. This pore size distribution governs the nature of the capillary pressure-saturation curve and thereby allows one to have reasonable confidence in using information obtained from the measurement of a capillary pressure-saturation curve in the construction of a relative permeability curves.

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