

Temperature Dependence of Water Retention Curves for Wettable and Water-Repellent Soils

J. Bachmann, R. Horton*, S. A. Grant, and R. R. van der Ploeg

ABSTRACT

The capillary pressure (ψ) in unsaturated porous media is known to be a function of temperature (T). Temperature affects the surface tension (σ) of the pore water, but possibly also the angle of contact (γ). Because information on the temperature dependence of γ in porous media is rare, we conducted experiments with three wettable soils and their hydrophobic counterparts. The objectives were (i) to determine the temperature dependence of the water retention curve (WRC) for wettable and water-repellent soils, (ii) to assess temperature effects on the apparent contact angle γ_A derived from those WRCs, and (iii) to evaluate two models (Philip-de Vries and Grant-Salehzadeh) that describe temperature effects on ψ . Columns packed with natural or hydrophobized soil materials were first water saturated, then drained at 5, 20, and 38°C, and rewetted again to saturation. Capillary pressure and water content, θ , at five depths in the columns were measured continuously. The observations were used to determine the change in γ_A with T , as well as a parameter β_0 that describes the change in ψ with T . It was found that the Philip-de Vries model did not adequately describe the observed relation between ψ and T . A mean value for β_0 of -457 K was measured, whereas the Philip-de Vries model predicts a value of -766 K. Our results seem to confirm the Grant-Salehzadeh model that predicts a temperature effect on γ_A . For the sand and the silt we studied, we found a decrease in γ_A between 1.0 to 8.5°, when the temperature was increased from 5 to 38°C. Both β_0 and γ_A were only weak functions of θ . Furthermore, it seemed that for the humic soil under study, surfactants, i.e., the dissolution of soil organic matter, may compound the contact angle effect of the soil solids.

TEMPERATURE AFFECTS the ψ of soil water, which is manifested as temperature-affected soil WRCs. Even though many investigators report WRC without considering temperature, Hopmans and Dane (1986), Nimmo and Miller (1986), Salehzadeh (1990), Constantz (1991), and She and Sleep (1998) among others have all observed that WRCs change with temperature. Philip and de Vries (1957) assumed that changes of ψ in unsaturated porous media with temperature were due entirely to changes in interfacial σ of pure liquid water. However, most later experiments indicated that temperature-induced changes in ψ were larger than the temperature effect on σ alone (Jury and Miller, 1974; Novak, 1975; Bach, 1992; Liu and Dane, 1993; Döll, 1996). Nimmo and Miller (1986) showed that the temperature effect in porous media exceeded the temperature dependence of the liquid-gas interface by a factor of one to

five. Hopmans and Dane (1986), following a suggestion of Chahal (1964, 1965), reported that neither entrapped air nor the temperature dependence on σ of the soil solution could account for the observed temperature-dependence of ψ .

As a further potential cause for the observed discrepancy, temperature effects on the γ may be considered. The γ at the three-phase boundary line is one of the fundamental quantities, besides the liquid σ , affecting water retention. A study of contact angle effects on water retention generally requires knowledge of γ of the dry-soil particle surface to describe the wetting properties of the solid surface. In this context, the definition of γ needs some clarification. When a liquid is in contact with a plane solid surface, γ is defined as the angle between the solid and a tangent aligned with the liquid at the point of contact with the solid. The contact angle is actually dependent on a balance of interfacial forces in the three-phase solid-liquid-gas system. This property can be assessed, e.g., with the sessile-drop method (sessile-drop contact angle, γ_{SD} ; see Adamson, 1990). However, when specifying the combined effect of wettability and pore system, one should derive γ directly from the three-phase system, i.e., the WRC of the wettable medium and its hydrophobic counterpart. The contact angle derived from such an experiment can be called the apparent contact angle (γ_A). The γ_A thus reflects the combined effect of interfacial tensions and factors like surface roughness, topology of the pore system, and dynamics of the flow process on water retention.

In a recent paper, Grant and Salehzadeh (1996) developed theory that connected assessable physical quantities like ψ with theory describing surface properties of the solid phase. In their derivation, they partitioned the temperature effect of σ and γ on the capillary pressure-saturation relationship. This derivation can be considered as a thermodynamic extension of the mechanistic Philip and de Vries (1957) model. First experimental results for some soil materials and a glass-bead sample showed that changes in γ contributed to the temperature sensitivity of ψ . Based on the theory of Grant and Salehzadeh (1996), She and Sleep (1998) derived an expression for predicting the temperature dependence of γ . Their theory predicts an increase of γ with increasing temperature. For quartz surfaces in contact with bulk water, also Derjaguin and Churaev (1986) predicted an increase of γ with increasing temperature. However, in contrast to current theory, there is experimental evi-

J. Bachmann and R.R. van der Ploeg, Institute of Soil Science, Univ. of Hannover, Herrenhaeuser Str. 2, 30419, Hannover, Germany; R. Horton, Dep. of Agronomy, Iowa State Univ., Ames, IA 50011; and S.A. Grant, U.S. Army Cold Regions Research and Engineering Lab., 72 Lyme Rd., Hanover, NH 03755. Journal Paper no. J-19022 of the Iowa Agric. and Home Econ. Exp. Stn., Ames; Project no. 3287, and supported in part by Hatch Act and State of Iowa funds. Received 8 Dec. 2000. *Corresponding author (rhorton@iastate.edu).

Abbreviations: SD, quartz sand; SD_{phob}, hydrophobic quartz sand; SL, wettable humic soil; SL_{phob}, hydrophobic humic soil; ST, wettable silt; ST_{phob}, hydrophobic silt; T , temperature; TDR, time domain reflectometry; WRC, water retention curve; θ , soil water content; σ , surface tension; σ^L , liquid-air surface tension; ψ , capillary pressure; γ , angle of contact; γ_A , apparent contact angle; γ_{SD} , sessile drop contact angle.

dence that γ decreases with increasing temperature (King, 1981).

To our knowledge, there have been no systematic studies of the temperature dependence of ψ in soils having a different contact angle. To resolve the discrepancy between observed and theoretical temperature effects on ψ , a careful study of temperature effects on WRCs for a group of soil materials with a wide range of contact angles is needed. The objectives of this study therefore were (i) to measure temperature effects on water retention curves of paired (wetable-hydrophobic) soil samples, (ii) to determine how temperature affects the γ_A of the paired soil samples, and (iii) to evaluate the Philip-de Vries and Grant-Salehzadeh models for describing temperature effects on capillary pressure.

THEORY

Capillary Pressure and Temperature Dependence

The pressure difference across a concave interface of a water meniscus under equilibrium conditions in a capillary can be expressed as (Grant and Salehzadeh, 1996; their Eq. [3])

$$\psi = \frac{2\sigma^{\text{lg}} \cos(\gamma)}{r} \quad [1]$$

where ψ [Pa] is the capillary pressure, σ^{lg} [N m⁻¹] is the surface tension of the liquid–gas interface tension, γ [°] is the contact angle, and r [m] is the average radius of the liquid–gas interface.

From Eq. [1], the partial derivative of ψ with respect to T can be written as (Grant and Salehzadeh, 1996; their Eq. [6])

$$\frac{\partial \psi}{\partial T} = \frac{\psi(\theta)}{\sigma^{\text{lg}}} \frac{\partial \sigma^{\text{lg}}}{\partial T} + \frac{\psi(\theta)}{\cos(\gamma)} \frac{\partial \cos(\gamma)}{\partial T} \quad [2]$$

The first term of the right-hand side of Eq. [2] represents the conventional approach of Philip and de Vries (1957), whereas the second term stands for the extension because of the contact-angle temperature effect, proposed by Grant and Salehzadeh (1996).

The temperature dependence of the liquid–air surface tension, σ^{lg} , in the range of -10 to 50°C is described closely by a linear function (see Grant and Salehzadeh, 1996) as

$$\sigma^{\text{lg}} = a' + b'T \quad [3]$$

where $a' = 0.11766 \pm 0.00045$ N m⁻¹ and $b' = -0.0001535 \pm 0.0000015$ N m⁻¹ K⁻¹, and (for later use) $a'/b' = -766.45$ K.

Frequently, it is assumed that the ψ is also a linear (decreasing) function of the temperature, T [K]. For soils with a given water content, θ (m³ m⁻³), this function can be expressed as

$$\psi(T, \theta) = a(\theta) + b(\theta)T \quad [4]$$

With use of Eq. [4], a soil-specific parameter, β_0 , can be defined (Grant and Salehzadeh, 1996; their Eq. [43]) as

$$\frac{\psi(T, \theta)}{\psi(T, \theta) \partial \psi(T, \theta) / \partial T} = \beta_0 + T \quad [5]$$

where $\beta_0 = a(\theta)/b(\theta)$.

Grant and Salehzadeh (1996) postulated that, in view of Eq. [2], [3], and [4], if the γ is independent of T the slope of a plot of T versus $\psi/(\partial\psi/\partial T)$ should be equal to one. In this case a value for β_0 should be found experimentally, that is, close to $a'/b' = -766.45$ K (see Grant and Salehzadeh, espe-

cially their Eq. [26]). Under this assumption, the temperature dependence of ψ is caused only by the temperature dependence of the surface tension, σ^{lg} , of pure water, which basically is the model of Philip and de Vries (1957).

However, if it is assumed that also the γ is temperature-dependent, the slope of the T versus $\psi/(\partial\psi/\partial T)$ plot still should be equal to one, but the value of β_0 should differ from $a'/b' = -766.45$ K. Now Eq. [5] applies and β_0 in this case is equal to $a'/b' \neq -766.45$ K. Hence, to find out which model should be used to describe the temperature dependence of the capillary pressure, $\psi(T, \theta)$, WRCs at different temperatures of wettable soil materials and their nonwettable counterparts should be determined.

Parameterization of Temperature-Dependent Water Retention Curves

For later use it is remarked here that separation of variables and integration of Eq. [5] leads to an expression that can be incorporated into any analytical model for a general description of the function $\psi(\theta, T)$, see Grant and Salehzadeh (1996). This expression can be given as

$$\psi(\theta, T) = \psi(\theta, T_r) \left(\frac{\beta_0 + T}{\beta_0 + T_r} \right) \quad [6]$$

where T is an arbitrary temperature [K], say 38°C , and T_r is a reference temperature [K], e.g., 5°C . Combination of Eq. [6] with the van Genuchten (1980) equation yields:

$$\theta(\psi, T) = \theta_r + \frac{\theta_s - \theta_r}{\{1 + [\alpha\psi(T)]^n\}^m} \quad [7]$$

In Eq. [7] the quantity θ_r is the residual water content, θ_s is the saturated water content, and α [m⁻¹], n , and m are empirical fitting parameters.

MATERIALS AND METHODS

Soils

We used three wettable soil materials and their hydrophobic counterparts as paired samples. The first material was a laboratory quartz sand, whereas the second one was a subsoil silt from a Weichselian loess under agricultural use. The wettable laboratory quartz sand (SD) and the wettable silt (ST) were hydrophobized by coating the grains with Dichlorodimethylsilane (C₂H₆Cl₂Si) (Shaw, 1975) to give hydrophobic materials (SD_{phob} and ST_{phob}) with identical texture to SD and ST, respectively, but with a different contact angle. Based upon soil texture, the amount of applied Silane was 7.5 mL kg⁻¹ air-dry soil for the sand and 50 mL kg⁻¹ for the silt. The third material was a humic soil, sampled at a former pine (*Pinus sylvestris*) stand that had been in horticultural use for the last 15 yr. This soil was a Spodosol formed on glacial till sand. The contact angle of the Ah-horizon of this soil varied between slight water repellency (sample SL) and strong water repellency (SL_{phob}). The initial γ_{SD} of air-dry samples of our soils, as a measure of potential repellency, was assessed by the modified sessile-drop method (Bachmann et al., 2000a,b). Selected physical and chemical properties of the three wettable soils and their hydrophobic counterparts are shown in Table 1.

Experimental Setup

All experiments were conducted with vertical acrylic columns having an i.d. of 8.85 cm and a height of 15.0 cm (Fig. 1). Each column was situated in an insulation box and was closed at the top and the bottom with a ceramic plate having an air

Table 1. Selected physical and chemical properties of the six soils (sieved <2000 μm) under study.

Soil	Bulk density Mg m^{-3}	Soil organic C $(\text{kg kg}^{-1}) \times 100$	Sessile-drop contact angle γ_{SD} (degree)	Particle-size fraction						
				Particle size class [μm]						
				<2	2–6	6–20	20–63	63–200	200–630	630–2000
Wettable sand SD	1.55	0.0	<5	0.0	0.1	0.1	0.2	8.5	90.5	0.4
Hydrophobic sand SD _{phob}	1.47	0.0	97.2 \pm 5.9	0.0	0.1	0.1	0.2	8.5	90.5	0.4
Wettable silt ST	1.54	0.0	<5	2.6	1.4	15.2	70.0	6.0	4.8	0.1
Hydrophobic silt ST _{phob}	1.52	0.0	78.1 \pm 5.3	2.6	1.4	15.2	70.0	6.0	4.8	0.1
Wettable humic soil SL	1.61	1.4	45.0 \pm 9.3	1.6	1.0	2.1	4.6	26.3	61.3	3.1
Hydrophobic humic soil SL _{phob}	1.48	1.4	92.6 \pm 5.2	1.8	0.5	1.6	4.3	28.7	60.1	3.0

entry value exceeding (more negative than) -80 kPa (KPM Company, Berlin).

The plates at the top and the bottom of each column were placed in permanent contact with water reservoirs of a given temperature. The temperature was adjusted for each drying-wetting cycle. Temperature control in the insulation box and in the water reservoirs at both ends of a column was maintained by circulating cold water through copper coils ($T < 20^\circ\text{C}$) and by a heating wire ($T > 20^\circ$). To minimize lateral heat fluxes, the sides of a column were sealed with three layers of 1-cm thick extruded polystyrene insulation and fitted with three additional temperature sensors (Fig. 1).

Column experiments were conducted with all six soil materials. To prepare a column, dry soil was poured into an initially water-filled column. To check for homogeneous packing, bulk density was determined after each centimeter of soil that was added. To minimize shrinking during an experiment, each soil was initially drained to create water tensions that were higher than those occurring during the following drying-wetting cycles. Because the soil materials differed in organic matter content, mineral composition, and contact angle, the final bulk densities differed slightly after the initial drainage-wetting cycle preparation (Table 1).

Soil water tension, water content, and temperature were measured at five positions along the axis of each column. Soil temperature was measured with semiconductor elements (KTY 10, Conrad Electronic, Hirschau, Germany) having an accuracy $<0.3^\circ\text{C}$, soil water tension with pressure transducer tensiometers (136 PC, Honeywell, Fort Washington, PA, ac-

curacy <0.15 kPa), and soil water content with time domain reflectometry (TDR) probes (TRIME-ES System, Imko, Karlsruhe, Germany). The TDR probes were calibrated individually for each soil at four different water contents and three temperatures (5, 20, and 38°C). Accuracy of the probes was within 1.0 to 1.5% (vol./vol.) after calibration. The temperature dependence of each TDR probe was evaluated for two ranges: from 5 to 20°C and from 20 to 38°C . Data were acquired and the system was controlled with two data loggers (Analog Devices) connected to a DOS operating personal computer.

With the soil columns just described, drying (drainage) and rewetting experiments were performed. During drying, columns were drained from the top with a constant water potential of -65 kPa being maintained at the upper ceramic plate. Columns were rewetted from the bottom with a constant positive water pressure of 2 kPa at the lower ceramic plate. During drying the lower outlet was closed, whereas during wetting the upper outlet was shut off. Rewetting was considered to be complete when the tensiometers in all depths indicated positive water pressure. Because the outflow rates varied for the different soils, the duration of a drying cycle was soil-dependent. Drainage from the sand columns was stopped when the change in ψ was <0.04 kPa h^{-1} . The corresponding value for the silt was <0.08 kPa h^{-1} , and for the humic soil <0.14 kPa h^{-1} . The corresponding water content at the reversal point was defined as θ_{min} . All three drying-wetting cycles were completed within 3 wk, i.e., one temperature cycle per week. In summary, a total of 180 WRCs (six soils, five depths, three temperatures, one wetting cycle, and one drying cycle) were collected.

Evaluation of β_0 from Water Retention Curves at Different Temperatures

The parameter β_0 was evaluated locally and globally in a column. For the local estimation of β_0 , we used Eq. [4] and estimated first, from a pair of $\psi(\theta, T)$ values (for the same θ -value, but for two temperatures) values for $a(\theta)$ and $b(\theta)$. From these values, β_0 was calculated as $a(\theta)/b(\theta)$, or as

$$\beta_0 = \frac{\psi_1(\theta, T_1)T_2 - \psi_2(\theta, T_2)T_1}{\psi_2(\theta, T_2) - \psi_1(\theta, T_1)} \quad [8]$$

In Eq. [8] T_1 and T_2 [K] are the temperatures (278 K and 311 K which correspond to 5°C and 38°C) at which the WRCs were measured. Curve fitting with a cubic spline function was performed with the Sigma Plot 5 software package (Jandel Corporation, Chicago, IL). Cubic splines were used in this part of the analysis to smooth the data with a high degree of flexibility.

Alternatively, we evaluated β_0 by using the data from five depths and three temperatures simultaneously (global estimates). For this analysis, we used two different approaches. First, we applied a two-dimensional cubic spline interpola-

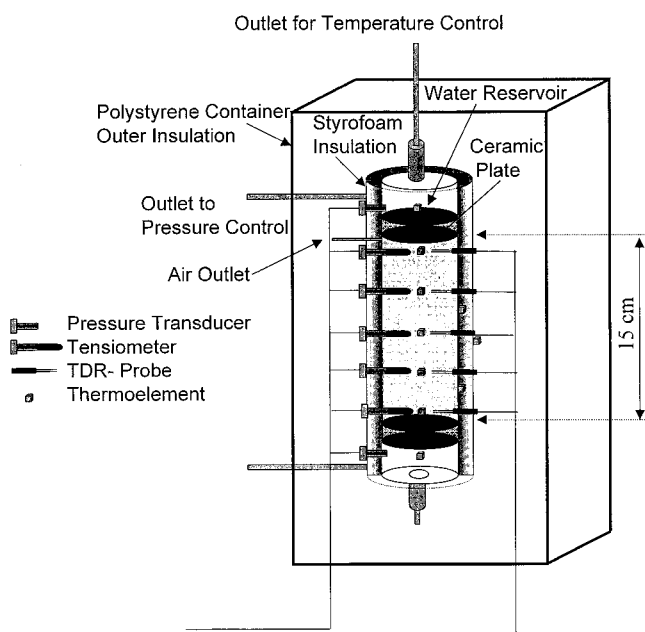
**Fig. 1.** Schematic representation of an instrumented soil column.

Table 2. Temperature dependence of the soil water content, θ_s , at saturation and the reversal (minimum) water content, θ_{\min} , at the end of a drying (drainage) cycle.

Soil	θ_s of drying WRC (mean)	$d\theta_s/dT$ [m ³ m ⁻³ °C ⁻¹]	θ_{\min} of wetting WRC (mean)	$d\theta_{\min}/dT$ [m ³ m ⁻³ °C ⁻¹]
SD [†]	35.3 ± 3.5	-0.173	8.2 ± 2.4	-0.060
SD _{phob} [‡]	32.0 ± 3.5	0.033	7.2 ± 4.0	-0.080
ST [§]	35.9 ± 2.0	-0.140	15.5 ± 3.0	0.026
ST _{phob}	40.1 ± 3.1	-0.084	13.8 ± 4.1	0.050
SL [#]	27.1 ± 4.0	0.032	10.5 ± 2.7	-0.080
SL _{phob} ^{††}	27.4 ± 4.9	-0.116	10.4 ± 2.4	-0.102

[†] Wettable sand.

[‡] Hydrophobic sand.

[§] Wettable silt.

^{||} Hydrophobic silt.

[#] Wettable humic soil.

^{††} Hydrophobic humic soil.

tion at each of the three temperatures for selected water contents according to Grant and Salehzadeh (1996) by using the CSAKM function of the IMSL routine package (International Mathematics and Statistics Libraries, 1989). Second, the parameter β_0 , as well as the van Genuchten-equation parameters α , n , m , θ_s , and θ_r , were fitted simultaneously to a complete data set of either wetting or drying by using Eq. [7] directly. The nonlinear least squares approximation of the extended van Genuchten equation was also determined with the Sigma Plot 5 software package.

The function $\psi(\theta, T)$ of Eq. [7]) was also used, in combination with Eq. [1], to estimate the γ_A of the nonwetable soils under study. Following Morrow (1976) and She and Sleep (1998), we assumed that the γ_A of a wettable soil was equal to zero, i.e., $\cos(\gamma_A) = 1$, and that the σ^w of the soil solution of a wettable soil was equal to that of its nonwetable counterpart. Using Eq. [1] for both a wettable soil and its nonwetable counterpart and building ratios, we calculated γ_A , for given values of θ and T , from the following expression:

$$\cos(\gamma_A) = \psi_{\text{phob}}/\psi_{\text{phil}} \quad [9]$$

where phil and phob stand for the hydrophilic (wetable) and hydrophobic (nonwetable) soil, respectively.

RESULTS AND DISCUSSION

All drying-wetting cycles were carried out in the same fashion. To control the duration of the hydrophobicity, γ_{SD} were measured before and after each experiment. It was found that differences in γ_{SD} , measured before and after an experiment, were smaller than the standard deviation of γ_{SD} (see Table 1). Therefore, it was assumed that the wettability of the soil particle surfaces remained constant during the entire experiment. Each drying (drainage) cycle of a soil column started after 1 to 2 d of saturation, as indicated by positive and depth-increasing matric potentials. A small increase or decrease of the matric potential of 0.1 to 0.2 kPa indicated variation of the temperature during saturation. Temperature dependence of the θ_s and the reversal (minimum) water content, θ_{\min} , at the end of a drying cycle are shown in Table 2. The θ_s had a tendency toward smaller values with increasing temperature, except for the hydrophobic sand (SD_{phob}) and the wettable soil (SL).

Matric potentials differed generally slightly, being depth-dependent at the reversal point, when drying was reversed to wetting. The temperature dependence was generally smaller for θ_{\min} than for θ_s . Except for ST and ST_{phob}, θ_{\min} showed a tendency to decrease with increas-

ing temperature. In contrast to the capillary model of Liu and Dane (1993), we assume, therefore, that θ_{\min} was constant with temperature. Because the depth dependence of the θ_{\min} values (initial water content for wetting curves) was relatively small, no hysteresis model was used to parametrize the wetting WRCs.

Collected data sets were used to construct the respective WRC. The data were parameterized with use of the van Genuchten (1980) model. Figure 2 shows the general tendency observed for all soils, that both wetting and drying WRCs were approximated satisfactorily with the closed-form equation of van Genuchten (1980).

A complete list with the tabulated data of all measurements can be obtained from the senior author.

The Effect of Temperature on Capillary Pressure

For SD and SD_{phob}, we found that the temperature effect was smaller than the accuracy of the pressure transducers. Therefore, only the ST and the SL were analyzed. In a first step, the experimental data for 5 and 38°C at each depth were fitted to a cubic spline function. Then the β_0 was determined as described by Eq. [7]. As an example, Fig. 3 shows β_0 values for the SL_{phob}, determined for each of the five depths. Because of the level of experimental error, we observed no statistically significant trend in depth dependence of β_0 .

Referring to Table 3, we can see that the temperature effect increased (β_0 is less negative) when the soil water content was increasing (wetting cycle, $\Delta\beta_0/\Delta\theta > 0$).

For wetting, the water content dependence of β_0 was approximately three times larger than for drying. Almost all water-content dependent β_0 values were found to be significantly larger than the temperature dependence predicted by the Philip-de Vries model. Table 3 shows further the considerable magnitude of the standard deviation associated with the depth-by-depth estimation of β_0 .

The simultaneous cubic spline interpolation, which was based on the entire data set from five depths and three temperatures, lowered the standard error of the estimated β_0 value markedly. As also shown in Table 3, the mean for all depths obtained by local estimation ($\beta_0 = -475$ K) was close to the value obtained by global estimation ($\beta_0 = -457$ K). A similar reduction of the standard error was obtained when global fits were performed with Eq. [7], see Table 3. A comparison of global

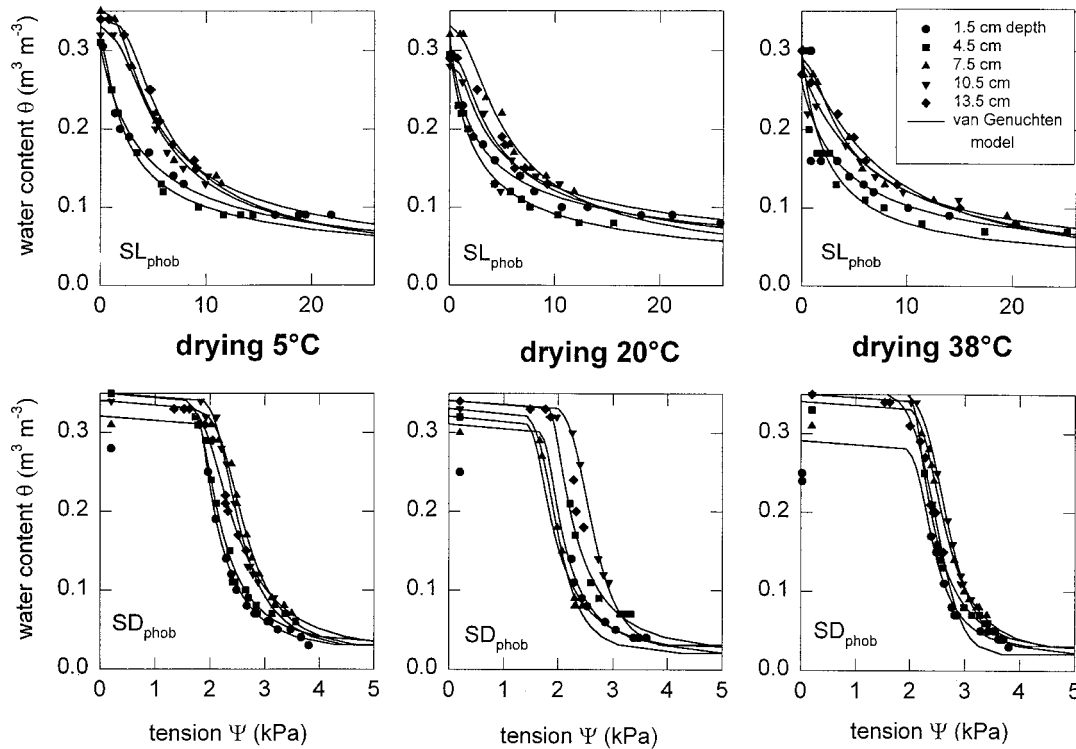


Fig. 2. Drying-wetting measured capillary pressure – water content (ψ – θ) data points for all column depths, and fitted van Genuchten water retention model for the hydrophobic soil SL_{phob} (upper graphs) and the hydrophobic sand (SD_{phob}) (lower graphs).

fits of either the cubic spline approximation or the van Genuchten equation yielded almost identical values. In summary, the local estimates of β_0 resulted in slightly smaller β_0 values (less negative) than global fits of β_0 . However, $\beta_0(\theta)$ values obtained locally for each depth were consistent with β_0 determined from global fits. If a constant β_0 was used instead of $\beta_0(\theta)$, the temperature effect was underestimated at high θ values and overestimated at low θ values. The error, however, is only slightly larger than the standard error of the global fit in the range of measured water contents. Table 3 shows further

that β_0 was larger (i.e., less negative) for wetting WRCs than for drying WRCs. Data from the literature are in agreement with this observation (Table 4).

All data strongly indicate that the temperature dependence of ψ was much larger than can be explained by the surface tension (σ^s) effect of pure bulk water alone. For instance, the β_0 value of -766 K derived for pure water leads to a reduction of ψ (less negative) by a factor of 0.93 if the soil temperature increases at constant water content from 5 to 38°C. However, the corresponding value for the hydrophobic humic soil (e.g., $\beta_0 =$

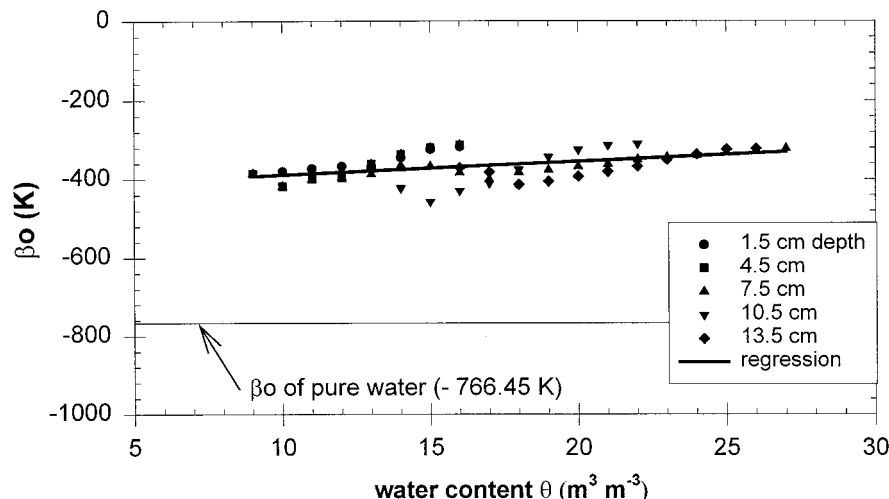


Fig. 3. Temperature parameter, β_0 , versus water content, θ , (drying) for the hydrophobic soil (SL_{phob}). Mean value of β_0 estimated from local analysis (mean of all depths) is -365 ± 35 K. Note that the value of β_0 for pure water is -766.45 K.

Table 3. Temperature parameter, β_0 , derived from cubic spline fitting and van Genuchten approximation, calculated for the temperature range of 5 to 38°C.

		Depth-dependent local fit of β_0 (cubic spline interpolation)						Global fit of β_0 ‡		
		Soil depth, cm					Mean and SE from data of all depths	$\Delta\beta_0/\Delta\theta$ §	Cubic spline	van Genuchten equation
Soil†		1.5	4.5	7.5	10.5	13.5				
		K							K	
SD	drying	n.m.¶	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	—	<−3500
SD	wetting	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	—	<−3500
SD _{phob}	drying	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	—	<−3500
SD _{phob}	wetting	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	−696 ± 919	<−3500
ST	drying	−471 ± 91	−505 ± 102	−475 ± 101	−483 ± 76	−378 ± 33	−467 ± 95	14.5	−507 ± 26	−526 ± 29
ST	wetting	−357 ± 28	−399 ± 49	−278 ± 180	−471 ± 136	−432 ± 99	−387 ± 92	1.8	−392 ± 17	−401 ± 19
ST _{phob}	drying	−604 ± 118	−680 ± 234	−789 ± 273	−686 ± 233	−472 ± 102	−657 ± 222	21.6	−603 ± 57	−598 ± 45
ST _{phob}	wetting	−461 ± 118	−494 ± 107	−290 ± 251	−457 ± 417	−399 ± 418	−481 ± 297	7.9	−434 ± 24	−428 ± 12
SL	drying	−866 ± 457	−681 ± 234	−789 ± 273	−686 ± 233	−475 ± 103	−705 ± 312	13.6	−674 ± 57	−542 ± 150
SL	wetting	n.m.	−494 ± 228	−360 ± 27	−343 ± 12	−336 ± 7	−391 ± 128	4.7	−364 ± 27	−361 ± 27
SL _{phob}	drying	−354 ± 25	−366 ± 39	−361 ± 21	−375 ± 55	−368 ± 3	−365 ± 35	3.6	−346 ± 12	−324 ± 5
SL _{phob}	wetting	−348 ± 30	−372 ± 171	−329 ± 35	−317 ± 171	−371 ± 92	−346 ± 115	1.2	−338 ± 8	−344 ± 11
Mean		−500	−499	−459	−477	−403	−475		−457	−441

† SD, wettable sand; SD_{phob}, hydrophobic sand; ST, wettable silt; ST_{phob}, hydrophobic silt; SL, wettable humic soil; SL_{phob}, hydrophobic humic soil.

‡ Simultaneous fit for data of all depths and all temperatures.

§ Slope of linear regression of plots similar to Fig. 5.

¶ n.m. = not measurable.

−350 K for drying) decreased ψ by a factor of 0.54, which is an effect about six times larger than described by the temperature dependence of σ^{lg} of pure water alone. Mixed mineral composition, surface roughness, and pore geometry, can be expected to influence adsorption and, hence, the capillary forces that control water retention. For the soils without soil organic matter, β_0 was larger for the hydrophilic variant. For the soil with an organic C content of 1.4%, the values were also much larger compared with water. This is particularly true for SL_{phob}, which shows strong repellency.

With known values for the parameters a and b of Eq. [4] and for β_0 of Eq. [5], Eq. [7] was used for any of the soils under study to construct the temperature-dependent WRCs. As an example, Fig. 4 presents measured data points and the $\psi(T, \theta)$ surface of the fitted two-dimensional van Genuchten equation for the SL_{phob}.

Evaluation of the Apparent Contact Angle

The depth-dependent spline functions were also used to calculate γ_A for the hydrophobic soils for each depth of a column (Eq. [9]). Table 5 shows such values derived from the WRCs measured at 5 and 38°C, both for wetting and drying. Generally, a tendency to lower γ_A values

was observed with increasing depth for both the drying and the wetting WRCs. The mean value of γ_A for all materials was 45.7°.

We examined also the dependence of γ_A on θ . With a linear regression the slope $\Delta\gamma_A/\Delta\theta$ of the function $\gamma_A = f(\theta)$ was determined. In Table 5 values of $\Delta\gamma_A/\Delta\theta$ for each soil at 5 and 38°C are shown. It can be seen that this value is generally small, but for half of the soils the value was significantly different from zero (t -test, Snedecor and Cochran, 1980). Hence, it can be assumed that γ_A is only a weak function of θ within the range of observed water contents (Fig. 5).

A comparison of the γ_{SD} with the γ_A shows further that the water content at the reversal point θ_{min} was obviously higher than the critical water content, where the transition from wettability to hydrophobicity for soils with a $\gamma_{\text{SD}} > 90^\circ$ may occur. A transition to repellency, indicated by positive potentials during the wetting process, was not observed at any position in the column. Morrow (1976) found for a hydrophobic porous medium and with the use of several liquids, having a wide range of σ^{lg} , that drying to a capillary pressure <3.5 times the liquid surface tension led to nonliquid uptake in the subsequent wetting cycle, when γ_{SD} was $>60^\circ$. During our experiments, water tensions higher than the numerical value of 3.5 multiplied by σ^{lg} (e.g., for water as testing liquid: 25 kPa) were reached at the reversal points for silt and soil. Other researchers (e.g., de Jonge et al., 1999) found that water repellency varied greatly with water content. Preliminary observations we made before our column experiments showed that water repellency occurred for the SL_{phob} at water contents around 1 to 2% by weight, which corresponded to a matric potential of about −75 MPa. For the ST, a corresponding transition was also observed between 1 and 2%, which corresponds to matric potentials of −2 to −3 MPa. In summary, our values of the critical capillary pressures for soil materials thus were considerably more negative than the values reported by Morrow (1976) for

Table 4. Estimates of the parameter β_0 of water retention curves as reported in the literature.

Porous medium	Drying (d) Wetting (w)	$\beta_0 \pm \text{SE}^\dagger$	Reference
K			
Oakley sand	d	−436 ± 11	Constantz (1991)
	w	−392 ± 4	Constantz (1991)
Glass beads	d	−451 ± 2	Nimmo and Miller (1986)
	w	−404 ± 1	Nimmo and Miller (1986)
Plainfield sand	d	−432 ± 5	Nimmo and Miller (1986)
	w	−415 ± 4	Nimmo and Miller (1986)
	d	−496 ± 4	Nimmo and Miller (1986)
	w	−334 ± 2	Nimmo and Miller (1986)
	w	−380 ± 2	Salehzadeh (1990)
	d	−356 ± 2	Salehzadeh (1990)

† SE = asymptotic standard error of the estimate.

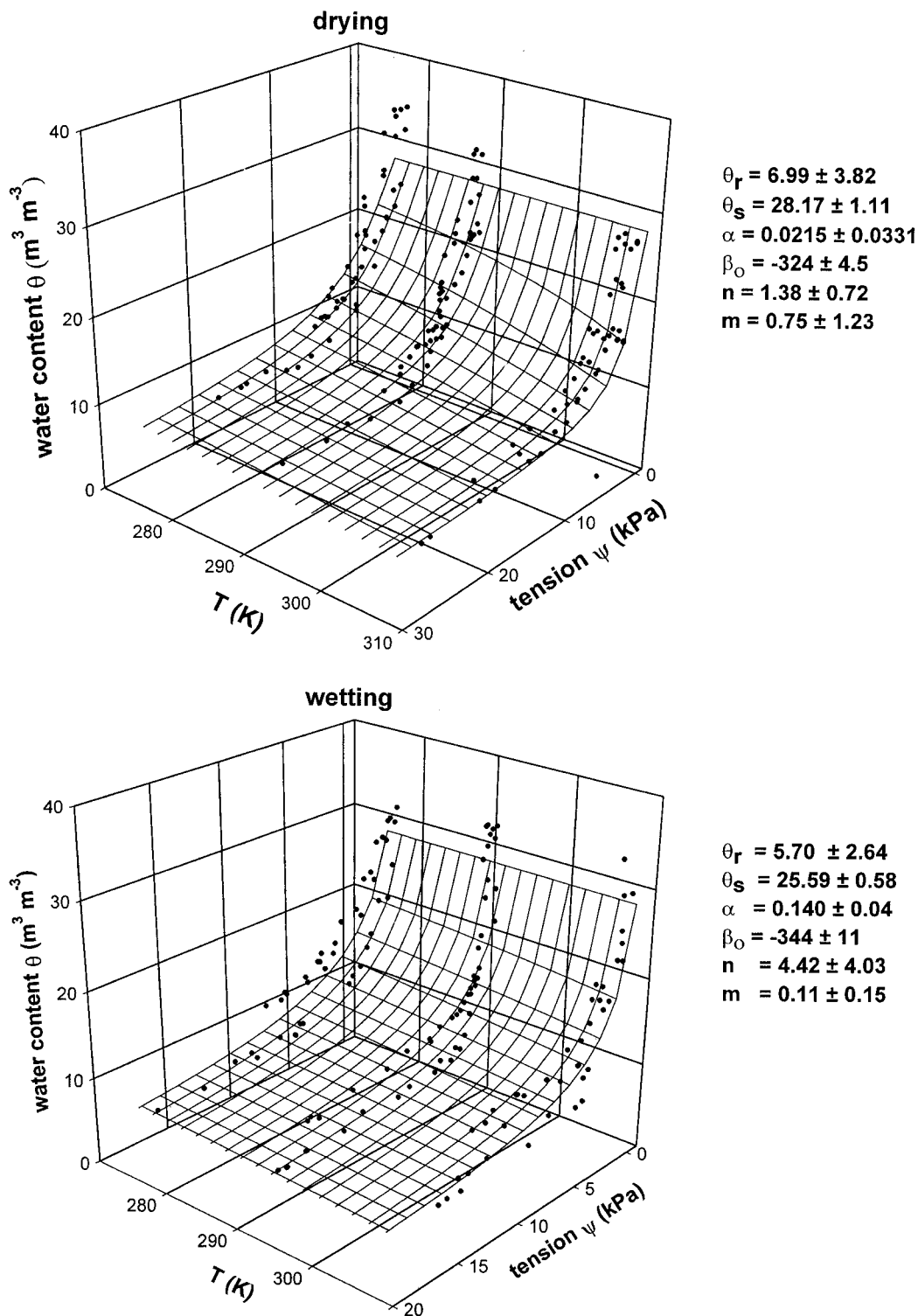


Fig. 4. Global fit of the temperature-dependent van Genuchten function for the hydrophobic soil (SL_{phob}) (drying and wetting).

a porous Teflon sample in combination with organic and nonorganic liquids.

Temperature Dependence of the Apparent Contact Angle

Table 5 indicates that the temperature dependence of γ_A has a tendency to smaller values with increasing

temperature, with the exception for the drying cycle of the paired soils SL and SL_{phob} . This result may be explained to some extent by the dissolution of soil organic substances. Generally, dissolved organic substances lower the liquid surface tension σ^{lg} of 72.6 mN m^{-1} for pure water. Chen and Schnitzer (1978) and Tschapek et al. (1976) reported a decrease in σ^{lg} of the soil solution to values around 63 mN m^{-1} , caused by humic acid. A

Table 5. Apparent contact angle γ_A for the hydrophobic soil materials (calculated with Eq. [9]), derived from water retention curves at 5°C and 38°C.

			Soil depth, cm					Mean and SE from data of all depths	$\Delta\gamma_A/\Delta T$	$\Delta\gamma_A/\Delta\theta^{\ddagger\ddagger}$	n#
Soil†	Temperature °C		1.5	4.5	7.5	10.5	13.5				
			degree								
SD _{phob}	d‡	5	52.0 ± 11.1	41.8 ± 6.7	30.3 ± 3.9	31.3 ± 3.0	36.9 ± 6.8	39.7 ± 9.4	−0.03	0.14 ± 0.15	96
		38	51.7 ± 12.0	55.4 ± 16.7	45.7 ± 16.3	29.1 ± 6.9	27.2 ± 1.3	38.7 ± 15.1		0.55 ± 0.26b‡‡	87
SD _{phob}	w§	5	76.3 ± 5.3	73.4 ± 8.9	49.0 ± 9.9	52.6 ± 4.1	46.9 ± 7.1	62.9 ± 14.4	−0.05	−0.27 ± 0.19	39
		38	71.6 ± 8.8	65.5 ± 12.1	58.8 ± 8.8	58.7 ± 11.8	50.1 ± 7.7	61.3 ± 12.2		0.90 ± 0.14b	110
ST _{phob}	d	5	37.2 ± 2.9	40.0 ± 2.3	29.1 ± 2.4	39.7 ± 2.7	16.8 ± 5.9	35.7 ± 6.9	−0.12a††	−0.41 ± 0.17b	61
		38	26.8 ± 4.3	32.8 ± 6.2	38.0 ± 3.0	33.4 ± 5.5	17.4	31.6 ± 6.6		−0.75 ± 0.20b	47
ST _{phob}	w	5	50.0 ± 6.3	51.0 ± 4.8	52.8 ± 3.2	54.0 ± 3.4	25.7 ± 9.3	47.9 ± 10.7	−0.26a	−0.23 ± 0.23	78
		38	27.0 ± 10.6	45.1 ± 8.2	47.4 ± 21.5	47.1 ± 14.7	20.0 ± 3.2	39.4 ± 15.4		−0.95 ± 0.48	44
SL _{phob}	d	5	36.5 ± 8.0	37.9 ± 7.1	32.8 ± 6.5	23.7 ± 11.9	13.4 ± 6.0	28.9 ± 11.3	0.50a	−0.44 ± 0.38	36
		38	51.9 ± 23.3	50.0 ± 20.3	47.3 ± 12.0	48.4 ± 20.7	36.5 ± 19.1	45.4 ± 18.3		2.22 ± 0.44b	55
SL _{phob}	w	5	56.4 ± 23.4	66.5 ± 13.0	64.6 ± 10.3	63.3 ± 8.3	53.0 ± 17.9	61.6 ± 14.7	−0.22a	1.56 ± 0.43b	53
		38	n.m.	52.4 ± 6.1	66.0 ± 5.5	47.7 ± 3.6	45.7 ± 18.2	54.2 ± 12.9		0.31 ± 0.31	57
Mean			48.9	51.0	46.8	44.1	32.4	45.7			

† SD_{phob}, hydrophobic sand; ST_{phob}, hydrophobic silt; SL_{phob}, hydrophobic humic soil.

‡ Drying

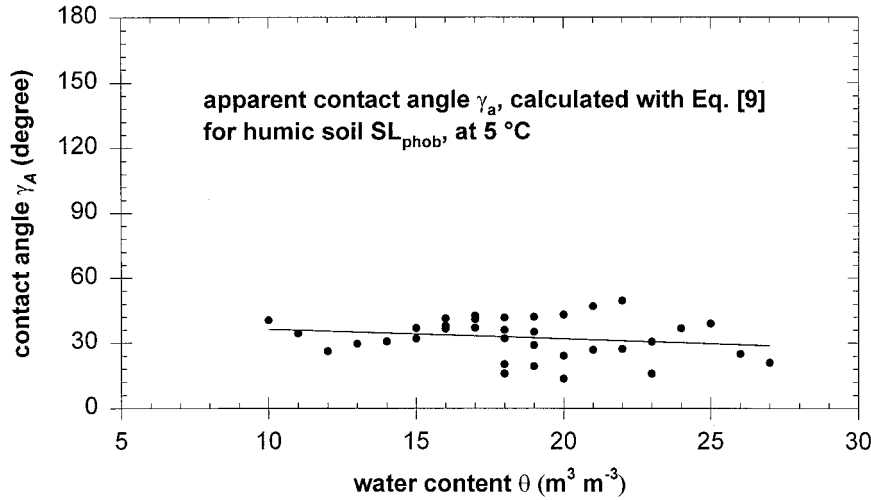
§ Wetting

¶ Slope of linear regression asymptotic standard error se of the estimates.

‡‡ Indicates significant difference between the contact angles measured at 5°C and 38°C. The letter a indicates 38°C.

‡‡‡ Slope significantly different from zero (95%). The letter b indicates the slope significantly is different from zero (95%).

n = number of data points.

**Fig. 5.** Apparent contact angle, γ_A , derived from drying water retention curves at 5°C, for the hydrophobic soil (SL_{phob}).

large reduction of σ_{lg} was reported by Chen and Schnitzer (1978), who found values as low as 44 mN m⁻¹. Singleton (1960, cited in Nimmo and Miller, 1986) found a three times higher solubility of fatty acids with a temperature increase from 0 to 60°C. This result is in line with the largest value of β_0 we observed for SL_{phob}, compared with the sand and silt samples without soil organic matter. Generally, a larger temperature factor results in lower capillary forces at high temperatures because increasing temperature affects the WRC in the same direction as an increasing γ . If the γ of the reference soil remains stable with temperature or shows at most a small increase, then the contact-angle difference increases with higher temperature. This effect, however, cannot be quantified without additional measurements of the temperature dependence of the soil solution surface tension.

In summary, the contact-angle decrease with temperature $\Delta\gamma_A/\Delta T$ is between $-0.03^\circ/\text{C}$ and $-0.26^\circ/\text{C}$. These values agree with those cited by She and Sleep

(1998), but are smaller than those reported by King (1981). These differences are statistically significant for all soils with exception of the paired sand (SD/SD_{phob}; Welch-test at the 5% level; see Snedecor and Cochran, 1980).

CONCLUSIONS

Generally, our results confirm the findings of others who determined the temperature dependence with WRCs under equilibrium conditions. Three possible mechanisms are expected to cause a six times higher temperature dependence of ψ than predicted by the temperature dependence of pure water only: (i) temperature-induced changes in contact angle, (ii) changes in liquid-gas interfacial tension because of solute effects, and probably (see Grant and Salehzadeh, 1996), (iii) changes of the enthalpy of immersion with temperature or capillary pressure.

Our results show that apparent contact angles are

temperature dependent and are decreasing with temperature in most cases. On the other hand, an apparent contact angle increase, as predicted by theory (She and Sleep, their Eq. [23]), was not observed, except for the humic soil during drying. For this soil it is likely, that surfactants, i.e., dissolved soil organic matter, compounds the contact angle effect caused by the properties of the solid surface. The temperature-dependent solution of surfactants and their impact on the liquid surface tension may enhance the temperature effect on drying and wetting WRCs. However, to determine quantitatively the solute effect, additional measurements of the liquid surface tension have to be made. Further research is necessary to evaluate the temperature effect on the contact angle γ_{SD} of the dry solid surface. Measurements of the enthalpy of immersion and direct evaluation of the contact angle at different temperatures would give further valuable information on the physical nature of water in porous media.

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