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Freezing Point Depression of Soil Water as a Function of Mineral Composition and Physical Properties

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Abstract

In the face of difficulties of a physico-chemical analysis, two semi-empirical methods have been worked out enabling one to calculate the equilibrium freezing point depression, Θ_0, as a function of soil water content and physical properties. Method A, based on the approximating power function, takes into account mineral composition, specific surface area and the values of soil consistency limits. Method B, making use of the approximated hyperbolic function, requires only the consistency limits, w_p and w_l. Verification of the methods has shown that the values for Θ_0, estimated at water content, w, between the interval $w_p < w < 1.2w_l$, have an average absolute error equal to 0.13 K (method A) and 0.08 K (method B). The average absolute errors at w between the interval $0.8w_p < w < 1.2w_l$ are 0.22 K and 0.32 K for methods A and B respectively.

1. Introduction

Despite the fundamental part played by the freezing point depression in most problems associated with frozen ground mechanics, no useful solutions are found in the references (Andersland and Anderson 1978, Cytowicz 1973, Farouki 1986, Jumikis 1977).

It is known that it is possible to describe the freezing point depression of soil water, Θ_0, as an approximating function of the object:

$$\Theta_0 = f(w, x_1, x_2, \ldots, x_n) \tag{1}$$

where w is the soil water content. Determination of the function (1) by means of direct measurements is very time-consuming; also special equipment and an experienced investigator are required. Therefore, it would be advisable to derive universal equations for sufficiently accurate calculating of Θ_0 in relation to w and other easily-determinable geotechnical parameters. In other words, function (1) should be presented in a form where chosen geotechnical parameters constitute a subset X_1 of the whole set X of parameters in Eq. (1). A set of constant coefficients is the complement of X_1 in X. This paper presents a proposal for solving the problem, however the relations need further verification and analysis.

2. Problems Connected with a Physico-Chemical Approach

Low et al. (1968) tried to find a theoretical form for the function (1) in terms of thermodynamics and physico-chemistry. Despite many assumed simplifications, the authors obtained a complicated equation involving the negative of the relative partial molar heat content of soil water $(H^0 - H)$, the relative molar free energy of soil water $(F - F^0)$ and the freezing point depression, Θ_0, at some assigned water content. It is possible to determine the value $(H^0 - H)$ from the differential heat of desorption and the value $(F - F^0)$ as a function of the swelling pressure. As can be seen, the solution, undoubtedly very interesting from the theoretical point of view, is of little practical value. Determination of the value Θ_0 at a given water content (including an error caused by the simplifications) needs two independent investigations which would require as much time as direct measurements. It seems that a strict thermodynamic approach cannot yield useful solutions.

Generally, change in the chemical potential of soil water is a function of such parameters as electric and magnetic forces associated with the charged mineral particles, radius of curvature, pressure, concentration of solutes, and temperature. These values are not always easily determinable. Therefore, it would be reasonable to select a number of geotechnical parameters which seem to be connected with the thermodynamic parameters mentioned above. There are three groups of such soil parameters.

1. Water content (particularly as a number of monomolecular water layers per unit of specific surface area).
2. Factors connected with the structure and composition of the mineral matrix:
   a) mineral composition,
   b) geometrical parameters of the mineral particles,
   c) geometrical parameters of the pores.
3. Chemical factors independent or partially dependent on mineral composition:
   a) the kind of exchangeable cations,
   b) concentration and kind of pore solutes.

One should not expect that all the factors mentioned will exert considerable influence on the freezing point depression value. Therefore, on the author's results of the investigation, a solution of maximum simplicity and usefulness is postulated.

3. Universal Semi-Empirical Equations

The author previously reported (Kozłowski 1990) the method and results of the investigation of the freezing point depression, Θ_0, vs. total water content, w, for three almost monomineral model soils: Ca-bentonie from Chmielnik (BCh), Na-bentonite MAD (BM) and kaolinite from Sedlec (KS). The results are shown in Fig. 1. It has been found that the freezing point depression is 20 K when the water content corresponds to about one (1.3 exactly) conventional monomolecular layer of bounded water in the bentonites and to about three monomolecular layers in the kaolinite. Thus, it has been assumed that the freezing point depression equal to 20 K depends only on the material composition of a soil. In that case, the maximum water content at which freezing does not begin at −20°C can be described by the following equation:

$$w_{\max,20} = 0.035S \cdot m \tag{2}$$

where $w_{\max,20}$ is the maximum water content, at which ice can be absent in the system at −20°C (in %). So $w_{\max,20}$ is slightly less than the water content at which the freezing point depression is 20 K. In Eq. (2), S is the specific surface area (m^2/g), m is the number of monomolecular layers and depends on the mineral composition. The value 0.035 is a water content corresponding to one monomolecular water layer covering 1 m^2 of mineral surface (thickness of monomolecular layer 2.76×10^{-10} m × average density of the bound water 1.27×10^6 $\mathrm{g/m}^3$ × 100%). The value 1.27×10^6 $\mathrm{g/m}^3$ is the density of sorbed water constituted of the bimolecular layer (Martin 1962) and in the author's opinion in can be regarded as the approximate density of water in 1.3 to 3.0 monomolecular layers.

The value of m numbers 1.3 in case of montmorillonite and 3.0 in case of kaolinite. On the authority of data indicating full additivity of surface properties of mineral components in mixture (Grabowska-Olszewska 1968), one can obtain:

$$m = 3k + 1.3(1 - k) \tag{3}$$

where k is the content of kaolinite as a fraction of dry soil mass (estimated e.g. by the method proposed by Stępkowska, 1977).

At temperature depressions near 0°C the value of the "maximum content of non-freezing water" $w_{u,\max}$ is affected by the grain size distribution and kind of main exchangeable cation. The available data for a small number of soils in the investigation did not permit inference of the influence of the dispersion and exchangeable cation complex. It is, however, known that the parameters are connected with the values of consistency limits w_p and w_l. When comparing the values of the freezing point depression, Θ_0, at water contents equal to the consistency limits in the given soil, the author noticed that the value of Θ_0 increased with the increase of the plasticity index, I_p (Fig. 2). Values of Θ_0 calculated from the

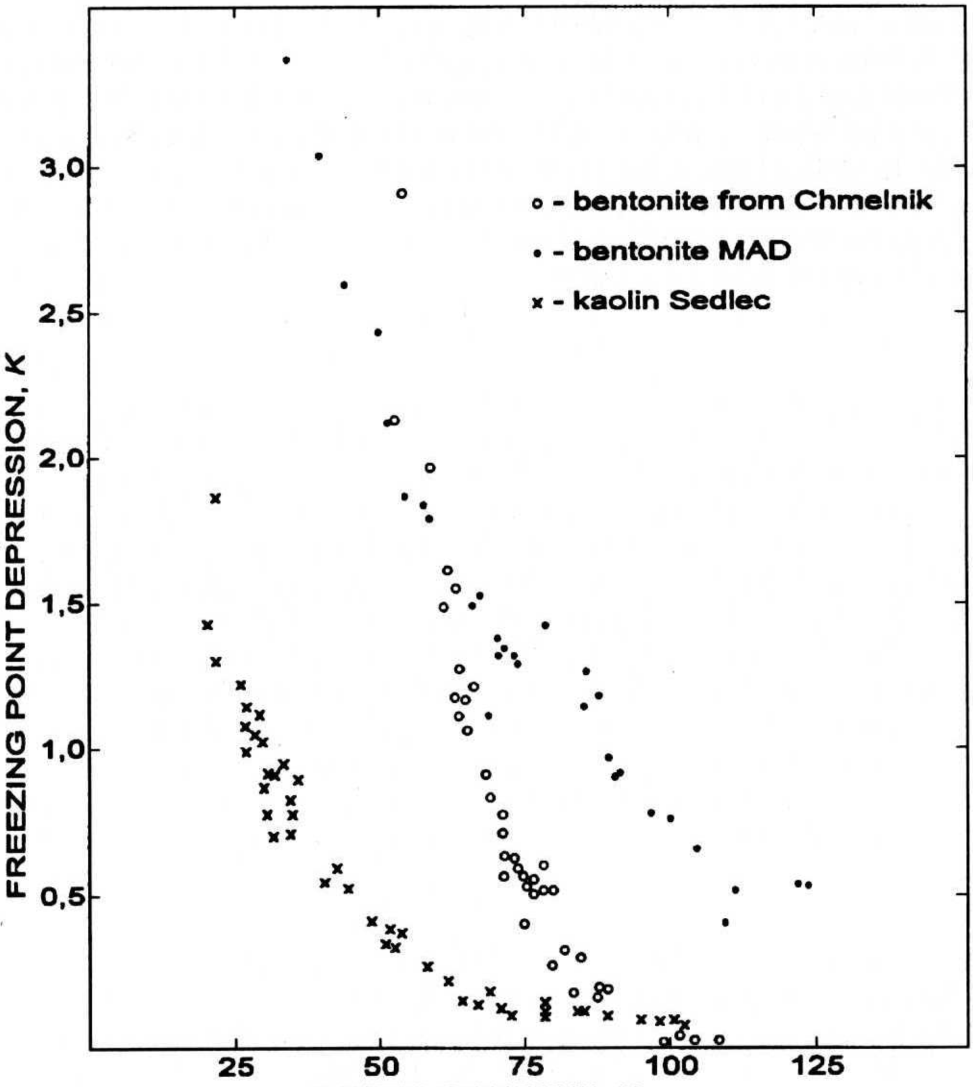

Fig. 1. The freezing point depression in three investigated monomineral soils vs water content

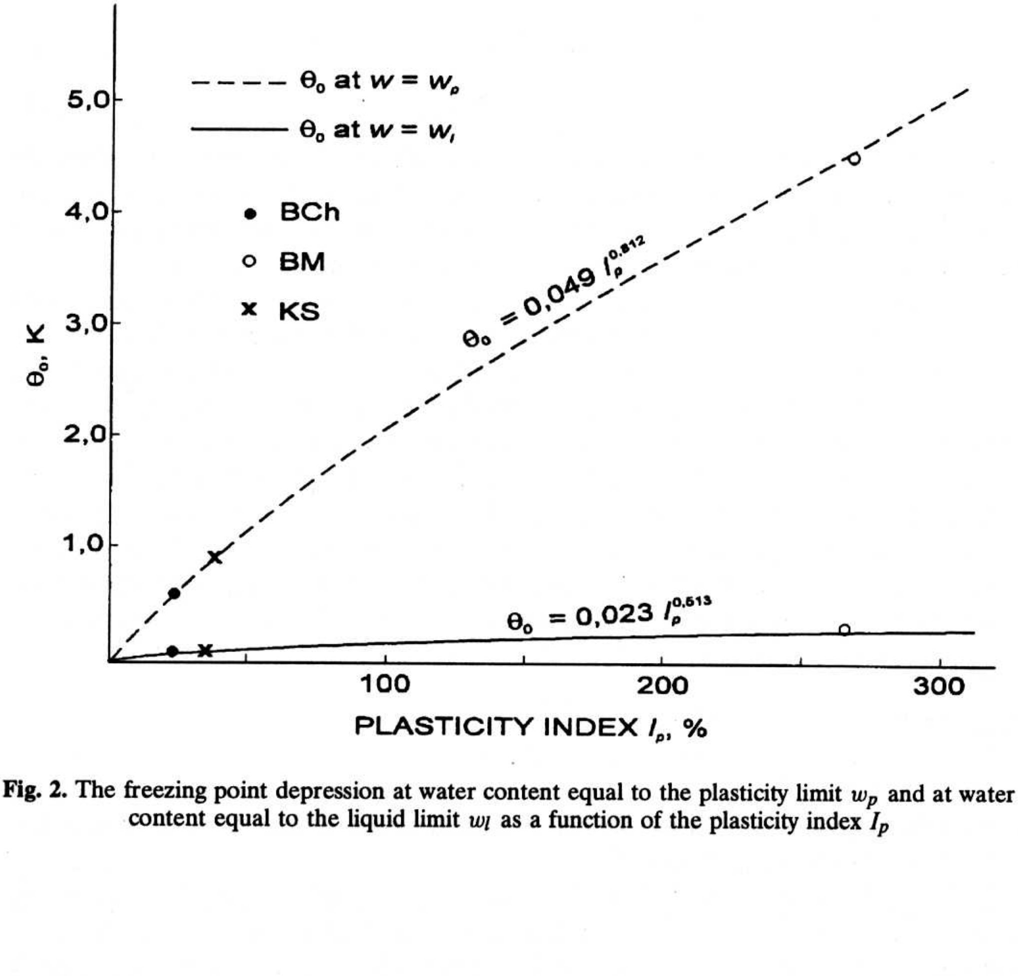

Fig. 2. The freezing point depression at water content equal to the plasticity limit w_p and at water content equal to the liquid limit w_l as a function of the plasticity index I_p

Table 1. Freezing point depression $\Theta_0(w_p)$ at the plasticity limit and $\Theta_0(w_l)$ at the liquid limit

Parameter	Bentonite Chmielnik	Bentonite MAD	Kaolinite Sedlec
w_p, %	74.1	27.0	33.7
w_l, %	96.0	290.6	70.4
I_p, %	21.9	263.6	36.7
$\Theta_0(w_p)$, K	0.60	4.50	0.90
$\Theta_0(w_l)$, K	0.11	0.40	0.15

correlation data $\Theta_0(w)$ relative to $w = w_p$ and $w = w_l$, are shown in Table 1. The values from Table 1 could be approximated by power functions:

$$\Theta_0(w_p) = 0.049\ I_p^{0.812}, \tag{4}$$

$$\Theta_0(w_l) = 0.023\ I_p^{0.513}. \tag{5}$$

The correlation coefficients for Eqs. (4) and (5) are respectively 0.99998 and 0.99941. The zero of these functions occurs at the zero value of the independent variable I_p, which agrees with the experimentally confirmed fact that noncohesive salt-free soils do not show the freezing point depression.

The author is aware of the fact that Eqs. (4) and (5) describe the freezing point only in the three soils under investigation. However, the assumption that the formulas are valid with reference to other cohesive soils is not baseless. The values of consistency limits in cohesive soils depend on mineral and granulometric composition, shape of mineral particles, kind of exchangeable cations, as well as on chemical composition and concentration of pore solution (Grabowska-Olszewska and Siergiejew 1977). Thus, information about most of the factors mentioned in section 2 of the paper in contained in the values of w_p and w_l. Therefore, the assumption was made that Eqs. (2), (4) and (5) have a universal implication. Two methods of predicting the freezing point depression Θ_0, have been worked out based on these equations.

Method A

The following data concerning the soil are required: approximate mineral composition (content of kaolinite), the specific surface area S in m^2/g and the consistency limits w_p and w_l in %.

An equation of a curve, $\Theta_0 = f(w)$, representing the empirical values of Θ_0 in the three soils was considered, when two points belonging to the curve were known, $(w_{\max,20}, 20)$ and $w_l, \Theta_0(w_l)$. Test calculations have shown that a good approximation of the following power function can be expected:

$$\Theta_0 = \Theta_A = a \cdot w^b. \tag{6}$$

Substituting Eqs. (2) and (5) into (6) and rearranging gives the following system of equations:

$$20 = a\ (0.035\ S\ m)^b, \tag{7a}$$

$$0.023\ I_p^{0.513} = a\ w_l^b, \tag{7b}$$

the solution of which gives values for the coefficients in Eq. (6):

$$b = \frac{6.768 - 0.513 \cdot \ln(I_p)}{\ln(0.035 \cdot S \cdot m / w_l)}, \tag{8}$$

$$a = 0.023\ I_p^{0.513}\ w_l^{-b}. \tag{9}$$

The value of m in Eq. (8) is given by Eq. (3).

Method B

If data for mineral composition and specific surface are not available, the function $\Theta_0 = f(w)$ can be estimated from the soil consistency limits, w_p and w_l. The curve in request passes two points: $(w_l, \Theta_0(w_l))$ and $(w_p, \Theta_0(w_p))$. It has been found that the power function (6) is not useful in this instance because of large errors in extrapolation for $w < w_p$. Better fitting is provided by the hyperbolic function:

$$\Theta_0 = \Theta_B = c + d/w. \tag{10}$$

Combining Eqs. (4), (5) and (10) yields a system of equations:

$$0.049\ I_p^{0.812} = c + d/w_p, \tag{11a}$$

$$0.023\ I_p^{0.513} = c + d/w_l. \tag{11b}$$

The solution determines values of the parameters of Eq. (10):

$$d = (x_1\ I_p^{x_2} - x_3\ I_p^{x_4})\ w_p\ w_l, \tag{12}$$

$$c = x_3\ I_p^{x_5} - d/w_l, \tag{13}$$

where $x_1 = 0.049$, $x_2 = -0.188$, $x_3 = 0.023$, $x_4 = -0.487$, $x_5 = 0.513$.

4. Verification of the Methods

Adequacy of the methods presented has been verified based on the data available from the references and the results of this investigation. Additionally, the freezing point depression was computed by use of the following empirical equation given by Fedorov (1989):

$$\Theta_0 = \Theta_F = 0.045\ (w/w_l)^{-4}. \tag{14}$$

This author had at his disposal two sets of soil data. The first comprised complete information about a given soil including specific surface area, S. In the set, the data on freezing point depression of Morin clay from the American center of frost investigations CRREL are specially reliable. The results of computations of Θ_A according to method A, of Θ_B according to method B, and of Θ_F according to Fedorov's equation (14) are given in Table 2. In Table 3, the results of the computations of Θ_B and Θ_F are given for soils with unknown specific surface area. The values of plasticity limit w_p of the soils investigated by Fedorov (only the values of liquid limit w_l are given in his paper) were calculated using the empirical Casagrande equation (Dumbleton and West 1966):

Table 2. Comparison of observed values of freezing point depression (Θ_{0e}), values calculated according to the author's methods (Θ_A, Θ_B) and from Fedorov's equation (Θ_F)

Name of soil	Source of data	w_p %	w_l %	S m^2/g	w %	Θ_{0e} K	Θ_A K	Θ_B K	Θ_F K
Bentonite Chmielnik	A	74.1	96.0	838	110.0	0.01	0.05	0.00	0.03
					100.0	0.06	0.09	0.05	0.04
					90.0	0.18	0.16	0.22	0.06
					80.0	0.38	0.31	0.44	0.09
					70.0	0.82	0.66	0.72	0.16
					60.0	1.85	1.58	1.10	0.29
Bentonite MAD	A	27.0	290.6	226	320.0	0.37	0.36	0.36	0.03
					260.0	0.41	0.46	0.45	0.07
					200.0	0.46	0.62	0.59	0.20
					140.0	0.54	0.95	0.86	0.84
					80.0	1.14	1.82	1.51	7.88
					20.0	8.37	9.21	6.12	?*
Kaolin Sedlec	A	33.7	70.4	46	75.0	0.14	0.13	0.10	0.03
					65.0	0.18	0.17	0.20	0.06
					55.0	0.43	0.23	0.34	0.12
					45.0	0.52	0.33	0.56	0.26
					35.0	0.76	0.52	0.87	0.72
					25.0	1.33	0.97	1.45	2.77
Morin Clay	B, C	22.8	38.3	60	41.2	0.09	0.08	0.06	0.03
					36.1	0.11	0.11	0.13	0.06
					30.9	0.19	0.15	0.22	0.11
					25.8	0.24	0.21	0.35	0.22
					19.4	0.41	0.37	0.61	0.68
					14.4	0.79	0.98	0.69	2.26
					9.3	2.04	1.68	1.77	13.2
					4.8	7.02	6.36	3.80	?*
Leda Clay	D, E, F	20.8	37.2	54	35.0	0.13	0.11	0.13	0.06
					30.0	0.20	0.15	0.21	0.11

?* – greatly values overestimated (up to 200 K) and not taken into account in calculation of the average errors (Table 4)

The sources:

A – own investigation
B – Xiaosu et al. (1985a)
C – Xiaosu et al. (1985b)
D – Dillon & Andersland (1966)
E – Williams (1964a)
F – Williams (1964b)

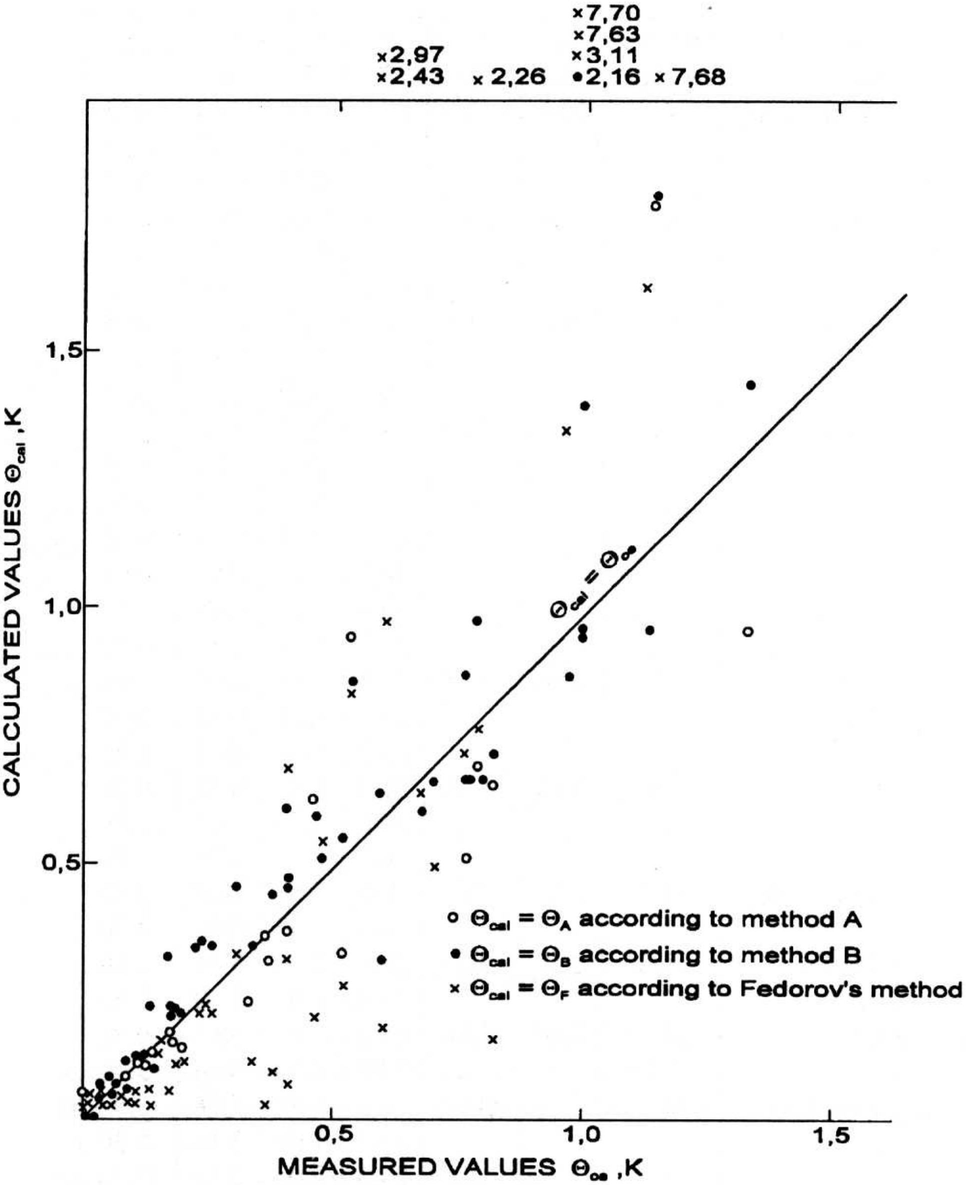

Fig. 3. Calculated values of the freezing point depression Θ_A, Θ_B, Θ_F versus experimental values Θ_{oe} vs water content

Table 3. Comparison of observed values of freezing point depression (Θ_{0e}), values calculated according to the author's methods B (Θ_B) and from Fedorov's equation (Θ_F)

Name of soil	Source of data	w_p %	w_l %	w %	Θ_{0e} K	Θ_B K	Θ_F K
Sandy loam	G	20.7	22.7	22.4	0.03	0.04	0.05
					0.14	0.22	0.14
					0.48	0.51	0.54
Loam	G	22.4	28.8	28.2	0.04	0.07	0.05
				19.3	0.23	0.34	0.22
				14.8	0.68	0.60	0.64
Loam	G	23.0	31.1	30.9	0.07	0.07	0.05
				21.1	0.26	0.34	0.21
				15.3	0.79	0.66	0.77
Loam	G	24.3	35.8	49.0	0.00	0.00	0.02
				41.1	0.06	0.09	0.04
				29.7	0.17	0.32	0.16
				25.1	0.41	0.47	0.31
				20.7	0.77	0.67	0.68
				16.6	1.13	0.96	1.64
				10.2	1.97	1.88	11.52
Loam	G	25.6	40.8	36.6	0.04	0.07	0.04
				22.0	0.31	0.45	0.32
				15.3	0.97	0.87	1.35
Clay	G	30.2	57.8	58.2	0.09	0.12	0.04
				31.8	0.70	0.66	0.49
				23.9	2.03	1.06	1.54
Sandy silt	H, I	13.7	21.7	8.0	0.60	0.65	2.43
				6.0	1.00	0.96	7.70
Kaolin	H, I	21.7	39.7	28.0	0.60	0.31	0.18
				11.0	1.00	1.40	7.63
Clay	H, I	19.6	34.6	16.0	0.60	0.64	0.98
				12.0	1.00	0.96	3.13
Bentonite	H, I	43.6	114.0	40.0	0.60	1.78	2.97
				34.5	1.00	2.16	5.38
				29.0	3.00	2.70	17.15

The sources:
G – Fedorov (1989)
H – Akimow (1978)
I – Jerszow (1979)

Table 4. Average absolute errors in the calculation of freezing point depression at different ranges of water content (from data shown in Tables 2 and 3)

Method of calculation	$0.8\,w_p < w < 1.2\,w_l$		$w_p < w < 1.2\,w_l$	
	Number of points	Error δ_1 K	Number of points	Error δ_z K
A	28	0.22	21	0.13
B	59	0.32	37	0.08
after Fedorov (1989)	57*	1.88	37	0.36

* – two particularly unfavourable values were not taken into account

$$I_p = 0.73\ (w_l - 20). \tag{15}$$

Assuming, for the purpose of the analysis, that the measured values of freezing point depression Θ_{0e} are free from errors, the average absolute error, δ_1, was calculated for the values Θ_A, Θ_B, Θ_F in the range of water content $w > 0.8\ w_p$ and the average absolute error, δ_z, in the restricted range of water content $w > w_p$. For each method δ_1 is greater than δ_z. This is the consequence of the existence of a point of discontinuity on the empirical curve Θ_0 vs w (Fig. 1), which does not allow successful one-function approximation. In this respect method A proved best ($\delta_1 = 0.22$ K, $\delta_z = 0.13$ K). It makes use of the approximating function (6) defined over a wide range of w. Instead, the error of method B, which is insignificant at $w > w_p (\delta_z = 0.08$ K), is four times bigger in the wider range of $w (\delta_1 = 0.32$ K). Both proposed methods seem to be suitable for an approximate calculation of the freezing point depression of soil water. An accuracy of 0.1 K at $w > w_p$ and 0.2–0.3 K at $w > 0.8\ w_p$ is sufficient in most thermal computations. On the other hand, the error of Fedorov's method was much higher ($\delta_1 = 1.88$ K, $\delta_z = 0.36$ K). The degree of agreement between the calculated values of freezing point depression Θ_A, Θ_B, Θ_F and the measured values Θ_{0e} is shown in Fig. 3.

5. Conclusions

1. In the face of difficulties of physico-chemical analysis, two semi-empirical methods have been developed enabling the calculation of the equilibrium freezing point depression, Θ_0, as a function of soil water content and physical properties of soil.
2. Method A, based on the approximating power function (6), takes into account the mineral composition, specific surface area and the values of soil consistency limits. Method B, making use of the approximated hyperbolic function (10), needs only data on the consistency limits, w_p and w_l.
3. Verification of the methods proved that the values of Θ_0 are estimated at water contents w from the interval $w_p < w < 1.2\ w_l$ with an average

absolute error equal to 0.13 K (method A) and 0.08 K (method B). The average absolute errors at w from the interval $0.8\ w_p < w < 1.2\ w_l$ are 0.22 K and 0.32 K, respectively for method A and method B. In most cases the above values are acceptable for engineering computations.

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