

PROPERTIES OF ICE AND PERMAFROST

PROPERTIES OF WATER IN DISPERSE ROCKS

Part I. Viscosity, Dielectric Permittivity, Density, Heat Capacity, Surface Tension

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The paper presents a synthesis of new data on the properties of water in disperse rocks, with a special focus on its viscosity, dielectric permittivity, density, and surface tension.

*Disperse rocks, bound water, phase composition, viscosity, dielectric permittivity, density, surface tension*

INTRODUCTION

Phase diagrams of water and complex fluids in pores of disperse rocks are indispensable to model the state of such rocks as multi-component heterogeneous systems, as well as heat and mass transfer in these systems at negative temperatures. The state of pore water in rocks and other disperse media has multiple controls, such as adsorption, electrical double layer effects, energy exchange, capillary effects, etc., which influence both the phase equilibrium conditions and the water structure and properties [Smirnov et al., 2003; Cheverev, 2003a,b, 2004].

Measuring the properties of bound water is difficult because its concentrations are commonly small, its state depends on many poorly constrained factors (impurities, etc.), and the results are very sensitive to

the experimental conditions. That was the cause of the story with “polymeric water”, which was predicted to have some special properties different from those of ordinary water based on experimental evidence [Deryagin, 1970], but the interpretation of the experiments turned out to be wrong [Ginzburg, 1971]. Water was claimed to form a new modification with the density  $1400 \text{ kg/m}^3$  and other particular properties under some conditions (e.g., in silica capillaries). Although that was a wrong idea, the very fact that water in disperse materials differs from bulk water has never been doubted [Kvlividze et al., 1988; Deryagin, 1989; Korolev, 1997; Giovambattista et al., 2006].

In order to avoid numerous uncontrollable effects in experiments with rock samples, it is reasonable to study the properties of pore water on model materials. Of course, the results cannot fully substitute for the natural rock data, but they can furnish useful information.

VISCOSITY

The viscosity of water bound in small pores is generally higher than that of free water. The molecules of water near mineral surfaces (vicinal water) have different orientations, which can be expected to show up especially as viscosity changes. Measurements in very fine pores (capillaries) in silica and glasses [Deryagin, 1989] show the viscosity of water films to increase as their thickness ( $h$ ) reduces to less than  $1 \text{ }\mu\text{m}$ . At the film thickness  $0.2\text{--}0.3 \text{ }\mu\text{m}$ , the water viscosity is 1.1 times higher than that of free water, and the difference reaches 1.6 times at  $h = 10 \text{ nm}$  (Fig. 1). Therefore, the viscosity of pore water has to be studied directly in rock samples.

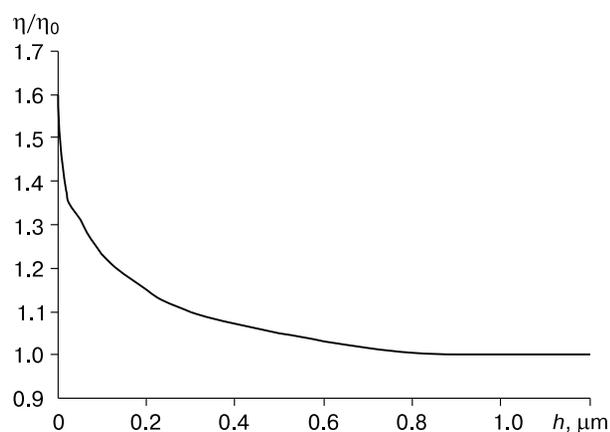


Fig. 1. Relative viscosity of water ( $\eta/\eta_0$ ) in quartz capillaries as a function of capillary radius ( $h$ ).

$\eta$  is the viscosity of vicinal water,  $\eta_0$  is the viscosity of bulk water.

### DIELECTRIC PERMITTIVITY

Pore water has its dielectric permittivity times lower than bulk water. The permittivity of water in montmorillonite, is 23–25 at a water film thickness of 5–8 nm and is as low as 3–4 in the case of 0.5–0.6 nm films [Deryagin, 1985]. There is evidence of low water permittivity in acetate-cellulose membranes, silica gel [Deryagin, 1985], and muscovite [Karnakov et al., 2006; Borisov et al., 2008]. The permittivity of 0.17 to 10  $\mu\text{m}$  adsorption water films exposed to electric fields of active surfaces in muscovite crystals reduces 40 times as the films thin down.

The data on permittivity of pore water were used to develop methods for studying it in rocks and soils, including estimating the content of water remaining unfrozen at negative temperatures [Mironov and Lukin, 2010; Savin and Mironov, 2010].

### DENSITY

Molecular dynamics simulations of water confined between heterogeneous plates reveal density changes [Giovambattista et al., 2006] which are however hard to detect experimentally for low relative contents of pore water and other problems [Churaev, 1990].

Clear evidence that both viscosity and density of water in fine pores differ from those in bulk liquid was obtained by studying water thermal expansion in pores of silica gel powder [Deryagin, 1985]. Namely, the volume minimum lying at 4 °C for bulk water [Karasev et al., 1967] was observed to disappear. The thermal expansion values estimated for water in silica gel at temperatures between 0 and 90 °C were used to calculate the absolute water density in SiO pores [Deryagin, 1983], which showed a 2 % increase at 0 °C relative to the bulk and decreased with temperature (Fig. 2) [Churaev, 1990].

The water density in nanoscale ( $r = 0.3\text{--}0.5\text{ nm}$ ) pores of zeolite (NaX) was found out to be ~10 % higher than in free water, and the density of vicinal water at the glass surface measured by pycnometry likewise showed high density at 25 °C [Deryagin, 1985]. Note however that results of this kind depend on the method of pore volume estimation.

Water in cement has a higher density than bulk water due to the adsorption effect, but the exact difference is unknown. The earliest density estimates of  $\rho = 1.1\text{ g/cm}^3$  for water in gel pores were obtained in 1948 by Powers and Brownyard and confirmed later through measurements of water entropy on adsorption in hardened Portland cement by Copland and others who derived an equation leading to the  $\rho = 1.01\text{ g/cm}^3$  density of water in cement [Lindmark, 1998 and references therein].

Alternatively, there is evidence that water in clay is 2–3 % less dense than bulk water [Anderson and

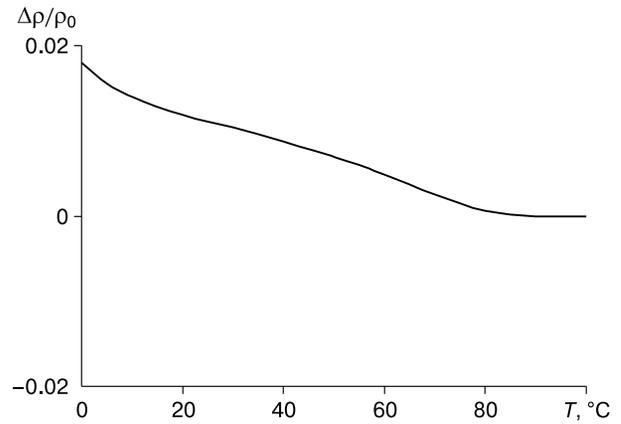


Fig. 2. Relative density of water ( $\Delta\rho/\rho_0$ ) in pores of silica gel powder (SiO) as a function of temperature ( $T$ ).

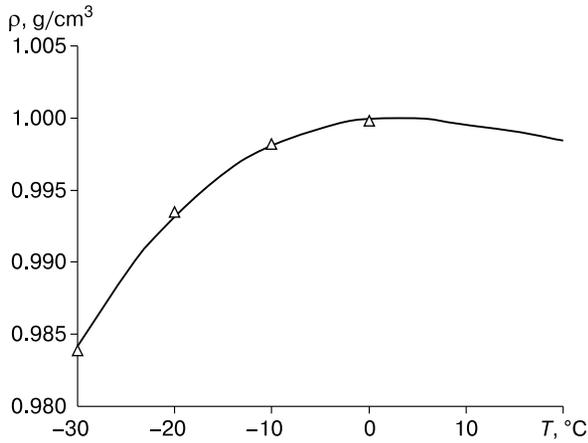
Low, 1958], presumably due to the effect of adsorbed cations on the water structure. The density data of water in clay, as well as in silica gel, also attest to distance dependence of the extent of vicinal structuring that extends to about 5 nm from the surface and then decreases almost exponentially [Etzler and Conners, 1990]. The density difference between pore and bulk water reduces with temperature increase.

Thus, the density of pore water has been a subject of discussions at least for the past fifty years [Anderson and Low, 1957], this being another proof for the difficulty of such research. For the lack of respective data, thermodynamic simulations often employ the properties of bulk water, including supercooled water [Grant and Sletten, 2002]. Supercooling highlights ever more the unusual properties of water. As the temperature decreases and approaches  $-45\text{ °C}$ , the extrapolated compressibility, heat capacity, and thermal expansion tend to zero, i.e., the temperature dependence of many properties becomes stronger on transition to the supercooling range [Stanley et al., 1997; Fedotova and Trostin, 2003; Sarkisov, 2006]. Therefore, extrapolation of the water properties estimated at positive temperatures to the domain of supercooling is inapplicable.

At atmospheric pressure (1 bar), the water density reaches its maximum about 4 °C and decreases below this temperature (Fig. 3). The density decrease accelerates and reaches 3 % of the maximum value at  $-35\text{ °C}$  [Stanley et al., 1998].

Different equations have been suggested to approximate the experimental data, including approximation by polynomials with their degree depending on the wanted accuracy [Lindmark, 1998]. In the interval  $243.15\text{ K} < T < 293.15\text{ K}$ , the water density ( $\text{kg/m}^3$ ) is found as

$$\rho = -3479.56 + 46.3T - 0.1591T^2 + 1.8171 \cdot 10^{-4}T^3.$$



**Fig. 3. Density of supercooled water ( $\rho$ ) as a function of temperature ( $T$ ).**

Triangles are experimental data; solid line shows theoretical data according to equation (1).

Then the molar volume is

$$V_{m,l} = -3.4228 \cdot 10^{-12} T^3 + 2.9896 \cdot 10^{-9} T^2 - 8.6806 \cdot 10^{-7} T + 1.0182 \cdot 10^{-4}. \quad (1)$$

This equation allows quite a good fit to observations (Fig. 3).

The extrapolation of the water density equation valid for positive temperatures to the case of supercooled water entails large errors because the density curve for supercooled water falls abruptly as the temperature decreases. For instance, the temperature ( $T$ ) dependence in the density ( $\rho_w$ ) equation of Gebhart–Mollendorf is [Zubkov *et al.*, 2001]

$$\rho_w = \rho_{\text{inv}} \left( 1 - \beta |T - T_{\text{inv}}|^\gamma \right),$$

where  $\beta = 9.297,173 \cdot 10^{-6}$  is the thermal expansion coefficient;  $\gamma = 1.894,816$ ;  $\rho_{\text{inv}}$  is the water density at the point of inversion corresponding to the density maximum at  $T_{\text{inv}} = 4^\circ\text{C}$ .

Thus estimated water density disagrees with the experimental data at negative temperatures, as well as the density found according to [Hindmarsh *et al.*, 2003]

$$\rho_w = -0.02T^2 + 10.8T - 470.$$

Curvature of rock-pore interfaces causes notable pressure difference between water phases. Therefore, it is necessary to constrain the influence of pressure on the thermodynamic properties of pore water and ice, e.g., using the relationship between pressure and temperature of density inversion [Kaye and Laby, 1959]:

$$T_m = 3.98 - 0.0225(p - 1),$$

where  $T_m$  is the temperature corresponding to the maximum water density, in  $^\circ\text{C}$ , and  $p$  is the pressure (bar).

The molecular dynamic simulations by Giovambattista *et al.* [2006] to study the behavior of water confined between hydrophobic, hydrophilic, and heterogeneous (patchy) nanoscale plates with separations from 0.4 to 1.6 nm, at  $T = 300$  K, were performed at different pressures from  $-0.15$  to  $0.2$  GPa. However, instead of a unique pressure dependence of water density, the authors got two theoretical pressure-density relationships depending on whether the water volumes were calculated with the real plate separations or with an effective distance based on the distribution of water molecules.

Jeffery and Austin [1997] derived an equation of state and estimated the properties of supercooled water in broad temperature and pressure ranges, which agreed with the experiment.

An original approach to estimating the density of pore water was suggested on the theoretical basis of hydration for a heterogeneous surface with water-saturated sedimentary layers of a polar order [Makeeva, 2010, 2012]. According to this approach, the density of water in disperse systems with the first-kind phase transition is given by

$$\rho_{sw} = \frac{W_{sw} z F}{S} \sqrt{\frac{8\pi c \epsilon}{RT}},$$

where  $W_{sw}$  is the water content in a single layer of saturated sediments (Curie point);  $S$  is the specific surface area;  $z$  is the cation valence;  $F$  is the Faraday number;  $\epsilon$  is the dielectric permittivity of water;  $T$  is the absolute temperature;  $R$  is the gas constant;  $c$  is the concentration of cations (hydronium ion) and anions (hydroxides) of water within the electrical double layer.

## HEAT CAPACITY

The heat capacity of an adsorption system measured in laboratory depends mostly on the adsorbent, which poses problems to measurements of the adsorbate. Namely, it requires a highly sensitive calorimeter, rigorous equilibrium conditions, account for the heat of partial desorption on heating of the calorimeter, etc. [Kiselev, 1986].

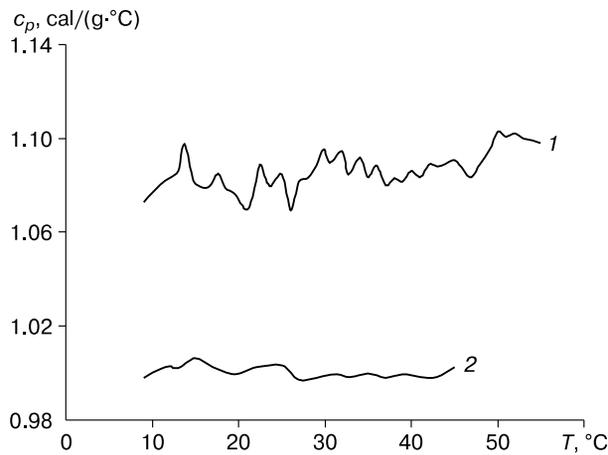
Pore water is often thought to have its heat capacity ( $0.7$  cal/(g·K)) lower than bulk water [Zlochovskaya, 1969], but experimental results show the heat capacity of vicinal water in some materials to exceed that of bulk water. For instance, Braun and Drost-Hansen [1976] measured the heat capacities of vicinal water adjacent to a variety of materials including silica glass, zeolite, diamond, and brown coal and obtained values about  $1.25$  cal/(g·K) irrespective of the substrate material. Drost-Hansen termed the apparent independence of vicinal water properties on the precise physico-chemical details of the substrate the “paradoxical effect”. Etzler and Connors [1990] measured the heat capacity of water in sili-

cas of varying pore radius and observed a maximum (about 25 % higher than in bulk water) near 7 nm pore radius.

According to measurements by *Kovalenko [1992]*, the heat capacities of vicinal water in tricalcium silicate and tricalcium aluminate are 0.22 cal/(g·K) and 0.42 cal/(g·K), respectively, the latter value being close to that of ice. Note that the data reported in [*Kovalenko, 1992*] were processed with too a simplified model allowing a different interpretation and, correspondingly, different heat capacity estimates.

Recent instrumental advances allowed measuring the heat capacity of water to high accuracy and in a large temperature range. The results of *Etzler and Connors [1990]* refer to heat capacity measurements by a Calve-type *Setaram DSC-111G* differential scanning calorimeter in 24 nm silica pores at temperatures varying from 5 to 55 °C (Fig. 4). The heat capacity of pore water showed a general increase with temperature and spikes about the Drost-Hansen transition temperatures, this being consistent with the idea that water undergoes structural transitions in this temperature region [*Etzler and Connors, 1990; Gutmann, 1991*].

The heat capacity of pore water depends also on its concentration. Certain patterns appear when comparing sine-shaped curves of differential adsorption heat and average molar heat capacity vs. the amount of adsorbed water in zeolite. Heat capacity is especially sensitive to phase and molecular transitions in the adsorbate. Low heat capacity corresponds to the highest initial adsorption heat, and the lows of adsorption heat correlate with heat capacity peaks. On heating, a part of associates formed by water molecules with zeolite and with one another dissociate in



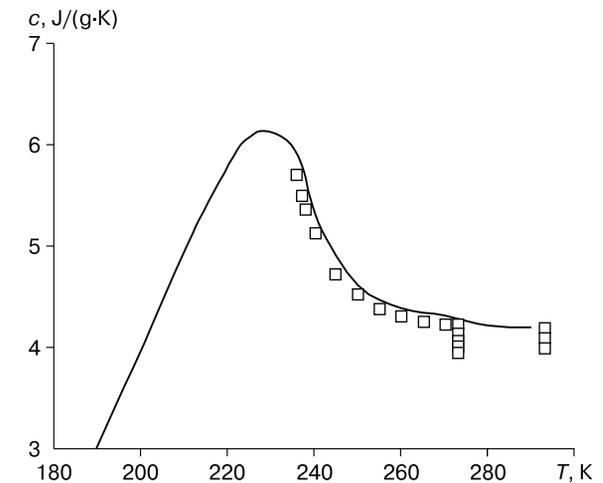
**Fig. 4.** Heat capacity of bulk water (curve 2) and water in 24 nm silica pores (curve 1) as a function of temperature.

endothermic reactions; inasmuch as the dissociation heat makes part of the heat capacity budget, the latter shows peaks in the curve of its water concentration dependence [*Kiselev, 1986*].

The heat capacity of capillary water is the lowest at 37.5 °C and increases dramatically below 0 °C; at -35 °C it is 35 % higher than at 100 °C [*Gutmann, 1991*].

The theoretical heat capacities of supercooled water obtained by *Jeffery and Austin [1997]* on the basis of their equation agree with the observations (Fig. 5). At high pressures, heat capacity is proportional to the degree of supercooling.

The existence of some temperature limit at which heat capacity increases dramatically was inferred in many publications [e.g., *Starr et al., 2003; Fuentesvilla and Anisimov, 2006*]. The heat capacity of supercooled water subject to further cooling was predicted to decrease abruptly. However, still many questions remain about the behavior of thermodynamic and dynamic properties of liquid water at atmospheric pressure in the temperature range between the lower limit of supercooling (235 K) and the onset of the glassy state, though it has been broadly investigated [*Starr et al., 2003*]. Direct measurements within these temperatures being largely infeasible, the authors inferred the respective temperature dependence of entropy and heat capacity from the available experimental data on entropy, specific heat, and enthalpy outside that range. The assumption of entropy being well defined in extreme metastable states and continuous at the atmospheric pressure was used to estimate the excess entropy, and then heat capacity, of the liquid over the crystal within relatively narrow limits [*Starr et al., 2003*]. The heat capacity calculations were based on the upper and lower limits of the temperature depen-



**Fig. 5.** Heat capacity of supercooled water as a function of temperature at different pressures.

Squares are experimental data; solid line shows theoretical data according to equation of state for water.

dence of entropy. The obtained two curves of water heat capacity at constant pressure are similar to that in Fig. 5.

Using self-consistent equations for thermodynamic properties of supercooled water by *Speedy* [1987], *Grant et al.* [1999] suggested the heat capacity equation

$$c_p = \sum_{n=0}^4 B_{c_p}^{(n)} \xi^n + 2C_{c_p} \xi^{-1/2},$$

where  $B_{c_p}^{(0)}$ , ...,  $B_{c_p}^{(4)}$ ,  $C_{c_p}$  are the fitted coefficients based on experimental data;  $\xi = (T - T_s)/T_s$  is the dimensionless reduced temperature;  $T_s$  is the apparent limiting temperature for supercooled water assumed to be 227.15 K ( $-46^\circ\text{C}$ ).

Unlike the relationships from [*Hindmarsh et al.*, 2003], the heat capacity of supercooled water between 203 and 273 K at constant pressure can be approximated as

$$c_p = -0.0011T^3 + 0.732T^2 - 163T + 16\,582,$$

according to which it grows more slowly as the temperature decreases to 203 K.

The structure changes of vicinal water control changes in its diffusivity, which becomes ever lower than in free water as the thickness of water films decreases below  $1\ \mu\text{m}$  [*Korolev*, 1996]; water in  $0.03\ \mu\text{m}$  films has its diffusivity about 30 % lower than free water. These and other features of pore water impart particular properties to the saturated rocks (see below), which is a main reason why the issue is a subject of interest for geoscientists worldwide, especially for engineering geologists, hydrogeologists, and geochemists.

The heat capacity of vicinal water can be calculated from adsorption isotherms [*Starostin*, 2000, 2002]. The equation for the heat capacity of adsorbate includes the temperature second derivative of heat capacity or pressure, while the third derivative is required to study the temperature dependence of heat capacity. Note that these heat capacity estimates cannot be fully reliable because of errors in measured adsorption isotherms and isosteres [*Kiselev*, 1986].

## SURFACE TENSION

The surface tension of water and aqueous solutions becomes a critical parameter of the phase equilibrium at curved interfaces. According to recommendations of the International Association for the Properties of Water and Steam (IAPWS), the equation for the water surface tension ( $\sigma$ ) in the interval from the triple point 273.16 K to the critical temperature  $T_c = 647.096\ \text{K}$  is

$$\sigma = B\tau^\mu(1 + b\tau),$$

where  $\tau = 1 - T/T_c$ ,  $T_c = 647.096\ \text{K}$ ,  $\mu = 1.256$ ,  $B = 235.8\ \text{mN/m}$ , and  $b = -0.625$ .

In studies of phase equilibrium conditions in rocks, the phase sizes and, hence, the interface curvatures vary in large ranges and control the properties at the interface. Below we consider the effect of the curvature radius and temperature on the surface tension of water (water-vapor interface).

The interface curvature dependence of surface tension shows up at small values of curvature radius. Surface tension is a basic thermodynamic parameter of heterogeneous systems and enters the basic equation of the capillarity theory and surface effects. According to Gibbs's adsorption equation obtained from thermodynamic analysis, the surface tension and curvature radius values vary concordantly [*Rusanov*, 1967]. Modified for single-component systems, this equation becomes

$$\frac{1}{\sigma} \left( \frac{d\sigma}{dr} \right)_r = \frac{2\delta}{r^2} \left[ 1 + \frac{\delta}{r} + \frac{1}{3} \left( \frac{\delta}{r} \right)^2 \right] \left\{ 1 + \frac{2\delta}{r} \left[ 1 + \frac{\delta}{r} + \frac{1}{3} \left( \frac{\delta}{r} \right)^2 \right] \right\}^{-1},$$

where  $\delta$  is the Tolman length, or the distance between the surface of tension and the equimolar surface satisfying the condition  $\Gamma = 0$ , while  $\Gamma$  refers to excess extensive thermodynamic values;  $r$  is the curvature radius.

If the curvature is relatively small, the approximate relationship is valid (Tolman's equation) [*Rusanov*, 1967; *Summ and Ivanova*, 2001]:

$$\frac{\sigma}{\sigma_0} = \frac{1}{1 + 2\delta/r},$$

where  $\sigma$  and  $\sigma_0$  are the surface tensions for the curvature radius  $r$  and a planar surface, respectively.

It follows from this equation that at  $\delta > 0$ , the surface tension decreases as the radius of drops becomes smaller. In the region of small curvature radii, the surface tension can decrease with decreasing radius of the surface until both become zero [*Rusanov*, 1967], according to

$$\sigma = Kr,$$

where  $K$  is the proportionality coefficient depending on the phase temperature and composition.

Thus, the curvature dependence of surface tension is controlled by Tolman's length, which was estimated in different ways [*Zhukhovitskii*, 1994, 2003; *Kiselev and Ely*, 2001].

The temperature dependence of Tolman's length in the case of an ice-water interface is described by the interpolation formula [*Kiselev and Ely*, 2001]

$$\delta(T) = -0.4 - 0.005(273 - T)$$

inferred from empirical data [*Bogdan*, 1997].

For the temperature dependence of surface tension at the water-air interface, from  $-8$  to  $0^\circ\text{C}$ , *Grant*

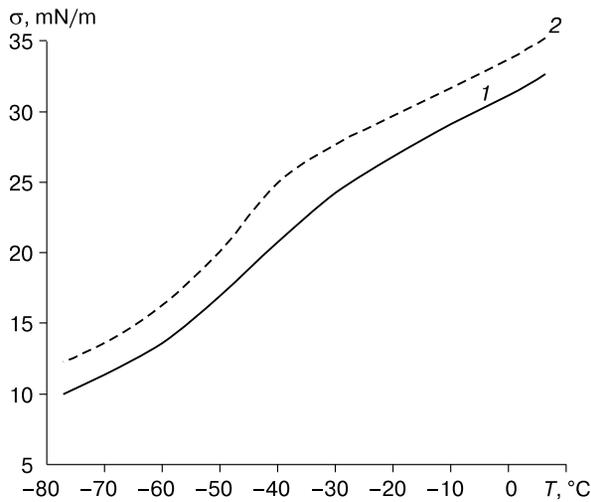


Fig. 6. Surface tension at the water-ice interface as a function of temperature at pressures 1 bar (1) and 550 bar (2).

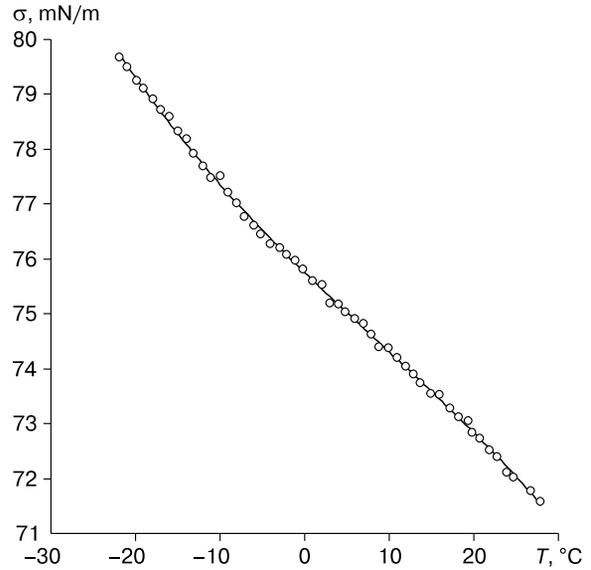


Fig. 7. Surface tension of water as a function of temperature.

[2000] suggested to use an equation originally derived for positive temperatures:

$$\sigma = \sigma_0 \left( \frac{T_1 - T}{T_1} \right)^u \left( 1 - v \frac{T_1 - T}{T_1} \right),$$

where  $\sigma_0 = 0.2358 \text{ N/m}$ ,  $T_1 = 647.15$ ,  $u = 1.256$ , and  $v = 0.625$ .

Jeffery and Austin [1997] studied the temperature dependence of surface tension and calculated ice-water surface energy of supercooled water to  $-80 \text{ }^\circ\text{C}$  (see the results for 1 and 550 bar in Fig. 6). The values predicted from the equation of state agree with the measured values between 25 and 38 mN/m for  $0 \text{ }^\circ\text{C}$  [Jeffery and Austin, 1997].

There are few experimental estimates of water surface tension at negative temperatures. Detailed measurements in the range from  $-22.2$  to  $27.0 \text{ }^\circ\text{C}$  were performed by visual observation of meniscus in a capillary [Hacker, 1951] and showed monotonic growth of surface tension with decreasing temperature over the entire range (Fig. 7).

Inasmuch as pore water makes part of a solution, the effect of dissolved components on surface tension is important for estimating the phase equilibrium conditions. Namely, surface tension increases under the effect of surfactants. Furthermore, the surface tension of dissolved salts that dissociate into ions is higher than in fresh water.

When dissolving, surfactants can change the surface tension and thus influence the phase equilibrium. The presence of insoluble liquid (e.g., oil) in pores

likewise affects the phase equilibrium of both water and this liquid.

## CONCLUSIONS

1. The properties of water in rocks and other disperse materials reasonably arouse much interest as water freezing and thawing largely influence the structure and properties of the substrate, as well as its mechanic and thermal state. The results obtained through these studies are used to substantiate the theory that accounts for the physical properties, stress, and strain of rocks, as well as to model related heat and mass transfer.

2. The state and properties of pore (vicinal) water are controlled by many factors in an intricate way. Predicting the properties of water in rocks has been impossible proceeding from the general theoretical assumptions but requires experimental studies in each specific case.

3. The properties of vicinal water differ markedly from those of free water. For instance, measurements show that the viscosity of water in quartz capillaries becomes 1.6 times higher as the water film thins down; the permittivity of bound water is likewise much lower than in free water. Direct extrapolation of these results on disperse rocks is problematic; rather, experimental studies are required to include the properties of pore water into heat and mass transfer models.

4. Investigation into the properties of bound water can shed light also on processes in permafrost. Modeling the state of rocks as multi-component

systems, as well as heat and mass transfer in these systems, is impossible without phase diagrams of pore water and complex fluids showing their thermodynamic properties as functions of temperature, salinity, etc.

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