

Remember the water – a comment on EPS colligative properties

K. Keiding, L. Wybrandt and P.H. Nielsen

Environmental Engineering Laboratory, Aalborg University, Sohngaardsholmsvej 57, DK-9000, Aalborg, Denmark

e-mail: i5kk@civil.auc.dk

Abstract The relationship between water and activated sludge components was examined. Reevaluation of published data on freezing point depression, drying rates and dewatering has been performed. The basis of this has been the assumption that the water/sludge relationship is considered to be a colligative effect. Since the results indicate this to be the case, we suggest that the published concepts of “pools of water” are false. Data on swelling properties of EPS as a function of pH suggests that the colligative properties are largely determined by the counterions of charged polymers and surfaces.

Keywords Activated sludge; biopolymers; charge density; colligative properties; EPS; extracellular polymeric substances

Introduction

A number of activated sludge features are related to the interplay between water and sludge components. Some, such as floc density, dewaterability and drying properties, have immediate relevance for the design of equipment for sludge handling. Others, such as freezing point analysis (dilatometry) and drying rate analysis, have been studied in order to devise sludge characterization methods. For all of the above-mentioned studies, it is noted that no theoretical interpretation of the observed phenomena is given or the results have been interpreted by the definition of different “pools of water”, i.e. different states of water binding.

Common to the mentioned phenomena is the relation to the class of properties, termed colligative properties. Colligative properties are in most physical chemistry textbooks presented by: elevation of boiling point, freezing point depression, osmotic pressure and water activity. Colligative properties are defined by the lowering of the solvent (water) chemical potential as a consequence of introducing a solute. If the chemical potential – or the free energy – of a species is altered, then the physical chemical properties of the species will change as well, which is expressed as colligative properties of a solution or suspension. As activated sludge and other structures containing extracellular polymers (EPS) are mixed solutions/suspensions in water, colligative effects must be present. Yet, it is of interest to assess the extent to which such are manifested.

In the crude perspective of a physical chemist, activated sludge is composed of dissolved solids and charged surfaces. This is so because colligative properties merely reflect the number of independent entities in the solution. Albeit the microbial particles and macromolecules are important in the metabolic aspects of sludge, they are numerically insignificant to the number of ions – either dissolved salt or counter ions to the charged surfaces – in the suspension. It is thus predictable that a number of sludge properties relates to the conductivity of the bulk water as a measure of dissolved solids and to the suspended solid content as a measure of the concentration of charged biopolymers. In the present paper, the discussion of water distribution, swelling/deswelling – hence the density – of sludge flocs and in part the dewaterability of sludge will be addressed to demonstrate the colligative properties of sludge EPS.

Results

Dilatometry

Dilatometric analysis of sludge samples has been used to discriminate between what is thought to be different pools of water in the sludge samples. These pools have been termed hydrated water, bound water, interstitial water and, most curiously, vicinal water (Smith and Vesilin, 1995). Yet, in the mentioned analysis it appears that the effect of freezing point depression has been overlooked. Reformulation of the general expression for the freezing point depression (in the unabbreviated form) permits reevaluation of dilatometric data from Smith and Vesilin (1995), where the ratio of unfrozen water to solid content of the sample, Y , can be expressed as a function of temperature:

The freezing point is defined as the temperature at which there is equilibrium between the liquid solvent and the corresponding solid state of the solvent. In the present context this means that equilibrium exists between the liquid water of the sample and the frozen water – ice. Throughout the following derivations it is assumed that the pressure is constant, thus the demand of equilibrium is formulated as:

$$\mu_{\text{liquidwater}}(T, x) = \mu_{\text{ice}}(T) \Leftrightarrow \mu_{\text{liquidwater}}^o(T) + RT \ln x = \mu_{\text{ice}}(T) \quad (1)$$

where μ_i denotes the chemical potential of the species i and x is the mole fraction of the liquid water.

Following Castellan (1975), this leads to the following general expression for the freezing point depression:

$$\ln x_w = \frac{\Delta H_f}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_f} \right) \Leftrightarrow T = \left(\frac{R \cdot \ln x_w}{\Delta H_f} + \frac{1}{T_f} \right)^{-1} \text{ and } Y = \frac{M_w}{M_s} \cdot \frac{x_w}{1 - x_w} + Y_{sc} \quad (2)$$

where ΔH_f is the enthalpy of fusion, R the gas constant, T the observed freezing point and T_f the freezing point of the pure solvent. The Y, x -relation, in which M_w is the molecular weight of water, M_s is the number average molecular weight of solutes and Y_{sc} is the amount of unfrozen, supercooled water per solid content, is developed in the appendix, Eq. (A4). The super cooled water is formed as a consequence of the anti-freeze effect of the EPS, as the solution is concentrated (Haymet *et al.*, 1999).

Fitting data published by Smith and Vesilin (1995) by the above equations (Figure 1), one obtains a value of Y_{sc} at 5.1 g of super cooled water per gram of solid and a value of M_s at 179 g/mol, i.e. the number average molecular weight of guest molecules in the sludge. This implies that the result of dilatometric experiment may be interpreted as a continuous

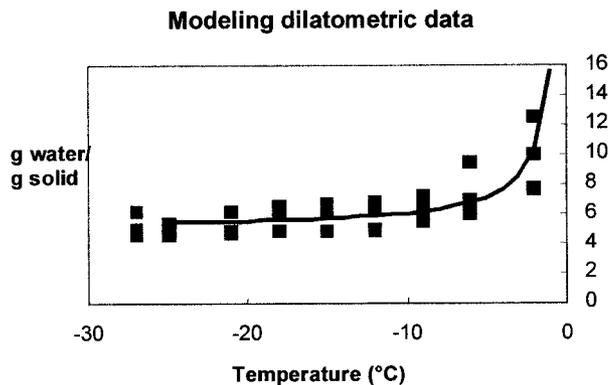


Figure 1 The figure shows the adaptation of Eq. (2a) and (2b) to data published by Smith and Vesilin (1995). The full line shows the least square fit of the model to the experimental data (given by dots)

freezing of liquid water in a solution containing a substance of average molecular weight of 179 g/mol and a formed content of super cooled water of 5.1 g water per g solid. Thus a priori, there is no argument for the definition of pools of water. This is much the same conclusion as drawn by Wu *et al.*, (1998).

Drying rates

Studies of sludge drying rates have immediate relevance to the technical design of sludge dryers. The group of Dichtl (Kopp and Dichtl, 2000) has demonstrated that drying characteristics of a sludge are closely related to centrifugational dewatering characteristics of the same sludge. The generation of experimental data on drying rates, suited for quantitative data treatment, is a difficult task. This is so because drying involves heat transfer, diffusional resistance to the transfer of water vapor from the slurry material to the drying air stream and equilibration of the liquid water in the slurry with the local atmosphere in and around the slurry. By applying thin films of sludge and conducting the drying process adiabatically, the group of Kopp and Dichtl, (2000) have obtained results where the kinetics of drying is proportional to the driving force of the mass transfer of water vapor from the slurry to the drying stream. In other words, the results may be regarded as if there at all time exists an equilibrium between the water vapor pressure, P , of the slurry and the liquid water content of the slurry. Hence the drying rate, R , is proportional to $P_{w,slurry} - P_{w,stream}$. Assuming now that $P_{w,stream} \approx 0$, which is a prerequisite of a drying process. Then the drying rate will be proportional to $x_w \cdot P^*$, where x_w is the mole fraction of liquid water in the sample and P^* is the vapor pressure of pure water at the temperature of the experiment – according to Raoult's law.

$$\text{Rate} = K \cdot \frac{Y \cdot \frac{M_s}{M_w}}{1 + Y \cdot \frac{M_s}{M_w}} \quad (3)$$

Utilizing, as above, Eq. (A3) and a proportionality factor, K , a result of least square fitting of Eq. (3) to experimental data from Kopp and Dichtl (2000) is shown in Figure 2.

The adaptation of the model to the experimental data yields a proportionality constant of 0.075 and a value of M_s at 89 g/mol. Thus, it is possible to describe the drying rate of sludge as a continuous evaporation of liquid water from a solution of molecules of average molecular weight at 89 g/mol. The constant of proportionality largely reflects the vapor pressure of pure water at the drying temperature. Again, no a priori need for defining pools of water can be argued.

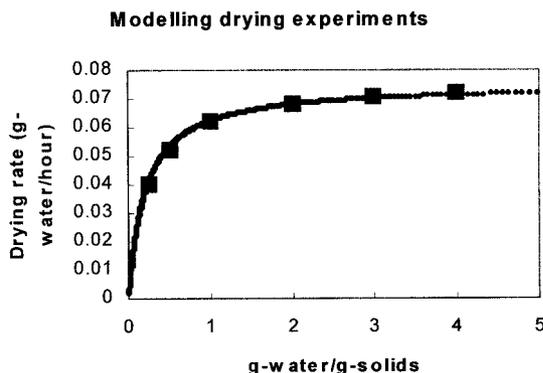


Figure 2 Experimentally determined drying rates, as indicated by dots, described as a function of water content (full line) by means of Eq. 3

Dewatering

The understanding of dewatering is mainly based on a mechanical description of the resistance to filtration and to a lesser extent the expression step (Sørensen and Sørensen, 1997). Apart from concerns of the particle size effects, no physical chemistry has been involved in understanding the dewatering process. Dewaterability of slurries is composed of a filtration step, in which the liquid pressure (the driving force of the filtration) is constant and equal to the external filtration pressure, and an expression step, in which the liquid pressure decreases, until the flow of water ceases. This latter phenomenon may amply be simulated, when utilizing that the osmotic pressure between the cake and the filtrate actually causes a counter pressure to filtration. The osmotic pressure of the sludge cake is now solely coming from the counter ions of the charged surfaces in the sludge, as the dissolved solid concentration is the same in the filtrate as in the bulk water of the filter cake (Keiding and Rasmussen, 2000).

Assuming a surface charge density of the sludge, σ , and a density of the hydrated, but not swelled, sludge particles of ρ , and a porosity of the cake of β – then the concentration of counter ions in the bulk water of the filter cake with a total volume of V_1 may be calculated from the following rationale: the concentration of counter ions per volume of solids is $\sigma \cdot \rho$; as the total solid concentration in the filter cake is $(1-\beta) \cdot V_1$, the total number of counter ions in the filter cake is $\sigma \cdot \rho \cdot (1-\beta) \cdot V_1$; as the water content of the filtercake is $\beta \cdot V_1$, the concentration of counter ions in the water of the filter cake is $\sigma \cdot \rho \cdot (1-\beta) \cdot V_1 / \beta \cdot V_1 = \sigma \cdot \rho \cdot (1-\beta) / \beta$ and hence the osmotic pressure $P = \sigma \cdot \rho \cdot (1-\beta) / \beta \cdot RT$. The agreement of these relations with experimental data is shown in Figure 3, with input data from Novak *et al.* (1999).

The agreement between the experimental determination of the liquid pressure at the top of the filter cake and the corresponding modeled data (Figure 3) indicate that the expression phase of the dewatering is identical to the physical chemical process of mechanical deswelling.

Swelling

Swelling is the increase of sample volume by uptake of water in order to reduce the osmotic pressure difference between the sample and the surrounding liquid water. Swelling is well known in e.g. ion exchanger systems, soils and other systems, where the sample consists of charged surfaces. The final example of colligative properties of sludge EPS relates again to the effect of osmotic pressure.

As the concept of a gel gains increasing acceptance by the scientific community as a precise way of describing biological aggregates, the osmotic pressure becomes a key parameter in understanding the swelling/deswelling of such aggregates. In this respect pH becomes an important parameter for the definition of the free surface charge of the biopolymers. Figure 4 shows the degree of swelling as a function of pH of a dialyzed (10 kD)

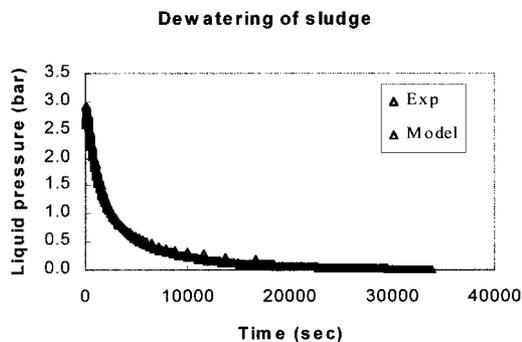


Figure 3 Experimental and modeled description of the liquid pressure during expression of activated sludge

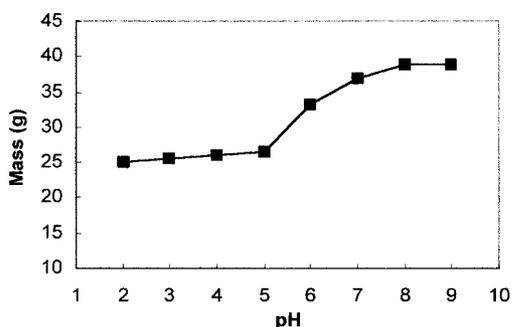


Figure 4 The figure shows that the water uptake of EPS in a dialysis bag is strongly dependent of the pH of the sample

EPS-sample, extracted from activated sludge by the ion exchange method (Frølund *et al.*, 1996). The dependency closely reflects the charge distribution as assessed from titrations (Keiding, 1998) of the sample.

As pH increases the number of charged groups at the macromolecule increases as subsequently does the number of counter ions. The resemblance of the swelling data in Figure 4 with the corresponding titration curve of extracted EPS is thus an indirect verification of the dominating effect of counter ions in the colligative effects of charged polymers.

Discussion

Four examples of colligative effects have been shown – namely freezing point depression, water vapor pressure reduction (drying rate), osmotic pressure in mechanical deswelling (dewatering) and in swelling. In none of these cases is a definite proof provided for the colligative effect. However, the simplicity of the argument presented here, combined with the convincing fits of the calculated values to the experimental values, do suggest that this straightforward description of water properties from basic chemical thermodynamics should be investigated further, before the spurious concept of pools of water is generally accepted.

It has been chosen to approach the mole fraction of water by the water content, Y , or the free charge density. In Eq. (A4) it is shown that this corresponds to the relation: $\sigma.M_s = 1$. In a further analysis of this relation it is found that $\sigma.M_s = \tau/(1+\tau)$, where τ is the molecular charge density, i.e. moles of free charge per moles macromolecules. These two relations concur for large values of τ . From titration of extracted sludge EPS σ is found in the order of 10^{-3} moles free charge per g solid EPS (Keiding, 1998). Assuming an average molecular weight in the order of 10^5 g/mole of the EPS, one obtains values of τ in the order of 10–100. This argument may be simplified as follows: as $x_w = 1 - x_s$ and $x_s = x_{\text{counter-ion}} + x_{\text{macromolecule}}$, we may neglect the mole fraction of the macromolecules as their number is small or insignificant to the number of counter ions. Hence $x_w \approx 1 - x_{\text{counterion}}$ is obtained. Thus the argument demonstrates that the density of counter ions, i.e. the charge density of the macromolecules, largely determines colligative properties of macromolecular suspensions. This argument is frequently encountered in literature on gels, e.g. Nieves *et al.* (2000). As EPSs are charged polymers and as they constitute a large fraction of microbial aggregates as found in e.g. activated sludge and biofilms, it is strongly suggested that the above phenomena are pertinent to such systems.

Conclusions

It has been argued that a number of properties related to suspensions of microbial aggregates may be explained by the colligative effects of such suspensions, and that

these effects largely are determined by the charge density of the extracellular biopolymers.

Rather frequently in research we look for effects of solutes, e.g. biopolymers, by studying properties of the solutes in order to understand the macroscopic properties of the solution. However, some properties of a solution will originate from the mere lowering of the solvent potential and not the specific properties of the solute. In fact, the binding energy in water binding is entropic in nature. This is the general argument behind the statement: remember the water!

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Appendix

The present appendix serves the purpose of relating the thermodynamic variable x_i , i.e. the mole fraction of species i , to generally applied variables such as total suspended matter, TS , and water content, Y . The relation between TS and Y is readily derived. Letting m_s denote the mass of suspended and dissolved matter and m_w denote the mass of liquid water, TS and Y are defined as follows:

$$TS = \frac{m_s}{m_s + m_w} \quad \text{and} \quad Y = \frac{m_s}{m_w} \quad \text{hence:} \quad TS = \frac{\frac{m_s}{m_w}}{\frac{m_s}{m_w} + 1} = \frac{Y}{Y + 1} \Leftrightarrow Y = \frac{TS}{1 - TS} \quad (\text{A1})$$

The mole fraction x is defined as the ratio of number of moles of species i to the total number of mole of the solution/suspension. In the present context we are interested in the total number of guest molecules (or non-water molecules), hence we define:

$$x_w = \frac{n_w}{n_s + n_w} \quad \text{and} \quad x_s = \frac{n_s}{n_s + n_w} \quad \text{which implies:} \quad x_w + x_s = 1$$

The relation between the mole fraction and the water content may be derived as follows:

$$x_s = \frac{n_s}{n_s + n_w} \Leftrightarrow \frac{1}{x} = 1 + \frac{n_w}{n_s} = 1 + \left(\frac{m_w}{M_w}\right) \cdot \left(\frac{m_s}{M_s}\right)^{-1} = 1 + \left(\frac{m_w}{m_s}\right) \cdot \left(\frac{M_s}{M_w}\right) = 1 + Y \cdot \frac{M_s}{M_w}$$

$$\Leftrightarrow x_s = \frac{1}{1 + Y \cdot \frac{M_s}{M_w}} \quad (\text{A2})$$

from which it follows that

$$x_w = \frac{Y \cdot \frac{M_s}{M_w}}{1 + Y \cdot \frac{M_s}{M_w}} \quad \text{and} \quad Y = \frac{M_w}{M_s} \cdot \frac{1 - x_s}{x_s} = \frac{M_w}{M_s} \cdot \frac{x_w}{1 - x_w} \quad (\text{A3})$$

Finally, the x, TS -relations may be derived from the TS, Y - and the x, Y -relations.

Two approaches have been used to describe the mole fraction – namely the average molecular weight of the suspended/dissolved matter and the concept of a charge density. The development below has been made to demonstrate that these two approaches are equivalent:

We have:

$$x_w = \frac{Y \cdot M_R}{1 + Y \cdot M_R} = 1 - \frac{\sigma \cdot \rho_L \cdot \frac{TS}{(1-TS)}}{\sigma \cdot \rho_L \cdot \frac{TS}{(1-TS)} + V_{m,w}} = 1 - \frac{\sigma \cdot \rho_L \cdot \frac{1}{Y}}{\sigma \cdot \rho_L \cdot \frac{1}{(Y)} + V_{m,w}} = \frac{\frac{\sigma}{Y}}{\frac{\sigma}{Y} + \frac{V_{m,w}}{\rho_L}}$$

$$\Downarrow$$

$$M_R \cdot \sigma = \frac{V_{m,w}}{\rho_L} \Rightarrow M_s \cdot \sigma = \frac{(M_w \cdot V_{m,w})}{\rho_L} = 1 \quad (\text{A4})$$

which shows that the concept of a mean molecular mass equivalates that of a free charge density.

Assuming this to be strictly a biopolymer problem we know that:

$$m_s = m_i + m_m = n_i \cdot M_i + n_m \cdot M_m$$

Introducing the concept of a charge density at a molecular level, we may define τ as n_i/n_m , i.e. as the number of charged group per macromolecule. Further, the mean molecular weight, M_s , may be defined as m_s/n_s , where $n_s = n_i + n_m$. Hence, we get:

$$M_s = \frac{1}{1 + \tau} \cdot (\tau \cdot M_i + M_m)$$

With the definition of $\sigma = n_i/(M_s \cdot n_s)$, we find:

$$\sigma \cdot M_s = \frac{\tau}{1 + \tau} \Leftrightarrow \tau = \frac{\sigma \cdot M_s}{1 - \sigma \cdot M_s} \quad (\text{A5})$$

which tells us that: 1) $\sigma \cdot M_s$ may take values between 0.5–1 and 2) $\sigma \cdot M_s$ approaches unity as τ increases, which was found appropriate in the study – see above.

