MHD

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1 Physics of saline water

Notations:

T : Temperature in K (Kelvins).

t : Temperature in ^{o}C (Celsius degrees).

ρ : Volumic mass, expressed in kg/m^3.

S : Salinity, defined as the mass ratio between the dissolved NaCl and the solution, expressed in ‰ (part per thousand or ppt or or g/kg).

M : Molarity, defined as the number of moles of NaCl present in 1 liter of solution, expressed in mol/L.

m : Molality, defined as the number of moles of NaCl present in 1 kg of solution, expressed in mol/kg.

M_{NaCl} : Molar mass of NaCl, constant value of 58.4428×10^{-3} kg/mol.

1.1 Density (volumic mass)

1.1.1 Density from salinity and temperature (El-Dessouky and Ettouney, 2002)

El-Dessouky and Ettouney [1] provide a model based on a Chebyshev fit for predicting the density (actually the volumic mass) of saline water from its measured salinity and temperature at a fixed pressure of 0.1 Mpa (reformulated):

$$\rho_{salinity}(S,t) = \sum_{i,j} c^E_{i,j} T_i \left(\frac{t-100}{80}\right) T_j \left(\frac{S-75}{75}\right) \tag{1}$$

where

$$c^E = \begin{pmatrix} 1008.05475 & 57.6565 & 0.163 \\ -54.0995 & 1.571 & -0.423 \\ -6.1235 & 1.74 & -0.009 \\ 0.346 & -0.087 & -0.053 \end{pmatrix} \tag{2}$$

and the T_i are the (type 1) Chebyshev polynomials:

$$\begin{aligned} T_0(x) &= 1 \\ T_1(x) &= x \\ T_2(x) &= 2x^2 - 1 \\ T_3(x) &= 4x^3 - 3x \end{aligned} \tag{3}$$

[1] indicates 0 ‰ $< S <$ 160 ‰ and $10 < t < 180$ °C as ranges of validity.

1.1.2 Density from molality and temperature

Molality and Salinity are related in a straightforward way via the molar mass of NaCl as:

$$S = 1000.m.M_{NaCl} \tag{4}$$

and we get:

$$\rho_{molality}(m,t) = \rho_{salinity}(1000.m.M_{NaCl}, t) \tag{5}$$

1.2 Viscosity

1.2.1 Viscosity from (El-Dessouky and Ettouney, 2002)

El-Dessouky and Ettouney [1] provide a model for predicting the dynamic viscosity of saline water from salinity S and temperature t at a fixed pressure of 0.1 Mpa:

$$\mu = (\mu_W)(\mu_R) \times 10^{-3} \tag{6}$$

with

$$\begin{array}{lcl} \ln(\mu_W) & = & -3.79418 + 604.129/(139.18 + t) \\ \mu_R & = & 1 + AS + BS^2 \\ A & = & 1.474 \times 10^{-3} + 1.5 \times 10^{-5}t - 3.927 \times 10^{-8}t^2 \\ B & = & 1.0734 \times 10^{-5} - 8.5 \times 10^{-8}t + 2.23 \times 10^{-10}t^2 \end{array} \tag{7}$$

[1] indicates 0 ‰ $< S <$ 130 ‰ and 10 °C $< t <$ 180 °C as ranges of validity.

1.3 Conductivity

1.3.1 Conductivity from molality using training data

Bešter-Rogač [2] provides molar conductivities Λ (in S.cm^2/mol) for a combination of seven temperatures T (in K) and eight NaCl concentrations, expressed in molalities m (mol/kg) for seven combinations of water and 1,4-Dioxane. The first of these combinations is with water only and this is the only one we are interested into. The relevant table excerpt is reproduced in table 1. Note that you do NOT get the conductivity just by multiplying Λ by m because, in order to get the conductivity σ, one needs to multiply the molar conductivities Λ by the *molarity* M (in mol/L), not by the *molality* m (in mol/kg). M and m are related through the volumic mass ρ (in kg/m^3) of the solution, itself dependent upon the concentration and the temperature, via $M = m.\rho/1000$. This is a bit complicated but it does make sense to have Λ related to volumic concentrations because conductivity is related to the geometry (lengths, areas, volumes) and to use mass concentrations for dosing solutions as these, unlike the volumic concentrations, do not vary with the temperature. As σ, Λ, m, and ρ are respectively expressed in S/m, S.cm^2/mol, mol/kg and kg/m^3, we obtain:

$$\sigma_{molality}(m,t) = \Lambda_{molality}(m,t).\rho_{molality}(m,t).m/10 \tag{8}$$

A model for $\Lambda(m,t)$ can be obtained using a Chebyshev fit[1] from the data displayed in table 1. In practice, we use $\sqrt{m}$ instead of m for the molality variable[2]. After a least square minimization of

[1] A Chebyshev fit is a particular case of polynomial fit known to be more numerically stable when the input data are normalized in the $[-1,+1]$ range.

[2] This is because we expect a linear behavior in $\sqrt{m}$, at least for small values of m because of the Kohlrausch law stating that we should have $\Lambda \sim \Lambda_0 - b\sqrt{M}$ in this case, Λ_0 and b being temperature-dependent constants. For small values of m and t, we also have $M \sim m$.

the residual squared relative error, the model is obtained as follows:

$$\Lambda_{molality}(m,t) = \sum_{i,j} c^B_{i,j} T_i\left(\frac{t-20}{15}\right) T_j\left(\frac{\sqrt{m}-1.099268}{0.994007}\right) \tag{9}$$

where

$$c^B = \begin{pmatrix} 74.172862 & -30.060878 & 0.178265 & -1.720127 & 0.755938 \\ 23.480611 & -10.081103 & 0.838633 & -0.412552 & 0.272767 \\ 0.588656 & -0.299116 & 0.066510 & 0.010868 & 0.073651 \end{pmatrix} \tag{10}$$

and the T_i are the (type 1) Chebyshev polynomials:

$$\begin{aligned} T_0(x) &= 1 \\ T_1(x) &= x \\ T_2(x) &= 2x^2 - 1 \\ T_3(x) &= 4x^3 - 3x \\ T_4(x) &= 8x^4 - 8x^2 + 1 \end{aligned} \tag{11}$$

The maximum and RMS of the relative error of the model on the training data are respectively of 0.35 % and 0.15 %, which is quite good considering that the model has only 15 trained parameters for 56 data points, indicating that the measurements were also very good. There is also an excellent fit with other independent measurements.

Table 1: From [2]: molar conductivity Λ (in S.cm^2/mol) of saline water at different combinations of temperatures t (converted in Celsius degrees) and molalities m (in mol/kg).

$m \setminus t$	5	10	15	20	25	30	35
0.01108	72.805	83.359	94.416	05.891	117.828	130.167	142.870
0.05608	68.355	78.163	88.507	99.093	110.178	121.586	133.340
0.10291	66.015	75.425	85.282	95.585	106.215	117.053	128.319
0.50981	58.434	66.452	74.833	83.553	92.536	101.692	111.198
1.0084	53.833	60.970	68.565	76.350	84.413	92.679	101.162
2.0099	46.627	52.714	59.084	65.657	72.463	79.523	86.690
3.0047	39.057	44.302	49.739	55.431	61.390	66.904	72.898
4.3818	29.670	33.873	38.326	42.893	47.679	52.595	57.950

In order to illustrate the difference between m and M, tables 2 and 3 shows the solution density and molarity for the training data points. Table 4 shows the conductivity values fro the data points. Densities are estimated using the method described in [1].

References

[1] H.T. El-Dessouky and H.M. Ettouney. *Fundamentals of Salt Water Desalination*. Chemical, Petrochemical & Process. Elsevier, 2002.

[2] Marija Bešter-Rogač, R. Neueder, and J. Barthel. Conductivity of sodium chloride in water + 1,4-dioxane mixtures from 5 to 35°c ii. concentrated solution. *Journal of Solution Chemistry*, 29:51–61, 01 2000.

Table 2: Salinity S in ‰, and density ρ in kg/m^3 computed with the method described in [1] for the training data points from [2]. Like molality, salinity does not depend upon the temperature.

m	$S \setminus t$	5	10	15	20	25	30	35
0.01108	0.65	1002.1	1001.2	1000.1	998.9	997.5	995.9	994.2
0.05608	3.28	1004.1	1003.2	1002.1	1000.8	999.4	997.8	996.1
0.10291	6.01	1006.1	1005.2	1004.1	1002.9	1001.4	999.9	998.1
0.50981	29.79	1024.1	1023.1	1021.9	1020.6	1019.1	1017.5	1015.7
1.0084	58.93	1046.6	1045.5	1044.2	1042.7	1041.1	1039.4	1037.5
2.0099	117.46	1093.3	1091.7	1090.0	1088.2	1086.3	1084.3	1082.2
3.0047	175.60	1141.6	1139.5	1137.3	1135.0	1132.7	1130.2	1127.8
4.3818	256.08	1211.8	1208.6	1205.4	1202.2	1199.1	1195.9	1192.8

Table 3: Molarity M in mol/L computed using the method described in [1] for density estimation for the training data points from [2].

$m \setminus t$	5	10	15	20	25	30	35
0.01108	0.01110	0.01109	0.01108	0.01107	0.01105	0.01103	0.01102
0.05608	0.05631	0.05626	0.05620	0.05613	0.05605	0.05596	0.05586
0.10291	0.10354	0.10345	0.10333	0.10320	0.10306	0.10290	0.10272
0.50981	0.52212	0.52160	0.52099	0.52032	0.51956	0.51873	0.51782
1.0084	1.05543	1.05425	1.05293	1.05147	1.04986	1.04811	1.04623
2.0099	2.19744	2.19428	2.19089	2.18727	2.18343	2.17938	2.17511
3.0047	3.43027	3.42384	3.41720	3.41035	3.40329	3.39604	3.38858
4.3818	5.30972	5.29573	5.28180	5.26792	5.25408	5.24027	5.22647

Table 4: Conductivity σ in S/m computed with the method described in [1] for density estimation for the training data points from [2].

m	$S \setminus t$	5	10	15	20	25	30	35
0.01108	0.65	0.08	0.09	0.10	0.12	0.13	0.14	0.16
0.05608	3.28	0.38	0.44	0.50	0.56	0.62	0.68	0.74
0.10291	6.01	0.68	0.78	0.88	0.99	1.09	1.20	1.32
0.50981	29.79	3.05	3.47	3.90	4.35	4.81	5.28	5.76
1.0084	58.93	5.68	6.43	7.22	8.03	8.86	9.71	10.58
2.0099	117.46	10.25	11.57	12.94	14.36	15.82	17.33	18.86
3.0047	175.60	13.40	15.17	17.00	18.90	20.89	22.72	24.70
4.3818	256.08	15.75	17.94	20.24	22.60	25.05	27.56	30.29