

# Estimation of Monoethylene Glycol (MEG) Content in Water + MEG + NaCl + NaHCO<sub>3</sub> Solutions

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Density and electrical conductivity have been measured for mixtures of 1,2-ethanediol (MEG) + water + NaCl + NaHCO<sub>3</sub> with MEG concentrations from 0 to 100 mass % in salt-free solvent (wt %) and salt contents approaching the solubility limits at temperatures between 20 and 25 °C. Empirical correlations for density and conductivity in (MEG + water + salt) mixtures have been proposed. These correlations have been utilized in a model that can predict MEG concentration and salt content merely on the basis of density and conductivity of a solution. The model provides a fast, easy, and inexpensive method for prediction of MEG concentration, with an accuracy of (2 to 3) wt %.

## Introduction

Transportation of hydrocarbons and water in long subsea flow lines from satellite fields to an onshore process plant results in new challenges to control hydrates, corrosion, and scale. As the fluids cool, water will condense and gas hydrates can form unless an inhibitor such as monoethylene glycol (MEG) is present. To avoid hydrate formation, hence possible plug formation and transport problems, it is very important to have good control of the MEG concentration in the pipeline. The MEG concentration must therefore be regularly measured.

A commonly used method to measure MEG concentration is simply to measure the density of the solution. Since the density of MEG is greater than that of water, the MEG concentration can be found from a calibration curve. The density also depends on quantity of dissolved salts, with NaCl usually being the dominating compound. If dissolved salts are present, it will appear as if the MEG concentration is higher than it really is, and the system may not have proper hydrate protection.

MEG concentration can be accurately measured by use of gas chromatography (GC). This, however, requires that the samples are shipped to an external laboratory, unless a well-equipped laboratory is available.

This work presents a new and simple method where measurements of conductivity and density are combined to give an estimate of both MEG and salt concentration. In cases where pH stabilization<sup>1</sup> is used to control corrosion, the main salt component is often NaHCO<sub>3</sub> and not NaCl. If the alkalinity is measured, (e.g., by titration), this can be corrected for.

## Theory

A density measurement is a fast, accurate, and simple method for estimation of alcohol content in aqueous solutions. Figure 1 shows the density of water/MEG solutions without salts at a temperature of 20 °C. From these data, it is possible to relate

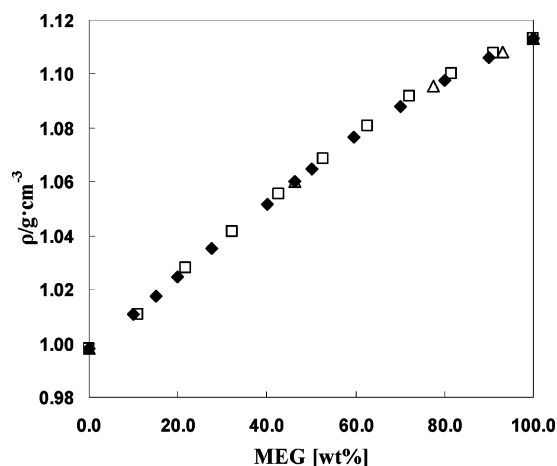


Figure 1. Density of water/MEG mixtures at a temperature of 20 °C.  $\Delta$ , this work;  $\blacklozenge$ , Tsierkezos and Molinou;<sup>2</sup>  $\square$ , Corradini et al.<sup>3</sup>

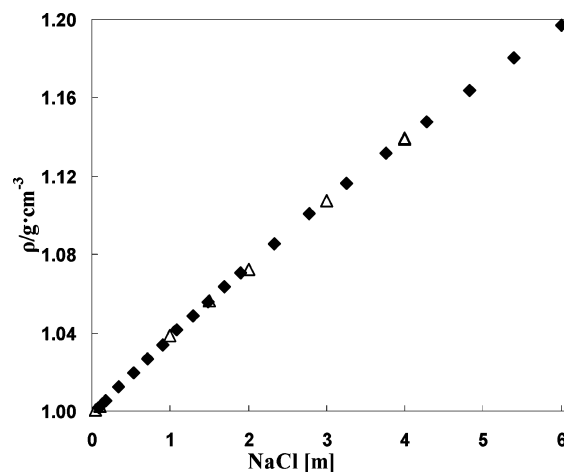


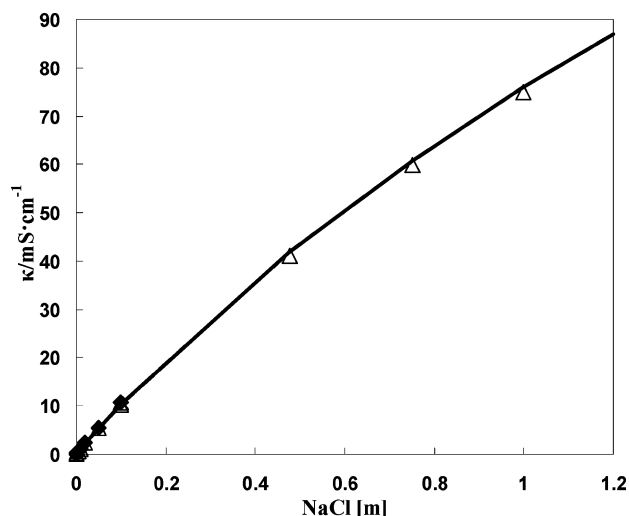
Figure 2. Density of water as function of NaCl concentration (mol/kg of solvent) at a temperature of 20 °C.  $\Delta$ , this work;  $\blacklozenge$ , Lide.<sup>4</sup>

density directly to the MEG concentration. The density of a solution is, however, also dependent on dissolved salt. Figure 2 shows the density of water containing NaCl.

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**Figure 3.** Conductivity at a temperature of 25 °C in aqueous solutions of varying NaCl content (mol/kg of solvent). The solid line gives the model in this work;  $\Delta$ , this work;  $\blacklozenge$ , Lide.<sup>4</sup>

Both NaCl and MEG increase the density, and a single density measurement is not sufficient to calculate the MEG concentration. One additional measurement is needed, and our choice is conductivity as it is fast and simple. Conductivity increases with the concentration of dissolved salt and is commonly used to measure salinity of waters. Figure 3 shows the response in aqueous solutions as a function of NaCl concentration. The effect of MEG is, however, opposite as an increase in MEG concentration will reduce the conductivity. Due to qualitatively different effects of MEG and salt on density and conductivity, the two measurements can be combined to calculate MEG and salt concentration in unknown samples.

Refractive index measurements are also commonly used for estimation of MEG content in unknown samples. The change due to both MEG and salt is, however, very similar for density and refractive index such that a combination of the two is not suited for determination of MEG content in saline samples. It is noted that a combination of refractive index and conductivity should yield good results.

## Experimental Section

Moisture can be a problem because MEG is hygroscopic. The MEG (p.a. >99.5 mass %) delivered by Merck was analyzed with a Methrom 831 KF Karl Fischer titration equipment and found to contain 720 ppm (0.07 wt %) of water.

MEG + water solutions of concentrations between 0 and 100 wt % MEG were prepared gravimetrically in 1-L screw-cap bottles. These samples were thereafter degassed by use of a water jet pump. NaCl (p.a. > 99.5 mass %, supplied by Merck) and MEG + water solutions were weighed into screw-cap bottles with an internal volume of about 100 mL to obtain samples of known salt and MEG content. Density measurements were performed with an Anton Paar DMA48 (with an accuracy of  $\pm 0.1 \text{ mg}\cdot\text{cm}^{-3}$ ) at temperatures of (15, 20, 25, and 50) °C. The electrical conductivity was measured both by a pIONneer30 conductivity meter from Radiometer, equipped with a CDC 30T probe, and by a Hanna Instruments HI 9932. Both were calibrated with an aqueous NaCl solution having a conductivity of 1.000 mS/cm at a temperature of 25 °C. The sensor was rinsed with deionized water and dried by use of pressured air between each measurement. Temperature was measured with a built-in sensor in the CDC 30T probe. The same experimental

**Table 1.** Density in Water (1) + MEG (2) + NaCl (3) at a Temperature of (15, 20, 25, and 50) °C, and Conductivity  $\kappa$  at a Temperature of 25 °C<sup>a</sup>

$x_2$	$m_3$	$\rho/\text{g}\cdot\text{cm}^{-3}$				$\kappa/\text{mS}\cdot\text{cm}^{-1}$
		$t = 15 \text{ }^\circ\text{C}$	$t = 20 \text{ }^\circ\text{C}$	$t = 25 \text{ }^\circ\text{C}$	$t = 50 \text{ }^\circ\text{C}$	
0.000	0.000	0.9991	0.9982	0.9970	0.9880	0.00
0.000	0.050		1.0003			5.45
0.000	0.100	1.0033	1.0024	1.0011	0.9920	10.24
0.000	0.477					41.22
0.000	0.750					60.09
0.000	1.000	1.0392	1.0387	1.0361	1.0260	75.02
0.000	1.500	1.058	1.0563			100.21
0.000	1.953		1.0723		1.0594	118.29
0.000	2.500	1.0933			1.0779	137.74
0.000	3.000	1.1099	1.1075		1.0945	150.67
0.000	4.000	1.1414	1.1391		1.1243	175.35
0.000	5.000	1.1712		1.1662	1.1531	181.54
0.000	6.000	1.1992		1.1939	1.1810	192.94
0.000	6.000	1.1993		1.1938	1.1810	189.38
0.100	1.000		1.0735			47.35
0.100	0.500		1.0533			25.22
0.181	1.635		1.1156			48.11
0.196	2.398		1.1436			56.92
0.200	0.000	1.0627	1.0600			0.00
0.200	0.100	1.0666	1.0641			3.85
0.200	0.925	1.0974	1.0945			28.13
0.200	0.500		1.0789			17.52
0.200	1.000	1.0999	1.0968			29.67
0.200	1.014		1.0971			30.49
0.200	1.500	1.1175	1.1140			39.93
0.200	2.000	1.1343	1.1314			48.48
0.265	0.681		1.0972			17.89
0.284	1.000		1.1133			22.26
0.291	0.310		1.0872			8.38
0.310	0.970		1.1110			19.85
0.321	0.804		1.1088			16.97
0.350	0.500		1.1010			9.64
0.400	1.000		1.1236			15.65
0.409	0.559		1.1091			9.74
0.409	0.281		1.0992			5.30
0.499	0.000	1.0988	1.0954	1.0921	1.0749	0.00
0.499	0.100	1.1049	1.0992	1.0958	1.0784	1.62
0.499	0.500	1.1165	1.1146	1.1101	1.0929	6.73
0.499	1.000	1.1336	1.1308	1.1271	1.1107	11.68
0.499	1.500	1.1476	1.1472	1.1439	1.1259	14.93
0.599	1.000		1.1364			9.45
0.650	0.500		1.1213			4.64
0.650	1.000		1.1382			7.79
0.699	1.000		1.1404			7.67
0.798	0.000	1.1120	1.1082			0.00
0.798	0.100	1.1156	1.1118			0.89
0.798	1.000	1.1467	1.1432			6.11
0.998	0.000	1.1169	1.1132	1.1097	1.0921	0.00
0.998	0.100	1.1205	1.1170	1.1134	1.0960	0.73
0.998	0.250		1.1223		1.1016	1.55
0.998	0.500	1.1341	1.1310		1.1103	2.71
0.998	0.750		1.1395		1.1190	3.74
0.998	1.000	1.1507	1.1477	1.1441	1.1273	4.43

<sup>a</sup> MEG concentration is given as mole fraction in the salt-free solvent and molality of NaCl as mol/kg of solvent.

procedure was used when preparing mixtures containing  $\text{NaHCO}_3$  (p.a. 99.8 to 100.2 %, supplied by Merck).

## Results and Discussion

The uncertainties in the measurements are  $\pm 0.0005 \text{ g}\cdot\text{cm}^{-3}$  for density and  $\pm 5 \%$  for the electrical conductivity.

**$\text{H}_2\text{O} + \text{MEG} + \text{NaCl}$ .** Experimental results for water + MEG + NaCl mixtures are given in Table 1. The MEG concentration is given as mole fraction, and the NaCl molality is given as mol/kg of solvent where the solvent is the salt-free (water + MEG). On the basis of the experimental and literature data,<sup>2–8</sup> functions for density and conductivity of (water + MEG +

**Table 2. Density  $\rho$  in Water (1) + MEG (2) + NaCl (3) + NaHCO<sub>3</sub> (4) at a Temperature of 20 °C and Conductivity  $\kappa$  at a Temperature of 25 °C<sup>a</sup>**

			$\rho$		$\kappa$					$\rho$		$\kappa$		
$x_2$	$m_3$	$m_4$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mS}\cdot\text{cm}^{-1}$	$x_2$	$m_3$	$m_4$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mS}\cdot\text{cm}^{-1}$	$x_2$	$m_3$	$m_4$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mS}\cdot\text{cm}^{-1}$
0.000	1.000	0.050	1.0407	79.29	0.100	1.000	0.100			0.500	0.000	0.100	1.1007	1.00
0.000	1.000	0.075	1.0421	80.00	0.100	0.500	0.100	1.0601	26.93	0.500	0.900	0.100	1.1318	10.41
0.000	0.000	0.100	1.0042	6.95	0.200	1.000	0.050		29.28	0.500	0.000	0.251	1.1084	2.20
0.000	0.100	0.100	1.0083	15.73	0.200	0.000	0.100	1.0656	2.45	0.650	0.500	0.099	1.1260	4.88
0.000	0.500	0.100	1.0244	47.64	0.200	0.100	0.100		5.87	0.650	1.000	0.099	1.1429	7.83
0.000	0.900	0.100	1.0394	74.82	0.200	0.500	0.100		17.47	0.800	0.100	0.050	1.1148	1.06
0.000	1.000	0.100	1.0436	81.80	0.200	0.900	0.100	1.0988	27.16	0.800	1.000	0.050	1.1457	5.87
0.000	2.000	0.100	1.0791	135.30	0.200	1.000	0.100		30.43	0.800	1.000	0.075	1.1469	5.69
0.000	0.900	0.107	1.0398	80.48	0.200	0.000	0.250	1.0738	5.62	0.800	0.100	0.100	1.1173	1.32
0.000	0.100	0.150	1.0113	18.45	0.200	0.100	0.250		8.57	0.800	1.000	0.100	1.1480	6.01
0.000	1.000	0.150	1.0464	82.75	0.200	1.000	0.250		30.34	0.800	0.000	0.100	1.1137	0.53
0.000	2.000	0.200	1.0841	135.67	0.200	0.749	0.251	1.1010	25.17	0.800	0.900	0.100	1.1446	5.69
0.000	0.000	0.250	1.0131	15.65	0.200	0.500	0.100	1.0844	18.80	0.800	1.000	0.150	1.1505	5.86
0.000	0.100	0.250	1.0171	24.34	0.200	1.014	0.050	1.0995	31.46	0.800	0.000	0.250	1.1213	1.11
0.000	0.749	0.250	1.0421	70.46	0.200	0.100	0.100	1.0693	6.19	0.800	0.100	0.250	1.1248	1.77
0.000	1.000	0.250	1.0521	85.32	0.200	1.014	0.100	1.1020	31.81	0.998	1.000	0.050	1.1500	4.21
0.000	0.100	0.300	1.0200	26.11	0.200	0.100	0.250	1.0765	9.02	0.998	0.000	0.100	1.1183	0.39
0.000	2.000	0.300	1.0890	137.51	0.200	1.014	0.250	1.1106	33.80	0.998	0.100	0.100	1.1218	0.92
0.000	0.100	0.400	1.0257	30.91	0.200	0.100	0.400	1.0855	10.73	0.998	0.900	0.100	1.1489	4.06
0.000	1.000	0.400	1.0604	89.71	0.350	0.500	0.100	1.1062	10.33	0.998	1.000	0.100	1.1524	4.37
0.000	2.000	0.400	1.0939	139.39	0.350	1.000	0.100		17.42	0.998	0.000	0.250	1.1258	0.81
0.000	0.100	0.450	1.0286	32.91	0.500	0.100	0.050	1.1018	1.91	0.998	0.100	0.250	1.1293	1.32
0.000	0.000	0.500	1.0274	28.07	0.500	1.000	0.050	1.1333	11.06	0.998	0.750	0.250	1.1510	3.60
0.000	0.500	0.500	1.0467	61.23	0.500	1.000	0.075	1.1346	11.22	0.998	1.000	0.250	1.1597	4.21
0.000	0.100	0.600	1.0369	38.56	0.500	0.100	0.100	1.1043	2.21	0.998	0.100	0.400	1.1366	1.56
0.000	0.000	0.750	1.0413	37.25	0.500	0.500	0.100	1.1187	6.92	0.998	1.000	0.400	1.1668	4.07
0.000	0.100	0.750	1.0452	45.41	0.500	1.000	0.100	1.1358	11.22	0.998	0.000	0.500	1.1377	1.35
0.000	1.000	0.750	1.0795	96.65	0.500	0.100	0.250	1.1121	3.18	0.998	0.500	0.500	1.1543	3.06
0.000	0.000	1.000	1.0547	48.06										

<sup>a</sup> MEG concentration is given as mole fraction in the salt-free solvent, and the salt concentrations as molality  $m$ ; mol/kg of solvent.

**Table 3. Parameters for Density  $\rho$  and Conductivity  $\kappa$  Functions**

$\rho/\text{g}\cdot\text{cm}^{-3}$	value at 15 °C	value at 20 °C	$\kappa/\text{mS}\cdot\text{cm}^{-1}$	value
MEG	1.1169	1.1134	$p_1$	107.5206
H <sub>2</sub> O	0.9991	0.9982	$p_2$	-28.6272
$d$	0.111916	0.109695	$p_3$	-0.0203
$e$	0.214501	0.209660	$q_1$	-3.7396
$s_1$	0.040247	0.040247	$q_2$	4.6799
$s_2$	-0.001214	-0.001214	$r_1$	8.0765
$s_3$	-0.005082	-0.005082	$r_2$	-3.7272
$b_1$	0.059715	0.059715	$r_3$	0.0714
$b_2$	-0.003501	-0.003501	$h_1$	2.9046
$b_3$	-0.009626	-0.009626	$h_2$	-3.0756
			$l_1$	64.2160
			$l_2$	-16.1611
			$l_3$	-0.7572
			$l_4$	7.0495

NaCl) mixtures were fitted. The density function is given in eq 1:

$$\rho = (x_{\text{MEG}}\rho_{\text{MEG}} + x_{\text{H}_2\text{O}}\rho_{\text{H}_2\text{O}}) + dx_{\text{MEG}}x_{\text{H}_2\text{O}} + ex_{\text{MEG}}x_{\text{H}_2\text{O}}^3 + ((S_1 + S_3\sqrt{x_{\text{MEG}}})m_{\text{NaCl}} + s_2m_{\text{NaCl}}^2) \quad (1)$$

where  $x_i$  is the mole fraction of pure water or MEG,  $\rho_i$  is the density of pure water or MEG, and  $m_{\text{NaCl}}$  is the NaCl concentration (mol/kg of solvent), which equals the ionic strength. The parameters  $d$  and  $e$  are used to calculate the density of the salt-free (water + MEG), and the parameters  $s_{1-3}$  include the effect of salt on the density. The values of all the parameters are given in Table 3. Temperatures of (15 and 20) °C were chosen because density is normally measured at one of these temperatures. Literature data and experimental data are generally reproduced by eq 1 to within 0.001  $\text{g}\cdot\text{cm}^{-3}$ .

The conductivity measurements were fitted to a three-parameter equation;

$$\kappa = (K_1e^{K_2})x_{\text{H}_2\text{O}}^2 + K_3x_{\text{MEG}}^2 \quad (2)$$

where  $K_1$  is the conductivity of an aqueous solution, as given in eq 3 where the first two terms have the same form as the Debye–Hückel–Onsager equation<sup>3</sup>, while the 3rd order term was added to fit the data at high concentrations.  $K_3$  is a similar expression that corresponds to conductivity in pure MEG, while  $K_2$  gives the mixing of water/MEG. The curve fitted parameters  $p$ ,  $q$ , and  $r$  are given in Table 3:

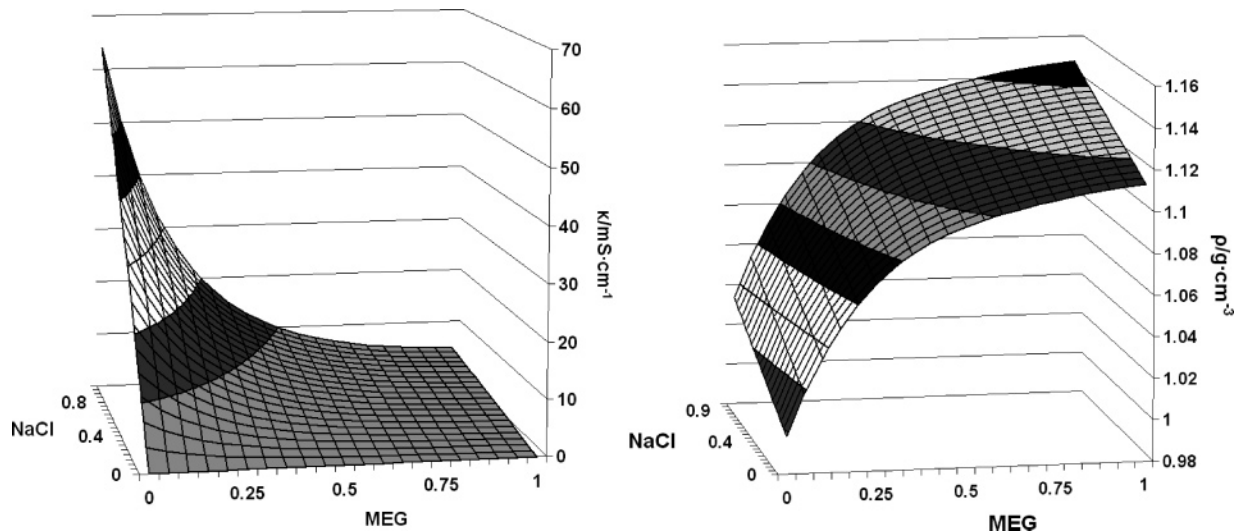
$$K_1 = p_1m_{\text{NaCl}} + p_2m_{\text{NaCl}}^{3/2} + p_3m_{\text{NaCl}}^3 \quad (3)$$

$$K_2 = q_1x_{\text{MEG}} + q_2x_{\text{MEG}}^2 \quad (4)$$

$$K_3 = r_1m_{\text{NaCl}} + r_2m_{\text{NaCl}}^{3/2} + r_3m_{\text{NaCl}}^3 \quad (5)$$

Since conductivity is strongly temperature-dependent, a reference temperature must be used. In this work, it was chosen to refer all measurements to a temperature of 25 °C. The measured conductivity  $\kappa_t$  at temperature  $t$  was therefore corrected using eq 6 to  $\kappa_{25}$ , which is the conductivity if the measurements had been done at a temperature of 25 °C. Most commercially available conductivity meters have built-in functions to do such temperature corrections from the actual temperature to a selected reference temperature:

$$\kappa_{25^\circ\text{C}} = \kappa_t + \frac{0.00054t^2 - 0.0669t + 3.381}{100}\kappa_t(25 - t) \quad (6)$$



**Figure 4.** Conductivity ( $\kappa$ ) at a temperature of 25 °C and density ( $\rho$ ) at a temperature of 20 °C as function of MEG [mole fraction] and NaCl [mol/kg of solvent].

Because of the strong temperature dependence, it is recommended to measure conductivity at a temperature close to the reference.

With the above expressions for density and conductivity, three-dimensional graphs of density and conductivity as a function of MEG and salt concentration were constructed and are shown in Figure 4. From the graphs, it is easy to see the qualitatively different behavior in density and conductivity with respect to MEG and salt concentration. When the density is measured, this gives a line in the salt–MEG plane. The conductivity gives another line with opposite curvature in the salt–MEG plane. The point where these two lines intersect determines both the MEG and salt concentrations of an unknown sample.

**Computer Modeling.** When density and conductivity are measured, eq 1 and eq 2 have to be solved to find the MEG and salt concentrations. The simplest but not very robust method is to use the “Solver” option in Excel. This gives fast and accurate results when a good start estimate is given. A more robust method is to solve eq 1 with respect to the NaCl concentration as a second order equation and insert it into eq 2. The system is then easily solved using either the “Goal Seek” function in Excel or by performing numerical iteration with respect to the MEG fraction using the by section method.

**Presence of Other Species.** Formation waters contain several other species, typically  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ , etc. These species have different molecular weight and mobility and hence have a different quantitative impact on solution density and conductivity. However, in most formation waters, NaCl contributes with typically 90 % of the ions, thus the model is very little affected by other species. In addition, it is noted that the output of the model should be interpreted in terms of ionic strength rather than NaCl concentration directly. Thus ionic strength will be a measure of all ions in solution as if they were NaCl (i.e., NaCl equivalents). If for example some of the NaCl is replaced with  $CaCl_2$ , but keeping the ionic strength constant, the density and conductivity will change very little and in such a way that the calculated MEG concentration will remain virtually unaffected. This was confirmed by making a solution containing 77.5 wt % MEG, with an ionic strength of 1 mol/kg where 10 % of this came from  $CaCl_2$  and the rest from NaCl. From the measured density and conductivity, the model predicted the MEG concentration at 76.2 wt % and that the ionic strength was 0.965 mol/kg. This is within the accuracy of the method. As a

curiosity, it is noted that the density ( $1.1301 \text{ g}\cdot\text{cm}^{-3}$ ) of this test solution is higher than the density for pure MEG ( $1.1169 \text{ g}\cdot\text{cm}^{-3}$ ). Thus, using only density to estimate MEG concentration would in this case give a meaningless result. This clearly demonstrates the effectiveness of linking density and conductivity in a model to calculate MEG concentration and salt content.

**$H_2O + MEG + NaCl + NaHCO_3$ .** One system will be given special attention. In cases where pH stabilization<sup>1</sup> is utilized for corrosion control, there can be significant amounts of  $NaHCO_3$  present and perhaps very little other salts. Because  $NaHCO_3$  has a slightly different effect on both density and conductivity than NaCl, the model was expanded such that  $Na^+$  is still the dominating cation, while both  $Cl^-$  and  $HCO_3^-$  are dominating anions. Table 2 summarizes additional measurements of density and conductivity with both NaCl and  $NaHCO_3$  present in the solution. The presence of  $NaHCO_3$  will shift the surfaces in Figure 4 upward, but their qualitative shape will remain unchanged.

The bicarbonate concentration can easily be found from an alkalinity titration<sup>9</sup> and can therefore be regarded as a known value. To model the effect of bicarbonate on the density, additional terms were added to eq 1:

$$\rho = (x_{MEG}\rho_{MEG} + x_{H_2O}\rho_{H_2O}) + dx_{MEG}x_{H_2O} + ex_{MEG}x_{H_2O}^3 + (S_1 + S_3\sqrt{x_{MEG}})m_{NaCl} + S_2m_{NaCl}^2 + (b_1 + b_3\sqrt{x_{MEG}})m_{NaHCO_3} + b_2m_{NaHCO_3}^2 \quad (7)$$

where  $b_{1-3}$  are empirical parameters given in Table 3, and  $m$  denotes concentration in mol/kg of solvent. The expression for the conductivity in eq 2 is unchanged, but  $NaHCO_3$  gives additional terms to parameters  $K_1$  and  $K_3$ :

$$K_1 = p_1m_{NaCl} + p_2m_{NaCl}^{3/2} + p_3m_{NaCl}^3 + l_1m_{NaHCO_3} \exp(l_3m_{NaCl}) + (l_2 + l_4m_{NaCl})m_{NaHCO_3}^2 \quad (8)$$

$$K_3 = r_1m_{NaCl} + rm_{NaCl}^{3/2} + r_3m_{NaCl}^3 + h_1m_{NaHCO_3} \exp(h_2m_{NaCl}) \quad (9)$$

A measured alkalinity ( $HCO_3^-$  concentration) is normally in mol/L solution or mol/kg of solution. The above models, however, require the concentrations to be in mol/kg of solvent. The following formula can be used to recalculate



**Table 4. Solutions Used To Test Model: Density  $\rho$  in Water (1) + MEG (2) + NaCl (3) + NaHCO<sub>3</sub> (4) at a Temperature of 20 °C and Conductivity  $\kappa$  at a Temperature of 25 °C<sup>a</sup>**

no.	$w_2$	$m_3$	$m_4$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\kappa/\text{mS}\cdot\text{cm}^{-1}$
1	50.86	0.574	0.095	1.0929	17.17
2	17.32	0.698	0.118	1.0551	44.17
3	45.39	0.380	0.013	1.0743	13.12
4	73.74	0.585	0.046	1.1155	8.64
5	42.43	0.248	0.017	1.0671	9.79
6 <sup>b</sup>	57.94			1.0745	0.13

<sup>a</sup> MEG concentration  $w$  is given as wt % in the salt-free solvent, and the salt concentrations as molality  $m$ ; mol/kg of solvent. <sup>b</sup> Oilfield sample from separator. MEG content measured with gas chromatography (GC). Salt content is unknown.

**Table 5. Results for Test Solutions: Water (1) + MEG (2) + NaCl (3) + NaHCO<sub>3</sub> (4)<sup>a</sup>**

no.	$w_2$	$m_3$	$m_4$	$E_2/(\text{wt } \%)$	$E_3/(\%)$
1	51.4	0.56	0.096	0.5	-3.0
2	19.1	0.66	0.117	1.8	-5.6
3	45.6	0.38	0.013	0.2	0.0
4	72.7	0.59	0.047	-1.0	0.3
5	43.5	0.25	0.017	1.1	2.5
6	57.1	0.01		0.8	

<sup>a</sup>  $E_2$  and  $E_3$  denote error in the MEG and NaCl determination, respectively.  $w$  is given in wt % and  $m$  as mol/kg of solvent.

alkalinity from molarity to molality:

$$\text{alk}[\text{mol}/\text{kg}] = \frac{\text{alk}[\text{mol}/\text{L}]}{\rho - \sum C_i \cdot M_w \cdot 10^{-3}} \quad (10)$$

$\rho/\text{g}\cdot\text{cm}^{-3}$  denotes the density of the solution, while  $C/\text{mol}\cdot\text{L}^{-1}$  and  $M_w/\text{g}\cdot\text{mol}^{-1}$  corresponds to concentration and molecular weight of dissolved species, respectively. This recalculation requires an estimate for the unknown concentration  $C$  of all species.

A simple iteration procedure is as follows; solve the model using the measured alkalinity, insert the calculated NaCl concentration and measured alkalinity in eq 10 to recalculate the alkalinity, and reapply the model with the updated alkalinity; iterate until convergence (2 to 3 cycles). The effect of using the uncorrected alkalinity is, however, small and will give a slightly too high estimation of NaCl content, but MEG estimation will remain virtually unchanged.

### Model Testing and Application

Testing was performed on the five synthetic solutions and the oilfield sample given in Table 4. The oilfield sample had a MEG content known from GC analysis. Bicarbonate content was analyzed by use of an HCl alkalinity titration,<sup>9</sup> and the MEG and salt concentration were calculated using the above equations. From the results given in Table 5, it is seen that the calculated MEG content was within  $\pm 2$  wt %. Estimation of NaCl content was generally good, although one measurement showed as large error as (5 to 6) %.

The accuracy of the model is generally  $\pm (2 \text{ to } 3)$  wt % for the estimation of MEG content, while it can vary as much as

10 % in the estimation of ionic strength. The most interesting systems typically have MEG concentrations of (40 to 90) wt %. In this range, the model has accuracy better than  $\pm 2$  wt % units, and ionic strength is generally within (5 to 6) %. To obtain the best result, density should be measured at a temperature of 20 °C and conductivity close to the reference temperature of 25 °C. Conductivity measurements are regarded as the most uncertain analysis. This is not only due to random error but also due to it being based on a one-point calibration. Thus there exists a possibility for systematic error if the test solution is significantly different from the standard of 1 mS/cm. It is noted that the model is developed for cases when NaCl and/or NaHCO<sub>3</sub> are the dominating salt species.

### Conclusions

New experimental measurements of density and conductivity have been performed in mixed water + MEG + NaCl + NaHCO<sub>3</sub> solutions. A model based on this data set enables an estimate for both MEG concentration and salt content merely from the density and conductivity of a solution. If also the alkalinity is measured, the model can separate between NaHCO<sub>3</sub> and other salts. The model is valid in the whole concentration interval of 0 to 100 wt % MEG and with ionic strengths from zero to the solubility limits of NaCl and NaHCO<sub>3</sub>. At intermediate MEG concentrations (40 to 90 wt %), the accuracy of the model is regarded as  $\pm 2$  wt % for calculation of MEG content.

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