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Solubility of NaHCO_3 in systems of aqueous glycols (monoethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol): The role of solvation

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ABSTRACT:

The solubility and density of NaHCO_3 in the systems: monoethylene glycol (MEG)-water, diethylene glycol (DEG)-water, triethylene glycol (TEG)-water, and tetraethylene glycol (TeEG)-water have been measured over the entire concentration range from pure water to pure glycol. Experimental measurements have been conducted at the temperatures 5, 20, 40, and 60 °C, and at atmospheric pressure.

The solubility of NaHCO_3 in all glycol mixtures were increasing with increasing temperatures. Solubility is largest in aqueous MEG and decreases with the higher molecular weights of glycol

used. Local minima were observed in all systems in the concentration range 80 to 90 wt% glycol, salt-free. On a mole fraction scale, minima were found at $x(\text{glycol, salt-free})=0.5$. There is a clear tendency that two solvate mechanisms exist with a 1:1 solvation relation. One type of solvation is formed in NaHCO_3 -water, and a second type is formed in NaHCO_3 -glycol.

The density results showed a linearly increase up to a glycol concentration ≈ 80 wt%. Above 80 wt% the density seemed to form a minima similar to the solubility phase diagrams.

KEYWORDS: glycols, NaHCO_3 , solubility, corrosion, gas drying, gas hydrates

1. Introduction

Formation of gas hydrates and CO_2 corrosion in wells, and pipelines are considered a major problem in the oil and gas industry¹⁻⁵. It has been a recognised topic since the discovery in 1934 by Hammerschmidt⁶. Gas hydrate formation can cause serious plugs and lead to costly shut downs in the production line. In addition, it also creates a safety concern. Several methods for reducing/preventing gas hydrates have been considered, including reduction of the water content, changing operational conditions, and addition of additives also known as hydrate inhibitors⁷. Addition of hydrate inhibitors change the chemical potential of hydration towards lower temperature and higher pressure⁸. Usually, hydrate inhibitors as methanol, ethanol, sodium chloride, monoethylene glycol (MEG), and diethylene glycol (DEG) have been used⁷⁻⁹. The use of DEG for dehydrating natural gas has been employed since 1936 and later triethylene glycol (TEG), and tetraethylene glycol (TeEG) have proved suitable for the purpose¹⁰. Most commonly, DEG has been used for low temperature dehydration and higher molecular weight glycols as TEG, and TeEG for temperatures above 10 °C¹⁰.

In the production of oil and gas, water and CO₂ are produced. Approximately, 25 % of the corrosion failures are related to CO₂ corrosion². Despite alternative materials with high corrosion resistance, the industry is widely using carbon steel for process equipment and pipelines due to its cost effective characteristics^{2,3,5}. Once the material is exposed to different environments, protective film layers are formed as a product of chemical and electrochemical reactions. The protective barrier towards corrosion depends on different parameters such as CO₂ partial pressure, solution pH, temperature, and type of steel material^{2,3,5}. At sweet conditions where no H₂S is present, the main corrosion product is FeCO₃. FeCO₃ is known to create protective layers extending the life of the pipelines. Increasing pH between 6-8^{1,2} stabilises FeCO₃. pH stabilisers such as ammonia, sodium carbonate, and sodium bicarbonate have been used and have proven to reduce the corrosion rate significantly^{2,3,9}.

Detailed knowledge of the solubility of bicarbonate in aqueous glycol systems are important for corrosion modelling of e.g. pipelines. The solubility of NaHCO₃ in MEG-H₂O and in DEG-H₂O have been investigated by several authors^{4,9,11-13}, whereas none have considered the solubility of NaHCO₃ in triethylene glycol (TEG)-H₂O and in tetraethylene glycol (TeEG)-H₂O. Fosbøl et al.¹¹ reported new data points for solubility and density in the mixed solvent NaHCO₃-MEG-H₂O in the temperature range 2 to 60 °C. They observed a minimum solubility at around 85 wt% MEG for all isotherms. X-ray powder diffraction (XRPD) analysis showed that the solid phase was NaHCO₃ at all MEG concentrations. Gärtner et al.¹² measured the solubility of NaHCO₃ in the MEG-H₂O system over the temperature range 50 to 90 °C. They also observed a minimum solubility around 80 to 90 wt% MEG (salt-free). Sandengen¹³ measured the solubility of NaHCO₃ in 60 and 90 wt% MEG at 4.0 and 21.9 °C. Only at 4.0 °C a solid phase of NaHCO₃ was present. He concluded that equilibrium had not been reached. Dugstad and Seiersten⁹ measured few data

points in the systems: $\text{NaHCO}_3\text{-MEG-H}_2\text{O}$ and in the $\text{NaHCO}_3\text{-DEG-H}_2\text{O}$. They studied the salt solubility in pure and in 90 wt% glycol mixtures and at the temperatures 20 and 124 °C.

The aim of this work is to provide solubility and density data of the ternary systems: $\text{NaHCO}_3\text{-MEG-H}_2\text{O}$, $\text{NaHCO}_3\text{-DEG-H}_2\text{O}$, $\text{NaHCO}_3\text{-TEG-H}_2\text{O}$ and $\text{NaHCO}_3\text{-TeEG-H}_2\text{O}$. Furthermore, this work also aims to support thermodynamic modelling of corrosion and gas drying. These data are also useful for generic electrolyte thermodynamics and molecular theory development.

2. Experimental details

2.1 Materials

The studied chemicals are listed in Table 1. The chemicals were used as received without any further purification. Chemicals were mixed with demineralized water, which had a conductivity of 0.2 μS . Standardized HCl (0.1 M) used for titration was supplied from J. T. Baker.

Table 1. Chemicals used in the experiments.

Chemical name	Source	CAS No.	Mass fraction purity	Purification method
Diethylene glycol	Fluka	111-46-6	≥ 99.0	none
Triethylene glycol	Fluka	112-27-6	≥ 99.0	none
Monoethylene glycol	Riedel-deHaën	107-21-1	≥ 99.0	none
Tetraethylene glycol	Sigma-Aldrich	112-60-7	≥ 99.0	none
Sodium hydrogen carbonate	MERCK	144-55-8	>99.7	none

2.2 Experimental method

Solubility measurements were conducted equivalent to the method outlined by Fosbøl et al.^{4,11,14}. The equilibrium experiments were performed at atmospheric conditions at the temperatures 5, 20, 40, and 60 °C.

The setup consisted of an equilibrium unit with seven cells connected in parallel to a heating/cooling bath (Julabo F25). The heating/cooling bath controlled the temperature within

± 0.01 °C. Each cell had a glass lid and a heat jacket surrounding an equilibrium chamber. Supersaturated NaHCO_3 mixtures were added to 50 mL closed polyethylene (PE) containers, each containing a magnetic stirrer. The PE containers were placed in the equilibrium chamber.

The supersaturated mixtures were stirred at approximately 3-500 rpm and equilibrated over a period of 24 to 120 h. The equilibration time needed for the analysis is short, but the time used was fixed to 24 hours on normal working days and 120 hours over weekends. The saturated liquid samples were filtered before analysis. A sample volume of 100-1000 mL was obtained by micropipette, taken in triplicate from each equilibrium chamber. Each sample volume was weighed and the density was determined as weight per volume. The accuracy of the density measurements is in the order of 0.01 g/cm^3 . Less than 5 minutes after filtering the samples they were analyzed by potentiometric titration using an autoburette (Radiometer, ABU93 triburette). The software used to control the titration unit and the pH measurement was developed in-house. The accuracy of the equivalence points is approximately 0.01 mL. Approximately, 15 g of demineralized water was added to the samples and titrated with 0.1 M HCl. The initial pH before the potentiometric titration is in the order of 9-11.

3. Results and discussion

The solubility of NaHCO_3 in the solvents: MEG- H_2O , DEG- H_2O , TEG- H_2O , and TeEG- H_2O and the density of the mixtures were determined at atmospheric pressure, and at the temperatures 5, 20, 40, and 60 °C. Experimental results, such as initial compositions, titration results, densities, the compositions of the saturated solutions, and the composition of the solid phase are presented in Table 2, Table 3, Table 4, and Table 5. The compositions of the saturated solutions and the solid phase were determined by the reverse Schreinemakers (RS) method previously explained¹⁴. The

composition is denoted S_{TNa} and is given as the total amount of sodium (moles of Na) per kg of solution. Experimental results are given as an average of three measurements together with standard deviations. The results obtained from the RS method are very accurate as standard deviations are low. The uncertainty given in Table 2, Table 3, Table 4, and Table 5 is an expression of the uncertainty of the triple titration during compositional analysis. The uncertainty does not include deviations caused by slight temperature differences, filtering efficiency, titrant standardization, sampling accuracy etc. The real uncertainty is most likely 10 times higher. This can be observed by plotting solubilities as function of temperature in the range of the minimum observed.

At higher temperatures, the NaHCO_3 solution has a tendency to break down into NaOH and CO_2 . For high temperature solubility analysis of NaCO_3 , this break down needs to be taken into account. Our analysis has shown¹⁴, that the S_{TNa} number very trust worthy independent of evaporated CO_2 content.

The solubility of NaHCO_3 in the aqueous glycol mixtures are graphically presented in Figure 1, Figure 2, Figure 3, and Figure 4. For all systems, a moderate solubility decline with increased glycol concentrations was observed until minima between 80 to 90 wt% were reached. Hereafter a gradual increase in the solubility at higher glycol content is seen. This behaviour is also seen in CaSO_4 -MEG- H_2O and CaCO_3 -MEG- H_2O ¹⁵. This phenomenon was studied and validated for the NaHCO_3 -MEG- H_2O system by Fosbøl et al.¹¹. In the study, the identity of the solid phase as pure NaHCO_3 was confirmed by XRPD. Fosbøl et al.¹¹ proposed that the increased solubility could be explained by the increase of CO_2 solubility at high MEG concentrations. Gärtner et al.¹² suggested that the increased NaHCO_3 solubility could be due to soluble complexes of MEG with HCO_3^- . In this study, XRPD was only applied to the system NaHCO_3 -MEG- H_2O and not to the systems

containing DEG, TEG, and TeEG. Precipitates may therefore be complexes of glycol and HCO_3^- . A further study on the precipitates using either Raman and/or infrared (IR) spectroscopy would be valuable.

The solubility of NaHCO_3 , in all glycols, is increasing by increasing the temperature. However, the temperature dependency decreases towards higher glycol concentrations. At glycol (salt-free) concentrations above 70 wt% the NaHCO_3 solubility is more or less identical comparing the results at the different temperatures.

Results obtained in this study for NaHCO_3 -MEG- H_2O (see Figure 1) are in line with the data published by Fosbøl⁴, and Fosbøl et al.¹¹ at the temperatures 20, 40, and 60 °C. The minima are located approximately at $w(\text{MEG}) \approx 85\%$ and $w(\text{NaHCO}_3) \approx 3\%$ corresponding to the findings of Fosbøl et al.^{4,11}.

The solubility trend of NaHCO_3 in DEG- H_2O , Figure 2, is similar to the solubility of NaHCO_3 in MEG- H_2O . The lowest value of the solubility is found in the range $85\% \leq w(\text{DEG}) \leq 90\%$. The minimum is more flat and the NaHCO_3 increase is not as pronounced as with MEG. The minimum solubility of NaHCO_3 is lower in TEG- H_2O (Figure 3) and in TeEG- H_2O (Figure 4) $w(\text{NaHCO}_3) \approx 1\%$ and $w(\text{NaHCO}_3) \approx 0.5\%$ respectively. The minima in these glycols are shifted towards higher glycol concentrations, which makes the solubility increase less distinct.

Table 2. Experimental data of the system NaHCO_3 -MEG- H_2O measured at 5, 20, 40 and 60 °C and at a pressure $p = 0.1 \text{ MPa}^a$. t is the equilibrium temperature. $\tilde{w}$ is the salt-free glycol concentration (wt%). σ is the standard deviation. The results of the RS method was calculated from equations of Fosbøl et al.^{4,14}. w_i is the weight percent of component i . The solid phase is assumed from a subset of analysis and not every sample was characterized by PXRD.

t	initial				equilibrium				reverse Schreinemakers				
	$\tilde{w}_{MEG}$	m_{H_2O}	m_{MEG}	m_{NaHCO}	S_{TNa}	$\sigma_{S_{TNa}}$	$\rho_{sat,liq}$	σ_ρ	w_{NaHCO_3}	σ_{NaHCO_3}	m_{H_2O}	w_{MEG}	P
°C	%	g	g	g	mol/kg	mol/kg	g/cm ³	g/cm ³	%	%	g	%	
5.20	0.00	10.045	0.000	1.003	0.869	0.006	1.005	0.016	7.30	0.054	10.045	0.00	B
5.10	3.32	9.742	0.335	1.006	0.825	0.003	1.012	0.017	6.93	0.023	9.742	3.09	B
5.00	15.05	8.502	1.506	0.950	0.690	0.005	1.005	0.014	5.80	0.046	8.502	14.17	B
5.05	28.04	7.201	2.806	0.804	0.585	0.006	1.034	0.015	4.91	0.051	7.201	26.66	B
5.50	53.00	4.725	5.328	0.745	0.373	0.0009	1.079	0.011	3.13	0.008	4.725	51.34	B
5.20	78.00	2.205	7.815	0.601	0.292	0.002	1.108	0.006	2.45	0.013	2.205	76.08	B
5.10	84.89	1.515	8.511	0.718	0.299	0.002	1.115	0.012	2.51	0.017	1.515	82.76	B
5.05	89.96	1.006	9.013	0.805	0.324	0.0004	1.137	0.013	2.72	0.003	1.006	87.52	B
5.10	94.66	0.536	9.511	1.055	0.392	0.0006	1.112	0.018	3.30	0.005	0.536	91.54	B
5.50	100	0.000	10.007	1.009	0.610	0.0004	1.165	0.019	5.12	0.003	0.000	94.88	B
20.1	0.00	9.997	0.000	1.365	1.090	0.005	1.059	0.007	9.16	0.046	9.9972	0.00	B
20.10	15.46	8.494	1.554	1.237	0.845	0.002	1.065	0.001	7.10	0.016	8.494	14.36	B
20.10	28.03	7.232	2.816	1.112	0.687	0.005	1.078	0.004	5.77	0.043	7.232	26.41	B
20.05	53.31	4.697	5.363	0.871	0.450	0.002	1.074	0.030	3.78	0.017	4.697	51.30	B
20.10	78.05	2.218	7.890	0.754	0.350	0.005	1.107	0.017	2.94	0.043	2.218	75.76	B
20.20	89.97	1.006	9.021	0.758	0.373	0.0009	1.130	0.006	3.13	0.008	1.006	87.15	B
20.10	94.90	0.511	9.514	0.993	0.451	0.0007	1.135	0.001	3.79	0.006	0.511	91.30	B
20.10	100.00	0.000	10.011	1.370	0.806	0.0003	1.157	0.002	6.77	0.002	0.000	93.23	B
40.10	0.00	10.009	0.000	1.767	1.441	0.005	1.116	0.012	12.11	0.042	10.009	0.00	B
40.20	15.09	8.510	1.513	1.628	1.129	0.013	1.069	0.052	9.48	0.108	8.510	13.66	B
40.20	27.88	7.245	2.801	1.499	0.905	0.008	1.087	0.008	7.60	0.065	7.245	25.76	B
40.20	52.90	4.730	5.313	1.241	0.579	0.006	1.083	0.006	4.87	0.051	4.73	50.33	B
40.10	77.57	2.259	7.813	0.755	0.423	0.0004	1.137	0.003	3.55	0.003	2.259	74.81	B
40.20	89.76	1.027	9.002	0.756	0.444	0.0005	1.144	0.010	3.73	0.004	1.027	86.42	B
40.20	94.72	0.530	9.507	0.990	0.533	0.003	1.145	0.005	4.48	0.025	0.530	90.47	B
40.20	100.00	0.000	10.019	1.366	0.913	0.001	1.177	0.005	7.67	0.009	0.000	92.33	B
57.60	96.97	0.303	9.704	1.401	0.712	0.0008	1.176	0.006	5.98	0.006	0.303	91.18	B
57.65	100.00	0.000	10.025	1.402	1.028	0.001	1.167	0.015	8.63	0.010	0.000	91.37	B
59.50	15.05	8.512	1.508	1.410	1.480	0.004	1.162	0.034	12.43	0.034	8.512	13.18	B
59.30	28.07	7.235	2.823	1.306	1.196	0.002	1.194	0.027	10.04	0.013	7.235	25.25	B
59.80	0.00	10.011	0.000	2.206	2.008	0.02	1.148	0.005	16.86	0.171	10.011	0.00	B
59.05	27.95	7.213	2.798	1.600	1.189	0.006	1.157	0.008	9.98	0.051	7.213	25.16	B
59.30	42.94	5.742	4.321	1.502	0.911	0.008	1.148	0.041	7.65	0.068	5.742	39.65	B
59.50	52.89	4.744	5.327	1.310	0.760	0.01	1.135	0.034	6.38	0.089	4.744	49.52	B
59.45	67.97	3.211	6.815	1.245	0.589	0.0003	1.112	0.011	4.95	0.003	3.211	64.61	B
59.10	77.98	2.210	7.827	0.707	0.522	0.0004	1.146	0.019	4.39	0.003	2.21	74.56	B
59.35	78.54	1.507	5.515	0.804	0.510	0.0006	1.155	0.015	4.28	0.005	1.507	75.18	B
59.45	89.88	1.014	9.008	0.916	0.533	0.001	1.150	0.023	4.48	0.010	1.014	85.85	B
59.40	94.88	0.514	9.519	1.202	0.630	0.002	1.167	0.013	5.29	0.021	0.514	89.86	B

^aStandard uncertainties (u) for temperature, wt%, density, pressure, are $u(T) = 0.01$ °C, $u(w) = 0.003 + 0.07$, $u(S_{TNa}) = 0.03$ mol/kg, $u(p) = 1$ kPa. Standard uncertainties of the densities are estimated as the standard deviations of the mean reported in the table.

Table 3. Experimental data of the system NaHCO_3 -DEG- H_2O measured at 5, 20, 40 and 60 °C and at a pressure $p = 0.1 \text{ MPa}^a$. t is the equilibrium temperature. $\tilde{w}$ is the salt-free glycol concentration (wt%). σ is the standard deviation. The results of the RS method was calculated from equations of Fosbøl et al.^{4,14}. w_i is the weight percent of component i . The solid phase is assumed from a subset of analysis and not every sample was characterized by PXRD.

t °C	initial				equilibrium				reverse Schreinemakers				P
	$\tilde{w}_{\text{DEG}}$ %	$m_{\text{H}_2\text{O}}$ g	m_{DEG} g	m_{NaHCO_3} g	S_{TNa} mol/kg	$\sigma_{S_{\text{TNa}}}$ mol/kg	$\rho_{\text{sat,liq}}$ g/cm ³	σ_ρ g/cm ³	w_{NaHCO_3} %	σ_{NaHCO_3} %	$m_{\text{H}_2\text{O}}$ g	w_{DEG} %	
5.2	0	10.004	0.000	1.515	0.87	0.002	1.021	0.009	7.31	0.018	10.004	0	B
5.1	3.1	9.701	0.311	1.401	0.818	0.008	1.017	0.004	6.87	0.068	9.701	2.89	B
5.05	15.17	8.528	1.525	1.307	0.626	0.014	1.033	0.007	5.26	0.119	8.528	14.38	B
5.1	40.12	6.023	4.036	1.223	0.295	0.0008	1.068	0.01	2.48	0.006	6.023	39.13	B
5.5	60	4.019	6.027	1.005	0.16	0.0003	1.096	0.007	1.35	0.003	4.019	59.19	B
5.5	71.88	2.816	7.198	0.910	0.113	0.0002	1.098	0.008	0.95	0.002	2.816	71.19	B
5.1	79.76	2.052	8.082	0.906	0.091	0.0002	1.108	0.01	0.76	0.002	2.052	79.15	B
5.05	87.5	1.259	8.811	1.227	0.08	0.0001	1.112	0.01	0.67	0.001	1.259	86.91	B
5.1	94.98	0.504	9.523	1.401	0.088	0.001	1.117	0.006	0.74	0.008	0.504	94.27	B
5.2	100	0.000	10.050	1.509	0.163	0.0001	1.118	0.009	1.37	0.001	0.000	98.63	B
19.8	0	10.004	0.000	1.500	1.095	0.0005	1.044	0.003	9.19	0.004	10.004	0	B
19.8	3.39	9.724	0.341	1.400	1.013	0.0006	1.04	0.003	8.51	0.005	9.724	3.1	B
19.75	15.04	8.571	1.518	1.303	0.777	0.001	1.049	0.008	6.53	0.01	8.571	14.06	B
19.75	39.98	6.052	4.031	1.205	0.392	0.0003	1.077	0.003	3.29	0.003	6.052	38.66	B
19.8	59.91	4.032	6.026	1.000	0.2	0.002	1.094	0.003	1.68	0.02	4.032	58.9	B
19.9	71.66	2.849	7.206	0.903	0.138	0.0003	1.105	0.002	1.16	0.003	2.849	70.84	B
19.8	79.05	2.124	8.013	0.914	0.112	0.0005	1.112	0.0007	0.94	0.004	2.124	78.3	B
19.8	87.79	1.235	8.878	1.225	0.096	0.0003	1.117	0.001	0.81	0.003	1.235	87.08	B
19.8	94.77	0.526	9.538	1.414	0.104	0.006	1.12	0.054	0.87	0.05	0.526	93.95	B
19.8	100	0.000	10.072	1.518	0.275	0.0005	1.123	0.004	2.31	0.005	0.000	97.69	B
40.25	0	10.022	0.000	2.022	1.441	0.009	1.107	0.009	12.11	0.004	10.022	0	B
40.35	3.06	9.725	0.307	1.903	1.36	0.002	1.112	0.007	11.43	0.079	9.725	2.71	B
40.4	15.08	8.545	1.517	1.800	1.053	0.002	1.113	0.006	8.85	0.019	8.545	13.74	B
40.4	39.88	6.034	4.003	1.611	0.543	0.001	1.09	0.019	4.56	0.016	6.034	38.07	B
39.5	59.98	4.003	6.000	1.000	0.268	0.002	1.104	0.013	2.25	0.008	4.003	58.63	B
40.3	71.94	2.827	7.246	1.130	0.18	0.0001	1.111	0.012	1.51	0.019	2.827	70.85	B
40.4	79.68	2.042	8.009	1.100	0.14	0.001	1.119	0.012	1.18	0.0008	2.042	78.75	B
40.5	87.74	1.239	8.867	1.302	0.117	0.001	1.122	0.011	0.98	0.01	1.239	86.88	B
40.4	94.73	0.529	9.514	1.602	0.128	0.001	1.122	0.011	1.07	0.011	0.529	93.72	B
39.5	100	0.000	10.024	1.911	0.353	0.001	1.134	0.01	2.97	0.01	0.000	97.03	B
59.75	0	10.039	0.000	2.206	1.856	0.023	1.141	0.032	15.59	0.195	10.039	0	B

60.2	3.2	9.738	0.322	2.106	1.751	0.007	1.037	0.012	14.71	0.058	9.738	2.73	B
60.25	15.17	8.528	1.525	2.027	1.366	0.011	1.146	0.028	11.48	0.094	8.528	13.43	B
60.2	40.01	6.013	4.010	1.817	0.716	0.0005	1.108	0.044	6.01	0.004	6.013	37.6	B
57.55	60.02	4.007	6.015	1.200	0.321	0.001	1.117	0.037	2.7	0.008	4.007	58.4	B
59.85	71.81	2.830	7.209	1.302	0.228	0.003	1.113	0.028	1.91	0.024	2.830	70.43	B
60.05	79.83	2.046	8.097	1.321	0.171	0.0006	1.121	0.023	1.44	0.005	2.046	78.68	B
60.3	87.95	1.208	8.818	1.501	0.139	0.0007	1.12	0.025	1.17	0.006	1.208	86.92	B
60.2	94.84	0.518	9.508	1.807	0.146	0.0005	1.118	0.019	1.22	0.004	0.518	93.67	B
58.3	100	0.000	10.041	2.038	0.396	0.002	1.129	0.019	3.32	0.018	0.000	96.68	B

^aStandard uncertainties (u) for temperature, wt%, density, pressure, are $u(^{\circ}\text{C}) = 0.01^{\circ}\text{C}$, $u(w) = 0.003 + 0.07$, $u(S_{TNA}) = 0.03 \text{ mol/kg}$, $u(p) = 1 \text{ kPa}$. Standard uncertainties of the densities are estimated as the standard deviations of the mean reported in the table.

Table 4: Experimental data of the system NaHCO_3 -TEG- H_2O measured at 5, 20, 40 and 60 °C and at a pressure $p = 0.1 \text{ MPa}^a$. t is the equilibrium temperature. $\tilde{w}$ is the salt-free glycol concentration (wt%). σ is the standard deviation. The results of the RS method was calculated from equations of Fosbøl et al.^{4,14}. w_i is the weight percent of component i . The solid phase is assumed from a subset of analysis and not every sample was characterized by PXRD.

t °C	initial				equilibrium				reverse Schreinemakers				P
	$\tilde{w}_{\text{TEG}}$ %	$m_{\text{H}_2\text{O}}$ g	m_{TEG} g	m_{NaHCO_3} g	S_{TNa} mol/kg	$\sigma_{S_{\text{TNa}}}$ mol/kg	$\rho_{\text{sat,liq}}$ g/cm ³	σ_ρ g/cm ³	w_{NaHCO_3} %	σ_{NaHCO_3} %	$m_{\text{H}_2\text{O}}$ g	w_{TEG} %	
5.00	76.88	4.63	15.393	0.829	0.085	0.004	1.124	0.028	0.71	0.029	4.63	76.33	B
5.00	84.94	3.014	17.002	0.844	0.068	0.0008	1.120	0.013	0.57	0.007	3.014	84.45	B
4.90	91.77	1.652	18.422	0.903	0.061	0.0005	1.091	0.025	0.51	0.004	1.652	91.30	B
4.90	96.80	0.642	19.412	0.931	0.075	0.0005	1.111	0.026	0.63	0.004	0.642	96.19	B
5.20	100.0	0.000	20.018	1.058	0.055	0.005	1.105	0.036	0.46	0.044	0.000	99.54	B
20.40	0.00	9.974	0.000	1.379	1.153	0.002	1.047	0.006	9.69	0.017	9.974	0.00	B
20.20	2.98	9.703	0.298	1.232	1.056	0.039	1.069	0.052	8.88	0.327	9.702	2.71	B
20.20	15.28	8.504	1.533	0.976	0.794	0.001	1.052	0.003	6.67	0.012	8.504	14.26	B
20.20	39.90	6.016	3.995	0.585	0.388	0.0008	1.076	0.007	3.26	0.007	6.016	38.60	B
20.20	65.08	3.5	6.522	0.349	0.154	0.002	1.098	0.013	1.29	0.021	3.5	64.24	B
20.30	76.91	2.313	7.702	0.367	0.105	0.011	1.108	0.021	0.88	0.09	2.313	76.23	B
20.30	85.01	1.500	8.509	0.439	0.073	0.001	1.059	0.053	0.61	0.01	1.500	84.49	B
20.20	91.77	0.829	9.246	0.341	0.070	0.001	1.082	0.055	0.59	0.027	0.829	91.23	B
20.20	96.95	0.305	9.701	0.45	0.078	0.002	1.080	0.09	0.65	0.02	0.305	96.32	B
20.20	100.0	0.000	10.004	0.563	0.190	0.003	1.139	0.059	1.60	0.024	0.000	98.40	B
41.10	76.92	4.635	15.445	1.1495	0.110	0.0005	1.126	0.017	0.62	0.534	4.635	76.44	B
41.30	84.80	3.052	17.020	1.1114	0.081	0.001	0.904	0.077	0.68	0.011	3.052	84.22	B
41.40	91.75	1.655	18.405	1.0542	0.069	0.003	1.121	0.003	0.58	0.025	1.655	91.22	B
41.30	96.94	0.613	19.4	1.2095	0.079	0.00003	1.129	0.035	0.66	0.0003	0.613	96.30	B
40.20	100.0	0.000	20.018	1.3155	0.210	0.002	1.168	0.018	1.77	0.021	0.000	98.23	B
59.40	0.00	10.009	0.000	2.501	1.937	0.01	1.089	0.059	16.27	0.069	10.009	0.00	B
59.60	3.18	9.730	0.319	2.348	1.801	0.004	1.080	0.065	15.13	0.037	9.730	2.70	B
59.80	15.13	8.501	1.515	1.614	1.413	0.01	1.065	0.064	11.87	0.087	8.501	13.33	B
59.80	39.89	6.02	3.994	0.988	0.659	0.011	1.104	0.01	5.54	0.093	6.02	37.68	B
59.10	64.98	3.507	6.506	0.638	0.216	0.0009	1.111	0.008	1.81	0.007	3.507	63.80	B
59.30	76.54	2.361	7.704	0.434	0.164	0.039	1.107	0.014	0.92	0.827	2.361	75.84	B
59.60	84.82	1.523	8.511	0.425	0.086	0.029	1.504	0.525	0.72	0.244	1.523	84.21	B
59.70	91.96	0.808	9.248	0.554	0.074	0.007	1.132	0.006	0.62	0.056	0.808	91.39	B
59.40	96.82	0.319	9.726	0.656	0.080	0.001	1.148	0.002	0.67	0.009	0.319	96.17	B
58.50	100.0	0.000	9.996	0.705	0.213	0.001	1.135	0.007	1.79	0.012	0.000	98.21	B

^aStandard uncertainties (u) for temperature, wt%, density, pressure, are $u(^{\circ}\text{C}) = 0.01^{\circ}\text{C}$, $u(w) = 0.003 + 0.07$, $u(S_{TNA}) = 0.03 \text{ mol/kg}$, $u(p) = 1 \text{ kPa}$. Standard uncertainties of the densities are estimated as the standard deviations of the mean reported in the table.

Table 5. Experimental data of the system NaHCO_3 -TeEG- H_2O measured at 5, 20, 40 and 60 $^{\circ}\text{C}$ and at a pressure $p = 0.1 \text{ MPa}^a$. t is the equilibrium temperature. $\tilde{w}$ is the salt-free glycol concentration (wt%). σ is the standard deviation. The results of the RS method was calculated from equations of Fosbøl et al.^{4,14}. w_i is the weight percent of component i . The solid phase is assumed from a subset of analysis and not every sample was characterized by PXRD.

t $^{\circ}\text{C}$	initial				equilibrium				reverse Schreinemakers				
	$\tilde{w}_{\text{TeEG}}$ %	$m_{\text{H}_2\text{O}}$ g	m_{TeEG} g	m_{NaHCO_3} g	S_{TNa} mol/kg	$\sigma_{S_{TNa}}$ mol/kg	$\rho_{\text{sat,liq}}$ g/cm ³	σ_{ρ} g/cm ³	w_{NaHCO_3} %	σ_{NaHCO_3} %	$m_{\text{H}_2\text{O}}$ g	w_{TeEG} %	P
5.40	0.00	20.010	0.000	2.479	0.842	0.004	1.052	0.012	7.08	0.034	20.010	0.00	B
5.40	3.00	19.422	0.6	2.238	0.780	0.008	1.050	0.013	6.55	0.067	19.422	2.80	B
5.30	14.96	17.035	2.998	2.062	0.584	0.005	1.048	0.006	4.90	0.041	17.035	14.23	B
5.30	39.88	12.058	7.999	1.264	0.263	0.003	1.081	0.011	2.21	0.026	12.058	39.00	B
5.70	66.81	6.658	13.399	0.901	0.094	0.005	1.130	0.018	0.79	0.045	6.658	66.28	B
4.90	78.49	4.337	15.829	0.872	0.063	0.001	1.116	0.016	0.53	0.011	4.337	78.08	B
4.90	87.82	2.441	17.604	0.899	0.041	0.001	1.107	0.053	0.35	0.009	2.441	87.52	B
4.80	93.90	1.222	18.822	0.870	0.037	0.0004	1.172	0.1	0.31	0.003	1.222	93.62	B
4.80	97.42	0.516	19.508	1.124	0.034	0.0004	1.157	0.109	0.28	0.0004	0.516	97.15	B
5.20	100.0	0.000	20.031	1.314	0.037	0.002	1.148	0.035	0.31	0.02	0.000	99.69	B
20.00	87.80	2.448	17.623	0.836	0.044	0.008	1.131	0.026	0.37	0.066	2.448	87.48	B
20.00	93.82	1.239	18.801	0.847	0.036	0.001	1.165	0.027	0.30	0.012	1.239	93.53	B
20.00	97.35	0.530	19.500	1.114	0.052	0.0005	1.142	0.01	0.43	0.005	0.530	96.93	B
20.00	100.0	0.000	20.056	1.275	0.136	0.013	1.097	0.033	1.14	0.108	0.000	98.86	B
20.10	3.00	19.418	0.602	3.533	1.021	0.001	1.079	0.015	8.58	0.01	19.418	2.75	B
39.60	0.00	9.994	0.000	1.723	1.492	0.0009	1.085	0.034	12.53	0.007	9.994	0.00	B
40.00	3.19	9.712	0.32	1.678	1.249	0.054	1.114	0.027	10.49	0.451	9.712	2.85	B
39.90	15.03	8.548	1.512	1.239	0.973	0.008	1.092	0.02	8.17	0.066	8.548	13.80	B
39.90	39.94	6.021	4.004	0.779	0.437	0.033	1.123	0.078	3.67	0.274	6.021	38.48	B
39.20	66.73	3.348	6.716	0.588	0.134	0.005	1.121	0.007	1.13	0.039	3.348	65.98	B
39.60	78.65	2.145	7.902	0.415	0.083	0.004	1.112	0.021	0.70	0.033	2.145	78.11	B
40.00	87.86	1.219	8.820	0.43	0.049	0.0002	1.120	0.01	0.41	0.001	1.219	87.50	B
40.00	93.81	0.621	9.41	0.418	0.039	0.001	1.136	0.008	0.33	0.012	0.621	93.50	B
39.90	97.09	0.293	9.747	0.662	0.039	0.0004	1.129	0.01	0.33	0.003	0.293	96.77	B
39.20	100.00	0.000	10.038	0.695	0.067	0.004	1.105	0.063	0.56	0.037	0.000	99.44	B
59.50	0.00	10.033	0.000	2.316	1.827	0.007	1.112	0.034	15.35	0.055	10.033	0.00	B
59.50	3.15	9.734	0.317	2.172	1.513	0.001	1.109	0.037	12.71	0.011	9.734	2.75	B
60.00	14.90	8.528	1.494	1.737	1.134	0.007	1.094	0.031	9.52	0.06	8.528	13.48	B

60.60	40.11	6.026	4.036	1.062	0.524	0.001	1.102	0.032	4.40	0.012	6.026	38.34	B
58.20	66.69	3.345	6.698	0.644	0.143	0.001	1.096	0.024	1.20	0.009	3.345	65.89	B
60.60	78.65	2.141	7.899	0.569	0.099	0.016	1.112	0.003	0.76	0.007	N/a	78.06	B
60.90	87.49	1.256	8.791	0.531	0.059	0.003	1.118	0.021	0.50	0.028	1.256	87.06	B
61.50	93.52	0.651	9.398	0.586	0.039	0.002	1.130	0.021	0.33	0.017	0.651	93.21	B
61.40	97.27	0.275	9.773	0.756	0.044	0.003	1.076	0.082	0.37	0.025	0.275	96.91	B
60.40	100.00	0.000	10.021	0.89	0.148	0.007	0.591	0.1	1.24	0.056	0.000	98.76	B

^aStandard uncertainties (u) for temperature, wt%, density, pressure, are $u(^{\circ}\text{C}) = 0.01^{\circ}\text{C}$, $u(w) = 0.003 + 0.07$, $u(S_{TNA}) = 0.03 \text{ mol/kg}$, $u(p) = 1 \text{ kPa}$. Standard uncertainties of the densities are estimated as the standard deviations of the mean reported in the table.

Figure 1. Solubility of NaHCO₃ in the aqueous MEG system measured in this work at atmospheric conditions in the temperature range 5 to 60 °C.

Figure 2. Solubility of NaHCO_3 in the aqueous DEG system measured in this work at atmospheric conditions in the temperature range 5 to 60°C .

Figure 3. Solubility of NaHCO_3 in the aqueous TEG system measured in this work at atmospheric conditions in the temperature range 5 to 60 °C.

Figure 4. Solubility of NaHCO_3 in the aqueous TeEG system measured in this work at atmospheric conditions in the temperature range 5 to 60 °C.

Figure 5 illustrates the solubility of NaHCO_3 in pure water and at constant glycol (salt-free) concentrations of ~15 and ~95 wt% as a function of temperature. Our experimental results for the solubility of NaHCO_3 in water are validated towards previously published data^{16–31}, Figure 5. The experimental data are in line with the previously published data up to 40 °C. At 60 °C our measured data tend to deviate with an upward trend compared with previously published data. The amount of published data available at this temperature is non-existent.

The NaHCO_3 solubility is highest in pure water and decreasing with increased amount of glycol. The solubility of NaHCO_3 is also decreasing with higher glycol molecular weight, and linearly increasing with temperature. At high glycol concentration, the temperature effect on the salt

solubility is scarcely seen except in the MEG-water system. The explanation may be increased CO_2 concentration at high glycol concentration or the formation of glycol-bicarbonate complexes.

Figure 5. NaHCO_3 solubility as a function of temperature. Previously published data¹⁶⁻³¹ for NaHCO_3 -water are plotted for comparison.

The NaHCO_3 solubility at 20 °C in four aqueous glycol systems are plotted in Figure 6. The NaHCO_3 solubility (wt%) is given on logarithmic scale and the glycol (salt-free) concentration is in weight percent on the horizontal axis.

It is evident that the solubility increases significantly from its value in aqueous MEG, through higher molecular weights of glycols. The minima in Figure 6 move toward higher glycol concentration increasing the molecular weight of the glycol homologues. In all glycol systems, the solubility is declining at low glycol concentrations compared to the value in pure water. After a minimum solubility, the solubility increases by adding more glycol.

An interesting phenomenon is observed by plotting the NaHCO_3 logarithmic solubility as function of glycol mole fraction. Comparing to the figure of weight percent of NaHCO_3 (Figure 7, Figure 8, Figure 9, and Figure 10) it graphically gives a rather different representation of the solubility curve. The curves all have a parabolic trend and the influence of the glycol molecular mass is even more distinct. The logarithmic scale indicates that the temperature has insignificant impact on the NaHCO_3 solubility but this is not quite the case as seen in Figure 1, Figure 2, Figure 3, and Figure 4. An outlier related to the increased viscosity for 100 wt% TEG is observed in Figure 7.

On a mole fraction scale, there is a clear and visible minimum at $x(\text{glycol, salt-free})=0.5$. The minimum remains quite constant at 50 mol% ($\pm 5\%$) in all systems at all temperatures. This minimum could be explained by a 1:1 NaHCO_3 solvation by either water or glycol. Water and NaHCO_3 apparently have a tendency to form one type of NaHCO_3 solvation while glycol- NaHCO_3 forms another. The affinity for NaHCO_3 appears to be equally shared by water and glycol. Therefore we see this minimum at $x(\text{glycol, salt-free})=0.5$ where NaHCO_3 is neither bound to water nor to glycol, but in a transition from one molecular relation to the other. The two solvent molecules tend to interact with each other, rather than with the sodium and the bicarbonate ions. This results in salting out of NaHCO_3 because the salt is unable to remain solubilized in the mixture.

The increased NaHCO_3 solubility at high glycol concentration can also be explained in a different way. It may be influenced as explained by Gärtner et al.¹² by soluble complexes of glycol and HCO_3^- or un-dissociated NaHCO_3 where water replaces HCO_3^- due to the capability of water to form hydrogen bonding. At higher content of water in the mixtures the solubility of HCO_3^- increases as cavity forms in the solvent making space for HCO_3^- . The solvating effect at high

glycol concentration indicates that glycol and HCO_3^- form complexes. Gärtner et al.³² explain that the solvation mechanism in almost pure glycol might be due to glycol forming hydrogen bridges with HCO_3^- , increasing the solubility of bicarbonate ions.

Solubilisation of salts and ions are often strongly related to the static permittivity of the solvent. The tendency of the solvent to shield or transfer the coulombic forces from Na^+ or HCO_3^- to one of the solvent molecules is given by this property. Therefore the solubility of molecules can have a strong relation to static permittivity. The clear minimum in solubility observed is not due to changes in static permittivity. Previous work³³ show that static permittivity for the mixed water-glycol solvent has no minimum in the static permittivity and the solubility minimum must therefore originate from other types of phenomena. This could be hydrogen bonds between NaHCO_3 and either of the solvent molecules. The minimum observed in this system is also very different from similar mixed solvent salt systems. The minimum is not observed in e.g. NaCl -MEG- H_2O ³⁴ or Na_2SO_4 -MEG- H_2O ³⁵, where the bond must be different apparently.

Figure 6. Solubility of NaHCO_3 (wt%) in glycol-water mixtures (wt%) at 20 °C.

Figure 7. Solubility of NaHCO_3 (wt%) in glycol-water mixtures (mole%) at 5 °C.

Figure 8. Solubility of NaHCO_3 (wt%) in glycol-water mixtures (mole%) at 20°C .

Figure 9. Solubility of NaHCO_3 (wt%) in glycol-water mixtures (mole%) at 40°C .

Figure 10. Solubility of NaHCO_3 (wt%) in glycol-water mixtures (mole%) at 60 °C.

The reproducibility of the density measurements are listed in Table 2, Table 3, Table 4, and Table 5. The density was measured by taking 100 to 1000 μL of a sample and weighing it. This method is giving standard deviations up to 2 %, which is relatively high. The reasons for the high deviations were explained by Fosbøl et al.¹¹ to be caused by air intake by the micropipette or too small sample sizes.

Figure 11, Figure 12, Figure 13, and Figure 14 depict the measured densities at different isotherms of NaHCO_3 -MEG- H_2O , NaHCO_3 -DEG- H_2O , NaHCO_3 -TEG- H_2O , and NaHCO_3 -TeEG- H_2O mixtures. The densities for all systems increase with increasing temperature. There seems to be a slight tendency in lower density from MEG to TeEG.

The results of the density measured for saturated NaHCO_3 -MEG- H_2O mixtures, Figure 11, were compared to the data by Fosbøl et al.¹¹. The density data seem to be more temperature dependent

at low MEG concentrations. From 60 wt% to 100 wt% MEG the density does not vary much with temperature. This was also observed in the solid-liquid equilibrium (SLE) diagram, Figure 1.

The density of measured NaHCO_3 -DEG- H_2O mixtures, Figure 12, has tendencies similar to those of NaHCO_3 -MEG- H_2O mixtures. At low DEG concentrations, the density is increasing linearly for the isotherms 5 and 20 °C. At 40 and 60 °C, the density is decreasing. The behaviour might be due to the experimental uncertainty. At high glycol concentrations, the density is following the solubility trend.

For the system, NaHCO_3 -TEG- H_2O the temperature only has little influence on the density. The density is weakly increasing up to 75 wt% TEG and around 85 wt% TEG the density may have a minimum similar to the one observed in the SLE phase diagram Figure 13. Two outliers are shown at 40 and 60 °C at a TEG concentration of approximately 85 wt%. The outliers are caused by the limitation of the density method. Figure 14 illustrates the density of NaHCO_3 -TeEG- H_2O . The trend of this system is deviating from the other glycol systems, as the temperature seems to have an insignificant impact on the density. The behaviour may be caused by density being difficult to measure due to high viscosity.

Figure 11: Density of saturated NaHCO_3 -MEG- H_2O solutions measured at selected isotherms at atmospheric pressure.

Figure 12: Density of saturated NaHCO_3 -DEG- H_2O solutions measured at selected isotherms at atmospheric pressure.

Figure 13: Density of saturated NaHCO₃-TEG-H₂O solutions measured at selected isotherms at atmospheric pressure.

Figure 14: Density of saturated NaHCO₃-TeEG-H₂O solutions measured at selected isotherms at atmospheric pressure.

4. Conclusion

The solubility of NaHCO_3 and the density of saturated mixtures of MEG- H_2O , DEG- H_2O , TEG- H_2O , and TeEG- H_2O were measured in this work. Potentiometric titration and the reverse Schreinemakers method were used to analyse and calculate the solubility.

For all systems, minima were found at $x(\text{glycol, salt-free})=0.5$. The minima remained constant at all temperatures. Two possible types of NaHCO_3 solvation exist in the systems: 1) between water and NaHCO_3 and 2) between glycol and NaHCO_3 . The affinity for NaHCO_3 was apparently equally shared by water and glycol. The bonds between the solvent molecules is apparently stronger than to the ions of NaHCO_3 .

The density was measured by knowing the volume and weight of a sample. The accuracy of this method is very low, giving standard deviations up to 2 %. The trend of the density values was similar to the trend of the solubility values. Minima were located in the range $w(\text{glycol, salt-free})$ 80 to 90 wt% glycol, salt-free.

The experimental data produced in this work can be used to enhance the quality of modelling of corrosion and gas drying. Furthermore the data can be used as a general test-bed for group-contribution thermodynamic modelling of electrolyte system.

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ABBREVIATIONS

DEG, diethylene glycol; IR, infrared; MEG, monoethylene glycol; PE, polyethylene; RS, reverse Schreinemakers; TeEG, tetraethylene glycol; TEG, triethylene glycol; XRPD, x-ray powder diffraction.

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