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Solubility of NaCl in Aqueous Electrolyte Solutions from 10 to 100 °C

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The solubilities of NaCl in aqueous KCl, $MgCl_2$, $CaCl_2$, and mixed $CaCl_2$–KCl solutions have been determined from 10 to 100 °C. The data were fit to an equation, and the equation was used to calculate values of the change in solubility of NaCl, $\partial[\mathrm{NaCl}]/\partial T$. These values are required for calculations of the rate of migration of fluids in a thermal gradient in rock salt. The data obtained here indicate that the values of $\partial[\mathrm{NaCl}]/\partial T$ are 36–73% greater for solutions containing divalent ions than for the NaCl–H_2O system.

Introduction

One of the potential problems with using halite (NaCl) formations for the long-term disposal of high-level nuclear waste is the migration of included fluids up the thermal gradient toward the waste. Several workers (*1–3*) have developed equations for calculating the migration rate of these included fluids provided that the temperature and temperature gradient are known. One of the key parameters for these calculations is the change in the solubility of NaCl as a function of temperature, $\partial[\mathrm{NaCl}]/\partial T$. To date, the migration of the included fluids has been modeled by using the data for the NaCl–H_2O system; however, the included fluids generally are brines in the system NaCl–$MgCl_2$–KCl–$CaCl_2$ (*4*). Hence, we have undertaken an experimental study of the solubility of NaCl in various electrolyte solutions.

Experimental Method

The experimental technique used in this study is a modification of the commonly applied visual or synthetic method and has been discussed in detail in an earlier report (*5*). To summarize: The method involves loading a Pyrex glass vessel with salt and water of a precisely known bulk composition. A stirring mechanism is inserted into the tube, and a layer of silicone oil added to prevent water gain or loss. The tube is then placed in a bath containing either water or ethylene glycol as a heating medium. The tube is thermally equilibrated, and the solution plus salt crystal assemblage vigorously stirred until dissolution of salt ceases. The bath is heated incrementally and the above procedure repeated. Heating increments are made progressively smaller as the amount of salt decreases. The temperature at which the last salt crystal dissolved is taken as the saturation point of the particular bulk composition.

The temperatures were measured with platinum resistance thermometers that had been calibrated against NBS-secondary standard thermometers and are accurate to ±0.03 °C on the IPTS-68 temperature scale.

Experimental Results

We investigated the solubility of NaCl in aqueous KCl, $MgCl_2$, $CaCl_2$, and mixed KCl–$CaCl_2$ solutions from 10 to 100 °C. The results are listed in Table I along with the deviation of the measured solubilities from empirical equations that describe the solubility for each of the aqueous electrolytes. The data were fit to equations of the form

$$[\mathrm{NaCl}] = a_0 + a_1 t + a_2 t^2 + a_3 \chi_{\mathrm{K}} + a_4 \chi_{\mathrm{Ca}} + a_5 t \chi_{\mathrm{Ca}} + a_6 \chi_{\mathrm{Ca}}^2 + a_7 \chi_{\mathrm{K}} \chi_{\mathrm{Ca}}^{0.5} + a_8 \chi_{\mathrm{K}} \chi_{\mathrm{Ca}} + a_9 \chi_{\mathrm{K}} \chi_{\mathrm{Ca}}^2 + a_{10} \chi_{\mathrm{Mg}} + a_{11} t \chi_{\mathrm{Mg}} + a_{12} \chi_{\mathrm{Mg}}^2 \quad (1)$$

where [NaCl] is the solubility of NaCl in g/100 g of solution; χ_i is the concentration of the other electrolysis in g/100 g of final solution; t is the temperature in degrees Celsius; and a_0–a_{12} are empirical constants determined from the least-squares fit of the data. The empirical constants are listed in Table II. The experimental data show a mean deviation of ±0.06 g/100 g of saturated solution from the empirical equations.

Discussion of Results

Much of the available solubility data for NaCl in mixed electrolytes have been summarized and partially evaluated (*6*). These data have a wide range of quality and commonly are characterized by a wide degree of scatter, frequently of the order of ±0.5 g/100 g of saturated solution. The limited data available for solutions saturated in NaCl show a mean deviation of ±3.5% (~±0.4 g/100 g saturated solution) from the values obtained by using eq 1 with the coefficients listed in Table II. This degree of scatter is within the precision of the older measurements (*7*). The equation represents the solubility data for NaCl in water (*5*) within the precision of the data, i.e., ±0.03 g/100 g of saturated solution.

Table III lists the values of $\partial[\mathrm{NaCl}]/\partial T$ determined from this study for aqueous electrolytes as compared with the values determined for the pure NaCl–H_2O system. The value of $\partial[\mathrm{NaCl}]/\partial T$ is the same for the NaCl–H_2O system and for the aqueous KCl solutions, but for all other solutions the value of $\partial[\mathrm{NaCl}]/\partial T$ is greater by 36–73%. Hence, if these values are

Table I. Experimental Solubilities of NaCl in Aqueous Electrolyte Solutions and the Deviation of the Values from Eq 1 in g/100 g of Saturated Final Solution

T, °C	[NaCl]	[KCl]	[$CaCl_2$]	[$MgCl_2$]	Δ
26.03	24.25	3.788			−0.00
47.01	24.61	3.770			−0.04
59.11	24.88	3.756			−0.03
74.82	25.26	3.737			−0.03
89.02	25.64	3.718			−0.02
94.59	25.82	3.709			−0.00
27.94	21.99	7.801			−0.10
41.95	22.29	7.771			−0.07
61.78	22.80	7.720			−0.00
79.12	23.28	7.672			0.04
97.42	23.79	7.621			0.03
43.88	20.01	11.999			−0.07
43.96	20.00	12.000			−0.08
62.61	20.49	11.927			−0.03
77.53	21.01	11.849			0.10
77.47	21.00	11.850			0.09
93.80	21.50	11.775			0.12
19.57	21.82			3.909	0.03
29.42	22.11			3.895	0.12
42.27	22.27			3.887	0.00
52.20	22.51			3.875	0.01
61.95	22.91			3.855	0.15
77.34	23.29			3.836	0.11
92.28	23.79			3.811	0.16
21.31	17.04			8.296	−0.09
29.21	17.27			8.273	−0.06
19.57	17.57			8.243	−0.03
29.42	17.82			8.218	−0.08
42.27	18.35			8.165	−0.09
52.20	18.85			8.115	0.03
61.95	19.33			8.067	0.10
19.86	12.26			13.161	0.03
31.40	12.51			13.124	−0.04
42.87	12.86			13.071	−0.04
56.15	13.22			13.017	−0.10
76.35	13.98			12.903	−0.07
86.37	14.47			12.829	0.03
19.31	7.16			18.568	−0.06
27.54	7.55			18.490	0.04
36.62	8.00			18.400	0.15
51.70	8.48			18.304	0.09
59.63	8.68			18.264	0.00
80.61	9.46			18.108	−0.07
87.79	9.81			18.038	−0.04
25.16	24.75		1.505		−0.05
47.78	25.18		1.496		−0.07
64.19	25.60		1.488		−0.03
86.97	26.00		1.480		−0.23
41.14	21.32		5.508		0.08
59.54	21.73		5.479		0.01
73.57	22.16		5.449		0.03
88.81	22.57		5.420		−0.03
25.77	16.57		10.012		−0.10
49.38	17.39		9.913		0.03
71.45	18.23		9.812		0.13
95.07	19.03		9.716		0.07
26.23	12.24		14.919		−0.03
43.56	12.85		14.815		−0.01
62.94	13.61		14.686		0.03
95.88	14.93		14.462		−0.00
25.32	22.87	3.857	1.543		0.09
38.61	23.05	3.848	1.539		0.01
63.68	23.65	3.818	1.527		0.03
77.87	24.26	3.787	1.515		0.26
30.23	20.75	7.925	1.585		0.01
33.05	20.83	7.917	1.583		0.03
51.38	21.00	7.900	1.580		−0.19
66.92	21.54	7.846	1.569		−0.05
82.58	22.03	7.797	1.559		0.01
34.99	18.55	12.218	1.629		−0.03
45.51	18.85	12.173	1.623		0.02
67.26	19.46	12.081	1.611		0.08
95.06	20.00	12.000	1.600		−0.17
20.43	18.71	4.065	5.690		0.12
33.91	18.99	4.051	5.671		0.09
66.79	19.77	4.012	5.616		−0.01
80.00	20.00	4.000	5.600		−0.17
52.35	19.52	4.024	5.634		0.14
16.57	16.26	8.374	5.862		0.06
30.59	16.67	8.333	5.833		0.13
41.12	17.02	8.298	5.809		0.21
58.18	17.36	8.264	5.785		0.09
70.20	17.66	8.234	5.764		0.03
80.90	17.82	8.218	5.753		−0.14
37.95	15.80	10.104	5.894		0.04
48.44	16.09	10.069	5.874		0.04
59.33	16.38	10.034	5.853		0.02
75.35	16.74	9.991	5.828		−0.10
87.02	17.11	9.947	5.802		−0.12
21.80	15.35	2.540	10.158		0.08
32.10	15.49	2.535	10.141		−0.05
43.65	15.84	2.525	10.099		−0.04
57.56	16.21	2.514	10.055		−0.10
63.25	16.39	2.508	10.033		−0.11
75.23	16.86	2.494	9.977		−0.06
95.05	17.64	2.471	9.883		−0.03
28.09	13.97	5.162	10.324		−0.11
39.20	14.21	5.147	10.295		−0.18
51.32	14.73	5.116	10.232		−0.05
58.05	15.03	5.098	10.196		0.02
69.90	15.41	5.075	10.151		−0.01
82.84	15.97	5.042	10.084		0.07
92.85	16.24	5.026	10.051		−0.03
12.18	10.96	1.781	15.137		−0.09
31.09	11.65	1.767	15.019		−0.00
55.05	12.54	1.749	14.868		0.04
63.82	13.00	1.740	14.790		0.14
85.80	13.71	1.726	14.669		−0.02
22.80	10.59	3.576	15.200		−0.02
46.92	11.41	3.544	15.060		−0.01
55.81	11.77	3.529	14.999		0.01
76.47	12.54	3.498	14.868		−0.02
91.62	13.18	3.473	14.759		−0.03
20.83	9.77	5.414	15.339		0.00
28.28	10.08	5.395	15.286		0.06
43.12	10.59	5.365	15.200		0.06
55.95	10.91	5.345	15.145		−0.06
68.35	11.44	5.314	15.055		−0.02
81.13	12.04	5.278	14.953		0.04
93.85	12.61	5.243	14.856		0.06

Table II. Empirical Regression Coefficients for Eq 1

$a_0 = 25.939$
$a_1 = 1.2695 \times 10^{-2}$
$a_2 = 7.9434 \times 10^{-5}$
$a_3 = -0.54749$
$a_4 = -1.0252$
$a_5 = 6.9850 \times 10^{-4}$
$a_6 = 4.3305 \times 10^{-3}$
$a_7 = 4.6061 \times 10^{-2}$
$a_8 = -1.7281 \times 10^{-2}$
$a_9 = 1.1288 \times 10^{-3}$
$a_{10} = -1.1726$
$a_{11} = 5.6785 \times 10^{-4}$
$a_{12} = 7.4778 \times 10^{-3}$

used for calculating the migration rate of the fluid inclusions, the resulting migration rates would be increased by 36–73%. This increase would mean a corresponding increase in the amount of brine predicted to reach the waste canister.

Table III. Values of $\partial[\mathrm{NaCl}]/\partial T$ of the Aqueous Electrolyte Solutions Compared to $\partial[\mathrm{NaCl}]/\partial T$ for NaCl-H_2O[a]

T, °C	NaCl	10.0 KCl	18.0 $MgCl_2$	15.0 $CaCl_2$	15.0 $CaCl_2$ + 10.0 KCl
10	0.0143	0.0143	0.0245	0.0248	0.0248
25	0.0167	0.0167	0.0269	0.0272	0.0272
50	0.0206	0.0206	0.0308	0.0311	0.0311
75	0.0246	0.0246	0.0348	0.0351	0.0351
100	0.0286	0.0286	0.0388	0.0391	0.0391

[a] Concentrations are in g/100 g of saturated solution, and $\partial[\mathrm{NaCl}]/\partial T$ is in g of NaCl/100 g of saturated solution per degree Celsius.

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Salt Effects in Vapor–Liquid Equilibria. Effects of Dissolved Salts on the Vapor–Liquid Equilibrium Relationships of Three Miscible Nonaqueous Binary Systems and One Partially Miscible Binary System

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The vapor-liquid equilibrium (VLE) data determined experimentally at 760 torr for three nonaqueous and completely miscible binary systems, viz., (i) carbon tetrachloride–2-propanol saturated with calcium chloride, (ii) acetone–carbon tetrachloride saturated with potassium iodide, and (iii) acetone–chloroform saturated with potassium iodide, and for the partially miscible binary system methyl ethyl ketone–water saturated with sodium chloride are reported. The second and third miscible systems exhibit anomalous behavior (viz., crossover effect) from the general theory of salt effects in vapor–liquid equilibria. The data for the three miscible systems have been checked for their thermodynamic consistency and also correlated satisfactorily by choosing the Wilson model for the activity coefficient–composition relationship.

Introduction

A salt dissolved in a mixed solvent is capable, through preferential association or other structure-related effects in the liquid phase, of altering the composition of the equilibrium vapor phase. Hence, salt effects on vapor–liquid equilibrium relationships provide a potential technique of extractive distillation for difficult separations. A good amount of work has been reported in the literature concerning salt effects on the vapor–liquid equilibria for many binary systems with a variety of salts (*1–3*). However, much of the reported work covers mainly aqueous miscible systems, and data on nonaqueous and partially miscible systems are rather fragmentary.

In a continuing study (*4–9*) of salt effects on the VLE of nonaqueous binary systems and salt-mixture effects on aqueous ones, the following systems have been studied in the present investigation: (i) carbon tetrachloride–2-propanol* in the presence of calcium chloride, (ii) acetone*-carbon tetrachloride in the presence of potassium iodide, and (iii) acetone* -chloroform in the presence of potassium iodide again, the salts being present under saturated conditions. To find out the effect of dissolved salt on the VLE of a partially miscible system, we have also studied the system methyl ethyl ketone–water*-sodium chloride. The asterisks shown above denote the components in which the salt in question is more soluble.

Table I. Physical Properties of Solvents

	lit. (*10, 11*)			obsd		
solvent	bp, K	sp gr at 303.2 K	n^a at 303.2 K	bp, K	sp gr at 303.2 K	n^a at 303.2 K
acetone	329.2	0.7790	1.3536	329.3	0.7780	1.3539
carbon tetrachloride	349.9	1.5748	1.4519	350.1	1.5625	1.452
chloroform	334.3	1.4706	1.3886	334.3	1.4685	1.360
methyl ethyl ketone	352.8	0.7946	1.3760	352.8	0.7905	1.373
2-propanol	355.7	0.7770	1.3732	355.7	0.7724	1.3715

[a] Refractive index.

Experimental Section

Chemicals. The components (both the liquid and the solid) used in the present investigation were of the AnalaR/LR quality. The solvents were further purified by fractional distillation. The physical properties of these solvents measured at 30 °C are compared with the corresponding literature values (*10*, *11*) in Table I.

Equilibrium Still and Analytical Technique. The vapor–liquid equilibrium data were determined in a Smith and Bonner type (*12*) of still with an arrangement for magnetic stirring the description of which is given elsewhere (*13*, *14*). This type of still was chosen so as to enable the study of the partially miscible system also. The experimental procedure and the analytical technique for the liquid- and vapor-phase samples were the same as outlined by one of us in earlier papers (*6–8*).

The equilibrium data were obtained at atmospheric pressure, viz., 760 ± 3 torr. The saturated condition of the salt in the liquid mixture was ensured by adding the salt slightly in excess before starting every run. As for the partially miscible system methyl ethyl ketone–water (in the presence of dissolved sodium chloride), cloudy or two-phase samples were analyzed by the density–composition method, after the addition of measured quantities of distilled water to bring them within the homogeneous region. The boiling temperature and concentration measurements for all of the systems studied were generally accurate to ±0.1 K and ±0.005 mole fraction, respectively.