Elevation of the Boiling Point of Water by Salts at Saturation: Data and Correlation

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Elevation of the boiling point of water by each of a series of 40 salts, individually present at saturated concentration, was studied. Data for 14 of the systems were determined experimentally; the remainder were taken from the literature. The data were correlated by an empirical equation. From the results it would appear that, in general, the degree of dissociation of salts present at saturation in boiling, aqueous solution is sufficiently small that its effect on boiling point rise is not significant. These findings support the contention that even salts which are highly dissociated at lower concentrations in aqueous solution tend to reassociate at saturation.

The vapor pressure of a solvent decreases when a nonvolatile component is dissolved in the liquid phase. The depression of the vapor pressure of the solution (at constant temperature) results in a rise of the boiling point of the solution (at constant pressure). The degree of the boiling point rise (BPR), being a colligative property, depends on the concentration of the dissolved particles and on the nature of the solvent. In dilute solutions it is observed to be relatively independent of the nature of the solute. BPR measurements of dilute solutions have been used for many years to obtain the molecular weight of the solute (*8*).

The molecular weights of nonelectrolytes in different solvents obtained from BPR measurements of dilute solutions are quite accurate and consistent. However, the same procedure for electrolytes in aqueous solution gives results which are not as accurate as those predicted, the postulated reason being that electrolytes dissociate in aqueous solution and thus increase the concentration of solute particles. If degree of dissociation is taken into account in calculating the molecular weight of the solute the results are better and more accurate. However, the same considerations, when applied to moderately concentrated aqueous solutions of electrolytes, fail once again to give accurate results. Data on BPR of aqueous solutions are available in the form of During lines, graphs, etc., in the literature. These data find wide use in the design of heat exchangers for evaporation equipment.

In the nomenclature to be used below, components 1 and 2 are water and salt, respectively.

Experimental Section

Boiling point rises for a total of 40 salts present at saturation in boiling, distilled water were established. Data for 14 of these systems were determined experimentally, while the remainder were obtained from the literature (*1–3, 5, 9–11*). For the data obtained experimentally the method was as follows.

A boiling flask of 300 mL capacity having three wide necks was employed. A reflux condenser was connected to one of the necks. A thermometer was immersed into the liquid through the second neck. The third neck was stoppered and used for adding water or salt when necessary, and also for removing samples of the boiling liquid. Heating was by an electrical jacket. When the system had been boiling for 30 min after having reached constant temperature with a slight excess of solid salt present to ensure saturation, the solution was sampled. The sampling procedure involved removing the heating jacket, allowing the solid salt particles to settle, and then removing a sample from the clear liquid. The samples were placed in weighing bottles, stoppered, weighed, and analyzed for salt concentration. Where a choice existed, titration methods were preferred to gravimetric determination. CH_3COO^- ions were determined by conductometric titration with HCl (*6*). I^- and Br^- ions were titrated with $AgNO_3$ using Mohr's method (*12*). All other salts were dried at 190–210 °C to constant weight and determined gravimetrically.

Results and Discussion

Isobaric BPR data at 760 ± 10 mmHg pressure are reported in Table I for boiling point and salt concentration, and plotted in Figure 1 as ΔT vs. N_2, where N_2 is the salt mole fraction and temperature is in °C. A single best straight line was obtained using the method of least squares. The equation of this line was found to be:

$$\Delta T = 104.9 N_2^{1.14} \qquad (1)$$

The activity coefficient of water in the solution was calculated according to

$$\gamma_1 = \frac{\pi}{P_1^0 N_1}$$

where π is the total pressure, N_1 is the water mole fraction, and P_1^0 is the vapor pressure of water at the boiling point of the solution (*4*).

Smoothed values of N_1 were taken from the figure using the least-squares straight line, and smoothed γ_1 calculated from these data are listed in Table II.

Obtaining accurate data on boiling temperature and concentration of saturated solutions is not an easy task. The difficulties that affect the accuracy of such an estimate are many and therefore the results should be looked upon accordingly. The boiling of saturated solutions is not even and smooth since the solution often tends to superheat and bump. As a result, the heating must be carried out very carefully and evenly. An elec-

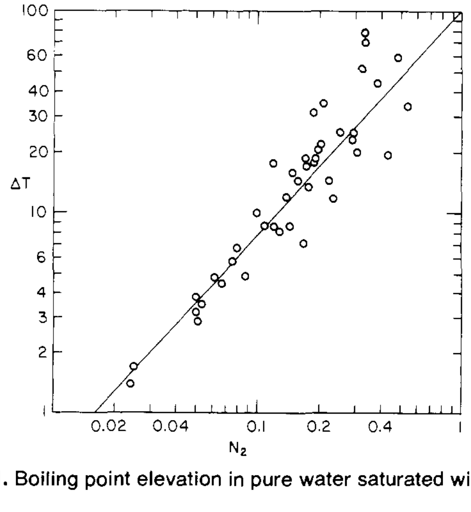

Figure 1. Boiling point elevation in pure water saturated with salt.

Table I. Boiling of Saturated Aqueous Solutions

System no.	Salt	N_2	T (°C)	ΔT	N_1	P_1^0 (mmHg)	γ_1	Ref
1	$CuCl_2$	0.150	116.0	16.0	0.850	1300	0.687	*a*
2	KOAc	0.490	159.8	59.8	0.510	4638	0.321	*a*
3	KBr	0.140	112.0	12.0	0.860	1150	0.768	*a*
4	KI	0.190	118.1	18.1	0.810	1390	0.675	*a*
5	KI	0.193	118.5	18.5	0.807	1410	0.667	5
6	KNO_3	0.380	117.2	17.2	0.620	1350	0.908	*a*
7	KNO_3	0.373	115.9	15.9	0.627	1300	0.932	11
8	KNO_3	0.405	115.5	15.5	0.595	1280	0.997	1–3
9	K_2SO_4	0.025	101.7	1.7	0.975	810	0.962	*a*
10	K_2SO_4	0.024	101.4	1.4	0.976	795	0.979	1–3
11	NaOAc	0.300	125.0	25.0	0.700	1610	0.674	*a*
12	NaOAc	0.252	125.0	25.0	0.748	1610	0.631	5
13	NaOAc	0.297	123.0	23.0	0.703	1630	0.663	10
14	Na_2SO_4	0.050	103.2	3.2	0.950	855	0.935	*a*
15	Na_2SO_4	0.051	102.9	2.9	0.950	850	0.941	5
16	Na_2SO_4	0.051	101.9	1.9	0.949	820	0.976	10
17	NaBr	0.173	118.9	18.9	0.827	1430	0.642	*a*
18	NaBr–KBr (1:1 mole ratio)	0.177	117.2	17.2	0.823	1350	0.684	*a*
19	NaBr–KBr (2:1 mole ratio)	0.204	122.0	22.0	0.796	1580	0.604	*a*
20	NaBr–KBr (3:1 mole ratio)	0.199	120.8	20.8	0.801	1520	0.624	*a*
21	NaI	0.390	144.0	44.0	0.610	3020	0.412	*a*
22	NaI–KI (1:1 mole ratio)	0.193	131.5	31.5	0.807	2140	0.440	*a*
23	NH_4Cl	0.227	114.7	14.7	0.773	1250	0.786	5
24	$(NH_4)_2SO_4$	0.130	108.1	8.1	0.870	1390	0.628	5
25	$ZnSO_4$	0.087	104.9	4.9	0.913	910	0.914	5
26	$Sr(NO_3)_2$	0.080	106.8	6.8	0.920	980	0.842	5
27	NaCl	0.109	108.7	8.7	0.891	1030	0.828	5
28	NaCl	0.111	108.7	8.7	0.889	1030	0.829	11
29	NaCl	0.109	108.7	8.7	0.891	1030	0.828	1–3
30	KCl	0.123	108.6	8.6	0.877	1030	0.841	5
31	K Tartarate	0.160	114.4	14.4	0.840	1230	0.735	5
32	K_2CrO_4	0.076	105.8	5.8	0.924	940	0.875	5
33	$K_2Cr_2O_7$	0.062	104.8	4.8	0.938	900	0.900	5
34	LiCl	0.343	165.4	65.4	0.657	5308	0.217	9
35	LiCl	0.376	168.6	68.6	0.624	5742	0.212	1–3
36	Li_2SO_4	0.050	103.8	3.8	0.950	880	0.909	1–3
37	$Ca(NO_3)_2$	0.329	152.0	52.0	0.671	3725	0.304	11
38	$CaCl_2$	0.347	179.5	79.5	0.653	7435	0.156	11
39	$BaCl_2$	0.067	104.5	4.5	0.933	900	0.905	11
40	K_2CO_3	0.210	135.0	35.0	0.790	2360	0.407	11
41	$CsClO_4$	0.145	108.6	8.6	0.855	1040	0.854	11
42	$AgNO_3$	0.557	134.1	34.1	0.443	2290	0.749	11
43	$SrCl_2$	0.118	117.9	17.9	0.882	1380	0.624	11
44	RbCl	0.180	113.51	13.5	0.820	1200	0.772	1–3
45	CsCl	0.237	119.9	11.9	0.763	1470	0.677	1–3
46	Rb_2SO_4	0.053	103.5	3.5	0.947	870	0.922	1–3
47	Cs_2SO_4	0.101	110.00	10.0	0.891	1080	0.782	1–3
48	$RbNO_3$	0.439	119.4	19.4	0.561	1450	0.934	1–3
49	$CsNO_3$	0.172	107.2	7.2	0.828	990	0.927	1–3
50	$TlNO_3$	0.450	104.7					1–3
51	$NaNO_3$	0.310	120.20	20.2	0.690	1480	0.744	1–3

[a] Experimental (this study).

trical jacket was found to be the best heating source. A magnetic stirrer is also advisable. Boiling chips and manual agitation are required to prevent superheating. The measurement of temperature can be erroneous at times due to scale formation on the thermometer stem immersed in the solution. The salt concentration sometimes tends to indicate a higher value than actual, due to fine crystals dispersed in the solution which do not settle out before sampling. In light of these difficulties the degree of data scatter observed is not unexpected.

The correlation of BPR vs. N_2 observed for saturated solutions disagrees with that observed for moderately concentrated solutions of electrolytes (*7*). The relation for saturated solutions demonstrates that BPR under such conditions is apparently a colligative property of the solution, such as in the case of dilute, nonelectrolyte solutes, and hence is relatively independent of the character of the solute. Therefore it must be concluded that, in saturated electrolytic solutions, either all salts used were dissociated to an equal degree, or the degree of dissociation was not significant, or, most likely, that they were in predominantly if not fully associated condition when present at saturation.

In summary, an empirical relation, which correlates BPR with salt concentration in boiling saturated solution, was obtained

Table II. Smoothed Values for γ_1

T (°C)	Smoothed ΔT	Smoothed N_2	N_1	P_1^0 (mmHg)	γ_1
105	5	0.068	0.932	906.07	0.8999
110	10	0.125	0.875	1074.56	0.8083
115	15	0.180	0.820	1267.98	0.7309
120	20	0.230	0.770	1489.14	0.6628
125	25	0.280	0.720	1740.93	0.6063
130	30	0.330	0.670	2026.16	0.5598
135	35	0.380	0.620	2347.26	0.5222
140	40	0.412	0.588	2710.92	0.4767
145	45	0.470	0.530	3116.76	0.4600
150	50	0.520	0.480	3570.48	0.4434
155	55	0.570	0.430	4075.88	0.4336
160	60	0.610	0.390	4636.00	0.4203

using data for 40 salt–water systems. From the results it is concluded that, in general, the degree of dissociation of these salts in boiling, saturated, aqueous solution appears to be sufficiently small that its effect on the BPR is not significant. This apparent behavior at saturation is in marked contrast to the strong dissociation tendencies of many of these salts at lower concentrations.

The behavior of boiling saturated solutions can be useful in elucidating solvent and solution structure. If the information obtained can be generalized, prediction of salt behavior in mixed, as well as single, solvents may become possible.

Literature Cited

(1) Applebey, M. P., Crawford, F. H., Gordon, K., *J. Chem. Soc.*, 1665 (1934).
(2) Earl of Berkeley, *Philos. Trans. R. Soc. London, Ser. A*, **203**, 189 (1904).
(3) Earl of Berkeley, Applebey, M. P., *Proc. R. Soc. London, Ser. A.*, **85**, 447 (1911), and 489 (1911).
(4) "Handbook of Chemistry and Physics", 42nd ed, Chemical Rubber Publishing Co., Cleveland (1960–1961).
(5) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology", McGraw-Hill, New York, N.Y., 1926.
(6) Kolthoff, I. M., Sandell, E. B., "Textbook of Quantitative Inorganic Analysis", 3rd ed, MacMillan, New York, N.Y., 1962.
(7) Millard, E. B., "Physical Chemistry for Colleges", 7th ed, McGraw-Hill, New York, N.Y., 1953.
(8) Prutton, C. F., Maron, S. H., "Fundamental Principles of Physical Chemistry" (revised edition), MacMillan, New York, N.Y., 1951.
(9) Rius Miro, A., Otero de la Gandara, J. L., Alvarez Gonzalez, J. R., *An. R. Soc. Esp. Fis. Quim., Ser. B*, **53**, 171 (1957).
(10) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds", 3rd ed, Van Nostrand, New York, N.Y., 1953.
(11) Timmermans, J., "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions", Interscience, New York, N.Y., 1960.
(12) Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis", 3rd ed, Longmans, London, 1962, p 261.

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Solubility of Hydrogen Sulfide and Carbon Dioxide in a Sulfinol Solution

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The solubility of H_2S and CO_2 individually in a Sulfinol solution (40 wt % DIPA, 40 wt % sulfolane, 20 wt % water) has been measured at 40 and 100 °C. Partial pressures of H_2S ranged from 5 to 3900 kPa while partial pressures of CO_2 ranged from 2.4 to 5700 kPa.

The removal of the acid gases (H_2S and CO_2) from natural and refinery gases is commonly accomplished by absorption in a suitable solvent. Many processes employ an aqueous alkanolamine solution and are classed as "chemical" processes. They have the advantage of being able to reduce the concentrations of H_2S and CO_2 to low levels, even at low total pressures of the gas stream. However, the alkanolamine solutions do not remove mercaptans and other sulfur compounds readily, and require the application of large quantities of heat for regeneration. These disadvantages have led to the development of "physical" processes which employ a solvent, usually nonaqueous, to remove the H_2S, CO_2, and other sulfur compounds and which require little energy for regeneration, as most of the absorbed gases come out of solution upon reduction of the pressure. In some cases, though, the physical processes are unable to reduce H_2S to pipeline specifications without excessively large circulation rates. Factors to be considered in the selection of processes have been discussed recently by Richardson and O'Connell (*10*).

The Sulfinol process (*1–3*), patented by Shell, was devised to combine the advantages of the chemical and physical processes. The solvent consists of sulfolane, a physical solvent, together with diisopropanolamine (DIPA) and water, a chemical solvent. DIPA has the advantages of being less corrosive (*3, 9*) and less sensitive to degradation (*2*) than primary amines. The relative amounts of these components can be varied in a given treating process. Little solubility data for the acid gases in Sulfinol solution have been released. Operating details have been provided in various publications (*1–4, 6*), but only qualitative solubility data were presented. The present investigation was undertaken to provide equilibrium solubility data for CO_2 and H_2S in a typical Sulfinol solution. These data may be useful in comparisons of alternate treating processes.

Experimental Section

The apparatus used in this study is the same as that used for previous studies of H_2S–CO_2–monoethanolamine, H_2S–CO_2–diethanolamine, and H_2S–CO_2–DIPA systems in this laboratory (*5, 7, 8*). The equilibrium cell consisted of a Jerguson gauge and a gas reservoir (250-mL capacity) mounted at the top. A magnetic pump was used to circulate the gas phase from the reservoir to the bottom of the gauge. The temperature of the cell was measured by ten-junction copper–Constantan thermopiles which had been calibrated at the ice and steam points. The pressure of the cell was measured by a Heise bourdon tube gauge. The equilibrium cell was housed in a constant temperature air bath controlled within ±0.5 °C. The chromatograph used in this work had a 10-ft long, ¼-in. o.d. column packed with Chromosorb 104. It was operated isothermally at 100 °C.

The Sulfinol solution, composed of 40 wt % DIPA, 40 wt % sulfolane (tetrahydrothiophene 1,1-dioxide), and 20 wt % water,