Solubilities of Sodium Gluconate in Water and in Aqueous Solutions of Ethanol and Methanol

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The solubility of sodium gluconate in water and in aqueous ethanol and methanol solutions was measured, over the temperature range 10 °C to 50 °C. The measurements were performed with ethanol solutions of (0 to 1.2) g of ethanol/g of water and with methanol solutions of (0 to 1.4) g of methanol/g of water. An equation was derived to calculate the solubility as a function of temperature and alcohol concentration, with the maximum relative deviation between experimental and calculated solubility values < 4% ($\cong$0.0035 g of sodium gluconate/g of water) for both ethanol and methanol systems.

Introduction

Sodium gluconate has found numerous practical applications, for example as a component of commercial cleansers and as a sizing agent in the paper industry. More recently it has been used for pharmaceutical purposes. Since the gluconate radical is nontoxic and is not metabolized in the animal body, the gluconic acid salts are utilized in mineral supplementation where the acid acts as a carrier of metal ions of therapeutic importance (Dutta and Bhattacharyya, 1975).

For use in industrial processes and scientific laboratories gluconate salts have to be separated and purified from mixtures obtained from glucose fermentative synthesis or from electrochemical or catalytic oxidation. Precipitation and crystallization are suitable for the separation of these salts. Because of their inherent solubility in water and partial solubility in alcoholic solutions, the utilization of aqueous alcoholic solutions as a precipitating agent is an interesting method.

These separation methods require the knowledge of the salt solubility. Some solubility data of sodium gluconate in water are found in the literature (Atkinson and Mavituna, 1991; *Ullmann's Encyclopaedia*, 1989), although nothing related to the purity of the compounds and to the experimental method used has been mentioned. No data are available on the solubility in ethanol and methanol aqueous solutions, and hence measurements were made.

Experimental Section

Solubility measurements were performed over the temperature range (10−50) °C using mainly the visual polythermal method developed by Clynne et al. (1981).

The experiments were carried out in a 50 mL glass vessel tightly closed with a ground glass stopper and equipped with a Teflon-coated magnetic stirrer. Solutions were prepared by mass with an uncertainty of ±0.1 mg. Analytical grade sodium gluconate (BDH, >99 mass%), ethanol (Merck, >99.8 mol %), and methanol (Riedel-de Haen, >99.8 mol %) were used without any additional purification. Deionized water (conductivity < 4 μS/cm) was also used. For each experiment, sodium gluconate, deionized water, and cosolvent were accurately weighed directly into the solubility cell, with the solid solute in excess. Methanol (or ethanol) was added to water in order to create solutions of various cosolvent + water mass ratios (between (0.0 and 1.2) g of ethanol/g of water and between (0.0 and 1.4) g of methanol/g of water). To prevent changes of solvent composition, due to evaporation, a minimum quantity of free volume was left in the inner part of the cell. This procedure is especially important at high temperatures. The vessel was immersed in a thermostated water bath controlled to ±0.1 K.

To dissolve the excess solid solute, the temperature of the solution was raised at a very slow rate. Prior to any temperature increase, the mixture was allowed to stand for a period of 3 h for temperature equilibration and to attain equilibrium between the remaining solid and the solution. It was found from independent studies that 3 h of agitation was sufficient to reach equilibration. The solution was moderately agitated to prevent the breakage of the crystals and, consequently, the supersaturation of the solution. Heating increments were made progressively smaller as the amount of salt decreased. The temperature at which the last crystal was dissolved is taken as the saturation point of the particular bulk composition.

Some solubility values were checked by means of the residue solid technique (Mullin, 1992). In this technique the solubility was determined by equilibrating the sodium gluconate crystals and the solution for 3 h at constant temperature. At the end of this time agitation was stopped and the equilibrium mixture was allowed to stand for about 2 h at constant temperature to enable any dispersed solid to settle. Samples of clear solutions (3 to 5) cm^3 were withdrawn using a syringe equipped with a microfilter (0.25 μm) and transferred to a container of known mass. The concentration of the saturated solution was determined from the mass of the solid residue obtained by evaporating to dryness a known mass of the sample. The difference between the results obtained by these two methods was <0.3%.

Temperature was measured in the thermostatic water bath with a mercury-in-glass thermometer (E 0.1/0/50 DIN12775) with a resolution of ±0.05 K. This thermometer was calibrated against the melting and normal boiling points of distilled water (maximum uncertainty of ±0.05 K). All solubility data reported in this study represent the average value of at least two independent measurements

Table 1. Solubility of Sodium Gluconate in Water

t/°C	S/(g/100 g of H_2O)	t/°C	S/(g/100 g of H_2O)
9.3	49.98	29.2	63.60
13.7	52.71	33.0	66.56
18.6	56.11	38.0	71.01
20.2	57.45	43.0	75.66
24.6	59.92	47.2	80.02

Table 2. Solubility of Sodium Gluconate in Ethanol Aqueous Solutions with Various Mass Ratios w (g of EtOH/100 g of water)

t/°C	S/(g/100 g of H_2O)	t/°C	S/(g/100 g of H_2O)
	$w = 5$		
9.6	40.11	27.6	53.23
12.9	42.50	34.0	58.40
16.2	44.90	39.4	63.48
22.8	49.46	45.6	69.07
	$w = 10$		
9.2	30.69	29.7	45.84
11.9	32.51	35.8	51.48
14.9	34.61	42.6	57.93
19.2	37.58	50.3	65.89
	$w = 20$		
9.2	17.99	33.3	35.36
13.5	20.79	38.1	39.84
19.9	25.22	46.6	47.84
26.0	29.49	49.3	50.54
	$w = 30$		
9.3	11.20	40.4	31.89
15.2	13.79	46.5	37.67
22.1	17.96	52.6	44.01
32.0	24.80		
	$w = 50$		
10.0	5.88	26.0	11.36
13.0	6.75	33.5	15.02
17.4	8.02	42.7	20.79
22.3	9.72	46.0	23.40
	$w = 80$		
9.7	3.12	33.0	8.02
13.1	3.48	38.9	9.73
21.3	5.02	44.0	11.80
27.7	6.34	52.0	15.78
	$w = 120$		
10.0	1.90	33.4	4.28
13.6	1.98	41.9	5.82
20.6	2.65	47.9	7.09
26.2	3.31		

Table 3. Solubility of Sodium Gluconate in Methanol Aqueous Solutions with Various Mass Ratios w (g of MeOH/100 g of water)

t/°C	S/(g/100 g of H_2O)	t/°C	S/(g/100 g of H_2O)
	$w = 10$		
10.2	32.24	37.2	54.56
15.2	35.81	41.3	58.03
19.8	39.71	45.3	62.45
24.5	43.29	51.2	69.13
31.5	49.32		
	$w = 20$		
10.1	20.42	30.0	34.56
14.8	23.05	33.4	37.17
17.6	25.32	41.2	44.24
25.2	30.53	45.3	48.33
28.0	32.71	51.1	54.21
	$w = 30$		
10.2	13.68	30.0	24.54
15.1	15.74	34.1	27.54
18.0	17.08	35.0	28.62
20.2	18.45	40.0	32.41
23.5	20.42	45.7	37.39
	$w = 50$		
10.5	7.56	27.8	13.21
13.6	8.34	30.0	14.20
15.6	8.92	36.0	17.42
18.2	9.53	40.2	19.37
23.4	11.42	44.6	22.46
		48.9	24.97
	$w = 80$		
10.4	4.19	30.0	7.67
14.7	4.66	36.6	9.63
17.1	5.10	39.5	10.36
20.2	5.61	44.7	12.17
26.6	6.91	48.7	13.79
	$w = 140$		
10.2	2.42	32.9	3.82
12.4	2.58	37.6	4.50
16.2	2.67	39.1	4.69
20.2	2.90	44.4	5.45
27.7	3.52	49.6	6.46

values, S/(g of salt/100 g of water), as a function of the alcohol content, W/(g of alcohol/100 g water), is

$$S = 1/(\sum_{i=0}^{3} A_i W^i) \qquad (1)$$

The A_i parameters were correlated with temperature (t/°C) for each type of alcohol, with the A_0 parameter being the solubility of sodium gluconate in water. The different correlations obtained as well as the regressed coefficient values are summarized in Table 4. Equation 1 allows us to predict the solubility of sodium gluconate for any temperature and any concentration of methanol or ethanol in the considered ranges. The mean relative standard deviation between the individual experimental data and those calculated by eq 1 is 1.02 and 1.12%, respectively, for the ethanol and methanol systems. As illustrated in Figures 1 and 2, the maximum relative deviation is <4% ($\cong$0.35 g of salt/100 g of water) for both systems.

Finally, the comparison to literature values is only possible for the solubility values obtained in pure water. As shown in Figure 3, the data available in the literature are scarce, showing the existence of some discrepancies even among literature data themselves. The estimated deviations from data in *Ullmann's Encyclopaedia* (1989) are about 5.7% and 2.6%, respectively, at 20 °C and 50 °C, while for the data of Atkinson et al. (1991), where the solubility value at 25 °C is presented, an acceptable

with a reproducibility of <±0.0003 g salt/g water. The solubility uncertainty is ±0.0005 g salt/g water, and the saturation temperature is accurate to ±0.1 K.

Results and Discussion

The experimental solubility results obtained in this work are reported in Tables 1−3. For all the systems studied the solubility of sodium gluconate in aqueous solutions of ethanol and methanol decreases with the increase in the alcohol content and the effect of temperature becomes less pronounced. The solubility of sodium gluconate in methanol solutions is slightly higher than that in ethanol solutions. Nevertheless, above 0.3 g of alcohol/g water and for the highest temperatures, the solubility values in both solutions became similar. As the alcohol content increases, the lower is the temperature value, which verifies that similarity.

To describe the solubility of sodium gluconate in the systems studied as a function of both composition and temperature, an equation was derived through the regression of the experimental results. Several equations were tested, and the one which best represents the solubility

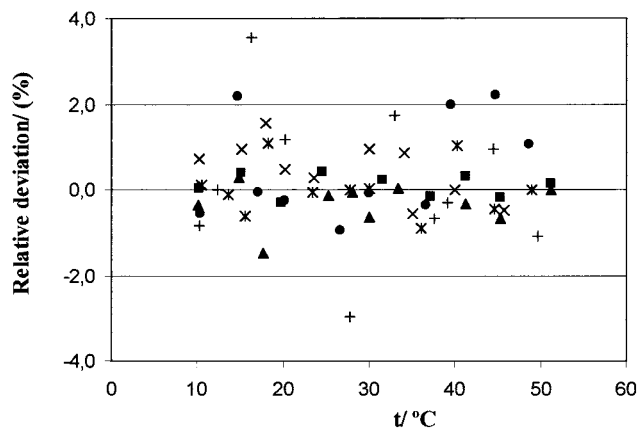**Table 4. Coefficients of the Model Eq 1[a]**

Water	
$A_0 = \exp(A_{00} + A_{01}t + A_{02}t^2)$	$A_{00} = -3.804\ 31$
	$A_{01} = -1.140\ 67 \times 10^{-2}$
	$A_{02} = -1.745\ 96 \times 10^{-5}$
Water + Ethanol System	
$A_1 = (A_{10} + A_{11}t + A_{12}t^2 + A_{13}/t) \times 10^{-4}$	$A_{10} = 8.754\ 99$
	$A_{11} = -1.801\ 27 \times 10^{-1}$
	$A_{12} = 1.271\ 70 \times 10^{-3}$
	$A_{13} = -4.320\ 00$
$A_2 = (A_{20} + A_{21}/t +$	$A_{20} = -1.820\ 00$
$A_{22}/t^2 + A_{23}/t^3) \times 10^{-5}$	$A_{21} = 1.160\ 00 \times 10^2$
	$A_{22} = -3.505\ 22 \times 10^2$
	$A_{23} = -4.740\ 00 \times 10^2$
$A_3 = (A_{30} + A_{31}/\ln t + A_{32}/(\ln t)^2 +$	$A_{30} = 9.980\ 00 \times 10^{-1}$
$A_{33}/(\ln t)^3) \times 10^{-7}$	$A_{31} = 6.007\ 15$
	$A_{32} = -4.175\ 03 \times 10$
	$A_{33} = 2.369\ 12 \times 10$
Water + Methanol System	
$A_1 = (A_{10} + A_{11}t + A_{12}t^2 + A_{13}t^3) \times 10^{-4}$	$A_{10} = 1.212\ 73 \times 10$
	$A_{11} = -5.772\ 60 \times 10^{-1}$
	$A_{12} = 1.301\ 11 \times 10^{-2}$
	$A_{13} = -1.103\ 46 \times 10^{-2}$
$A_2 = (A_{20} + A_{21}t + A_{22}t^2 + A_{23}/t) \times 10^{-5}$	$A_{20} = 6.792\ 01$
	$A_{21} = -2.236\ 93 \times 10^{-1}$
	$A_{22} = 2.115\ 47 \times 10^{-3}$
	$A_{23} = -8.329\ 03$
$A_3 = (A_{30} + A_{31}\ln t + A_{32}(\ln t)^2 +$	$A_{30} = 1.676\ 94 \times 10$
$A_{33}(\ln t)^3) \times 10^{-7}$	$A_{31} = -2.032\ 61 \times 10$
	$A_{32} = 7.116\ 86$
	$A_{33} = -7.728\ 80 \times 10^{-1}$

[a] $t^{all} \rightarrow (t/°C)$.
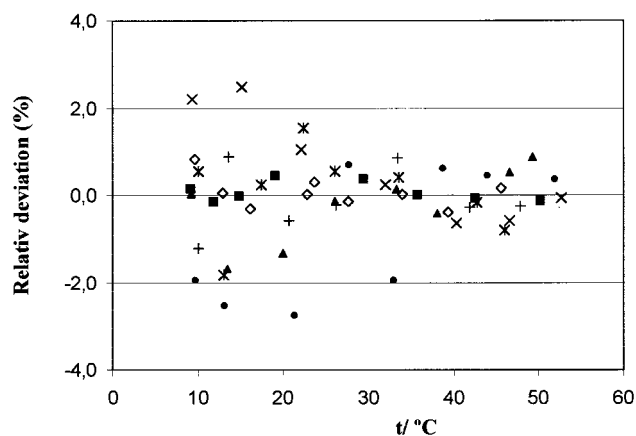
Figure 1. Relative deviations between measured solubility values and the ones calculated by eq 1 for ethanol aqueous solutions: ◇, 5 g/100 g; ■, 10 g/100 g; ▲, 20 g/100 g; ×, 30 g/100 g; ∗, 50 g/100 g; ●, 80 g/100 g; +, 120 g/100 g.
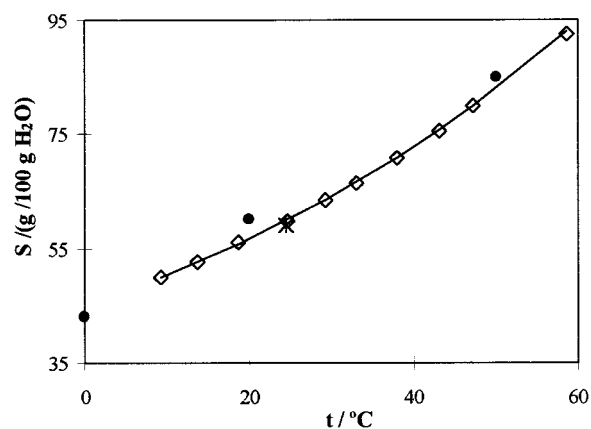

Figure 2. Relative deviations between measured solubility values and the ones calculated by eq 1 for methanol aqueous solutions: ■, 10 g/100 g; ▲, 20 g/100 g; ×, 30 g/100 g; ∗, 50 g/100 g; ●, 80 g/100 g; +, 120 g/100 g.

Figure 3. Solubility of sodium gluconate in water as a function of temperature: ◇, experimental values in this study; ●, *Ullmann's Encyclopaedia* (1989); ∗, Atkinson and Mavituna (1991); solid line, calculated by eq 1.

Literature Cited

Atkinson, B.; Mavituna, F. *Biochemical Engineering and Biotechnology Handbook*, 2nd ed.; Macmillan: Riverside, NJ,1991; p 1178.

Clynne, M. A.; Potter, R. W.; Haas, J. L., Jr. Solubility of NaCl in Aqueous Electrolyte Solutions from 10 to 100 °C. *J. Chem. Eng. Data* **1981**, *26*, 396−398.

Dutta, S. K.; Bhattacharyya, A. Preparation and Study of Some Alkali Metal Salts of Gluconic Acid Including Lithium Gluconate. *J. Appl. Chem. Biotechnol.* **1975**, *25*, 441−443.

Mullin, J. W. *Crystallisation*, 3rd ed.; Butterworth: Oxford, 1992; pp 108.

Ullmann's Encyclopaedia of Industrial Chemistry, 5th Completely rev. ed.; VCH: Weinheim, 1989; Vol. A12, p 454.

deviation of 1.5% is found. The differences observed can be related to the purity of the salt used in the determinations or to the experimental techniques employed. The solid line plotted in Figure 3 represents the solubility values calculated also by eq 1, where a good fitting is observed (deviations $<\pm 0.3\%$).