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USE OF SODIUM-SENSITIVE GLASS ELECTRODES FOR SOLUBILITY DETERMINATIONS

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Abstract.—A method applicable to concentrated solutions is described for converting activities, measured by cation-sensitive glass electrodes, to concentrations. The usual difficulty of assigning accurate values to activity coefficients is avoided by the use of a dilution technique. The method is applied to the determinations of the solubilities of borax, ulexite, and sodium chloride.

Following the initial discovery by Eisenman and others (1957) of practical sodium- and potassium-sensitive glasses, Garrels and others (1962) developed glasses specifically sensitive to divalent cations (Ca^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2}). An electrode fashioned from one of these glasses offers a convenient and rapid means of directly measuring cationic activity (conventionally defined), or of indirectly measuring concentration in aqueous solution.

Although only the sodium-sensitive electrode was used to measure the solubilities of sodium salts, the same procedure could be used for any salt containing a cation for which an electrode having the proper response is available, for example, potassium or ammonium salts, or the alkaline-earth salts. Similarly, the solubility of a given salt in the presence of any ionic medium not affording a common cation could be determined.

In general, the conversion of a measured ionic activity (a_i) to a concentration (c_i) requires the use of an accurate value of the appropriate ionic-activity coefficient (γ_i), where $c_i = a_i/\gamma_i$. The activity coefficient depends upon the total ionic strength of the solution. In saturated solutions of many readily soluble salts, such as the sodium borates, the concentration, and hence the ionic strength (I) is high, and the cation is complexed in an unknown way. As a result, there is no way to assign accurate values of cation-activity coefficients. We have evolved a technique that bypasses this difficulty. This technique involves making cation-activity measurements on successive ten-fold dilutions of a saturated solution of the salt whose solubility is to be measured. When the solution becomes very dilute, this fact is revealed by its electrochemical behavior. Because the solution is very dilute and any complexing will be vanishingly small, the cation-activity coefficient can be calculated from the Debye-Hückel equation. The concentration of this dilute solution can be calculated, and because the number of dilutions is known, the original concentration can then be established.

Using a sodium-sensitive electrode we have determined the solubilities of borax (at 25°C and 40°C), ulexite (at 25°C, incongruent solution), and sodium chloride (at 25°C). The values determined by the present method are in excellent agreement with those determined by conventional methods, as shown in table 156.1.

PROCEDURE AND THEORETICAL BASIS

The sodium-sensitive electrode used in this work was the Electronics Instruments Laboratory model Na GNA 23. This electrode was paired with a saturated-KCl calomel reference electrode (wick type), and the developed potential was measured with a vibrating capacitor high-impedance electrometer, and a potentiometer. Potential measurements were made on solutions maintained at 25°C±0.05°C in a constant-temperature bath and stirred with a magnetic stirrer. The voltage measurements were generally accurate to ±0.1 mV, with an occasional reading doubtful to ±0.2 mV. Because the electrode is also sensitive to hydrogen ions, pH must be maintained ≥7; at sodium-ion concentrations below about 10^{-4} m (molal), the hydrogen-ion response of the electrode introduces error. The usual precautions were maintained with regard to adequate electrical shielding in working with the high resistance glass electrode (Mattock, 1961). The electrode was conditioned by soaking for several days in 0.1 m NaCl solution.

TABLE 156.1.—*Values of solubilities of sodium chloride, borax, and the sodium-ion concentration resulting from the incongruent solution of ulexite, determined by* Na-*sensitive electrode, compared with literature values* [1]

This study			Literature	
f [2]	M [3]	Weight percentage [4]	Weight percentage [4]	Reference
Sodium chloride, 25°C				
....	5. 40	26. 4	26. 48	Gillespie (1928, p. 105).
....	5. 41	26. 4		
4. 62	....	27. 0	....	Density $= 1.1978$ g/cm³ (Gillspie, 1928, p. 105).
4. 53	....	26. 5		
Borax (as $Na_2B_4O_7$), 25°C				
0. 151	....	3. 04	3. 06	Menzel and Schulz (1940).
0. 150		3. 03		
0. 152	....	3. 05	3. 13	Blasdale and Slansky (1939).
Borax (as $Na_2B_4O_7$), 40°C				
0. 308	....	6. 20	6. 00	Menzel and Schulz (1940), and Blasdale and Slansky. (1939).
Ulexite (as $NaCaB_5O_9$), 25°C				
....	0. 0187	[5] 0. 49	....	....
....	0. 0186	0. 49	....	....

[1] The accuracy of the experimental results is best judged by internal consistency, and by comparison with the literature values. The limiting precision is determined by the ±0.1 mV reproducibility of the voltage measurements; an error of 0.1 mV leads to an error of about 0.4 percent in the solubility determination.
[2] Weight dilution method.
[3] Volume dilution method.
[4] Grams of solute per 100 g of solution.
[5] Incongruent solution; only sodium-ion concentration measured.

The potential of the cell, E, is given by a Nernst-type equation

$$E \text{ (volts)} = E' + (RT/\mathcal{F})ln[Na^{+1}], \qquad (1)$$

where R, T, and $\mathcal{F}$ have their usual significance. E' is a constant voltage and includes any liquid junction potential. E' has the value E at unit activity of sodium ion, $[Na^{+1}] = 1$. At 25°C, equation 1 becomes

$$E = E' + 0.0592 \log [Na^{+1}]. \qquad (2)$$

In practice, E' is not evaluated, but rather the difference in potential of the cell is determined with the unknown solution and with a solution whose sodium ion activity is known. This procedure minimizes the uncertainty due to the liquid-junction potential. From equation 2 we obtain the following operational equation:

$$E_x - E_s = 0.0592 (\log [Na^{+1}]_x - \log [Na^{+1}]_s), \qquad (3)$$

or

$$E_x - E_s = 0.0592 (pNa_s - pNa_x), \qquad (4)$$

where x=unknown and s=standard. Equation 4 is of exactly the same form as the one on which the measurement of pH is based (Bates, 1954).

The Na GNA 23 electrode was checked against a series of standard NaCl solutions (1 m to 10^{-4} m), and found to have exactly the theoretical slope predicted by equation 4, namely

$$dE_s/dpNa_s = 0.0592 \text{ volts}.$$

The sodium molality of each standard solution was converted to sodium activity by the relation

$$[Na^{+1}] = \gamma_{Na^{+1}} \times m_{Na^{+1}}, \qquad (5)$$

where the activity coefficient $\gamma_{Na^{+1}}$ was obtained by the "mean-salt" method (Garrels, 1960), in which

$$\gamma_{Na^{+1}} = \gamma^2_{\pm NaCl}/\gamma_{\pm KCl}$$

for ionic strength $I \geq 0.1$, and by the Debye-Hückel equation for $I < 0.1$ (Klotz, 1950, p. 329). Values of $\gamma_{\pm KCl}$ and $\gamma_{\pm NaCl}$ were taken from Lewis and Randall (rev. ed., 1961, p. 643), and Robinson and Stokes (1959, p. 492), respectively.

The standard solution used in a given determination was either 0.1 m NaCl, with $\gamma_{Na^{+1}} = 0.79$ (mean-salt), $pNa = 1.10_2$; or 0.01 m NaCl with $\gamma_{Na^{+1}} = 0.902$ (Debye-Hückel), $pNa = 2.04_5$, or both. It was found that the solubility determinations were completely consistent with both of these single-ion activity coefficients, which attests to the validity of their value in practical problems.

Saturated solutions of the salts were prepared by shaking the solutions in contact with excess solids, over a period of about 3 weeks. One method of doing this was to impart mechanically a rocking motion to a 125-ml rubber-stoppered flask containing solution plus solid, in a constant-temperature bath maintained at ±1°C. In a second method the solution plus solids, contained in 125-ml Teflon bottles, were immersed in a constant-temperature bath held at ±0.1°C; the bottles were removed twice daily and vigorously shaken by hand. In the case of the mechanically shaken system, the grain size of the excess NaCl was sufficiently large that the supernatant liquid could be sampled directly with a pipet; this was not true with the less soluble borax and ulexite. In those experiments in which the bottles were shaken by hand all the solids remained finely crystalline, and the liquid was drawn by suction through a coarse-frit filter in order to remove small crystals.

As previously stated, the voltage measurements were all made at 25°C. For the 25°C solubility measurements, the potential of the cell was measured with the

saturated solution as the test solution. Following this, in one set of experiments, a 10-ml portion of the saturated solution was delivered to a calibrated 100-ml volumetric flask by means of a calibrated pipet, and diluted to 100 ml; the potential of this solution was then measured. This procedure was repeated stepwise to and including the 1:1,000 dilution.

The volume-dilution procedure leads to concentrations in units of molarity (M, moles of solute per 1,000 ml solution). In a second set of experiments a weight-dilution technique was employed; this technique leads to concentrations in units of formality (f, moles of solute per 1,000 solution). Whether volume dilution or weight dilution was used in a particular determination is indicated in table 156.1.

There is an internal formal inconsistency in the calculations because the values of the activity coefficients employed are based on the molal scale (m, moles of solute per 1,000 g solvent). However, for $\gamma_{Na^{+1}}$ values from the mean-salt method, and especially for $\gamma_{Na^{+1}}$ values calculated by the Debye-Hückel method for the very dilute range, any changes resulting from a change in scale from molal to molar or formal would be outside the limits of error of the method.

As the test solution becomes progressively dilute, with fewer sodium ions available to ensure stable equilibrium between the electrode surface and the solution, fluctuations in the voltage readings become larger. At the same time, the relative activity of hydrogen ions increases and the electrode begins to respond to these ions. For these reasons a decision must be made concerning the best dilution stage at which to calculate the concentration. This stage will depend upon the solubility of the salt, and will reveal itself through the magnitude of the measured activity. In general, it is best to use the highest concentration that shows the Nernst-type behavior of equation 2. In this study we choose the 1:1,000 dilution (of the saturated solution) of NaCl, the 1:100 dilution of borax, and the 1:10 dilution of ulexite.

The tabulated values given by Klotz (1950, p. 332) for the Debye-Hückel equation

$$-\log \gamma_i = \frac{Az^2 I^{\frac{1}{2}}}{1 + Ba_i I^{\frac{1}{2}}},$$

for $10^8 a_i = 4$, and for 25°C, were used to construct a plot of $\gamma_{Na^{+1}}$ vs. I; values of $\gamma_{Na^{+1}}$ were read from this plot for the diluted solutions. The ionic strength, $I = \frac{1}{2}\sum_i m_i z_i^2$, must be evaluated differently for each substance, depending upon the charges of the anions assumed to be present to balance the Na^{+1}. For NaCl, $I = m_{Na^{+1}}$; for borax, in the absence of specific knowledge, it was assumed that each Na^{+1} is balanced by a singly charged

borate anion (Ingri and others, 1957), so that here also $I = m_{Na^{+1}}$. Ulexite, $NaCaB_5O_9 \cdot 8H_2O$, in excess, in equilibrium with water at 25°C, yields a Na-rich borate solution and inyoite, $Ca_2B_6O_{11} \cdot 13H_2O$ (Kurnakova and Nikolaev, 1948). Thus, the measurement here yields the sodium-ion concentration in equilibrium with excess ulexite and in the presence of inyoite. From the data of Kurnakova and Nikolaev (1948) on the CaO-B_2O_3-H_2O system, the solution in equilibrium with inyoite at 25°C is $1.32 \times 10^{-2} M$ with respect to Ca^{+2}. We assume as a rough guess that the presence of the common singly charged borate ion depresses this value to one-half in the case of the solution in equilibrium with both ulexite and inyoite, and calculate the ionic strength on this basis.

In all cases, in calculating I it is first assumed that the measured activity is equal to the molality, and a provisional γ_i found. This provisional γ_i is divided into the activity to find the next approximation to the molality and a new γ_i is looked up, following which a new molality is calculated (see table 156.2); in this work, only two stages of iteration were necessary. Fortunately, γ_i changes relatively slowly as a function of I over the dilute-solution region, so that no appreciable error results in the calculated concentration in those cases where I cannot be evaluated precisely.

TABLE 156.2.—*Determination of solubility of NaCl at 25° C by volume-dilution method*

$$E_x - E_s = 0.0592 \, (pNa_s - pNa_x)$$

$E_s = 41.0$ mV for 0.1 m NaCl; $pNa_s = 1.102$ [1]
$E_s = -14.9$ mV for 0.01 m NaCl; $pNa_s = 2.045$ [1]

Dilution stage	E_x (mV)	pNa_x (0.1 m std.)
Sat. sol.	168.2	−1.047
1:10	84.3	0.371
1:100	27.0	1.338
1:1,000	−30.0	2.301

For the 1:1,000 dilution

$$-pNa_x = \frac{-30.0 - 41.0}{59.2} - 1.102 = -2.301$$

$$pNa_x = 2.301 \, [1]$$

or

$$-pNa_x = \frac{-30.0 + 14.9}{59.2} - 2.045 = -2.300$$

$$pNa_x = 2.300 \, [1]$$

$[Na^{+1}] = 5.00 \times 10^{-3}$; $\gamma_1 = 0.927$; $c_1 = (5.00 \times 10^{-3})/(0.927) = 5.39 \times 10^{-3}$; $\gamma_2 = 0.925$; $c_2 = (5.00 \times 10^{-3})/(0.925) = 5.40 \times 10^{-3}$; $M = 5.40$

[1] Third place after the decimal uncertain.

RESULTS AND SUMMARY

The final solubility values determined by the electrode method are listed in table 156.1. To show how the experimental procedure leads to a solubility value,

the details of one determination on NaCl are given in summary form in table 156.2.

The investigation reported upon here was an exploratory one only, and had as its sole purpose the testing of the principle of the method; no real attempt was made to achieve the best possible accuracy. It seems clear that this dilution technique can be used to measure solubilities with a fair degree of confidence, even with simple techniques. To measure accurately the solubility of a substance at an elevated temperature, a better technique than that employed by us of separating solids from liquid would be needed.

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