Activity Coefficients of NaCl in the System $NaCl$-$NaClO_4$-H_2O at 25° C, and the Use of Amalgam Electrodes

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A sodium amalgam electrode was used to measure the activity coefficients of NaCl in $NaCl$-$NaClO_4$-H_2O mixtures at ionic strengths of 0.1 and 1.0 mole kg^{-1}. The results at the lower ionic strength agree with the predictions of the Brønsted-Guggenheim specific interaction theory and the results at the higher ionic strength are in accord with isopiestic measurements. The use of alkali amalgam electrodes in mixed electrolyte solutions is discussed.

THERE has been renewed interest (*1, 5*) in measuring activity coefficients in mixed electrolyte solutions by emf methods. In this paper the results are given for the measurement of the activity coefficients of NaCl in $NaCl$-$NaClO_4$-H_2O mixtures at total ionic strengths of 0.1 and 1.0 mole kg^{-1}. The purpose of the measurements at the lower ionic strength is to test the validity of the Brønsted-Guggenheim specific interaction theory (*3*) for mixed electrolyte solutions. Such direct tests have previously been restricted to mixed acid-salt systems (*6*) and the results have supported the theory in these 1 to 1–1 to 1 systems. Measurements were made at the higher ionic strength, for comparison with the results obtained by the isopiestic method, to confirm that the amalgam electrode was operating reversibly.

EXPERIMENTAL

Materials. The sodium chloride was prepared from British Drug Houses' analytical reagent grade material by the method of Pinching and Bates (*8*), and was shown by test (*12*) to contain less than 0.002 mole % bromide. The same manufacturer's laboratory reagent sodium perchlorate "low in chloride" (<0.002%) was used. This material has since been shown to contain traces of carbonate (*7*). A stock solution of sodium perchlorate was analyzed by evaporating weighed portions to dryness and then heating the solid at 175° C for 28 hours before weighing. Further heating at 350° to 400° C produced no significant change in weight. Agreement among the three determinations was ±0.002%. Solutions were prepared by combining suitable amounts of this stock solution with weighed amounts of solid sodium chloride and distilled water.

Apparatus and Method. The emf of cells of the following type were measured:

$$NaHg_x|NaCl(m_2), NaClO_4(m_3)|AgCl|Ag$$

Mean activity coefficients of NaCl in the mixtures were calculated using the relation

$$E = E^\circ - 0.059158 \log m_{Na^{+}} \cdot m_{Cl^{-}} \gamma_2^2 \qquad (1)$$

The same amalgam concentration was used for all the reported measurements; checks of the emf of cells containing $0.1m$ NaCl alone were made during the course of the work and this enabled an E° for the cell to be calculated from Equation 1 by using a published value (*10*) for the mean activity coefficient of $0.1m$ NaCl.

The cell vessel and technique were similar to those used by Smith and Taylor (*11*). Care was taken to exclude oxygen from the cells by repeated evacuation of the apparatus and flushing with pure nitrogen. A flowing amalgam, of concentration about 0.02% by weight, was used; there was some indication that the emf was dependent on the flow rate of the amalgam. This effect was of the order of a few hundredths of a millivolt over the range of flow rates that was possible. A constant flow rate of about 2-ml per minute was achieved for all the reported measurements by having the stopcock on the amalgam electrode completely open while the emf was being determined. It is essential to deoxygenate the electrolyte completely for the satisfactory operation of the amalgam electrode. In this case nitrogen which had been freed of oxygen by passing over hot reduced copper was bubbled through a presaturator and then through the cell solution to displace dissolved oxygen. Under these circumstances it is not essential that the electrolyte should flow through the cell but, as this was not difficult to achieve with the apparatus used, the solution was set flowing past the amalgam electrode at the rate of 4 to 6 ml per minute while the emf was being measured. The cells were thermostated at 25° ± 0.01° C.

Bases for the thermal-electrolytic silver–silver chloride electrodes were formed by sealing pairs of platinum spirals

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Table I. Mean Activity Coefficients of NaCl in System NaCl-$NaClO_4$-H_2O, at 25° C

Cell $NaHg_x|NaCl(m_2), NaClO_4(m_3)|AgCl|Ag$ $E^\circ = 2.04243$ volts

m_2, Mole Kg^{-1}	m_3, Mole Kg^{-1}	E, Volts	$-\log \gamma_2$	Δ	
0.1	0	2.17362	0.1088	−2	$\log \gamma_{2(0)} = -0.10878 \pm 0.00009$ $\alpha_{23} = -0.0098 \pm 0.0017$
0.09	0.01	2.17632	0.1087	−2	
0.07	0.03	2.18274	0.1084	+9	
0.05	0.05	2.19136	0.1082	+9	
0.03	0.07	2.20449	0.1083	−21	
0.01	0.09	2.23266	0.1078	+10	
1.0	0	2.06402	0.1825	−29	$\log \gamma_{2(0)} = -0.18221 \pm 0.00027$ $\alpha_{23} = -0.0019 \pm 0.0005$
0.9	0.1	2.06669	0.1821	−8	
0.7	0.3	2.07307	0.1815	+14	
0.5	0.5	2.08163	0.1808	+45	
0.3	0.7	2.09473	0.1806	+27	
0.1	0.9	2.12300	0.1810	−51	

Δ = (log of experimental activity coefficient − log of value calculated by least squares) × 10^5.

in extended soda glass joints. The electrodes were aged in 0.1m NaCl which was deoxygenated by bubbling nitrogen. A day after preparation the bias potentials of a batch were usually less than ±0.02 mv on comparison with an aged reference electrode.

The experimental cells were opposed by an unsaturated Eppley cell and the resultant emf was measured with a Pye potentiometer (catalog No. 7565), used in conjunction with a Scalamp galvanometer (catalog No. 7904/S) and a certified Weston standard cell. The makers guarantee the accuracy of the potentiometer to 0.1 mv, but it is likely that the difference in potential of two cells can be determined more accurately.

Errors. The square root of the sum of the squares of the errors due to temperature fluctuation, concentration of solution, and response of the electrodes is about 0.03 to 0.04 mv. The scatter of the experimental results suggests that the error due to the potentiometer is small.

RESULTS AND DISCUSSION

The activity coefficients of NaCl in the mixed solutions are listed in Table I. A least squares calculation was used to fit the mean activity coefficients to the Harned rule (*4*) expression,

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{23} m_3$$

where subscript 2 refers to NaCl, subscript 3 to $NaClO_4$, and α_{23} is a constant at constant total ionic strength. The errors listed are the standard errors obtained in the least squares calculation.

It is obvious that the variation of the mean activity coefficients of NaCl in these solutions obeys Harned's rule. The value of α_{23} at an ionic strength of 0.1 mole kg^{-1} may be calculated from the following equation, using the accepted values of the specific interaction coefficients (*3*), $\beta_{Na, Cl} = 0.15$ mole^{-1} kg and $\beta_{Na, ClO_4} = 0.13$ mole^{-1} kg,

$$\alpha_{23} = \frac{1}{2.303} (\beta_{Na, Cl} - \beta_{Na, ClO_4})$$

This is the equation given by Pitzer and Brewer (*6*) except that their interaction coefficients B have been replaced by $2/2.303\ \beta$. The value obtained for α_{23} is +0.009. An increase in $\log \gamma_\pm$ for $NaClO_4$ at 0.1m, of 0.0035 would increase β_{Na, ClO_4} by 0.04. As the activity coefficient of $NaClO_4$ was deduced from isopiestic measurements, an error of this magnitude is possible. The calculated value of α_{23} would then be within a standard deviation of the experimental result. Therefore, within the limits imposed by the errors, the value of α_{23} calculated by the Brønsted-Guggenheim theory agrees with the experimental value.

Two other investigations support the claim that the cells were operating reversibly. Lanier (*5*) investigated this system using a glass electrode responsive to sodium ions and he also quotes the results which Scatchard and Yoest (*13*) obtained using the isopiestic method. These results are compared in Table II.

Amalgam Electrodes in Mixed Electrolyte Systems. The use of alkali amalgam electrodes in mixed electrolyte systems requires close scrutiny. In the experiments reported above, the potentials appeared to be completely reversible and the agreement with the isopiestic results indicates that the perchlorate ion is not susceptible to reduction by the amalgam.

A system for which this type of measurement might be expected to fail is NaCl-KCl-H_2O. Butler, Huston, and Hsu (*2*) have shown recently that this is so, using a sodium amalgam electrode. Prior to the publication of their report we had attempted to measure the activity coefficients of NaCl and KCl in this system using amalgam electrodes. We can confirm their conclusion that the sodium amalgam electrode behaves irreversibly and their prediction that the potassium amalgam electrode would behave similarly. Comparison of our results with Robinson's (*9*) isopiestic data shows that the potassium amalgam electrode gives values in even greater error than those obtained with the sodium amalgam electrode. An additional observation is that it is not obvious that an amalgam electrode is malfunctioning when it is operated in a solution in which the main cation component is that to which it is supposedly reversible—the electrode appears to be well poised. However, as the fraction of the foreign cation is increased the irreversible behavior becomes apparent.

Table II. α_{23} for NaCl-$NaClO_4$-H_2O System by Three Methods

Ionic Strength, Mole Kg^{-1}	Scatchard and Yoest (*13*)	Lanier (*5*)	Present Work
0.1	. . .	. . .	−0.0098 ± 0.0017
1.0	−0.003	0.000	−0.0019 ± 0.0005
3.0	0.003	0.003	. . .
6.0	0.011	0.010	. . .

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Vapor-Liquid Equilibrium at Atmospheric Pressure

Carbon Disulfide–Methanol System

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Isobaric vapor-liquid equilibrium was established for the heterogeneous system carbon disulfide–methanol at 760 mm of Hg pressure, using a modified Smith-Bonner still. Liquid-phase activity coefficients were calculated; the data were thermodynamically consistent. The binary constants for the NRTL (nonrandom, two-liquid) equation of Renon and Prausnitz were determined.

SEVERAL industrial processes, particularly those for manufacturing rayon, pulp, and related products, require separating carbon disulfide from methanol. Vapor-liquid equilibrium values of this system, however, have been reported only at 20° C (*3*). Therefore, vapor-liquid equilibrium data at atmospheric pressure and the boiling point were determined.

MATERIALS

A commercially available 99.9 mole % carbon disulfide was used. Chromatographic analysis was carried out on a 6-foot column of Porapak Type Q (120- to 150-mesh) (*1*) at 100° C. Analysis indicated three trace impurities. The methanol, commercial practical grade, was dried over calcium chloride and distilled three times. The distillate was 99.9 mole % methanol; the impurity was less than 0.10 mole % water. Table I compares the literature and experimental values of the physical properties of these materials.

EXPERIMENTAL PROCEDURE AND ANALYSIS

The vapor-liquid experimental procedure was reported by Smith and Bonner (*7*). Samples of carbon disulfide and methanol were weighed and mixed in various concentrations. These heterogeneous samples were made homogeneous by adding an equal volume of dry 2-propanol. The calibration curve of carbon disulfide–methanol was determined by gas chromatography.

Approximately 500 ml of a carbon disulfide–methanol mixture were weighed into the still. The still was allowed to operate for about 1 hour, the 5° C differential between liquid and vapor temperature being maintained as closely as possible. The temperature was recorded and a 2-ml condensate sample drawn off through an auxiliary cooler, with an equal volume of dry 2-propanol added to make the samples homogeneous for gas chromatographic analysis. The composition of the liquid phase was assumed that of the still. Between runs, the still was cleaned by refluxing acetone in it for 20 minutes and then drying it under vacuum.