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W. Van Doorne
Calvin University

T. P. Dirkse
Calvin University

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W. Van Doorne and T. P. Dirkse*

Department of Chemistry, Calvin College, Grand Rapids, Michigan 49506

ABSTRACT

A study of supersaturated zincate solutions is made using light scattering and nuclear magnetic resonance techniques. The results indicate strongly that the excess zinc is present as a solute species rather than in a colloidal form. The solute species appears to be the same as that in solutions of ZnO in aqueous KOH, viz., $Zn(OH)_4^{2-}$. There is no strong evidence to indicate the presence of other solute species.

When metallic zinc is treated anodically in aqueous KOH the surface often becomes dark in color and, if the treatment is continued long enough, a white solid precipitates from the solution. Both the white solid and the dark film on the metal are zinc oxide. Thus, the end product of the anodic treatment appears to be ZnO. However, ZnO is soluble in aqueous KOH. For some time it was believed that the solution from which the white solid precipitated was a saturated solution of ZnO in KOH. But further investigation (1) disproved this assumption. Instead, it was shown that the dissolved Zn(II) content of the electrolyte decreased and after about a year approached that of a saturated solution of ZnO. Meanwhile, a white solid continued to precipitate from the solution.

This phenomenon has been known for some 20 years and it is of significance for batteries containing a metallic zinc electrode and an aqueous KOH electrolyte. However, very little work has been done with these so-called "supersaturated" zincate solutions (szs).

A variety of evidence suggests that in a saturated solution of ZnO in aqueous KOH the dissolved Zn(II) species is primarily $Zn(OH)_4^{2-}$ (2-4). Very little work has been done to determine the nature of the dissolved Zn(II) species in the szs. Dirkse (1) measured the emf of a zinc electrode in various szs and interpreted the results as indicating that $Zn(OH)_4^{2-}$ is also the predominant species in szs. However, this suggestion has been called into question. It has been suggested, e.g., that the excess Zn(II) in the szs is in a colloidal form and there is evidence to support this, e.g., the slow precipitation of the excess Zn(II) as ZnO. Hampson et al. (5) on the basis of emf measurements concluded that the excess Zn(II) in szs is electrochemically inactive. A Raman spectra investigation (6) showed that the Zn(II) species in saturated solutions of ZnO in aqueous KOH is a tetrahedral zinc-hydroxy arrangement. With anodic treatment of zinc in a 40% KOH solution saturated with ZnO the dissolved Zn(II) content increased about 70%, but the area under a band typical of $Zn(OH)_4^{2-}$ increased only about 12% and no new bands were observed. The conclusion is that about 1/6 of the excess Zn(II) is converted to

$Zn(OH)_4^{2-}$. The nature of the remaining 5/6 was not determined.

In the early work with szs, it was observed (1) that the specific conductance of the solution decreased with increasing excess Zn(II). This may have been due to increased viscosity of the solutions and/or to replacement of OH^- ions by the zinc-hydroxy species.

In summary, on the basis of the work done to date it is not possible to describe precisely the nature of the excess Zn(II) in the szs. The work reported here was carried out in an attempt to gather more information about these szs solutions. Two techniques were used: (i) light scattering, and (ii) nuclear magnetic resonance (NMR). The light scattering technique may give information as to whether or not the Zn(II) in the szs is in a colloidal form. The NMR technique provides information about the environment of the protons in the solutions. This environment is averaged over all possible proton locations (i.e., in water, hydroxide ions, and Zn species). Because of rapid exchange of protons among these locations the NMR technique cannot distinguish between the various proton-containing species.

The initial investigation of the ZnO-aqueous KOH system by NMR techniques was reported by Newman and Blomgren (4). Their investigation covered a series of KOH concentrations ranging from 3.89 to 13.62 molal and ZnO concentrations nearly up to the saturation point for each of the KOH solutions. The analysis of Newman and Blomgren shows that the formulation $Zn(OH)_4^{2-}$, as the primary Zn(II) species, is consistent with the chemical shift values. The present work employs a similar technique but extends the range of ZnO concentrations into those of the szs.

Experimental

The light scattering results were obtained by the use of a Coleman Universal spectrophotometer with a nephelometric attachment. The NMR spectra were obtained using a Jeolco MH60 spectrometer, operating at 60 MHz. Water was used as the external reference. After allowing time for obtaining temperature equilibrium in the sample, each spectrum was scanned five consecutive times.

Three stock solutions of KOH were prepared using reagent grade KOH. Saturated solutions of ZnO were made by dissolving the maximum of reagent grade

ZnO in each of the KOH solutions, followed by filtration through a Pyrex frit. Unsaturated solutions of varying ZnO concentrations were prepared by mixing appropriate amounts of pure KOH solution and the KOH solutions saturated with ZnO. A supersaturated Zn(II) solution was made by anodic oxidation of metallic zinc in a saturated ZnO solution. Solutions with varying degrees of supersaturation were made by mixing the saturated and supersaturated solutions in varying ratios. All zinc analyses were made by titration with EDTA.

Results and Discussion

Light scattering.—A saturated solution of ZnO in $2.8M$ KOH [$0.13M$ in Zn(II)] was used as a reference and to set the galvanometer to 0. Next a szs solution [$2.8M$ KOH $+ 0.35M$ Zn(II)] was placed in the same cuvette and the galvanometer then read 3%. This is within the experimental uncertainty associated with making these measurements. In a second run a saturated solution of ZnO [$10.2M$ KOH $+ 1.12M$ Zn(II)] was placed in the cuvette and the galvanometer set to read 0. When a szs [$10.2M$ KOH $+ 1.5M$ Zn(II)] was placed in the same cuvette the galvanometer read 0%. Thus, in both these cases the szs showed no or negligible increased light scattering compared to the saturated ZnO solutions. These results indicate the absence of colloidal material. It has been argued that the light scattering results are dependent on the refractive indices of the substances involved and that in these cases the refractive indices are such that even though there is colloidal material present no light scattering is observed. It has been observed under magnification that a pronounced refractive index change occurred around the zinc electrodes during discharge, *i.e.*, during anodic treatment (6, p. 34). This argument has been used often when solutions of ZnO in aqueous KOH are said to be optically clear. However, the fact that NMR results also support the absence of colloidal material (see below), seems to make it reasonable to state that the szs solutions contain no appreciable amounts of colloidal material.

Nuclear Magnetic Resonance.—All spectra showed a single peak for the external reference and a sharp, single, downfield peak for the KOH-ZnO solution. A typical scan is shown on Fig. 1.
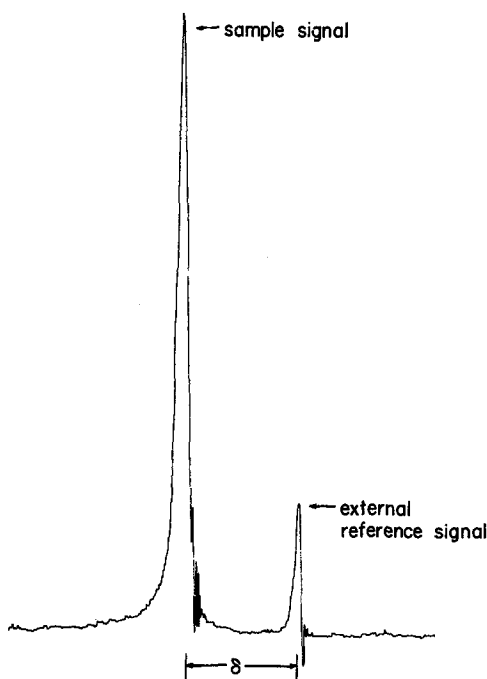
The five chemical shifts relative to water were measured for each sample and averaged to give the uncorrected chemical shift, δ. The standard deviation was 0.4 Hz for a typical set of five values.

Since an external reference was used, bulk susceptibility corrections were made using the equation given by Pople, Schneider, and Bernstein (7)

$$\delta = [(H - H_r)/H_r] + (2\pi/3)(\chi_{v,r} - \chi_v) \qquad [1]$$

χ_{v1} and χ_v refer to the volume magnetic susceptibilities of reference and sample. χ values were obtained from the table given by Selwood (8) and it was assumed that the additivity law

$$\chi_v = \phi_1\chi_1 + \phi_2\chi_2 + \ldots + \phi_n\chi_n \qquad [2]$$

was obeyed. (ϕ represents the volume fraction of each component.)

The change in the chemical shift, δ, from that of the pure KOH solution, caused by the addition of ZnO, is defined as $\Delta\delta$.

As is shown in Fig. 2, $\Delta\delta$ increases with increasing Zn concentrations, and the slope of the lines increases with increasing KOH concentrations. The linearity of these plots, as has been observed by Newman and Blomgren (4), is consistent with the existence of a single Zn-containing species. Evidence from other authors suggests that this species is the tetra-coordinated ion Zn(OH)$_4^{2-}$ (2, 3).

Figure 3 gives a plot of $\Delta\delta$ *vs.* the increasing mole ratio of KOH to ZnO. In a similar graph, Newman and Blomgren found possible discontinuities in the two curves of lowest KOH concentrations (2.89 and 4.83M).

These discontinuities were tentatively attributed to second coordination sphere effects. Although our curve for the lowest KOH concentration (2.9M) also shows an increase at a mole ratio of about 11, we feel that this must be viewed with caution since the increase is less than twice the standard deviation of the δ-values, and may be due to normal statistical scatter.

In Fig. 2, 3, and 4 the dotted vertical line indicates the limit of normal solubility of ZnO in each of the KOH solutions. Neither Fig. 2 nor Fig. 3 shows a statistically significant discontinuity or change of slope on passing from the unsaturated into the supersaturated region. The absence of such a discontinuity is consistent with the view that in both the unsaturated and supersaturated regions only one type of Zn complex exists, namely Zn(OH)$_4^{2-}$.

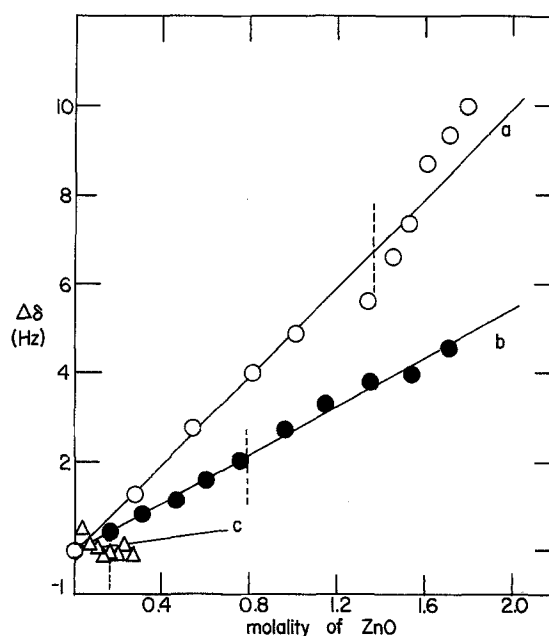Fig. 1. Typical nuclear magnetic resonance scan

Fig. 2. Change in chemical shift with added ZnO at different base strengths: *a*, 12.2M KOH; *b*, 7.3M KOH; *c*, 2.9M KOH.
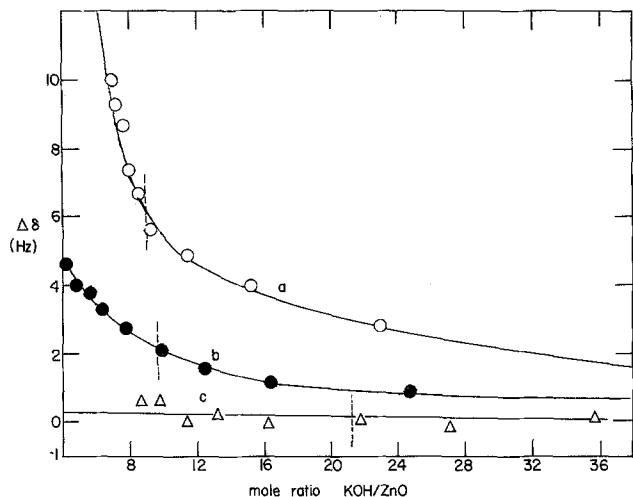
Fig. 3. Change of chemical shift with increasing mole ratio of KOH to ZnO at different base strengths: a, 12.2M KOH; b, 7.3M KOH; c, 2.9M KOH.
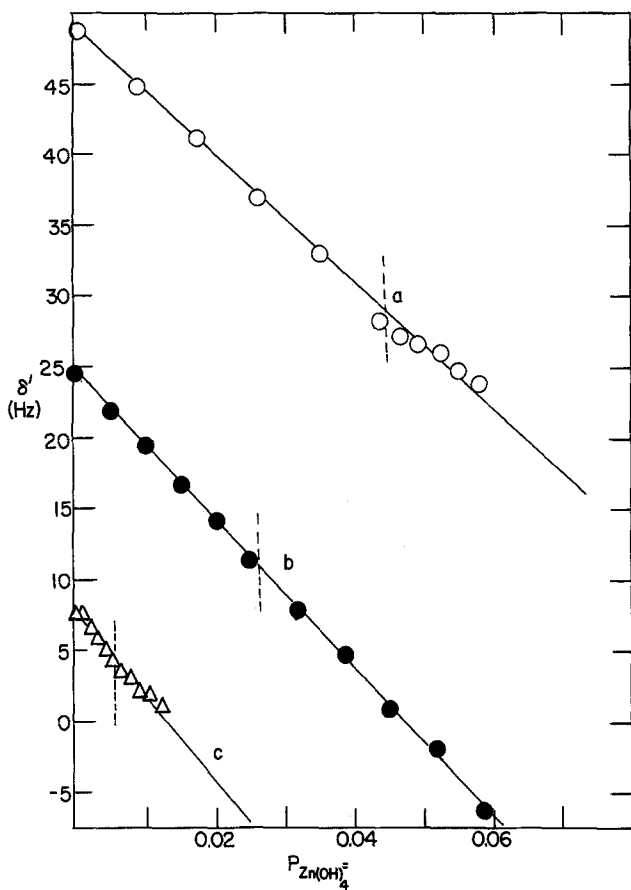

Fig. 4. Plot of δ' with increasing proton fraction of $Zn(OH)_4^{2-}$ at different base strengths: a, 12.2M KOH; b, 7.3M KOH; c, 2.9M KOH.

The total chemical shift with respect to the reference signal may be expressed by the equation

$$\delta = P_{OH^-}\,\delta^{\circ}_{OH^-} + P_{Zn(OH)_4^{2-}}\,\delta^{\circ}_{Zn(OH)_4^{2-}} \qquad [3]$$

in which the following definitions apply

δ = chemical shift corrected for bulk susceptibility

P_{OH^-} = proton fraction of OH^- in solution

$$= (M_{KOH} - 2M_{ZnO})/(M_{KOH} + 2 \times 55.51) \qquad [4]$$

$P_{Zn(OH)_4^{2-}}$ = proton fraction of $Zn(OH)_4^{2-}$ in solution

$$P_{Zn(OH)_4^{2-}} = 4M_{ZnO}/M_{KOH} + 2 \times 55.51) \qquad [5]$$

$\delta^{\circ}_{OH^-}$ = ratio of change of chemical shift with change in mole fraction of OH^- at infinite dilution

$\delta^{\circ}_{Zn(OH)_4^{2-}}$ = ratio of change of chemical shift with change in proton fraction of $Zn(OH)_4^{2-}$

The above definitions are identical to those used by Newman and Blomgren (4).

The value for $\delta^{\circ}_{OH^-}$ found by Newman and Blomgren is 20.0 ppm or 1200 Hz.

This value was found by measuring the chemical shift, δ, vs. the proton fraction of OH^- ion and measuring the slope of the curve at zero concentration.

Both our values and those of Newman and Blomgren (4) show positive deviations from linearity which the latter authors have attributed to ion-pairing between the K^+ and OH^- ions. The magnitude of this deviation should depend on the concentration of KOH and, since water solutions are strongly hydrogen-bonded, the deviation should also be temperature dependent (7, p. 400).

The differences in the deviation from linearity (Fig. 5) for identical KOH concentrations may be attributed to different spectrometer probe temperatures.

Newman and Blomgren do not report a temperature value. Ambient probe temperature in our instrument is $40° \pm 2°C$. In any case, the value of the slope of the curve extrapolated to zero concentration corroborates the value of 20.0 ppm for $\delta^{\circ}_{OH^-}$.

From the value of $\delta^{\circ}_{OH^-}$ and the known KOH concentration the value of δ' may be calculated for each solution.

$$\delta' = P_{Zn(OH)_4^{2-}}\,\delta^{\circ}_{Zn(OH)_4^{2-}} = \delta - P_{OH^-}\,\delta^{\circ}_{OH^-} \qquad [6]$$

A plot of δ' vs. $P_{Zn(OH)_4^{2-}}$ will then give as its slope, the value of $\delta^{\circ}_{Zn(OH)_4^{2-}}$ (Fig. 4).

The following values were found:

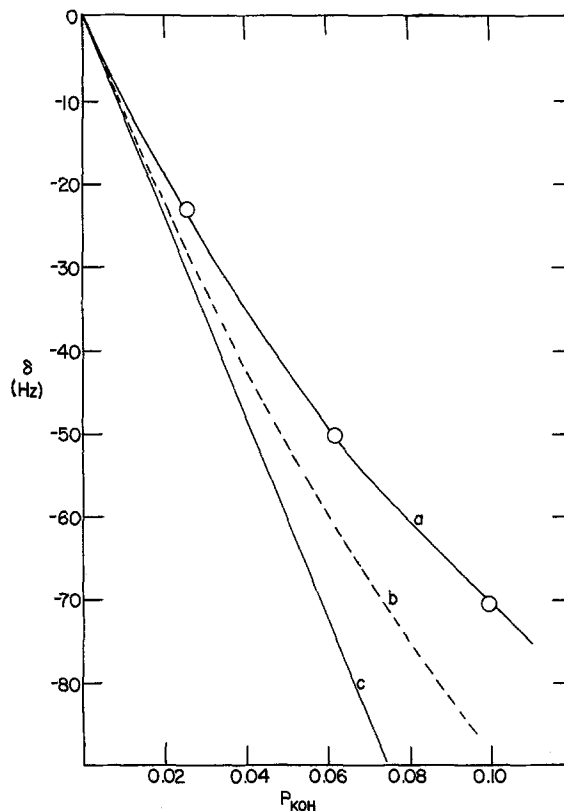| Molality of KOH	$\delta^{\circ}_{Zn(OH)_4^{2-}}$, ppm
2.9	−9.60
7.3	−8.60
12.2	−7.32

Fig. 5. Plot of proton resonance shift, δ, with increasing proton fraction of base: a, our values; b, approximate experimental values of Newman and Blomgren (4); c, slope of curves at $P_{KOH} = 0$. Used as values of δ°_{KOH}.

In view of the small magnitude of the effect being measured and the uncertainty in the temperature, these values compare well with those found by Newman and Blomgren (4) which ranged from -6.44 to -6.04 ppm. Although our values are slightly higher, the change in $\delta_{Zn(OH)_4{}^{2-}}$ with changing KOH concentrations is similar, though somewhat more pronounced.

In calculating the data in Fig. 4, it was assumed that $\delta^{\circ}_{OH^-}$ has a constant value of 20.0 ppm. The error introduced by the deviations from this value (see Fig. 5) causes the nonzero intercepts of the curves in Fig. 4, but should not affect the slopes appreciably.

The plots of δ' vs. $P_{Zn(OH)_4{}^{2-}}$ do not show a significant deviation from linearity on passing from the unsaturated to the supersaturated region. In view of this, no difference in the zinc-containing species existing in those two regions is indicated. Should a second, different, zinc species exist in the supersaturated region, a change in slope might be expected.

If, for example, the excess zinc (above the normal limit of solubility) existed as simple Zn^{++} ions, the slope of the curves in Fig. 4 should approach zero in the supersaturated region. The species which cannot be eliminated by those arguments are other complexes of zinc containing 4 protons, namely, $Zn(H_2O)_2{}^{++}$ and $Zn(OH)_2(H_2O)$. The existence of these, however, is placed in doubt by the work of Fordyce and Baum (3).

Finally, the linearity of the plots in Fig. 4, and the lack of signal broadening in the spectra eliminate the possibility that the excess zinc exists as a colloid or suspended solid.

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The Sealed Nickel-Hydrogen Secondary Cell

Jose Giner*,[1]

Tyco Laboratories, Waltham, Massachusetts 02154

and James D. Dunlop*

COMSAT Laboratories, Clarksburg, Maryland 20734

ABSTRACT

A recently developed sealed nickel-hydrogen cell offers considerable promise to develop lightweight, long-life, rechargeable batteries. The most apparent advantages of this cell are its higher energy and power density as compared with other rechargeable systems including nickel-cadmium, lead-acid, and silver-zinc cells and the regenerative H_2-O_2 fuel cell. The energy density for lightweight 50 A-hr cells shown is 28 W-hr/lb. The cell enjoys a unique overdischarge protection mechanism which allows for long cycle life at high depth of discharge. Experimental data are presented to define the characteristics of the cell. Over 5000 high rate cycles have been completed on small 1.5 A-hr cells with good voltage performance. A 50 A-hr cell has completed to date over 800 cycles discharge to 70% of measured capacity in 1.2 hr.

A recently developed sealed nickel-hydrogen cell (1) offers considerable promise for the development of light, long-life, rechargeable batteries. This system competes favorably in many applications with such rechargeable systems as the lead-acid and nickel-cadmium (Ni-Cd) cells and with systems in the developmental stage, such as the regenerative H_2-O_2 fuel cells and Cd-O_2 cells. The most apparent advantages of the cell are its attractive ·energy and power densities for both charge and discharge. In addition, it shows high reliability, long cycle life,

storage life which is insensitive to the state of charge, considerable overcharge protection, and a unique overdischarge protection mechanism which makes it eminently suited for connecting cells in series. It also promises attractive low-temperature performance. The specific application of this system to synchronous satellite operation has already been discussed (2). In the following the characteristics of the cell are defined, based on experimental measurements, and the lightweight 66 W-hr (50 A-hr) cell design.

Description of the System

In its construction the nickel-hydrogen cell resembles the Ni-Cd cell, except that the cadmium electrode is replaced by a catalyst electrode capable of oxidiz-