

ELECTROANALYTICAL CHEMISTRY

A SERIES OF ADVANCES

Edited by
ALLEN J. BARD

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN, TEXAS

VOLUME 5

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PREFACE TO VOLUME 5

Several aspects of the chapters in Volume 5 call for a brief introduction—a departure from previous practice for volumes in this series.

The concept of the involvement of the hydrated electron in electrode processes is rather new and still controversial. Chapter 1, by G. A. Kenney and D. C. Walker, presents an introduction to the history and properties of the hydrated electron and gives what evidence is available for its role in electrochemistry. It is hoped that this brief review will stimulate thought and experimentation in this developing field.

Although electrodeposition is one of the oldest fields in electrochemistry and forms the basis of the oldest electroanalytical techniques, the nature of the mechanism of electrocrystallization is still actively being investigated. The Newcastle group has made many contributions to the field and Chapter 2, by J. A. Harrison and H. R. Thirsk, reviews the methods and models employed in current research.

The involvement of chemical reactions in polarography has been the subject of numerous theoretical and experimental studies, but a general review of the nature of the processes or the mathematical methods for dealing with them has not been given. R. Guidelli has accomplished this in Chapter 3, using models taken from the thermodynamics of irreversible processes and the concepts of diffusion and reaction overpotential. Although this approach to problems of this type is not conventional in most of the electroanalytical chemistry literature, it forms a satisfying unification of the field and hopefully will be useful in the attack of new problems in this area.

A. J. B.

INTRODUCTION TO THE SERIES

This series is designed to provide authoritative reviews in the field of modern electroanalytical chemistry defined in its broadest sense. Coverage will be comprehensive and critical. Enough space will be devoted to each chapter of each volume so that derivations of fundamental equations, detailed descriptions of apparatus and techniques, and complete discussions of important articles can be provided, so that the chapters may be useful without repeated reference to the periodical literature. Chapters will vary in length and subject area. Some will be reviews of recent developments and applications of well-established techniques, whereas others will contain discussion of the background and problems in areas still being investigated extensively and in which many statements may still be tentative. Finally, chapters on techniques generally outside the scope of electroanalytical chemistry, but which can be applied fruitfully to electrochemical problems, will be included.

Electroanalytical chemists and others are concerned not only with the application of new and classical techniques to analytical problems, but also with the fundamental theoretical principles upon which these techniques are based. Electroanalytical techniques are proving useful in such diverse fields as electro-organic synthesis, fuel cell studies, and radical ion formation, as well as with such problems as the kinetics and mechanism of electrode reactions, and the effects of electrode surface phenomena, adsorption, and the electrical double layer on electrode reactions.

It is hoped that the series will prove useful to the specialist and non-specialist alike—that it will provide a background and a starting point for graduate students undertaking research in the areas mentioned, and that it will also prove valuable to practicing analytical chemists interested in learning about and applying electroanalytical techniques. Furthermore, electrochemists and industrial chemists with problems of electrosynthesis, electroplating, corrosion, and fuel cells, as well as other chemists wishing to apply electrochemical techniques to chemical problems, may find useful material in these volumes.

A. J. B.

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- Digital Simulation: A General Method for Solving Electrochemical Diffusion-Kinetic Problems, STEPHEN W. FELDBERG, *Brookhaven National Laboratory, Upton, New York*

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- Sine Wave Methods in the Study of Electrode Processes, MARGARETHA SLUYTERS-REHBACH AND JAN H. SLUYTERS, *Laboratory of Analytical Chemistry, State University, Utrecht, The Netherlands*
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- Application of Controlled Potential Coulometry to the Study of Electrode Reactions, ALLEN J. BARD, *Department of Chemistry, The University of Texas at Austin, Austin, Texas*; and K. S. V. SANTHANAM, *Tata Institute of Fundamental Research, Colaba, Bombay, India*

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Hydrated Electrons and Electrochemistry

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AUTHORS' PREFACE

"Curiouser and curiouser," said Alice in amazement at the White Rabbit's words and then hastily poured him another cup of tea so that he should not stop this exciting tale. Wiping his whiskers and paws very carefully the rabbit repeated grandly,

"Yes, *quite* an exciting discovery, in my opinion one whose impact still has to be explored. And the machines they used, you cannot imagine how complicated they were!"

"Yes, yes," stamped Alice a little impatiently, "but *what* did they discover?"

"Why the hydrated electron, of course."

"The what?"

Breathing heavily the White Rabbit pushed back his chair.

"The hydrated electron."

"What is that? It sounds a very curious thing to be excited about."

"Ah—how can I describe it—A species older than homosapiens, a transient blueness when the lightning plays upon the rain . . ."

"That's all nonsense," interrupted Alice sharply, "you are making fun of me." With a supercilious shrug the White Rabbit continued in his prosaic vein, "... the hydrated electron is an elusive phantom charge that's never still in its watery trap, so quick to react that . . ."

"Gobbledygook!" retorted Alice, "I won't stand for these ridiculous ideas."

The White Rabbit stood up, gave her a quelling look and tucking his paws into his white coat returned to the laboratory. Over his shoulder came the mutterings . . . "What did she want me to say? That it is an excess electron bound in a self-induced stable quantum state of the polarized dielectric?"

"Well that *is* a little clearer and a lot more logical," admitted Alice to herself as she began to clear away the cups and saucers.

I. AN INTRODUCTION

The demand for a serious study of the possible involvement of hydrated electrons (e_{aq}^-) in the cathode discharge process in dilute aqueous solution can be justified for several reasons. First, some of the experimental data on the nature of the species involved finds a simple and logical explanation in terms of hydrated electrons. Second, these hydrated electrons have usurped the position of the hydrogen atoms as the primary reactive species produced during the reduction of water by most other physical and chemical means. A

third reason comes from the analogy with liquid ammonia where solvated electrons are produced and observed visually at a noble cathode when the cations are nonreducible (1). Finally, since none of the presently advocated mechanisms for the evolution of hydrogen appears to be universally acceptable (particularly in accounting for data at $\text{pH} > 9$), there is clearly room for a fourth candidate to add to the more familiar slow discharge, catalytic and electrochemical explanations (2).

It should be noted at the outset that no attempt is made here to discuss the considerable wealth of information on the hydrogen evolution reaction at intermediate and high pH which resulted in the formulation of these more familiar mechanisms. This chapter presents only information which can be seen to be pertinent to the question of the existence of hydrated electrons, and thus the reader is left to assess its merit in the perspective of seventy years of electrochemical studies relating to this fundamental process.

Sixty-two years ago Cameron and Ramsey (3) suggested an analogy between the action of ionizing radiations and that of electrolysis, but decided that this could not be formulated as a grand generalization when they failed to deposit copper from CuSO_4 solution using radium α particles. Actually the Cu^{2+} would have been reduced to copper by radiolysis but not necessarily "deposited." Cameron and Ramsey's analogy would achieve considerable thrust if it were shown that the principal primary oxidizing (OH) and reducing (e_{aq}^-) species formed in the radiolysis of water were the very same species formed initially at the anode and cathode, respectively, during the electrolytic decomposition of water.

Hydrated electrons were first discovered in studies on the radiolysis of water (4-8). For several decades prior to this it was believed that the net effect of high-energy radiations on water was simply to create H atoms and OH radicals, but a transition in ideas spanning 1957 to 1962 led to the eventual unanimous acceptance that the principal reducing species was a new agent, the hydrated electron and not the hydrogen atom. Naturally, a reassessment followed not only of basic physiochemical interactions and diffusions in radiation processes, but also of the previous notions of reactivity and the mechanistic details of reductions in general. This discovery of e_{aq}^- was a very important step with consequences that were felt beyond radiation chemistry in the studies of fundamental reduction processes that occur in aqueous media.

Having acquired status and respectability as a self-sufficient chemical entity in at least one discipline, the hydrated electron has been subjected to numerous reviews in recent years (9-20) many of them both comprehensive and searching. Consequently, this chapter leaves many things unsaid about

hydrated electrons, some intentionally, and the references listed are selective rather than exhaustive. Particular aspects are emphasized in different reviews: Anbar (14), for instance, deals very thoroughly with the reactions of e_{aq}^- ; Schindewolf (19) highlights the analogies between electrons solvated in aqueous systems and those in ammonia; Dainton (11) makes useful comparisons between e_{aq}^- and electrons trapped in various media while discussing the thermodynamics of the different systems; in contrast, both Hart (9) and Thomas (15) concentrate on radiation chemical studies. Anbar and Neta (21) have compiled tables of rate constants for reactions of e_{aq}^- (also H and OH radicals) from which all quoted rate constants in this chapter are taken.

A. Hydrated Electrons

Hydrated electrons are a novel species of the genus solvated electron which appears in many forms; these range from excess electrons caught momentarily by short-range repulsive forces in nonpolar liquids such as liquid helium to those electrons permanently trapped as F centers at anion vacancies in ionic crystals. Despite the extreme differences in their immediate environments these electrons share several common characteristics. Their optical absorption bands are all intense, broad, structureless, and asymmetric (see Fig. 1) while the ESR absorption bands are very sharp and narrow. Their equivalent conductancies are well in excess of other ions in the same environment and they exhibit strong chemical reactivity as reducing agents. For our purpose electrons solvated in liquid ammonia—the first discovered and probably the best understood of these species (24)—provide the most useful analogies for hydrated electrons, even with such inherent striking differences reflected by their relative lifetimes, cavity size, and so on.

A wealth of information has been accumulated concerning the chemical behavior of e_{aq}^- in its role as a very powerful and reactive reducing agent, but the structure of e_{aq}^- and the nature of the electron binding remain a subject for conjecture. Perhaps a useful, if vague, description of e_{aq}^- is that of an excess electron associated with, and smeared over, a region of polarized and oriented solvent molecules such that it possesses diffusion and reaction rate parameters comparable to normal charged chemical species. Or, more succinctly, the hydrated electron is an electron caught in a stable quantum state of the polarized dielectric.

The recently reported ESR spectrum of e_{aq}^- (25) indicates that it cannot be described as a solvated H_2O^- ion because there is no preferred association

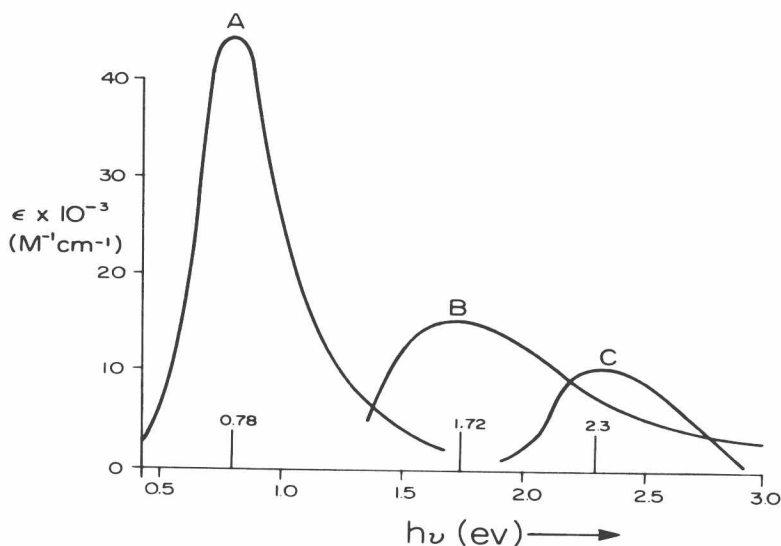


Fig. 1. Optical absorption spectra of solvated electrons in various media. A = liquid NH_3 (alkali metal solution (19)), B = liquid water (transient in pulse radiolysis (22)) and C = F center (KCl crystals (23)).

with any two protons and the splitting shows only very weak interactions. Nor is it likely, for reasons presented previously (20), that the e_{aq}^- is a true polaron (in the sense of inducing its own solvation sheath wherever it moves) but rather, it is suggested, e_{aq}^- exists in and jumps between pre-existing, suitably oriented sites, though this idea is far from proven. The mobility of e_{aq}^- is very high ($1.8 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$) (26), substantially higher than all other ions in aqueous solution (27) except OH_{aq}^- ($2.0 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$) and H_{aq}^+ ($3.5 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$). In comparison, the mobility of F^- , equivalent to that of K^+ , is $7.5 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$. Since OH^- and H^+ derive their phenomenal mobilities from the presence of hydrogen bonded chains of molecules of liquid water (in which the transfer of a proton merely corresponds to the shift of an electron in the opposite direction), it is not unreasonable to suppose that the mobility of e_{aq}^- also may be derived from some mechanisms not available to other ions—such as the jumping or tunneling between the sites described above. Nevertheless e_{aq}^- quickly acquires an ionic atmosphere with which, for example, equilibrium is achieved in less than 3 nsec after its formation in a solution whose ionic strength is 0.23 M (28).

Despite this very high mobility, the diameter of the sphere of influence of

e_{aq}^- —its effective collision diameter which can be derived from kinetic data—is relatively large, being of the order 6 Å. A similar number has also been deduced from theoretical treatments of e_{aq}^- based on a polaron model (29) and in further consideration of the Heisenberg uncertainty principle the position of the electron could not be located with greater precision than a few angstroms because of its small momentum when in thermal equilibrium with its solvent surroundings at about 300°K. Thus e_{aq}^- has a size, corresponding in fact to a dispersed charge distributed over the solvent sheath, that is similar to an iodide ion. The I_{aq}^- ion has a comparatively small free energy of hydration consistent with its bulkiness and these features, too, are exhibited by e_{aq}^- whose free energy of hydration is only about 40 kcal mole⁻¹. This latter value and the size of the charge distribution for e_{aq}^- fit excellently the Noyes semi-empirical relationship (30) developed for univalent anions in aqueous solution.

$$\Delta G_h^\circ = 1.58r^2 - 0.568 - 163.89/r + 19.79/r^2$$

ΔG_h° also corresponds very closely to the photon energy of maximum absorption in the optical absorption band of e_{aq}^- (shown in Fig. 1, $\lambda_{max} = 7200 \text{ Å} = 40 \text{ kcal mole}^{-1}$), which would be expected if the excitation process occurred as the direct photo release (i.e., photoionization) of the electron from its solvation shell. However, these values would be within 75% of each other on another model of electron binding formulated by Jortner in which the excitation of e_{aq}^- is considered to be a ($2p \leftarrow 1s$) transition between levels described by hydrogenic wave functions.

In summary hydrated electrons are ordinary chemical entities to which reaction rate parameters (perhaps even energies of activation), diffusion constant, collision diameter, hydration energy, and third-law entropy can be assigned. If this were not so, then of course there would be no difficulty in distinguishing chemically between e_{aq}^- and hydrogen atoms, and the questions we ask in this chapter either would not have arisen or would have been answered long ago.

B. Hydrogen Atoms and Hydrated Electrons

As it is a problem *does* exist because hydrogen atoms and e_{aq}^- are barely chemically distinguishable, both being extremely reactive and very powerful reducing agents that frequently react with additives at comparable (often

diffusion-controlled) rates to yield the same product. A distinction was possible, however, based on marked differences between their physical characteristics of charge, ESR, and optical absorption spectra.

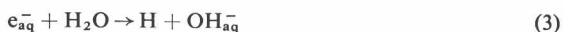
These two species constitute a conjugate acid-base pair given by the equilibrium (1)



The hydrogen atom exhibits a pK_a of about 9.5 (17), which implies that although the hydrogen atom is rather a weak acid e_{aq}^- is also a weak base, being comparable to the cyanide or phenolate ions. Equilibrium (1) is seldom, if ever, established under experimental conditions because in most systems in which the chemistry of H or e_{aq}^- can be studied, either or both have lifetimes that will not exceed tens of microseconds. Consequently, they may be interconverted through pH adjustments but it is still improbable that process (1) as an equilibrium is ever attained. Their rate of interconversion can be calculated readily for any pH using the known rate constants for reaction (1), $k_1 = 2.3 \times 10^{10} M^{-1} \text{ sec}^{-1}$, and reaction (2), $k_2 = 2 \times 10^7 M^{-1} \text{ sec}^{-1}$,



The spontaneous decomposition of e_{aq}^- , its natural lifetime being governed by the rate of reaction with its solvent molecules as given by the rate of reaction (3),



is very slow—that is, $k_3 \leq 16 M^{-1} \text{ sec}^{-1}$ (31)—but probably many orders of magnitude faster than the analogous reaction of the solvated electron in liquid ammonia. The very small value of k_3 shows that e_{aq}^- is not simply a precursor of hydrogen atoms (except at $\text{pH} < 3$ in a typical system) and cannot be dismissed as a transient of little chemical importance. Reaction (3) is one of the most crucial and fascinating reactions of e_{aq}^- since its rate constant with that of the reverse reaction are the cornerstones for calculations of the thermodynamic properties of e_{aq}^- including its standard potential. It is important to realize, however, that reaction (3) will not contribute significantly ($< 10\%$) to the events in any chemical system when either (a) the local mean concentration of e_{aq}^- exceeds $\sim 2 \times 10^{-6} M$, because of reaction (4) (see below), or (b) when the pH is less than 6.3 at which stage reaction (1) dominates.

C. Reactions of the Hydrated Electron in Pure Water

Even in perfectly pure water a high concentration of e_{aq}^- cannot easily be reached because of reaction (4)



which has a rate constant only slightly less than that of the analogous bimolecular combination reaction of hydrogen atoms ($H + H \rightarrow H_2$, $k = 1.2 \times 10^{10} M^{-1} \text{ sec}^{-1}$). If e_{aq}^- were produced in water at a rate R ($M \text{ sec}^{-1}$), then the steady-state concentration of hydrated electrons $(e_{aq}^-)_s$ would be given by the relationship,

$$(e_{aq}^-)_s \leq (2R \times 10^{-10})^{1/2} M$$

In order to produce a concentration of $10^{-4} M$ under steady-state conditions in a radiation chemical study with continuous radiations, we would require the incredibly high dose rate of $> 2 \times 10^{10} \text{ rad sec}^{-1}$. For electrolysis, if one gram-mole of hydrated electrons could be generated at an electrode by the passage of a Faraday of charge, then in order to produce $10^{-4} M$ of hydrated electrons within a layer only 10^3 \AA thick at the electrode surface, we would need a current density of 50 mA cm^{-2} . Since the mean lifetime of e_{aq}^- at $10^{-4} M$ would be about $1 \mu \text{ sec}$, it is impossible to obtain a layer thicker than $\sim 10^3 \text{ \AA}$ because that is the maximum distance e_{aq}^- could diffuse in $1 \mu \text{ sec}$ (the diffusion constant D is $5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ (26) and the electric field strength beyond the double layer will be insufficient to induce a mobility significantly greater than this).

Under pulsed conditions, however, a concentration of $10^{-4} M$ can be achieved with a radiation dose of $4 \times 10^4 \text{ rad}$ delivered in a period significantly shorter than the lifetime of e_{aq}^- ($\sim 1 \mu \text{ sec}$). This radiation intensity is readily available, yet in most pulse radiolysis studies it is unnecessary and often undesirable (32) to utilize concentrations greater than 10^{-5} to $10^{-6} M$. Likewise, a concentration of $\sim 10^{-4} M$ of e_{aq}^- could be achieved by pulse electrolysis using $\sim 10^{-7} \text{ C cm}^{-2} / \mu \text{ sec}$ pulse, but here the nonhomogeneity of the concentration of e_{aq}^- away from the electrode surface will cause difficulty in lifetime studies because this "concentration" will be changing by virtue of diffusion.

These rough data have been presented to emphasize the problem anticipated in any experimental investigation of e_{aq}^- that have been generated electrolytically. The higher the concentration of e_{aq}^- required for detection and