

HOW CAME THE RESEARCH OF ION-SELECTIVE ELECTRODES INTO BEING?

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Summary

The author describes his way leading from pH measurements with the glass electrode through his research work about adsorption indicators to the development and examination of his ion-selective electrodes. On this occasion he reaches methodological conclusions how different fields of research work excite and influence the thoughts of the investigator.

As Prof. Fujiwara put me the surprising question: how the research of ion-selective electrodes had taken shape in my research work, I thought it would be easy to answer this question. I believed this, despite that I am aware that the emerging of a new thought is the result of complicated processes. After a short oral reply Fujiwara professor honored me by telling that he would like to have a written report on this story. As I reflected upon all the precedents and momentary effects which had started the research of ion-selective electrodes, I became conscious that I had undertaken a very difficult task.

I was still a student as in the years towards the end of the war I first met the problem of working with the glass electrode. To our laboratory measurements we had to blow plates from Schott-glass and with these to determine pH values. I think it is not necessary to mention that our measuring results obtained by means of these electrodes were not satisfactory. The potential change was pro decade 10–15 mV and the measurement of this could only be performed with the electroscopic method because the resistance of the measuring system was high. So, in the forties, due to the above mentioned problems, I got the impression that if possible, I have to neglect the application of the glass electrode.

From 1948 I worked at the Institute of Inorganic and Analytical Chemistry of the University of Budapest where under the guidance of Prof. Schulek we began to deal with the problems of adsorption indicators. A known phenomenon, detected earlier by Prof. Schulek, was that paraethoxychrysoidine indicates the end-point of titrations yielding silver iodide precipitate. However, the mechanism of the indication could not be fitted in with the already known Fajans indicators and Prof. Schulek supposed that the new

indicator does not work with adsorption but with desorption mechanism. So, we started to work in order to prove this suggestion.

To work with prof. Schulek was extremely interesting. I think, we might say as well that he was the last of those Hungarian university professors, working in the field of classical analysis, who gave preference to own experimental work, and our experimental activity was in fact from every point of view also common. We were observing together the formation of the precipitates, their colour and since in that time he was already over 50, he inspected the reactions through his glasses.

Since after the war in Hungary there was not a big selection in the quality of glasses, in Prof. Schulek's spectacles there was a shade of green. At the beginning of the titration of silver nitrate with iodide the slightly reddish solution becomes yellowish. Due to his specs Prof. Schulek could not observe this clearly and the whole desorption theory was actually based on the observation that the colour of the solution turned suddenly fresh red at the end-point of the titration. However, if the colour change occurs not only at the end point of the titration but also at the beginning of it, it is evident that such a simple explanation could not hold on. I remember the afternoon, when I first noticed the colour change at the beginning of the titration and, we stood there with Prof. Schulek puzzled, what can then be the cause of the phenomenon if it cannot be explained by the desorption theory?

In the course of my university studies I learned a lot from Prof. Aladár Buzágh, one of the founders of colloid chemistry, in whose laboratories I performed also my predissertation laboratory work. (In those days there was a possibility for the students to perform such a preliminary work before preparing the dissertation for the Ph. D.-degree.) However, since at the Department for Colloid Chemistry there was no vacant appointment, I was compelled to accept a position where I could deal with scientific investigations for a salary.

Based upon my studies in colloid chemistry I speculated during a whole night upon the problem when I struck on a bold idea. According to this, the p-ethoxychrysoidine suitable for acid-base indication is being adsorbed on the surface of the precipitate during the whole titration process before as well as after the end-point and the indication occurring in dependence of the quality (positive or negative) of the surface charge is actually an acid-base indication. But if this is true and either silver or iodide ions are in excess, then the dye must deliver protons into the solution or take up protons from there. Consequently the pH of the solution must change.

The following day I reported Prof. Schulek on my hypothesis, who under the influence of the Fajans theory, simplified and generalized by Kolthoff, could not judge the explanation as an acceptable one. However, as an excellent researcher he did not only want that we look for arguments and contra-arguments but made immediately arrangements that I could perform

measurements on the only Radiometer type pH-meter available in those days in Hungary. The Radiometer glass electrodes gave a signal with a slope of 59 mV/decade. These experiments carried out at the end of 1948 convinced me that the measuring technique despised earlier by me is good. So, I began to look for the appropriate theory of function mechanism. It was strange that I found in most of the books the Donnan model despite the fact that, more than 15 years earlier the very inventive ion-exchange theory of Nikolsky had already been established. The activity of Lengyel and Blum in connection with the indication with sodium glass electrodes also was performed for about 15 years.

It seemed that the Nikolsky equation gives a correct qualitative picture of the electrode function and as far as I was concerned I thought that this "strange" indicator would serve in the course of my scientific activity in the best case as a help for pH measurements.

My working hypothesis regarding the adsorption indication proved to be correct and for nearly one decade, beside other works, I investigated with my coworkers the details of the above mechanism. We elaborated with Prof. Schulek an adsorption indicator theory of general validity. We rehabilitated also Fajans who performed with fluorescein and eosin such experiments on the basis of which it was not necessary to suppose some nebulous theory of molecule deformation, since the experiments clearly showed that in the presence of silver in excess these dyes form on the surface of silver halides a precipitate. In order to detect every detail, we carried out examinations in many directions. We examined the adsorption data of the dyes, the dispersity grade of the precipitates, the effect exerted upon the dispersity grade by the various substances being present in the solution, etc. We stated that if p-ethoxychrysoidine is present when precipitating silver iodide, then the dispersity grade becomes in a reproducible way very high. In a very interesting experiment we stated also that the halide ions are bound onto the surface of silver halides "naked", i.e. without any hydrate shell.

In 1958 I was invited by the organizers of a Hungarian Analytical Discussion Meeting to give a general survey on the development of electroanalytical measuring techniques. Up to this time I dealt with oscillometry and polarography as my research field. I did not see any special fantasy in potentiometry. Also in the mentioned review paper I dealt first of all with the polarographic measuring technique and its development and with methods based on conductivity measurements. Of course, during my data collecting work I looked through also works belonging to the potentiometric topic and my attention was attracted by the fact that many researchers had dealt with zeolites. These researchers intended with the help of zeolites—being a good ion-exchanger—to develop ion-sensing electrodes. However, from their results it could be seen that these electrodes were not selective. Of the many works the paper of Fischer and Babcock stroke my eye. These

researchers dispersing barium sulphate in paraffin had obtained some kind of a not very selective signal.

At the beginning of this century Prof. L. Winkler elaborated the error compensation method of gravimetric analysis. He used as a "magic salt" NH_4Cl in very high concentrations and by a very big number of measurements he determined "correction factors" for the precipitates. By correcting the measured weights, it is possible to get accurate results. This method of Winkler gave rise to many debates. In the forties, Prof. Schulek as new member of the Hungarian Academy of Sciences in his inaugural address defended the method of Winkler. However, the fundamental question was still open. Why can the composition of the precipitates be kept in hand in the presence of the "magic salt" NH_4Cl ? In the middle of the fifties we performed many electron microscopic examinations in order to detect what happens with BaSO_4 in the presence of NH_4Cl . Why is it necessary to work at pH 2? Some other questions of smaller significance were also unsolved.

Many researchers, among others, also Prof. Buzágh dealt with BaSO_4 . He stated, that from morphological aspect the BaSO_4 precipitate is greatly influenced by various additive materials.

Also we examined to what extent would the morphology of the precipitate be influenced by strictly keeping or not keeping the prescriptions of Winkler. We stated that Winkler worked correctly, he found instinctively the optimum conditions. We examined also the adsorption ability of this precipitate but could not find such a distinct adsorption as in the case of silver salts.

This short insertion explains why Fischer and Babcock found that barium sulphate is not a good model for preparing electrodes. Since meanwhile I collected a lot of experiences in connection with silver iodide it seemed to me evident that in the knowledge of the adsorption effects I should examine AgI instead of BaSO_4 . From the aspect of iodide and silver response we examined in 1959 AgI precipitated according to the earlier developed technique and dispersed in paraffin.

My coworker Elisabeth Rokosinyi and myself, were very lucky. The first experiments gave immediately electrodes with Nernstian response for iodide as well as for silver. We were happy with the results and examined thereafter the influence of chloride. My first supposition was that the interfering effect would evidently be connected with the solubility of the precipitate and since between the solubilities there exists a thousandfold index number I counted with about the same value in the interfering effect. To our greatest surprise up to millionfold excess of Cl^- the electrode still gave the iodide response. It seemed that the selectivity is in connection with the quotient of the solubility products. By neglecting the deduction of the above relation we published the first results in 1961. At my new working place, in the Institute for Analytical Chemistry at the University for Chemical Industries in Veszprém we restarted in 1962 our

investigations on selective sensors first with Klára Tóth, later also with Jenő Havas and thereafter with other coworkers. The first period was the epoch of great enthusiasm. We examined systematically a series of materials whether they show potential signals or not, and to our greatest surprise we found such signals in many cases. Then later, as we began to control as to whether the signals are selective or not, it turned out that the number of those ions to which selective electrodes could be prepared became significantly reduced. Non selective phase boundary potentials deceived us and although the first age of ecstasy took an end, an examination technique of reliability was established in our laboratory.

In 1964 I presented at the ACHEMA exposition some electrode species, first of all halide electrodes and a few metal ion electrodes with precipitates embedded in silicone rubber, which was used then already as carrier.

In the course of a detailed examination of literature we found a publication according to which Kolthoff used in the thirties a silver chloride disk for tracing argentometric titrations. Fundamentally, an electrode of the very same type had already been prepared as that we used in our laboratory, but since the chloride electrode can show a theoretical relation rather hardly, I suppose this was the cause why Kolthoff and his excellent school had not further insisted on clearing this problem.

The electrodes displayed at the ACHEMA excited an unexpected interest. Professor Belcher who also attended the exposition discussed with me the problem and offered that he would acquire a grant for the purpose that one of my coworkers could work in his Institute in order that we could elaborate a measuring method for fluoride. Some months later I sent Klára Tóth to Birmingham with the task that she should examine CaF_2 , LaF_3 and ThF_4 precipitates for the above purpose. After 1965 our laboratories in Veszprém were visited by many foreigners, among others several times also by one of the managers of Corning Glass, and to my best knowledge the same big number of people visited the Institute of Prof. Belcher, too. Klára Tóth completed meanwhile her experiments with the electrodes, but the results in connection with fluoride measurements were published only in 1969.

Meanwhile, periods of enthusiasm and periods of despair alternated one another until in 1968 we organized in Veszprém the first international symposium on ion-selective electrodes. Of earlier meetings I can lay emphasis only. The Conference held in Budapest in 1966 was attended by several researchers who were later accepted as well-known experts in this field. So among others also Prof. Rechnitz was present who performed experiments with our electrodes in the United States and gave information about his observations to American journals.

In 1968 our research was already over its landmark. Our earlier activity characterized mainly by collecting statistical data was developed for a

systematic research activity, concentrated on theoretical fundamentals. The strategy of our work could be described first of all by the endeavour to develop methods suitable for the measurement of important electrode-parameters. We wanted to examine the changes of E_0 as function of the vacancies. We carried out this work together with Aurel Marton. We elaborated with Klara Tóth and István Gavallér a technique for the examination of transient potential signals.

Meditating about the ways according to which the behaviour of ion-selective electrodes could be detected my opinion was from the second half of the sixties that beside the equilibrium data of the measurements and instead of them first of all the dynamic properties of the electrodes like response time, relaxation effects, must be examined.

Unfortunately our early hopes that with the help of response times we could obtain results which would clear up the mechanism of the electrodes, were not fulfilled. Our examinations showed that the rate-determining process is the ion diffusion from the solution onto the electrode or into the inside of the electrode. Naturally in the course of the work we struck upon prognostic signals useful to our future activities. So e.g. we stated that the response time on a disc electrode, prepared of silver halide, is about the same as the response time to be obtained on metals. It turned out also that the response time is nearly the same as that of glass electrodes if the silver halides are embedded in silicone rubber. However, if we polish the surface of the above electrode, embedded in silicone rubber matrix, e.g. by removing the silicone layer with abrasive paper, the response time would decrease.

Deeper information we acquired however, only towards the end of the seventies, when we analysed the initial periods of response times on the one hand, and on the other we measured the response times in the presence of interfering ions at the beginning of the interference range.

Parallel with theoretical investigations our aim was also to extend the analytical application of ion-selective electrodes and to develop new techniques in analysis. The development of newer and newer types of electrodes was also very important. In practical use several anomalous phenomena emerged and to a part of these we gave the name "memory effect" in general. In the course of the examination of these phenomena we obtained some useful information also regarding the operation mechanism of the electrodes.

As from the above described follows, the individual cannot emancipate himself from his earlier experiences since these would exert an effect upon him even in topics which are seemingly far from the original one. But this is absolutely right. Perhaps just therefore it is unfavourable if a researcher works and gets experiences in a very narrow field because in this case at the solution of problems he would be able to consider the questions only in a narrowed down horizon.