# 查全性先生苏联进修期间的研究论文和解读
# ——查全性先生苏联进修补遗
# Notes on the Visiting Research Stay of Professor Chuan-Sin Tza in the Soviet Union

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## 前 言

1957 年初，武汉大学化学系青年教师查全性，被选派到苏联莫斯科大学进修。虽仅约两年，这次进修却深刻塑造了查先生本人及其所创建的武汉大学电化学学派的学术风格。 因年代久远， 查先生去苏联进修这一历史事件的公开文献资料，零散各处。为此，我收集了（部分）公开资料，包括这次访问的主要成果——查先生发表在苏联科学院院刊上的三篇论文的英文翻译件，并加以解读。此外，我还特意请弗鲁姆金（A. Frumkin）学派第四代电化学家泽琳娜教授（G. Tsirlina），帮助搜集苏联方面的一些信息（包括一些未公开的历史资料）。于是在查先生诞辰百年之际， 冒不务正业之不韪， 把我所整理的信息连同我的解读和感想，借着久不练而渐生疏的笔头写出来，以纪念这位中国现代电化学的先驱，并以飨同样对“新中国电化学是如何发展起来”的这一科学史问题感兴趣的同行。当然，我既非历史亲历者，又缺乏科学史的严谨训练，同时囿于极有限的获取相关资料的渠道和不多的业余时间，所以本文定有很多可以商榷的地方，还望不吝指教。

## 背 景

这次进修前，他仅“开展了粗浅的研究工作”[1]，抱着弗鲁姆金领衔的《电极过程动力学》，和一群同样对电极动力学这一新兴学科感兴趣的年轻同事自修 [2]。

在 1988 年为弗鲁姆金写的纪念文章中，查先生写道，“新中国成立后，弗鲁姆金领衔撰写了《电极过程动力学》专著。当时电极动力学不仅对于中国科学家是新鲜事物，对全世界大多数科学家亦如此。这本书上架后，立刻引起了中国各地几个研究单位的研究人员的注意。武汉大学化学系的一群年轻老师，包括我本人（我可能是最积极的），开始组织研讨会，自修这本巨著。这便是作为当今中国几个电化学研究团队之一的武汉电化学研究团队的起源。”（俄文原文截图附在文末，这里的译文是根据泽琳娜教授提供的英文翻译）

2011 年，武汉大学电化学研究室为查先生写了一篇小传[1]，其中特意提到，“这些（自修）活动曾得到应用化学所朱荣昭先生的鼓励”。朱先生长查先生六岁， 新中国成立之初从法国获得博士回国。两位先生颇有渊源：籍贯安徽，生在江苏，在武汉大学和大同大学学习过，终身致力于电化学研究和教学。查先生 1951 年曾去长春应用化学所，在志方益三和章咏华的实验室学习极谱技术。朱先生 1954 年从大连化学物理研究所调到长春应用化学所，在那里建立了电化学研究室。今年是朱先生去世四十周年，我也有打算写一篇短文纪念他。

值得一提的是，在查先生访学前夕，也就是 1956 年的十月，年仅 37 岁的朱荣昭受中国科学院的委托，作为中国电化学界的代表，出席了在莫斯科举办的第四届苏联电化学会。这次大会的主席，正是弗鲁姆金院士。回来后，朱先生写了一篇详实的大会综述《苏联第四次电化学会议》，发表在 1957 年的《中国科学》杂志上。朱先生在文末写道，“苏联的电化学研究工作无论是在质还是量上都保持着世界的领导地位，其中尤其是弗鲁姆金院士及其学派的理论工作获得了与会的各国科学家的一致推崇。”

以朱先生一贯的性格，笔下如此热情而肯定，实属罕见。大家可以对比读一读他在 1960 年写的《对电化学发展的几点希望》，在那个热火朝天的年代，他的笔调依然冷静。可见他在莫斯科受到的震撼，和他对弗鲁姆金的推崇。

我没有史料证明，但我猜测查先生可能读了朱先生写的《苏联第四次电化学会议》，或者从朱先生那里了解到了弗鲁姆金学派的一些情况。这或许促使了他 1957 年到了莫斯科后，“主动请求变更进修计划，改派至弗鲁姆金院士主持的莫斯科大学化学系电化学教研室研修”。武汉大学陆君涛教授指出：“查先生当年属于分析教研室，电极过程动力学只是他的‘业余爱好’，此新学科大概率不会在有决定权的分析化学教研室领导考虑之中”。

**约法 (Z. Iofa)**

在莫斯科大学化学系，查先生实际是在以实验电化学为主的约法教授的课题组。约法是弗鲁姆金学派的重要骨干，《电极过程动力学》的四位作者之一。

弗鲁姆金这颗星星太亮眼，约法的光芒不免被遮掩。他的公开资料很少。于是我写信，向现居斯洛文尼亚的泽琳娜教授求助。她身上有一种罕见的历史责任感，视梳理和讲述莫斯科大学电化学历史为己任。近年来，她发表了一系列的回忆文章，收集整理相关的文档，并在她同样是科学家的儿子的帮助下，正在建立一个网站把这些资料永久保留下来。顺便一提，我最近和她一起做了一个历史研究，翻译并校正了列维奇（V. Levich）于 1949 和 1959 年写的两篇非平衡双电层理论的文章，即将出版 [3]。

泽琳娜在给我的邮件中写道，约法是弗鲁姆金学派中极为重要和特殊的一个存在。作为莫斯科大学化学系前任领袖斯皮塔尔斯基教授（G. Spitalsky）的学生和继任者，约法是弗鲁姆金学派中唯一一个，在弗鲁姆金加入莫斯科大学化学系之前，就已经开展电化学研究的人。

陆君涛教授提到：“弗鲁姆金对其工作是十分尊重的。查先生留苏期间正式发表的 3 篇论文署名皆为‘查全性，约法’，并无弗鲁姆金。现存的一篇手写初稿可见，查先生原来写的署名是‘弗鲁姆金，约法，查全性’，弗鲁姆金对全文进行了修改，并将自己的名字划掉，保留了约法，而将查全性移到前面。”

这和查先生自己的回忆是一致的。查先生在 1988 年的文章中，回忆道，“我保留着我的文章的手稿，上面有弗鲁姆金院士通篇修改的痕迹，但他把自己从合著者一列拿掉了。”（泽琳娜提供的译文：I carefully keep the drafts of my works, which Alexander Naumovich thoroughly corrected, but declined to be included as coauthor）

弗鲁姆金本人热衷于基础电化学的理论思考。因此，弗鲁姆金学派的很多基础和工业电化学实验研究，实际上是约法主持的[4]。特别是，约法建立了非常精密的滴汞电极实验方法，并培养了一大批能够在滴汞电极上做精密测量的实验科学家。约法课题组，为弗鲁姆金学派在电化学界面和电极过程动力学两个支柱性课题上开疆拓土，打下了坚实基础。约法在 1936 年的政治运动中受到迫害，曾被短暂关押，“不可逆转地”（泽琳娜的原话）影响了他的科学研究。泽琳娜强调，尽管经历了这些磨难，约法依然是一个极为友善、乐于助人、异常谦逊的人。这对查先生是一件幸事。

查先生加入约法的实验室，跟随他学习滴汞电极和阻抗等实验电化学研究方法，并有机会接触约法实验室其他工业电化学研究方向，是极其符合当时以学习技术、服务工业为导向的外派政策的。值得指出的是，约法实验室当时就开展了一些电池研究，这些或许对查先生后来在武汉大学电化学研究室开展电源研究，奠定了初步基础。

查先生的三篇论文经弗鲁姆金院士推荐，发表在苏联科学院院刊（Doklady Akademii Nauk SSSR）。苏联科学院院刊是苏联科学界的顶级杂志，从 1933 年至 1992 年陆续出版，涵盖物理、数学、化学、地质、生物等领域的原创论文。查先生的三篇文章都能够在这个杂志上发表，帮助查先生建立了自己在科学探索上的自信。他在 1988 年的回忆文章中写道，“我个人的经历表明，自信的重要性，不亚于天资和努力。获得科研上的自信最好的方式，就是在一个很强的课题组做出成绩。”

二战后，美国有一家出版和翻译公司 Consultant Bureau，最初专门翻译盟军从德国缴获的技术文件，后来转向翻译苏联的文献。所以今天我们得以看到查先生的三篇论文的英文翻译件。下面就是我根据这三份英文翻译件（详见文后附录），对查先生访学期间工作较为详细的解读。

## 入门

查先生进修期间的第一个研究，是关于离子特性吸附对滴汞电极上析氢反应的影响。在当时及后面很长一段时间，莫斯科电化学学派的最核心题目，就是如何理解电化学反应的双电层效应。

我曾在中科大陈艳霞教授负责的《电化学研究方法》课堂上，讲过一点这个方向的研究的缘起和发展。感兴趣的读者，可以在蔻享学术网站上找到这个视频：https://www.koushare.com/video/details/55447。受到他人实验结果的启发，弗鲁姆金曾在 1933 年，将双电层模型和电极过程动力学理论首次结合起来，提出了著名的弗鲁姆金修正理论。这个理论预测，阴离子的特性吸附，使得双电层内的电势相对于溶液本体电势更负，从而促进了析氢反应动力学，降低了其过电势。相反，阳离子特性吸附，会增大析氢反应的过电势。

约法本人曾在 1939 年亲自做实验验证了弗鲁姆金的理论。他证实了有机阳离子的特性吸附，的确会增大析氢反应的过电势。约法教授交给查先生的第一个题目，是在原有的工作基础上拓展，即同时引入阴离子和阳离子的特性吸附，分析其如何影响滴汞电极上析氢反应的过电势。

从这个题目的选择上，可以窥见约法训练学生的方法，即让学生从自己亲自做过的一个工作上开始。这个安排，一方面将自己的研究手法和规范可靠地传授给学生，另一方面又让学生在可预期的时间内取得有可发表的结果。这两个方面都很重要，前一个方面是打基础、控质量，后一个方面是养兴趣、护信心。有些导师一开始就丢给学生一个很有挑战、甚至自己也没相关经验的课题。从培养人的角度来看，这是不利的。新人的信心很脆弱，而热情很容易褪去。当然，有人可能会说，放手让学生一开始就去做一个很有挑战的题目，才是培养人的做法。但我认为，这是在筛选人，而不是在培养人。

查先生的实验做得很漂亮。他首先复现了阴阳离子分别特性吸附时，对滴汞电极上析氢反应的影响。然后，他设计了一个新实验，考察了阴阳离子的共吸附现象及其对析氢反应的影响。在同时存在可能特性吸附的阴阳离子的溶液中，他发现随着电极电势负移，析氢过电位相对于没有特性吸附离子的参考情况，先是降低，然后增大，最后趋于相同。前面的降低和增大阶段，分别对应阴离子和阳离子的特性吸附。但是怎么理解最后的反常现象呢？

查先生提出，在很负的电势下，有机阳离子的特性吸附会引发阴离子的特性吸附，从而抵消了有机阳离子特性吸附的影响。他接着用当时新兴的阻抗桥方法，测量了不同溶液中的单个频率点的双电层电容，试图佐证从过电势曲线分析中得出的双电层图像。虽然这两个实验的结果吻合很好，但我认为这部分的测量和分析有一定瑕疵。不同溶液选取的频率点相差两个数量级，所得到的界面电容的可比性自然就存疑。此外，这个方法测量得到的电容，是总的电容，而非对应双电层中反离子浓度的真正的双电层电容。

放眼国际电化学，远在美国的格雷厄姆（D. Grahame），早几年已经提出了类似的观点，认为特性吸附离子会改变双电层内电势和离子浓度的分布。因此，查先生的苏联进修期间的第一个研究产生的结果，并非首创。但实属有水平的工作。它一方面支持了格雷厄姆的双电层模型，另一方面也有力佐证了弗鲁姆金修正理论。从历史角度来看，这个工作对中国电化学更为重要的意义是，它把一个中国青年带到了电化学研究最核心也是最前沿的领域。

查先生在 1988 年亲笔写道：“尽管遭遇了种种‘不幸’——无论是汞的泼洒，还是特定直径的薄壁毛细管的断裂——我却始终感到，自己在电极/电解液的界面上‘吸附’得越来越牢固。”（泽琳娜译文：Despite “terrible misfortunes” like spilled mercury, or broken thin-wall capillary of desired diameter, I had a feeling that I am stronger and stronger “adsorbing” at the electrode/electrolyte interface.）

略显遗憾的是，查先生没有进一步提出第二个零电荷电势的概念。他在很负的电极电势下，观察到的阴阳离子共吸附从而导致离子特性吸附对过电势的影响基本消失的现象，已经暗示了第二个零电荷电势的

存在。多年以后，弗鲁姆金提出了铂电极存在第二个零电荷电势。这被认为是他对基础电化学的一个不平凡的、有想象力的贡献。当弗鲁姆金在构思这个概念时，查先生的实验结果，也许在他脑海中曾浮现过吧。

## 深化

不到四个月后，弗鲁姆金旋即推荐查先生和约法的第二篇文章在苏联科学院院刊发表。第二个工作看似比第一个入门的工作更简单，仅研究了卤素阴离子特性吸附对滴汞电极上析氢过电位的影响，但在我看来，水平实则更高。判断一个工作的水平，工作量甚至难度都不是首要的，想象力更可贵。公认的二十世纪最重要的科学成就之一，沃森和克里克的 DNA 模型的提出，用的可是别人的数据，几乎没有什么工作量可言。

在这个工作中，查先生测量了滴汞电极在 1 $mol \cdot L^{-1}$ HCl 和 1 $mol \cdot L^{-1}$ KX（X=Cl, Br, I）混合溶液中的界面电容和析氢过电位曲线。从界面电容曲线，他可以计算表面电荷密度。值得指出的是，限于当时的实验条件，查先生测量的是总的界面电容和总的表面电荷，而不是真正的自由电荷。所幸的是，查先生后续的分析，聚焦在表面电势很负、没有阴离子特性吸附的点位区间，这时候的总表面电荷密度就等于自由电荷密度。

作为全文的亮点，他定义了某一固定过电位下析氢电流对表面电荷密度的偏导数。基于弗鲁姆金修正理论，他推导这个偏导数的具体表达式，发现它可以表达成界面电容和反应传递系数的函数。用独立测量得到的界面电容数值和合理的反应传递函数数值，他计算得到这个偏导数约等于 0.5，与实验测量结果非常吻合。

我之所以说这个工作水平较他前一个工作更胜一筹，就在于他超越了实验现象的定性描述和不同实验之间的定性吻合的初级阶段，进入了在不同物理量之间寻找关联并将其理论化的高级阶段。这种高阶的研究，就需要对研究对象的深入理解，以及想象力。

最近几年，以表面电荷作为电催化反应活性的描述符的相关研究，时有出现。六十多年前，查先生的这个工作，应当被看作是这个研究方向的开创性工作。我提议，如果后续证实这个偏导数是这篇文章首次提出的，我们就叫它，Tza-Iofa 系数，以纪念查先生和约法教授。

## 开拓

如果说前两个工作分别是入门和深化，那么第三个工作更具有开拓的意义。通过用电化学阻抗谱方法准确测量锌单晶的零电荷电位，查先生的第三个工作，有力推动了界面电化学研究从液态滴汞电极到固态单晶金属的转变。

这个工作得到了弗鲁姆金的高度认可。弗鲁姆金在 1960 年美国电化学会的获奖报告中评价道：双电层结构的研究，在固态电极上变得更为复杂。在这种情况下，在液态金属上行之有效的、通过界面张力测量认识双电层的方法是不现实的。接着他就引用查先生的这个工作，指出研究固态电极双电层的一个行之有效的方法，就是通过电化学阻抗谱方法，跳过界面张力这个物理量，直接测量界面电容。

客观来讲，查先生的这个工作，不是第一个测量锌电极界面电容和零电荷电位的，更不是第一个在固态电极上开展基础电化学研究的，但的确是第一个把锌单晶界面电容和零电荷电位测准的。查先生的测量结果，后来被特拉萨蒂（S. Trasatti）和勒斯特（E. Lust）推荐作为锌单晶零电荷电位的参考值，收录在这两位名家为《当代电化学概观》（Modern Aspects of Electrochemistry）写的零电荷电位一章中。

在科学上，把一件事情做对的意义，常常被轻视。大家普遍对做一件新的事情更有激情。近年来，国内外很多有影响力的科学家，在向公众或者年轻学生介绍自己的科研体会时，往往只强调求新的重要性，甚至“唯新”。然而，任何做研究的人都知道，任何科研上的进展，都离不开前人的经验和积累。只强调自己工作新的一面，而有意或者无意不提前人的经验和贡献，对于科学的健康发展、对培养具备健康科研素养的学生，是极为不利的。因此，我建议大家去看查先生的第三篇文章的原文。查先生客观地评价了前人在这个课题上的相关积累。并且，他在具体介绍某一个实验方法或者思路时，总是要提到，是受到了谁的启发。

## 结 语

1959 年，查先生结束进修，带着弗鲁姆金院士修改过的三篇论文手稿，回到武汉大学。他带着黄德东、敖锡英、叶世沅、戚兆欣等师生，采用全国产的仪表和元件，在不到一年时间内，就设计组装了恒电位仪，并搭建了精密的滴汞电极实验平台。年轻的武汉大学电化学研究室，迅速开展了滴汞电极/溶液界面上吸附现象的系列研究。尽管相关研究结果发表在中文杂志上，但通过对比同一时期在国际主流杂志上的类似的工作，我可以判断这些研究结果是国际水准的。

1963 年 11 月 5-11 日，朱荣昭在长春主持召开，全国第一次电化学报告会 [5]。时年 38 岁的查先生，是 55 名参会代表之一。他做了两个报告，一个是关于他在苏联期间做的有机阳离子和阴离子在汞电极上的联合吸附，也就是本文介绍的三篇论文的第一个工作。另一个报告是氯离子对镍的阳极行为的影响，这是他回到武汉大学后开展的新的工作。陆君涛教授补充道，“这次会议还交流了各校所用电化学自编教材，一致推崇武大的讲义，并由此作出了一个与查先生有关并影响深远的决定：建议查先生在其《电极过程动力学》选修课自编教材的基础上撰写专著，以填补国内该学科教学参考书的空白。这才有了今天大家熟知的滋养了一代又一代中国电化学人的《电极过程动力学导论》(1976，1987，2002 共三版)。”

一九六三年，十一月的长春，寒冬将至。我常设想，44 岁的朱先生和 38 岁的查先生，或许在会议期间曾绕着南湖散步、抑或是秉烛长谈。查先生定当饶有兴致地给朱先生讲述，在莫斯科进修期间的二三事。被追忆的，当然也少不了，弗鲁姆金给他修改三篇论文的点点滴滴。查先生在 1988 年写道：“或许，我从弗鲁姆金和约法那里学到的最重要的东西，就是要有自己的看法，不害怕说不，并且相信自己做得不会比别人差。我的父亲曾告诉我，他在明尼苏达大学最后一年时，密立根曾要我（查父）和索末菲握手，并提示到‘你和伟大的科学家握手后，你能更快读懂其写的书’”（泽琳娜译文：It looks like the most valuable what I accepted in Moscow from A.N. Frumkin and Z.A. Iofa, was to have my own opinion, not to be afraid to say ‘no’, and to trust that I am able to do something no worse than others. My father told me that when he was last year student in the Univ of Minnesota (USA), Millikan asked him to shake hands with Sommerfeld, and then noticed: “shaking hands with great scientists, you start to understand his books faster）

“要有自己的看法，不害怕说不” 的精神，在 1977 年查先生谏言邓小平恢复高考一事得到了充分体现。

六十二年后的十一月，将在武汉迎来类似的追忆和缅怀。只不过，当年的追忆者，今天成了被追忆的先人。

## 致 谢

武汉大学陆君涛、陈胜利、艾新平教授为本文提出了宝贵意见，一并表示感谢。

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[2] 武汉大学陆君涛教授在校正本文初稿时写道，“1954 年，正值全国高校教师突击学俄语的热潮中。他在汉口外文书店发现新到俄文原版弗鲁姆金等著《电极过程动力学（1952)》，如获至宝，即购回自学，并与几位有共同兴趣的青年同事一起研讨并开展初步实验工作。”

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# 查先生发表在苏联科学院院刊上的三篇论文的英文翻译件

## THE COMBINED ACTION OF ORGANIC CATIONS AND HALIDE ANIONS ON THE EVOLUTION OF HYDROGEN ON A MERCURY ELECTRODE

Tza Chyuan-hsin and Z. A. Iofa

M. V. Lomonosov Moscow State University

(Presented by Academician A. N. Frumkin, December 8, 1958)

The hydrogen overvoltage on mercury cathode depends on the nature and concentration of the surface-active agents present in solution, for the adsorption of these products at the boundary between the electrode and solution changes the structure of the electrical double layer in which the elementary processes of hydrogen ion discharge occur.

By taking into consideration the effect of double-layer structure on the surface concentration of discharging ions and the activation energy for the discharge, A. N. Frumkin derived [1] the following equation for the hydrogen overvoltage in acid solutions

$$\eta = \frac{RT}{\alpha F} \ln i - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln[H_3O^+] + \frac{1-\alpha}{\alpha} \psi_1 + \text{const}, \qquad (1)$$

where $\psi_1$, is the average potential one ionic radius away from the electrode surface.

The action of various surface-active ions differs in that, first of all, their adsorption may vary differently with changes in electrode potential, and second, that when adsorbed they may produce different (in magnitude and sign) changes in the potential $\psi_1$. Halide ions become predominantly adsorbed on a neutral or positively charged electrode surface, displace the $\psi_1$ potential in the negative direction, and (in accordance with equation 1) decrease the hydrogen overvoltage. Tetraalkylammonium cations displace the $\psi_1$ potential towards more positive values and increase the hydrogen overvoltage [2].

The present work was undertaken to explain the mechanism of a joint action by organic cations and halide anions. We often encounter such combined systems in practice, so it was interesting to find out if the effects of individual ions on the kinetics of electrochemical reduction of hydrogen ions are preserved when above-mentioned ions are present in solution together.

In Fig. 1 we have plotted curves of $\eta$ vs. log $i$ obtained on a dropping-mercury electrode by a method described in paper [3]. The electrode was polarized at a constant potential ( $\varphi$ = const.) during the lifetime of a drop; the true current density* in this case was,

$$i = {}^5/_3 \frac{\bar{I}}{S_2}, \qquad (2)$$

*The condition $\varphi$ = const. was attained at minimum resistance in the polarization circuit. In such a case (according to Tafel's equation) i = const., while current I changes with increase in drop area. Since $I_2 = iS_2$ (where $I_2$ and $S_2$ are the current and drop area at $\tau_d$ – the moment the drop is detached) then $S = S_2 t^{2/3} \tau_d^{-2/3}$, $I = iS_2^{2/3} \tau_d^{-2/3}$, and the average current $\bar{I} = \frac{1}{\tau_d} \int_0^{\tau_2} I_2 t^{2/3} \tau_d^{-2/3} dt = {}^3/_5 I_2 = {}^3/_5 i S_2$.

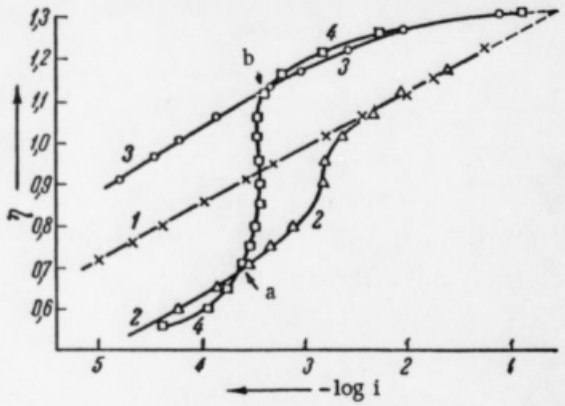


Fig. 1. Overvoltage curves in solutions of: 1) 2 N HCl + + 2 N KCl; 2) 2 N HCl + 2 N KI; 3) 2 N HCl + 2 N KCl + + $4.5 \cdot 10^{-4}$ moles/liter of $N(C_4H_9)_4Br$; 4) 2 N HCl + 2 N KI + $4.5 \cdot 10^{-4}$ moles/liter of $N(C_4H_9)_4Br$.

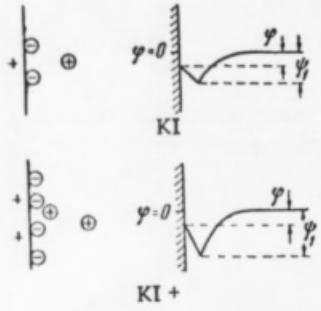


Fig. 2. Schematic representation of an electrical double layer at $\varphi_r = -0.6$ v.

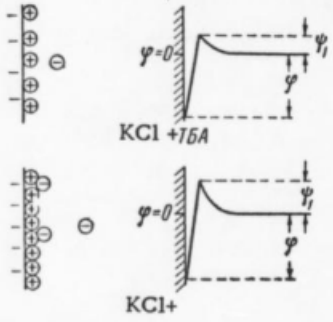


Fig. 3. Schematic representation of an electrical double layer at $\varphi_r = -1.2$ v.

where $\bar{I}$ is the average current measured with a well-damped mirror galvanometer; $S_2$ is the maximum area of a drop, calculated from the formula $S_2 = 0.850\ (\tau_d m)^{2/3}$ cm$^2$ ($\tau_d$ = dropping period, m = rate of mercury flow). Experiments were conducted at 20 ± 1°. An equilibrium hydrogen electrode in 2 N HCl + 2 N KCl was used as reference.

One can see from curve 1 in Fig. 1 that in the range of potentials where it was possible to measure hydrogen overvoltage on a dropping-mercury electrode the adsorption of $Cl^-$ ions was small, and one could not detect any effects on the overvoltage. Addition of some $N(C_4H_9)_4^+$ cations increased the overvoltage considerably (curve 3). Iodide ions, which were strongly adsorbed over a wide range of potentials at low current densities, decreased the overvoltage (curve 2). The introduction of $N(C_4H_9)_4^+$ cations in this case produced an additional decrease in the overvoltage in the region of low overvoltages (compare curves 2 and 4). With increasing current density the overvoltage increased sharply and attained a value greater than that in a solution of 2 N HCl + + 2 N KCl + $N(C_4H_9)_4^+$. When the current density was increased some more the excessive overvoltage decreased and the $\eta$ vs. log $\bar{i}$ curve coincided with the same curve for solutions free of organic cations (curve 4). The reduced action of organic cations in regions of high negative potentials has already been described [4].

It is obvious that the section of decreased $\eta$ in the region of low polarizations is associated with a predominant adsorption of iodide anions; the section of increased $\eta$ corresponds to predominant adsorption of organic cations, and finally the decreased effect of cations adsorption at higher polarizations corresponds to desorption of these cations.

The observed mutual reinforcement in the action of the adsorbed ions can be explained by some "secondary adsorption" of oppositely charged surface-active ions on the neutral surface of the electrode. Secondary adsorption enhances the adsorption of those same ions, which are already predominantly adsorbed in the given range of potentials, and thus produces a greater change in potential $\psi_1$ (see Fig. 2 and 3).

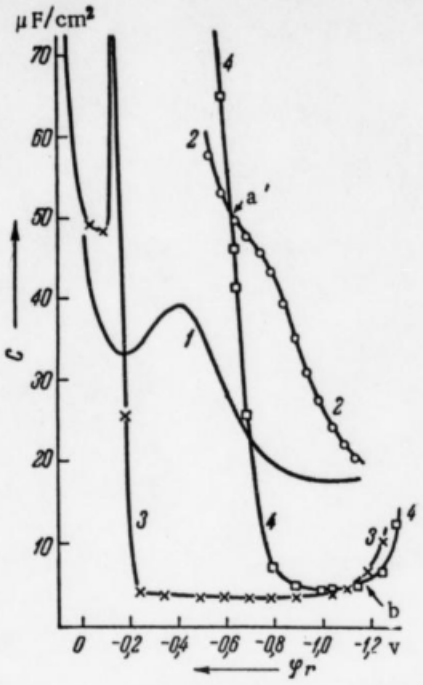


Fig. 4. Differential capacitance curves as a function of potential. The solutions are labeled just as in Fig. 1. Curves 1 and 2 were recorded at a frequency of 400 hertz, curves 3 and 4 at 5000 hertz.

This description of the combined ionic action is confirmed by the differential capacitance of an electrical double layer determined on a dropping-mercury electrode in those same solutions. The impedance bridge used in this work did not differ in its basic design from those described in papers [5-7]. The time interval between the detachment of a drop and the subsequent achievement of bridge balance was determined accurately with an electronic relay and an electric timer.

As one can see from Fig. 4 (where differential capacitance was plotted as a function of electrode potential $\varphi_r$), at potentials more negative than $-0.63$ v, curve 4, obtained with a solution containing quaternary salt cations, fell above the one with just HCl + KI in solution (curve 2). This means that with increasing potential at $\varphi_r > -0.63$ v, the electrode surface becomes charged more rapidly under the influence of quaternary cations. It is quite obvious that if only anions had any effect on the structure of the double layer at low polarizations then the left portions of curve 2 and 4 would have to coincide.

Iodide anions act similarly at high polarizations. Comparing curve 3 and 4 one can see that at potentials more negative than $-1.13$ v, the adsorption of quaternary cations in the presence of iodide anions decreases the capacitance more abruptly (with increasing potential), whereas the desorption of the organic cation begins at more negative potentials.

It is interesting to note that the potentials at the intersections of curves 2 and 4 and curves 3 and 4 (points a' and b' in Fig. 4) practically coincide with the potentials at the intersections of the corresponding polarization curves (points a and b in Fig. 1). It seems that to the first approximation this coincidence can be used to support the proposed hypothesis on the mutual reinforcement of adsorbed ions, although it would be more appropriate to compare the locations of a and b at the intersections of ($\eta$, log i) curves with the intersections of curves representing not the differential capacitance, but the electrode charge as a function of potential.

We wish to thank Academician A. N. Frumkin for his interest in this work and valuable advice.

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Received December 1, 1958

*In Russian.

# THE EFFECTS OF ABSORBED ANIONS ON HYDROGEN OVERVOLTAGE

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(Presented by Academician A. N. Frumkin, March 20, 1959)

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According to the theory of retarded discharge [1], the equation for the overvoltage for the liberation of hydrogen from acid solutions has the form:

$$\eta = \frac{RT}{\alpha F} \ln i - \frac{1-\alpha}{\alpha} \frac{RT}{F} \ln [H_3O^+] + \frac{1-\alpha}{\alpha} \psi_{10} + \text{const}, \quad (1)$$

where $\psi_{10}$ is the mean value of the potential at a distance of one ionic radius from the surface of the electrode (the potential of "the external Helmholtz layer").

In [2] an experimental comparison was made of the overvoltage curves with the electrocapillary curves for the same solution. It was found that, in qualitative agreement with the above equation (1), the halide ions $Cl^-$, $Br^-$ and $I^-$ reduced the hydrogen overvoltage at mercury in the low polarization regions, and that, in approximately the same potential regions, they lowered the interfacial tension at the mercury-solution boundary. But, deviations from linearity in the $\eta$ - log i curve, and an initial reduction in overvoltage, were observed at considerably more negative potentials than those corresponding to the beginning of divergences between the electrocapillary curves for the given soltuion and for solutions not containing surface active anions. It was therefore, considered that the lack of agreement between the desorption potentials of these anions, as determined by the two methods, might be explained on the assumption that small amounts of adsorbed material did not affect the electrocapillary curve, but, had a considerable influence on the overvoltage.

As the result of improvements in the technique of measurement, we now have available a more sensitive method of investigating the structure of the double layer, namely, the differential capacity method. It was therefore, of interest to carry out more precise measurements on the effects of adsorbed anions on the hydrogen overvoltage, using this method.

Figure 1 shows curves for the hydrogen overvoltage in acid solutions containing KCl, KBr and KI. These curves were obtained, using a dropping electrode at 20°, by the method described in [3]. Fig. 2 shows differential capacity curves, obtained with the same solutions at a dropping mercury electrode, by the method of [4]. Since, at sufficiently negative potentials, hydrogen evolution began in these acid solutions, and the system showed conductivity with alternating current, the true value of the capacity of the double layer, in these regions of potential, was calculated from the formula

$$C_{\text{true}} = \frac{C_M}{1 + 4\pi^2 f^2 C_M^2 (R_M - R_p)^2},$$

where $C_M$ and $R_M$ were the values of capacity and resistance, obtained directly by means of a bridge, in which the standard resistance and capacitor boxes were connected in series; f was the frequency of the alternating current used; $R_p$ was the total resistance of capillary and solution.

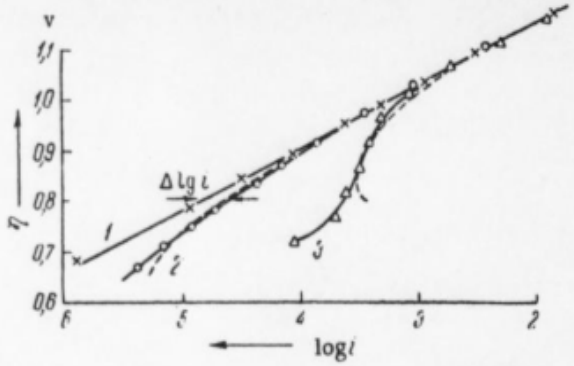


Fig. 1. Overvoltage curves in solutions: 1) N HCl + + 2N KCl, 2) N HCl + 2N KBr, 3) NHCl + 2N KI.

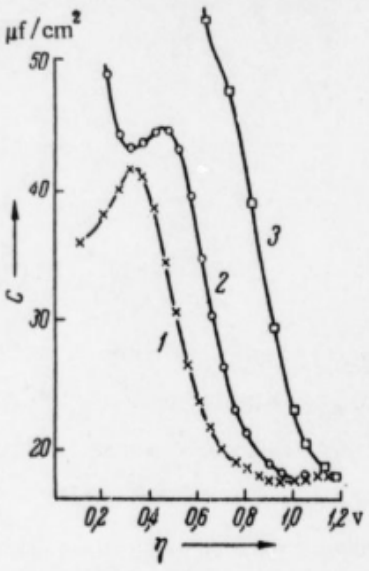


Fig. 2. Differential capacity curves, for the same solutions as in Fig. 1, at a frequency of 5000 cps.

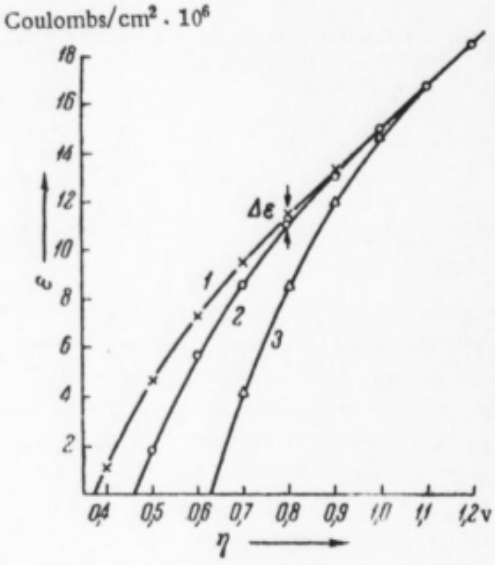


Fig. 3. Relation between discharge density, $\epsilon$, and potential for the same solutions.

Comparison of the overvoltage and capacity curves showed that the differential capacity was more sensitive to the absorption of anions than were the interfacial tension or the overvoltage. Divergences between the differential capacity curves were observed at considerably more negative potentials than divergences between the overvoltage curves. As will be shown below, in order to elucidate the effect of the double layer structure on the kinetics of electrochemical processes, it is convenient to use the value of the discharge density, $\epsilon$, rather than the interfacial tension or the differential capacity.

To calculate $\epsilon$, we first used the values of $\varphi_{\epsilon=0}$ found from the electrocapillary curves for the same solutions. But the values of $\epsilon$, obtained in this way, for the three solutions differed from each other by about 1-2% at $\eta$ = 1.2 v, where the capacity curves converged. This difference showed a lack of precision in the determination of $\varphi_{\epsilon=0}$ by the electrocapillary curve method, so we took the mean value of $\epsilon$ at $\eta$ = = 1.2 v as an integration constant for all three solutions, and integrated in the reverse order, starting with $\eta$ = = 1.2 v. The relation between $\epsilon$ and potential is shown in Fig. 3.

There was satisfactory agreement between the curves for $\epsilon$, $\eta$ and $\eta$ -log i. In the potential regions where the $\epsilon$ -$\eta$ curves were practically straight lines, the $\eta$ -log i curves were also straight. With KCl solutions, the curve remained a straight line over the range of potential investigated. The potentials at which deviations from linearity began for KBr and KI were of the same order (−0.95 v for KBr and −1.05 v for KI).

For the range of potential in which the absorption of anions was still not very great, the following empirical relation was found:

$$\left(\frac{\Delta \lg i}{\Delta \varepsilon}\right)_{\eta} \approx 0{,}5, \qquad (2)$$

where $\Delta$ log i and $\Delta\epsilon$ were the deviations of log i and $\epsilon$ from the corresponding values determined for KCl solutions at the same potential, and $\epsilon$ was expressed in $\mu$ coulombs/cm$^2$ (see Fig. 1 and 3). Fig. 1 shows both the experimental points (continuous curves) and the values of log i calculated from the relation $\Delta \log i = 0.5\Delta\epsilon$ (dotted curves). It is clear that the calculated and experimental curves agreed satisfactorily up to $\eta < 0.70$ v for KBr and $\eta < 0.65$ v for KI.

It is not difficult to derive Relation(2) from Equation (1) and some elementary considerations on the structure of the double layer.

From Equation (1) we obtain:

$$\left(\frac{\partial \lg i}{\partial \psi_{10}}\right)_\eta = -\frac{(1-\alpha)F}{2{,}3RT}. \tag{3}$$

So long as the adsorption of anions is small, we can reckon, without serious error, that the electric field in the close part of the double layer is determined only by the value of $\epsilon$ at the electrode surface, and we obtain:

$$\varepsilon = C_r(\varphi - \psi_{10}), \tag{4}$$

where $C_r$ is the capacity of the outer Helmholtz layer in the presence of adsorbed anions. It follows from (4) that:

$$\left(\frac{\partial \psi_{10}}{\partial \epsilon}\right)_\eta = -\frac{1}{C_r}. \tag{5}$$

Since, in the presence of adsorbed anions, the capacity alters little with potential over the range of potential considered, the value of $C_r$ can be put equal to the differential capacity of the outer Helmholtz layer. The latter, with solutions of the concentration considered, hardly differs from the capacity of the double layer as a whole. From (3) and (5) it follows that:

$$\left(\frac{\partial \lg i}{\partial \epsilon}\right)_\eta = \left(\frac{\partial \lg i}{\partial \psi_{10}}\right)_\eta \left(\frac{\partial \psi_{10}}{\partial \epsilon}\right)_\eta = \frac{(1-\alpha)F}{2{,}3RTC_r}. \tag{6}$$

Putting $C_r = 18$ $\mu$f/cm$^2$ and $\alpha = 0.5$ in (6), we obtain:

$$\left(\frac{\partial \lg i}{\partial \epsilon}\right)_\eta \approx 0{,}5. \tag{7}$$

When the adsorption of anions became greater, $\psi_{10}$ was determined, not only by the value of $\epsilon$ at the electrode surface, but, also by the charge of the adsorbed anions, so that Equation (3) was no longer correct. But, according to Grahame's latest data for KI [5], when $|\epsilon| > 10$ $\mu$coulombs/cm$^2$ ($\eta > 0.85$ v), the adsorbed ions were still at some distance from the electrode surface, so that our assumption was evidently still applicable as a first approximation.

It is clear from the above that the effect of adsorption of halide anions on the hydrogen overvoltage can be related quantitatively to the change in surface charge, $\epsilon$. Measurements of overvoltage should therefore, be compared with the values of $\epsilon$, and not with the interfacial tension or differential capacity. The interfacial tension – the result of integrating the charge density $\left(\sigma = \int \varepsilon\, d\varphi\right)$, – is not sensitive enough to small changes in the structure of the double layer. The differential capacity, which is a derivative of $\epsilon$, is too sensitive to small changes in structure which are not reflected in the polarization curves.

Using the same solutions, $\eta - \log i$ curves were recorded at a large stationary mercury cathode. The absence of hysteresis loops in the curves for direct and reverse polarization indicated that the adsorption of $I^-$ ions proceeded rapidly. The hysteresis loops observed previously [2] were possibly due to traces of iodine or of mercury ions in the solution.

We would like to thank Academician A. N. Frumkin for his interest and advice during the progress of the work and the interpretation of the results.

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# A DIFFERENTIAL CAPACITY STUDY OF THE ADSORPTION OF SURFACE-ACTIVE IONS ON A ZINC ELECTRODE

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The differential capacity of the double layer was first used by T. I. Borisova, B. V. Érshler, and A. N. Frumkin [1] in determining the potential of zero charge $\varphi_{\epsilon=0}$ on electrodes and solid metals (Pb, Tl, Cd). They showed that the capacity vs potential curves for these metals were similar to the well-known C, $\varphi$ curves for the mercury electrode. C, $\varphi$ curves have been used for determining $\varphi_{\epsilon=0}$ values and for adsorption studies on Fe [2], $PbO_2$ [3], Zn [4], and on other metals [5].

On solid metals the capacity varies with the frequency of the applied alternating current (capacity dispersion). Based on the fact that capacity dispersion is less on a smooth metal surface, for example a molten metal [1] or a single crystal [6], it was suggested [2] that the numerous microcracks in the surface of a polycrystalline metal screen part of the surface as the frequency is increased. This decrease in effective surface of the electrode explains the decrease in capacity at high frequencies. On the other hand, Bockris and Conway [7] explain capacity dispersion as being due to slow relaxation of water molecules on the surface of a solid electrode.

The object of the present work was to study the structure of the double layer at the zinc electrode by measuring the differential capacity.

B. S. Krasikov and V. V. Sysoeva [4] measured the capacity at the zinc electrode to determine $\varphi_{\epsilon=0}$. However, we were unable to obtain a potential close to the value $\varphi_{\epsilon=0} = -0.63$ v found by these authors (the normal potential of the zinc electrode $\varphi^0_{Zn} = -0.76$ v) because, when the negative potential was decreased, dissolution of zinc occurred and an anodic current was observed even at -0.85 v. Therefore, the accuracy of $\varphi_{\epsilon=0}$ values for zinc are questionable where the measurements were made in aqueous solutions. Electrocapillary measurements on molten salts at high temperatures [8] offer an independent method of finding $\varphi_{\epsilon=0}$, assuming a constant potential difference between the maxima of the electrocapillary curves for a given metal in a melt and in an aqueous solution. For zinc this method gave $\varphi_{\epsilon=0} \approx -0.65$ v.

We used an ordinary impedance bridge to measure the capacity. The electrode was prepared by growing a single crystal of spectrally pure zinc in a hard glass tube (i.d. 0.4-0.5 mm) so that the plate of the base was parallel* to the axis of the resulting fine wire. The area of the electrode immersed in the solution was measured with a microscope.

Figure 1 (curves 1 and 2) shows that the variation of differential capacity at a zinc single crystal in 0.2-1.0 N KCl was only 5-8% over the frequency range 0.4-1.0 kc/sec. In dilute solutions the variation was much greater, but in this case it was due to a parasitic bridge to ground, because the capacity–frequency curve for 0.01 N KCl at $\varphi = -1.22$ v was completely compensated when a compensating capacitor was inserted into the bridge circuit, as described by B. B. Damaskin [9]. Such a correction, however, can only be applied when the

* As in the Russian original.

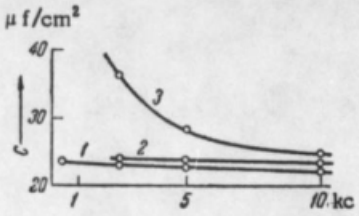


Fig. 1. Dependence of double-layer capacity on frequency at $\varphi$ = - 1.22 v. 1) Zinc single crystal in 1.0 N KCl; 2) same in 0.2 N KCl; 3) polycrystalline zinc in 1.0 N KCl.

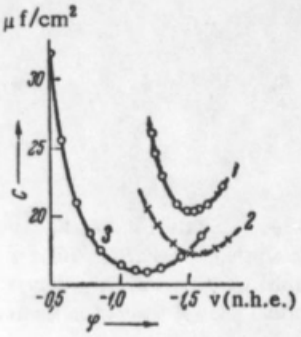


Fig. 2. Differential capacity of the double layer at different metals in 0.1 N KCl (frequency 10 kc/sec). 1) Zn; 2) Ga; 3) Hg.

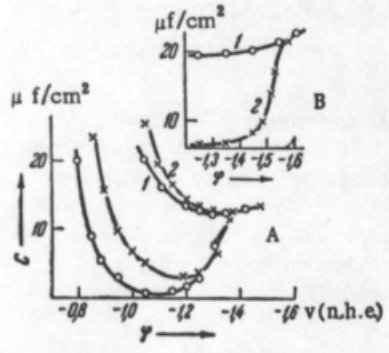


Fig. 3. Differential capacity at zinc single crystal (frequency 10 kc/sec). A: 1) 0.5 N KCl 2) 0.5 N KI; 3) 0.5 N KCl + 0.00024 N $N(C_4H_9)_4^+$; 4) 0.5 N KI + 0.00024 N $N(C_4H_9)_4^+$. B: 1) 1.0 N KCl; 2) 1.0 N KCl + 0.001 N $N(C_4H_9)_4^+$.

cell resistance is less than 100 ohms. In 0.001 N KCl (R = 5000 ohms) this method of compensation is not satisfactory. The effect of the state of the metal surface on capacity variation with frequency can be seen by comparing Curve 3 for polycrystalline zinc with Curve 1 (Fig. 1).

Figure 2, Curve 1 shows the variation of C with $\varphi$ at a zinc single crystal in 0.1 N KCl. The curves for Hg and Ga in the same solution, based on the data of Grahame [10], are given for comparison. It is seen that the three curves are similar in form, especially if they are moved along the abscissa until the minima coincide. The branches of the curves rise more steeply from the minima, however, for Ga and Zn than for Hg. It was suggested that the rise of the C, $\varphi$ curve for zinc when the cathodic potential was decreased might be due to pseudocapacity as the normal potential of the metal was approached. However, a simple calculation showed that pseudocapacity was insignificant in the region of the rise of the curve.• It is evident therefore that the positive branch of Curve 1 in Fig. 2 is due to adsorption of chlorine ions.

Figure 3A shows C, $\varphi$ curves for the zinc electrode in solutions containing surface-active ions. The general form of these curves resembles that of the corresponding curves for mercury, which indicates a similar structure of the double layer on zinc and mercury. However, the difference between the C, $\varphi$ curves 1 and 2 in Fig. 3A is much less than that between the corresponding curve on mercury [12], which is obviously related to the smaller adsorption of $I^-$ on zinc. It should be noted that the instability constant of the halide complexes with mercury is much less than that for zinc, and also that the difference between these constants for $Cl^-$ and $I^-$ is much less in the case of zinc than for mercury [13].

$N(C_4H_9)_4^+$ ions are strongly adsorbed on zinc (Fig. 3 A). These ions are desorbed from the mercury electrode when the potential becomes sufficiently negative ($\varphi$ = = - 1.58 v), but no desorption peak was observed in the zinc electrode curves (Fig. 3 B). This fact indicates that adsorption equilibrium is reached very slowly on zinc as compared with mercury. The desorption potential for $N(C_4H_9)_4^+$ ions on zinc in a solution of 1 N KCl + 0.001 N $N(C_4H_9)_4^+$ (Fig. 3 B) and the desorption peak for mercury in the same solution [14] are almost identical when

• The pseudocapacity was calculated using the formula [11] $C_p = \frac{n^2F^2D^{1/2}C}{RT\ \omega}$, assuming n = 2, F = $10^5$ $\frac{\text{coulombs}}{\text{mole}}$ R = 8.3 $\frac{\text{joules}}{\text{mole}}$, D = $10^{-5}$ $cm^2/sec$, $\omega = 10000 \cdot 2\pi$. For E = - 0.76 v, c = $10^{-3}$ mole/$cm^3$, C = $2 \cdot 10^5$ $\mu f/cm^2$; for E = - 0.88 v, c = $10^{-7}$ mole/$cm^3$, C = 20 $\mu f/cm^2$; for E = -0.91 v, c = $10^{-8}$ mole/$cm^3$, C = 2 $\mu f/cm^2$. Since all the potentials were more negative than - 0.91 v, therefore the pseudocapacity in our experiments was less than 2 $\mu f/cm^2$.

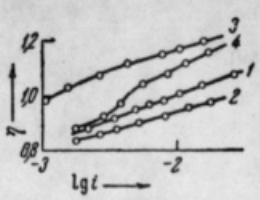


Fig. 4. Hydrogen overvoltage at zinc single crystal. 1) 0.5 N HCl + 0.5 N KCl; 2) 0.5 N HCl + 0.5 N KI; 3) 0.5 N HCl + 0.5 N KCl + 0.0004 N $N(C_4H_9)_4^+$; 4) 0.5 N HCl + + 0.5 N KI + 0.0004 N $N(C_4H_9)_4^+$.

referred to the $\varphi_{\epsilon=0}$ of the respective metals. Thus, the desorption peak for mercury in 1 N KCl + 0.001 N $N(C_4H_9)_4^+$ was observed at - 1.28 v, $\varphi_{\epsilon=0}$ = - 0.28 v, giving a difference of - 1.0 v. For zinc the potential of complete desorption was - 1.58 v, $\varphi_{\epsilon=0}$ = - 0.65 v, the difference being - 0.93 v.

Figure 4 shows the relationship between the hydrogen overvoltage at a zinc single crystal and the logarithm of the current density in a solution containing surface-active ions. These curves, like the capacity curves, resemble the corresponding ones for mercury. The adsorption of iodine ions lowered the overvoltage, but as in the case of the C, $\varphi$ curves the effect was less at the zinc electrode than at the mercury electrode [15]. Lowering of the hydrogen overvoltage owing to adsorption of $Cl^-$ and $Br^-$ ions at a zinc amalgam electrode was observed by Ya. V. Durdin and E. G. Tsventarnyi [16]. The curves in Fig. 4 show that as in the case of mercury $N(C_4H_9)_4^+$ ions increased the hydrogen overvoltage at zinc considerably. Unfortunately, we did not reach the desorption potential for these ions while measuring the overvoltage. When the $N(C_4H_9)_4^+$ and $I^-$ ions were present simultaneously the $\eta$, log i curves lay between Curves 2 and 3 in Fig. 4. As the negative potential is decreased, the adsorption of iodine ions increases, and the overvoltage decreases. This effect, which is due to a mutual increase in adsorption, was observed at the mercury cathode [15] but not at the zinc electrode over the potential range studied.

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查先生 1988 年为弗鲁姆金纪念文集写的一段话

*Ча Чуань-син*

Монография А. Н. Фрумкина и его сотрудников «Кинетика электродных процессов» была опубликована после освобождения Китая, когда термин «электродная кинетика» был еще новинкой не только для китайских ученых, но и для большинства ученых всего мира. Появление этой книги на прилавках книжных магазинов немедленно привлекло внимание нескольких групп ученых в различных научных учреждениях Китая. Группа молодых преподавателей химического факультета Уханьского университета, среди которых был и я (возможно, я был наибольшим энтузиастом), организовала семинар, основной задачей которого было внимательное изучение монографии А. Н. Фрумкина. Так была создана Уханьская группа электрохимиков, одна из многочисленных в настоящее время электрохимических групп в Китае.

В 1957—1959 гг. я получил возможность поработать в качестве приглашенного ученого на кафедре электрохимии МГУ, которую возглавлял А. Н. Фрумкин. Несмотря на «страшные бедствия» вроде пролитой ртути или сломанного тонкостенного капилляра нужного диаметра, я ощущал, что все сильнее и сильнее «адсорбируюсь» на границе раздела электрода и электролита. Пожалуй, самое ценное, чему я научился в Москве у А. Н. Фрумкина и З. А. Иофа,— это иметь собственное мнение, не бояться сказать «нет» и верить, что я могу сделать что-то не хуже других. Мой отец рассказывал мне, что, когда он был студентом последнего курса Университета Миннесоты (США), профессор Милликен попросил его обменяться рукопожатием с Зоммерфельдом и потом заметил: «Пожав руку великому ученому, ты начинаешь быстрее понимать его книги».

Мой собственный опыт показывает, что уверенность в своих силах не менее важна, чем талант и усердие. Такая уверенность в научной деятельности может быть лучше всего достигнута в подлинно творческой академической обстановке, в которой я находился на кафедре Александра Наумовича.

Я бережно храню и ценю те рукописи своих работ, которые Александр Наумович тщательно исправлял, отказываясь включить себя в число авторов. Его имя связано с работами по электрохимии и традициями электрохимиков всего мира, а Китай — часть этого мира.

*Ухань, 1988 г.*