

DIANHUAXUE YU DIANFENXI HUAXUE

电化学与电分析化学

——李启隆学术论文选

李启隆 等◎著



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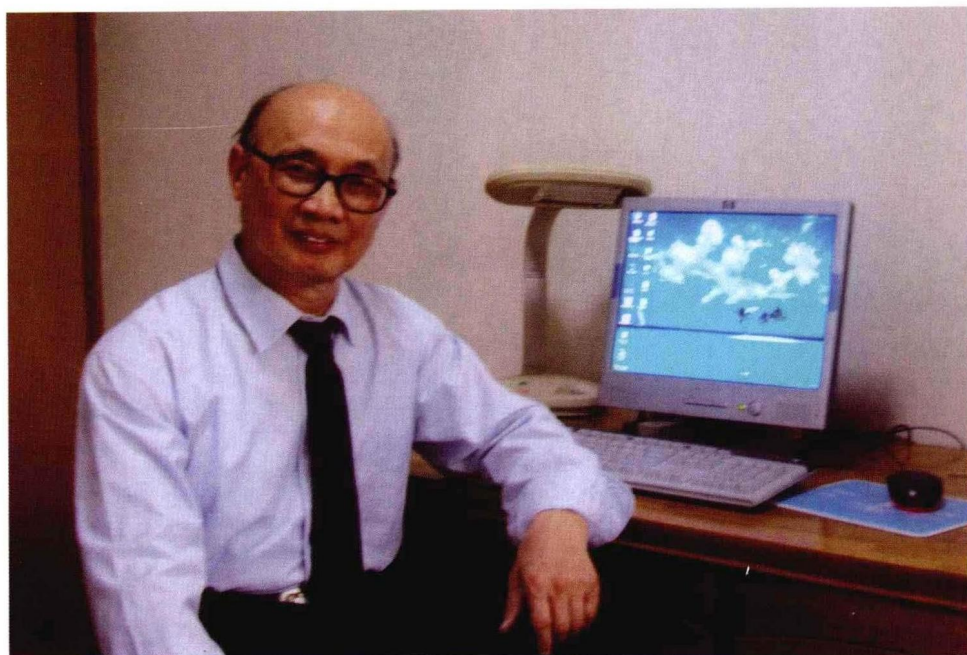
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李启隆，教授，博士，博士生导师。1937 年生于广东省大埔县湖寮区岭下乡。1956 年考上北京师范大学化学系本科，1960 年毕业留校任教。同年在北京大学化学系进修，师从高小霞教授，1962 年回到北京师范大学。1979 年在布加勒斯特工学院化学系当访问学者，后在导师 C. Luca 教授和 A. Calusaru 教授的鼓励和支持下，经双方教育部批准，转为博士生，并于 1982 年获化学博士学位后回国。讲授基础课《仪器分析》、《分析化学》、《食品分析》和研究生专业基础课《电分析化学》、《化学文献》等课程。从事电化学和电分析化学、药物和生物电分析化学等领域研究，获国家自然科学基金和博士点基金等资助。在《Anal. Chim. Acta》、《Analyst》、《Anal. Biochem》、《J. Electroanal. Chem》、《化学学报》、《高等学校化学学报》、《科学通报》等国内外重要杂志上发表学术论文 170 多篇。出版编著《电分析化学》，合编《仪器分析》和《食品分析科学》等。



与合作者尚军高级实验师(右 1)、胡劲波教授(左)和于泳研究员(右 2)在一起



1999 年 11 月，胡劲波博士论文答辩后合影。左起：吴仲达教授、张月霞教授、李南强教授、周同惠院士、胡劲波博士、慈云祥教授、李启隆教授



2002 年参加国家基金委委托扬州大学举办的国家自然科学基金重点项目结项报告时合影



1987 年参加北京 BCEIA 国际会议，与金文睿教授(左 1)、赵藻藩教授(左 2)、李南强教授(右 2)合影



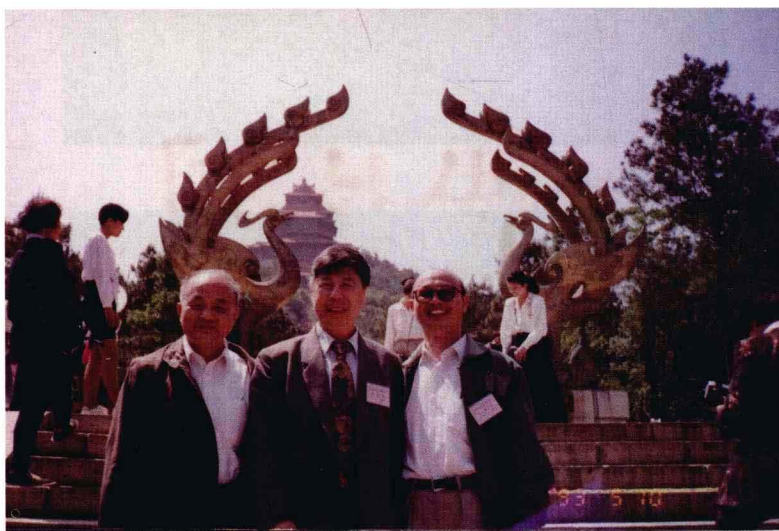
1999 年在美国新奥尔良匹斯堡分析化学和光谱应用展览会楼前



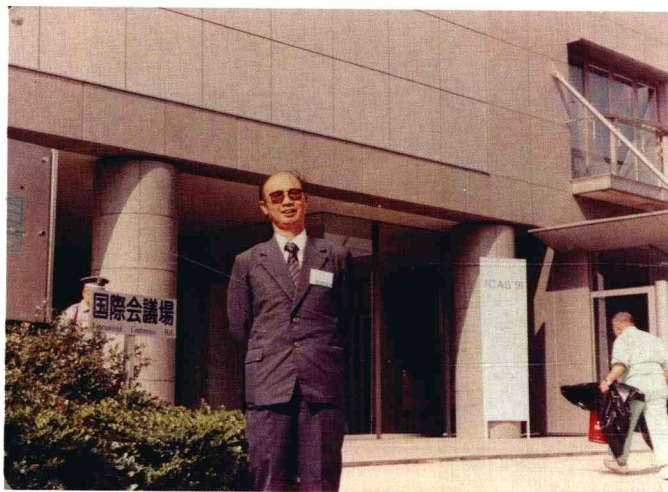
20 世纪 80 年代末与访问北京的美国电
分析化学家 Wang J 合影



与毕业学生在一起



1993 年参加武汉全国电分析化学学术会议时与莫金垣教授(左)、汪尔
康教授(中)合影



1991 年 8 月参加日本分析科学会议会场前



与研究生答辩后合影



与科研组的老师和研究生在一起

自序

这本论文选收集了我们 37 篇论文，大多是从我与我的学生们共同发表的 150 多篇论文中筛选出来的，是我们多年科研工作的结晶。

出版这本论文选旨在回顾和总结我们的科研工作，并借此机会与同行专家交流。

当我回忆往昔所走过的科研道路时，心潮澎湃，百感交集。我的科研经历并不是一帆风顺，而是充满了艰难和曲折的。不过，这也铸就了我不畏艰苦、百折不挠的性格。我凡事尽心尽责，不屈不挠，矢志不渝，用自己劳动的双手辛勤地培育科研之花和科研之果。花可以共赏，果可以同享。值得庆幸的是，我遇到了许多关怀我、教育我的好老师和鼓励我、帮助我的好同学、好同事、好朋友。我所取得的成果是与他们的教育和帮助分不开的。

自 1982 年起至今，28 年间，我们主要研究了 5 个专题：

1. 极谱催化波与络合吸附波及其机理；
2. 吸附伏安法及其在药物分析中的应用；
3. 金属离子注入修饰电极(包括超微电极)的研制及其药物、DNA 和蛋白质的电化学；
4. 有机官能团离子注入修饰电极及其与纳米技术相结合的 DNA 和蛋白质电化学；
5. 化学修饰电极及生物传感器等。

这些专题得到了国家自然科学基金和博士点基金等的资助。

在 20 世纪 80 年代，我们开展了极谱催化波、络合吸附波的研究。提出了 $Al(III)$ -邻苯二酚紫、 $Cu(II)$ -丁二酮肟和金属离子-环丝氨酸催化氢等 10 多个新的体系，并对其络合性、吸附性和电活性进行了深入的研究，建立了检测它们的新方法。曾多次被邀请在全国学术会议上作专题报告，得到同行专家的好评。吸附伏安法是一种简单而灵敏的方法，在 20 世纪 80 年代末到 90 年代初，被用于金属离子的测定，而用于有机药物的研究和测定才刚刚起步。我们在国家自然科学基金的资助下，研究了舒乐安定、抗痫灵、头抱氨苄及其衍生物、抗癌药物博来霉素、阿霉素、长春新碱、紫杉醇等及其与 DNA 或微管蛋白的相互作用，取得了一系列的成果。

1990 年，我在一次研究生毕业论文答辩会上，提出了将离子注入这种新的材料表面改性技术可用于分析化学的理念，当时有人提出异议。第二年即 1991 年 8 月间，我在日本参加分析科学国际会议时，参观了东京理化学研究所。该所向我们展示了他们研究的新成果：一个闪闪发光的小球。他们说，这是普通铁球的表面上用离子注入手段注入了微量的铂，既漂亮，又耐腐蚀。这个发光的小球又激发了我原来的理念。回国后获得了国家自然科学基金的支持和资助，开展了长达近十年的不懈的、艰苦的研究工作。先后注入了钴、镍、铂等金属，成功制成了各种各样的离子注入修饰的常规电极和超微电极，用 XPS、AES、SEM 等多种表面分析手段进行表征，并用于抗癌药物、蛋白质和 DNA

等的研究,取得了开拓性的创新成果。这类新的修饰电极具有灵敏度高、稳定性好、催化活性强和简便耐用等特点。国际杂志 *Analyst* 评为“Discovered an interesting electrode material and analysis method described appears useful”(发现了一种有意义的电极材料和有用的分析方法)。后来有些国家,例如日本,也开展了这方面的研究工作。

化学修饰电极自 1973 年诞生以来,一直是分析化学领域中研究的热点。它是用吸附或键合的方法将带有某种特定功能团的有机化合物修饰到基体电极表面而制成的。这种电极的主要缺点是稳定性较差,因而产生了用离子注入的手段把有机官能团直接注入而制成稳定的新电极的设想。我们将 $-\text{NH}_2$ 、 $-\text{COOH}$ 和 $-\text{OH}$ 等有机官能团注入到 ITO 等基体电极上,或与纳米技术结合,制成纳米金、纳米钴、纳米镍和碳纳米管修饰电极或传感器,研究抗癌药物、蛋白质和 DNA 电化学反应及其相互作用,取得了开拓性的创新成果。这类电极的研究具有重要的理论意义和广泛的应用前景。

我们也在化学修饰电极方面做了一些工作,主要将其与金纳米和非金纳米(包括纳米钴、纳米镍和碳纳米管)相结合,制成各种电化学传感器和生物传感器,用于检测 DNA、谷胱甘肽、细胞色素 c 等蛋白质及抗癌药物等,也取得了创新性的成果。

这本文选原本筛出 54 篇论文,由于篇幅的限制,除删弃一些研究论文外,还将较能全面反映我们工作的专题报告或综述统统割爱放弃了。这些论文由于发表的时间和杂志不同,其中使用的各种符号不一致,为保持原貌,未做统一。

值此论文选出版之际,感谢老师们对我的关怀与教诲和同学、同事、朋友对我的鼓励与帮助。

感谢国家自然科学基金、博士点基金和其他基金的资助。

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感谢北京师范大学低能所来永春、白桂彬和薛文彬等老师的支持和帮助。

感谢 28 年来历届本科生、硕士生和博士生的辛勤而创新的工作。这些成果也渗透着他们的汗水。他们那种废寝忘食、踏踏实实的态度和不怕困难、开拓进取的精神,深深地感动了我。

感谢合作者尚军高级实验师、胡劲波教授和中国科学院力学研究所于泳研究员和北京科技大学鲁毅强教授等。他们为科研工作作出了重要的贡献。我们曾一起经历过“山穷水尽疑无路”的艰难时期,也经历过“柳暗花明又一村”的光辉前景。

感谢博士生李硕琦。他帮助我从网上查找有关论文和扫描一些资料,使我的收集和整理工作得以顺利完成。

感谢我的哥哥、姐姐及家人。无论过去和现在,他们一直在关心我和帮助我。

最后还感谢 40 多年来与我同甘共苦的爱人王家英。她默默地、无怨无悔地承担了教育孩子的重任和繁重的家务。她对我始终如一的支持,使我能专心致志地工作。

李启隆

2010 年 9 月 22 日

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第一部分 极谱催化波与络合吸附波及其机理研究

1. Catalytic Hydrogen Discharge by Cycloserine in Metal-Ion Containing Ammonia Buffer

Li Qi Long, C. Luca, A. Călusaru and F. G. Bănică

National Institute of Chemistry, Spl. Independentei No 202, 77208-Bucharest, Romania

Catalytic hydrogen discharge was studied in ammonia buffer containing cycloserine and Ni^{2+} , Zn^{2+} , Cd^{2+} and Cu^{2+} ions. It has been found that the catalytic wave is enhanced in the presence of these ions. There is no essential difference on the species of metal ion, but the half-wave potential of the catalytic wave increases in the above-mentioned order of cations. The effect of the characteristic parameters was studied and it has been concluded that the catalytic wave is very similar to a wave of pre-sodium type. The enhancement of the wave can be explained by the convective transport of the metal ion due to electrolyte streaming as in the case of maxima of the first kind. Cycloserine transport toward the electrode in ligand form also plays an important role.

The heterocyclic compound D-4-amino-3-isoxazolidone is an important substance from the standpoint of its use as an antibiotic. It is called also cycloserine, oxamycin, seromycin or orientomycin. Among these commercial names the first is the widest used.

In a previous work the polarographic properties of the cycloserine in the presence of cobalt ions was studied.¹ Although this compound has a formally simple structure in the presence of cobalt it shows complex properties in polarography.

In buffer solutions, cycloserine alone forms a catalytic hydrogen wave of the pre-sodium type. In cobalt-containing solution the behaviour of this substance depends strongly on cobalt concentration. At 10^{-5} M Co^{2+} the hydrogen wave produced by cobalt-cycloserine complex is diffusion-controlled and separated from the pre-sodium wave. Within the cobalt concentration range $10^{-5} - 2.5 \times 10^{-5}$ M, the pre-sodium wave is progressively displaced towards more positive potentials and over these concentrations only one wave can be found, which is identical with the so-called Brdička wave. This process was called the "superposition effect of catalytic hydrogen waves";¹ its particular importance for the mechanism of the catalytic hydrogen discharge consists especially in explaining the inde-

pendence of the Brdička wave of the mercury reservoir height. This apparent independence is due to the composite character of the Brdička wave, which contains a diffusion-controlled and a pre-sodium component. Therefore the invariance of the Brdička wave cannot be ascertained to the kinetic character of the discharge, although the chemical reaction occurs at the same time with, or before the discharge of the proton proper.

The aim of the present work is to study the catalytic hydrogen discharge in ammonia buffer containing cycloserine and metal ions: Ni^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} . It has been found that there is no essential difference in the presence of one or another of the above-mentioned ions. In contrast to the Co-containing system, no catalytic hydrogen wave due to metal ion-cycloserine complex forms; as a consequence, the effect of metal ions on the pre-sodium wave can be studied without any interference.

EXPERIMENTAL PART

The purity of cycloserine, determined potentiometrically, was found to be 98%. The melting point of 154 °C and the dissociation constants $\text{p}K_{\text{a},1}=4.45$ and $\text{p}K_{\text{a},2}=7.45$ correspond to the values given in the literature.²⁻⁴ The other substances were of analytical grade.

The polarograms were recorded under nitrogen atmosphere with a LP 7 e polarograph using a cell with a saturated calomel electrode as anode. The constants of the capillary were: $t_1=4.60$ s and $m=2.44$ $\text{mg} \cdot \text{s}^{-1}$ in 0.1 M ammonia buffer, open circuit at $h=50$ cm.

EXPERIMENTAL RESULTS

1. Effect of metal ion concentration on catalytic hydrogen wave

In 0.1 M $\text{NH}_3\text{-NH}_4\text{Cl}$ solution containing 2×10^{-3} M cycloserine and 10^{-3} M Me^{2+} (Me is Ni, Cd, Zn and Cu), two polarographic waves are formed: (1) a diffusion wave of Me^{2+} reduction and (2) a catalytic hydrogen wave. The half-wave potential of the catalytic wave depends on the nature of Me^{2+} as follows: $E_{1/2,\text{Co}} = -1.72$ V; $E_{1/2,\text{Ni}^{2+}} = -1.87$ V; $E_{1/2,\text{Cd}^{2+}} = -1.91$ V; $E_{1/2,\text{Zn}^{2+}} = -1.92$ V and $E_{1/2,\text{Cu}^{2+}} = -1.96$ V.

In Fig. 1 the polarographic wave of catalytic hydrogen discharge of cycloserine both in the absence and presence of nickel ions is shown. In the absence of nickel (Fig. 1, Curve 1), the catalytic wave is not defined well enough. When the nickel ion concentration increases, the height of the catalytic wave also increases and the corresponding limiting current becomes more clearly defined (Fig. 1, Curve 4). A similar behaviour is observed in the presence of Cd^{2+} , Zn^{2+} and Cu^{2+} ions.

The variation of the catalytic current with nickel ion concentration is shown in Fig. 2. At higher nickel ion concentration, the catalytic current tends towards a limiting

value, as in the case of other systems, where this kind of discharge was studied.⁵

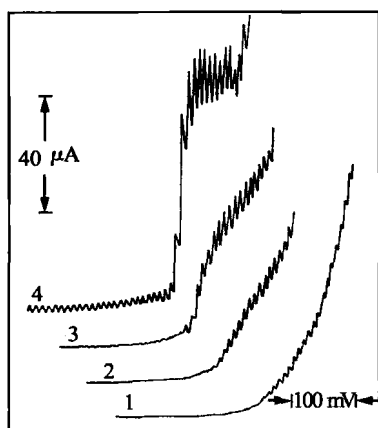


Fig. 1 Effect of nickel ion concentration on catalytic hydrogen wave of 2×10^{-3} M cycloserine in 0.1 M $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer. Ni^{2+} concentration: 1—0; 2— 8×10^{-5} ; 3— 3×10^{-4} ; 4— 10^{-3} M. Start potential, -1.60 V

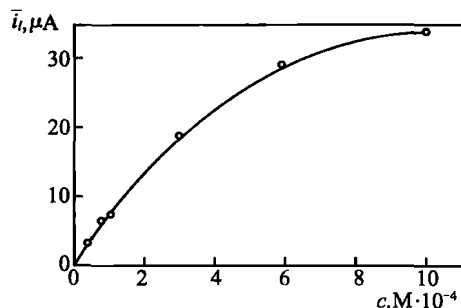


Fig. 2 Variation of catalytic current with nickel ion concentration in 0.1 M $\text{NH}_3\text{--NH}_4\text{Cl}$ and 2×10^{-3} M cycloserine

The catalytic current is enhanced not only by metal ions but also by several non-metallic depolarisers like oxygen, quinone and phenolphthalein. As in the works of Biezina and Kütova,^{6,7} this fact proves the lack of specific effects of complex formation.

2. Effect of cycloserine concentration

One of the most characteristic behaviours of the catalytic currents is that the relationship between the limiting current and the catalyst concentration is not linear. This kind of variation was found also in the present case. In Fig. 3 the variation of the catalytic hydrogen wave with cycloserine concentration is shown in 0.1 M $\text{NH}_3\text{--NH}_4\text{Cl}$ solution at three nickel ion concentrations: (1) 5×10^{-4} M; (2) 1×10^{-3} M and (3) 2×10^{-3} M. In all cases the height of the catalytic wave increases with the catalyst concentration, but only at higher cycloserine concentrations the current does not vary linearly with this parameter.

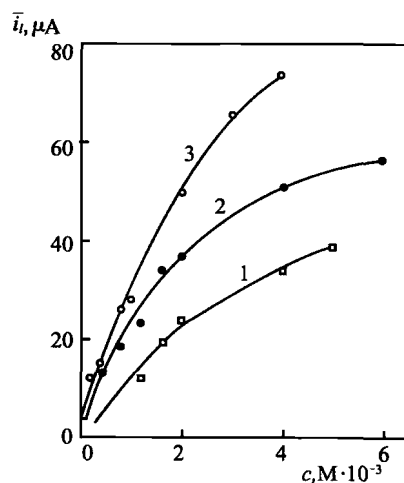


Fig. 3 Variation of catalytic hydrogen current with cycloserine concentration in 0.1 M $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer. Ni^{2+} concentration: 1— 5×10^{-4} ; 2— 1×10^{-3} ; 3— 2×10^{-3} M

3. Effect of mercury reservoir height

The effect of mercury reservoir height on the polarographic waves gives valuable information on the process which is rate determining in the overall

reaction. The Brdička-type catalytic waves are independent of the mercury reservoir height, but in the cycloserine-cobalt system it has been shown¹ that this behaviour is produced by the superposition effect on catalytic hydrogen waves. In the presence of nickel ions the catalytic current formed by cycloserine decreases with the increase of the mercury reservoir height, showing the influence of the adsorption process of the catalyst on the mercury surface. This behaviour is always encountered in the pre-sodium type waves and therefore also in the cycloserine nickel system the catalytic wave may be of this type.

4. Effect of buffer capacity

Since the catalytic wave is formed by the discharge of the proton, the increase of the buffer capacity produces in general a visible increase of this wave height. This behaviour is considered to be one of the most peculiar concerning the catalytic hydrogen discharge. In the case of the cycloserine-nickel system, the variation of the catalytic current with the buffer capacity is given in Fig. 4. The increase of the limiting current with the increase of the buffer capacity shows the determining role of the protonation reaction. The same behaviour was found in cycloserine-cobalt system.¹

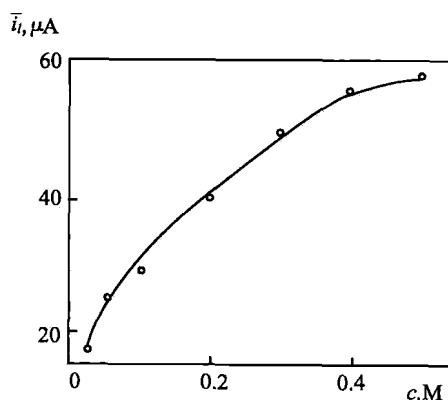


Fig. 4 Effect of buffer capacity on catalytic wave

$NH_4Cl/NH_3=1$; $10^{-3} M Ni^{2+}$; $2 \times 10^{-3} M$ cycloserine

5. Effect of temperature

The catalytic current increases sharply with the rise in the temperature. Experimental measurements were carried out within the temperature range $25^\circ C \sim 35^\circ C$ only, owing to the instability of cycloserine at higher temperatures. For this temperature range the temperature coefficient is $10.4\%/^\circ C$. This high value is characteristic to the currents where the chemical reaction is the rate-determining step. In the present case the most probable chemical reaction is the protonation of the catalyst. It has been found, the same as in other systems, that the rate of protonation reaction is faster as compared with the

catalyst adsorption.⁸ However the effect of temperature depends on the cation present in solution. In the same conditions in the presence of Cd^{2+} the height of the catalytic wave reaches a maximum value at 27°C ; for the higher temperatures, the wave height decreases. This complex behaviour can be explained by the concurrence of the reaction rate and the rate of adsorption. The latter becomes rate determining over 27°C .

6. Effect of ammonia concentration

In solution of ammonia buffer the increase of NH_3 concentration produces also an increase of the pH. This is why the height of the catalytic wave decreases with the increase of NH_3 concentration. This variations is of a general character in the case of catalytic hydrogen currents.

In Fig. 5 the variation of the limiting current is given as a function of NH_3 concentration. The polarographic catalytic wave decreases sharply in the initial part of the curve and then reaches a low limiting value.

7. Effect of ammonium chloride concentration

The increase of the ammonium chloride concentration results in two effects: (1) the decrease of pH; (2) the increase of the proton donor concentration. Both these effects contribute to increase the height of the catalytic wave. The variation of the catalytic wave in the presence of nickel ions as a function of ammonium chloride concentration is given in Fig. 6. The catalytic current increases with the increase of NH_4Cl concentration and tends to a limiting value for higher concentrations.

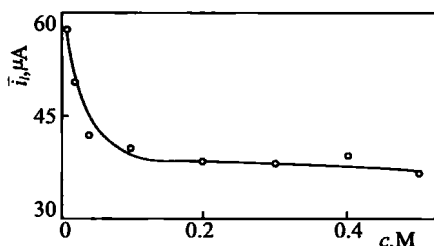


Fig. 5 Variation of catalytic current with ammonium concentration

Solution: $10^{-3} \text{ M Ni}^{2+}$; $2 \times 10^{-3} \text{ M cycloserine}$; $10^{-1} \text{ M NH}_4\text{Cl}$

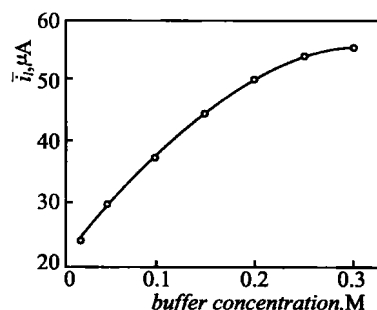


Fig. 6 Variation of catalytic wave with ammonium chloride concentration

Solution: $10^{-3} \text{ M Ni}^{2+}$; $2 \times 10^{-3} \text{ M cycloserine}$; 10^{-1} M NH_3

8. Effect of ionic strength

The ionic strength modifies the structure and the pH of the electrical double layer. Therefore the discharge process is influenced by the variation of ionic strength, especially

when the catalyst is adsorbed on electrode surface, as it occurs in the case of cycloserine containing system. The variation of the catalytic wave as a function of concentration of several alkali chlorides is shown in Fig. 7. The same variation is shown in Fig. 8 for the alkali-earth chlorides. In the first case (Fig. 7) the character of variation is influenced by the cation species in a rather complex manner. A similar variation has been found in other systems.^{1,5} In the second case the height of the wave is increased at higher concentrations of the alkali-earth ion (Fig. 8) due to the increase of adsorption via the salting-out effect.

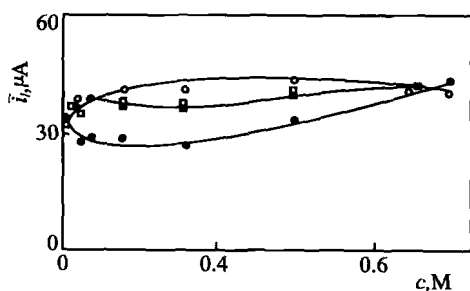


Fig. 7 Effect of ionic strength on the catalytic wave in the presence of alkali chlorides. Solution: 0.1 M $\text{NH}_3\text{-NH}_4\text{Cl}$; 10^{-3} M Ni^{2+} ; 2×10^{-3} M cycloserine. \circ LiCl; \square KCl; \blacksquare NaCl; \bullet CsCl

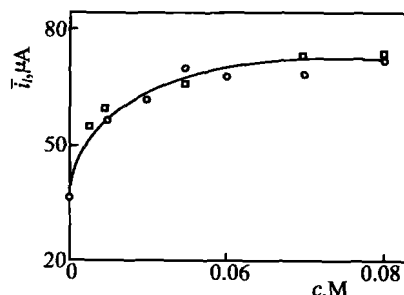


Fig. 8 Effect of ionic strength on catalytic hydrogen wave in the presence of alkali-earth chlorides. Solution: 10^{-1} M $\text{NH}_3\text{-NH}_4\text{Cl}$; 10^{-3} M Ni^{2+} ; 2×10^{-3} M cycloserine. \circ BaCl_2 ; \square CaCl_2

9. Effect of surface-active substances

Among the surface-active substances the effect of gelatine, Triton X-100 and tetramethylammonium cation was studied. As it has been shown previously, the catalytic wave produced by cycloserine in the presence of nickel is influenced by adsorption processes. The presence of another surfactant can act by a concurrent adsorption; in this way it is possible to explain the opposite effects found in the presence of each substance.

The height of the catalytic wave increases in the presence of gelatine. This means that the cycloserine molecules may be bound by the gelatine which is stronger absorbed at the electrode surface. By this process a higher cycloserine concentration participates in the hydrogen discharge. Unlike the gelatine influence, both Triton and tetramethylammonium ion produce a decrease of the wave height. This effect can be explained by the partial coverage of the electrode surface by the added substance and no binding with the cycloserine molecules. In the presence of tetramethylammonium cation the half-wave potential of the catalytic wave is displaced towards more positive values. It is possible in this case that the character of the current changes by transition from surface into bulk catalytic current.⁹

10. Electrolyte streaming

Electrolyte streaming around the mercury drop is a salient feature of the pre-sodium