

Taste sensing with polyacrylic acid grafted cellulose membrane

Sarmishtha Majumdar^a, Joykrishna Dey^b, Basudam Adhikari^{a,*}

^a Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

^b Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

Received 14 June 2005; received in revised form 8 September 2005; accepted 8 September 2005

Available online 2 November 2005

Abstract

There are reports of fabrication of taste sensor by adsorbing lipids into Millipore filter paper, which improved the taste sensing efficiency of membrane remarkably. We have made an attempt to prepare taste sensor material by grafting polyacrylic acid (PAA) to cellulose. The research work covers polymer membrane preparation, morphology study, and structural characterization of the membrane and study of the taste sensing characteristics of this membrane for five different taste substances. FTIR spectroscopic analysis and SEM were done to get an idea about the structure and morphology of the PAA grafted cellulose membrane. Surface charge density of the membrane was estimated. The sensor characteristics like temporal stability, response stability, response to different taste substances, and reproducibility of sensing performance were studied using PAA grafted cellulose membrane. Sensor device prepared with this membrane has shown distinct response patterns for different taste substances in terms of membrane potential. Threshold concentrations of PAA grafted cellulose membrane for HCl, NaCl, quinine-hydrochloride (Q-HCl), sucrose and monosodium glutamate are 0.001 mM, 0.01 mM, 0.08 mM, 0.08 mM and 0.01 mM, respectively. The threshold concentrations except that in Q-HCl are below human threshold concentrations. Membranes also showed characteristic response patterns for organic acids like acetic acid, citric acid, formic acid, etc., mineral acids like HCl, H₂SO₄ and HNO₃, etc., salts, bitter substances, sweet substances and umami substances. Sensor device prepared with this membrane has excellent shelf life.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Taste sensor; Taste substances; Membrane; Functionalized polymer

1. Introduction

Sense of taste occurs as a result of interaction between taste buds of tongue and taste substance. Different lipid molecules in taste buds of tongue are known to play the key role in sensing tastes of food materials [1,2]. Lipid based multichannel artificial taste sensor was constructed for mimicking the taste sensing ability of humans [3–7]. In these taste sensors various lipids were immobilized, such as *n*-decyl alcohol, oleic acid, dioctyl phosphate (DOP), Tetradodecylammonium bromide (TDAB), etc., in plasticized PVC for sensing of sourness, saltiness, bitterness, sweetness and umami. Tanaka et al. [8] have prepared membranes for taste sensing by mixing lipids like dioctyl phosphate (DOP), trioctyl methyl ammonium chloride (TOMA) with silicone rubber. Lee et al. [9] developed a multichannel taste sensor using evanescent field absorption in fibre optics. Dye incorporated silicone polymer and

dye/lipid/polyvinyl chloride-polyvinyl acetate-polyvinyl alcohol copolymer membranes have been used as sensing material. *Kimchi*, a Korean traditional pickle fermented with lactic acid bacteria, is expanding its consumption worldwide [10]. Eight polymer membranes, used in monitoring *Kimchi* fermentation, were prepared by mixing electroactive materials such as tridodecylamine (TDDA), tri-*n*-octylmethylammoniumchloride (TOMA), etc., bis(2-ethylhexyl)sebacate as the plasticizer and polyvinyl chloride in the ratio 1:66:33.

A model membrane [11,12] for taste sensing was developed with Millipore filter and lipids extracted from bovine tongue epithelium. Lipids were adsorbed into Millipore filter paper for this purpose. It was observed that dioleoyl phosphate (DOPH)-adsorbed membrane changed its oscillatory amplitude and frequency in the presence of taste substances [13,14]. DOPH is an unsaturated negatively charged lipid analogue, which is a reaction product of oleyl alcohol and POCl₃ [15]. In its non-oscillatory state, the effect of taste substances on its resting potential showed a good agreement with the tendency observed in biological systems regarding the order of the sensing threshold to such chemicals as quinine (bitter), NaCl (salt) and HCl

* Corresponding author. Tel.: +91 3222 283966; fax: +91 3222 255303.
E-mail address: ba@matssc.iitkgp.ernet.in (B. Adhikari).

(sour) [16]. Hayashi et al. [17] investigated the effect of taste substances for a lipid membrane by casting complexes of synthetic lipid (double-chain ammonium salt) and sodium polystyrene-sulphonate on a silicon wafer with a single minute pore. Reproducibility of the electric properties was improved remarkably by the use of the present construction method for the lipid membrane. These authors also [18] examined lipid and ion exchange cellulose for transducer materials of a taste sensor. The membrane was constructed with lipid, protein, and glycocalyx. These transducers can detect all basic tastes, excepting sweet substances. Ethanol was also detected with the lipid/cellulose membrane. Chitosan was alternated with sulfonated polystyrene (PSS) to build layer-by-layer (LBL) films that are used as sensing units in electronic tongue [19]. Using impedance spectroscopy as the principal method of detection, an array using chitosan/PSS LBL film and a bare gold electrode as the sensing unit was capable of distinguishing the basic tastes (salty, sweet, bitter, and sour) to a concentration below that of human threshold. So it is apparent that people have used lipids as taste sensing material with polymer as supporting material.

Toko and his coworkers [3–5,7] used different lipids directly in the polymer matrix for taste sensor application. The lipids viz., DOP, oleic acid, TOMA, *n*-decyl alcohol, etc., were either dispersed in a suitable polymer membrane, viz., PVC [3–5] or adsorbed onto Millipore filter [11,12]. In case of dispersion, there might not be uniform distribution of lipid molecules on the membrane surface exposed for sensing. We anticipated that the lipid molecules, which are in random orientation in the bulk of the membrane, being small and discrete, might be slowly depleted or leached out after multiple use of the membrane electrode device, although no report has been seen regarding the repeat performances of those lipid membranes. In case of lipid monolayer adsorbed polymer membrane taste sensor [20], where the lipid molecules were adsorbed on to a substrate polymer membrane surface by hydrophobic–hydrophobic interaction, but stronger polar–polar interaction between ionic heads of the lipid molecules and electrolytes in taste solution might also cause depletion of lipid molecules from the monolayer. These might be one limitation of the physically bound lipid membranes. Our scientific interest, therefore, lies in the use of chemically bound functional groups to a polymer backbone, which may avoid such limitations.

In the present work, instead of using lipids for taste sensing, we have grafted polyacrylic acid (PAA) to cellulose. The PAA grafted cellulose was characterized by FTIR spectroscopy and scanning electron microscopy. Response characteristics of this material to different tastants were evaluated in terms of membrane potential. Taste sensing properties of the membrane was studied.

2. Materials and methods

2.1. Materials

Ceric ammonium nitrate $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (CAN), glacial acetic acid, potassium bromide and oxalic acid were purchased from Qualigens, Fine Chemicals, Mumbai (India). Acrylic

acid was taken from Fluka AG (Switzerland). Ashless filter paper (Whatman 41) was procured from Whatman International Limited (England). Quinine-hydrochloride was purchased from E-Merck (Germany). Sodium sulphate (Na_2SO_4), sodium chloride (NaCl), fructose, glucose, citric acid, sulphuric acid (H_2SO_4), nitric acid (HNO_3) and lactic acid were purchased from E-Merck (India) Limited, Mumbai (India). Monosodium glutamate (MSG), inosine monophosphate (IMP), guanosine monophosphate (GMP), sucrose and glycine were purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai (India). Sodium nitrate (NaNO_3), sodium acetate (NaAc), sodium bicarbonate (NaHCO_3), magnesium sulphate (MgSO_4), potassium chloride (KCl) and magnesium chloride (MgCl_2) were purchased from S.d. Fine-Chem Ltd., Boisar (India). Formic acid was purchased from Sarabhai M Chemicals, Baroda (India).

2.2. Membrane preparation

Grafting of cellulose with polyacrylic acid was done using ceric ammonium nitrate (CAN) as initiator. Grafting is an important technique for modifying physical and chemical properties of polymers. A particular advantage of grafting is that the modification can be performed on pre-existing polymers, which may or may not be in the form of a shaped object such as fiber or film. This is of particular importance in dealing with natural polymers such as cellulose [21]. The grafting methods that have been developed can be classified into three groups: (1) free radical; (2) ionic; and (3) condensation and ring opening polymerizations. The free radical methods have become more common due to their practicality. Free radicals are formed on the cellulose molecules either by chemical means or by irradiation. The general field of grafting onto cellulose has been reviewed by a number of authors [22–29], and also in a monograph [30]. Mino and Kaizerman first discussed the use of ceric ions to initiate graft polymerization in 1958 [31]. Schwab et al. [32] were among the first to extend this method to the grafting of cellulose. The Ce^{IV} ion method has gained considerable importance in the grafting reaction, because of its ease of application as well as its grafting efficiency. It is based on the fact that when cellulose is oxidized by ceric salts such as ceric ammonium nitrate $(\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6)$, free radicals capable of initiating vinyl polymerization are formed on cellulose.

Acrylic acid was purified by distillation under reduced pressure at 30 °C. 1.04 g cellulose (Whatman 41 filter paper) was soaked with 5.2 ml acrylic acid, 20.7 ml 0.1N HNO_3 and 42 ml water [33] in a 100 ml three-necked round-bottomed flask. Nitrogen gas was bubbled into the system for 30 min. Then 1.4 ml 0.00125 M CAN solution was added with 20 ml water. The reaction was carried out at 20 °C for 3 h with constant nitrogen bubbling. The grafted cellulose was isolated and washed with hot water for 5 h. Then the film was dried in vacuum oven at 60 °C, weighed and stored in desiccators.

2.3. Measurements

2.3.1. FTIR—study

For structural analysis, FTIR study of cellulose and PAA grafted cellulose were done using Thermo Nicolet, NEXUS

870 FTIR spectrophotometer. The spectra were recorded in absorbance mode. Cellulose and grafted cellulose films were finely chopped and KBr pellet was prepared.

2.3.2. Scanning electron microscopy

Study of surface morphology of the cellulose and PAA grafted cellulose was done using JEOL-JSM 5800 scanning electron microscope. The polymer films were gold coated before the study. Photographs were taken at 500 magnifications.

2.4. Taste sensor property study

2.4.1. Temporal stability

In order to judge the time required for obtaining stable response of electric potential (temporal stability) across PAA grafted cellulose membrane, the membrane electrode device, was dipped in 1 mM KCl solution and then the potential was measured using a Ag/AgCl reference electrode immediately after dipping at an interval of 1 min. The measurement was continued till stable response [3].

2.4.2. Response stability of the membrane

In order to study the stability of response of electric potential across PAA grafted cellulose membrane in HCl, NaCl, Q-HCl, sucrose and MSG, the membrane electrode device was dipped into 1 mM solution of the analytes in 1 mM KCl and the potential was measured using a Ag/AgCl reference electrode at an interval of 30 s upto 15 min. The measurement was done after preconditioning in 1 mM KCl for 30 min.

2.4.3. Response to taste substances

The membrane electrode was preconditioned in 1 mM KCl solution for 30 min. The effect of change in concentration of taste solutions, i.e. HCl, NaCl, Q-HCl, sucrose and MSG on the potential was measured. Responses to organic acids, mineral acids, salty substances, bitter, sweet and umami substances were also studied. Taste substances were dissolved in 1 mM KCl solution [20]. All experiments were carried out at room temperature (25 °C).

2.4.4. Changes in response with repetitive use

The change in response in terms of electric potential of PAA grafted cellulose membrane to each taste substance was studied in three consecutive cycles of use. After each cycle of measurement the membrane device was rinsed with water and kept immersed in 1 mM KCl solution for 5 min prior to next cycle of measurement.

3. Results and discussion

The physical properties of cellulose and PAA-g-C membranes are summarized in Table 1. Grafting of cellulose caused 9.7% incorporation of polyacrylic acid. For measurement of taste sensing in terms of membrane potential, wetting of the membrane surface by the taste solution is essential. So, water absorption behavior of the cellulose and PAA-g-C was studied. The polymer membrane was immersed in water for 24 h at 25 °C.

Table 1

Physical properties of cellulose (C) and PAA grafted cellulose (PAA-g-C) membranes

Polymer membrane	Polymer loading (%)	Color	Water absorption (%)	Thickness (μm)
C	–	White	43.5	180
PAA-g-C	9.7	White	42.0	200

After wiping the surface adhered water the increase in weight of the membrane was recorded. The result was expressed as percentage of water absorption, which is the percentage of increase in weight of the sample with respect to the weight of the desiccated sample before dipping into water. The water absorption values were taken as an average of four samples. The data in Table 1 show that there is only a minor change in water absorption of cellulose (43.5%) after grafting of PAA (42%). This result indicates that the grafted membrane has sufficient wettability in aqueous medium. Moisture absorption study was also done to have an idea about the affinity of the membranes to atmospheric moisture. Moisture absorption behavior of the cellulose and PAA grafted cellulose membranes were assessed by exposing the membranes to laboratory environment within a range of 51–81% relative humidity (RH) at 30 °C to 32 °C. Moisture absorption of the membranes was measured as percentage of increase in weight of the sample with respect to the initial weight of the desiccated sample before exposure to the laboratory environment. The moisture absorption values were measured at an interval of 24 h upto 7 days and recorded as an average of four samples. The Table 2 shows that there is negligible change in moisture absorption of cellulose after grafting with PAA. It is seen that the moisture absorption fluctuates with variation of relative humidity (RH) from 58% to 80% at temperatures between 30 °C to 33.5 °C for the duration of 7 days. In case of cellulose the moisture absorption value ranges from 0.21% to 3.55% and in case of PAA grafted cellulose the same ranges from 0.20% to 3.38%. Thus, as evident from Table 2 moisture absorption values of cellulose and PAA-g-C were higher within the period of first 72 h due to high relative humidity of about 80%. The decrease in moisture absorption of the membranes in the next 48 h is due to a fall in relative humidity to 51%. Again the increase in moisture absorption values of cellulose and grafted cellulose in the last 48 h is due to a rise in RH to 75%. Thus water absorption and moisture absorption studies show sufficient hydrophilicity of the membranes for taste sensor property study in aqueous medium.

3.1. Membrane characterization

The membrane was characterized by FTIR study, scanning electron microscopy and surface charge density measurement. The change in structures of cellulose on grafting with PAA was studied by FTIR analysis. FTIR spectra of cellulose and PAA grafted cellulose membranes are shown in Fig. 1. Cellulose and PAA grafted cellulose membranes show peak at 3340 cm^{−1} and 3411 cm^{−1}, respectively, for hydrogen bonded –OH group of cellulose. Both cellulose and PAA-g-C show peak at 2905 cm^{−1} for asymmetric stretching of –CH₂– in –CH₂OH group of

Table 2
Moisture absorption characteristics of cellulose (C) and PAA grafted cellulose (PAA-g-C) membranes after exposure to 51–81% RH at 30–32 °C for different time periods

Polymer membrane	Moisture absorption (%) ^a					
	24 (h)	48 (h)	72 (h)	96 (h)	120 (h)	144 (h)
Cellulose	2.95	3.55	3.55	0.84	0.21	3.34
PAA-g-C	2.91	3.14	3.38	0.82	0.20	3.24

^a Relative humidity was about 80% for 72 h and later reduced to 51% in the next 48 h and again increased to about 75% in the last 48 h.

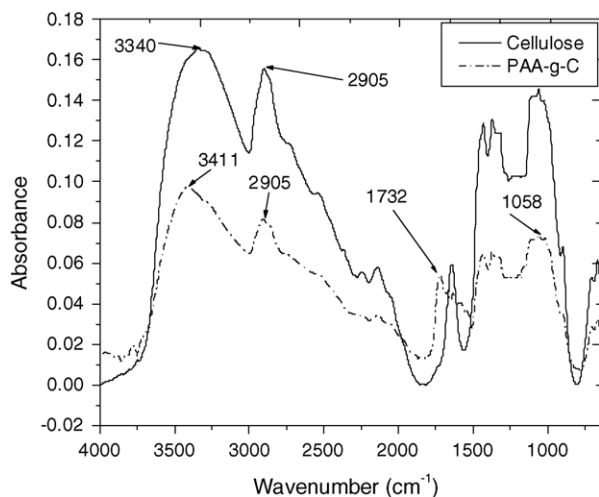
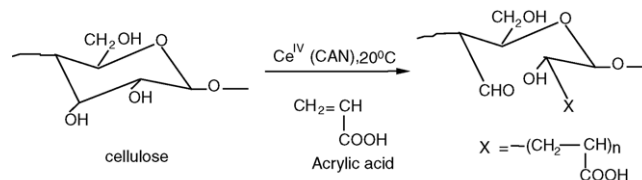


Fig. 1. FTIR spectra of cellulose and PAA grafted cellulose in the range 4000–650 cm⁻¹.

cellulose. A broad peak has appeared at 2905 cm⁻¹ for the grafted polymer. This may be due to the merging of peak for C–H stretching of aldehyde (–CHO), which is supposed to appear in the region between 2830 and 2695 cm⁻¹, with the peak for asymmetric stretching of –CH₂– in –CH₂OH. In case of PAA-g-C a broad peak has appeared in the region 1725–1533 cm⁻¹, which may be due to merging of peak for >C=O stretching of –COOH group of grafted polyacrylic acid and >C=O stretching of aldehyde group (–CHO). This indicates the presence of polyacrylic acid in the grafted cellulose membrane. PAA-g-C shows peak at 1058 cm⁻¹ for –C–CHO linkage. Thus the peaks at 2905 cm⁻¹, 1732 cm⁻¹ and 1058 cm⁻¹ prove the formation of aldehydic group in cellulose during grafting with polyacrylic



Scheme 1.

acid by CAN initiator. Thus FTIR study supports the grafting of polyacrylic acid to cellulose as shown in Scheme 1.

The scanning electron micrographs of cellulose and PAA grafted cellulose membranes are shown in Fig. 2. The study of surface morphology by scanning electron microscopy revealed the presence of cellulose fibre entanglements on the surface of the membranes. Fig. 2(a) shows cellulose membrane before grafting with PAA and Fig. 2(b) shows the surface morphology after PAA grafting. After grafting, as some polymer chains are incorporated into cellulose membrane, the fibres in the inner layers of cellulose membrane become invisible as shown in Fig. 2(b). Although some diffused features as well as some open fibrils are visible in the ungrafted cellulose but the fibre boundaries are to some extent smoothened due to coating of the open fibrils after PAA grafting.

The potentiometric titration was done to estimate α , the degree of dissociation of –COOH groups of PAA on the membrane surface, in order to estimate the surface charge density of the membrane. Estimation of –COOH groups on the PAA-g-C membrane surface was done by potentiometric titration with 10 mM KOH. The membrane electrode was stabilized by dipping into a 1 mM HCl solution in a beaker for complete protonation of dissociated –COOH groups, if any, on the membrane

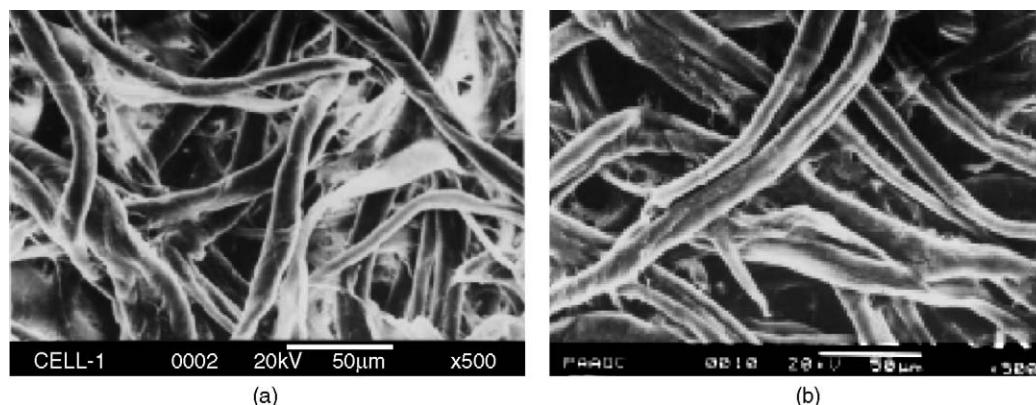


Fig. 2. Scanning electron micrograph of the surface of (a) cellulose, and (b) PAA grafted cellulose.

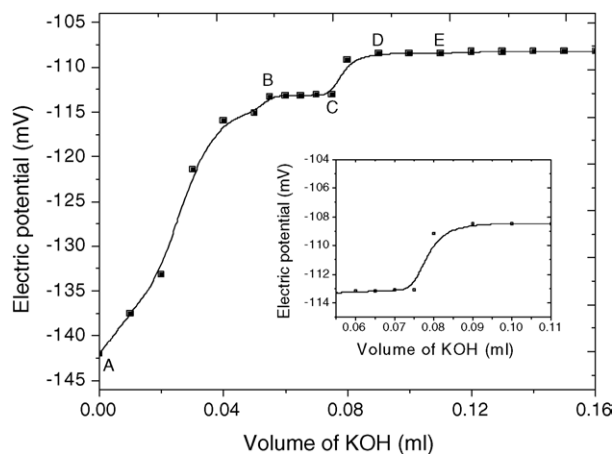
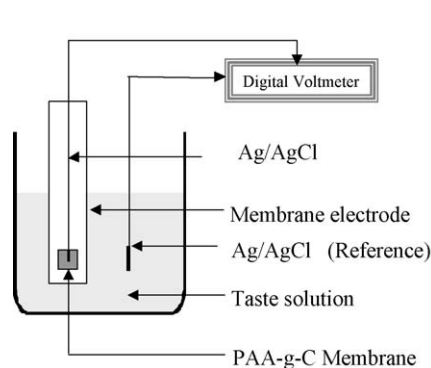


Fig. 3. Electric potential vs. volume of KOH plot of polyacrylic acid grafted cellulose membrane electrode [35]. The potential change from point A to point B occurred due to neutralization of HCl in the bulk solution. Potential change from the point C to point D occurred due to the complete neutralization of $-\text{COOH}$ groups on the membrane surface. The point D has been accepted for complete dissociation of all $-\text{COOH}$ groups ($\alpha = 1$) (A part of the curve from point B to point E is shown in the inset which was used for calculation of α of the membrane surface in 1 mM KCl prior to the addition of taste solution).

surface. This was followed by potentiometric titration of the surface $-\text{COOH}$ groups with 10 mM KOH using a Ag/AgCl reference electrode. Addition of KOH resulted a gradual change in membrane potential. The membrane potential is plotted against the volume of KOH added (Fig. 3). At the end point of this titration the value of α was considered to be unity indicating complete dissociation of all $-\text{COOH}$ groups of PAA present on the surface. The membrane potential value at the end point (at $\alpha = 1$) was used to calculate the value of α on the membrane surface in contact with 1 mM KCl prior to the addition of taste solution (Fig. 3 inset). Then the surface charge density on the membrane [34] prior to the addition of taste solution in 1 mM KCl was calculated using the Eq. (1).

$$\sigma = -\frac{e}{A} \times \alpha \quad (1)$$



Measurement Set-up

(a)

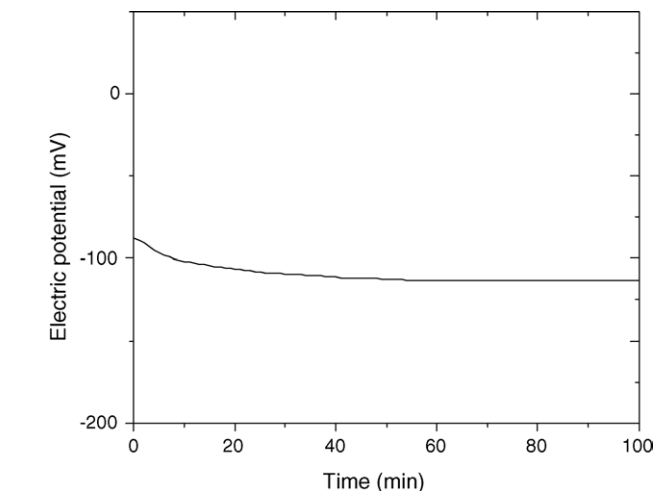
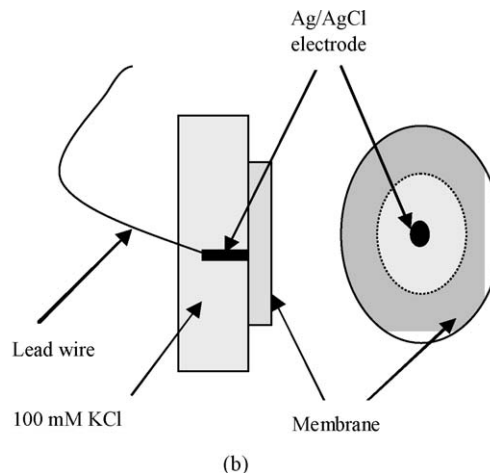


Fig. 5. Temporal stability of PAA grafted cellulose membrane in 1 mM KCl.

where e = electronic charge, A = area of membrane surface exposed to 1 mM KCl solution.

It has been found that the surface charge density of the membrane σ calculated from volume of KOH versus electric potential plot prior to the addition of taste solution in 1 mM KCl is $-6.12 \times 10^{-16} \text{ C/m}^2$. As calculated from Fig. 3 the $-\text{COOH}$ groups on the membrane surface shows a degree of dissociation of 0.42 just after dipping into the 1 mM KCl solution. After dissociation the $-\text{COO}^-$ groups develop charged layers with K^+ and Cl^- ions. When the analyte solution is added, the ions of the analytes interact with these charged layers. Repulsion between the ions in the charged layers and the ions from the analytes leads to increase in membrane potential with increase in concentrations of NaCl, HCl, Q-HCl and MSG solutions. Sucrose is a weak electrolyte. Still there is a possibility of development of weak dipole-dipole interaction between the polar groups of sucrose and $-\text{OH}$ and $-\text{COOH}$ groups of PAA-g-C causing slight increase in potential at higher concentrations (from 50 mM to 100 mM).



(b)

Fig. 4. (a) Experimental set-up for measurement of taste sensing in terms of potential; (b) membrane electrode device used in the set-up.

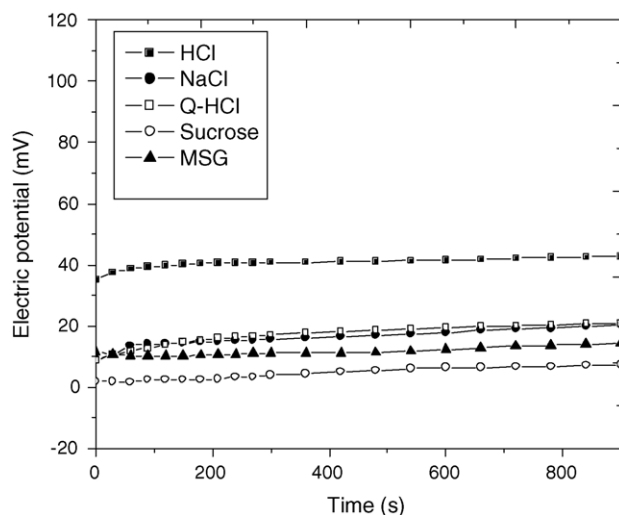


Fig. 6. Stability of response potential of PAA grafted cellulose in 1 mM taste solutions (HCl, NaCl, Q-HCl, sucrose and MSG).

3.2. Taste sensor property study

3.2.1. Sensor set-up

The experimental set-up shown in Fig. 4(a) was used for the measurement of tastes of five basic taste substances, for example, NaCl for saltiness, HCl for sourness, quinine-HCl for bitterness, sucrose for sweetness and monosodium glutamate (MSG) for umami. As shown in Fig. 4(b) the membrane electrode device was fabricated by mounting PAA grafted cellulose membrane over a circular cavity on a perspex block. The cavity was filled with 100 mM KCl solution [3,20] through a narrow hole and one

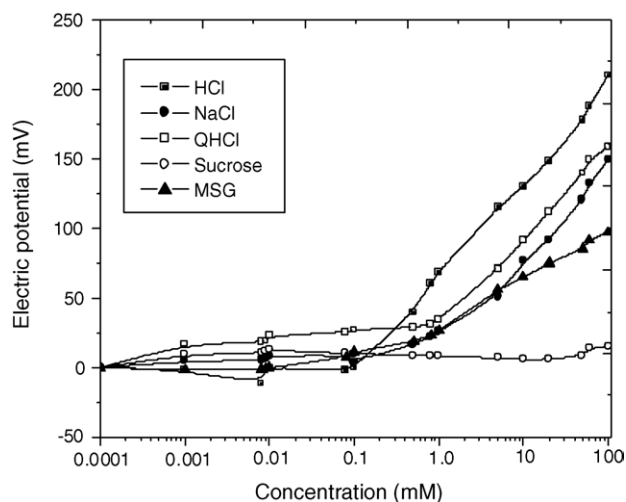


Fig. 7. Responses of PAA grafted cellulose to HCl, NaCl, sucrose, monosodium glutamate (MSG) and quinine-HCl (Q-HCl).

Ag/AgCl electrode was inserted into the cavity. The reference electrode was Ag/AgCl electrode [3,20]. The two electrode terminals were connected to a digital multimeter for measuring the potential across the polymer membrane.

3.2.2. Temporal stability of the membrane

The temporal stability of the potential of the PAA grafted cellulose membrane in 1 mM KCl is shown in Fig. 5. The potentials were measured immediately after immersion of the membrane electrode device in 1 mM KCl solution and the membrane potential was measured at intervals of 1 min. As revealed from Fig. 5 PAA grafted cellulose membrane shows stable response after

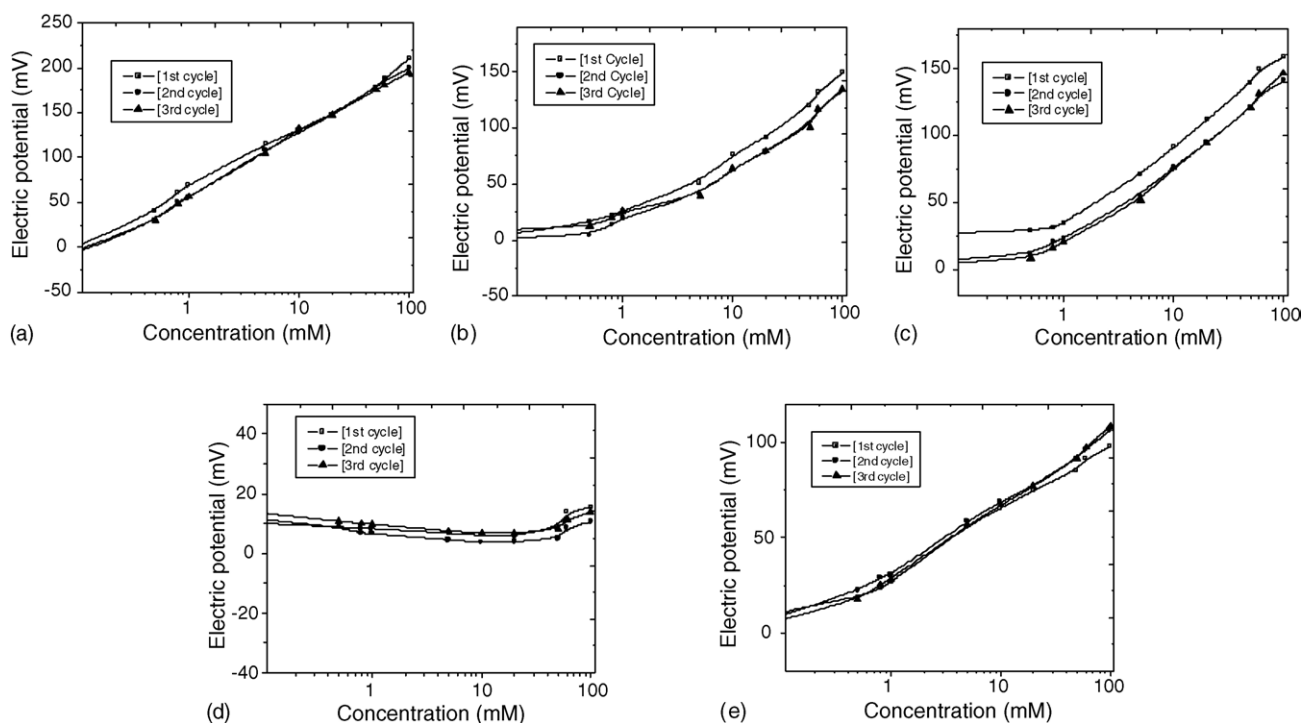


Fig. 8. Responses in terms of membrane potential of PAA grafted cellulose for (a) HCl; (b) NaCl; (c) Q-HCl; (d) sucrose and (e) MSG solutions at an interval of 5 min.

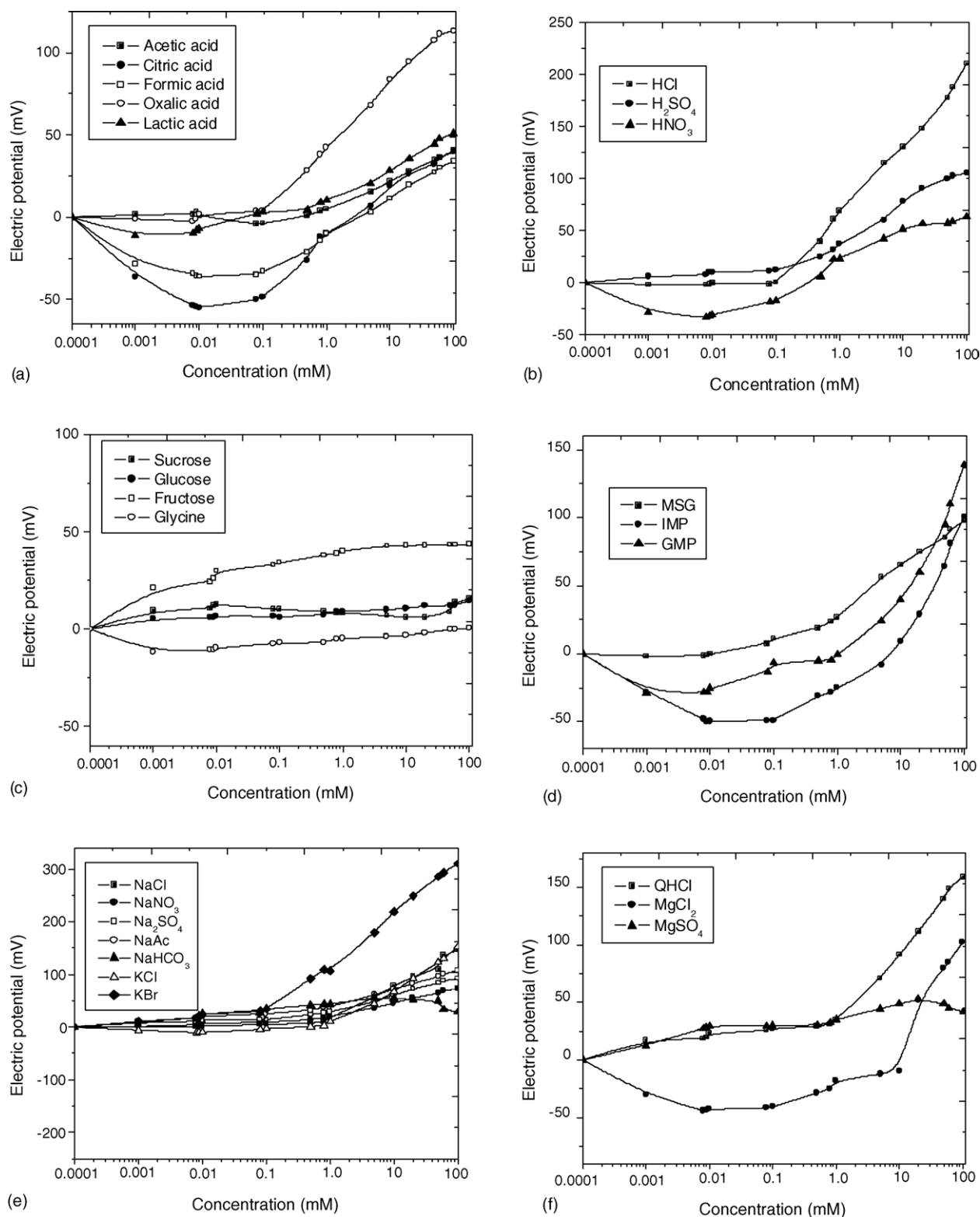


Fig. 9. Responses in terms of membrane potential of PAA grafted cellulose to different (a) organic acids; (b) mineral acids; (c) sweet substances; (d) umami substances; (e) salts; and (f) bitter substances.

about 40 min. Based on this observation the membrane electrode device was preconditioned for 40 min in 1 mM KCl solution before measuring the response of taste solutions. Lipid membrane constructed by Hayashi et al. [3] showed stable response in 1 mM KCl after 30 min.

3.2.3. Response stability of the membrane

In order to judge the response stability of the membrane in a particular taste solution the membrane electrode device was dipped into a taste solutions of 1 mM concentration containing 1 mM KCl and the potential was measured upto 15 min at an

interval of 30 s. Fig. 6 shows the stability of response with time to HCl, NaCl, Q-HCl, sucrose and MSG for PAA grafted cellulose membrane. This observation indicates that the membrane is suitable for sensing tastes of different substances. Since the magnitude of response potential is different for different taste substances the membrane is able to recognize different tastes.

3.2.4. Responses to taste substances

The responses of polyacrylic acid grafted cellulose membranes to five taste substances were studied for a concentration range of 0.001–100 mM solution and the results are shown in Fig. 7. The figure shows that with increase in concentration of HCl, NaCl, Q-HCl and MSG the membrane potential increases. In case of sucrose, which is a non-electrolyte, there is negligible change in potential. When dipped into analyte solutions, increase in ion concentration leads to increase in charge repulsion on the membrane surface. This leads to increase in membrane potential with increase in analyte concentration.

It has been observed that PAA grafted cellulose membrane shows detection threshold values of 0.001 mM, 0.01 mM, 0.08 mM, 0.08 mM and 0.01 mM for HCl, NaCl, Q-HCl, sucrose and MSG, respectively. These threshold concentrations excepting that for Q-HCl were below that of human threshold concentrations, which are 0.9 mM, 30 mM, 0.03 mM, 170 mM and 1.6 mM for HCl, NaCl, Q-HCl, sucrose [36] and MSG [37], respectively. We have been able to improve the detection threshold values of the membrane for HCl, NaCl and MSG in comparison to that of lipid membranes prepared by Hayashi et al. [3], which are 0.009 mM, 0.25 mM and 0.08 mM, respectively. The errors (%) defined by the standard deviations divided by the averaged values were 1.75, 0.40, 2.60, 0.42, and 0.82 for HCl, NaCl, Q-HCl, sucrose and MSG, respectively, at 1 mM concentration in each case.

3.2.5. Changes in response with repetitive use

In order to see the reproducibility of response pattern of the membrane to a particular taste solution the membrane electrode device was tested for repeatability by three consecutive measurements of response potential in each taste solution for the concentration range of 0.001–100 mM. Fig. 8 shows the reproducibility of response by PAA grafted cellulose membrane to five taste substances. It was found that PAA grafted cellulose membrane shows almost identical response patterns on repeated measurements though there is little drift of about 1 to 5 mV in each cycle excepting in case of Q-HCl and NaCl. For Q-HCl there is a drift of about 25 mV between the first and the next two consecutive cycles. For NaCl a drift of about 10–12 mV between the first and the next two consecutive cycles was observed.

3.2.6. Response to organic acids, mineral acids, salts, bitter, sweet and umami substances

PAA grafted cellulose membrane shows characteristic response to organic acids like acetic acid, citric acid, formic acid, oxalic acid and lactic acid, respectively, as shown in Fig. 9(a). Responses of PAA grafted cellulose membrane to mineral acids like hydrochloric, sulphuric and nitric acids are shown in Fig. 9(b). Responses for salts (NaCl, KCl, KBr, NaNO₃,

Na₂SO₄, NaAc, NaHCO₃), bitter substances (Q-HCl, MgSO₄, MgCl₂), sweet substances (sucrose, glucose, fructose, glycine), umami substances (MSG, IMP, GMP) are shown in Fig. 9(c–f). The variation in slopes of the curves is due to their difference in dissociation constants.

4. Conclusions

The main objective of our work was to develop taste sensing membrane material using tailor-made polymer. In PAA grafted cellulose the taste sensing groups are chemically bonded to the membrane material thus improving the sensing reproducibility of the material. The taste sensing property of PAA grafted cellulose membrane thus prepared was evaluated by studying the change in membrane potential with concentration of taste substances. The membrane shows characteristic curve pattern with each of the taste substances. Threshold values of membrane response for different taste substances excepting that of Q-HCl were below human threshold values. The detection threshold values of PAA-g-C membrane for HCl, NaCl and MSG is lower than that of PVC-lipid membranes which are 0.009 mM, 0.25 mM and 0.08 mM, respectively. The membranes showed good stability of response in 1 mM taste solutions. Repeatability in response is quite good with small drift in potential (1–5 mV) excepting in the case of Q-HCl (~25 mV) and NaCl (~10–12 mV). PAA grafted cellulose membrane also shows characteristic response patterns for different organic acids, mineral acids, salts, bitter substances, sweet substances and umami substances.

References

- [1] K. Kurihara, K. Yoshii, M. Kashiwayanagi, *Comp. Biochem. Physiol.* 85A (1986) 1.
- [2] M. Miyake, N. Kamo, K. Kurihara, Y. Kobatake, *Biochim. Biophys. Acta* 436 (1976) 856.
- [3] K. Hayashi, M. Yamanaka, K. Toko, K. Yamafuji, *Sens. Actuators B* 2 (1990) 205.
- [4] K. Toko, K. Hayashi, M. Yamanaka, K. Yamafuji, *Tech Digest 9th Sens. Symp.* (1990) 193.
- [5] Y. Kikkawa, K. Toko, T. Matsuno, K. Yamafuji, *Jpn. J. Appl. Phys.* 32 (1993) 5731.
- [6] K.N. Mikhelson, *Sens. Actuators B* 18 (1994) 31.
- [7] M. Habara, H. Ikezaki, K. Toko, *Biosens. Bioelectron.* 19 (2004) 1559.
- [8] K. Tanaka, M. Iwakura, T. Onodera, T. Adachi, K. Toko, *Chem. Sens. (Suppl. B)* 17 (2001) 412.
- [9] S.-M. Lee, S.-W. Jang, S.-H. Lee, J.-H. Kim, S.-H. Kim, S.-W. Kang, *Sens. Mater.* 14 (2002) 11.
- [10] N. Kim, K. Park, I.-S. Park, Y.-J. Cho, Y.M. Bae, *Biosens. Bioelectron.* 20 (2005) 2283.
- [11] K. Kurihara, N. Kamo, Y. Kobatake, *Adv. Biophys.* 10 (1978) 27.
- [12] M. Miyake, N. Kamo, K. Kurihara, Y. Kobatake, *J. Membr. Biol.* 22 (1975) 197.
- [13] K. Toko, M. Tsukiji, S. Iiyama, K. Yamafuji, *Biophys. Chem.* 23 (1986) 201.
- [14] S. Iiyama, K. Toko, K. Yamafuji, *Agr. Biol. Chem.* 50 (1986) 2709.
- [15] M. Yoshida, Y. Kobatake, M. Hashimoto, S. Morita, *J. Membr. Biol.* 5 (1971) 185.
- [16] S. Iiyama, K. Toko, K. Yamafuji, *Maku. (Membrane)* 12 (1987) 231 (in Japanese).
- [17] K. Hayashi, K. Yamafuji, K. Toko, N. Ozaki, T. Yoshida, S. Iiyama, N. Nakashima, *Sens. Actuators* 16 (1989) 25.

- [18] K. Hayashi, Y. Wakita, K. Moriyama, Kagoshima Daigaku Kogakubu Kenkyu Hokoku 37 (1995) 27.
- [19] D.S. dos Santos Jr., A. Riul Jr., R.R. Malmegrim, F.J. Fonseca, O.N. Oliviera Jr., L.H.C. Mattoso, *Macromol. Biosci.* 3 (2003) 591.
- [20] K. Hayashi, K. Toko, M. Yamanaka, H. Yoshihara, K. Yamafuji, H. Ikezaki, R. Toukubo, K. Sato, *Sens. Actuators B* 23 (1995) 55.
- [21] D.J. McDowell, V.S. Gupta, V.T. Stannett, *Prog. Polym. Sci.* 10 (1984) 1.
- [22] R.B. Phillips, J. Quéré, G. Guioy, V.T. Stannett, *Tappi* 55 (1972) 858.
- [23] V.T. Stannett, H.B. Hopfenberg, in: N. Bikales, L. Segal (Eds.), *Cellulose and Cellulose derivatives*, vol. 5, John Wiley & Sons, New York, 1971, pp. 907–936, Pt. 5.
- [24] H.A. Krässig, V.T. Stannett, *Adv. Polym. Sci.* 4 (1965) 111.
- [25] M.S. Bains, *J. Polym. Sci. C* 37 (1972) 125.
- [26] J.C. Arthur Jr., *Adv. Macromol. Chem.* 2 (1970) 1.
- [27] A. Hebeish, *Kolorad. Ert.* 13 (1971) 12.
- [28] J.C. Arthur Jr., *J. Macromol. Sci. Chem. A* 4 (1970) 1057.
- [29] H. Krässig, *Svensk. Papperstidn.* 74 (1971) 417.
- [30] A. Hebeish, J.T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, Berlin, 1981.
- [31] G. Mino, S. Kaizerman, *J. Polym. Sci.* 31 (1958) 242.
- [32] E. Schwab, V. Stannett, D.H. Rakowitz, J.K. Magrane, *Tappi* 45 (1962) 390.
- [33] Y. Ogiwara, H. Kubota, S. Hayashi, K. Sekine, *J. Appl. Polym. Sci.* 16 (1972) 2197.
- [34] K. Oohira, K. Toko, *Biophys. Chem.* 61 (1996) 29.
- [35] H. Träuble, M. Teubner, P. Woolley, H. Eibl, *Biophys. Chem.* 4 (1976) 319.
- [36] C. Pfaffmann, in: J. Field (Ed.), *Handbook of Physiology*, section 1, *Neurophysiology*, vol. 1, American Physiological Society, Washington, DC, 1959, p. 507.
- [37] S. Yamaguchi, *J. Food Sci.* 32 (1967) 473.