REPONSE OF POLYMERIC MEMBRANES AS SENSING ELEMENTS FOR ELECTRONIC TOUGUE

Y. M. Bae and S. I. Cho

School of Biological Resources and Materials Engineering
College of Agriculture and Life Science, Seoul National University
Suwon, Kyunggi-Do 441-744, Korea
E-mail : syk@snu.ac.kr

ABSTRACT

The study was executed for development of sensing elements of electronic tongue which could discriminate taste of liquid and semi-liquid foods. Five polymeric membranes which were composed of polymer, plasticizer, electro-active materials were prepared. After each polymeric membranes were mounted in an electrode body, membrane potentials due to electrochemical reaction with taste stimuli were measured. The experimental results were interpreted in view of the membrane's non-selective responses to stimuli.

Keywords : Electronic tongue, Liquid food, Polymer membrane , Non-selectivity

INTRODUCTION

Gustation and olfaction are chemical senses of human' five senses. Especially, Gustation is the sense due to gustory cell receptors' reaction with taste stimuli contained in solutions. Taste is recognized as complex of four primary taste ; sourness, saltiness, sweetness, and bitterness. The sourness is mainly due to proton ion produced in organic acids, saltiness to cations and anions of salts, sweetness to various sugar, and bitterness to alkoroids. Recently, reaction mechanisms of taste stimuli on surface of gustory cell receptors were studied in worldwide research groups(Mclaughlin and Margolskee (1994)). As results of the studies, it was known that sourenss and saltiness approximately resulted from non-selective potential's change of cell membranes. However, sweetness and bitterness resulted from contact between specialized receptors in cell membrane and taste stimuli. Therefore, while mechanism of sweetness and bitterness was difficult to realize because of too many receptors, it was considered that model system of sourness and saltiness is possible to be constructed. Murata et al.(1992) constructed a multichannel lipid membrane sensor to quantify sourness and saltiness and, Legin et al.(1997) developed a sensor array composed of specially designed non-specific glass electrodes for qualitative analysis of beverages. The combination system of these sensor array and signal process unit is called as electronic tongue and approximately mimics human gustation. Toko (1998) reviewed feasibility of application of an electronic tongue which was composed of multichannel lipid membrane sensors and singal process unit to panel test of liquid foods such as beer, mineral water, coffee, and tomato juice. Natale et al. (1997) used an electronic tongue for analysis of polluted waters. In future, it is guessed that the electronic tongue as model system of human gustation will be applied to analytical areas of foods and environment.

In this paper, as plase 1 of development of an electronic tongue for sourness and saltiness, a work on development of sensing elements for extraction of ionic information from solutions was described. To mimic human tongue, the elements must had to be non-selective responses to ionic taste stimuli. Various polymeric membranes were prepared, and their non-selectivity was surveyed as interpreting the change of membrane potentials due to electrochemical reaction between membrane and stimuli.

MATERIALS AND METHODS

Materials

Ion selective electrodes(ISEs) in analytical chemistry are useful tools in measurement of ion's activity in solutions. The pH electrode is representative, and else ISEs as sodium, potassium, and chloride are developed. However, these ISEs are not suitable in quantifying ions in complex solution, because of alkaline error where detectors respond to non-target ions. The alkaline error is serious problem in development of ISE. However, such a characteristic of non-selectivity of ISEs is analogous to behavior of human cell membrane which responds to ions in different patterns. Therefore, it is considered that ISE detector could be used as sensing element of electronic tongue. Glass type and polymer membrane type are in ISE detector materials. Because polymeric membrane are easy to prepare and can be minimzed for sensor array, it is used as sensing element for the electronic tongue.

Polymeric membrane is composed of polymer matrix, plasticizer, and electro-active materials. The characteristics of polymer membranes' responses to electrolytes are due to electro-active materials. Therefore, as replacing electro-active materials, various characteristics of polymeric membrane response could appear.

In this paper, poly vinyl chloride(PVC) was used as matrix for the polymeric membrane. The DOS(bis(2-ethylhexyl) adipate), DOA(bis(2-ethylhexyl) sebacate), NPOE(2-nitrodiphenyl ether) (Fluka) were used as plasticizers. The valinomycin(Sigma), sodium ionophore X, monensin decyl ester, TDMACl (Tridodecylmethylammonium chloride), and chloride ionophore I(Fluka) were purchased for electro-active materials.

Preparation of membrane

Preparation of membrane was referred to Craggs et al.(1974). Firstly, appropriate amount of PVC, plasticizer, and electro-active materials(PVC, 33 wt %, plasticizer 66 wt %, and electro-active material 1 wt%) were solved in THF solvent. The cocktail solution was poured in a glass ring frame(diameter 22mm) which was on glass plate. After the solvent in the solution evaporated during 24hours, only master membrane was left in the bottom of frame. The membrane was about 350μm thick and stored in dark room.

Measurement of membrane potential

After a piece of membrane (diameter 5mm) from the master membrane was cut, it was mounted in a tip of IS-561 electrode body(Glassblaserei moller, Switzerland). KCl 0.1 M or NaCl 0.1 M solution was used as inner filling solution of the electrode body. The electrode body mounted with membrane was soaked in distilled water during 12 hours.

Fig. 1 shows the measurement system of membrane potential. The external reference electrode was Orion sleeve-type double junction(Model90-02). Potential values between working electrode and reference electrode were acquired using a computer equipped with A/D board(AT-MIO-10 series, National instrument) and home-made high impedance amplifier. Sampling rate was 1000Hz and the average values of 1000 data were stored.

To measure membrane potential due to electrochemical reaction between membrane and taste stimuli, one taste stimulus was injected into buffer solution in each plot. Taste stimuli were sodium chloride, potassium chloride, sodium bromide, and sodium iodide for saltiness, and citric acid, tartaric acid, and lactic acid for sourness.

After the stimulus injected, the potentials were acquired during 100sec. The range of concentration of stimulus was between 1μM and 0.1M in 10 decade. The buffer solution used were 0.05M Tris buffer(pH 7.0 HCl) for salt taste stimuli, and 0.05M Bis-tris buffer(pH 7.0 HCl) for sour taste stimuli.

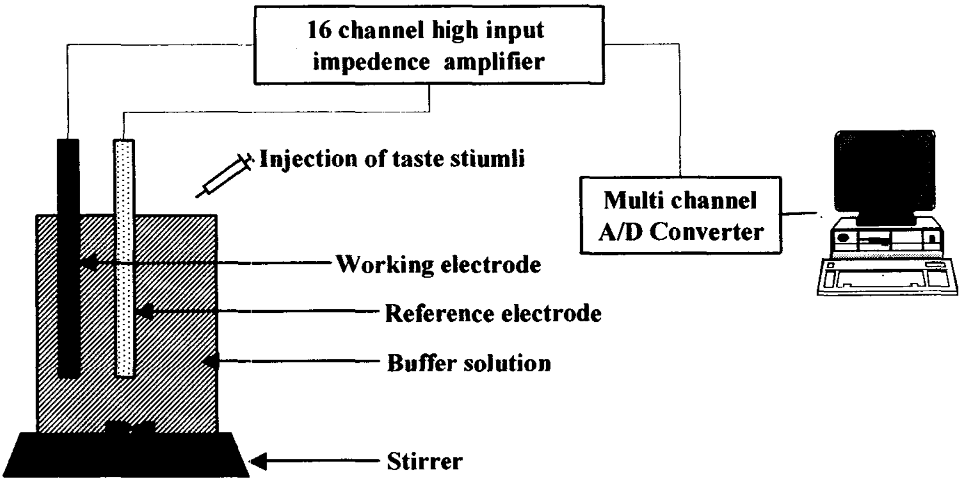
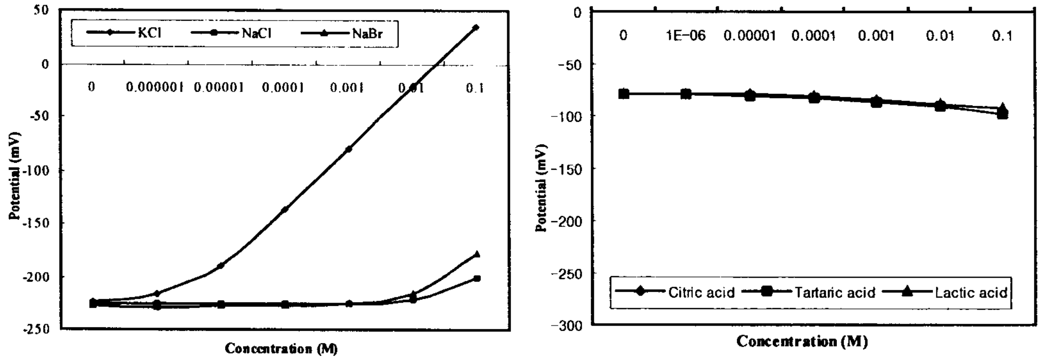


Fig. 1 Measurement system of membrane potential

RESULTS AND DISCUSSION

Theoretically, electrochemical reaction between electro-active material and electrolyte results in the change of membrane potential which is the sum of outer surface (interface with buffer solution) potential, diffuse potential in membrane, and inner surface potential. However, it can be assumed that diffuse potential is constant because complex of electro-active material and target ion is transmitted to the opposite surface immediately. Also, inner surface potential is constant if the inner filling solution is not changed. In ISEs of analytical chemistry, therefore, the change of outer surface potential of ISE membrane is equal to that of membrane potential and is described in Nernstian equation in which surface potential is proportional to logarithmic value of the activity of target ion in buffer solution(Crow, 1994). However because electro-active material may react with non-target ion, non-selective reactions occurrs in real ISEs. In this work, non-selective responses of polymer membranes doped with electro-active materials as sensing elements for electronic tongue to seven taste stimuli were observed and interpreted.

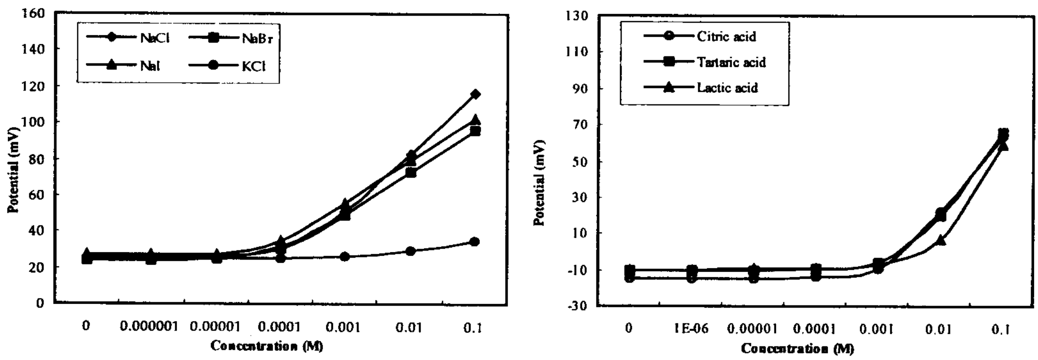
Fig. 2 shows valinomycin membrane's responses to the taste stimuli. The potential increased as concentration of ions increased. The increases of potential meant that valinomycin membrane was sensitive to cationic electrolytes. Because valinomycin was originally used for potassium ISE, the response to potassium ion was very high more than the response to the others. The repeatability was 0.9mV in 0.01M, and 0.8mV in 0.1M of potassium solution. But, as concentration of organic acids increased, the membrane potential decreased tinily in high concentration. The decreases of the potential might be due to effect of anionic sites of organic acids.



(a) The response to salts (b) The response to organic acids

Fig. 2 The response of valinomycin membrane

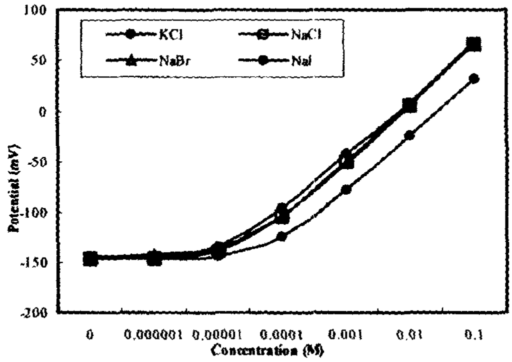
Fig. 3 shows sodium ionophore X membrane' responses to the taste stimuli. As same as behavior of valinomycin membrane, the sodium ionophore X was sensitive to cationic electrolytes. The responses to sodium ion were larger than the responses to potassium. And, though small, the responses to potassium ion occured in high concentration. Such a result means that the sodium ionophore X membrane shows non-selective responses. The repeatability was 1.9mV in 0.01M, and 2.1mV in 0.1M of concentration of sodium chloride selectivity of the membrane. The repeatability was 0.4mV in 0.01M, and 0.1mV in 0.1M of sodium chloride solution.



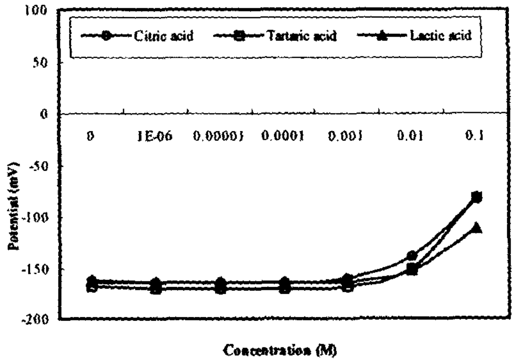
(a) The response to salts (b) The response to organic acids

Fig. 3 The responses of sodium ionophore X membrane

The potential of the membrane increased in the responses to organic acids. The change of membrane potential was in the order of the citric acid >= tartaric acid > lactic acid. The order agreed to the order of the dissociation coefficient of proton.



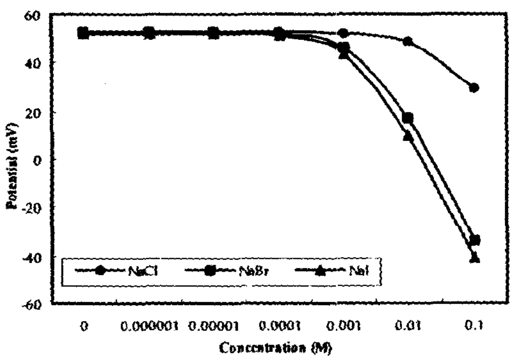
(a) The response to salts



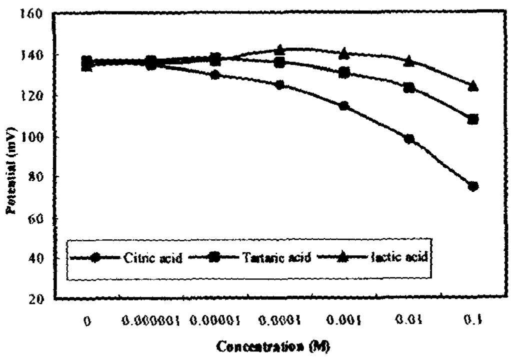
(b) The response to organic acids

Fig. 4 The responses of Monensin decyl ester membrane

Fig. 5 shows TDMACl membrane's responses to the taste stimuli. The membrane potential decreased as the concentration of stimuli increased. This response pattern meant that the TDMACl membrane was sensitive to anionic electrolytes. The change of membrane potential was in the order of the bromide > iodide > sodium. The order was in the Hofmeister series which followed the lipophilic order of anions(Rothmaier, 1993). Generally, the characteristic of anion ISE's was dominated by anions' lipophilic order. Therefore, each anion ISEs was only different in the magnitude of the change of membranes. The repeatability was 0.1 mV in 0.01M, and 0.3mV in 0.1M of sodium chloride solution.



(a) response to salts

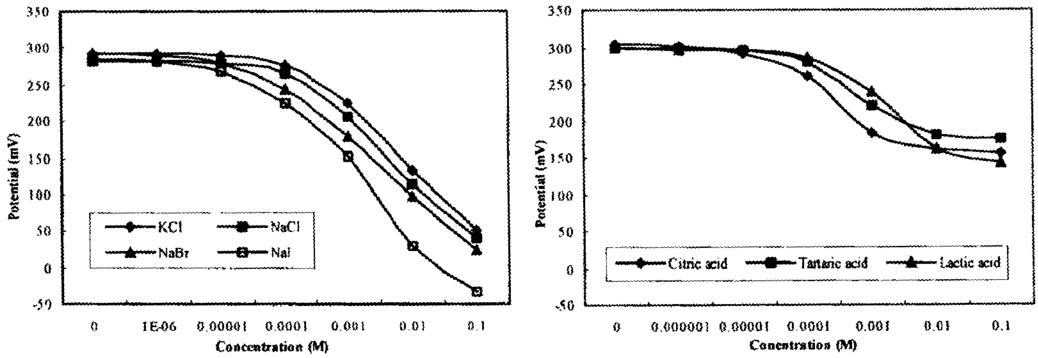


(b) response to organic acids

Fig. 5 The responses of TDMACl membrane by lipophilicity.

Also, the potential of the membrane decreased as the concentration of organic acids increased. The change of membrane potential was in the order of citric acid > tartaric acid > lactic acid. Because the order was in the order of the number of carbon contained in the molecules, it was judged that the characteristic of responses to organic acid was affected

Fig. 6 shows Chloride ionophore I membrane's responses to the taste stimuli. The membrane was sensitive to anionic electrolytes. The change of membrane potential was the same as that of TDMACl membrane. However, the change of potential to chloride was almost similar to that of bromide. This meant that Chloride ionophore X was deviated from the Hofmeister series. The repeatability was 1.6mV in 0.01M, and 1.1mV in 0.1M of sodium chloride solution. In responses to organic acids, the change of membrane potential was in the order of lactic > citric acid > tartaric acid. This fact also showed the deviation of the change of potential of chloride ionophore I membrane from lipophilicity.



(a) response tos salt (b) responses to organic acids

Fig. 6 The response of Chloride ionophore I

CONCLUSIONS

The study was executed for development of sensing elements of electronic tongue which could discriminate taste of foods. Five polymer membranes doped with electro-active material were prepared, and the measurements of membrane potential due to electrochemical reaction with seven taste stimuli were conducted. Three polymer membranes doped with valinomycin, sodium ionophore X, and monensin decyl ester were sensitive to cationic electrolytes, and two polymer membranes with TDMACl, and chloride ionophore X were sensitive to anionic electrolytes. These polymer membranes showed the non-selective responses to salts and organic acids analogous to response of human tongue.

It was concluded that the five polymer membranes mentioned above were the promise candidates for sensing elements of the electronic tongue.

REFERENCES

1. Craggs, A., G. J. Moody, and J. D. Thomas. 1974. PVC matrix membrane ion-selective electrode. Journal of Chemical Education 51(8):541-544
2. Crow, D.R. 1994. Principles and application of electrochemistry. Blackie Academica & Professional, Glasgow UK
3. Legin, A., A. Rudnitskaya, Y. Vlasov, C. D. Natale, F. Davide, A. D'Amico. 1997. Tasting of beverages using electronic tongue. Sensors and Acturators B 44 : 291-296
4. McLaughlin S. and R. F. Margolskee. 1994. The sense of taste. American Scienctist 82(November-December):538-545
5. Murata, T., K. Hayashi, K. Toko, H. Ikezaki, K. Sato, R. Toukubo, and K. Yamafuji. 1992. Quantification of sourness and saltiness using a mutichannel sensor with lipid membranes. Sensors and materials 4(2) : 81-88
6. Natale, C. D., A. Macagnano, F. Davide, A. D'Amico, A. Legin, Y. Vlasov, A. Rudnitskays, B. Selezenev. 1997. Multicomponent analysis on polluted waters by means of an electronic tongue. Sensors and Actuators B 44 : 423-428
7. Rothmaier, M., and W. Simon. 1993. Chloride-selective electrodes based on mercury organic compounds as neutral carriers. Analytica Chimica Acta. 271:135-141
8. Toko, K. 1998. Electronic tongue. Biosensors & Bioelectronics 13 : 701-709