

## Analysis of Several Ions and Thiols Using $\text{Ag}_2\text{S}$ -Membrane Electrode in Aqueous—Organic Mixed Solvents

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### 〈Abstract〉

It was well known that  $\text{Ag}_2\text{S}$ -membrane electrode is very suitable for determination of some anions and thiols in aqueous solution. But the properties and applications of this electrode in mixed solvents have not been established. The present study deals the properties of  $\text{Ag}_2\text{S}$ -membrane electrode by direct potentiometry in aqueous-organic mixed solvents. From the results, the behaviors of this electrode are discussed in terms of solute-solvent interaction. And some experiments were also carried out to determine the end-points of several anions, anion mixtures and thiols by potentiometric titration in aqueous-organic mixed solutions.

### 물—유기 혼합용매에서 $\text{Ag}_2\text{S}$ -막 전극을 이용한 몇가지 이온과 Thiol 화합물의 분석

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### 〈요 약〉

수용액에서 여러 음이온과 Thiol 화합물을 정량하는데  $\text{Ag}_2\text{S}$ -막 전극이 유용함을 잘 알려져 있다. 그러나 혼합용매계에서 이 전극의 성질과 그 응용성에 대해서는 널리 알려진 바가 없다. 본 연구는 물—유기 혼합용매에서  $\text{Ag}_2\text{S}$ -막 전극의 성질을 직접전위차법에 의해 측정하여 그 결과로부터 이 전극의 행동을 용질—용매 상호작용에 의해 고찰하였다. 또한 물—유기 혼합용매에서 몇가지 음이온, 음이온 혼합물 및 Thiol 화합물을 전위차 적정법에 의해 정량하였다.

### I. Introduction

The development of  $\text{Ag}_2\text{S}$ -membrane electrode has made possible selective, highly sensitive and rapid determinations of several compounds by means of direct potentiometric method or potentiometric titration.<sup>1-3)</sup> Some

studies on the determination of thiol by direct potentiometry have been made with  $\text{Ag}_2\text{S}$ -membrane electrode.<sup>4,5)</sup> Recently the results obtained in a study of ion-selective membrane electrodes used in some non-aqueous solvents were summarized.<sup>6)</sup> It was pointed out that the equations derived for aqueous media are also valid in non-aqueous media, if the solvents

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applied are alcohols.<sup>7</sup>

J. Papp and J. Havas<sup>8</sup> were the first to use an ion selective electrode for the titration of thiols. The electrode used was  $S^{2-}$ -selective (Radelkis, Type OPS-711). This electrode is also reversible to  $Hg^{2+}$ . The thiols examined were methyl mercaptan, potassium thiophenolate, mercaptoethanol and thiocresol. Water-soluble mercaptans were determined in 0.1M aqueous sodium hydroxide, and water-insoluble thiols were determined in ethanol. An ethanol-benzene mixture was used with good results by F. Peter and R. Rosset<sup>4</sup> for the potentiometric titration of thiols with the  $Ag_2S$ -membrane electrode as indicator electrode. Dioxane has a more limited applicability as the solvent and requires addition of an electrolyte to increase the dielectric constant of the titration medium. L.C. Gruen and B.S. Harrap<sup>9</sup> used  $Ag^+$  as titrant for the determination of L-cysteine, mercaptoethanol and glutathione. When  $Ag^+$  was added to the thiol there was very little change in potential until the end-point was almost reached.

This study presents the results of some experiments which were carried out to determine the properties and applications of  $Ag_2S$ -membrane electrode by direct potentiometry and end-point of some anions and thiols by potentiometric titration in water-organic mixed solvents, such as 50%-methanol(MeOH), 50%-ethanol(EtOH), 50%-1-propanol(1-PrOH), 50%-acetonitrile (AN) and 50%-dimethylsulfoxide (DMSO). The aim of this paper is to study how the application of mixed solvents alters the correlations valid for the  $Ag_2S$ -membrane electrode in aqueous media, and furthermore, to what extent these alternations can be used for analytical purposes.

## II. Experimental

Conductivity water was used and all other

reagents used were analytical grade. Conductivity water was obtained by passing distilled water through a deionizing column containing Amberlite MB-1 mixed bed resin. Stock solution of 0.01M thiols were prepared using either water or solvent mixture by volume without buffer solution, as the pH of titration mixture does not appear to be much of significance over the range of 2.5-9.<sup>9</sup>

All potentiometric measurements were made with the Fisher Accumet 525 Digital pH/Ion Meter. Solutions were stirred with a magnetic stirrer during potential measurement and solution temperatures were ambient at  $25 \pm 0.1^\circ C$ . Indicator electrode employed in this study was  $Ag_2S$ -membrane electrode of Broadley-James Co. type AG1015M and the reference electrode used was a calomel electrode of Fisher Co. with 0.1M  $NaNO_3$  salt bridge solution. In direct potentiometric measurement, the ionic strengths of solutions were fixed in 0.1 with anhydrous  $NaNO_3$ .

## III. Results and Discussion

END-POINT TITRATIONS, In studies on the potentiometric determination of  $CN^-$ , F.J. Conrad<sup>10</sup> used  $Ag_2S$ -membrane electrode as a indicator electrode in aqueous solution. Fig.1 shows potentiometric titration curves for the titration of  $CN^-$  with  $Ag^+$  using  $Ag_2S$ -membrane electrode in aqueous and 50% MeOH solutions. The stoichiometric reactions that form  $Ag(CN)_2^-$  and  $AgCN$  were proceeded during titrations, so the titration curves show two potential jumps and both may be used for the evaluation of quantity of  $CN^-$ . It is quite possible that  $Ag_2S$ -membrane electrode is suitable for determination of  $CN^-$  by potentiometric titration without difficulty in mixtures of MeOH and water as well as in aqueous solution.<sup>10</sup>

Fig.2 and 3 show the titration curves for

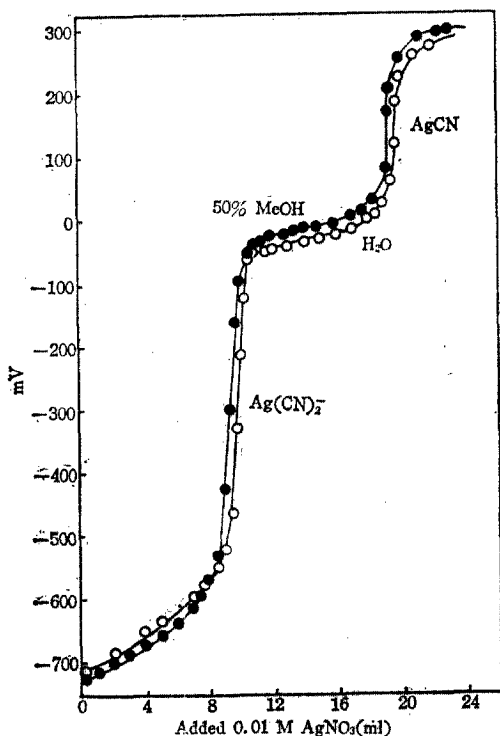


Fig. 1. Potentiometric titrations of  $\text{CN}^-$  with  $0.01\text{M AgNO}_3$  in aqueous and  $50\%$  MeOH solutions. Sample,  $20.0\text{ml}$  of  $0.01\text{M KCN}$  in water,  $20.0\text{ml}$  of  $0.01\text{M KCN}$  in  $50\%$  MeOH

$\text{CN}^-$  and  $\text{SCN}^-$  mixtures with  $\text{AgNO}_3$  in aqueous and three aqueous-alcohol mixed solutions. From the shapes of curves, two potential jumps are observed rather than three. In theoretical value of formation of  $\text{AgCN}$  at  $10.0\text{ml}$  of added  $\text{AgNO}_3$  solution, very weak evidences of endpoint can be found but it seems that these observations can not be helpful to determine  $\text{CN}^-$ . Fortunately, the first potential jump enables to determine  $\text{CN}^-$  and the second does  $\text{SCN}^-$  in each solution.

The  $\text{Ag}_2\text{S}$ -membrane electrode has previously been used for the analysis of various thiol compounds in aqueous solution.<sup>5,9)</sup> As yet, few

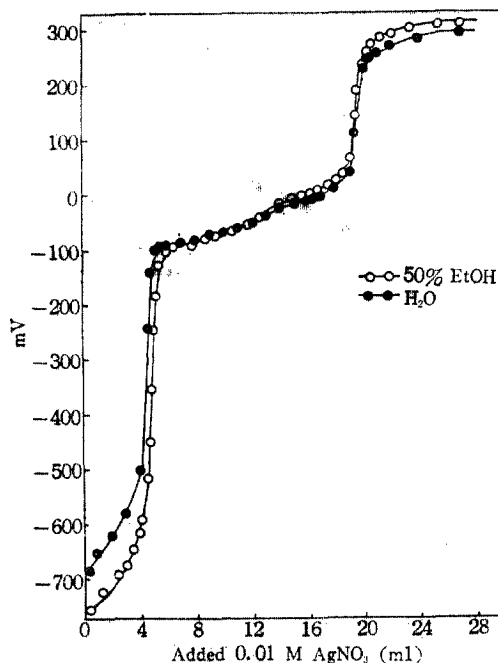


Fig. 2. Potentiometric titrations of  $\text{CN}^-$  and  $\text{SCN}^-$  mixture in aqueous and  $50\%$  EtOH solutions. Sample, mixture of  $10.0\text{ml}$  of  $0.01\text{M KCN}$  and  $10.0\text{ml}$  of  $0.01\text{M KSCN}$  in each solvent.

investigations have been made in organic and mixed solvents. In Fig. 4 and 5, the titration curves of glutathione with  $\text{AgNO}_3$  in aqueous,  $50\%$  MeOH,  $50\%$  DMSO and  $50\%$  AN solutions are presented. Satisfactory titration curves were obtained in all three aqueous-organic mixed solutions as well as in aqueous solution.<sup>9)</sup> The white precipitates of  $\text{Ag}$ -glutathione complex were formed and there were large potential jumps at the equivalence points, making it easy to locate the end-points accurately. But in  $50\%$  AN and  $50\%$  DMSO, the end-points were always within  $3.5\%$  of value predicted from stoichiometric equivalent point.

There have been doubts as to the stoichiometry of reaction with certain thiol. For instance, when cysteine was titrated in Tris

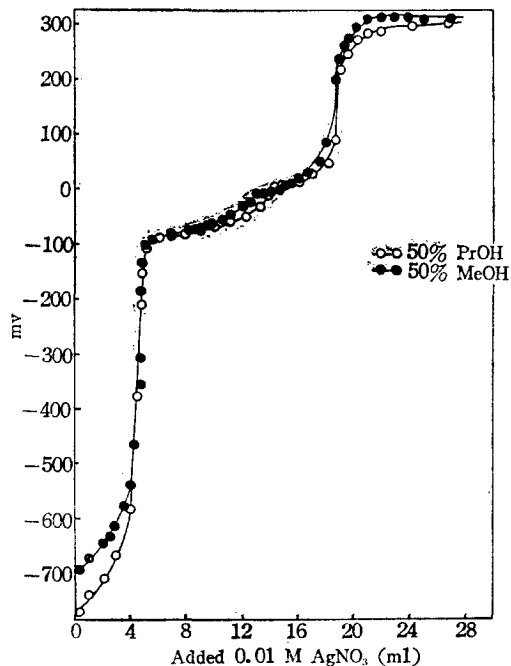


Fig. 3. Potentiometric titrations of  $\text{CN}^-$  and  $\text{SCN}^-$  mixtures in 50% 1-PrOH solutions. Sample, mixture of 10.0ml of 0.01M KCN and 10.0ml of 0.01M KSCN in each solvent.

or ammonia buffers with  $\text{AgNO}_3$ , the  $\text{Ag}^+$  consumed at the apparent end-point was 30–40% higher than that required for the 1:1 ratio.<sup>9,11</sup> Fig. 6 shows the titration curves for L-cysteine with  $\text{AgNO}_3$  in aqueous and 50% MeOH solutions. The results obtained in aqueous solution are identical to the previous workers'.<sup>9</sup> In determination of some thiols by potentiometric titration, L.C. Gruen and B.S. Harrap<sup>9</sup> took the end-points as the intersection between the linear baseline and curve of potential vs excess  $\text{Ag}^+$ , fitted with aid of french curves. The same methods were employed, so the satisfactory end-points were obtained in Fig. 6. The reasons of excess consumption of  $\text{Ag}^+$  were interpreted in formation of higher than 1:1 complex<sup>9</sup>, but there have been no

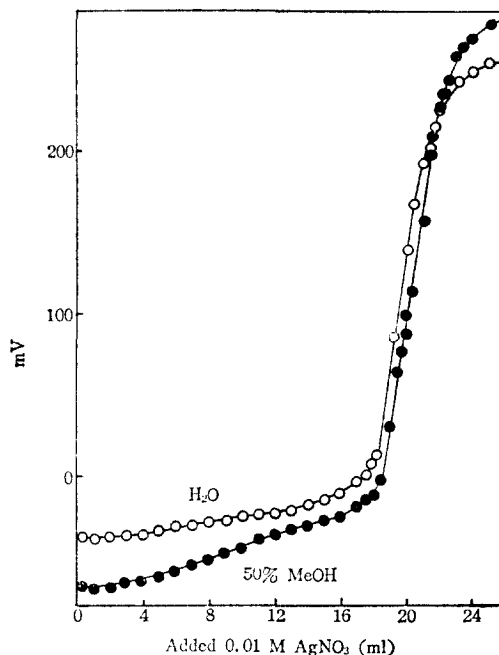


Fig. 4. Potentiometric titrations of glutathione with 0.01M  $\text{AgNO}_3$  in aqueous and 50% MeOH solutions. Sample, 20.0 ml of 0.01M glutathione in water, 20.0ml of 0.01M glutathione in 50% MeOH.

information concerning the structure or composition of such complexes.

DIRECT POTENTIOMETRY, Fig. 7 shows the responses of  $\text{Ag}_2\text{S}$ -membrane electrode to  $\text{Ag}^+$  concentrations in aqueous and several aqueous-organic mixed solvents. In aqueous solution, the slope of the curve (59.5mV/decade) has nearly Nernstian value but in aqueous-organic mixed solutions, those are lower than the Nernstians'.

J.E. McClure and T.B. Reddy<sup>12</sup>) have studied the behaviors of cationic glass electrode in propylene carbonate, AN and dimethylformamide. The electrode functions showed that the responses were linear over the range of  $10^{-5}$ – $10^{-2}$ M for all solvents, but the slopes of curves were lower than the Nernstian value, the difference being explained by dehydration of the glass in non-aqueous solvents.

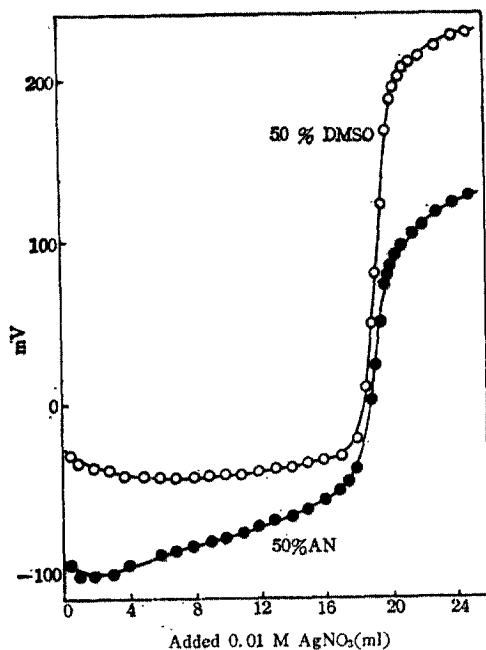


Fig. 5. Potentiometric titrations of glutathione with 0.01M  $\text{AgNO}_3$  in 50% AN and 50% DMSO solutions. Sample, 20.0ml of 0.01M glutathione in 50% AN, 20.0ml of 0.01M glutathione in 50% DMSO.

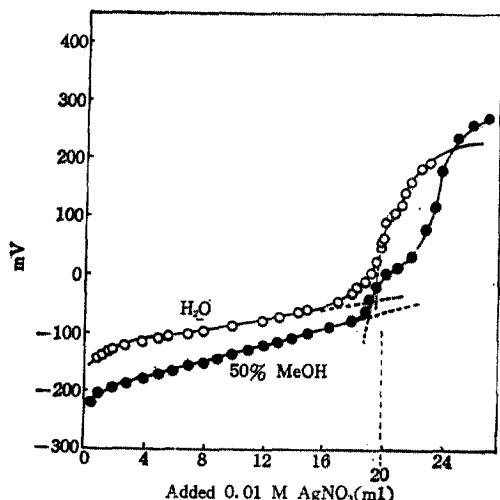


Fig. 6. Potentiometric titrations of L-cysteine with 0.01M  $\text{AgNO}_3$  in aqueous and 50% MeOH solutions. Vertical dashed line indicates stoichiometric end-point.

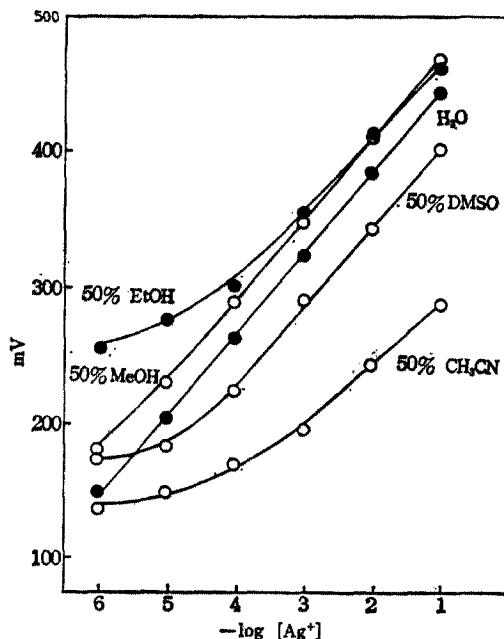


Fig. 7. The potential responses of  $\text{Ag}_2\text{S}$ -membrane electrode to the concentration of  $\text{Ag}^+$  in aqueous and several aqueous-organic mixed solvents at 25.0°C.

But in this study, it seems that the reasons are different from above and the origins are in solute-solvent interactions. H. Schneider and H. Strehlow<sup>13-15</sup> have studied the  $\text{Ag}^+$  solvation in aqueous-organic mixed solvents. The favorable interactions of  $\text{Ag}^+$  with dipolar aprotic solvents, such as DMSO and AN, were observed. These preferential solvation of  $\text{Ag}^+$  with DMSO and AN in aqueous-organic mixed solvents were explained by Pearson's HSAB concept<sup>16</sup> and back bonding interaction.<sup>17</sup> Low-lying vacant orbitals of the correct symmetry of a nitrile group forms  $\pi$ -back bondings by accepting electrons from filled  $d$  orbitals of  $d^{10}$  cations, such as  $\text{Ag}^+$ ,  $\text{Cu}^+$  and  $\text{Au}^+$ .<sup>20</sup> The interaction can be presented as  $\text{CH}_3\text{C}\equiv\text{N}\rightarrow\text{Ag}^+$ , and allows singly charged  $d^{10}$  cations to be much more strongly solvated by nitriles than would be expected from the solvation of less gifted cations (eg.  $\text{K}^+$ ) by nitriles. Thus  $\Delta G_{i,\text{K}^+}$

from water to AN is  $+9.5\text{KJ/g ion}$ , but  $\Delta G_r$ ,  $\text{Ag}^+$  is exergonic  $-22\text{KJ}$ , because the later, unlike  $\text{K}^+$ , are capable of back bonding to AN.<sup>18,19)</sup>

Cause of such specific ion-solvent interactions, the activities of  $\text{Ag}^+$  were decreased in these media and these effects are the major reasons of slope of  $\text{Ag}^+$  response to below Nernstian. Otherwise, in some aqueous-alcohol mixed solvents the responses of  $\text{Ag}^+$  are very similar to that of aqueous solution. These are explained as the characters of alcohol solvents, the most water-like structured.

The electrodes have linear responses over the concentration range  $10^{-6}$ – $10^{-1}\text{M}$  in these solvents are recommended for analytical use, but other solvents, such as 50% AN and 50% DMSO, are not suitable for this purpose. But from these phenomena, reversibly, it seems that the informations of solute-solvent interactions can be obtained, at least, qualitatively.

### References

1. T. M. Hsen and G. A. Rechnitz, *Anal. Chem.*, **40**, 1054(1968).
2. M. J. Brand and G. A. Rechnitz, *ibid.*, **42**, 478(1970).
3. C. J. Yoon, S. S. Lee and S. J. Kim, *J. Inst. Nat. Sci.*, Songsim Coll. for Women, Korea, **12**, 189(1981).
4. F. Peter and R. Rosset, *Anal. Chim. Acta*, **64**, 397(1973).
5. P. Tseng and W. F. Gutknecht, *Anal. Chem.*, **47**, 2316(1975).
6. G. Baiulescu, *Ion Selective Electrode in Organic Analysis*, pp.99–106, Ellis-Horwood Co., Sussex, England, 1977.
7. N. A. Kazarian and E. Pungor, *Anal. Chim. Acta*, **51**, 213(1970).
8. J. Papp and J. Havas, *Magy. Kem. Foly.*, **76**, 307(1970).
9. L. C. Gruen and B. S. Harrap, *Anal. Biochem.*, **42**, 377(1971).
10. F. J. Conrad, *Talanta*, **18**, 952(1971).
11. I. M. Kolthoff and J. E. Eisenstäter, *Anal. Chim. Acta*, **24**, 83(1961).
12. J. E. McClure and T. B. Reddy, *Anal. Chem.*, **40**, 2064(1968).
13. H. Strehlow and H. Schneider, *J. Chim. Phys.*, 118(1969).
14. H. Schneider, *Electroanal. Chem.*, **46**, 225 (1973).
15. L. Rodehüser and H. Schneider, *Z. Phys. Chem.*, 119(1976).
16. R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533(1963).
17. D. A. Owenby, A. J. Paker and J. W. Diggle, *ibid.*, **96**, 2682(1974).
18. A. J. Paker, *Electrochim. Acta*, **21**, 671 (1976).
19. G. S. Choi, M. S. Thesis, Korea Univ., 1982.
20. J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, p.29, University Science Books, Mill Valley, USA. 1980.