1986

Studies of Sodium Dodecylbenzenesulfonate-Water-Electrolyte Interactions

Xiaoxiang Zhu

Eastern Illinois University

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Studies of Sodium Dodecylbenzenesulfonate-

Water-Electrolyte Interactions
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BY

Xiaoxiang Zhu

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ABSTRACT

A surfactant selective electrode using a PVC membrane was constructed. A surfactant (sodium dodecylbenzene -sulfonate)-H_2O system was studied at 15°, 19°, 25°, and $40^\circ C$ with the PVC electrodes, a Na^+ selective electrode, and a conductivity bridge. Pre-micelle regions at the above temparatures were observed. The critical micelle concentrations (CMC^b) obtained by the PVC electrodes in salt-free systems are: 1.63×10^{-3} M at $15^\circ C$, 1.48×10^{-3} M at $19.1^\circ C$, 1.52×10^{-3} M at $25^\circ C$, and 1.73×10^{-3} M at $41.6^\circ C$. The CMC'c obtained by the Na^+ electrode are: 1.62×10^{-3} M at $15.0^\circ C$, 1.37×10^{-3} M at $19.3^\circ C$, 1.47×10^{-3} M at $25^\circ C$, and 1.98×10^{-3} M at $40.5^\circ C$. The CMC obtained by the conductivity measurement is: 1.62×10^{-3} M at $25^\circ C$. The counterion binding was calculated and it was found that it is not constant. An equation, $\log[DBS^-] = \text{constant} - r\log[Na^+]$, was obtained. The r value was calculated mathematically and it was found that it is related only to the slopes of the plots of EMF vs log [NaDBS] obtained by the PVC electrode and the Na^+ electrode. Hence the equality of r and the counterion binding proposed by the charged phase separation model is questionable. A decrease of the CMC by the addition of salts ($NaNO_3$ and NaCl) was observed with the PVC electrodes. The surfactant system with Cu^{2+} and Na^+ present was also investigated by the PVC electrodes and by a Cu^{2+} electrode. Complexation between Cu^{2+} and

the micelles was observed and the solubility product of Cu(DBS)$_2$ was calculated to be about $5\mathrm{x}10^{-10}$.

VITA

Name: Xiaoxiang Zhu

Degree and date to be conferred: M.S., 1986.

Major: Physical Chemistry.

Place of birth: Guangdong, PRC

Secondary education: Huang Tong High School, Meixian

County, Guangdong, PRC, 1970-1974

Collegiate institution attended:

South China Normal University, B.S., 1978-1982.

Eastern Illinois University, M.S., 1984-1986.

Positions held:

Teaching Assistant, Department of Chemistry,

South China Normal University, 1982-1984.

Graduate Assistant, Department of Chemistry,

Eastern Illinois University, 1984-1986.

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I. INTRODUCTION

Sodium dodecylbenzenesulfonate, NaDBS, belongs to the family of surfactants, a shorthand term for surface active agents.

Since the 1930's sulfonated petroleum products have found numerous applications for their surface active properties. After the Second World War alkyl aryl sulfonates began replacing animal soaps as industrial and household detergents because of their desirable low temperature solubility.[1] With the hundreds of millions of pounds of sulfonated petroleum produced annually comes the need for sulfonate analysis, both at the production end for quality control and at the disposal end for pollution control.

The oil industry has recently begun using large quantities of petroleum sulfonates in the tertiary oil recovery program,[2] which has great significance in this highly energy-consuming society. During the application of petroleum sulfonates to tertiary oil recovery, researchers found that the increase oil recovery was not as great as expected because there are many inorganic ions underground which can interact with the injected sulfonates.

The present work deals with the analyses of NaDBS-H_2O-electrolyte systems containing Na^+ and Cu^{2+} salts

using PVC anionic selective electrodes for DBS$^-$, cation selective electrodes for Na$^+$ and Cu^{2+}, and conductivity measurements to gain some insight into the micellar systems.

A. Anionic Surfactant-Aqueous System

A surfactant is an amphiphilic substance. An important class of surfactants is the anionic one. NaDBS, an anionic surfactant and a 1-1 type strong electrolyte, consists of a hydrophobic tail (carbon chain) and a hydrophilic head (SO_3^{2-}). When it is dissolved in water, it is separated by water molecules with its tail subjected to a repulsion force from water solvent due to a thermody-namic preference for elimination of hydrocarbon-water contacts.[3] When the NaDBS concentration is low, the repulsion is weak. However at higher concentrations this force becomes significant. At a certain NaDBS concentra-tion (or in a narrow concentration range), the repulsion force becomes so great that the hydrophobic tails have to interact with each other to form some kind of aggregate which is referred to as a micelle.[3] The concentra tion at which micelle formation first occurs or the narrow concen-tration range at which micelle formation is occurring is called the "critical micelle concentration" (CMC). The concept of a "critical concentration" for the formation of micelles from free amphiphiles is inexact but convenient.

It would be exact if micelle formation could be regarded as separation of a distinct phase, and free amphiphile in solution could coexist with the micellar phase at only a single value equal to either the total added concentration at which phase separation first occurs or the free concentration in solution as analytically measured in the presence of the micellar phase. In fact, micelle formation is not equivalent to phase separation. When micelles and free amphiphiles coexist, the free amphiphile concentration is a variable, depending on the concentration of micelles present. However, if the number average aggregation number m^* (the average number of monomer amphiphiles which make up the micelles) is reasonably large ($m^* > 50$) the free monomer concentration changes only slowly with the total added surfactant concentration after micelle formation occurs, and the transition from the predominantly unassociated amphiphile to the micellar state does in fact occur over a narrow critical range of concentration, approaching true phase separation. It is customary to define a single concentration within this transition range as a CMC. This is usually done by empirical graphical procedures.

Micelles can be small spheres or disks, oblate or prolate ellipsoids, or long cylinders. They can also be in the form of bilayers, that is, two parallel layers of amphiphile molecules with the polar groups facing out[3].

Frank Blum reported that micelles might even be undergoing interconversion between planar liquid crystal, liposome (multilamellar) and vesicle (unilamellar) forms.[4]   Figure 1 shows these possible micellar structures.

The hydrocarbon chains in such micelles are generally regarded as disordered, so that the hydrophobic core is in effect a small volume of liquid hydrocarbon.[3]

The striking characteristic of aggregation of the surfactant monomer amphiphiles at the CMC is the fact that the aggregation leads to an abrupt change in the solution properties such as surface tension, osmotic pressure, intensity of scattered light, electrical conductivity, and so on.   In micellar solutions micelles have certain size distributions and high formal charges.   The electrostatic repulsion energy inherent in the aggregation of amphiphilic ions of like charge is partly compensated by the binding of counterions (gegenions) to the micelle. The CMC, aggregation number n (the number of surfactant ions which make up the micelle), and the degree of counterion binding B are important parameters charaterizing the micellization process.

The process for micelle formation in the NaDBS-aqueous system can be represented by

$$n \ Na^+ + n \ X^- = (X_n Na_m)^{-(n-m)} + (n-m) \ Na^+ \qquad (1)$$

$$or, \ m \ Na^+ + n \ X^- = (X_n Na_m)^{-(n-m)}, \qquad (1a)$$
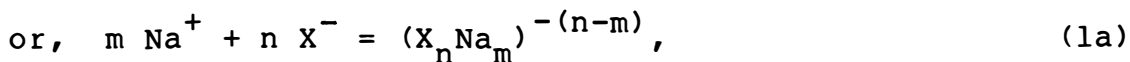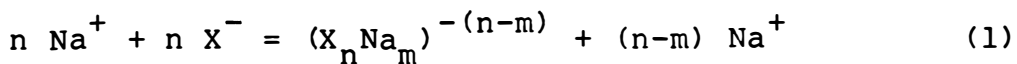
where n is the aggregation number, m is the number of Na^+ ions associated in a micelle, $-(n-m)$ is the micelle
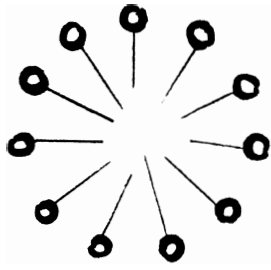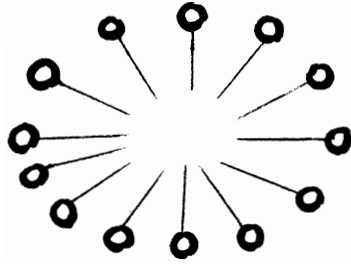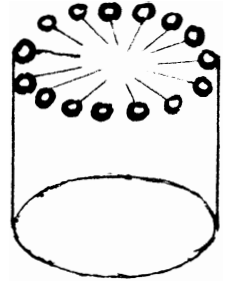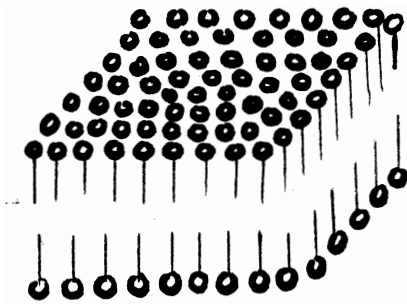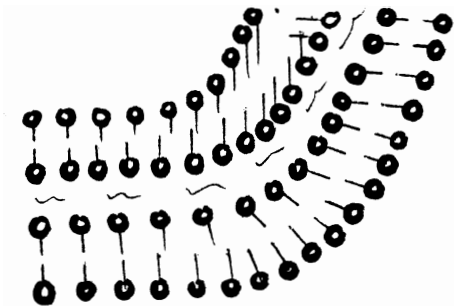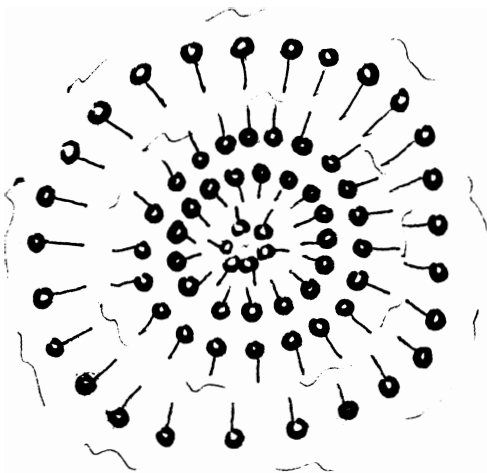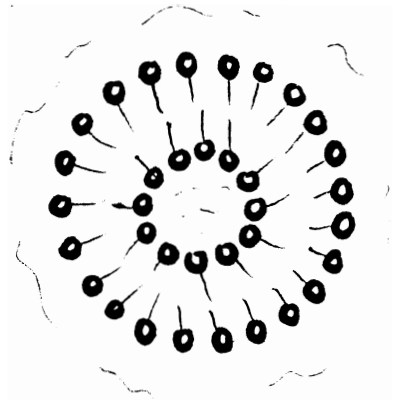
Figure 1. Micelle Structures

(a) sphere   (b) ellipsoid   (c) cylinder   (d) bilayer

(e) planar liquid crystal (f) liposome   (g) vesicle

charge, X^- is the anionic surfactant ion (DBS$^-$), and n > m.

The degree of counterion binding , B, is defined as :

B = 1 - a

= m* / n*

= Total number of Na$^+$ associated in all micelles / Total

number of monomer amphophiles in all micelles. (2)

Here m* and n* are number average values, and a is the

degree of counterion dissociation of a micelle (the

extent to which the surfactant molecules are ionized).

It is well known that electrolytes have a marked

influence on the micellar properties of surfactant

solutions, and systems in which the added electrolye has

an ion common to the surfactant salt have been extensively

studied.[6-7] These studies have shown that the depression

of the CMC by common ion electrolytes depends on the

counterion concentration and distribution in the vicinity

of the micelles. Large depression in the CMC of anionic

surfactants caused by the addition of electrolytes with

polyvalent cations were observed by some researchers[7-8].

They also found that the coexistence of Ca^{2+} and Na$^+$ as

counterions in the micelles and the precipitation of Ca^{2+}-

surfactant salt in these surfactant systems.

Many physical methods such as light scattering,[9-10]

NMR,[4, 11-13] electrophoresis,[14] conductivity measure-

ments,[15-16] electromotive force measurements,[17-21] density

measurements,[22-23] direct enthalpies of micellization

6

measurements,[24] ultrafiltration methods,[25] and chemical relaxation methods[26] (ultrasonic absorption, T-jump, P-jump and shock tube) have allowed researchers, through various theories, to account for the ionic environment of the micelles. Light scattering yields information primarily about aggregates. Conductance gives data which combine contributions of micelles, surfactant monomers, and counterions. The electromotive force measurement is more practical, since it requires a very common material. Another advantage of this procedure is that it does not require introduction into the medium of a chemical probe capable of influencing the distribution of the species. Surfactant ion electrodes provide a direct measure of the surfactant monomer activity alone. Above the CMC, such measurements allow determination of the activity of the surfactant monomer in equilibrium with the micell. When used with other ion electrodes specific for the counterions, surfactant ion electrodes provide data which are difficul to obtain by any other technique and thus constitute an unexploited method for studying micellar solutions.

B. Evolution of Micelle Formation Theory

B.1. Phase separation model (pseudophase model)[27-31]

This model assumes that the micelle is a separate phase from the solution, and the activity of the free monomer amphiphile and counterion remains constant above the CMC. This can be represented by

$$n \text{ Na}^+ + n \text{ X}^- = (\text{NaX})_n \qquad \text{(separate phase)} \qquad (3)$$

or, $\quad \text{Na}^+ + \text{ X}^- = 1/n \text{ (NaX)}_n \qquad \text{(separate phase)} \qquad (3a)$
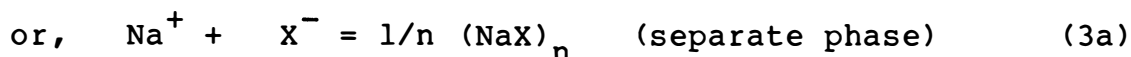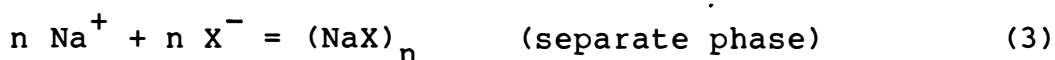
The free energy change for this process (Equation 3a) is

$$\Delta G^0_m = -RT \ln K_m$$
$$= -RT \ln \{ [(\text{NaX})_n]^{(1/n)} / ([\text{Na}^+][\text{X}^-]) \} \qquad (4)$$

Because the micelle is a separate phase, its activity is equal to unity, and $[\text{Na}^+] = [\text{X}^-] = \text{CMC}$, equation (4) becomes

$$\Delta G^0_m = 2RT \ln \text{CMC} \qquad (4a)$$

Some authors[9] treat the micelle formation as follows

$$\text{X}^- = 1/n \text{ (X}_n)^{-n} \qquad \text{(separate phase)} \qquad (5)$$

The free energy change can be easily derived :

$$\Delta G^0_m = RT \ln \text{CMC} \qquad (6)$$

The phase separation model was criticized later when it was discovered that the free monomer amphiphile concentration was not constant above the CMC , but decreased with the added surfactant. Moreover, the assumption of the micelle as a separate phase was brought into question by the mass action model, which will be

discussed below. The major advantage of the phase
separation model is that ΔG^O_m is easily obtained by
knowing only the experimental CMC value and the ΔG^O_m so
calculated is in good agreement with that calculated by
other methods.

B.2. Mass Action Model (Stepwise Self Association Model)[32-35]

The mass action model, which has been used since the
discovery of micelles, considers a micelle not as a
separate phase but as a chemical species. It recognizes
the polydispersity and the rapid association-dissociation
multiple equilibria in a micellar system.

In a nonionic micellar system with large micelles,
the step-wise association reaction

$$X_{n-1} + X_1 = X_n \quad \text{(not a separate phase)} \tag{7}$$
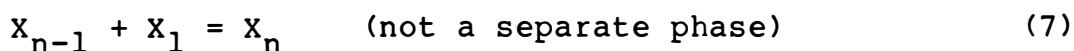
is governed by a stepwise association constant, K_n, given
by

$$K_n = [X_n] / ([X_{n-1}][X_1]). \tag{8}$$

Then the overall association constant, B_n, becomes

$$B_n = K_2 * K_3 * \ldots * K_n \tag{9}$$

For ionic micelles, the micellization process is
represented by Equation 1a:

$$m \, Na^+ + n \, X^- = (Na_m X_n)^{-(n-m)} \quad \text{(not a separate phase)} \tag{1a}$$
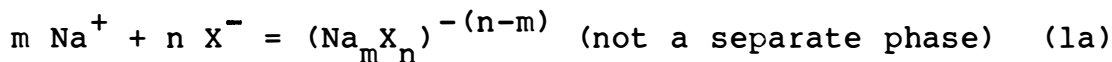
The free energy change accompanying this process can be

obtained by

$$\Delta G^O = -RT \ln B_n$$

$$= -RT \ln \{ [X_m/n] / ([Na^+]^m [X^-]^n) \}, \tag{10}$$

where brackets stand for activity, n is the aggregation number, and X_m is the total monomer amphiphile concentration aassociated in micelles of size n.

If Equation (1a) is rewritten as:

$$m/n \ Na^+ + X^- = 1/n \ (Na_m X_n)^{-(n-m)}, \tag{11}$$

then the free energy change is given by

$$\Delta G^O_m = 1/n \ \Delta G^O$$

$$= -RT/n \ \ln \{ [X_m/n] / ([Na^+]^m [X^-]^n) \}$$

$$= -RT \ \ln \{ [X_m/n]^{1/n} / ([Na^+]^{m/n} [X^-]) \}$$

$$= -RT \ \ln K_m \tag{12}$$

where m/n is the degree of counterion binding of micelles of size n.

Equation (12) can be used as a basis for the prediction of micellar properties from estimates of the free energy of micellization, and conversely, it can be used to obtain information about the free energy of micellization from experimental data.

However, the mass action model must have the size distribution or every association constant over all stepwise associations from monomer to micelle, which is almost impossible to achieve experimentally. Therefore, this model has the disadvantage that either monodispersity of the micellar aggregation or numerical values of each association constant have to be assumed.

If the micelle is assumed to have a unique size of n^* and m^* (number average size), then micellization for an ionic surfactant can be treated as one stepwise equilibrium similar to Equation (11):

$$m^*/n^*\ Na^+ + X^- = 1/n^*\ (Na_{m*}X_{n*})^{-(n^* - m^*)}. \qquad (13)$$

Then Equation (12) becomes:

$$\Delta G^O_m* = -RT\ \ln\ \{\ [X_m*/n^*]^{1/n^*}/([Na^+]^{m*/n^*}\ *\ [X^-])\ \} \qquad (14)$$

where $\Delta G^O_{m*} > \Delta G^O_m$ because $X_{m*} > X_m$. Here n^* is the average micelle size, m^*/n^*, the counterion binding of micelles of size n^*, and X_{m*}, the total monomer concentration in all micelles.

Although this model did not allow for the concentration dependence of m^*, n^*, $[Na^+]$ and $[X^-]$, and hence X_{m*} and ΔG^O_{m*} at the time it was proposed, it can still be employed if these factors are taken into account.

B.3.   Charged Phase Separation Model [36-42]

Sasuki et. al. proposed this model based on the experimental fact that above the CMC, log $[X^-]$ and log $[Na^+]$ were linear functions which were related by

$$\log\ [X^-] = constant - r\ \log\ [Na^+]. \qquad (15)$$

Thus when log $[X^-]$ was plotted against log $[Na^+]$, a straight line with slope equal to -r was obtained. They believed that r was the counterion binding because they believed that the micellization process had a charged

phase separation mechanism, which is illustracted below:

$$m \, Na^+ + n \, X^- = (Na_m X_n)^{-(n-m)} \quad \text{(separate phase)} \quad (16)$$
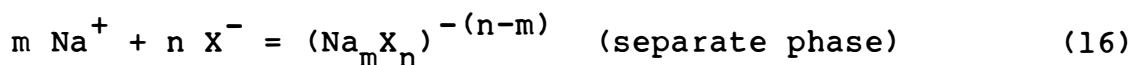
The equilibrium constant was obtained as:

$$K = 1 \, / \, ([Na^+]^m * [X^-]^n) \quad (17)$$

or, $\quad [Na^+]^m * [X^-]^n = 1/K = \text{constant} \quad (17a)$

Taking the logarithm and rearranging, one obtains an equation similar to Equation 15:

$$\log [X^-] = 1/n \log 1/K - m/n \log [Na^+] \quad (18)$$

Comparing Equation 15 and Equation 18, Sasuki et. al. believed that (1/n log 1/K) is a constant and r = m/n = B (counterion binding). The free energy change for the micellization process (Equation 16) is given by

$$\Delta G^O = RT \ln \{ [Na^+]^m * [X^-]^n \}$$

$$= nRT \ln \{ [Na^+]^B * [X^-] \} \quad (19)$$

or, $\Delta G^O_m = 1/n \, \Delta G^O = RT \ln [Na^+]^B * [X^-], \quad (20)$

where B is the counterion binding, and $[Na^+]$ and $[X^-]$ the activities of the sodium ion and the surfactant ion, respectively, at the CMC.

II. EXPERIMENTAL

A. Apparatus

Electrode potentials were measured with an Orion 701A digital ionalyzer (accurate to ± 0.1 mv). Electrodes used were plastic PVC membrane-Ag/AgCl internal electrodes, a Na^+ ion selective electrode (Orion 94-11), a Cu^{2+} ion selective electrode (CuS and PbS as the solid membrane), and an Orion double junction electrode. The potential cell was a water-jacketed cell in a magnetic stirrer assembly. Conductances were measured with a Beckman conductivity bridge (accurate to ± 0.01 Ohms), and the cell was kept at constant temperature.

B. Reagents

Sodium dodecylbenzenesulfonate (NaDBS) (Pfaltz and Bauer, D56340), Benzylcetyl dimethylammonium chloride·H_2O (95%), Hyamine 1622, NaCl, $NaNO_3$, $Cu(NO_3)_2$ and sodium tetraphenylboron were used without further purification. NaDBS solutions were titrated with benzylcetyldimethyl-ammonium chloride·H_2O using PVC electrodes as end point detectors. The $Cu(NO_3)_2$ concentration was determined by first passing the solution through a cation exchange resin (Dowex 50 W) then titrating with a standard base. The molecular formulas of NaDBS, and benzylcetyldimethyl-

ammonium chloride H_2O are shown below:

NaDBS: $p-C_{12}H_{25}C_6H_4SO_3Na$

Benzylcetyldimethylammonium chloride·H_2O:

   $C_6H_5CH_2N[(CH_2)_{15}CH_3](CH_3)_2Cl·H_2O$
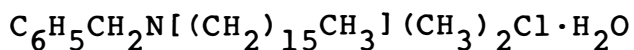
C. Construction of PVC Electrode Membranes

There have been many types of surfactant selective electrodes ranging from liquid membranes,[43-45] silicone-rubber,[46] coated wire,[47] and PVC membranes.[48-49] PVC membrane electrodes are very easy to construct, and their lifetimes are reasonably long, which has attracted more and more attention recently. The PVC membrane is the most important part in the potential measurements of NaDBS-aqueous systems. The membrane consists of three ingredients: PVC, plasticizer, and membrane exchanger. PVC is presumably serving as a network through which the surfactant ions can pass. A variety of compositions for making the PVC membranes have been tested, and the best one among them was employed throughout the measurements. The construction of the optimized electrodes will be discussed below.

MEMBRANE EXCHANGER-1: About 1 millimole NaDBS and 1 millimole benzylcetyldimethylammonium chloride·H_2O were dissolved in separate containers in just enough water to effect dissolution. Gentle warming was sometimes

necessary. The two solutions were mixed with stirring, and a white precipitate formed. The precipitate was allowed to stand for about one half hour before decanting the liquid portion. Excess water was removed by vacuum filtration. The precipitate was placed in a vacuum oven at room temperature for about one hour and then stored in a dessicator. Membrane Exchanger-1, Benzylcetyldimethyl-ammonium-DBS, was thus obtained.

MEMBRANE EXCHANGER-2: About 1 millimole sodium tetraphenyl boron and 1 millimole Hyamine 1622 were treated as above and Hyamine-tetraphenylboron, membrane exchanger-2, was thus obtained.

MEMBRANE SOLUTION-1: 0.4 grams of PVC (low molecular weight, Aldrich 18,958-81), 0.6 grams of tri-tolyl phosphate as the plasticizer (Aldrich 26,891-7) and 0.8 mg of Membrane Exchanger-1 were dissolved in about 11 ml cyclohexanone. Thus solution-1 was obtained.

MEMBRANE SOLUTION-2: 0.4 grams of PVC, 0.6 grams of tri-tolyl phosphate and 0.8 mg Membrane Exchanger-2 were dissolved in about 11 ml cyclohexanone. Thus solution-2 was obtained.

PVC ELECTRODE-1: An electrode body (polypropylene tube) with the conical tip cut off to give an ID of 2-4 mm was dipped into solution-1 and then suspended above a hot plate where the electrode membrane was allowed to dry at 50°-55°C for over one week. Thus electrode-1 was obtained.

PVC ELECTRODE-2: The same procedure was used to make this

electrode as was used in making electrode-1, but with solution-2 replacing solution-1. Electrode-2 thus was obtained.

PVC ELECTRODE-3: One part of solution-1 and one part of solution-2 were mixed together. The same dipping and drying procedure as discribed above was then used to make Electrode-3.

Good PVC electrode membranes should look transparent.

D. Determination of the Critical Micelle Concentration (CMC) of NaDBS and the Interactions between Electrolytes and Surfactant Monomers and Micelles

Electrode-3 was used to determine the CMC's for all the measurements in the salt free NaDBS-H_2O system, NaDBS-H_2O-NaCl (and NaNO$_3$) system, and NaDBS-H_2O-Cu(NO$_3$)$_2$ system. A conductivity bridge was employed to confirm the CMC obtained by PVC electrodes. A Cu^{2+} electrode and a Na$^+$ electrode were also employed to investigate the systems. Stock solutions were prepared, and all the solutions used in the experiments were diluted from the stock solutions. All the measurements were done at constant temperature in a water-jacketed cell for the potential measurements or in an oil bath for conductivity measurements.

D. (1) CMC Determinations at 15°, 19°, 25°,

and 40°C in Salt-Free NaDBS-H$_2$O System

D.(1) (a). CMC Measurements by PVC Electrode-3

in Salt-Free System

A detailed description of the PVC electrode and measuring circuit is shown in Figure-2. The potential cell can be represented by

PVC membrane
↓
Ag/AgCl/ NaCl, NaDBS   // test solution / <u>KNO$_3$/KCl/AgCl/Ag</u>

0.02 M, 10^{-3} M   reference electrode
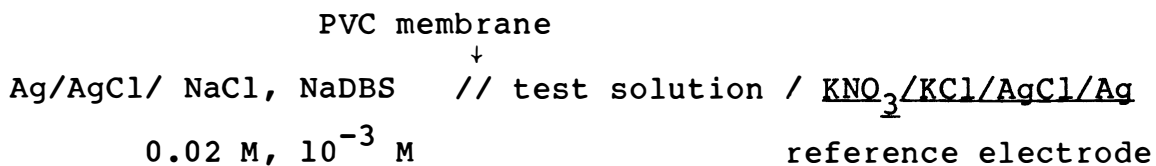
Before the measurements, the electrode was soaked for about 1-2 hours in a solution of 10^{-3} M NaDBS. To 75 ml of H$_2$O were added stock solutions of NaDBS to bring the test solution to about 4.7 x 10^{-3} M NaDBS. Potentials were recorded upon reaching a stable reading ($\pm$0.5 mv/min drift). Then successive additions were made with the potential recorded after each addition. It was found that in the lower concentration range, the response time was longer (usually about 10-15 mins) than that in the higher concentration range (usually about one min). Usually, a PVC electrode could be used for about 10 runs if the elec-trode was dried out after each run. With the PVC electrod-3, the CMC's of NaDBS in H$_2$O were determined at 15.0^O, 19.1^O, 25.0^O, and 41.6^{O}C respectively from the intersections in the plots of EMF vs log [NaDBS] which are

volt
meter

polypropylene tube

reference
electrode

Ag/AgCl

0.02 NaCl, 10^{-3} M NaDBS

PVC membrane

test solution

water-jacketed cell
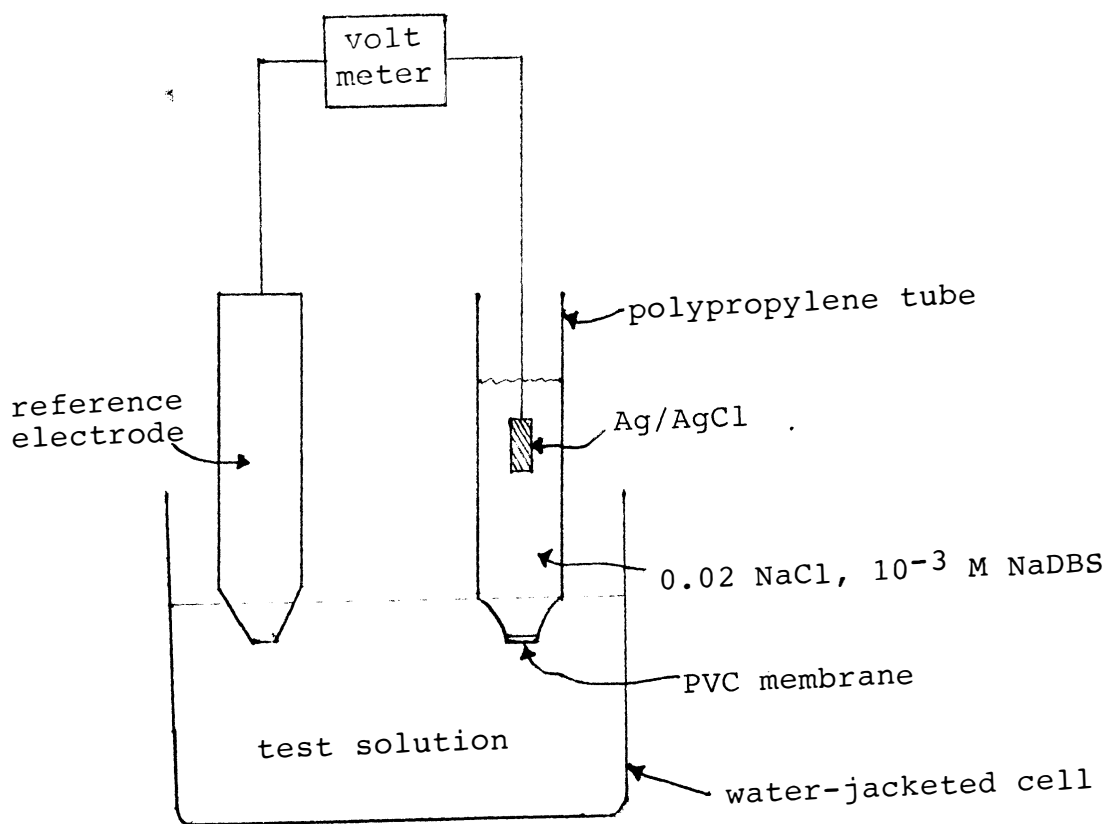
Figure 2.   PVC Membrane and Measuring Circuit

shown in Figure-3.

D.1.(b). CMC Determined by a Na^+ Electrode

A calibration curve obtained by adding 0.02 M $NaNO_3$
t0 75 ml water is shown in Figure-4 (a).

To 75 ml H_2O were added stock solutions of NaDBS to
bring the concentration of the system to about 2.8 x 10^{-2}
M NaDBS. Potentials were recorded after each successive
addition upon reaching a stable reading (±0.2 mv/min
drife). The measurements were done at 15.0^O, 19.3^O,
25.0^O,and $40.5^O C$, respectively. Plots of EMF (mv) vs log
[NaDBS] are shown in Figure-4 (b-e). Critical micelle
concentrations were obtained by extrapolating the two
straight lines to a point of intersection and taking the
concentration at this intersection as the CMC. The Na^+
electrode response became sluggish after each run in the
surfactant solution. Before each run, the Na^+ electrode
was soaked in 10^{-3} M $NaNO_3$ solution for a few hours, or if
necessary, was soaked in 0.1 M $NH_4F \cdot HF$ for about 30
seconds.

D.1 (c). CMC Determined by a Conductivity Bridge
           in Salt-Free system at $25^O C$

Before measurements were made, the cell was soaked in
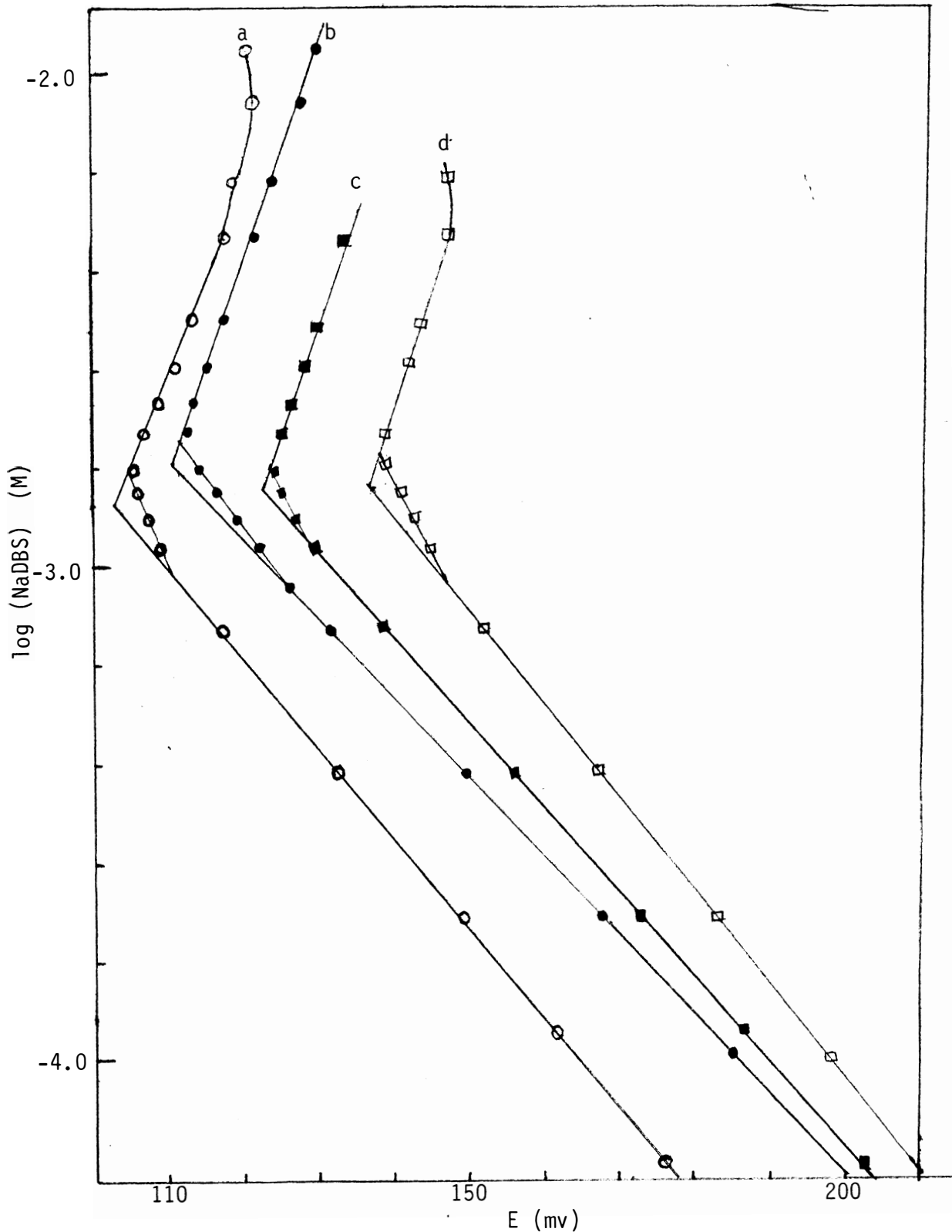
Figure 3. Response of PVC Electrodes to NaDBS Activity
(a) at 19.1°C (b) at 41.6°C (c) at 25.0°C (d) at 15.0°C

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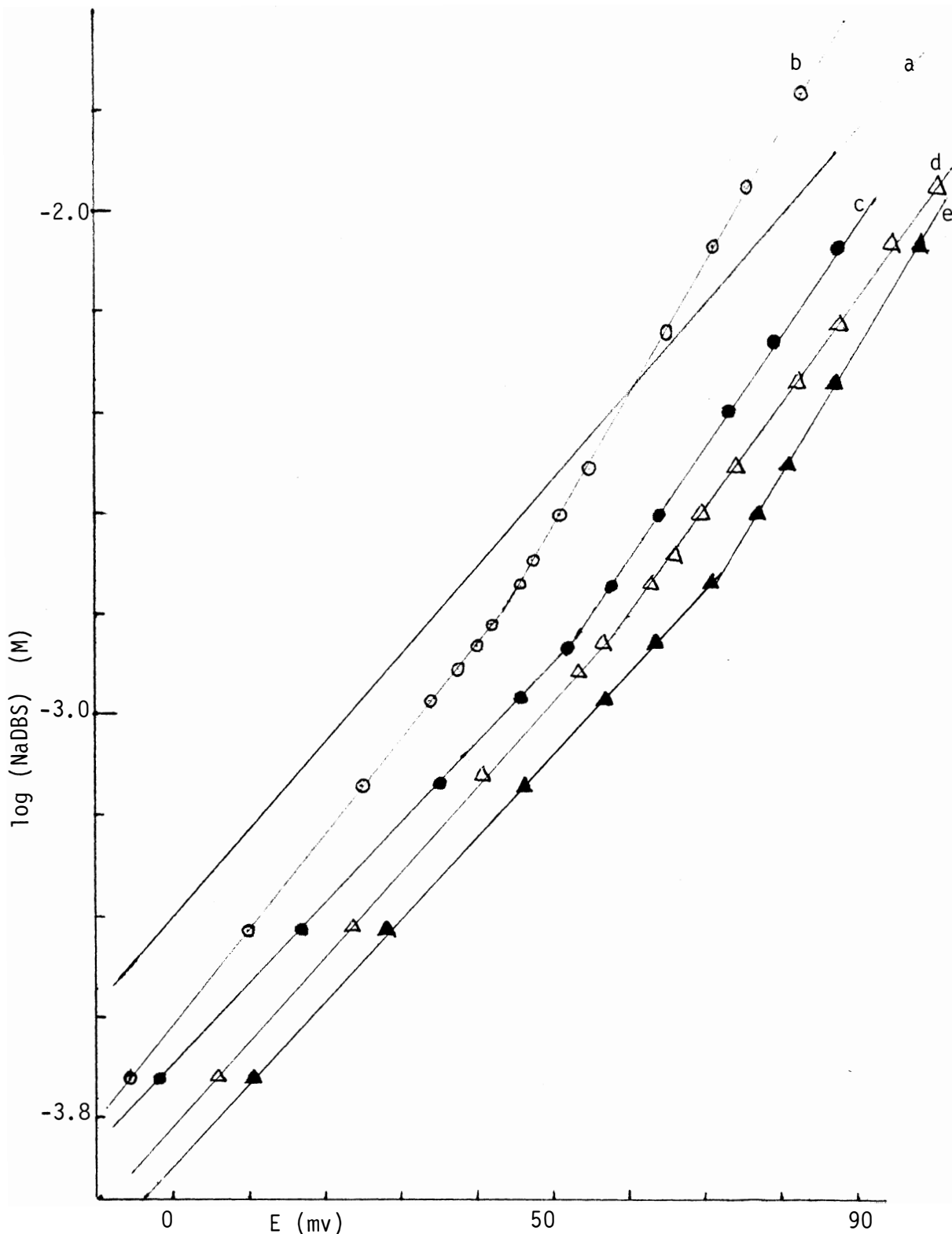
Figure 4.   Response of Sodium Electrode to NaDBS Activity
(a) Calibration run   (b) 15°C   (c) 19.3°C   (d) 25.0°C
(e) 40.5°C

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200 mL water overnight with constant stirring and temperature (25.0°C). The conductance of water was recorded as R^{-1}_{solv}. Aliquots of the stock NaDBS solution was added to the 200 mL of water to bring the concentration to about 2.8 x 10^{-2} M NaDBS with conductance recorded after each successive addition. The CMC was obtained as the intersection of the plot of log k (specific conductance) vs log [NaDBS], which is shown in Figure-5(a). The cell constant (1/A) was also determined by measuring the conductance of a 0.0200 M KCl solution.

D.2. CMC Determinations in NaDBS-H$_2$O-
Electrolyte (NaNO$_3$ and NaCl) Systems

All the measurements in this part were done at certain ionic strengths maintained constant by NaCl or NaNO$_3$. Usually three solutions were prepared from stock solutions for each run. A typical experiment is illustrated below:

solution-1   solution-2   solution-3
X M NaNO$_3$ X M NaNO$_3$ X M NaNO$_3$
6.60 x 10^{-4} M NaDBS   1.32 x 10^{-2} M NaDBS

50 mL of solution-1 was the starting solution, to which solution-2 or solution-3 was added to increase the concentration of NaDBS.
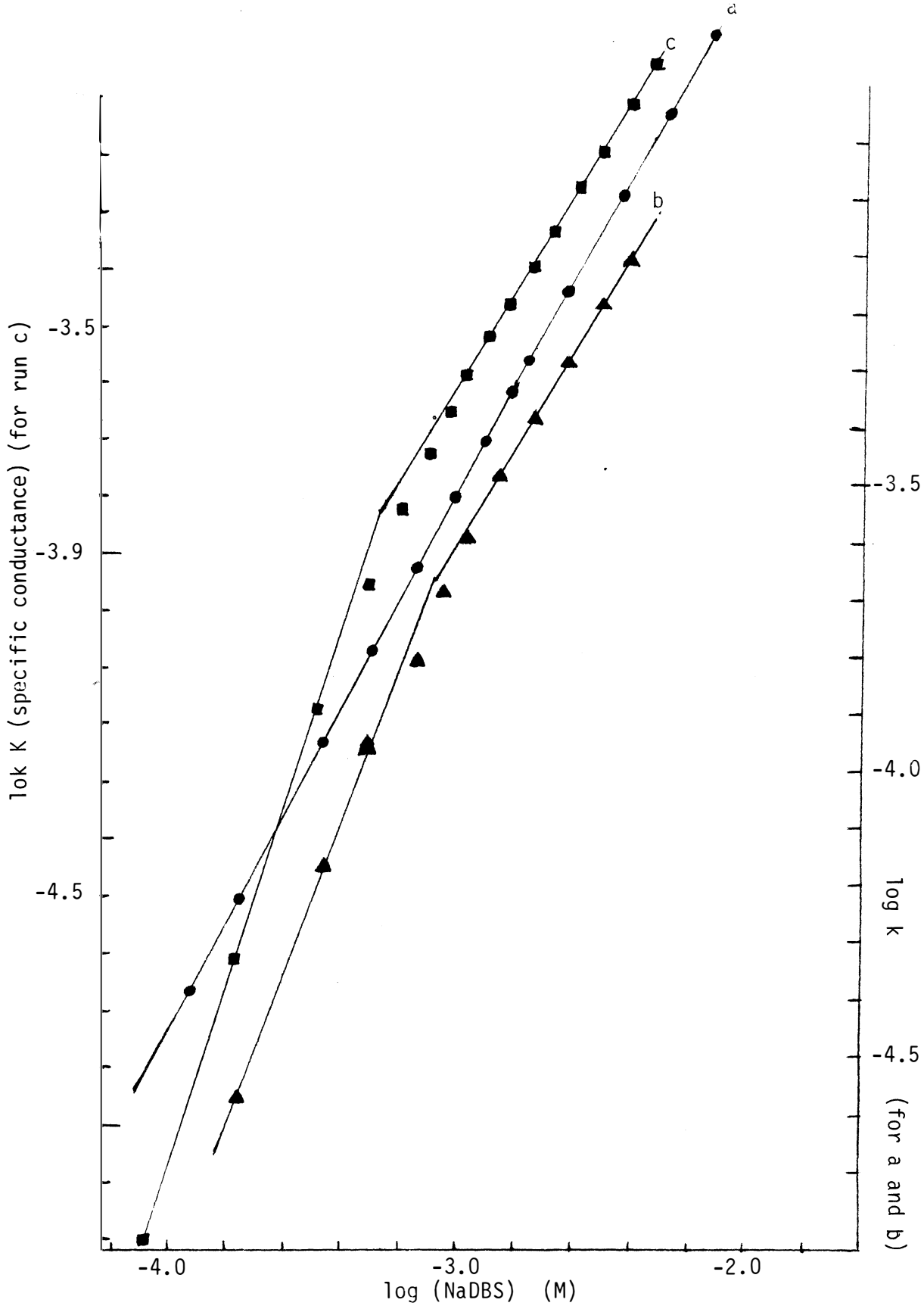
Figure 5. Conductivity Measurements at 25°C

(a) salt-free   (b) 0.02 M sodium nitrate

(c) 0.02 M sodium nitrate, and 0.001 M cupric nitrate

D.2 (a). CMC's Determined by PVC Electrode-3
with Added Salts (NaCl or $NaNO_3$)

A PVC electrode was soaked in 0.001 M $NaNO_3$ and 0.001 M NaDBS solution for about 1-2 hours before the following experiments. The responses of the PVC electrode to the additions of NaCl or $NaNO_3$ were measured. It was found that the PVC electrode did not respond to the additions of NaCl or $NaNO_3$. The systems studied by PVC electrodes measuring the responses to surfactant activities at a variety of ionic strengths are shown in Table-1.

Solution-2 or solution-3 was added to 50 mL of starting solution-1 with potentials recorded after each successive addition when a stable potential ($\pm$0.5 mv/min drift) was obtained. Plots of EMF vs log [NaDBS] are shown in Figure-6 for NaDBS-H_2O-$NaNO_3$ systems and in Figure-7 for NaDBS-H_2O-NaCl systems, from which CMC's were determined as the intersection points.

D.2 (b). CMC Determined by a Conductivity Bridge
with Added $NaNO_3$ at 25°C

The conductivity cell was soaked overnight in a starting solution-1, 200 ml 0.0200 M $NaNO_3$, and its conductance was recorded. Then solution-3 containing 0.0200 M $NaNO_3$ and 1.32×10^{-2} M NaDBS was added with the conductances recorded after each successive addition. A

Table-1.[*] Response of PVC Electrodes to the Activity of NaDBS at a Variety of Ionic Strengths at $25^{\circ}C$

Expt			Soln-1	Soln-2	Soln-3
1	x	(M)	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
2	x	(M)	1.00×10^{-3}	1.00×10^{-3}	1.00×10^{-3}
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
3	x	(M)	0.0100	0.0100	0.0100
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
4	x	(M)	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
5	z	(M)	1.00×10^{-5}	1.00×10^{-5}	1.00×10^{-5}
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
6	z	(M)	0.00100	0.00100	0.00100
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
7	z	(M)	0.00500	0.00500	0.0050
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
8	z	(M)	0.0100	0.0100	0.0100
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
9	z	(M)	0.0200	0.0200	0.0200
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
10	z	(M)	0.0500	0.0500	0.0500
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}
11	z	(M)	0.100	0.100	0.100
	y	(M)	0	6.60×10^{-4}	1.32×10^{-2}

*: x, y, and z are the concentrations of $NaNO_3$, NaDBS, and NaCl, respectively.
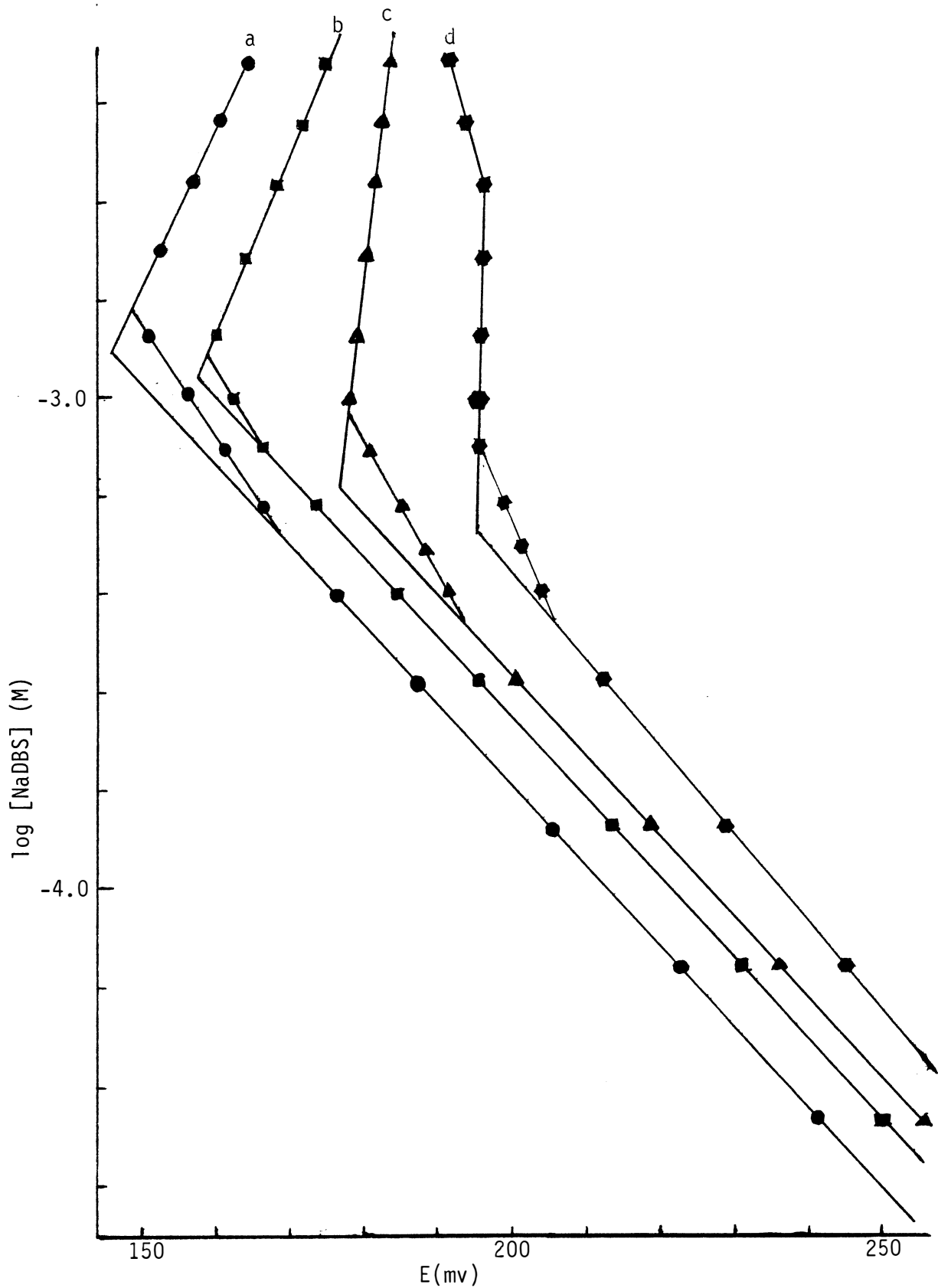
Figure 6. Response of PVC Electrode to NaDBS with Sodium Nitrate
Present at 25°C

(a) 0.0001 M (b) 0.001 M (c) 0.01 M (d) 0.02 M

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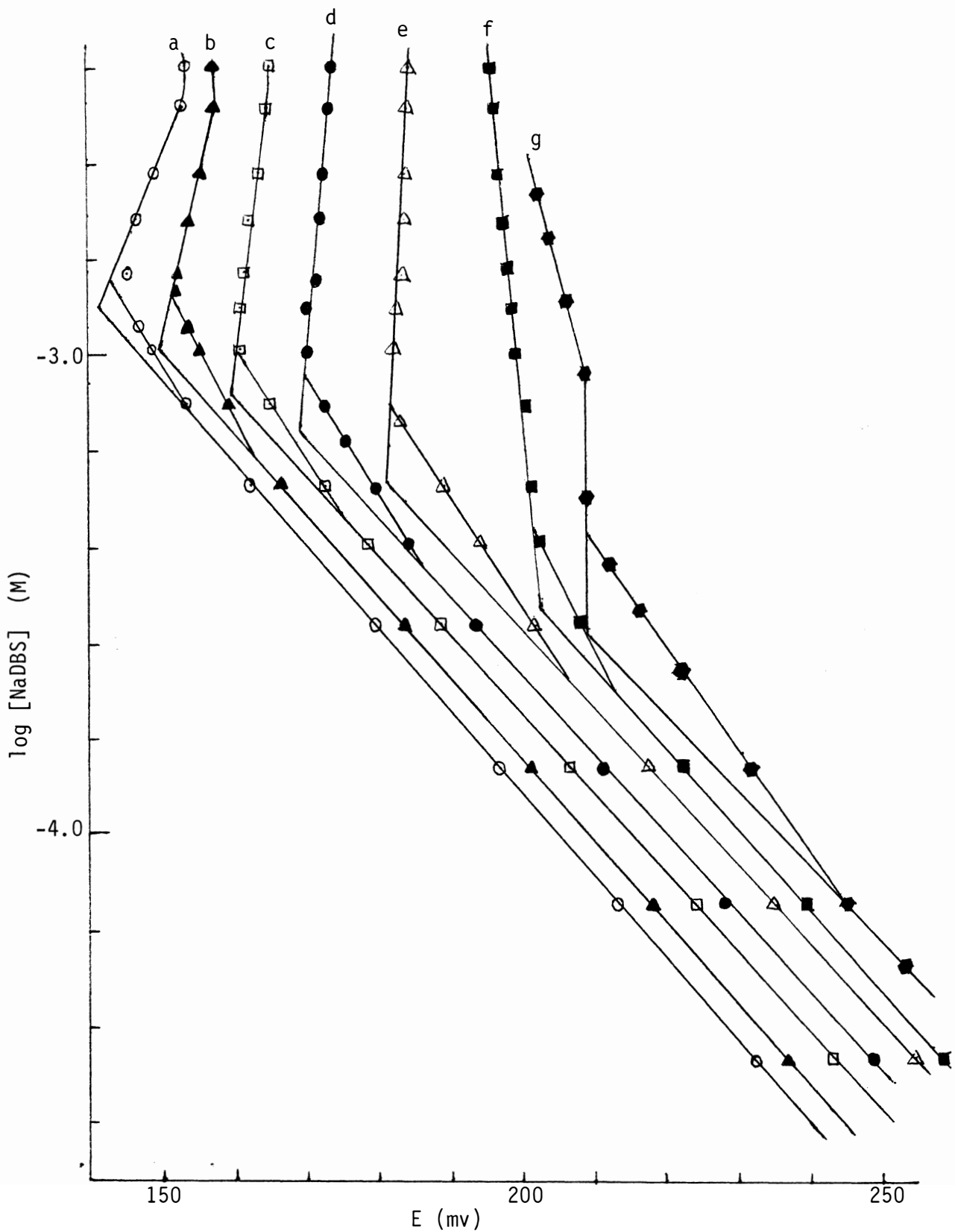
Figure 7. Response of PVC Electrode to NaDBS with
Sodium Chloride Present at 25°C
(a) 0.00001 M (b) 0.001 (c) 0.005 (d) 0.01 (e) 0.02
(f) 0.05 (g) 0.1

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plot of log k, the specific conductance, vs log [NaDBS] is shown in Figure-5(b). The CMC was determined by extrapolation as before.

D.3. NaDBS-H_2O-Cu$(NO_3)_2$-NaNO$_3$ Systems

D.3 (a). CMC Determinations at 25°C
with Added Cu$(NO_3)_2$ and ÑaNO$_3$

A PVC electrode-3 was soaked in about 5×10^{-4} M Cu$(NO_3)_2$ and 0.002 M NaDBS solution for about 1-2 hours and then the response of PVC electrode-3 to the additions of Cu$(NO_3)_2$ was carried out with or without the presence of NaNO$_3$ before the following experiments. The plots of EMF vs log [Cu$(NO_3)_2$] are shown in Figure-8.

The following experiments used PVC electrodes to investigate the solutions with NaDBS concentration varying and Cu$(NO_3)_2$ or both Cu$(NO_3)_2$ and NaNO$_3$ constant. The systems investigated by PVC electrodes with the presence of Cu^{2+} and Na$^+$ are shown in Table-2(1-6).

An experiment using the conductivity bridge to determine the CMC of a solution containing 0.0200 M NaNO$_3$, 1.00×10^{-3} M and NaDBS was carried out and shown in Figure 5(c) and listed in Table-2(7).

Solution-2 or solution-3 was added to 50 mL of starting solution-1 with potentials recorded after each
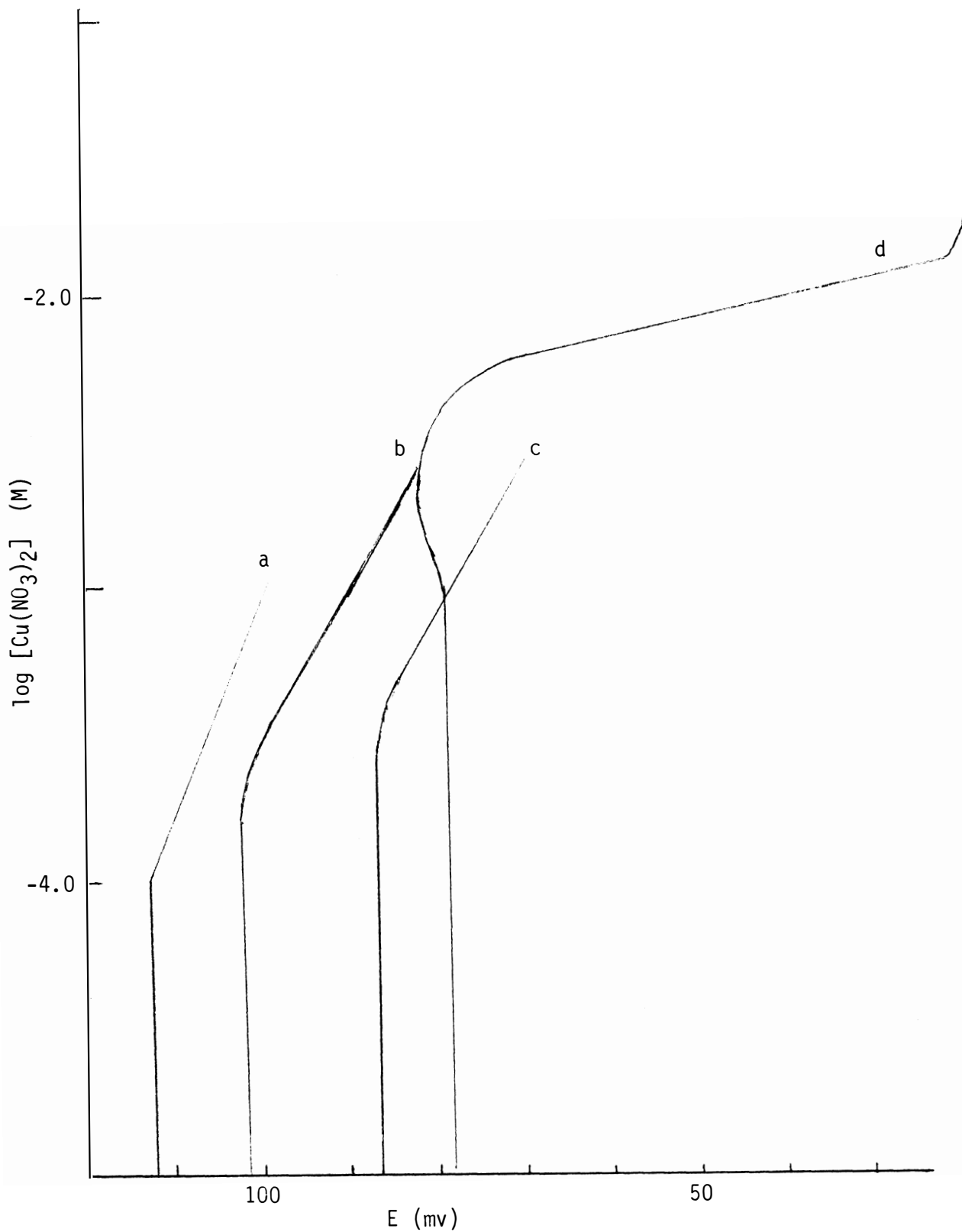
Figure 8. Response of PVC Electrode to $Cu(NO_3)_2$

(a) H_2O (b) 0.02 M $NaNO_3$, and 2×10^{-3} M NaDBS
(c) 0.02 M $NaNO_3$, and 3×10^{-3} M NaDBS (d) 0.02 M NaDBS

Table-2. NaDBS-Cu^{2+}-Na^{+} Systems Studied by PVC

Electrodes and a Conductivity Bridge at $25^{O}C$

Expt	Soln-1 (M)	Soln-2 (M)	Soln-3 (M)	S_1 mv	S_2 mv	CMC^b (x 10^3) (M)	Int
1. $Cu(NO_3)_2$	1.00×10^{-5}	1.00×10^{-5}	1.00×10^{-5}	-57	13	1.58	.92
NaDBS	0	0.000660	0.0132				
2. $Cu(NO_3)_2$	0.000100	0.000100	0.000100	-57	34	1.25	1.25
NaDBS	0	0.000660	0.0132				
3. $Cu(NO_3)_2$	0.00100	0.00100	0.00100	-56			0.13
NaDBS	0	0.000660	0.0132				
4. $NaNO_3$	0.0200	0.0200	0.0200	-58	5	.79	.66
$Cu(NO_3)_2$	0.000100	0.000100	0.000100				
NaDBS	0	0.000660	0.0132				
5. $NaNO_3$	0.0200	0.0200	0.0200	-57	3	0.70	.70
$Cu(NO_3)_2$	0.000200	0.000200	0.000200				
NaDBS	0	0.000660	0.0132				
6. $NaNO_3$	0.0200	0.0200	0.0200	-56			0.66
$Cu(NO_3)_2$	0.000500	0.000500	0.000500				
NaDBS	0	0.000660	0.0132				
7. $NaNO_3$	0.0200	0.0200	0.0200	.15	.11	.56	.56
$Cu(NO_3)_2$	0.00100	0.00100	0.00100				
NaDBS			0.0132				

(S_1 and S_2 are the slopes below and above the CMC's,

respectively, and CMC^b is the break point at which the

system had maximum free monomer activity, and the Int the

intersection point of upper and lower straight lines in

Figure 9).

successive addition upon reaching a stable potential ($\pm$0.5 mv/min drift). Plots of EMF vs log [NaDBS] for Experiment 1-6 are shown in Figure-9.

D.3 (b). Complexation between Cu^{2+} and Micelles Observed by a Cu^{2+} Electrode

The Cu^{2+} electrode was soaked in 0.001 M $Cu(NO_3)_2$ solution for about 2 hours and then the calibration of the Cu^{2+} electrode was carried out before the following experiments. A representative plot is shown later in Figure-12 (a). The responses of the Cu^{2+} electrode to Na^+ and DBS^- were also checked, and it was found that the Cu^{2+} electrode had little response to Na^+ but had some positive response to DBS^-, which is shown in Figure 10.

The following experiments used a Cu^{2+} electrode to observe the interaction between Cu^{2+} and Surfactant in the solutions with NaDBS concentration varying and $Cu(NO_3)_2$ and $NaNO_3$ constant. The systems studied are listed in Table-3.

Solution-2 or solution-3 was added to 50 mL of solution-1 with the potentials recorded after each successive addition. The plots of EMF vs log [NaDBS] are shown in Figure-11.
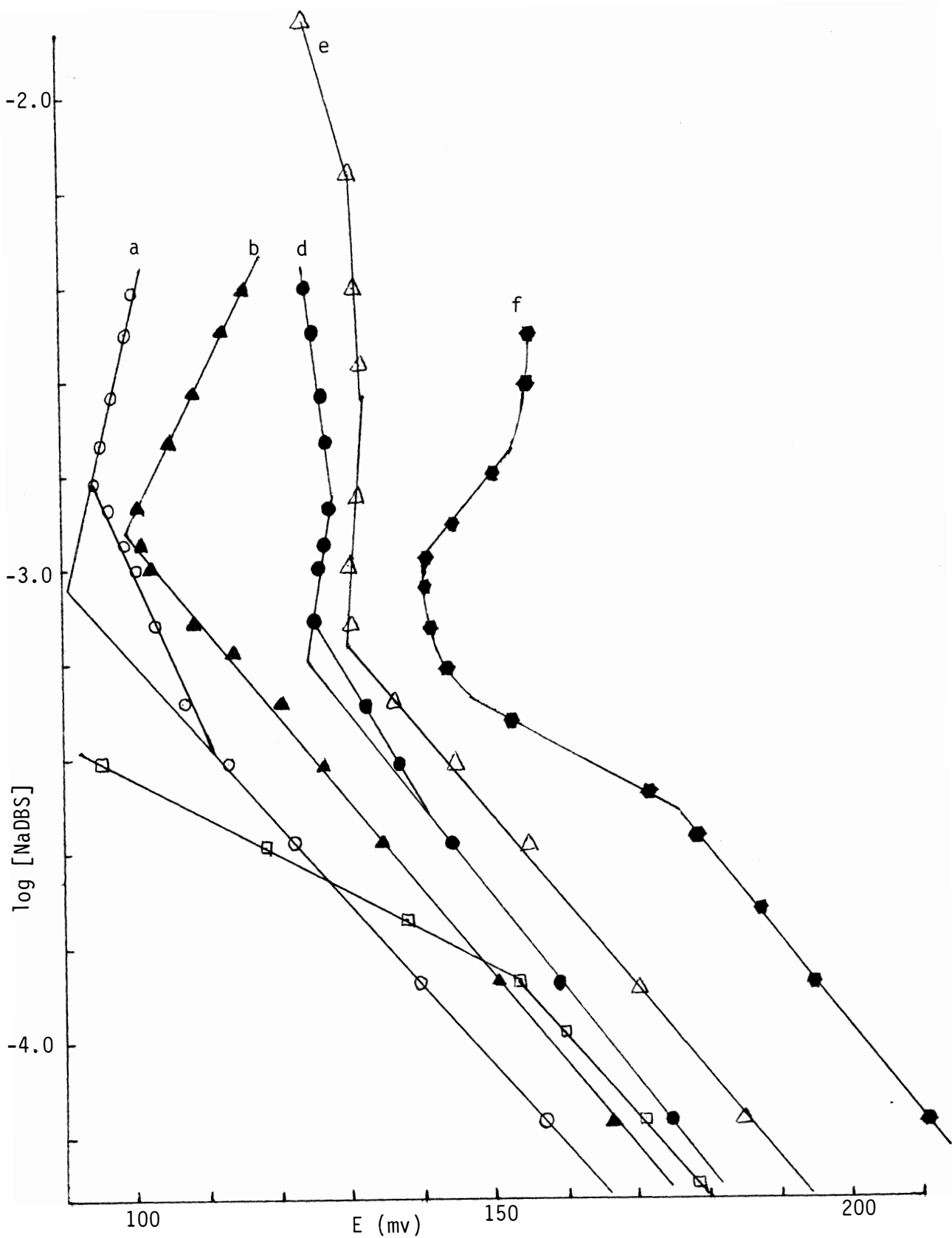
Figure 9. Response of PVC Electrodes to [NaDBS] with Cu^{2+} and Na^+ Present
a. 10^{-5} M Cu^{2+} b. 10^{-4} M Cu^{2+} c. 10^{-3} M Cu^{2+} d. 0.02 M Na^+, 10^{-4} M Cu^{2+}
e. 0.02 M Na^{2+}, 2×10^{-4} M Cu^{2+} f. 0.02 M Na^+, 5×10^{-4} M Cu^{2+}
g. 0.02 M Na^+, 0.001 Cu^{2+}

Table-3. Systems Studied to Observe the Interaction between Cu^{2+} and Surfactant solution by a Cu^{2+} Electrode at 25°C

Expt	Soln-1	Soln-2	Soln-3	[NaDBS]$_I$ *
1. NaNO$_3$	0.0200	0.0200	0.0200	
Cu(NO$_3$)$_2$	0.00600	0.00600	0.00600	5.6x10^{-3}
NaDBS		0.0132	0.0660	
2. NaNO$_3$	0.0200	0.0200	0.0200	
Cu (NO$_3$)$_2$	0.00400	0.00400	0.00400	4.6x10^{-3}
NaDBS		0.0132	0.0660	
3. NaNO$_3$	0.0200	0.0200	0.0200	
Cu(NO$_3$)$_2$	0.00100	0.00100	0.00100	2.2x10^{-3}
NaDBS		0.0132	0.0660	
4. NaNO$_3$	0.0200	0.0200	0.0200	
Cu(NO$_3$)$_2$	0.000500	0.000500	0.000500	1.6x10^{-3}
NaDBS		0.0132	0.0660	
5. NaNO$_3$	0.0200	0.0200	0.0200	
Cu(NO$_3$)$_2$	0.000200	0.000200	0.000200	1.3x10^{-3}
NaDBS		0.0132	0.0660	
6. NaNO$_3$	0.0200	0.0200	0.0200	
Cu(NO$_3$)$_2$	0.000100	0.000100	0.000100	1.0x10^{-3}
NaDBS		0.0132	0.0660	

*: [NaDBS] is the concentration at the intersection point.

All of the upper straight lines have slopes of about 22 mv.
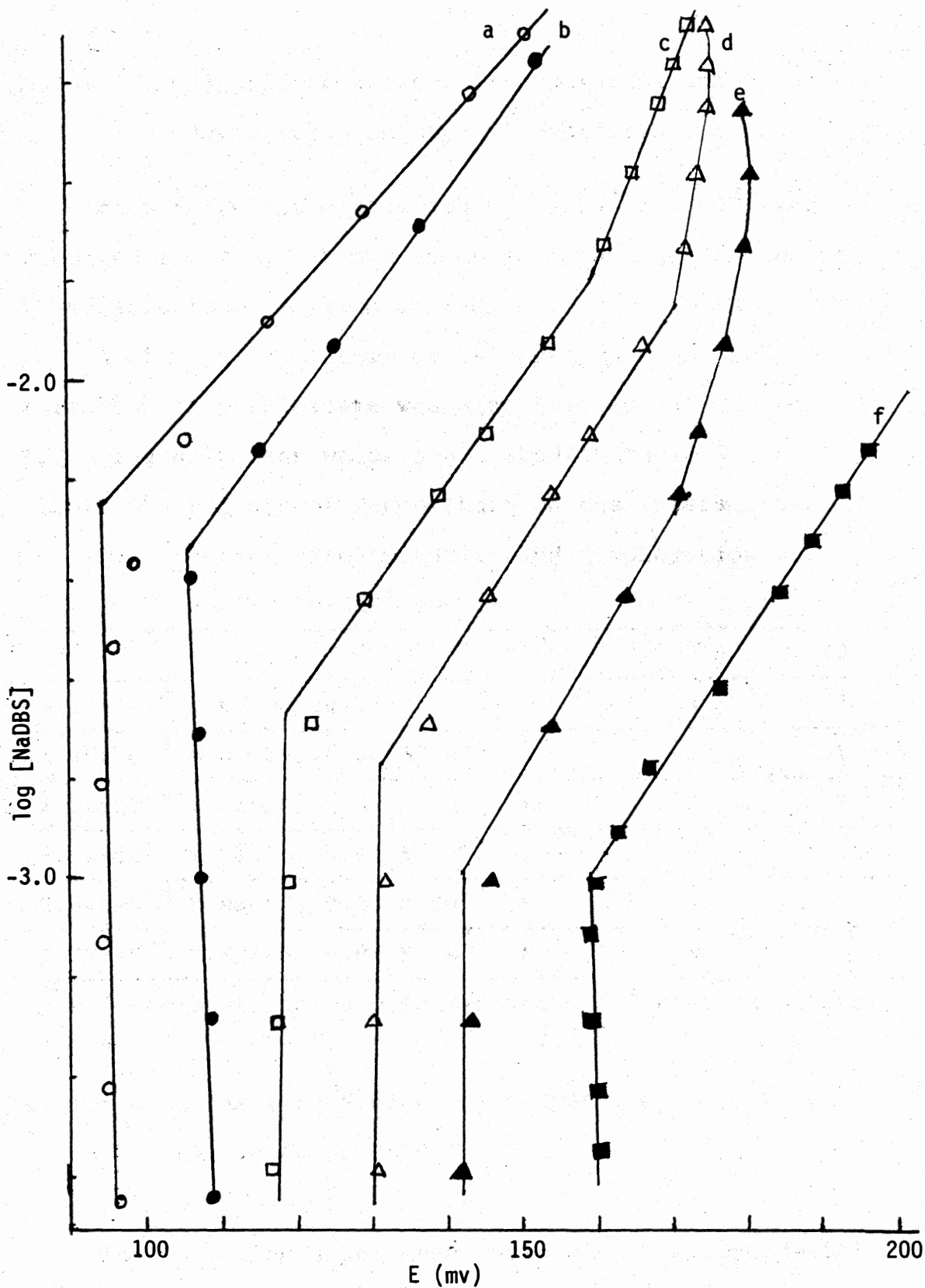
Figure 11. Experiment to observe the Complexation between Cu^{2+} and NaDBS by a Cu^{2+} Electrode at 25°C.

(a) 0.006 M Cu^{2+}, 0.02 M Na^+ (b) 0.004 M Cu^{2+}, 0.02 M Na^+
(c) 0.001 M Cu^{2+}, 0.02 M Na^+ (d) 0.0005 M Cu^{2+}, 0.02 M Na^+
(e) 0.0002 M Cu^{2+}, 0.02 M Na^+ (f) 0.0001 M Cu^{2+}, 0.02 M Na^+

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D.3 (c). Competition between Precipitation and

Complexation in the Cu^{2+}-Surfactant System

Many solutions containing DBS^-, Na^+ and Cu^{2+} were
prepared for visual tests for precipitation. A list of
these solutions is shown in Table-4.

A study of the temperature dependence of the
formation of precipitate was also carried out in the
following solutions which are listed in Table-5.

Table-5. Effects of Temperature on the Interaction
Between Precipitation and Complexation of
the NaDBS-Cu^{2+} system

	$25^{O}C$	5°	70°
1.32×10^{-3} M NaDBS, 0.01 M Cu^{2+}	N	N	Y
1.06×10^{-3} M NaDBS, 0.01 M Cu^{2+}	Y	Y	Y
7.92×10^{-4} M NaDBS, 0.01 M Cu^{2+}	Y	Y	Y
6.60×10^{-4} M NaDBS, 0.01 M Cu^{2+}	Y	Y	Y
2.64×10^{-4} M NaDBS, 0.01 M Cu^{2+}	Y	Y	Y
1.32×10^{-4} M NaDBS, 0.01 M Cu^{2+}	N	N	N

" Y " means pricipitate formed and " N " no precipitate.

D.3 (d). Solubility Product of $Cu(DBS)_2$ by a Cu^{2+}
Electrode at $25^{O}C$

The following experiments used a Cu^{2+} electrode to
investigate the systems with $Cu(NO_3)_2$ concentration
varying and $NaNO_3$ or NaDBS constant or both constant.

Table-4. Visual test for precipitate in NaDBS-NaNO_3-Cu(NO_3)_2 system

[NaDBS] (M)	[Cu(NO_3)_2] (M)	[NaNO_3] (M)	precipitate
0.132	0.1		Y
0.2	0.0001		N
0.0132	0.00001		N
0.005	0.001		N
0.0132	0.001		N
0.00053	0.01		Y
0.00026	0.005		Y
0.00013	0.0025		N
0.0005	0.01	0.02	Y
0.066	0.0002	0.02	N
0.066	0.0001	0.02	N
0.00046	0.02	0.02	Y
0.00046	0.001	0.02	N
0.00066	0.02	0.02	Y
0.00066	0.01	0.02	Y
0.00066	0.001	0.02	N
0.00132	0.001	0.02	N
0.0026	0.02	0.02	N
0.0026	0.006	0.02	N
0.00066	0.006	0.02	N
0.0132	0.006	0.02	N
0.066	0.006	0.02	N
0.0132	0.01	0.05	N

The systems studied by the Cu^{2+} electrode for the
solubility product of $Cu(DBS)_2$ are shown in Table 6.

Solution-2 or solution-3 was added to 50 ml of
solution-1 with the potentials recorded after each
successive addition upon reaching a stable potential (± 0.3
mv/min drifting). The plots of EMF vs log $[Cu(NO_3)_2]$ are
shown in Figure 12 (b-i).

D.3 (e). Competition of Cu^{2+} and Na^+
in Micellar Solutions

The experiments carried out are listed in Table 7.

Solution-2 or solution-3 was added to solution-1 with
potentials recorded after each successive addition. The
plots of EMF vs log [NaDBS] for Experiment 1-5 are shown
in Figure 13. The plots of EMF vs log $[Cu(NO_3)_2]$ obtained
in Experiment 6 are shown in Figure 14.

E. Determination of the concentration of NaDBS solution
by Means of Titration

A 25.0 mL sample of about 0.02 M NaDBS solution was
pipetted into the potential cell and titrated with 4.75 x
10^{-2} M benzylcetyldimethylammonium chloride$\cdot H_2O$ using a
PVC electrode-1 and electrode-3 as the end point
detectors. A white precipitate formed during the

Table 6. Experiments Studied to Obtain the Solubility Product of $Cu(DBS)_2$ by a Cu^{2+} Electrode

Expt	Soln-1	Soln-2	Soln-3	S_1 (mv)	$[Cu^{2+}]_p^*$
1. $NaNO_3$ (M)	0.0200	0.0200	0.0200	28.2	
$Cu(NO_3)_2$		0.00100	0.0200		
2. $NaNO_3$	0.0200	0.0200	0.0200		
NaDBS	6.60×10^{-5}	6.60×10^{-5}	6.60×10^{-5}	27.5	
$Cu(NO_3)_2$		0.00100	0.0200		
3. $NaNO_3$	0.0200	0.0200	0.0200		
NaDBS	0.000260	0.000260	0.000260	27.6	
$Cu(NO_3)_2$		0.00100	0.0200		
4. $NaNO_3$	0.0200	0.0200	0.0200		
NaDBS	0.000480	0.000480	0.000480	26.8	
$Cu(NO_3)_2$		0.00100	0.0200		
5. $NaNO_3$	0.0200	0.0200	0.0200		
NaDBS	0.000530	0.000530	0.000530	30	2.8×10^{-3}
$Cu(NO_3)_2$		0.00100	0.0200		
6. $NaNO_3$	0.0200	0.0200	0.0200		
NaDBS	0.000660	0.000660	0.00066	30	1.85×10^{-3}
$Cu(NO_3)_2$		0.00100	0.0200		
7. $NaNO_3$	0.0200	0.0200	0.0200		
NaDBS	0.00132	0.00132	0.00132	31	1.7×10^{-3}
$Cu(NO_3)_2$		0.00100	0.0200		
8. $NaNO_3$	0.0200	0.0200	0.0200		
NaDBS	0.00198	0.00198	0.00198	33	1.8×10^{-3}
$Cu(NO_3)_2$		0.00100	0.0200		

($[Cu^{2+}]_p^*$ are the concentrations at which the precipitate occurred).
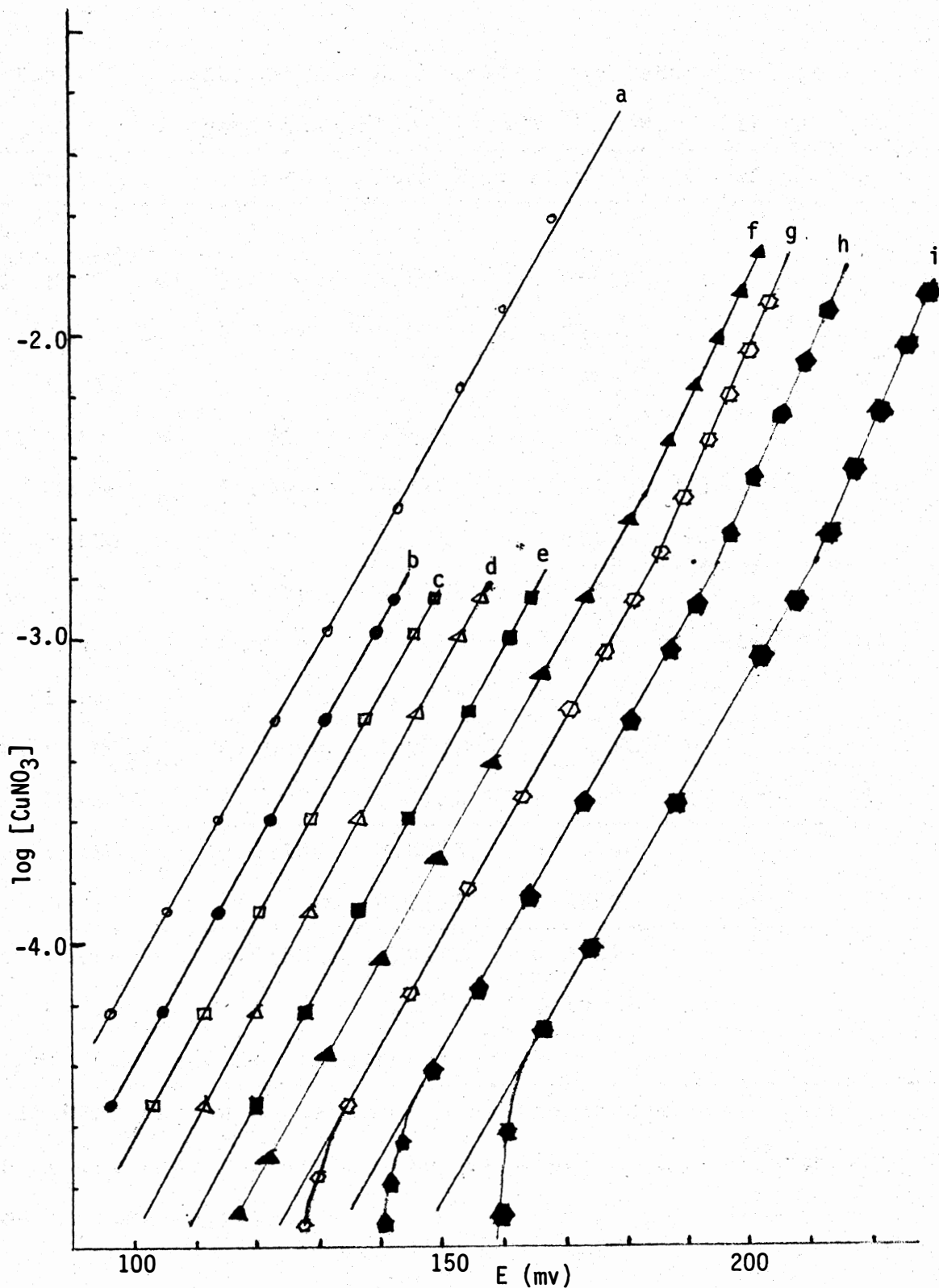
Figure 12. Solubility Product of Cu(DBS)$_2$ Measurement by a Cu^{2+} Electrode

a. Calibration Run b. 0.02 M Na$^+$ c. 0.02 M Na$^+$, 6.6x10^{-5} M NaDBS
d. 0.02 M NaNO$_3$, 2.6x10^{-4} M NaDBS e. 0.02 M Na$^+$, 4.8x10^{-4} M NaDBS
f. 0.02 M Na$^+$, 5.3x10^{-4} M NaDBS g. 0.02 M NaNO$_3$, 6.6x10^{-4} M NaDBS
h. 0.02 M Na$^+$, 0.00132 M NaDBS i. 0.02 M Na$^+$, 0.00198 M NaDBS

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Table 7. Lists of the Experiments for Detecting the Competition of Cu^{2+} and Na^+ in Micellar Solutions

Expt	Soln-1	Soln-2	Soln-3	$[NaDBS]_I$	S (mv)
Cu^{2+} electrode					
1. $NaNO_3$ (M)	0.0500	0.0500	0.0500		
$Cu(NO_3)_2$	0.0100	0.0100	0.0100	7.4×10^{-3}	18
NaDBS		0.0132	0.0660		
2. $NaNO_3$ (M)	0.0200	0.0200	0.0200		
$Cu(NO_3)_2$	0.000100	0.000100	0.000100	1.0×10^{-3}	22
NaDBS		0.0132	0.0660		
3. $NaNO_3$	0.0200	0.0200	0.0200		
$Cu(NO_3)_2$	0.00100	0.00100	0.00100	2.2×10^{-3}	22
NaDBS		0.0132	0.0660		
4. $Cu(NO_3)_2$	0.000100	0.000100	0.000100		
NaDBS		0.0132	0.0660	1.0×10^{-3}	67
5. $Cu(NO_3)_2$	0.00100	0.00100	0.00100		
NaDBS		0.0132	0.0660	1.8×10^{-3}	72
6. NaDBS	0.0132	0.0132	0.0132		
$Cu(NO_3)_2$		0.00100	0.100		

(Both Cu^{2+} and Na^+ electrodes).

($[NaDBS]$ is the concentration at the intersection point, and S is the slope of upper straight line in the Cu^{2+} activity decreasing region).
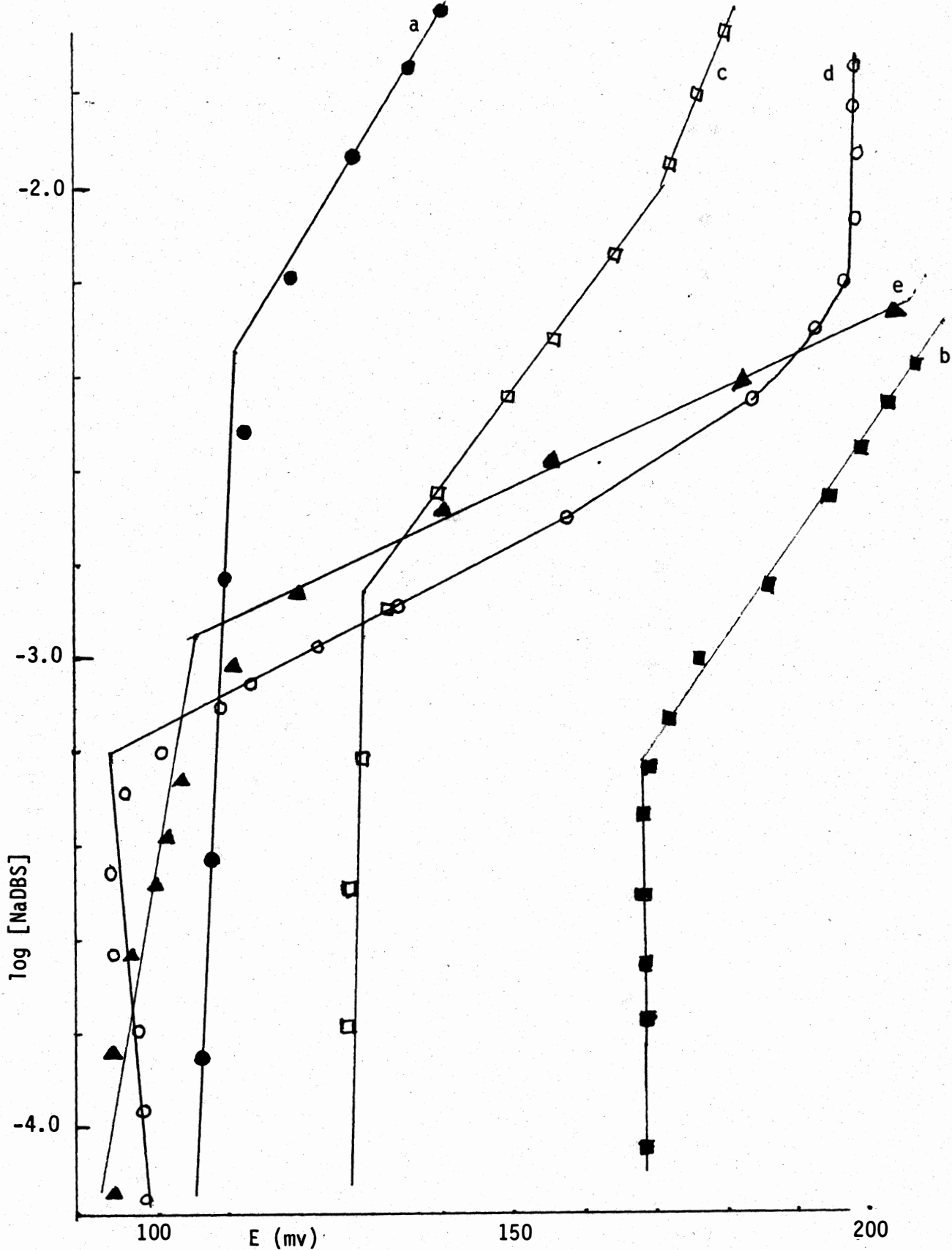
Figure 13.   Response of the Cu^{2+} Electrode to NaDBS at the presence
             Cu^{2+} and Na^+

a. 0.05 M Na^+, 0.01 M Cu^{2+} b. 0.02 Na^+, 10^{-4} M Cu^{2+} c. 0.02 Cu^{2+}, 10^{-3} Cu^{2+}
d. 10^{-4} M Cu^{2+} e. 0.001 M Cu^{2+}
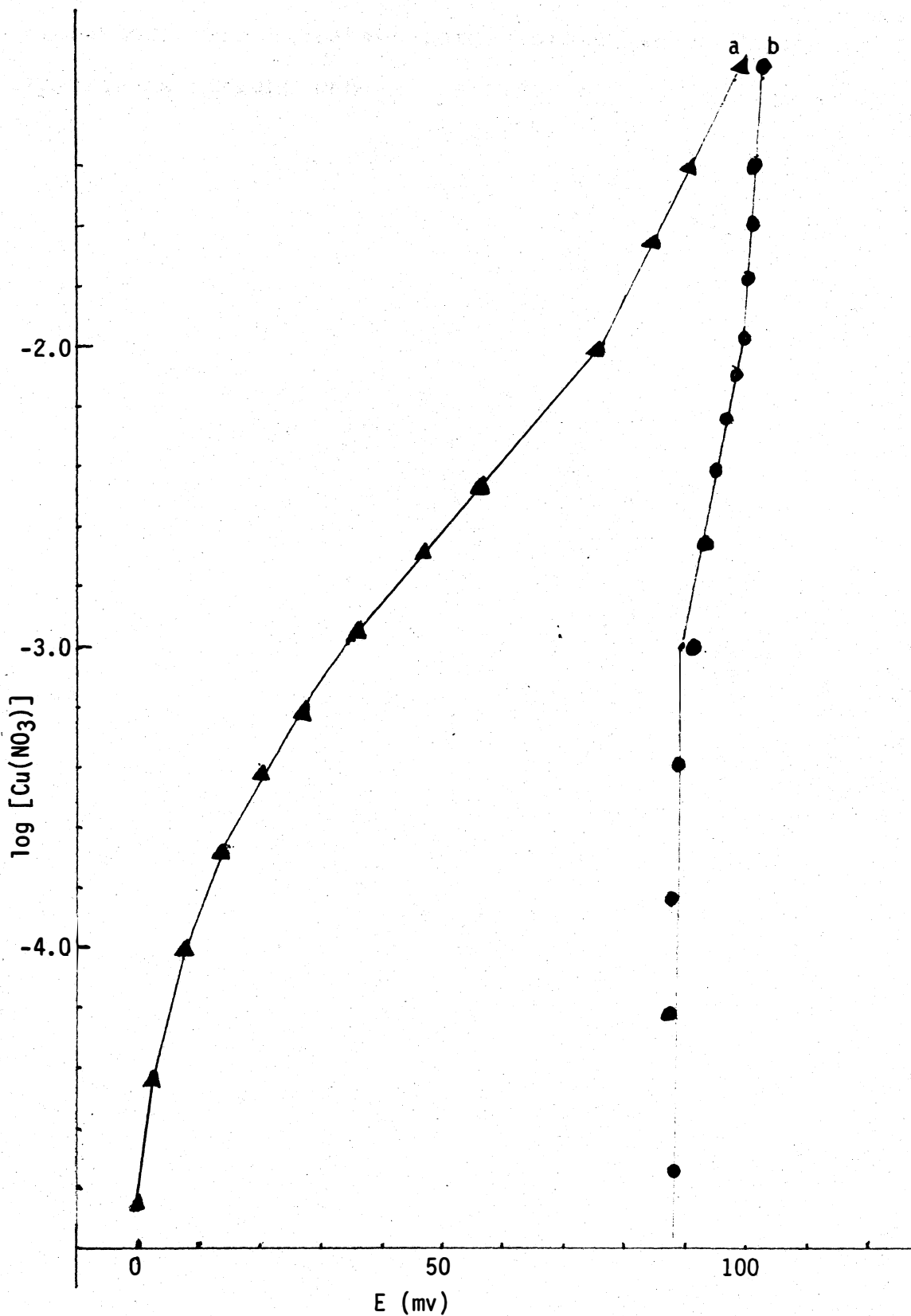
Figure 14. Response of a Cu^{2+} and a Na^+ Electrodes to Cu^{2+} in the Solution of 0.02 M NaDBS

a. Cu^{2+} electrode   b. Na^+ electrode

titration.   The titration curves are shown in Figure 15.
Hyamine as titrant was also tried.
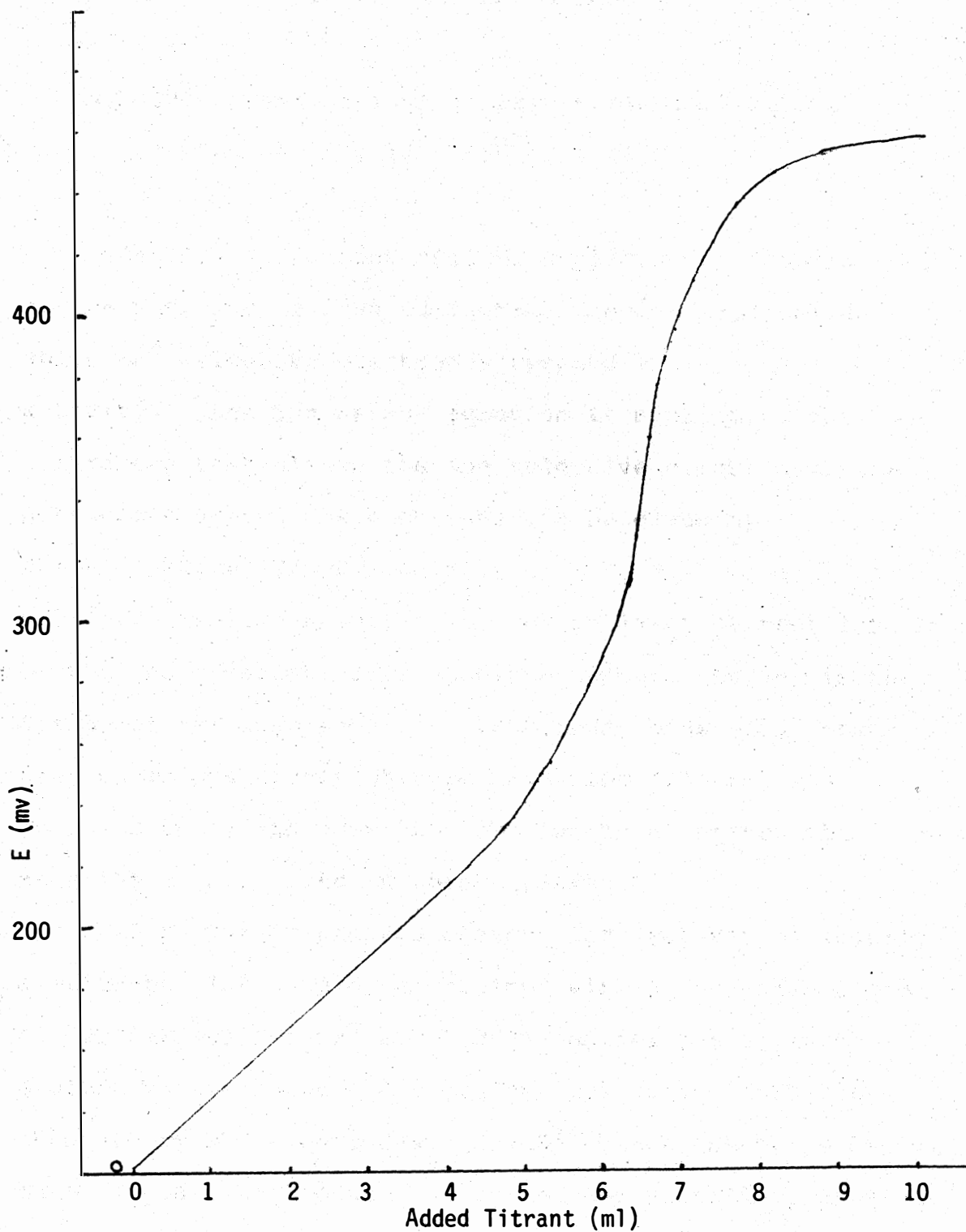
Figure 15. Titration Curve of NaDBS
Titrant: 4.75×10^{-2} M Benzylcetyldimethylammonium Chloride$\cdot H_2O$
NaDBS: 25.0 ml

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III. RESULTS AND DISCUSSION

A. CMC Determinations in Salt-Free NaDBS-H_2O System at 15°, 19°, 25°, and 40^OC

Ideally, surfactant selective electrodes respond only to the activity of free surfactant monomer amphiphiles, while Na^+ selective electrodes respond only to Na^+ activity. When the Nernst equation is applied to the membrane potentials in the ion selective electrodes, the potentials across the membranes can be given by

$$E = E^{o'} \pm 2.303RT/n_iF \log [a_i], \qquad (21)$$

where $E^{o'}$ is a constant, a_i is the activity of test ion, R is the gas constant, T is absolute temperature, n_i is the charge of the ion, and F is the Faraday constant. When the ion is positively charged, Equation (21) takes a positive sign, and when the test ion is negative, the negative sign is used in this equation.

When E (mv) is plotted against log (activity), ideally a straight line should be obtained with a Nernstian slope of $+2.302RT/nF$ for Na^+ or $-2.303RT/nF$ for DBS^-. In the present work all the plots of EMF (mv) vs log (activity) obtained by PVC electrodes and a Na^+ electrode below CMC's have slopes close to the Nernstian one, which implies that NaDBS is a strong electrolyte and the activities of DBS^- and Na^+ could be assumed to be equal to their concentra-

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tions at the concentration ranges studied here (Figure 3 and 4 (b-e)).

All the plots in Figure 3 obtained by PVC electrodes show similar trends. At first, all the straight lines have slopes (S_1) close to $-2.303RT/nF$ (mv) which are listed in Table 8. At certain concentration ranges (transition regions), the slopes are reduced to smaller absolute values than before, which implies possible premicellar formations. At certain break points, designated CMC^b in Table 8, the lines reverse and have positive slopes (S_2), which indicates that the activities of free monomer were decreasing above the CMC's in the micellar solutions. The decrease of free monomer activiy above the CMC is not in agreement with the earlier assumption that the activity of free monomers was constant above the CMC[50-52] but is in agreement with more recent work[36,38,40,41]. The CMC's as the intersections of upper and lower lines are also listed in Table 8.

Plots in Figure 4(b-e) obtained by a sodium electrode also have closely Nernstian responses below the intersections, which are designated as CMC's in Table 8. It can be seen that Na^+ activities increased at lower rates above the CMC's compared to the rates below the CMC's.

Figure 5(a) was obtained by a conductivity measurement using a basic equation:

$$k = R^{-1}_{solu} * (1/A) \qquad (22a)$$

$$= (R^{-1}_{soln} - R^{-1}_{solv})(1/A) \qquad (22b)$$

$$= (L_{solu}/1000) N_{solu} \qquad (22c)$$

$$= [(L_+ * N_+) + (L_- * N_-)]/1000 \qquad (22d)$$

where k is the specific conductance (ohm^{-1} cm^{-1}), R^{-1}_{solu} the conductance (ohm^{-1}) contributed by " solute " , R^{-1}_{soln} is the conductance of the solution, R^{-1}_{solv} the conductance of the solvent, (1/A) the cell constant (cm^{-1}), L_{solu} the equivalent conductance of "solute" (cm^2 ohm^{-1} equivalent^{-1}), N_{solu} the equivalent concentration of " solute " (equivalent /liter), and 1000 a constant (cm^3/liter).

When k is plotted against N in Equation (22c), a straight line with a slope of $L_{solu}/1000$ is obtained. Figure 5(a) shows two straight lines with slopes of S_1 and S_2 and an intersection point which is the CMC and which is listed in Table 8.

The counterion binding, B, can be calculated from Figure 3 and 4 by using Equation (2). The result listed in Table 9 shows that the counterion binding is not a constant.

When log [DBS$^-$] is plotted agaist log [Na$^+$], a straight line is obtained with a slope of 0.42, which is shown in Figure 16.

Table 8[*]. Slopes, CMC's and Thermodynamic parameters from plots

obtained by PVC and sodium Electrodes and by Conductivity

Measurement in Salt-Free System

Method	Temp (^{o}C)	S_1	S_2	CMC^b (M)	CMC (M)	lnCMC	ΔG^o_m (Cal)	ΔH^o_m (Cal)	ΔS^o_m (Cal/T)
PVC	15.0	53mv	24mv	1.63×10^{-3}	1.42×10^{-3}	-6.557	-3750	4	13
	19.1	55	27	1.48×10^{-3}	1.31×10^{-3}	-6.638	-3860	2	13
	25.0	58	20	1.52×10^{-3}	1.36×10^{-3}	-6.600	-3910	0	13
	41.6	63	23	1.73×10^{-3}	1.57×10^{-3}	-6.457	-4040	-9	13
Na^+	15.0	54	38		1.62×10^{-3}	-6.425	-3680	12	13
	19.3	63	44		1.37×10^{-3}	-6.593	-3830	6	13
	25.0	59	48		1.47×10^{-3}	-6.522	-3860	-3	13
	40.5	62	39		1.98×10^{-3}	-6.225	-3880	-28	12
Conductivity	25.0	0.148	0.104		1.62×10^{-3}	-6.383	-3780		

[*]: S_1, S_2, CMC^b and CMC are obtained from Figure 3, 4 and 5.

The cell constant (1/A) is 0.122.
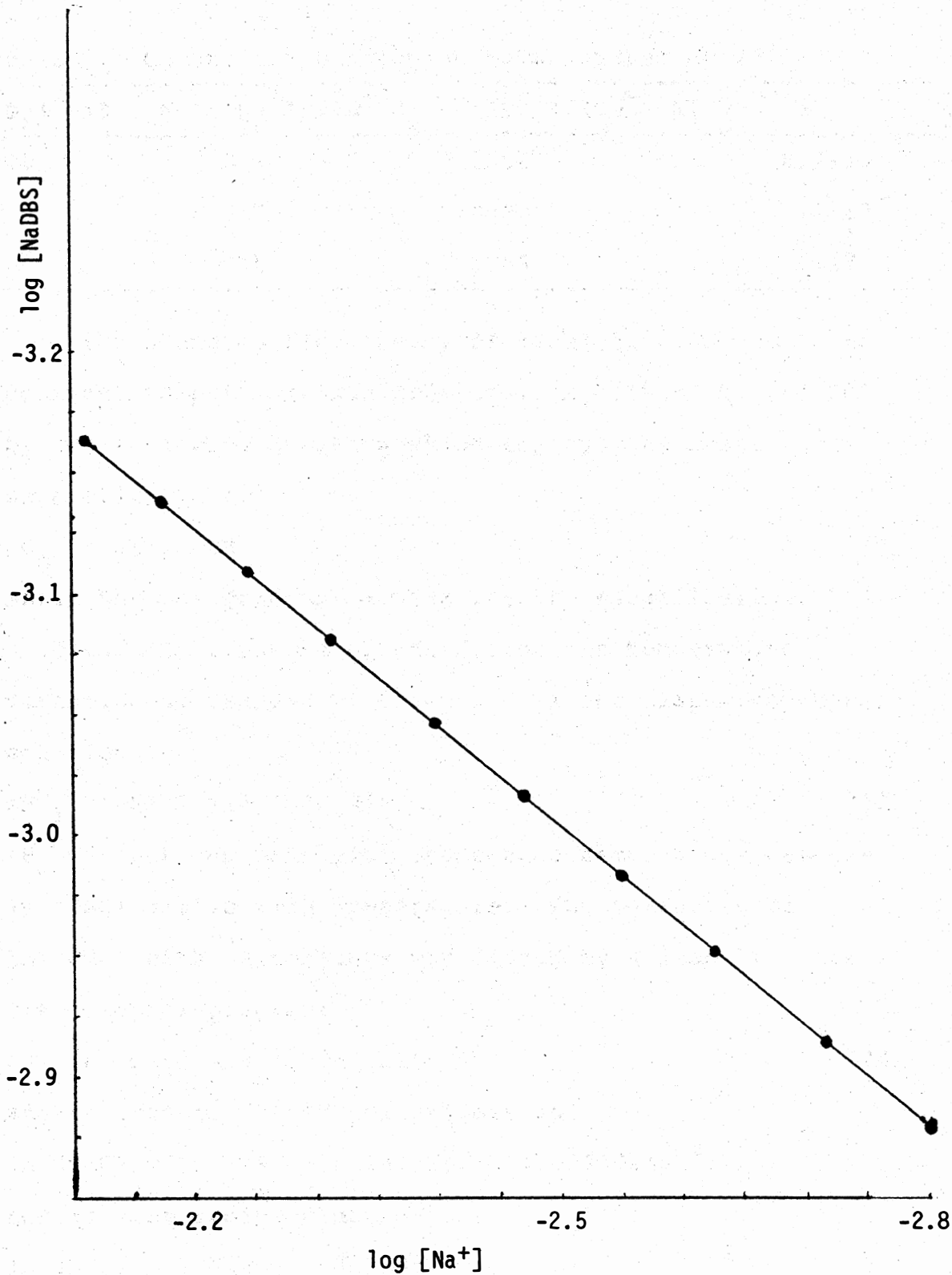
Figure 16.   Plot of log [DBS⁻] vs log [Na⁺] in Salt-Free System

Table 9. Counterion Binding in NaDBS System at 25°C

[D_t] (10^{-3} M)	[Na^+] (10^{-3}M)	[DBS^-] (10^{-3} M]	B
3.0	2.8	1.04	8.7×10^{-2}
5.0	4.3	0.88	1.7×10^{-1}
10	7.5	0.69	0.27

The standard free energy of micellization, ΔG_m°, at constant temperature and pressure, is related to the CMC by the following equation which employs the phase separation model:

$$\Delta G_m^{\circ} = RT \ln CMC \tag{6}$$

while the standard enthalpies for the micellization process, ΔH_m°, can be obtained from the temperature variation of the CMC by using a Clausius–Clapeyron type of equation:

$$\Delta H_m^{\circ} = -RT [\partial \ln CMC / \partial T] \tag{23}$$

ΔH_m° is not constant with respect to temperature because ln (CMC) varies with temperature. The variation of ln (CMC) with temperature was fitted by a least squares fit computer program:

$$\ln (CMC) = a + bT + cT^2 \tag{24}$$

and the result for PVC electrodes is

$$\ln (CMC) = 29.2797 - 0.241378T + 4.05940 \times 10^{-4}T^2 \tag{25}$$

and for the sodium electrode is

$$\ln (CMC) = 107.466 - 0.769517T + 1.29838 \times 10^{-3}T^2 \tag{26}$$

The plots of Equation (25) and Equation (26) are shown in Figure 17.
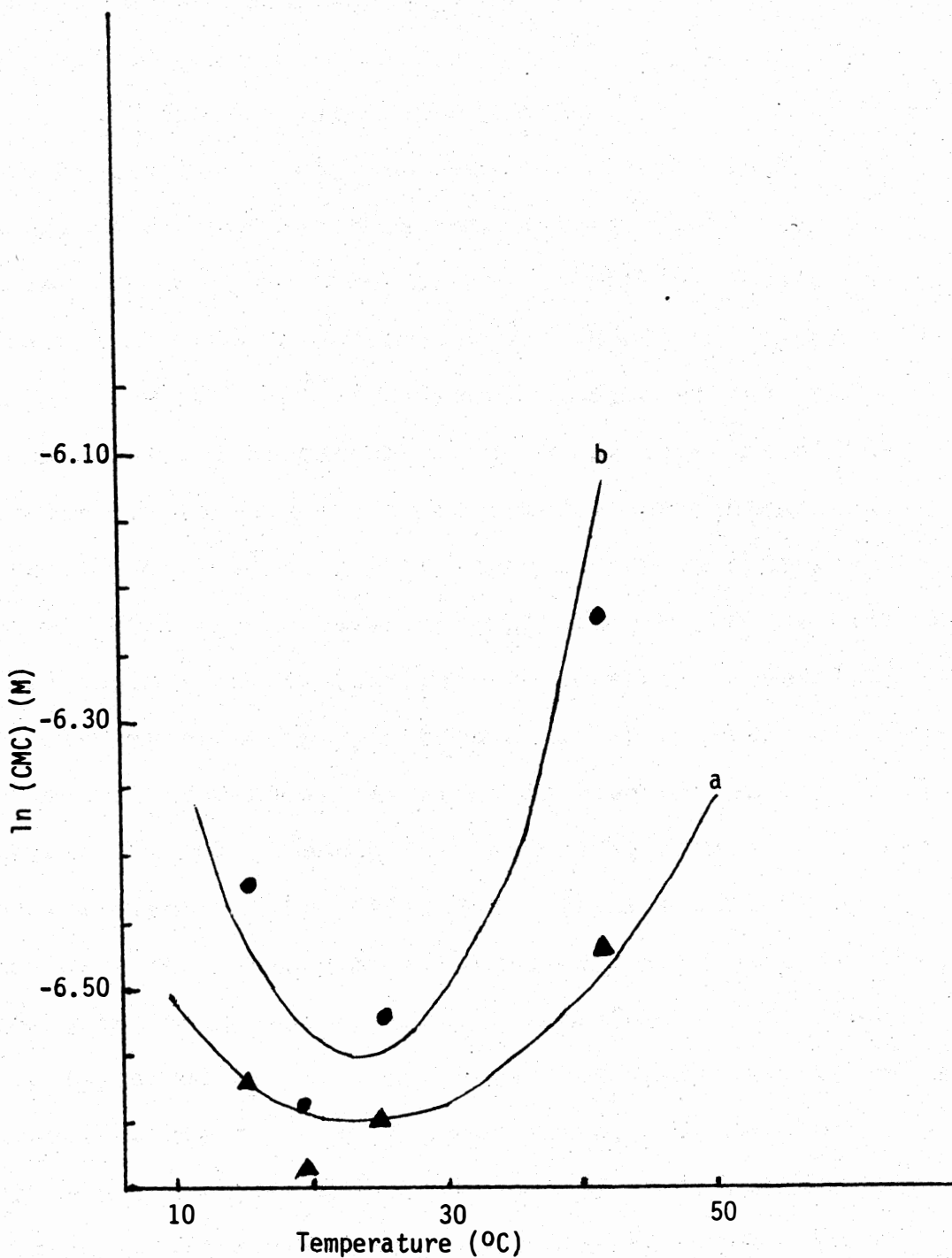
Figure 17.   Temperature Effect on the CMC

(a) PVC electrode (▲)   (b) Na$^+$ electrode (●)

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The standard entropies of micellization were calculated from ΔG_m^O and ΔH_m^O as

$$\Delta S_m^O = (-\Delta G_m^O + \Delta H_m^O)/T \qquad (27)$$

ΔG_m^O, ΔH_m^O and ΔS_m^O are listed in Table 8.
From Figure 17, it can be seen that the CMC initially decreases with temperature and then increases with a further increase in temperature. A similar result was obtained for sodium dodecylsulfate (NaDS)-H_2O systems by H. N. Singh et. al.[30] The result indicates that the transfer of a hydrocarbon group to the interior of the micelle is probably endothermic below the minimum temperature in Figure 17 as can be expected due to hydrophobic bonds. Further increase in temperature makes the micelle less stable. As the temperature increases, several effects may arise; e.g., the dielectric constant of the medium will decrease, resulting in greater repulsion between the ionic head groups of the surfactant molecules, thus causing a higher CMC value. It is also possible to visualize that as the temperature is raised, the "icebergs" around the monomeric surfactant ions "melt"[53-55], and the enthalpy of micellization becomes less positive, which is however counteracted by a progressively smaller positive contribution to the entropy change of the micellization process. Thus a postulated predominance of hydrophobic and enthalpy factors at low temperature and of dielectric and entropy factors at higher temperature may explain the

observed fact.

B. CMC Determinations in NaDBS-H_2O-Electrolyte (NaCl and NaNO$_3$) Systems at 25°C

The CMC of ionic surfactants decreases markedly upon addition of a simple salt of the counterion. Figure 7 and Figure 8 show the effects of NaCl and NaNO$_3$ on the CMC of NaDBS. The CMC's are listed in Table 10. It can be seen in Table 10 that the effects of NaNO$_3$ and NaCl on the CMC are similar and the slopes (S_2) above the CMC decrease as the added electrolyte concentration increases. Thus with more electrolytes added, the micelles appear to approach a separate phase. This might be explained by the neutralization of high formal charge in the micelles by counterion Na^+. With more Na^+ present in a micellar solution, the high formal charge of a micelle would be reduced by means of counterion bonding. With the decrease of formal charge, it becomes possible for micelles to grow larger. When micelles grow larger, their behavior approaches that of a separate phase. By analogy with a solubility product, one can relate the slope of the log (CMC) vs log (total counterion concentration) in terms of the degree of dissociation, a, to the following:[56]:

$$\log CMC = A - (1 - s/n) \log (C + CMC) \qquad (28)$$

where C is the concentration of added salt, s is the

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effective charge of the micelle, and A a constant. In accordance with general experience, the data presented here define good straight lines up to 0.020 M added salt (Figure 18). The degree of dissociation values s/n (= 1 + slope) thus obtained are listed in Table 10.

Table 10. Effects of NaCl and $NaNO_3$ on the CMC of NaDBS and the Degree of Counterion Dissociation (s/n) at $25^{O}C$

Salt (M)	S_1 (mv)	S_2	CMC^b_3 10^{-3} (M)	CMC_3 10^{-3} (M)	logCMC	log(C+CMC)	s/n
$NaNO_3$							
0	-58	20		1.36	-2.866	-2.866	
$1.00x10^{-4}$	-61	31	1.49	1.23	-2.909	-2.875	
$1.00x10^{-3}$	-60	27	1.20	1.09	-2.963	-2.680	0.72
0.0100	-61	6	0.92	6.60	-3.180	-1.972	
0.0200	-57	1	0.79	5.28	-3.277	-1.688	
NaCl							
$1.00x10^{-5}$	-59	27	1.45	1.26	-2.899	-2.896	
$1.00x10^{-3}$	-59	15	1.35	1.06	-2.975	-2.686	
$5.00x10^{-3}$	-58	7	1.02	8.32	-3.080	-2.234	0.69
0.0100	-60	4	0.92	6.93	-3.159	-1.971	
0.0200	-59	3	0.78	5.48	-3.261	-1.687	
0.0500	-60	-6	0.46	2.90	-3.537	-1.299	
0.100	-63	-1	0.44	2.64	-3.578	-0.999	
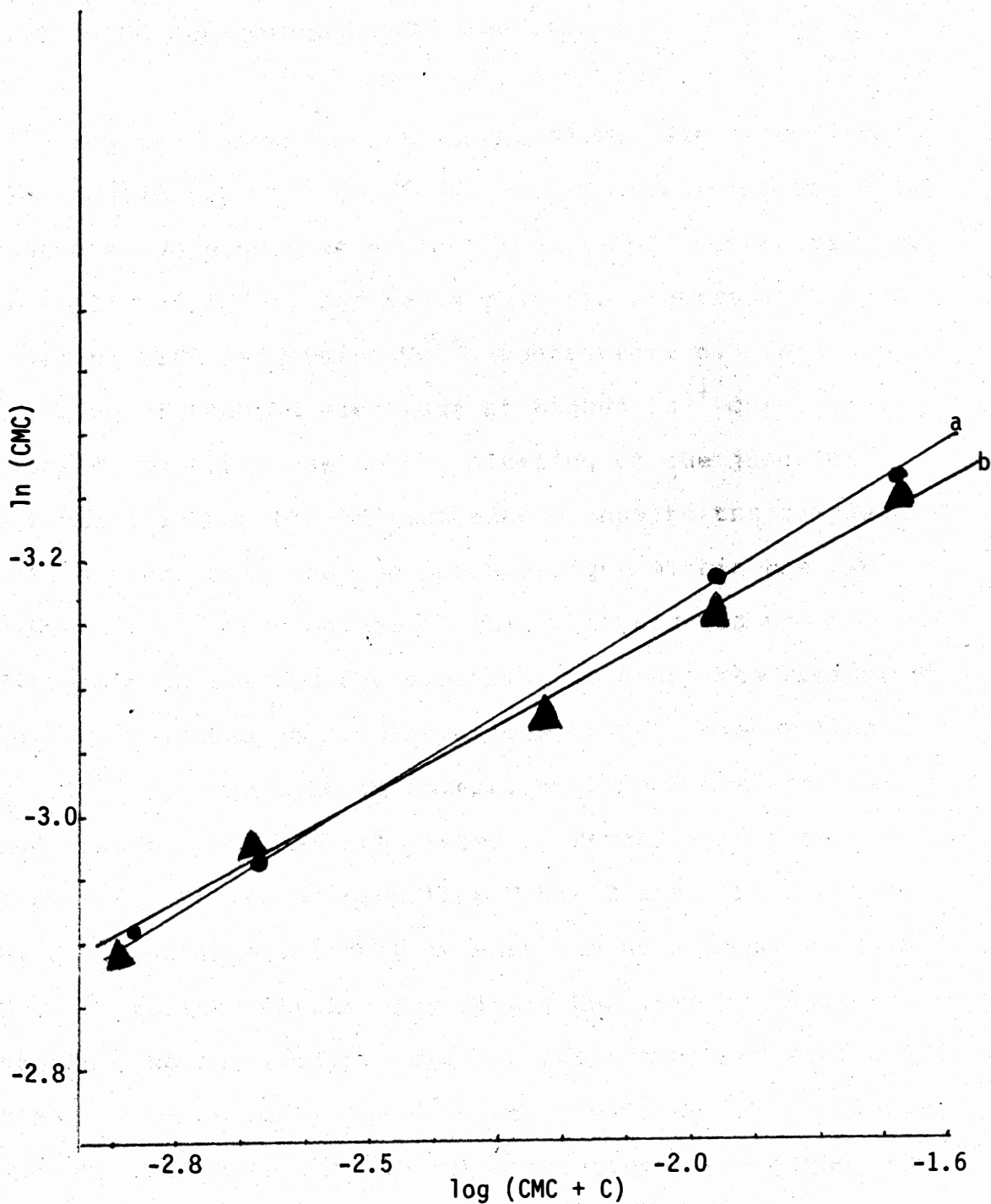
Figure 18. Plots to Obtain the Degree of Dissociation in Added
Salt System

(a) $NaNO_3$ (b) NaCl system

C. NaDBS-H_2O-Cu$(NO_3)_2$-NaNO$_3$ Systems

C.1. CMC Determined by PVC Electrodes

Figure 8 shows the responses of PVC electrode-3 to the addition of Cu^{2+} solution. It is seen in Figure 8 (a) that the PVC electrode could tolerate Cu^{2+} concentrations up to 1.0×10^{-4} M, and above that the electrode started drifting with increasing Cu^{2+} concentration. This drifting of the PVC electrode at higher Cu^{2+} concentrations is probably due to the altering of the junction potential across the PVC membrane or due to the complexation between Cu^{2+} and the ion exchanger within the PVC membrane. Because of the drifting, it becomes too difficult to use the PVC electrode to study the surfactant $-H_2O$-Cu^{2+} system at concentrations of Cu^{2+} higher than 2×10^{-4} M. The systems investigated by PVC electrode-3 and results obtained are listed in Table 2 and shown in Figure 9. It can be seen from Table 2 that CMC lowering by Cu^{2+} was observed only in that one experiment with 10^{-4} M Cu^{2+} present; others show little CMC lowering because the Cu^{2+} concentrations were too small compared with 0.020 M NaNO$_3$, which was present together with Cu^{2+}. In Figure 9(c and f), where the Cu^{2+} concentrations were higher than 2×10^{-4} M, the interaction between Cu^{2+} and the PVC membrane or DBS$^-$ in solution became so great that it proved impossible to determine the correct CMC values in

these solutions due to the enhanced responses at the electrode. It was found that the transition region just before the CMC sometimes appeared but sometimes did not in the same experiment. The break points (CMC[b] in Table 2) in those runs where there were transition points (also intersections) were always the same as the intersections in those runs where there were no transition points in the same experiment. The same deviation was also observed when Ca^{2+} was used instead of Cu^{2+}. With higher Cu^{2+} concentration present, the same deviations were found when other electrodes (e.g. Birch-Clarke[45] liquid membrane electrode, electrode-1 and electrode-2, and so on) were uesd. It was found that the PVC electrodes responded better after pretreating in Cu^{2+}-DBS^- solution.

C.2. Complexation between Surfactant micelles and Cu^{2+} Observed by a Cu^{2+} Electrode

Divalent ions have dramatic effects on the surfactant system. Ca^{2+} effects on the surfactant system have been studied thoroughly.[7-8] Investigators have found that Ca^{2+} lowers the CMC of a surfactant to a much greater extent than univalent ions and that it formed precipitates with surfactant ions in certain concentration ranges. Little research has been done on Cu^{2+} so far.

A Cu^{2+} electrode was employed to study the interac-

tion between Cu^{2+} and DBS^- in the present work. A

calibration experiment of the Cu^{2+} electrode with a slope

of 27.5 mv at 25^OC is shown in Figure-12(a). The Cu^{2+}

electrode was also checked to determine whether or not it

responded to Na^+ and DBS^- (Figure 10). It was found that

Na^+ did not interfere with the Cu^{2+} electrode's response,

but DBS^- showed a little response.

The complexation between Cu^{2+} and surfactant micelles

can be observed in Figure 11. Below the CMC (in these

cases CMC is about 5×10^{-4} M due to 0.020 M $NaNO_3$ present

in the system), there is no indication of decreasing Cu^{2+}

activity. The system with the lowest Cu^{2+} concentration

showed a decrease in Cu^{2+} activity at the lowest concen-

tration of surfactant. When the surfactant was added at

concentrations above the CMC, a decrease in Cu^{2+} activity

was observed due to complexation between Cu^{2+} and

micelles. The system with the highest Cu^{2+} concentration

showed a decrease in Cu^{2+} activity at the highest

surfactant concentration. This result is obtained because

a little decrease of Cu^{2+} activity will not change the

potential much in a system with a large amount of Cu^{2+} in

it. The potential will change considerably in a system

with less Cu^{2+}. The complexation process can be

represented by

$$m \ Cu^{2+} + n \ DBS^- = (mCu^{2+}nDBS^-) \qquad (29)$$

Let $m/n = B$, then the above equation becomes:

$$B \ Cu^{2+} + DBS^- = 1/n \ [Cu_m(DBS)_n]^{2m-n} \qquad (29a)$$

where n is the aggregation number, and 2m-n is the micelle charge.

The equilibrium constant then is given by

$$B_n = [Cu_m(DBS)_n^{(2m-n)}]^{1/n}/([Cu^{2+}]^B*[DBS^-]) \qquad (30)$$

or,

$$\log B_n = 1/n \ \log \ [Cu_m(DBS)_n^{2m-n}] - \log \ [Cu^{2+}][DBS^-] \qquad (30a)$$

If the micelle is treated as a separate phase, the above equation can be rewritten as:

$$\log B_n = - B \ \log \ [Cu^{2+}] - \log \ [DBS^-] \qquad (30b)$$

where the activities of copper and DBS$^-$ can be obtained, but the counterion binding B is unable to be obtained in these experiments.

C.3. Precipitation and Complexation in NaDBS-Cu^{2+} system

The precipitate of Cu(DBS)$_2$ appeared only after a long time in most cases. The result shown in Table 5 is very interesting. At 25°C, the precipitate first appeared at 0.010 M Cu(NO$_3$)$_2$ and 2.64×10^{-4} M NaDBS, which would indicate a solubility product, K$_{sp}$, approximately equal to but less than $0.010 \times (2.64 \times 10^{-4})^2$, which is

$$K_{sp} = 7 \times 10^{-10}$$

The amount of precipitate appeared most in the solution of 0.010 M Cu(NO$_3$)$_2$ and 7.92×10^{-4} M NaDBS around the CMC. As the concentration of DBS$^-$ rose, the amount of

precipitate decreased, and finally disappeared at 0.010 M Cu^{2+} and 1.32×10^{-3} M NaDBS solution. The result indicated the formation of complexes or a kind of strong interaction between micelles and Cu^{2+} above the CMC. When the temperature was raised, the amount of precipitate became more only in the solutions above the CMC at $25^{\circ}C$ (e.g. the precipitate appeared in the solution of 0.010 M Cu^{2+} and 1.32×10^{-4} M NaDBS). This result can be explained by the increase of the CMC with temperature, which has been discussed previously.

C.4. K_{sp} Measured by a Cu^{2+} Electrode

The CMC (or the activity of DBS^-) in these solutions with 0.020 M $NaNO_3$ added is 5.28×10^{-4} M (Table 10). In Figure 12 (c, d and e), the CMC was not reached and no micelle was formed, so the earlier addition of Cu^{2+} resulted in Nernstian responses at the Cu^{2+} electrode. In Figure 12 (e), Cu^{2+} concentration was high enough so that the precipitate of $Cu(DBS)_2$ was able to be observed at 2.8×10^{-3} M Cu^{2+}. In Figure 12 (f, g, h, and i), in the early portion of these plots, the addition of Cu^{2+} had considerablely reduced response at the Cu^{2+} electrode. After the reduced regions, the responses returned to normal (Nernstian response), and after the normal response regions the responses were reduced again. This result can

be explained by taking account of the competition between precipitation and complexation. The solutions were above the CMC aleady, so the very first addition of Cu^{2+} was consumed by forming complexes with micelles resulting in the considerably reduced responses. After this region, the micelles had probably been satuated by Cu^{2+}, so that the responses of the Cu^{2+} electrode to the addition of Cu^{2+} became normal. The reduced responses after the normal response regions were believed to be due to the formation of precipitate, and the intersections in those plots were therefore the concentrations at which the precipitate first occurred. From the concentrations corresponding to the intersections, the solubility product was obtained and is listed in Table 11. The enhanced slopes in Figure 12 (h and i) were due to the fact that the potential E was not a function of the activity but of the analytical concentration, which means that the first addition of Cu^{2+} just after the considerably reduced response regions bring very large activity differences as shown by largely enhanced slopes.

Table 11. Solubility Product of $Cu(DBS)_2$ Measured by a Cu^{2+} Electrode at 25°C

Number of plots in Figure 12	e	f	g	h
$[DBS^-]$ *	4.49×10^{-4}	5.15×10^{-4}	5.28×10^{-4}	5.28×10^{-4}
$[Cu^{2+}]$	2.8×10^{-3}	1.85×10^{-3}	1.7×10^{-3}	1.8×10^{-3}
K_{sp}	5.6×10^{-10}	4.9×10^{-10}	4.7×10^{-10}	5.0×10^{-10}

*: activity of DBS^- can be obtained in Figure 6 (d).

D. Competition between Cu^{2+} and Na^+ in Counterion Binding in Micellar Solutions

Some authors[8] reported the competition in counterion binding between Ca^+ and Na^+ in sodium dodecylsulfate micellar systems and found that the Na^+ bound in the micelles was replaced by added Ca^{2+} in a ratio of 1:2 (e.g. one Ca^{2+} added resulting in two Na^+ being removed from the micelles).

The competition between Cu^{2+} and Na^+ was observed by employing a Cu^{2+} electrode, and the results are shown in Figure 13, as well as in Table 7. The competition can be observed by examining the slopes in the regions of decreasing Cu^{2+} activity and knowing the difference in the slopes among $NaNO_3$-free, 0.0200 M $NaNO_3$, and 0.0500 M $NaNO_3$ systems. In the $NaNO_3$-free system, the rate of Cu^{2+} decrease was greater than in the system with 0.0200 M $NaNO_3$ added, which is in turn greater than the system with

0.0500 M $NaNO_3$ added. This fact can only be explained by the competition between these two ions during the counterion binding to the micelles.

The attepmt to obtain the extent of competition quantitatively by adding Cu^{2+} to the NaDBS micellar solution using a Na^+ electrode to detect the amount of Na^+ released after being replaced by Cu^{2+} failed because the Na^+ electrode was found to respond to Cu^{2+}. The two plots in Figure 14 have corresponding turning points which are probably due to the changing of Cu^{2+} activity at these points.

   E.   Determination of the Concentration of NaDBS
        Solution by Means of Titration

The result (Figure 15) showed that the stock solution of NaDBS was 66% in purity. Benzylcetyldimethylammonium-chloride·H_2O is a good titrant but hyamine is not.

4. Comments on the Phase Separation Model and
   Charged Phase Separation Model for Dealing with
   Surfactant-Aqueous Systems and a Refined Charged
   Phase Separation Model

With the development of many new techniques, the
nature of surfactant-aqueous solution interaction becomes
more and more understood. As early as 1974, the phase
separation model was questioned because the assumption of
constant free surfactant monomer activity and counterion
activity above the CMC was proved not valid by Sasaki et.
al.[36] in the study of NaDS aqueous system using a surfac-
tant selective electrode and a sodium selective eletrode.
They found that the free monomer activity decreased but
counterion activity increased with a reduced slope above
the CMC instead of remaining constant. Subsquently, more
and more investigators reported the same results as those
obtained by Sasaki et. al. The results obtained in the
present work also agree with those of Sasaki et. al.
There is now a common agreement that the free monomer
activity decreases and the counterion activity increases
above the CMC, and the phase separation model thus has
been proved invalid in surfactant-aqueous systems.

The charged phase separation model, presented first
by Sasaki et. al., has been in widespread use by many
investigators since 1975[36-42] because of the experimental
fact shown in Equation (15):

$$\log [X^-] = \text{constant} - r \log [Na^+] \tag{15}$$

With the experimental fact shown in Equation (15), Sasaki et. al. believed that the micellization process has a charged phase separation mechanism represented by

$$m\, Na^+ + n\, X^- = (Na_m X_n)^{-(n-m)} \tag{16}$$
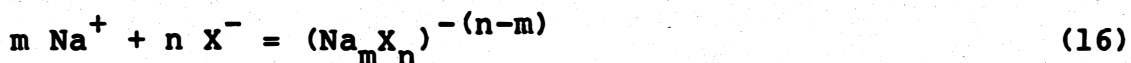
They believe that the slope r in Equation (15) is equal to the counterion binding B (m/n). So far the criticism of this model has been based on the assumption by some authors[21] that micelles exist as a separate phase. They used the phase rule from the viewpoint of degrees of freedom to account for the fact that micelles of order 10^2 could not be treated as separate phases. There is another experimental fact that the counterion binding B varies with the total analytical concentration of surfactant above the CMC, which has been shown by many authors[41] and verified in the present work. This result has also been assumed, but not declared explicitly, by those authors who used the charged phase separation model. Although the variation of counterion binding has been observed, no one has disproved the equality of r in Equation (15) to the counterion binding B. In the present work r is proved not equal to B. Methods are disccussed below:

Figure 19 is a plot of EMF vs log (surfactant) obtained by measuring the free surfactant monomer activity ($[X^-]$) by a surfactant selective electrode and the counterion sodium activity ($[Na^+]$) by a Na^+ selective electrode, respectively. In Figure 19(a), the response of
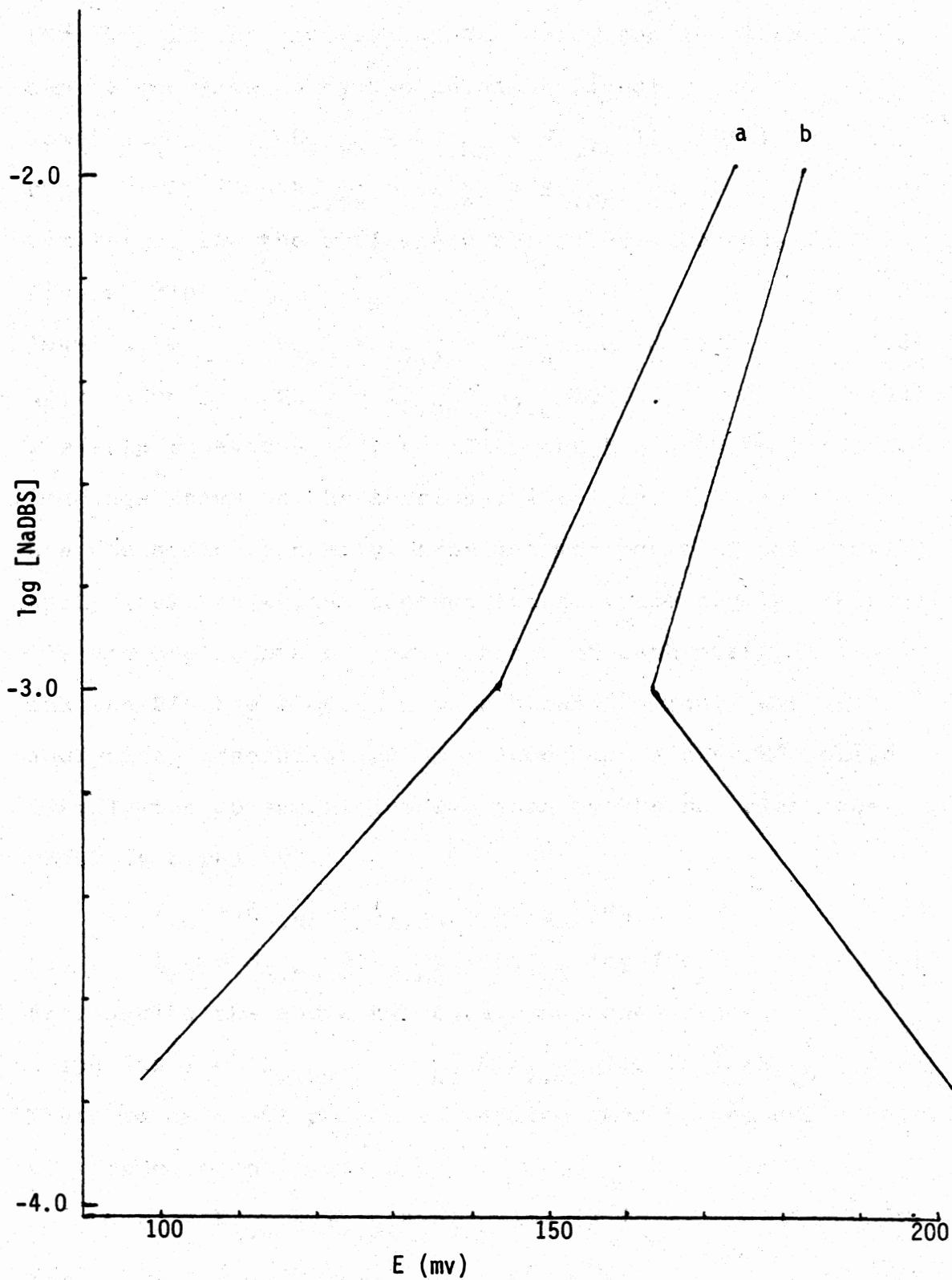
Figure 19. Arbitriry Plots of thr Response of a Na⁺ Electrode and a PVC Electrode to NaDBS

a. by Na⁺ electrode   b. by PVC electrode

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EMF (mv) to the activity of Na^+ below and above the CMC can be represented by two straight lines:

lower line, $\quad E_{1,Na} = I_{1,Na} + S_{1,Na} \log [Na^+]$ $\qquad$ (31)

upper line, $\quad E_{2,Na} = I_{2,Na} + S_{2,Na} \log (D_t)$ $\qquad$ (32)

Similarly, for the surfactant selective electrode in Figure 19(b):

lower line, $\quad E_{1,s} = I_{1,s} + S_{1,s} \log [X^-]$ $\qquad$ (33)

upper line, $\quad E_{2,s} = I_{2,s} + S_{2,s} \log (D_t)$ $\qquad$ (34)

where in Equations (31) to (34), the E's are the potential readings shown on the abscissa; $[Na^+]$ and $[X^-]$ and (D_t) are the sodium activity, free monomer activity and total analytical surfactant concentration, respectively; the I's are the points of intersection of each straight line, and the S's the slopes of each straight line. With total analytical concentration (D_t) added above the CMC, there is only one potential reading seen by the Na^+ electrode, which is given by

$$E_{Na} = E_{1,Na} = I_{1,Na} + S_{1,Na} \log [Na^+] \qquad (35)$$

or, $\quad E_{Na} = E_{2,Na} = I_{2,Na} + S_{1,Na} \log (D_t)$ $\qquad$ (36)

Rearranging the above two equations, one obtains

$$\log [Na^+] = (I_{2,Na} - I_{1,Na} + S_{2,Na} \log [D_t])/S_{1,Na}. \qquad (37)$$

There is only one potential reading seen by the surfactant electrode which is given by

$$E_s = E_{1,s} = I_{1,s} + S_{1,s} \log [X^-] \qquad (38)$$

or, $\quad E_s = E_{2,s} = I_{2,s} + S_{2,s} \log (D_t).$ $\qquad$ (39)

Rearranging the above two equations, one obtains

$$\log [X^-] = [I_{2,s} - I_{1,s} + S_{2,s} \log (D_t)]. \qquad (40)$$

Recalling Equation (15) and the slope (-r), one can write

$$-r = d(\log [X^-])/d(\log [Na^+]) \tag{41a}$$

$$= (S_{2,s} * S_{1,Na})/(S_{1,s} * S_{2,Na}) \tag{41b}$$

where $S_{1,s}$ is a negative value.

If the responses are Nernstian, then $-S_{1,s} = S_{1,Na} = 59.2$ mv at 25°C. Then Equation (41b) becomes:

$$r = S_{2,s}/S_{2,Na} \tag{42}$$

Substituting Equation (42) into Equation (15), one obtains the relationship

$$\log [X^-] = \text{constant} - S_{2,s}/S_{2,Na} \log [Na^+] \tag{43}$$

Consider a situation in which $S_{2,Na} = 50$ mv, and $S_{2,s} = -50$ mv. The amount of activity deviation from Nernstian responses is the same for both ions, therefore, the counterion binding is 1, but $r = -1$. Consider another situation in which $S_{2,Na} = 50$, and $S_{2,s} = 50$. Apparently this situation is not the same as the previous one. Therefore, the counterion binding m/n is not 1, but $r = 1$. The situation can be viewed from the other point. If $S_{2,s}/S_{2,Na} = m/n$, when $S_{2,Na} = 59.2$, m/n must be zero, and $S_{2,s}$ must be zero too. When $S_{2,Na} = 0$, $S_{2,s}$ also must be zero, then m/n = 1. This shows that the assumption, $S_{2,Na}/S_{2,s} = m/n$, is internally inconsistent.

Since the charged phase separation model has been shown to be inadequate, an improved charged phase separation model is now presented below:

Rearranging Equation (16), one obtains

$$[X^-] + m/n[Na^+] = 1/n (Na_m X_n)^{-(n-m)} = 1/n [M]. \tag{43}$$

The equilibrium constant K can be obtained as follows:

$$K = [M]^{1/n}/([Na^+]^B [X^-]) \qquad (44)$$

The free energy change for the micellization process then is given by

$$\Delta G^O_m = -RT(1/n \ln [M] -B \ln [Na^+] - \ln [X^-]) \qquad (45)$$

where K and ΔG^O_m are also functions of total analytical concentration. At the concentration just above the CMC, the counterion binding B is approximately equal to zero. Thus Equation (45) can be rewritten as

$$\Delta G^O_m = -RT(1/n \ln [M] - \ln [X^-]) \qquad (46)$$

There are two ways to simplify Equation (46):

(1). Assuming the micelle a separate phase, then [M] equals unity, and $[X^-]$ = CMC. Then Equation (46) becomes:

$$\Delta G^O_m = RT \ln CMC \qquad (47)$$

(2). Although the micelle is not a separate phase, the first term in Equation (46) can be neglected compared to the second term because in a solution just above the CMC (usually 10^{-3}- 0.01 M) the micelles usually have aggregation numbers of 60 or so. Then Equation (46) is simplified to Equation (47). The error is about equal to the experimental error.

Equation (47) has the same form as Equation (6), but they are derived under two different basic assumptions.

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