Role of Interfacial Potential in Coagulation of Cuprammonium Cellulose Solution

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SYNOPSIS

The electric potential, copper ion flux, and ammonia flux across the interface of cuprammonium cellulose solution (CCS) and various 1.0 equiv/L electrolyte solutions (ES) at 25°C were measured. The interfacial potentials were strongly negative (−10 to −35 mV) with H_2SO_4, HCl, and $(NH_4)_2SO_4$ as ES, weakly positive (6 to 8 mV) with NaCl, KCl, LiCl, CsCL, and RbCl as ES, and strongly positive (19 to 34 mV) with KOH and NaOH as ES, generally showing values similar to the diffusion potentials for electrolyte solutions comprising ions of the same absolute charge. The ammonia flux (about 1×10^{-4} mol/cm^2/s) was relatively unaffected by the interfacial potential, but the copper ion flux was clearly dependent on it. These results, together with the observed rates of CCS coagulation, indicate that the mechanism of the coagulation was largely determined by the interfacial potential, with strongly negative potential gradients accelerating the Cu^{2+} flux into the ES and CCS coagulation proceeding rapidly by Cu^{2+} removal, strongly positive potential gradients accelerating the Na^+ flux into the CCS and coagulation proceeding rapidly via the formation of cellulose–Na^+ complex, and the absence of a strong potential gradient capable of accelerating the ion flux resulting in slow coagulation by ammonia removal. It may therefore be possible to control the interfacial potential and the ion flux by the ES composition, and thus to influence the structure of regenerated cellulosic fibers and membranes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Cuprammonium cellulose solution (CCS) was first described by Shweizer in 1857,[1] and has through much of this century been employed in the production of Bemberg Rayon, one of the main types of regenerated cellulose. Continuing developments in CCS-based fiber production have helped maintain Bemberg Rayon as a major man-made fiber, and have led to new fields of application.

Since 1970, commercial utilization of CCS has broadened to include hollow fiber membranes for blood purification[2] and virus removal,[3] nonwoven fabrics, and microcarriers for mammalian cell cultures.[4]

Regenerated cellulose fiber is produced industrially from CCS by wet spinning, with coagulation by acid solution, hot water, or Normann reaction.[5] Production of fibers for fabrics generally involves coagulation with H_2SO_4 solution, which dissolves copper ion and rapidly neutralizes alkali, or with hot water, which rapidly dissolves ammonia. Production of hollow fiber membranes for blood purification involves coagulation with NaOH solution, for the formation of cellulose and Na^+ complex by

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Journal of Applied Polymer Science, Vol. 59, 15–21 (1996)
 CCC 0021-8995/96/010015-07

the Normann reaction.[6] The Normann reaction was first proposed to explain such CCS coagulation more than a century ago. It has not been investigated systematically since that time, but apparently involves crosslinking between the cellulose molecular chains by ionic bonding of the sodium ion, analogous to that described for high-strength poly(vinyl alcohol)[7] and other similarly crosslinked polymers, and has become the subject of renewed interest because of the need to control the membrane structure and characteristics.

Hollow fiber membranes produced from CCS are widely used in hemodialytic therapy. Higher hemodialytic performance, and particularly the more rapid transport of solutes with molecular weights of 5,000 to 66,000, is currently a major development goal for such membranes, and will require a better understanding and control of the CCS coagulation process.

The characteristics of CCS coagulation vary substantially with the electrolytes present in the coagulant solution, making characterization of the mechanism difficult. It has generally been assumed that CCS coagulation is dependent on the ability of the coagulant solution to dissolve copper and ammonia and induce the formation of stable salts or complexes,[8] but this assumption does not provide a sufficient basis for description of the coagulation mechanism.

Both the CCS and the coagulant solution generally contain electrolytes. An electric potential may therefore be expected to develop at their interface and to play a role in the coagulation process, by affecting the rate of ion transfer between the CCS and the coagulant solution, and thus the rate of coagulation in the CCS solution.

In the present work, we measured the electric potential and the copper and ammonia flux between the CCS and various electrolyte solutions, and the rate of coagulation, and examined the relation between the interfacial potential and the coagulation mechanism.

EXPERIMENTAL

Cuprammonium Cellulose Solution (CCS)

CCS was prepared by the method of Gibson et al.[9] with minor modifications, and held at 4°C until its use in the experiments within 30 h. Its composition was determined by calculation from the starting materials, except that its hydroxide ion content was determined by titration after evaporation of ammonia from the CCS for 1.5 h at 520°C. Its viscosity was determined on a standard viscometer (Mettler Rheomat 115).

Coagulant Solutions

The coagulant solutions were prepared by adjustment of reagent-grade electrolytes shown in Table II with distilled water, to obtain a concentration of 1.0 equiv/L.

Coagulating Effect

The coagulating effect of each coagulant solution, as judged by tactile examination of CCS immersed in 1.0 equiv/L coagulant solution at 25°C, was classified as strong (coagulation within 1 s after immersion), moderate (coagulation at 1 to 30 s), and weak or nil (no coagulation within 30 s). Each test was repeated 10 or more times, to confirm the assessment. Visual or optical detection of the coagulation was not employed because of the opacity of the CCS.

Copper and Ammonia Flux

The CCS (0.1 mL) was placed in the bottom of a test tube and 1 mL of the electrolyte solution was then added so as to form a layer on the CCS with a contact area of 0.2 cm^2 between the two solutions. After 10 s, the electrolyte solution was removed and subjected to atomic adsorption analysis (Shimazu AA-670) to determine its copper content and Keldahl analysis (Mitsubishi Chemical KN-01) to determine its ammonia content. Both solutions were kept at 25°C throughout the experiment.

Interfacial Potential

The interfacial potential between the CCS and the electrolyte solution was measured with the apparatus shown schematically in Figure 1. The vessel on the left held a 1.0 equiv/L KCl solution, and that on the right held the 1.0 equiv/L electrolyte solution. In cases where the electrolyte itself contributed no Cl^-, KCl (0.05 M) was added to ensure a stable, reproducible interfacial potential between the electrolyte solution and the Ag/AgCl electrode.

The two vessels were connected electrically by a U-shaped glass tube loaded with CCS or agar gel containing saturated KCl. The potential ($\Delta\phi$) of the right terminal relative to the left was measured with an electrometer (TOA Electronics, PM-18R) at 25°C.

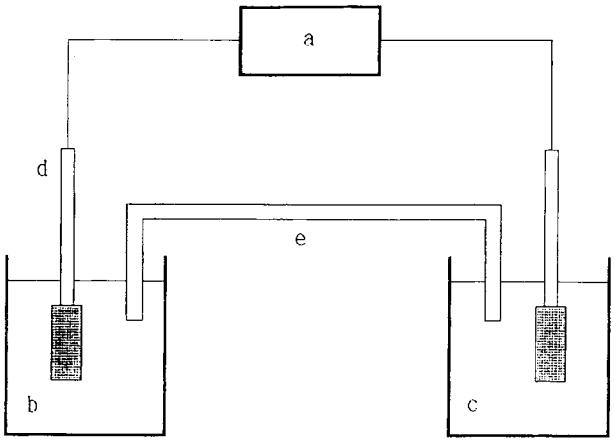

Figure 1 Experimental apparatus for determination of interfacial potential (*a*, electrometer; *b*, 1.0*M* KCl; *c*, 1.0 equiv/L electrolyte solution; *d*, Ag/AgCl electrodes; *e*, *U*-shaped glass tube loaded with CCS or agar gel containing saturated KCl.

RESULTS

The composition of the CCS is shown in Table I. The calculation based on component materials showed an excess of cationic species over anionic species. It was therefore assumed that hydroxyl groups dissociated from the cellulose sufficiently to maintain the necessary electric neutrality of the solution. The measured viscosity of the CCS was about 100 Pa · S at 25°C, which is sufficient to maintain a physical interface between the CCS and the electrolyte solution and thus permitted the investigation of the mass transfer rates and interfacial potential between the two solutions.

As summarized in Table II, the rate of CCS coagulation was extremely rapid (1 s or less) in contact with the electrolyte solutions NaOH, KOH, $(NH_4)_2SO_4$, HCl, and H_2SO_4, moderate (1 to 30 s) with K_2SO_4, NH_4Cl, and $CaCl_2$, and slow to nil (more than 30 s) with all other electrolytes tested.

Table I Composition of Cuprammonium Cellulose Solution (Cellulose Content, 8.0 wt %)

Species	Concentration (*M*)
NH_3	3.79
Na^+	0.382
Cu^{2+}	0.460
SO_4^{2-}	0.127
OH^-	0.078

As shown in Figure 2, the ammonia flux across the interface of the CCS and the electrolyte solution was generally about 1.0×10^{-4} mol/cm^2/s, with relatively little variation among the various electrolytes. The copper flux, on the other hand, was clearly dependent on the electrolyte. The highest copper fluxes were observed with HCl, H_2SO_4, $(NH_4)_2SO_4$, and NH_4Cl, in that order.

The interfacial potentials as determined in the present study are shown in Table II. They were obtained by measurement of the overall cell potential with the CCS and with saturated KCl in its place, and calculation from these measured values on the following basis.

The two systems are defined as:

System 1: Ag|AgCl|I|II|III|AgCl|Ag

System 2: Ag|AgCl|I|II′|III|AgCl|Ag

where I is 1.0*M* KCl, II is CCS, II′ is saturated KCl agar gel solution, and III is 1.0 equiv/L electrolyte solution, and the potentials of Ag|AgCl at the left and right are designated ϕ_L and ϕ_R, respectively. The overall cell potential in System 1 is then

$$\Delta\phi_1 = \phi_{R,1} - \phi_{L,1}$$
$$= (\phi_{R,1} - \phi_{III,1}) + (\phi_{III,1} - \phi_{II}) + (\phi_{II} - \phi_{I,1}) + (\phi_{I,1} - \phi_{L,1})$$

and that in System 2 is

$$\Delta\phi_2 = \phi_{R,2} - \phi_{L,2}$$
$$= (\phi_{R,2} - \phi_{III,2}) + (\phi_{III,2} - \phi_{II'}) + (\phi_{II'} - \phi_{I,2}) + (\phi_{I,2} - \phi_{L,2})$$

The potential differences $\phi_{R,1} - \phi_{III,1}$ and $\phi_{R,2} - \phi_{III,2}$ are presumably equal, as are $\phi_{I,1} - \phi_{L,1}$ and $\phi_{I,2} - \phi_{L,2}$. The values of $\phi_{III,2} - \phi_{II'}$ and $\phi_{II'} - \phi_{I,2}$, moreover, may be presumed sufficiently small to be taken as zero, since ion transport through these two interfaces is dominated by the massive quantities of KCl present. The difference between the two overall cell potentials may therefore be written

$$\Delta\phi_1 - \Delta\phi_2 = (\phi_{III,1} - \phi_{II}) + (\phi_{II} - \phi_{I,1})$$

The value of $(\phi_{II} - \phi_{I,1})$, which represents the interfacial potential between the CCS and 1.0 Eq/L KCl, can be shown by theoretical calculation (Henderson equation, as described below) to be −5.6 mV.

Table II Diffusion and Interfacial Potentials, Copper and Ammonia Fluxes, and Coagulation Speed and Mechanism, for CCS and 1.0 Eq/L Electrolyte Solution at 25°C

	Potential (mV)		Flux (mol/cm^2/s × 10^4)		Coagulation	
Electrolyte	Diff.[a]	Interf.[b]	Copper	Ammonia	Speed[c]	Type[d]
NaCl	10.2	7.6	0.084	0.86	S	A/R
Na_2SO_4	8.4	−7.4	0.134	0.89	S	A/R
NaOH	21.7	18.6	0.244	1.22	F	N/R
KCl	5.6	5.8	0.137	0.96	S	A/R
K_2SO_4	5.0	−6.4	0.236	0.84	M	C/R
KOH	18.4	33.6	0.197	1.44	F	N/R
NH_4Cl	5.6	4.9	0.667	—[e]	M	C/R
$(NH_4)_2SO_4$	5.0	−10.4	1.196	—[e]	F	C/R
$CaCl_2$	6.9	15.4	0.433	1.55	M	C/R
HCl	−22.0	−14.4	1.558	1.05	F	C/R
H_2SO_4	−19.5	−34.4	1.401	1.29	F	C/R
LiCl	12.5	8.0	0.081	0.96	S	A/R
CsCl	5.0	6.6	0.189	1.12	S	A/R
RbCl	4.9	7.4	0.172	1.02	S	A/R

[a] Diffusion potential (theoretical).
[b] Interfacial potential (experimental).
[c] F, 1 s or less; M, 1 ~ 30 s; S, over 30 s.
[d] A/R, ammonia removal; N/R, normal reaction; C/R, copper removal.
[e] Indeterminate.

The interfacial potential between the CCS and the electrolyte solution was therefore calculated as the measured overall cell voltage ($\Delta\phi_1 - \Delta\phi_2$) plus 5.6 mV.

DISCUSSION

As summarized in Table II, the results of this study are in accord with the classification of the CCS coagulation mechanism into the following three types.

- Copper removal: High to moderate copper flux, high to moderate coagulation rate; coagulation apparently led by copper removal from the CCS; observed with K_2SO_4, NH_4Cl, $(NH_4)_2SO_4$, HCl, and H_2SO_4 solutions.
- Normann reaction: Low copper flux, high coagulation rate; coagulation apparently led by complex formation via Normann reaction; observed with NaOH and KOH solutions.
- Ammonia removal: Low copper flux, low coagulation rate; coagulation apparently led by ammonia removal from CCS; observed with most other electrolyte solutions.

In the highly alkaline environment of the CCS, copper mostly exists as a divalent cation, but ammonia (with its pK_a value of 9.25) is not ionized. The results of the present study (Fig. 2) show that the copper flux, but not the ammonia flux, is clearly dependent on the type of electrolyte solution present, and therefore indicate that the ion transport across the interface is dependent not only on the

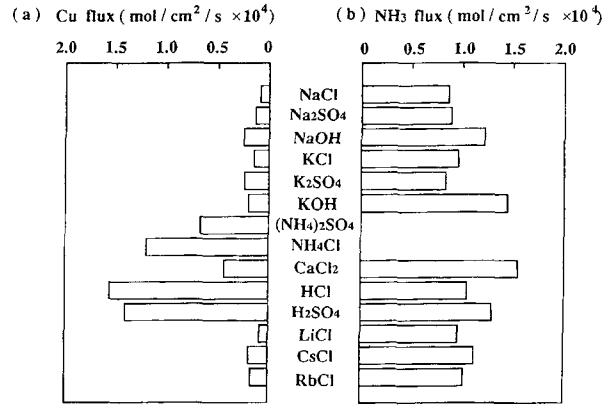

Figure 2 Copper ion and ammonia flux from CCS to various electrolyte solutions (1.0 equiv/L) at 25°C.

concentration gradient across the interface but also on the interfacial potential.

Interfacial Potential and Copper Flux

Figure 3 shows the relation between the copper flux from the CCS to the 1.0 equiv/L electrolyte solution and the interfacial potential between the two solutions ($\phi_{III} - \phi_{II}$), for all of the electrolyte solutions tested. Negative interfacial potentials imply a negative potential in the electrolyte solution, relative to the potential in the CCS, and thus an accelerated Cu^{2+} movement across the interface and into the electrolyte solution. Positive interfacial potentials imply a positive potential in the electrolyte solution relative to the CCS, and thus a retarded Cu^{2+} movement across the interface. The close relationship shown in Figure 3, between the copper flux and the interfacial potential, indicates that the main factor affecting the rate of copper transport in the CCS–electrolyte solution system is the potential difference between the two solutions at their interface.

On the basis of the measured values of the interfacial potential and copper flux, the observed coagulation characteristics, and the presumed influence of the interfacial potential on Na^+ transfer across the interface, the CCS–electrolyte solution systems are grouped by coagulation mechanism in Figure 3 as (a) copper removal, in which Cu^{2+} movement to the electrolyte solution is accelerated by its relatively negative potential; (b) Normann reaction, in which the Cu^{2+} movement is retarded but Na^+ or K^+ movement in the opposite direction is accelerated by its relatively positive potential and cellulose complexes form in the CCS; and (c) ammonia removal, in which no strong interfacial potential develops, ion movement across the interface is largely unaffected by an electric field, and coagulation proceeds by ammonia removal.

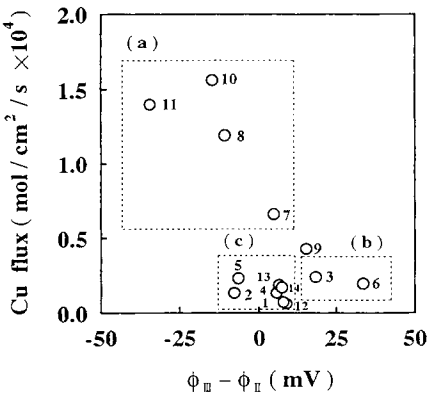

Figure 3 Copper ion flux from CCS to 1.0 equiv/L electrolyte solution vs. interfacial potential ($\phi_{III,1} - \phi_{II}$) at 25°C, and regions of coagulation (a) by copper removal, (b) by Normann reaction complexes of cellulose and Na^+ or K^+, and (c) ammonia removal. Electrolyte solutions: 1, NaCl; 2, Na_2SO_4; 3, NaOH; 4, KCl; 5, K_2SO_4; 6, KOH; 7, NH_4Cl; 8, $(NH_4)_2SO_4$; 9, $CaCl_2$; 10, HCl; 11, H_2SO_4; 12, LiCl; 13, CsCl; 14, RbCl.

Mechanism of Interfacial Potential Development

The development of the interfacial potential between the CCS and the 1.0 equiv/L electrolyte solution can be explained in terms of the diffusion potential, as expressed by the well-known Henderson equation.[10] In general, when two electrolyte solutions of different composition are in mutual contact, ions tend to diffuse through their interface because of the ion concentration gradient between the two. Different ion species generally have different mobilities, and some species therefore diffuse across the interface more rapidly than others. This separation of electric charge sets up a boundary potential difference. The resulting electric field then tends to slow the movement of ion species having high mobility, and speed the movement of those having low mobility.

The diffusion potential between two solutions (phase α and phase β) is expressed by the Henderson equation as

$$\Delta\phi = \phi_\beta - \phi_\alpha = \frac{RT}{F} \frac{\sum z_i \omega_i [c_i(\beta) - c_i(\alpha)]}{\sum z_i^2 \omega_i [c_i(\beta) - c_i(\alpha)]} \ln \frac{\sum z_i^2 \omega_i c_i(\alpha)}{\sum z_i^2 \omega_i c_i(\beta)}$$

where ω_i is the molar mobility of species i, z_i its charge, and C_i its molar concentration. The theoretical value of the diffusion potential for each of the CCS–electrolyte solution systems tested, as calculated from the Henderson equation, is shown in Table II together with the value of the interfacial potential ($\phi_{III} - \phi_{II}$) obtained for that system.

The results shown in Table II are in agreement with the observation by Buck[11] that the Henderson equation is a good approximation for systems with ions of the same absolute charge. Though deviation from the Henderson equation values occurred with the electrolyte solutions containing ions of differing absolute charge (involving SO_4^{2-} or Ca^{2+}), the overall correlation between the observed interfacial potentials and the diffusion potentials, as shown in Figure 4, indicates that the Henderson equation

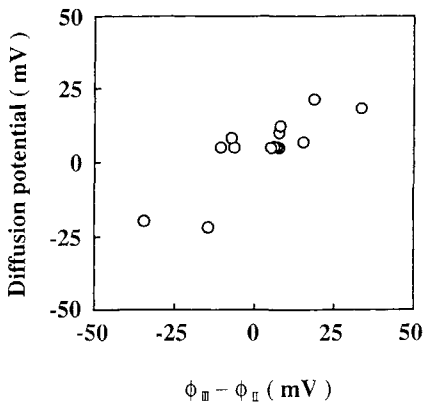

Figure 4 Correlation between experimental interfacial potentials and Henderson-equation diffusion potentials, for CCS and 1.0 equiv/L electrolytes at 25°C.

provides a valid starting point for explanation of the occurrence and strength of the interfacial potential.

CCS Coagulation Mechanism

The key role of the interfacial potential in determining the type of coagulation that occurs in the CCS may be inferred from the theoretical description of ion species movement in an electric field.

Strathmann and other researchers have provided excellent descriptions of mass flux in phase separation processes wholly in terms of chemical potential gradients, with no need for consideration of electrochemical potentials, and the relation of the mass flux to the coagulation of many polymer systems.[12] Such polymer/solvent/nonsolvent systems, however, contain no charged species among their components. CCS and the electrolyte solution used for its coagulation, in contrast, both contain ion species.

In the presence of an electric field, such as that of the interfacial potential observed in the present study, the movement of a given ion species in the system is generally expressed by the Nernst–Planck equation

$$J_i = -\omega_i RT(dc_i/dx) - z_i F\omega_i c_i(d\phi/dx)$$

where J_i is the flux of ion species i.[13] As shown by this equation, the movement of ion species such as those present in the CCS–electrolyte solution is a function not only of the concentration gradient, as expressed in the first term on the right, but also of the electrochemical potential gradient, as expressed by the second term.

The interfacial potential and the charge and relative mobility of each of the species in the CCS–electrolyte solution are therefore essential for an accurate description of the coagulation mechanism, and present a possible means of controlling the coagulation. Figure 5 is a schematic representation of

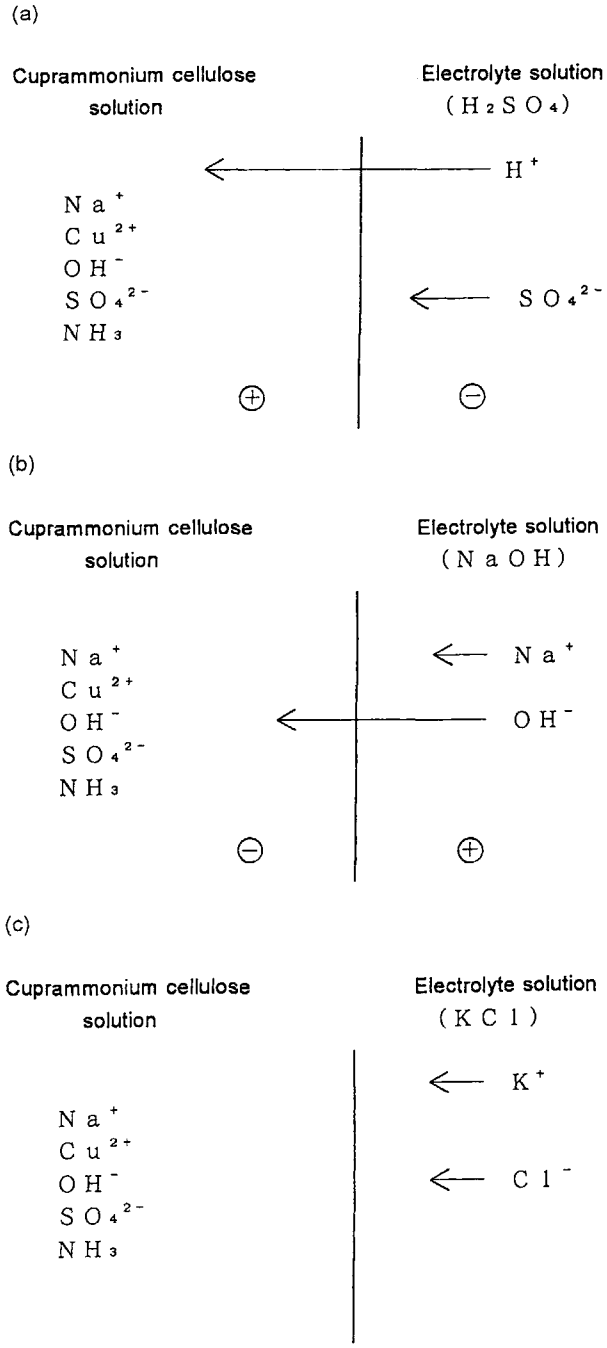

Figure 5 Development of interfacial potential in coagulation by (a) copper removal, (b) Normann reaction, and (c) ammonia removal (relative mobility of ion shown by arrow length; polarity of resulting interfacial potential shown by plus and minus).

the initial stage of the three types of coagulation mechanism, in which the arrow length represents the relative mobility of the ion species present in each system, and thus its net transfer by diffusion across the interface of the CCS–electrolyte system immediately following contact between its two solutions.

Diagram *a* represents the "copper removal" type of coagulation, with H_2SO_4 as the electrolyte solution. Upon contact between the CCS and the electrolyte solution, the diffusion of H^+ into the CCS is much faster than that of SO_4^{2-}. The differing diffusion rates of these two species sets up a potential gradient at the interface. Because the gradient is negative in the direction of the electrolyte solution, it accelerates the movement of Cu^{2+} from the CCS to the electrolyte solution, and CCS coagulation is thus led by the removal of this ion species.

Diagram *b* illustrates the "Normann reaction" coagulation system, shown here with NaOH as the electrolyte solution. With its far higher mobility, the OH^- ion diffuses more rapidly than the Na^+ ion through the interface and into the CCS, setting up a positive potential gradient which then speeds the movement of the Na^+ ion into the CCS, leading to the formation of the cellulose–Na^+ complex by the Normann reaction.

Diagram *c* illustrates the "ammonia removal" coagulation type. Since the ions K^+ and Cl^- have similar mobilities, their rate of diffusion into the CCS is approximately equal and only a slight interfacial potential develops. Ammonia has a higher mobility than any other species in the CCS, and in the absence of an electric field at the interface it is the diffusion of this species into the electrolyte that leads the coagulation.

CURRENT AND FUTURE STUDIES

The three types of coagulation mechanism found here for CCS may also apply to any polymer coagulation system involving electrolytic solutions, and investigation of this possibility may be expected to bring further understanding and control of their coagulation mechanisms and the related polymer characteristics.

We are currently investigating the relationship between the CCS coagulation mechanism and the structure of the resulting cellulosic membrane. A full description is not yet possible, but the results to date indicate that coagulation by the Normann reaction tends to result in a membrane of relatively dense, uniform structure, while copper removal and ammonia removal coagulation both tend to result in membranes having pore size gradients and asymmetrical surface structures, with a skin tending to form on the side facing the coagulant solution in the former and on the opposite side in the latter.

The authors are grateful to Asahi Chemical Ind. Co., Ltd. for its financial support and permission to publish these findings, and to Sachiyo Yamana for her help in elemental analysis.

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Received December 20, 1994
Accepted May 19, 1995