

Ionically Crosslinked Poly(acrylic Acid) Membranes.

I. Wet Technique

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Synopsis

A study has been made of the ionic crosslinking of poly(acrylic acid) membranes for possible applications in dialysis and reverse osmosis. The technique consists of casting a film of poly(acrylic acid) neutralized with sodium hydroxide, followed by immersion in appropriate metal salts (aluminum, zinc, and chromium salts). A qualitative rate model has been developed to guide this synthesis. Since both metal cations and protons in solution compete for the carboxylic acid sites, acid-base properties of the metal and polycarboxylic acid appear to be important for successful membrane formation. The use of a nonsolvent for the polymer in the crosslinking solution was tested and found to give improved membranes under some conditions. The nonsolvents tested were methanol, acetone, benzene, and dimethylformamide, dimethylformamide being the most successful. Crosslinking agents such as the Zn^{2+} and Cr^{3+} salts were tried but were not as successful as the Al^{3+} salts. A series of membranes was synthesized in aluminum/dimethylformamide crosslinking baths under various conditions in order to determine suitable procedures for preparation of membranes.

INTRODUCTION

In this paper we report research designed to produce permselective ionically crosslinked membranes for use in dialysis and reverse osmosis. Poly(acrylic acid)-based membranes are of particular interest because of their hydrophilicity and because of the fact that the carboxylic groups can dissociate to give a charged character to the membrane material. The term ionic crosslinking was perhaps originated in the work of Brown¹ in order to explain the role of metal oxides, such as ZnO, in the vulcanization of carboxylate rubber. It was then realized that the introduction of charged groups in polymers, and therefore the potential to form ionic bonds, added in fact a new dimension to the spectrum of properties of these polymers. Consequently, "ionomers"² were developed in the early 1960s, characterized by relatively small concentrations of carboxylic groups and neutralized in general by alkali metals. A review of the area of ionomers has recently been published by Holliday.³

Although the morphology of ionomers is still a subject of controversy, there seems to be evidence^{4,5} that the metal ions are concentrated in aggregates or clusters dispersed in the amorphous phases of the polymer (Fig. 1).

The formation and properties of ionically crosslinked membranes via polyvalent metals such as those reported here and in the literature⁵ are dependent upon the properties, concentration, and distribution of the metal and the polymer. The lack of quantitative data in the literature with regard to concentrated

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THREE PHASE MODEL OF IONOMER STRUCTURE

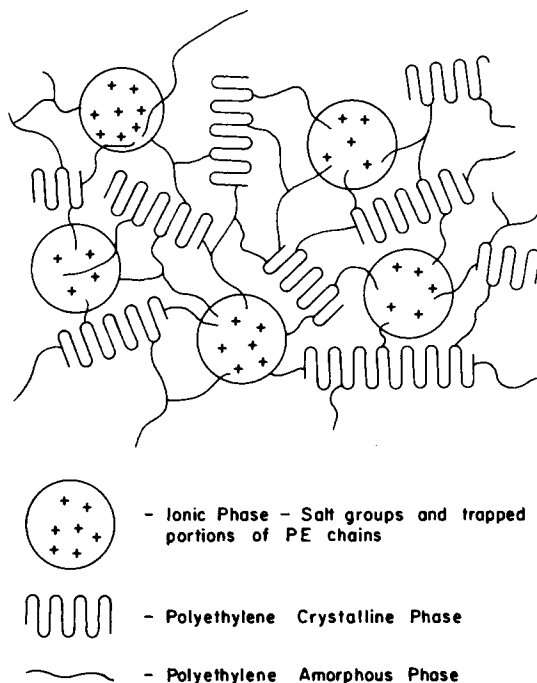


Fig. 1. Structure of ionomers. Adapted from Longworth and Vaughan.⁴

solutions of polyelectrolytes seriously limits attempts to analyze the mechanisms of membrane formation by the ionic crosslinking of carboxylic polymers in metal salt solutions.

The phenomenon known as ion binding occurs in solutions of anionic polyelectrolytes and cations because of the strong electrostatic forces surrounding the polymer chains. The cations (counterions) are attracted to, and constrained to remain in, the vicinity of the polyanions. The exact nature of the ion binding is not clear, but it has been found that the amount of bound ions increases with the extent of neutralization and with the valence. It is believed that small-valence counterions (e.g., Na, K) are generally surrounded in an electric field created by the charged polymer molecules, while higher-valence counterions (Cu, Ca, Mg) are located more specifically at the carboxylic sites.⁷

Research on the gelation of poly(carboxylic acids) has shown that addition of multivalent cations caused the formation of clusters. Eventually the clusters may become large enough to precipitate.⁸ Michaeli,⁹ working with divalent cations, supports the assumption that this precipitation is primarily a change in the solubility properties of the single polymer molecule and is not due to crosslinking. Near the precipitation point the molecule is in a coiled conformation and the precipitate would be a matrix consisting of spherical polymer molecules with the inorganic ions imbedded in each molecule.

Ikegami and Imai¹⁰ found that the precipitation of poly(acrylic acid) with divalent cations (M) could generally be classified into two types with respect to the minimum concentration of salt (\bar{C}_s) at which precipitation begins. In the first case (type L, for relatively lower values of \bar{C}_s), it was observed that \bar{C}_s in-

creased linearly with the concentration of polymer, and the formation of the salt bridge $\text{COO}-\text{M}-\text{OOC}$ was accompanied by considerable dehydration of the polyanion. In the other case (type H, for higher values of \bar{C}_s), \bar{C}_s was almost independent of the concentration of polymer, and the formation of the pendent half-salt $\text{COO}-\text{M}^{+-}\text{OOC}$ occurred with a smaller dehydration of the polyanion. The appearance of the L or H type depended on charge density (degree of neutralization) of the polyacid and on the nature of the cation added. Hence, more hydrated cations such as Mg^{2+} (compared to Ca^{2+} and Ba^{2+}) tended to be of the H type at low degrees of neutralization (α) and of the L type for higher α values.

In this paper we develop a qualitative rate model for the formation of ionically crosslinked polyacid membranes using a crosslinking bath external to the film. We then use the model as a guide in the preparation of poly(acrylic acid) membranes in two extensive studies, namely, an investigation of the use of nonaqueous solvents in the crosslinking bath which are nonsolvents for the poly(acrylic acid) and an investigation of a wide variety of polyvalent ionic salts as crosslinking agents in aqueous solution.

QUALITATIVE RATE MODEL

In the "wet" technique discussed here, a solution of the carboxylic polymer [in this work an aqueous solution of poly(acrylic acid)] and a crosslinking solution of a metal salt are prepared separately. Then, two steps characterize the preparation of the membrane: (i) A film of the solution of polymer is cast on an appropriate surface (such as a glass plate) with a predetermined drawdown thickness. (ii) The plate is carefully immersed in the "gelling" solution for crosslinking at a certain temperature for a certain time, as sketched in Figure 2. After its synthesis the membrane is soaked in deionized water.

For the purposes of this work it was found convenient to establish a simple qualitative description of the mechanism of formation of the membrane. Basically, the formation of the membrane is considered to be the result of the combination of two independent rate processes, namely, diffusion of metal ion and chemical reaction: (i) The metallic ion must diffuse from the outer solution into the polymer phase. (ii) It must react with the pendent carboxylic groups for crosslinking to occur.

Depending on the relative and absolute magnitudes of the rates of the two processes mentioned above, several idealized situations may arise. These situations are qualitatively represented in Figure 3 and are discussed below.

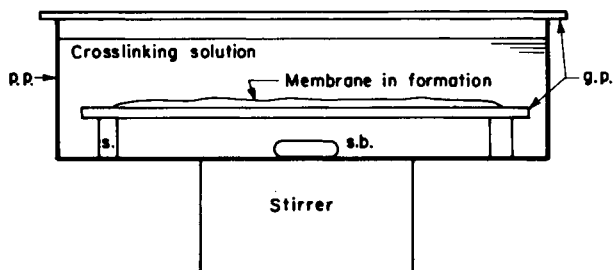


Fig. 2. Ionic crosslinking system (wet technique): g.p. = glass plate; p.p. = Pyrex pan; s. = support; s.b. = stirring bar.

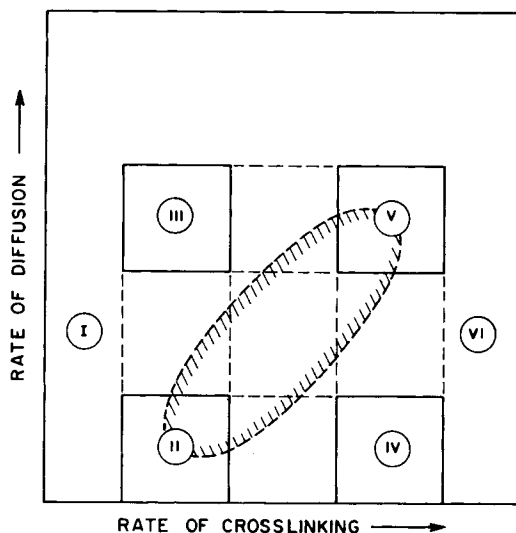


Fig. 3. Qualitative model for homogeneous membrane formation in the wet technique. Shaded area is optimum.

Case I

Reaction is very slow; the rate of reaction is comparable to the low rate of diffusion of the polymer outward into the crosslinking solution. Disruption and dispersal of the polymer phase occur, with a substantial proportion of the reaction occurring outside the original cast film.

Case II (and V)

Reaction is slow (or fast for case V) but fast enough to allow insolubilization of the film surface preventing any outward diffusion of the polymer. Since the reaction rate is now of the same order of magnitude as the diffusion rate of the metal ion, film formation by an approximately uniform gelling proceeds. Crosslink density increases with time. Both cases II and V lead to successful membranes and differ only in time scales. Case II may be transformed into case V by an increase of the temperature of the crosslinking bath when the activation energies of diffusion and reaction are of suitable magnitudes.

Case III

Here, diffusion of metal ion is fast relative to chemical reaction, and chemical reaction, although slow, is faster than diffusion of polymer out of the film. A uniform distribution of metal ion occurs through the cast film, and the rate of formation depends on the rate of crosslinking. It is still possible to have successful membrane formation if enough time is allowed for the appropriate crosslink density to be achieved.

Case IV

The crosslinking reaction is fast compared to diffusion, the situation opposite to case III. Here, as the reaction proceeds, the crosslink density is much larger than in case III. The process soon becomes diffusion controlled, as metal mobility through the initial uppermost layers of the film becomes first restricted and eventually interrupted by crosslinking of the surface resulting in a skin.

Case VI

Here, the reaction is very fast on an absolute scale. A skin quickly forms at the polymer-solution interface. Further penetration is practically impossible; the bulk of the cast film solution remains unreacted.

From this scheme it can be concluded that the most successful membranes should be obtained if conditions of cases II or V are present. In other words, it is desirable to have both the rates of diffusion and of reaction controlling the overall rate of formation of the membrane.

Nonsolvent Crosslinking System

In this case the aqueous cast film is in a solution of the crosslinking agent in an organic nonsolvent for the polymer. Besides stopping the diffusion of polymer into the bath, osmotic exchange of solvents takes place between the bath and the film. Eventually, the solvent system in the polymer phase becomes poorer and phase separation may start. Although precipitation of the polymer is the desired effect, it still has to be slow enough to allow the concurrent diffusion and crosslinking reaction of the metal ion to occur homogeneously in order to obtain a successful membrane. The inclusion of a nonsolvent therefore increases the complexity of the analysis since phase separation and changes in reactivity may need to be taken into account. Qualitatively, however, the description remains the same, that is, the formation of the membrane is a result of competing processes.

EXPERIMENTAL**Polymer Preparation**

Acrylic acid (Eastman Chemical Co.) was polymerized in a precipitating medium at 70°C under nitrogen, with benzoyl peroxide (Fisher Chemical Co.) as initiator. The recipe was 0.36% (by weight) benzoyl peroxide, 10.0% acrylic acid, 30.0% ethyl benzene, 59.64% toluene. The reaction was halted after 90 min by cooling. The product (termed polymer B in this report) was washed five times with benzene and dried at 60°C to constant weight. The conversion was 77%. The average molecular weight, measured by viscometry in dioxane, was $\bar{M}_v = 165,000$ using the Mark-Houwink constants for this system found in the literature.¹¹ Also used were poly(acrylic acid) (PAA) solutions (25% by weight) of the series Acrysol A-1 (MW 50,000), A-3 (MW 150,000), and A-5 (MW 300,000) as well as the polyacrylate sodium salt Acrysol GS (12.5% by weight), all from Rohm and Haas.

Membrane Synthesis

The method of preparation of the membrane has been outlined above and is illustrated in Figure 2. In detail, the polymer was dissolved in water at the desired concentration and then, in many cases, neutralized with NaOH. The film was cast on a polished glass plate using a Gardner casting knife with the clearance adjusted to the desired height. The plate was then immersed in a crosslinking solution containing, when possible, 10% by weight of the hydrated salt. All of the solvents and inorganic salts were reagent grade and used as received. About 2 liters of the crosslinking solution was filtered before being added to a shallow Pyrex pan for use. After a desired time in this bath, the plate was transferred to a deionized water bath for at least 24 hr, with frequent changes of water.

Membrane Characteristics

Both the water and aluminum contents of the membrane were determined gravimetrically. Samples preequilibrated in deionized water at room temperature were quickly blotted dry with a Kim-wipe and weighed. They were then transferred to a muffle furnace at 950°C, with the door left partially open to ensure excess of oxygen. When constant weight of ash was obtained, the aluminum content was calculated from the weight of residual ash, Al_2O_3 . The results were expressed in weight percent of water based on the wet film weight, with a reproducibility of 5%. Aluminum content was expressed in wt. % of Al based on the dry membrane, with a reproducibility of $\pm 10\%$. Wet thicknesses were measured with a precision micrometer.

RESULTS AND DISCUSSION

Nonaqueous Crosslinking Bath with Aluminum Salts

The results reported here represent the "wet" casting technique as applied to aqueous solutions of poly(acrylic acid) crosslinked in a nonsolvent bath which contained aluminum ions. Compatibility of the nonsolvent with the polymer solvent, water, would allow osmotic exchange of solvents to occur. Nonsolvents were then selected that had a wide range of acid-base properties, as listed in Table I. Hydrated $\text{Al}(\text{NO}_3)_3$ showed a relatively good solubility in polar organic solvents and served as a source of metal cations for ionic crosslinking.

The results of tests conducted with these nonsolvents are shown in Table II and can be interpreted by the qualitative rate model discussed in the preceding

TABLE I
Properties of Solvents Used^a

Solvent	Class	ϵ	EF	SP, (cal/cm ³) ^{1/2}
Water	Amphiprotic	78.4	144.4	23.4
Methanol	Amphiprotic	32.6	54.1	14.5
Dimethylformamide	Aprotic, dipolar	36.7	140.3	12.1
Acetone	Aprotic, dipolar	20.7	59.6	9.9
Benzene	Aprotic	2.3	0	9.1

^a ϵ = Dielectric constant; EF = $\epsilon\nu$, electrostatic factor, where ν is the dipole moment in debyes, reflects magnitude of electrostatic interactions; SP = solubility parameter.^{12,13}

TABLE II
Membrane Synthesis in Nonsolvent Ionic Crosslinking Media^a

Nonsolvent	$\Delta(\text{SP}),$ (cal/cm ³) ^{1/2}	Treatment and results		
		In pure nonsolvent ($C_{\text{Al}} = 0$)	Rate of exchange	In crosslinking nonsolvent ($C_{\text{Al}} = C^*$)
Methanol	8.9	glassy hazy film (within 10 min)	very fast	very thin "skin" film protecting polymer solution only when at 60°C
Dimethylformamide	12.3	glassy film (within 2-3 hr)	moderate	membrane formation (under strong swelling)
Acetone	13.5	glassy film (within 8-10 hr)	slow	incipient film formation
Benzene	14.3	very slow vitrification (>18 hr)	very slow	no satisfactory film

^a The polymer solutions used, GS (1.25% by weight) and B (25% by weight), both completely neutralized ($\alpha = 1$), showed only small differences in the rates of exchange. C^* is the concentration of the aluminum salt used for crosslinking, which was limited by solubility to 10% (by weight) of hydrated $\text{Al}(\text{NO}_3)_3$ for methanol and DMF, and 2% (by weight) for acetone, probably limiting crosslinking.

section. To assess the effect of the pure nonsolvent, it can be seen that the relative compatibility with water as measured by the difference of solubility parameter $\Delta(\text{SP})$ is an indication of the rate of osmotic exchange. In the case of methanol, a very fast solvent exchange takes place leading to the appearance of opacity within 10 min and resulting in a hard (glassy) film (case III). For the extreme case with benzene, the film formation is extremely slow, even at high concentrations of polymer (similar to cases I and II). Successful membrane formation occurred with dimethylformamide (DMF), which exhibited a moderate rate of exchange with H_2O allowing diffusion and reaction of Al^{3+} (cases II-V). In the case of the methanolic crosslinking solution, a higher temperature was used to increase the crosslinking reaction rate with respect to the rate of vitrification of the polymer gel. Even so, only a very thin clear skin of polymer film was formed which acted practically as a seal, protecting the remaining polymer solution from further crosslinking. One can attribute the skin effect to the faster rate of crosslinking (case IV) at higher temperatures.

TABLE III
Membrane Synthesis in Dimethylformamide

PAA	Film thickness,		$T, ^\circ\text{C}$	Results ^a
	mils	$C_{\text{salt}}, \text{wt. } \%$		
B	8	20	40	strong gel, detaches and disrupts upon swelling in medium
	12	10	50	film formation, with swollen gel (XLT = 9 hr)
	7	10	45	idem, wrinkled upon soaking in H_2O
GS	12	10	24	(XLT = 7 hr) film formation, with "microwrinkled" surfaces
	12	6.5	24	disrupted swollen gel
	12	2	24	cracking upon solvent depletion (glass formation)
	15	10	60	wrinkled film

^a XLT is crosslinking time.

Further experiments with the dimethylformamide system altering the variables, film thickness, salt concentration, and bath temperature again demonstrated the general feasibility of the nonsolvent technique, as can be seen in Table III. Successful films were obtained both with the poly(acrylic acid) prepared in the laboratory (B) and with the commercial Acrysol GS solution.

Although good film formation may be obtained, the strong swelling upon solvent exchange with water appears to cause wrinkles. This swelling appears to be an electrostatic effect, and a knowledge of the interaction of aluminum and carboxylate in the presence of water and dimethylformamide is needed in order to have better control over the process. This wrinkling and swelling in turn was a handicap in measuring their transport properties. Some transport properties of these films will be reported in the second paper in this series.

Aqueous Crosslinking Bath with Various Metal Ions

Previous work in this laboratory¹⁴ had indicated the possibility of employing metals other than Al for ionically crosslinking acrylic acid copolymers, and a more extensive investigation was made presently using poly(acrylic acid).

Two criteria were used for selecting a potential metal ion. The first, based on a metal ion classification, relied on Pearson's hard-soft acid-base principle (HSAB), which assumed that in all generalized Lewis acid-base reactions, "hard acids prefer to bind to hard bases."¹⁵ Accordingly, the carboxylate group which is a hard base would rather associate with a hard acid such as Cr³⁺. Secondly, from a kinetic point of view, the crosslinking reaction is assumed to occur similar to a complex formation in solution, that is, the carboxylic group acts as a substitute ligand to the H₂O (or other) ligand of the hydrated metal ion (for example, the octahedral [Al(H₂O)₆]³⁺). According to Cotton and Wilkinson,¹⁶ extensive studies have led to the remarkable rule that the rates at which a hydrated metal cation combines with a ligand to form a complex are practically the same as, or

TABLE IV
Physical Properties of Metal Ions^a

Metal cation	r , Å	Z/r	Class	k_{ex} , sec ⁻¹
K ⁺	1.33	0.75	H	10 ⁹
Na ⁺	0.95	1.05	H	10 ⁹
Be ²⁺	0.31	6.45	H	10 ²
Mg ²⁺	0.65	3.07	H	10 ⁵
Fe ²⁺	0.76	2.63	BL	2 × 10 ⁶
Co ²⁺	0.74	2.70	BL	4 × 10 ⁵
Ni ²⁺	0.72	2.77	BL	2 × 10 ⁴
Cu ²⁺	0.72	2.77	BL	5 × 10 ⁸
Zn ²⁺	0.74	2.70	BL	4 × 10 ⁷
Pb ²⁺	1.20	1.66	BL	
Cr ³⁺	0.69	4.34	H	2 × 10 ⁻⁶
Fe ³⁺	0.64	4.68	H	10 ²
Al ³⁺	0.50	6.0	H	1
Zr ⁴⁺	0.80	5.0	H	
UO ₂ ²⁺			H	

^a r = Pauling ionic radius; does not represent the "effective" (hydrated) radius in solution; Z = charge of cation; k_{ex} = approximate value for the rate constant of the exchange of ligand H₂O.¹⁶ Class refers to Pearson's hard (H)-soft classification of metals; BL = borderline.^{15,17}

TABLE V
 Membrane Synthesis in Aqueous Solutions of Polyvalent Metal Salts^a

Zn ²⁺			Be ²⁺			UO ₂ ²⁺		
Salt	PAA	Results	Salt	PAA	Results	Salt	PAA	Results
C	B	film formation fast precipit. (white)	S	B	rubbery film	N	GS	rubbery skin
	GS	film formation slow precipit. (white)		GS	weak rubbery no change at $T = 60^\circ\text{C}$		B	film formation yellow leathery ($T = 50^\circ\text{C}$)
	GS (7% by wt)	film formation; weak	C	GS (7% by wt)	weak rubbery			
Zr ⁴⁺			Al ³⁺			Cr ³⁺		
Salt	PAA	Results	Salt	PAA	Results	Salt	PAA	Results
C	B	weak gel	N	GS	film formation	C	B	skin, rubbery film
	GS	$T = 60^\circ\text{C}$ weak wrinkled film		B	film formation		GS	skin, rubbery film
N	B	no cross- linking				S	GS	($T = 60^\circ\text{C}$) hard surface film
S	B	no cross- linking				Alum	GS	film formation

^a C = Chloride; S = sulfate; N = nitrate. Most syntheses at room temperature.

within one order of magnitude of, the rate of water exchange for that ion. This latter process involves the exchange of one H₂O molecule from the "inner" sphere of coordination of the hydrated cation with one H₂O molecule from the bulk solvent. Characteristic rate constants for this exchange of a H₂O molecule (k_{ex}) of selected metal ions are reported in Table IV, along with their classifications.

One can observe that Al³⁺ has a relatively low k_{ex} (1 sec⁻¹) and hence a pseudo first-order rate constant of 10⁻¹ sec. This value is within the same order of magnitude as the range suggested by previous estimates of the rate model. If a relatively low k_{ex} is a necessary condition, Be²⁺ and Cr³⁺ also appear to be candidates for effective crosslinking of PAA membranes, particularly the former, which has a higher charge/radius value and would be expected to behave similar to Al³⁺. Therefore, suitable (water soluble) salts of these were selected. Also tested were the Zr⁴⁺, UO₂²⁺, and Zn²⁺ ions. The results are summarized in Table V.

In general, all these potential crosslinking agents did produce insoluble products. However, they were of different natures, and some, such as those crosslinked in Be salts, slowly disintegrated when soaked in water. Particularly promising were the Zn²⁺ and Cr³⁺ ions as well as the Al³⁺. Additional membrane syntheses were therefore done with Cr³⁺ and are reported in Table VI.

TABLE VI
 Chromium-Based Membranes (Wet Technique)^a

Salt	Reaction conditions	Results
Cr ₂ (SO ₄) ₃	pH 1.5, T = 60°C	hard skin; precipitated polymer underneath
	pH 4, T = 24°C	polymer diffuses out
	pH 2.5, T = 24°C	skin film
	5 min in pH 1, 1 hr in pH 2.5 at 24°C	surface film detaches, weak rubbery upon soaking
	3 min in pH 1, 1 hr in pH 2.5 at 40°C	surface film disrupts; swollen gel upon soaking
	10 min in pH 2 at 60°C, 40 min at 40°C	hard film surface

^a The hydrated salts Cr₂(SO₄)₃, CrCl₃, and chromium alum, CrK(SO₄)₂, were used in these experiments. The polymer solution was 25% (by weight) PAA, A-3, MW < 150,000, neutralized with NaOH. (Similar results were found with other MWs.) Variations in the conditions of the experiments were done in attempts to control the rates of crosslinking and diffusion. Different pHs resulted from dilution of the initial crosslinking solution. Tests conducted with CrCl₃ as crosslinking agent gave similar results to the above. For the tests with CrK(SO₄)₂, the polymer solution was the synthesized poly(acrylic acid) (B) neutralized with NaOH and with 26% (by weight) of polymer in solution. The pH of the 10% (by weight) crosslinking solution of CrK(SO₄)₂ was ~3.

The apparently unique efficiency of Al³⁺ in crosslinking carboxylic polymers can be explained according to the qualitative rate model developed earlier. The formation of a weak rubbery film or gel (such as those observed with Be²⁺ and Zr⁴⁺, for example) can be attributed to a low rate of crosslinking (cases II and III in Fig. 3). Even at high temperatures or at longer crosslinking times, the gel condition persisted. Kinetic inhibition, then, appears to be occurring and could be attributed to two causes, both influenced by pH: (i) The concentration of carboxylic groups is limited, due to only partial ionization. The pH, then, must be high enough to avoid suppression of ionization of the polyacid. (ii) The predominant metal species in solution was not polyvalent. The pH, then, must be low enough to still allow an appreciable concentration of polyvalent cationic species to exist and crosslink.

Thus, effective crosslinking can result with several metals only if a proper choice of salt or pH is made. One quantitative indication of the hydrolysis of the metal cation can be pK_a values, which refer in fact to the equilibrium constant (K₁₁) of the first hydrolysis product of the mononuclear species:



A pH of solution below the value of pK_a is a situation favoring the presence of the more positively charged species. Table VII contains values of pK_a of selected metal ions. Since they have not all been determined under the same conditions, they should be used cautiously. Also included are the predominant mononuclear species within certain pH ranges as well as the pH of crosslinking solutions of typical salts used in this work and by Jarvis.¹⁴

Keeping in mind the limitations of such analysis (which includes concentration effects, such as lower activities and the formation of polynuclear species; the influence of the anion of the salt, such as the possibility to form complexes with the metal cation; and the unknown equilibrium constant for the metal-carboxylate reaction), it is still possible to propose explanations and indicate trends. The effectiveness of Al can be attributed to the salts used because they produced

crosslinking solutions with pH 3–4, in which the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion still predominates and the low concentration of H^+ still allows the carboxylate to react with the metal. (One can further extend the analysis that the concentration of carboxylate is relatively low to justify the relatively slow overall synthesis of the membrane at room temperature.) The ZnCl_2 success can be rationalized similarly. On the other hand, the Be^{2+} , Zr^{4+} , and UO_2^{2+} salts used all produced relatively acidic solutions; and by suppressing the ionization of the carboxylates, they could not be effective.

To test the qualitative predictability of the pH effect, the use of acetates was considered since they would produce less acidic solutions. For both Zn^{2+} and Cr^{3+} , the pH for crosslinking is 6 to 6.5. However, under these conditions only Zn^{2+} remains polyvalent in solution while Cr^{3+} suffers extensive hydrolysis and the predominant species is monovalent. One should expect effective crosslinking only from Zn^{2+} . This was fully confirmed experimentally in the synthesis at room temperature conducted similar to the previous ones. (Note that Cr did produce some effective crosslinking when the chloride or the sulfate salt was used.) Cupric nitrate also selected under the same consideration gave a very good and clear greenish film.

CONCLUSIONS

An exact overall description of the reaction of crosslinking carboxylic groups by metal ions (and therefore the synthesis of membranes) is too complex to fit into a general model. A comparative analysis would certainly have to await a unifying theory of the behavior of metals in solution. However, judicious use of some available physicochemical parameters may still allow some insight into the phenomenon and serve as a guide for a desired application.

Although the wet technique is successful in producing membranes with good mechanical stability with certain salts under proper pH conditions, its rate dependence requires a careful control of the processing parameters.

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