

# An infra-red spectroscopic study of cement formation between metal oxides and aqueous solutions of poly(acrylic acid)

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An infra-red spectroscopic study of the formation of cements between metal oxides and aqueous solutions of poly(acrylic acid) is reported. Oxides of divalent metals form cement gels more readily than oxides of trivalent metals. An attempt was made to gain structural information from the observed frequency shifts of the absorption bands of the carboxylate groups in the metal poly(acrylate) gels relative to those recorded for the purely ionic form. The form of cation binding to the polyanion chain is discussed.

## 1. Introduction

Ionic polymer cements, some of which find a practical application in dentistry [1-3] are formed when certain powdered metal oxides or ion-leachable silicates are reacted with concentrated aqueous solutions of poly(alkenoic acid)s. Cations are extracted into the polyelectrolyte phase of the cement paste where they become bound to polyanionic chains [4]. A hard glass-like gel is formed which binds unreacted powder particles into a cement mass. Wall and Drennan [5] in 1951 considered that the gelation of PAA, poly(acrylic acid), by divalent ions was the consequence of the binding of metal ions to the polyion leading to the formation of salt-bridges.

The nature of the binding of cations to polyanions, which is the cause of phase changes such as gelation and precipitation, has been discussed at length in the literature [6, 7]. The consensus of opinion is that: (i) the counter ions are constrained to remain in the vicinity of the polyanion chain by a general electrostatic field and (ii) that under certain conditions, depending on the chemical nature of the cations and the anionic sites, specific ion binding may also occur. There is evidence for the formation of complexes in some cases [8-10].

There are a number of associated phenomena: the configurational changes of the polyelectrolyte

consequence upon ionization [11] and the disturbance of shells of water of hydration [7, 12]. Indeed certain workers have sought to explain ion-binding in these terms [7, 12].

The evidence for these theories comes from the many methods for the study of ion-binding in solution: electrometric determination of activity coefficient, permeability, chemical analysis, electrolysis studies, observation of molar volume changes, titrimetric and conductimetric techniques [6, 7]. However, these methods are obviously not available for the study of solids and gels, nor can it be certain that the results from solution studies can be extrapolated to solids.

Infra-red spectroscopy offers a useful means of studying interactions between cations and carboxylate groups in liquids, solids and gels. A voluminous literature exists on the subject for mono-, di-, and tri-substituted carboxylic acids. Vibrations due to the carboxylic acid (COOH) group ( $\sim 1700\text{ cm}^{-1}$ ) can be distinguished from those of the carboxylates ( $\text{CO}_2^-$ ) ion and are affected by hydrogen bonding [13-15]. The C-O stretching vibrations of the carboxylate ion are influenced markedly by the cation; the asymmetric mode is more sensitive than the symmetric mode and frequencies vary from 1500 to 1650  $\text{cm}^{-1}$ .

The cause of this variation has been the subject of much discussion [16-29]. Certain workers

have sought to correlate the frequency shifts with the ionic radius of the cation [15, 16], its electro-negativity [17], the bond strength, character and stability complex of the metal-ligand complex [19–23]. Other workers consider that the symmetry of the carboxylate group and the angle of the O–C–O bonds are the determining factor [21, 24, 25].

Donaldson *et al.* [27] and Warriar and his co-workers [28, 29] in reviewing the topic lay emphasis on the role both of bond character and the type of co-ordination in interpreting the direction and magnitude of frequency shifts, an approach which seems the most apposite.

Few studies have been made on poly(carboxylic) acids. Leyte *et al.* [30] studying the counter ion interactions between poly(alkenoic acid)s and alkali and alkaline earth metals could not detect any frequency shifts and concluded, therefore, that there was no specific site binding. Crisp *et al.* [31] used an attenuated total reflectance technique (ATR), developed by Wilson and Mesley [32, 33] for dental cements, to monitor the reaction between an ion-leachable aluminosilicate glass and PAA solutions – the glass-ionomer cement system. They found a frequency shift as between the aluminium and calcium salts. In this study infra-red spectroscopy (ATR) was used to improve the understanding of the character of the bonding in a range of metal oxide–PAA cements.

## 2. Experimental

### 2.1. Materials

The PAA used in this work has been described previously [34] and was prepared by aqueous phase polymerization using ammonium persulphate as the initiator and propan-2-ol as the chain transfer agent. The product had a weight average molecular weight of  $2.3 \times 10^4$  and was concentrated to 50%wt/wt. A sample of PAA was deuterated by evaporating the solution at 37°C and successively dissolving and evaporating from deuterium oxide three times. The final product was ground and sieved through a 170 mesh (90  $\mu\text{m}$ ) sieve.

Good laboratory quality metal oxides were selected for use in this experimental study. Indium (III), lanthanum (III) and copper (II) oxides were used as-received while those of magnesium, calcium and zinc were heated at 1100°C for several hours to reduce their reactivity. Aluminium

oxide was used as-received and, in addition, a sample of  $\alpha$ -alumina was prepared by heating aluminium ammonium sulphate to 1000°C, and  $\gamma$ -alumina by heating the freshly precipitated hydroxide at 840°C. Ferric oxide was prepared by the thermal degradation of hydrated ferric sulphate at 300°C. An alternative sample was prepared from the freshly precipitated hydroxide by heating at 50°C for 5 h.

### 2.2. Methods

Pastes were prepared at 21°C by mixing a weighed amount of metal oxide powder with a known volume of PAA solution on a glass block for 1 min using a dental spatula. The powder/liquid proportion employed was normally 1.5  $\text{g ml}^{-1}$  but in some cases this had to be reduced.

For reactions with deuterated PAA the powdered solid acid was first blended with the metal oxide in the required proportion. The solid mixture was mixed with the required volume of deuterium oxide, using the technique described above.

Part of a prepared paste was transferred to an ATR cell which was placed in the spectrometer as quickly as possible. Spectra were recorded on a Parkin Elmer 621 spectrometer with transmission scale expansion up to  $\times 3$ , and a scan rate of 450  $\text{cm}^{-1} \text{min}^{-1}$ . The ATR unit was a Research and Industrial Instruments Co Model TR5 with a KRS-5 crystal, a hemicylinder of thallium bromide-iodide. The angle of incidence was 55°.

ATR spectra were recorded 3 and 10 min and 1, 3, 6 and 24 h following the preparation of a paste. In some experiments it became necessary to tighten the back plate of the ATR cell which invalidated a direct comparison between the absorptions of a particular band in different spectra. However, relative intensities of different bands could still be compared.

## 3. Results

The spectra of pastes formed by the metal oxides which react with PAA in  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  solution are given in Figs. 1 to 7 and assignments made in Tables I to VII. Reference spectra for PAA, and sodium poly(acrylate), are given in Table VIII.

Band assignments are based on the standard texts by Bellamy [35] and Nakamoto [36], and the general literature. Bands of particular importance to the present study were the carbonyl C=O stretching mode of the carboxylic acid group

and the asymmetric and symmetric  $\text{CO}_2^-$  stretching modes of the carboxylate groups which are summarized for the various systems in Table IX. There was a water band at  $1630\text{ cm}^{-1}$  which interfered with certain assignments and was eliminated in the deuterated systems. Other bands were recorded and assignments, some of which are speculative, have been made. However, these have little relevance to the present study.

The general pattern of behaviour observed in the reacting cementitious pastes was for the  $\text{C}=\text{O}$  stretching band (at  $1700\text{ cm}^{-1}$ ) of the carboxylic acid group to decline coincidentally with the appearance and enhancement of the  $\text{CO}_2^-$  stretching bands of the metal carboxylates observed in the regions  $1530$  to  $1610\text{ cm}^{-1}$  (asymmetric stretch) and  $1390$  to  $1420\text{ cm}^{-1}$  (symmetric stretch). These results are, of course, indicative of an acid-base reaction.

The reaction between magnesium oxide and PAA is very rapid; no carboxylic acid groups could be detected in the 3 min ATR spectrum, which contained only carboxylate,  $\text{CO}_2^-$ , stretching bands, at  $1535$  and  $1405\text{ cm}^{-1}$ , and there was no detectable change in the spectrum in the following 24 h. These results are illustrated by the 3 h

spectrum (Table I, Fig. 1). Deactivated magnesium oxide had been used, prepared by heat-treatment which according to Livey *et al.* [37] reduces the surface area of the powder, so there was no further possibility of reducing the rate of reaction.

Calcium oxide reacts more slowly (Table II, Fig. 2). Carboxylic acid bands at  $1690$ ,  $1250$  and  $1165\text{ cm}^{-1}$  are prominent in the 3 min ATR spectrum, attenuated in the 1 h spectrum and absent altogether when the paste is 24 h old. Carboxylate bands, at  $1540$  and  $1403\text{ cm}^{-1}$ , are

TABLE I Spectra of MgO-PAA cement gels (all frequencies in  $\text{cm}^{-1}$ )

ATR (3 h)	KBr	Assignment
1640 m	—	Water
1535 s	1530 sb	Asymmetric C—O stretch of salt
1450 w	1450 m	$\text{CH}_2$ deformation
1405 s	1400 s	Symmetric C—O stretch of salt
1350 wsh		$\text{CH}_2$ or CH wagging
1320 m	c.a. 1320 m	$\text{CH}_2$ or CH wagging or in-plane OH deformation
1105 m	c.a. 1100 w	

Abbreviations: s, strong; m, medium; w, weak; b, broad; sh, shoulder; v, very.

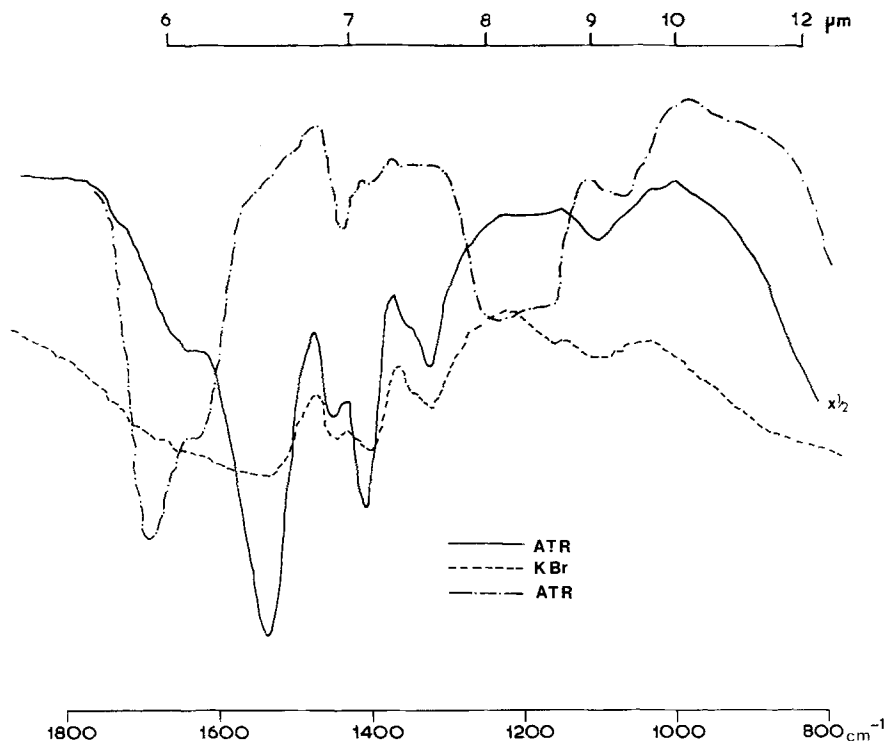


Figure 1 ATR spectrum of MgO/PPA at  $P/L = 1.5$  (—), KBr disc of MgO/PPA at  $P/L = 1.5$  (---), and ATR spectrum of PAA (-.-.).

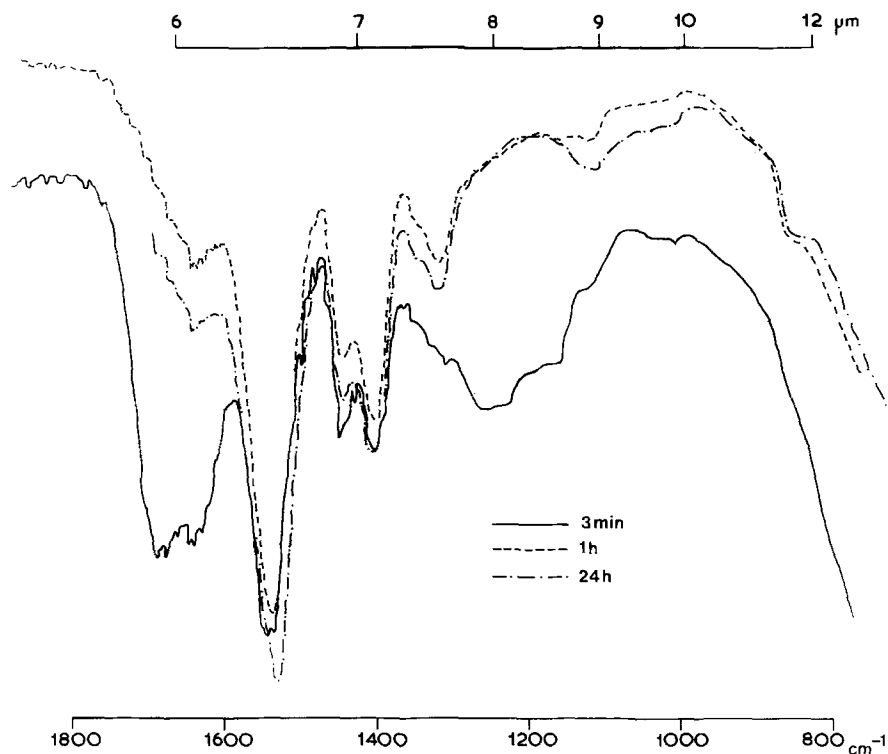


Figure 2 ATR spectra of CaO/PAA at  $P/L = 0.75$  after 3 min, 1 and 24 h after commencement of mixing.

TABLE II Spectra of CaO-PAA cements gels

ATR (3 min)	ATR (1 h)	ATR (24 h)	Assignment
1685 s	1690 sh	—	C—O stretch of acid
1640 s	1640 s	1645 w	Water
1540 s	1538 s	1530 s	Asymmetric C—O stretch of salt
1450 m	1450 m	1450 m	CH <sub>2</sub> deformation
1403 m	1405 m	1405 m	Symmetric C—O stretch of salt
—	1320 m	1320 m	CH <sub>2</sub> or CH wagging or in-plane OH deformation
1250 m	1260 vw	—	C—O/OH deformation combination
1165 w	1160 vw	—	COOH or CH <sub>2</sub>
1130 w	1130 w	1120 m	
1110 vw	1110 vw	1110 wsh	
—	750 msh	750 msh	OCO wagging in salt

strongly represented in the 3 min spectra.

The reaction between cupric oxide and PAA is slower and ideally suited for monitoring by the ATR technique. (Table III, Fig. 3). Deuteration has no discernable effect on reaction rate but enables certain regions of the spectra to be interpreted unequivocally. Carboxylate bands develop slowly and in the 24 h spectrum bands at 1675, 1440 and 1190  $\text{cm}^{-1}$  indicate that some acid groups remain unreacted. There are two  $\text{CO}_2^-$  (carboxylate) asymmetric stretching modes, one characterized by a sharp band at 1605  $\text{cm}^{-1}$  and the other by a broad band in the region of 1540  $\text{cm}^{-1}$  in the 3 min spectrum. The former pre-

dominates in the earlier spectra (up to 1 h) and the latter in the later spectra (after 6 h). There is one symmetric  $\text{CO}_2^-$  stretching mode at 1400  $\text{cm}^{-1}$  possibly common to both carboxylate forms.

The reaction with zinc oxide is moderately rapid (Table IV, Fig. 4) and both the carboxylic acid C=O stretching band (1675  $\text{cm}^{-1}$ ) and the asymmetric  $\text{CO}_2^-$  carboxylate stretching band (1550  $\text{cm}^{-1}$ ) are strong in the 3 min spectrum. The carboxylic acid band is greatly reduced after 1 h even so there are indications of unreacted groups in the 24 h spectrum. The deuterated system reacts a little more slowly. The broadening of the asymmetric  $\text{CO}_2^-$  stretching band towards higher fre-

TABLE III Spectra of CuO-PAA cement gels

ATR (3 min)	ATR (3 h)	KBr	Assignment
1700 s	1700 m	1700 m	C-O stretch of acid
1660 } to } 1610 } s	1630	-	Water
1540 sh	1600 s	1590 to 1520 sb	Asymmetric C-O stretch of salt
1445 m	c.a. 1540 s	-	Asymmetric C-O stretch of salt
1410 m	1445 m	1440 w	CH <sub>2</sub> deformation
-	1405 s	1395 s	Symmetric C-O stretch of salt
1320 to 1120 sb	1315 m	-	CH <sub>2</sub> or CH wagging or in-plane OH deformation
	1170 sb	1160 w	COOH or CH <sub>2</sub> twisting

Deuterated system

ATR (2½ min)	ATR (9 min)	ATR (1 h)	ATR (3 h)	ATR (6 h)	ATR (24 h)	Assignment
1685 s	1685 s	1680 s	1675 s	1675 w	-	C-O stretch of acid
1615 vw	1605 m	1605 s	1600 s	1600 sh	1605 sh	Asymmetric C-O stretch of salt
1530 sh	1525 sh	1545 sh	1560 s	1550 s	1540 s	Asymmetric C-O stretch of salt
1440 m	1440 m	1435 m	1445 m	1440 sh	1440 m	CH <sub>2</sub> deformation
1400 m	1410 m	1405 s	1405 s	1400 s	1400 s	Symmetric C-O stretch of salt
-	-	1310 w	1310 w	1310 m	1295 sh	CH <sub>2</sub> or CH wagging or in-plane OH deformation CH <sub>2</sub> twisting
1195 m	1190 m	1195 m	1195 m	1190 m	1190 w	COOH/CH <sub>2</sub> twisting or D <sub>2</sub> O deformation
1110 m	1090 m		1105 w	1095 w	1110 w	
1030 m	1030 m	1030 m	1010 w	1010 w	1010 w	
755 m	760 m	755 m	765 m	765 m	765 m	OCO wagging in salt

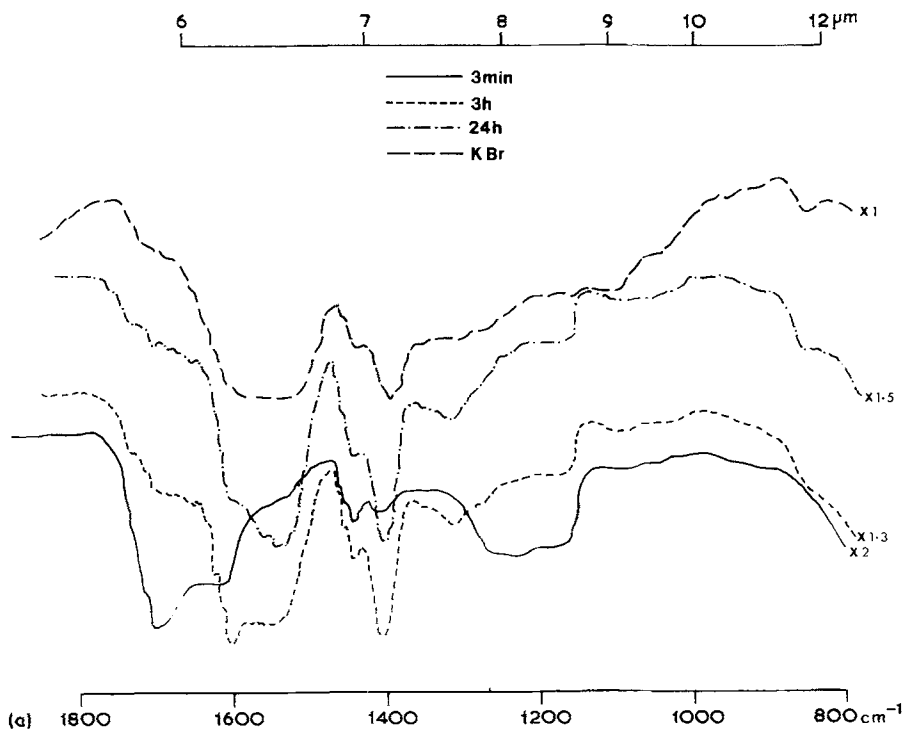


Figure 3(a) ATR spectra after 3 min, 3 h and 24 h from commencement of mixing and KBr disc of CuO/PAA at  $P/L = 1.5$ ; and (b) ATR spectra of the deuterated system at 2.5, 9 min, 1, 3, 6 and 24 h.

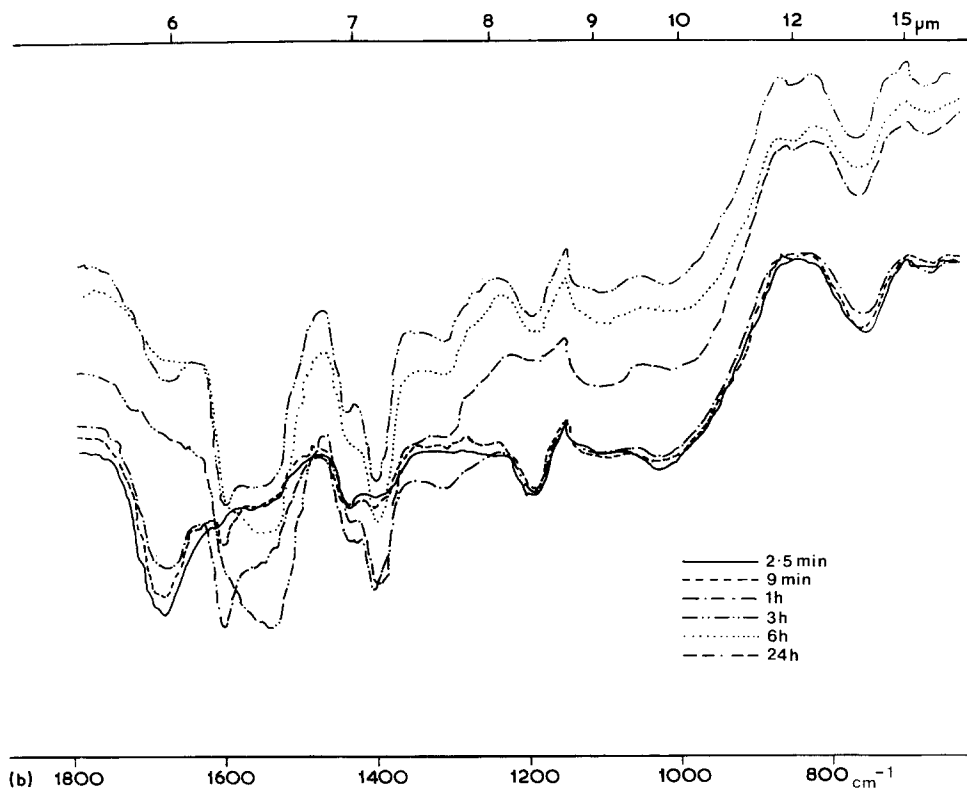


Figure 3 continued.

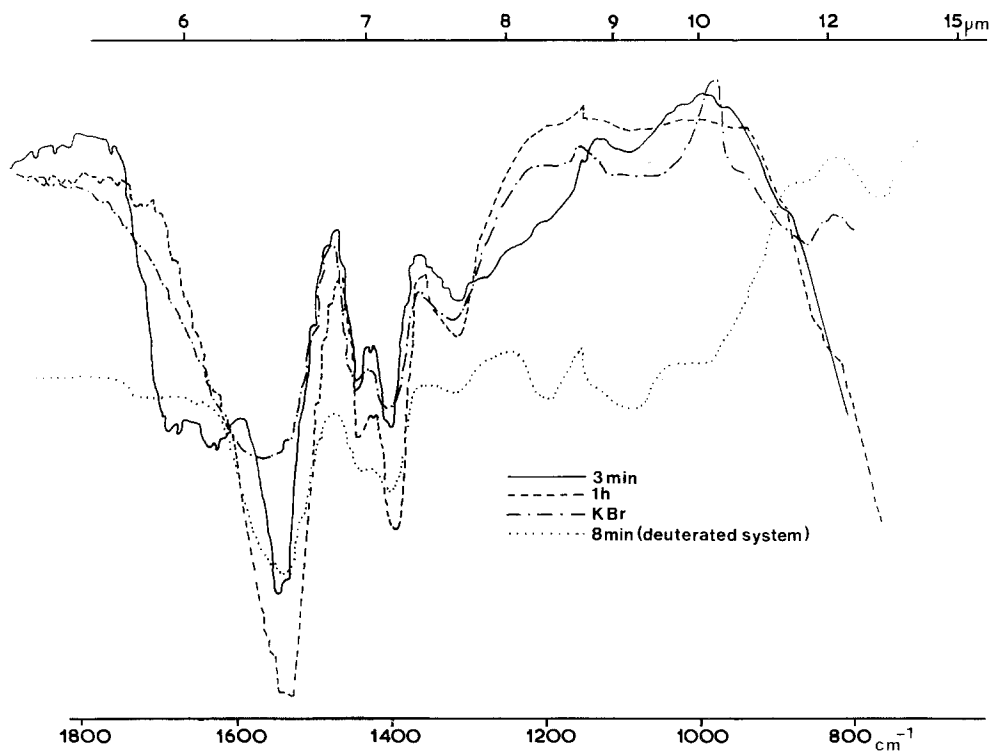


Figure 4 ATR spectra after 3 min and 1 h from commencement of mixing and KBr disc of ZnO/PAA at  $P/L = 1.5$  and ATR spectra of the deuterated system at 8 min.

TABLE IV Spectra of ZnO–PAA cement gels

ATR (3 min)	ATR (1 h)	KBr	ATR (deuterated, 8 min)	Assignment
1680 s	—	—	1740	C–O stretch of acid
1635 s	—	—	—	Water
1545 s	1540 s	1570 s	1540 s	Asymmetric C–O stretch of salt
1445 m	1445 m	1445 m	1440 m	CH <sub>2</sub> deformation
1405 s	1395 s	1405 s	1405 s	Symmetric C–O stretch of salt
1315 m	1315 m	1320 m	1315 w	CH <sub>2</sub> or CH wagging or in-plane OH deformation
—	—	—	1200 m	
1180 w	1180 w	1175 w	1180* sh	COOH or CH <sub>2</sub> twisting
1090 w	1080 vw	1080 vw	1080 m	
—	—	—	980 sh	
—	—	—	850 w	
790 sh	750 sh	—	765 m	OCO wagging in salt

\* D<sub>2</sub>O deformation may contribute.

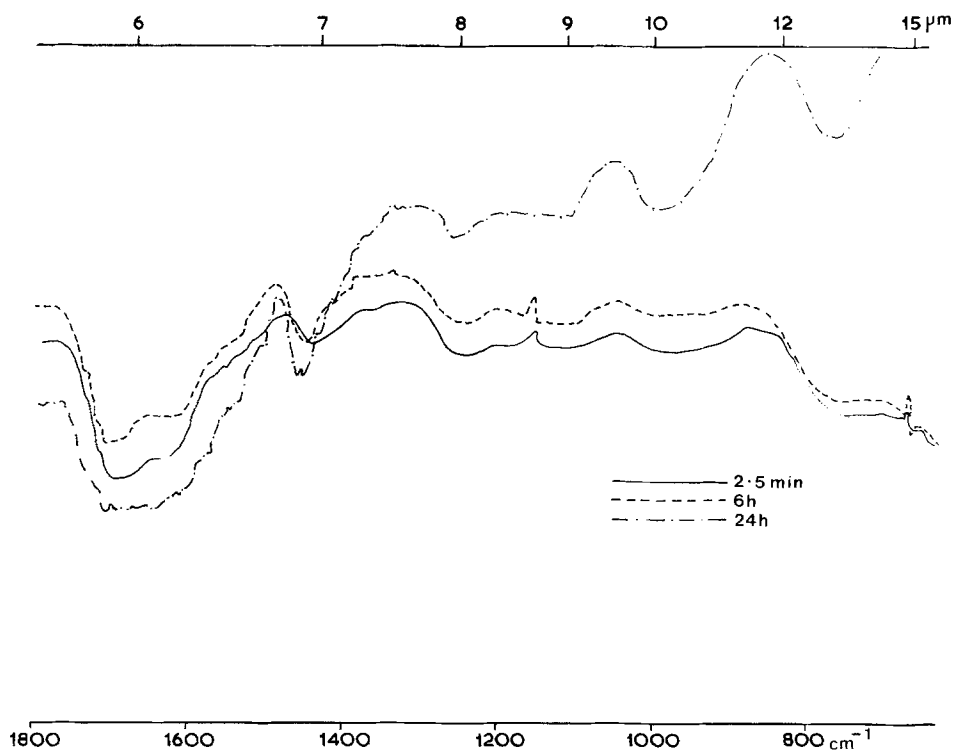


Figure 5 ATR spectra after 2.5 min, 6 and 24 h from commencement of mixing of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/PAA at  $P/L = 0.75$ .

TABLE V Spectra of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–PAA cement gels

ATR (2½ min)	ATR (6 h)	ATR (24 h)	Assignment
1690 s	1705 s	1710	C–O stretch of acid
1630 s	1615 s	to 1600	Water or asymmetric C–O stretch of salt
—	1530 sh	1540 sh	Asymmetric C–O stretch of salt
1440 m	1450 m	1455 m	CH <sub>2</sub> deformation
1250 m	1260 m	1260 m	CH <sub>2</sub> twist
1120 bw	1120 bw	1105 sh	
960 bw	980 bw	990 m	
—	—	765 m	OCO wagging in salt

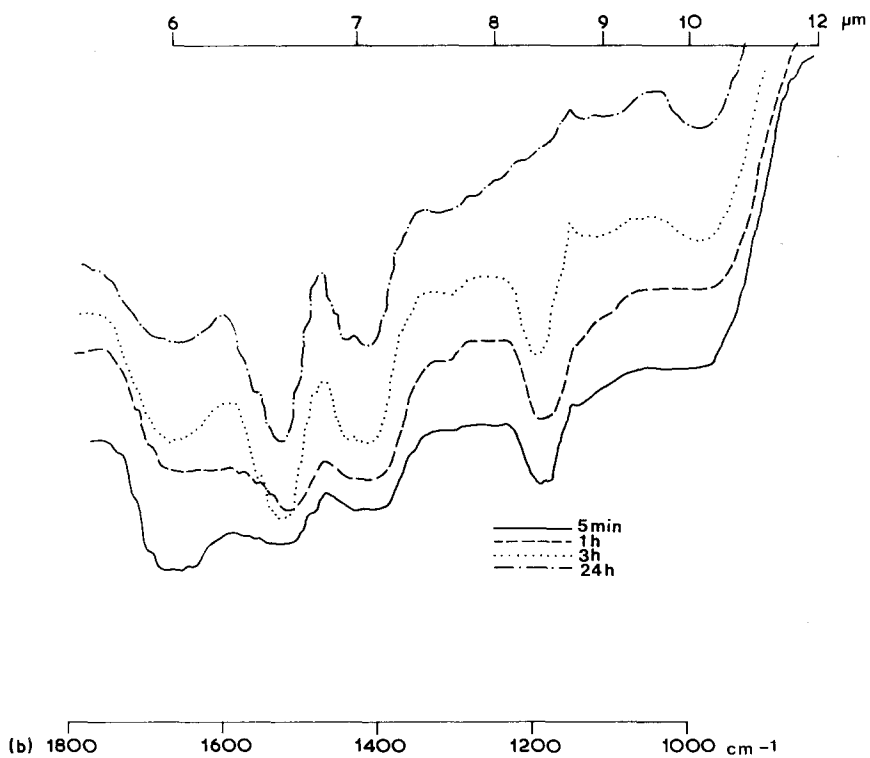
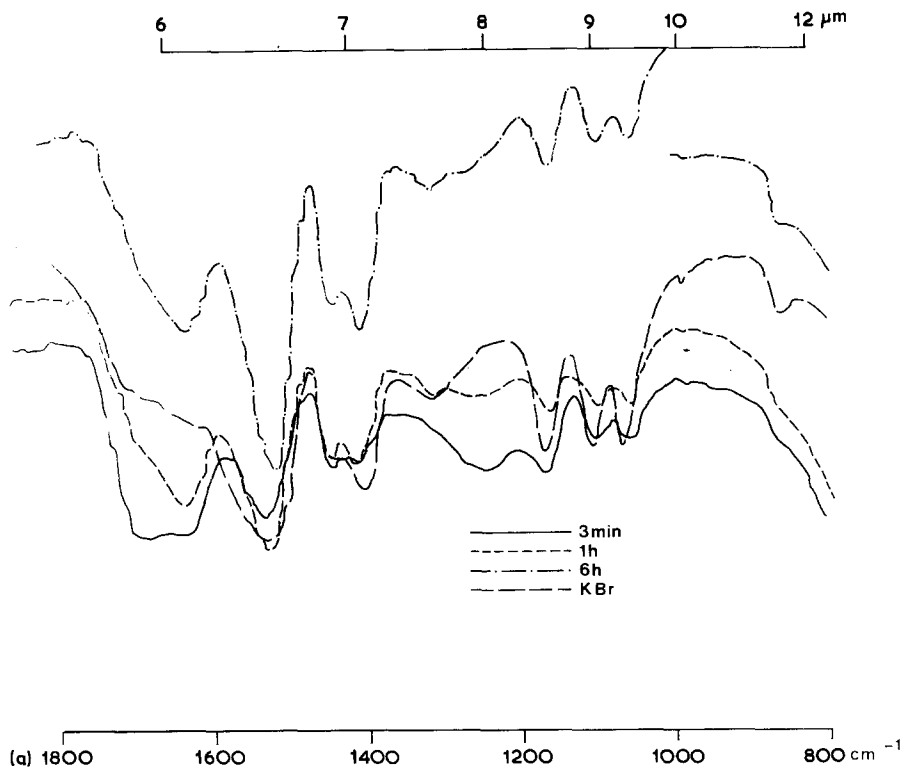


Figure 6(a) ATR spectra after 3 min, 1 and 6 h from commencement of mixing and KBr disc of  $\text{La}_2\text{O}_3/\text{PAA}$  at  $P/L = 1.5$ ; and (b) ATR spectra of deuterated system at 5 min, 1, 3 and 24 h.



TABLE VI Spectra of  $\text{La}_2\text{O}_3$ -PAA cement gels

ATR (3½ min)	ATR (1 h)	ATR (6 h)	K Br	Deuterated				Assignment
				ATR (5 min)	ATR (1 h)	ATR (3 h)	ATR (24 h)	
1700 s	1700 sh	1700 sh	1700 sh	1660 s	1685 sh	1670 s	1660 m	C–O stretch of acid
1640 s	1640 s	1640 s	–	–	–	–	–	Water
1535 s	1530 s	1525 s	1535 s	1530 s	1515 s	1525 s	1525 s	Asymmetric C–O stretch of salt
1445 s	1450 m	1450 m	1450 m	–	1440 sh	1440 m	1445 m	$\text{CH}_2$ deformation
1415 s	1415 s	1415 s	1405 s	1415 s	1410 s	1415 s	1415 s	Symmetric C–O stretch of salt
–	1325 w	1325 w	1325 w	–	1305 w	1310 w	1310 w	$\text{CH}_2$ or CH wagging or in-plane OH deformation
1250 bm	1260 bw	1260 vw	–	–	–	–	–	
1170 s	1168 m	1170 m	1170 m	1180* s	1180* s	1195* s	–	COOH or $\text{CH}_2$ twisting, or from $\text{La}_2\text{O}_3$
1105 m	1105 m	1105 m	1110 m	–	–	1120 w	1120 m	$\text{La}_2\text{O}_3$
1060 m	1060 m	1060 m	1070 m	–	–	–	–	$\text{La}_2\text{O}_3$
–	–	–	–	960 sh	960 sh	980 m	985 m	

\*  $\text{D}_2\text{O}$  deformation may contribute.

quencies in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  systems suggests that the possibility of a second band at  $1600\text{ cm}^{-1}$  cannot be entirely discounted.

Three forms of alumina were used in this study: (I)  $\alpha$ - $\text{Al}_2\text{O}_3$  heated at  $1100^\circ\text{C}$  for several hours, (II)  $\alpha$ - $\text{Al}_2\text{O}_3$  prepared in a fine form by heating ammonium aluminium sulphate at  $1000^\circ\text{C}$  and (III)  $\gamma$ - $\text{Al}_2\text{O}_3$ . The evidence from the ATR spectra shows that form I does not react with PAA for 6 h. The 24 h spectrum shows that the carboxylic acid band ( $1700\text{ cm}^{-1}$ ) and water band ( $1630\text{ cm}^{-1}$ ) broaden towards  $1600\text{ cm}^{-1}$  and coalesce to one band. The carboxylic acid band at  $1200\text{ cm}^{-1}$  broadens towards  $1400\text{ cm}^{-1}$ . Form II does not react with PAA. There is evidence of some reaction between  $\gamma$ - $\text{Al}_2\text{O}_3$  and PAA after some hours (Table V, Fig. 5). However, the carboxylic acid bands remain strong in the 24 h spectrum and the formation of carboxylate is limited. The band at

$1455\text{ cm}^{-1}$  is to be attributed to the ionization of PAA and not to an aluminium carboxylate, since the work by Crisp *et al.* [31] has shown that aluminium polyacrylate has one asymmetric band only at  $1600\text{ cm}^{-1}$ .

Lanthanum oxide reacts moderately rapidly with PAA and carboxylate bands ( $1525$  and  $1415\text{ cm}^{-1}$ ) indicative of salt formation are to be found in the 3 min spectrum. (Table VI, Fig. 6). However, unreacted acid groups persist even in the 24 h spectrum although the intensity of their spectral bands is diminished. The band in the region of  $1700\text{ cm}^{-1}$  is unusually broad and the possibility of a band in addition to the C–O stretch cannot be dismissed.

Bismuth oxide reacts slowly with PAA in  $\text{H}_2\text{O}$  and the rate of reaction is even less in  $\text{D}_2\text{O}$  (Table VII, Fig. 7). In the 3 min spectrum there is a weak shoulder at  $1530\text{ cm}^{-1}$  and a weak band  $\sim 1400$

TABLE VII Spectra of  $\text{Bi}_2\text{O}_3$ -PAA cement gels

ATR (2 min)	ATR (1 h)	ATR (24 h)	Deuterated		Assignment
			ATR (10 min)	ATR (24 h)	
1690 s	1685 s	1690 s	1685 s	1680 s	C–O stretch of acid
1630 m	1625 sh	1630 sh	1650 shw	–	Water
–	1530 sh	1530 sh	1520 sh	1520 sh	Asymmetric C–O stretch of salt
1440 m	1445 } to } 1390 } bm	1440 m	1440 m	1440 m	$\text{CH}_2$ deformation
–		1400 m	1400 m	1390 m	Symmetric C–O stretch of salt
			1255 w	1255 w	
1170–1250 m	1170–1250 m	1170–1250 m	1195* m	1195* m	COOH/ $\text{CH}_2$ twisting
c.a. 1100	1115 m	1140 m	–	–	
985 m	990 m	990 m	1020 m	1010 m	
750 m	750 m	765 m	775 m	765 m	OCO wagging in salt

\*  $\text{D}_2\text{O}$  deformation may contribute.

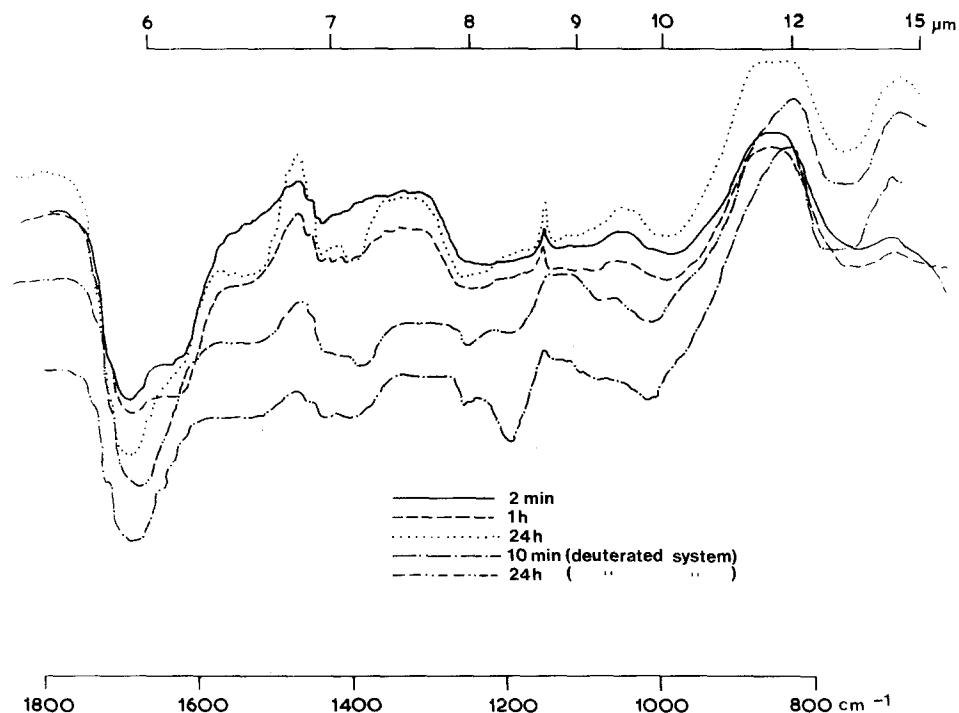


Figure 7 ATR spectra at 2 min, 1 and 24 h from commencement of mixing of  $\text{Bi}_2\text{O}_3/\text{PAA}$  at  $P/L = 1.5$  and ATR of deuterated system at 10 min and 24 h.

$\text{cm}^{-1}$  indicative of only slight salt formation. Even in the 24 h spectrum the carboxylic acid band at  $1690 \text{ cm}^{-1}$  dominates the spectrum. There is, however, some decline in all the carboxylic acid bands ( $1690$ ,  $1440$  and  $1200 \text{ cm}^{-1}$ ) and a definite carboxylate band at  $1400 \text{ cm}^{-1}$  confirming that some acid–base reaction has taken place.

Neither indium oxide nor ferric oxide showed any signs of reaction with PAA, although a reactive form of the latter oxide was prepared by ignition of the oxide [38].

#### 4. Discussion

Results from this infra-red spectroscopic study indicate that salts are formed when PAA in  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  solution is reacted with the oxides of Mg, Ca,  $\text{Cu}^{\text{II}}$ , Zn, Al,  $\text{La}^{\text{III}}$  and  $\text{Bi}^{\text{III}}$ .

The acid–base reaction with divalent metals goes virtually to completion, the rate of reaction decreasing in the order  $\text{Mg} > \text{Ca} > \text{Zn} > \text{Cu}$ . The trivalent metal oxides appear to only partly react with PAA and the reaction may be confined to the surface layer.

The exact position of the asymmetrical and symmetrical  $\text{CO}_2$  stretching modes can be used to gain structural information. In considering possible structures for carboxylate salts it should be remembered that it is the C–O band stretching

frequency which is measured. If the metal–carboxylate band is not purely ionic and co-ordination complexes are formed where there are bands with some covalent character then frequency shifts are to be expected. These shifts will depend on the M–O interaction and the nature of the co-ordination of the metal.

Nakamoto [36] has suggested that there are four types of metal carboxylate structure:

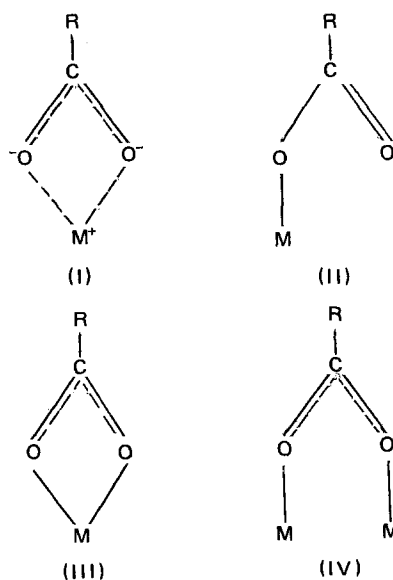


TABLE VIII Spectra of PAA, NaPAA

PAA aq	NaPAA (ATR)	Assignment
1690 s		C–O stretch
1630 m	1640 m	Water
	1540 s	Asymmetric C–O stretch
1435 m	1435 m	CH <sub>2</sub> deformation
1405 vw	1406 s	Symmetric C–O stretch of anion
1350 vw	1310 m	CH <sub>2</sub> wagging
1230 m		
1160 m		
1070 m		

These structures can be envisaged as possible ways in which cations can be bound to poly(acrylate) chains in ionic polymer cements. It should be noted in addition that these structures could be seen as representing half a metal bridge structure linking two polymer chains.

Structure I is purely ionic. Structures II, III and IV admit some degree of covalency in their bonding and the position of the absorption stretching bands in these structures is displaced from the corresponding bands in the ionic model. Several workers have discussed the effects of different coordination on the direction and magnitude of these frequency shifts [27–29, 36]. In structure II the asymmetric stretching frequency increases and the symmetric stretching frequency decreases with the strength of the M–O bond. In the bridge structure IV both asymmetric and symmetric stretching frequencies shift in the same directions probably to increase. The situation in structure III is complex and CO<sub>2</sub> stretching modes may couple with bending and M–O stretching modes [27]. Nakamoto [36] suggests that both stretching modes shift in the same direction while Warriar and Krishnan [29] consider that the asymmetric stretching frequency decreases an observation supported by Patel and Faniran [39].

The asymmetric and symmetric stretching vibrations of the CO<sub>2</sub> group in the various carboxylate salt-gels are compared in Table IX. The asymmetric stretching modes for Mg, Ca and Zn PAA salts are all in the region 1533 to 1540 cm<sup>-1</sup>. Despite differences in charge and ionic radii all are comparable with that of the free ion, the Na PAA salts (1540 cm<sup>-1</sup>). Clearly all these PAA salts are purely ionic (structure I) and these cations are, therefore, not bound to specific sites on the polyanionic chain but held in its vicinity by general electrostatic attraction only.

TABLE IX CO<sub>2</sub> Stretching frequencies of some MO–PAA mixtures. Symmetric and asymmetric stretching frequencies of metal poly(acrylates) measured by ATR

Metal	Asymmetric stretch (cm <sup>-1</sup> )	Symmetric stretch (cm <sup>-1</sup> )
Mg	1535	1403
Ca	1533	1404
Cu	1605, 1545	1405
Zn	~ 1540	1398
Al	1600, 1530	1390
La	1528	1415
Bi	1525	1415
Na	1540	1406
H	1690	1435

Although the Zn PAA spectra implies a pure salt form and there is no definite band at 1600 cm<sup>-1</sup>, there is a suggestion in the broadening of the spectra in this region that there may be a minor proportion of a second complex Zn PAA form.

The La<sup>III</sup> and Bi<sup>III</sup> PAA salt-gels have asymmetric CO<sub>2</sub> stretching modes of lower frequency than those of the pure salt (–12 to –15 cm<sup>-1</sup>) and symmetric stretching modes of higher frequency (+15 cm<sup>-1</sup>). According to Warriar and Krishnan [29] a shift of the asymmetric mode to a lower frequency occurs when the metal is bonded to both oxygens of the carboxylate groups. Therefore, structure III may be tentatively assigned to the La<sup>III</sup> and Bi<sup>III</sup> PAA salts. However, there is a considerable proportion of unreacted carboxylic acid groups present in these reaction mixtures and the free OH groups may play a role in complex formation.

There is evidence that two Cu<sup>II</sup> PAA salt forms co-exist, since there are asymmetric CO<sub>2</sub> stretching modes at 1545 and 1600 cm<sup>-1</sup>. The band at 1545 cm<sup>-1</sup> indicates that one form is purely ionic (structure I), while the other band at 1600 cm<sup>-1</sup> in Cu<sup>II</sup> poly(methacrylate) has been attributed by Leyte *et al.* [40] to a complexing carboxylate group since absorptions at this frequency have been observed for a number of Cu<sup>II</sup> carboxylate complexes [36, 41]. It seems reasonable to apply the same observation to the Cu<sup>II</sup> PAA salt gel. On present evidence it cannot be exactly ascertained whether the Cu<sup>II</sup> PAA complex has the mononuclear structure (II) or the binuclear structure (IV), however the lack of a frequency shift in the symmetric mode suggests the former. There is evidence from solution chemistry (which may not be admissible here) that both forms can co-exist [8]. Again it must be noted that there is a pro-

portion of unreacted COOH groups which may play a role in complex formation. The infra-red spectroscopic data presented here indicate that in the early stages of cement formation the complex Cu-PAA form predominates, but that as the reaction proceeds and the PAA is neutralized, the degree of decomposition of this complex increases and the proportion of the salt form increases.

There are apparently two Al PAA salt forms, since there are asymmetric CO<sub>2</sub><sup>-</sup> stretching frequencies at 1615 and 1530 cm<sup>-1</sup>; in this case the complex form would seem to predominate over the ionic form. Firm conclusions cannot be drawn because the extent of the reaction is small; however, previous work on aluminium poly(acrylate) salt [31] confirms results obtained here. From these results it would appear that both Cu<sup>2+</sup> and Al<sup>3+</sup> are not held by purely ionic forces and both are therefore site bound, in part at least, to the poly(acrylate) chain.

These results receive some support by evidence from stress relaxation studies, reported by Paddon and Wilson [42], on two ionic polymer cements where the matrix is based on metal-poly(acrylate) salts. These cements, which are used in dentistry, are based on the reactions between PAA or related poly(alkenoic acid)s and (a) ZnO containing some MgO: the zinc polycarboxylate cement [1], and (b) ion-leachable glass which releases Ca<sup>2+</sup> and Al<sup>3+</sup> ions: the glass ionomer cement [2, 3]. Stress relaxation measurements show that the polycarboxylate cements shows some plastic behaviour whereas the glass-ionomer cement does not. This observation implies that when Zn<sup>2+</sup> and Mg<sup>2+</sup> ions are bound to poly(acrylate) chain, the chains can slip over each other when a stress is applied, but cannot do so when the Al<sup>3+</sup> ion is bound. These observations would seem to confirm the findings reported here that Zn<sup>2+</sup> and Mg<sup>2+</sup> are held to the poly(anion) chain by general electrostatic interaction whereas Al<sup>3+</sup> ions are site-bound.

## 5. Conclusions

The oxides of the divalent metals Mg, Ca and Zn and the trivalent metals Al, La and Bi, react (after appropriate heat-treatment) with PAA to form carboxylate salt gels. The reaction between the PAA and the oxides of trivalent metals is, however, far from complete. The oxides of In<sup>III</sup> and Fe<sup>III</sup> are unreactive.

The Mg, Ca and Zn PAA salt gels are purely ionic and are therefore bound to the poly(anion)

chains by general electrostatic interactions. There is evidence of some complex formation in the Cu and Al PAA salt gels, which therefore exist in two forms one of which, the complex form, is site bound. There is also some evidence that La<sup>III</sup> and Bi<sup>III</sup> may form weak complexes but of a different co-ordination to those of Cu and Al. The results for Mg, Ca, Zn and Al are supported by stress relaxation studies of dental cements.

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## References

1. D. C. SMITH, *Brit. Dent. J.* **125** (1968) 381.
2. A. D. WILSON and B. E. KENT, *J. Appl. Chem. Biotechnol.* **21** (1971) 313.
3. J. H. ELLIOT, K. A. HODD, L. HOLLIDAY, P. R. HORNBY and A. L. READER, private communications (1974) unpublished data.
4. S. CRISP and A. D. WILSON, *J. Appl. Chem. Biotechnol.* **23** (1973) 811.
5. F. T. WALL and J. W. DRENNAN, *J. Polymer Sci.* **7** (1951) 83.
6. M. L. MILLER, "The Structure of Polymers" (Reinhold, New York, 1966) Chp. 12.
7. A. J. BEGALA, Thesis, Rutgers University, New Jersey (1971).
8. F. T. WALL and S. J. GILL, *J. Phys. Chem.* **58** (1954) 1128.
9. H. P. GREGOR, L. B. LUTTINGER and E. M. LOEBL, *J. Phys. Chem.* **59** (1955) 34.
10. *Idem, ibid* **59** (1955) 990.
11. A. L. JACOBSON, *J. Polymer Sci.* **57** (1962) 321.
12. A. IKEGAMI, *ibid* **A2** (1964) 907.
13. D. CHAPMAN, D. R. LLOYD and R. H. PRINCE, *J. Chem. Soc.* (1964) 550.
14. L. EBERSON, *Acta Chem. Scand.* **13** (1959) 203, 211, 224.
15. D. T. SAWYER and P. J. PAULSEN, *J. Amer. Chem. Soc.* **81** (1959) 816.
16. R. THEIMER and O. THEIMER, *Montansh. Chem.* **81** (1950) 313.
17. R. E. KAGARISE, *J. Phys. Chem.* **59** (1955) 271.
18. B. ELLIS and H. PYSZORA, *Nature* **181** (1958) 181.
19. D. T. SAWYER and P. J. PAULSEN, *J. Amer. Chem. Soc.* **80** (1958) 1597.
20. D. T. SAWYER and J. M. MCKINNIE, *ibid* **82** (1960) 4191.
21. K. NAKAMOTO, Y. MORIMOTO and A. E. MARTELL, *ibid* **83** (1961) 4528.
22. K. NAKAMOTO, P. J. MCCARTHY and B. MINIATAS, *Spectrochem. Acta.* **21** (1965) 379.
23. J. FUJITA, K. NAKAMOTO and M. KOBAYASHI, *J. Phys. Chem.* **61** (1957) 1014.

24. A. I. GRIGOR'EV, *Russ. J. Inorg. Chem.* **8** (1963) 409.
25. A. I. GRIGOR'EV and V. N. MAKSIMOV, *ibid* **9** (1964) 580.
26. D. T. SAWYER, *Ann. NY Acad. Sci.* **88** (1960) 307.
27. J. D. DONALDSON, J. F. KNIFTON and S. D. ROSS, *Spectrochim. Acta.* **20** (1964) 847.
28. A. V. R. WARRIER and P. S. NARAYANAN, *ibid* **23A** (1967) 1061.
29. A. V. R. WARRIER and R. S. KRISHNAN, *ibid* **27A** (1971) 1243.
30. J. C. LEYTE, L. D. ZUIDERWEG and H. J. VLEDDER, *ibid* **23A** (1967) 1397.
31. S. CRISP, M. A. PRINGUER, D. WARDLEWORTH and A. D. WILSON *J. Dent. Res.* **53** (1974) 1414.
32. A. D. WILSON and R. J. MESLEY, *ibid* **47** (1968) 644.
33. *Idem*, *ibid* **51** (1972) 1581.
34. B. E. KENT, B. G. LEWIS and A. D. WILSON, *Brit. Dent. J.* **135** (1973) 322.
35. L. J. BELLAMY "The Infra-red Spectra of Complex Molecules" (Methuen, London, 1954).
36. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds" (John Wiley, New York, 1963).
37. D. T. LIVEY, B. W. WANKLYN, M. HEWITT and P. MURRAY, A.E.R.E., Harwell (1957) HD 2233.
38. S. J. GREGG and K. J. HILL, *J. Chem. Soc.* (1953) 3945.
39. K. S. PATEL and J. A. FANIRAN, *Spectrochim. Acta* **31A** (1975) 123.
40. J. C. LEYTE, L. H. ZUIDERWEG and M. VAN REISEN, *J. Phys. Chem.* **72** (1968) 1127.
41. L. L. SHEVCHENKO, *Ukr. Khim. Zh.* **29** (1963) 1247 (Chem. Abs. **60** (1964) 10063e).
42. J. M. PADDON and A. D. WILSON (1974) unpublished report.

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