

In situ infrared spectroscopic analysis of the adsorption of aromatic carboxylic acids to TiO_2 , ZrO_2 , Al_2O_3 , and Ta_2O_5 from aqueous solutions

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Abstract

In situ infrared spectroscopy has been used to investigate the adsorption of a range of simple aromatic carboxylic acids from aqueous solution to metal oxides. Thin films of TiO_2 , ZrO_2 , Al_2O_3 and Ta_2O_5 were prepared by evaporation of aqueous sols on single reflection ZnSe prisms. Benzoic acid adsorbed very strongly to ZrO_2 , in a bridging bidentate fashion, but showed only weak adsorption to TiO_2 and Ta_2O_5 . Substituted aromatic carboxylic acids; salicylic, phthalic and thiosalicylic, were found to adsorb to each metal oxide. Salicylic and phthalic acids adsorbed to the metal oxides via bidentate interactions, involving coordination through both carboxylate and substituent groups. Thiosalicylic acid adsorbed to the metal oxides as a bridging bidentate carboxylate with no coordination through the thiol substituent group. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Adsorption at metal oxide surfaces in aqueous environments is an important aspect of a number of technological and natural processes, including photosensitisation of semiconductors, the retention of fertilisers and pesticides in soils, catalysis, and photodegradation of pollutants [1–3]. A knowledge of surface processes is required for an

understanding of such systems. Carboxylic acids are commonly found in both natural and technological systems. Carboxylic acid adsorption occurs at metal oxide surfaces, generally through coordination via the carboxyl group, which acts as a ligand for vacant coordination sites of surface metal ions. The mode of carboxylic acid coordination in coordination complexes [4,5] or adsorbed to surfaces [6–8] can be determined using infrared spectroscopy. It has been previously shown that coordination via both functional groups occurs on adsorption of simple dicarboxylic [9] and α -hydroxycarboxylic acids [10] to metal oxides. The metal oxides utilised in this study TiO_2 , ZrO_2 ,

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Al_2O_3 and Ta_2O_5 are industrially important materials [11].

The use of infrared spectroscopy to investigate aqueous systems has been previously hindered by the strong absorptions of water. However, recently a number of in situ infrared spectroscopic studies of the surfaces of thin films have been reported. These studies have used internal reflection (attenuated total reflectance) spectroscopy, which overcomes the water absorptions, to probe processes occurring at thin films of metal oxides [12–17] and other semiconductors [10,18]. Recent publications from this group have reported the application of in situ internal reflectance infrared spectroscopy to determine the nature of adsorption processes of simple α -hydroxycarboxylic acids [10], carboxylated Ru(II) bipyridyl dyes [19] and amino acids [20] with metal oxide films. Recently we reported [9] an in situ infrared study of the adsorption of some aliphatic carboxylic acids to TiO_2 , ZrO_2 , Al_2O_3 and Ta_2O_5 films from aqueous solutions. In the present paper we report a similar such study of the adsorption of some simple aromatic carboxylic acids onto the same substrates and have considered the effect of substituent functionality on the nature of adsorption.

2. Experimental

The preparation of titanium(IV) oxide, zirconium(IV) oxide, aluminium(III) oxide and tantalum(V) oxide hydrosols, containing 1×10^{-1} , 5×10^{-2} , 2.5×10^{-2} and 5×10^{-2} mol dm $^{-3}$ of each oxide respectively, have been reported previously [9,14]. Thin metal oxide films were prepared by overnight room-temperature evaporation of 100 mm 3 of hydrosol on the horizontal face of a 45° single reflection ZnSe ATR prism (Harrick).

Adsorption studies were carried out by placing approximately 1 cm 3 of 1×10^{-3} mol dm $^{-3}$ aqueous adsorbate solutions in contact with the sol–gel films using a hemispherical glass chamber sealed to the prism surface with an O-ring. The infrared spectra of the adsorbate solution species were undetectable at this concentration. Spectra of adsorbed species were obtained with respect to H_2O in contact with the sol–gel films. Adsorption

was indicated by significant enhancement of adsorbate infrared absorptions under these conditions. Infrared spectra of 0.1 mol dm $^{-3}$ adsorbate aqueous solutions were recorded on a bare ZnSe prism with respect to H_2O on the bare prism. Infrared spectra were recorded using a Digilab FTS60 spectrometer fitted with a DTGS detector and Harrick prism liquid cell accessory and calculated from 64 scans at 4 cm $^{-1}$ resolution.

All solutions were prepared with MilliQ (18 M Ω) H_2O . Benzoic acid, potassium hydrogen phthalate, sodium salicylate (BDH), thiosalicylic acid (Aldrich) and NaOH (Merck) were analytical grade and were used as received.

3. Results and discussion

Coordination of a carboxylic acid usually occurs as the deprotonated carboxylate. There are three common carboxylate coordination modes; monodentate, chelating bidentate, and bridging bidentate [4]. The mode of coordination can be distinguished in infrared spectra by their differing separations between the carboxylate antisymmetric and symmetric stretch absorption bands ($\Delta\nu$). Band separations are generally 350–500 cm $^{-1}$ for monodentate binding, 150–180 cm $^{-1}$ for bridging, and 60–100 cm $^{-1}$ for chelating [4,5]. In general, there is little difference in $\Delta\nu$ between the spectra of the solution and bridging carboxylate species. These criteria have recently been successfully applied to the infrared spectroscopic analysis of adsorption of aliphatic carboxylic acids to metal oxide films [9].

3.1. Benzoic acid

Benzoic acid is the simplest aromatic carboxylic acid. Fig. 1a shows the intense spectrum of species adsorbed to ZrO_2 from a 1×10^{-3} mol dm $^{-3}$ aqueous benzoic acid solution. The wavenumbers of the prominent bands in the spectra of benzoic acid adsorbed to metal oxides and of the aqueous benzoate ion are presented in Table 1. The Fig. 1a spectrum contains strong bands at 1595, 1533 and 1392 cm $^{-1}$, with weaker bands occurring at 1442, 1307 and 1179 cm $^{-1}$. A negative band at 1645

cm^{-1} is also present in Fig. 1a and is coupled with a strong broad negative absorption at 3330 cm^{-1} (not shown). The spectrum of the aqueous benzoate ion, shown in Fig. 1b, contains absorption bands at 1542 and 1386 cm^{-1} with a weaker band at 1592 cm^{-1} .

The strong absorptions at 1542 and 1386 cm^{-1} of the aqueous benzoate ion (Fig. 1b) have been assigned to the carboxylate stretch modes [21,22], while the 1592 cm^{-1} band is assigned to a ring stretch vibration. The strong 1533 and 1392 cm^{-1} absorptions in Fig. 1a can therefore also be assigned to the carboxylate stretch modes of benzoate adsorbed to ZrO_2 . The similarity of the carboxylate band splitting of the adsorbed species and the aqueous benzoate ion ($\Delta\nu = 141$ and 156 cm^{-1} , respectively) indicates that a bridging bidentate coordinated benzoate species is formed on ZrO_2 . The bands in Fig. 1a at 1595 , 1499 and 1442 cm^{-1} , and at 1179 , 1070 and 1024 cm^{-1} can be assigned to ring stretch modes and ring C–H

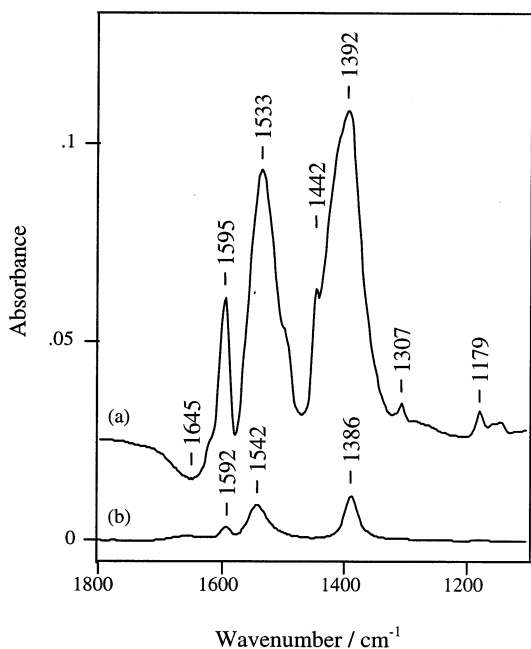


Fig. 1. Internal reflection infrared spectra of (a) $1 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous benzoic acid solution on ZrO_2 sol-gel film and (b) $1 \times 10^{-1} \text{ mol dm}^{-3}$ benzoic acid in $2.5 \times 10^{-1} \text{ mol dm}^{-3}$ aqueous NaOH solution. Reference spectra were of water in contact with (a) ZrO_2 film and (b) bare ZnSe prism.

Table 1

Wavenumber/ cm^{-1} of the absorption maxima in the infrared spectra of benzoic acid adsorbed to metal oxide films from $1 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous solutions and of $1 \times 10^{-1} \text{ mol dm}^{-3}$ aqueous benzoate ion solution

TiO ₂	ZrO ₂	Ta ₂ O ₅	Benzoate ^a	Assignment ^b
1603	1595		1592	v(ring C=C)
1516	1533	1535	1542	v _{as} (CO ₂ ⁻)
	1499			v(ring C=C)
1447	1442			v(ring C=C)
1407	1392	1418	1386	v _s (CO ₂ ⁻)
	1307			
	1179			δ(C–H)
1116	1144			
	1070			δ(C–H)
	1024			δ(C–H)
	869			
	718			

^a $1 \times 10^{-1} \text{ mol dm}^{-3}$ benzoic acid in $2.5 \times 10^{-1} \text{ mol dm}^{-1}$ aqueous NaOH solution.

^b See Refs. [21,22].

bend modes, respectively [21]. The aliphatic monocarboxylic acids, formic and acetic acid, have been shown, using in situ infrared spectroscopy, to adsorb to ZrO_2 films, also forming bridging bidentate surface complexes [9]. The negative absorptions at 1645 and 3330 cm^{-1} (not shown) in Fig. 1a, are assigned to interfacial solvent water displaced following uptake of benzoic acid to the ZrO_2 surface. These negative features are generally more prominent in the spectra of adsorbed aromatic carboxylic acids than in the spectra of smaller carboxylic acids because a greater number of interfacial water molecules are displaced in the adsorption process.

Comparatively weak spectra were obtained from the corresponding experiments with TiO_2 and with Ta_2O_5 (spectra not shown), while no adsorption of benzoic acid was found to occur on Al_2O_3 . The spectrum of benzoic acid adsorbed to TiO_2 contained carboxylate stretch absorptions at 1516 and 1407 cm^{-1} and a ring stretch mode at 1603 cm^{-1} (Table 1). On Ta_2O_5 , adsorption of benzoic acid produced only weak carboxylate stretch absorptions at 1535 and 1418 cm^{-1} . The smaller $\Delta\nu$ values of 109 and 117 cm^{-1} , for TiO_2 and Ta_2O_5 , respectively, possibly indicates the formation of chelating bidentate surface species

on each metal oxide. Tunesi and Anderson [21] have proposed previously the formation of a chelate bidentate surface species ($\Delta\nu = 109 \text{ cm}^{-1}$) from previous in situ infrared studies of adsorption of benzoic acid to aqueous TiO_2 colloids. Formic and acetic acids have been reported previously to adsorb weakly to Ta_2O_5 , but not to TiO_2 or Al_2O_3 films [9]. In situ infrared spectroscopic investigations found formate adsorbed to Ta_2O_5 in a bridging bidentate fashion, while acetate was found to form a chelating bidentate surface species. The difference in adsorption properties between ZrO_2 and Ta_2O_5 was proposed to be a result of the higher Ta(V) charge and coordination number [9].

3.2. Salicylic acid (2-hydroxybenzoic acid)

The infrared spectrum of a $1 \times 10^{-1} \text{ mol dm}^{-3}$ aqueous sodium salicylate solution is shown in Fig. 2a. Analysis of the vibrational spectrum of

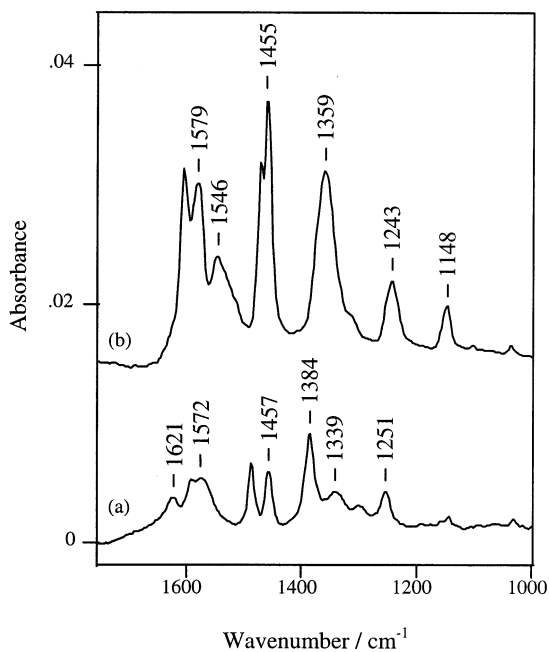


Fig. 2. Internal reflection infrared spectra of (a) $1 \times 10^{-1} \text{ mol dm}^{-3}$ aqueous sodium salicylate solution and (b) $1 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous salicylic acid solution in contact with Ta_2O_5 sol-gel film. Reference spectra were of water in contact with (a) bare ZnSe prism and (b) Ta_2O_5 film.

the aqueous salicylate ion has been discussed previously [21,23]. The absorption band at 1572 cm^{-1} has been assigned [21,23] to the antisymmetric carboxylate stretch mode. The 1384 and 1339 cm^{-1} bands are generated by coupling of the carboxylate stretch mode and the phenolic C–O–H bend mode, while the 1251 cm^{-1} band is assigned to the phenolic C–OH stretch vibration. Absorption bands at 1590 , 1484 , and 1457 cm^{-1} , and 1160 , 1143 and 1029 cm^{-1} are attributed to ring stretch and ring C–H bend modes, respectively. The absorption band at 1621 cm^{-1} is assigned to incompletely compensated solvent.

Fig. 2b shows the infrared spectrum of species adsorbed to a Ta_2O_5 film from a $1 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous sodium salicylate solution. The wavenumbers of bands present in the spectra of salicylate adsorbed to TiO_2 , ZrO_2 , Al_2O_3 and Ta_2O_5 and of the aqueous salicylate ion are presented in Table 2. The similarity in the spectra obtained for adsorbed salicylate on all the metal oxide substrates indicates that a similar mode of binding occurs in each case. On adsorption of salicylate to the metal oxides, the antisymmetric carboxylate stretch mode appears as a weak band at $\sim 1540 \text{ cm}^{-1}$. Following adsorption, the doublet bands at 1384 and 1339 cm^{-1} in the spectrum of the aqueous salicylate ion have been replaced by a single broad feature between 1360 and 1390 cm^{-1} . Similar results have been previously noted in infrared spectra of salicylic acid adsorbed to aqueous TiO_2 [21] and goethite [23] colloids. This band has been assigned [21] to the symmetric carboxylate stretch mode of the adsorbed species. The phenolic C–O–H bending mode, previously coupled with the symmetric carboxylate vibration, is absent from the spectrum of the surface complex. The phenolic C–O stretch band of the salicylate ion (1251 cm^{-1}) appears at 1242 cm^{-1} on TiO_2 , 1243 cm^{-1} on Ta_2O_5 , 1261 cm^{-1} on Al_2O_3 and 1253 cm^{-1} on ZrO_2 . The aromatic ring C=C vibrations of the adsorbed species now occur at ~ 1600 , ~ 1570 , ~ 1470 and $\sim 1460 \text{ cm}^{-1}$, while the C–H bending modes are not greatly affected.

The magnitude of the splitting of the carboxylate bands in the spectra of the adsorbed species ($\Delta\nu = 187$, 168 , 152 and 149 cm^{-1} for Ta_2O_5 ,

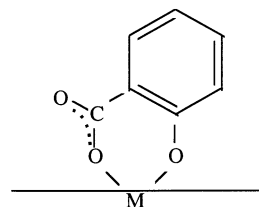
Table 2

Wavenumber/cm⁻¹ of absorption maxima in the infrared spectra of salicylate adsorbed to metal oxide films from 1 × 10⁻³ mol dm⁻³ aqueous sodium salicylate solutions and of 1 × 10⁻¹ mol dm⁻³ aqueous sodium salicylate solution

TiO ₂	ZrO ₂	Al ₂ O ₃	Ta ₂ O ₅	Salicylate	Assignment ^a
				1621	Solvent
1602	1604	1610	1603	1590	v(ring C=C)
1573	1571	1574	1579		v(ring C=C)
				1572	v _{as} (CO ₂ ⁻)
1539	1528	1539	1546		v _{as} (CO ₂ ⁻)
1469	1468	1474	1470	1484	v(ring C=C)
1458	1457	1461	1455	1457	v(ring C=C)
				1384	v _s (CO ₂ ⁻) + δ(C-OH)
1371	1379	1387	1359		v _s (CO ₂ ⁻)
				1339	v _s (CO ₂ ⁻) + δ(C-OH)
				1297	
1242	1253	1261	1243	1251	v(C-O)
				1160	δ(CH)
1149	1145	1150	1148	1143	δ(CH)
	1036		1037	1029	δ(CH)
881	885		886	859	
	762		763		

^a See Refs. [21,23].

TiO₂, Al₂O₃ and ZrO₂, respectively) may indicate the formation of a bridging bidentate bound carboxylate complex. However, the loss of the phenolic OH bending mode and shift of the phenolic C-O(H) stretch vibration on adsorption at each metal oxide indicates that the substituent hydroxy group is possibly involved in salicylate surface coordination [10,21]. Therefore, a chelating bidentate surface salicylate species, coordinated via a C-O bond of the carboxylate group and the C-O bond of the substituent group, is the most likely resulting structure at each metal oxide. This type of adsorption mode, while rarely found for salicylate complexes, is common for complexes of a number of α-hydroxy acids. Steric considerations are likely to forbid tridentate coordination. The Δν values for the adsorbed species are too low to normally consider monodentate carboxylate coordination, but lie, in general, within the range expected for bridging bidentate coordination or for an aqueous carboxylate ion. This indicates that the carboxylate group may remain delocalised following adsorption, as represented below (M is the surface metal ion).



Similar binding modes were also proposed for salicylate adsorbed to TiO₂ [21] and goethite [23] colloids. The carboxylate bond remaining delocalised following coordination as a monodentate carboxylate group may be due to an extended delocalisation of the aromatic ring of the adsorbate or from the 6-membered ring formed at the surface on coordination of salicylate. The change in the ring C=C stretching frequencies can be attributed to the new electronic distribution of the adsorbed ligand [21].

3.3. Phthalic acid (1,2-dicarboxybenzene)

The infrared spectrum of species adsorbed to a ZrO₂ film from a 1 × 10⁻³ mol dm⁻³ aqueous potassium hydrogen phthalate (Hphth) solution is shown Fig. 3. The wavenumbers of prominent

infrared absorption bands of phthalate species adsorbed to the metal oxide films and of aqueous Hphth and phthalate ions are presented in Table 3. The spectrum of a 0.1 mol dm^{-3} aqueous potassium Hphth solution (not shown) contains features due to both the deprotonated carboxylate, with the carboxylate stretch modes occurring at 1550 and 1381 cm^{-1} , and the protonated carboxylic acid group, with the $\text{C}=\text{O}$ stretch at 1704 cm^{-1} (Table 3). The spectrum of a 0.1 mol dm^{-3} aqueous potassium phthalate (0.1 mol dm^{-3} KHphth in $2.5 \times 10^{-1} \text{ mol dm}^{-3}$ NaOH) solution (not shown) contains only features due to the deprotonated carboxylate (Table 3). The strong absorption occurring at $\sim 1400 \text{ cm}^{-1}$ in the spectra of the solution and adsorbed species, while easily mistaken for the symmetric carboxylate stretch, has been assigned previously to a ring stretch mode [21,24].

The spectra of adsorbed Hphth are very similar for each metal oxide, indicating that the same binding mode occurs in each system. The absence of an absorption at $\sim 1705 \text{ cm}^{-1}$ in these spectra indicates that adsorption of Hphth to the metal

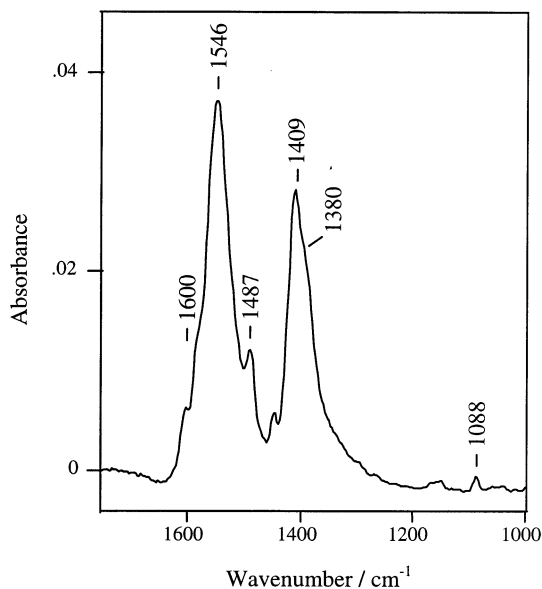


Fig. 3. Internal reflection infrared spectrum of $1 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous potassium hydrogen phthalate solution in contact with ZrO_2 sol-gel film. Reference spectrum was of water in contact with ZrO_2 film.

oxides occurs as the completely deprotonated phthalate species. Each spectrum contains two predominant bands at $\sim 1545 \text{ cm}^{-1}$, due to the antisymmetric carboxylate stretch, and at $\sim 1400 \text{ cm}^{-1}$, assigned to the ring stretch mode as mentioned previously. The absorption of the symmetric carboxylate mode of the adsorbed species occurs as a weak shoulder on the strong $\sim 1400 \text{ cm}^{-1}$ band. The carboxylate stretch absorptions are not enhanced following adsorption. The ring stretching absorptions are not greatly affected on adsorption of Hphth. Previous *in situ* infrared investigations have obtained similar spectral results for phthalate adsorbed to TiO_2 [21] and goethite [23] colloids.

The spectra of the adsorbed species exhibits a carboxylate band splitting of $\sim 160 \text{ cm}^{-1}$ for each substrate, compared with $\Delta\nu \sim 170 \text{ cm}^{-1}$ for the aqueous Hphth and phthalate ions. The similarity of the $\Delta\nu$ values for the adsorbed and solution species may indicate the formation of a phthalate surface complex containing bridging bidentate carboxylate linkages. However, the involvement of each oxygen atom in coordination of the adsorbate seems unlikely on steric grounds. At goethite colloids, phthalate [24] has been proposed to coordinate through a bidentate bridging mode involving only one carboxylate group with the second carboxylate group remaining deprotonated and unbound. While this mode can be confirmed from the $\Delta\nu$ values, adsorption of monocarboxylic acids, e.g. formic, acetic [9], benzoic and thiosalicylic (see later) acids, to TiO_2 and Ta_2O_5 films has been found to be either very weak or to not occur. While the absence of the $\text{C}=\text{O}$ stretch mode from the spectra of adsorbed phthalate rules out the formation of a bidentate surface structure bound to the surface via two formal monodentate carboxylates, Tunesi and Anderson proposed the formation of a similar surface structure, coordinated via delocalised carboxylate groups as represented below. This situation is similar to that proposed for adsorption of salicylate to metal oxides, and the formation of delocalised coordinated carboxylates may account for the absence of enhancement of the carboxylate bands following adsorption.

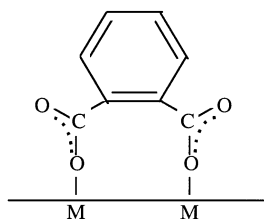
Table 3

Wavenumber/cm⁻¹ of absorption maxima in the infrared spectra of phthalate ion adsorbed to metal oxide films from 1 × 10⁻³ mol dm⁻³ aqueous Hphthalate solutions, of 1 × 10⁻¹ mol dm⁻³ aqueous Hphthalate ion solution and of 1 × 10⁻¹ mol dm⁻³ aqueous phthalate ion solution

TiO ₂	ZrO ₂	Al ₂ O ₃	Ta ₂ O ₅	Hphth	Phthalate ^a	Assignment ^b
				1704		v(C=O)
	1600	1604	1603		1600	v(ring C=C)
	1576(sh)	1576(sh)	1577(sh)			
		1557(sh)				
1547(sh)	1546	1548	1543	1555	1550	v _{as} (CO ₂ ⁻)
1528						
1487	1487	1487	1487		1484	v(ring C=C)
	1445	1449	1444			v(ring C=C)
1404	1409	1406	1405	1401	1402	v(ring C=C)
~1380(sh)	~1380(sh)	1390	~1383(sh)	~1380(sh)	1381	v _s (CO ₂ ⁻)
			1297			
			1266		1288	v(C–O)
			1166			
	1149	1143	1137	1144		δ(C–H)
		1106				
	1088	1087	1088	1077	1089	δ(C–H)
	824					
	754		754			

^a 1 × 10⁻¹ mol dm⁻³ Hphthalate in 2.5 × 10⁻¹ mol dm⁻³ aqueous NaOH solution.

^b See Refs. [21,24].



3.4. Thiosalicylic acid (2-thiobenzoic acid)

Thiosalicylic acid, which contains a thiol substituent group, was found to adsorb strongly from aqueous solution to ZrO₂ and Al₂O₃ films, but only weakly to TiO₂ and Ta₂O₅. The infrared spectrum of species adsorbed to a ZrO₂ film from a 1 × 10⁻³ mol dm⁻³ aqueous thiosalicylic acid solution is shown in Fig. 4. Wavenumbers of bands present in the spectra of aqueous thiosalicylate and of thiosalicylic acid adsorbed to TiO₂, ZrO₂, Al₂O₃ and Ta₂O₅ are presented in Table 4. The Fig. 4 spectrum is dominated by strong absorptions at 1534 and

1390 cm⁻¹, which we have assigned to the carboxylate stretch modes. Other strong bands at 1590 and 1571 cm⁻¹ are, along with the ~1460 cm⁻¹ absorption, assigned to ring C=C stretch modes. The band at 2546 cm⁻¹ is assigned to the thiol (SH) stretch mode [25]. This band was detected only in the spectra of thiosalicylic acid adsorbed to ZrO₂ and Al₂O₃, probably being too weak to be observed in the spectra of species adsorbed to TiO₂ and Ta₂O₅. However, the similarity of the carboxylate absorption bands (Table 4) indicates that an identical mode of adsorption occurs at each substrate. The negative band at ~1620 cm⁻¹ in Fig. 4 can be assigned to the bending mode of displaced interfacial solvent water following adsorption of thiosalicylic acid. The spectrum of thiosalicylic acid in aqueous solution could not be obtained due to low solubility. The spectrum of the aqueous thiosalicylate ion (not shown) contains prominent carboxylate stretch modes at 1543 and 1398 cm⁻¹ (Table 4).

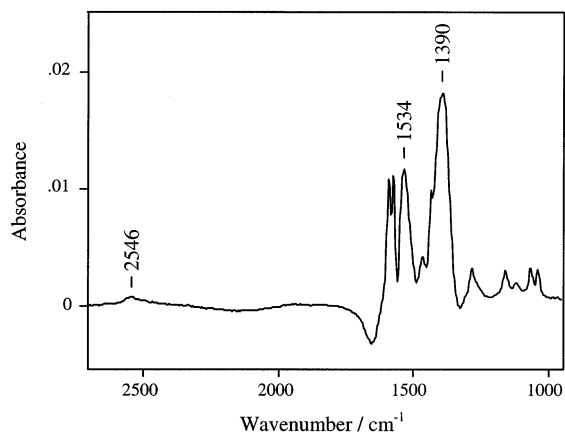


Fig. 4. Internal reflection infrared spectrum of 1×10^{-3} mol dm^{-3} aqueous thiosalicylic acid solution in contact with ZrO_2 sol-gel film. Reference spectrum was of water in contact with ZrO_2 film.

The similarity of $\Delta\nu$ for adsorbed thiosalicylic acid ($\Delta\nu = 126 \text{ cm}^{-1}$ on TiO_2 , 144 cm^{-1} on ZrO_2 , 158 cm^{-1} on Al_2O_3 , 163 cm^{-1} on Ta_2O_5) and the aqueous thiosalicylate ion ($\Delta\nu = 145 \text{ cm}^{-1}$) indicates the surface complex is likely to be bound as a bridging bidentate carboxylate. The presence of the S–H stretch absorption in the spectra ob-

tained on ZrO_2 and Al_2O_3 indicates that the substituent groups are not involved in surface binding of thiosalicylic acid and hence the species is coordinated only via the carboxylate group. This is confirmed on comparison with results for adsorption of benzoic acid to TiO_2 and ZrO_2 (see earlier), where very similar wavenumbers were obtained for the carboxylate absorption bands. This is not surprising, as the soft sulfur-containing substituent group is expected to not participate in coordination to the hard high oxidation state metal ions. This is in direct contrast with salicylic and phthalic acids where the oxygen-containing substituent groups are strongly involved in coordination to the surface metal ions.

3.5. Adsorption of aromatic carboxylates to metal oxides

The nature of adsorption of a range of aromatic carboxylic acids has been determined using infrared spectroscopy. The results obtained have been consistent with previous in situ infrared spectroscopic investigations [9,10] of adsorption of aliphatic carboxylic acids to metal oxides. These have shown that adsorptions of monocar-

Table 4

Wavenumber/ cm^{-1} of absorption maxima in the infrared spectra of thiosalicylic acid adsorbed to metal oxide films from 1×10^{-3} mol dm^{-3} aqueous solutions and of 1×10^{-1} mol dm^{-3} aqueous thiosalicylate ion solution

TiO_2	ZrO_2	Al_2O_3	Ta_2O_5	Thiosalicylate ^a	Assignment
	2546	2543			$\nu(\text{SH})$
1587	1590	1586	1590		$\nu(\text{ring C=C})$
1570	1572	1572	1572	1573	$\nu(\text{ring C=C})$
1522	1534	1543	1537	1543	$\nu_{\text{as}}(\text{CO}_2^-)$
				1504	
1458	1465	1457	1460		$\nu(\text{ring C=C})$
1437	1432	1436	1432	1427	
			1405		
1396	1390	1385	1374	1398	$\nu_s(\text{CO}_2^-)$
1376(sh)				1389	
1280	1281	1283	1282	1279	
1259		1259		1248	
1153	1158	1150	1153	1149	$\delta(\text{CH})$
	1119	1112	1119	1120	
1056	1066	1057	1063	1058	$\delta(\text{CH})$
1037	1038	1037	1039	1031	$\delta(\text{CH})$
	872	979		841	
	745	751		753	

^a 1×10^{-1} mol dm^{-3} thiosalicylic acid in 1.5×10^{-1} mol dm^{-3} aqueous NaOH solution.

boxylic acids to TiO_2 , Ta_2O_5 and Al_2O_3 are weak or do not occur, while these species adsorb strongly on ZrO_2 . The differences in adsorption behaviour of the substrates may be as a result of the magnitude of surface charge on the films. For example, ZrO_2 films prepared by this method exhibit an isoelectric point of ~ 9 [26] while TiO_2 films have a lower isoelectric point close to 5 [15]. The ZrO_2 substrate, with higher positive surface charge at the pH of the adsorbate solutions, may therefore allow greater adsorption of carboxylates from aqueous solution. However when a second possible coordinating functional group is present (e.g. dicarboxylic and ohydroxycarboxylic acids), strong adsorption occurs at all the substrates investigated. Adsorption of substituted aromatic carboxylic acids to metal oxides was found to involve the substituent group in surface coordination when the group contained an oxygen atom. However, when the substituent group was considered to be soft, for example the thiol substituent of thiosalicylic acid, surface coordination to metal oxides occurred only via the carboxylate group.

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