Caesium Fluoride Solutions in Carboxylic Acids

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The systems CsF–HCO_2H, CsF–$MeCO_2H$, CsF–$EtCO_2H$, and CsF–$PrCO_2H$ have been investigated. The results show that the chemical shift of the carboxylic proton, δ(OH), is dependent on the nature of the acid and varies with its pK_a. The i.r. spectra of saturated solutions and solvates, however, display two broad bands characteristic of hydrogen bonding at *ca.* 2 120 and *ca.* 1 550 cm^{-1} which are independent of the acid. These arise from the very strong hydrogen bonding between the fluoride ion and the proton of a carboxyl group.

VERY strong hydrogen bonding between the fluoride ion and the carboxyl group has been the subject of our studies.[1-4] Recently Harmon and Gennick[5] reported similar strong hydrogen bonding between F^- and water.

We have been particularly interested in the chemical shift of the hydrogen-bonding proton[3,4] and we have found this to vary widely from system to system. The actual value of δ(OH) is dependent on factors such as a shift contribution from the magnetically anisotropic carboxylate group, the symmetry of the hydrogen bond, and the electron-withdrawing nature of the group attached to the carboxylate group. Our studies so far have been confined to acetic acid and its halogenated derivatives. In this paper we compare the behaviours of the four acids formic, acetic, propionic, and butyric.

In earlier studies[3] on alkali-metal fluoride solutions it was noted that these gave higher δ(OH) values than the corresponding tetramethylammonium and tetra-n-butylammonium fluorides. This anomaly may now be partly explained by the possibility of contributions from $C-H \cdots F^-$ hydrogen bonding in these fluorides. Harmon *et al.*[6] found i.r. evidence for this sort of bonding in $[NMe_4]F$. Because such quaternary ammonium fluorides can no longer be taken as inert in terms of hydrogen bonding, we have chosen CsF as the salt most suitable for this work.

EXPERIMENTAL

Instruments.—Measurements were made on a Perkin-Elmer R12B spectrometer operating at 60 MHz at 25 °C and referenced internally to $SiMe_4$. Under these conditions there was no evidence of splitting due to coupling with ^{19}F. Infrared spectra were recorded in the range 650—4 000 cm^{-1} on a Perkin-Elmer 457 instrument with NaCl optics. Solutions were studied as liquid films and the solvates as Nujol mulls and as evaporated films. The spectra were aligned against the polystyrene band at 1 601 cm^{-1}.

Materials.—Formic, acetic, propionic, and butyric acids were dried over molecular sieves for a long period. Commercial caesium fluoride was dried by heating *in vacuo*. Caesium fluoride is very soluble in these acids. The concentrations of saturated solutions are: 3 962 g of CsF per kg of HCO_2H, which represents a molality of 26.03 mol kg^{-1} and a CsF : HCO_2H mol ratio of 1.20 : 1; 1 456 g of CsF per kg $MeCO_2H$, 9.58 mol kg^{-1}, ratio 0.51 : 1; 718.4 g of CsF per kg of $EtCO_2H$, 4.72 mol kg^{-1}, ratio 0.42 : 1; and 694.0 g of $PrCO_2H$, 4.57 mol kg^{-1}, ratio 0.39 : 1. The solutions are very viscous and because of this they were unsuitable for n.m.r. study beyond a certain concentration of fluoride. The saturated solution of CsF in HCO_2H turned black on standing.

Crystals of solvate grown from the saturated solutions were separated and analysed by titrating the acid component. In all cases it was the disolvate, $CsF \cdot 2RCO_2H$, which crystallized out of solution. The acetic acid system produced the best sample of crystals which were fine white needles. From the other solvents crystal growth was slower. On heating, the disolvates begin to decompose at 30—40 °C with loss of one molecule of solvent to form the monosolvates, $CsF \cdot RCO_2H$. These are stable up to *ca.* 80—100 °C when they melt, the CsF being in effect soluble in the remaining solvent of crystallization at these temperatures.

DISCUSSION

^1H *N.M.R. Spectroscopic Studies.*—It has been known for some time that an inert solute, inert that is with respect to hydrogen bonding, produces changes in the chemical shift of the carboxylic proton.[7,8] Acetic acid is particularly sensitive in this respect,[3,8] and studies have shown that it is composed mainly of cyclic dimers and trimers in equilibrium. Dilution increases the concentration of the former, which has a higher value of δ(OH), and so the observed value rises on dilution until the acid is very dilute when an appreciable concentration of the acid monomer appears, and this has a low δ(OH) of *ca.* 5.7 p.p.m. with respect to $SiMe_4$.[9,10]

Because of these changes, it is necessary to allow for them in the studies of any solute in carboxylic acids. The effects of diluting acetic, propionic, and butyric acids with cyclohexane are shown in Figure 1, and the equations governing these plots are given in Table 1. Unfortunately C_6H_{12} and other inert solutes are immiscible with formic acid and the only diluant suitable for this solvent was dichloromethane. That this solute may not be inert in hydrogen-bonding terms is suggested by the negative gradient in Figure 1.

The changes in δ(OH) of these acids on addition of CsF are shown in Figure 2, and the equations derived from the plots are in Table 1. After allowing for the dilution effect, these equations were used to calculate the chemical shift of the hydrogen-bonding proton by assuming that extrapolation of the plots of Figure 2 to a 1 : 1 ratio of CsF : acid would be linear. In a previous paper this method was shown to be justified.[3]

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[7] L. W. Reeves and W. G. Schneider, *Trans. Faraday Soc.*, 1958, **54**, 314.

[8] L. W. Reeves, *Trans. Faraday Soc.*, 1959, **55**, 1684.

[9] U. Jentschura and E. Lippert, *Chem. Ber.*, 1971, **75**, 556.

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The value for the $F^- \cdots H{-}O(O)CH$ system is larger than expected but this probably stems from the correction factor from the CH_2Cl_2 studies. If the dilution gradient of C_6H_{12} in acetic acid is taken as representative of the effect this solute would have on formic acid, then a value of 17.9 p.p.m. is obtained for the chemical shift of the very strong hydrogen-bonding proton between the fluoride ion and formic acid. Support for the contention that CH_2Cl_2 was not an inert solute was obtained when it was used as a solute for the other acids. With propionic and butyric acids it produced negative gradients also.

TABLE 1

Hydrogen-1 n.m.r. studies on CsF solutions in carboxylic acids

Solvent acid	δ(OH) solvent [a]	Effect of inert diluant on δ(OH) [a]	Effect of CsF on δ(OH) [a]	Extrapolated and corrected δ(OH) for $F^- \cdots H{-}O$
HCO_2H	11.06	$11.06 - 0.047m$	$11.07 + 0.384m$	19.7 [b]
$MeCO_2H$	11.60	$11.57 + 0.303m$	$11.50 + 0.244m$	15.0
$EtCO_2H$	11.92	$12.00 + 0.014m$	$11.95 + 0.150m$	13.8
$PrCO_2H$	12.04	$12.07 + 0.009m$	$12.00 + 0.160m$	13.8

[a] In p.p.m. with respect to $SiMe_4$. [b] See text.

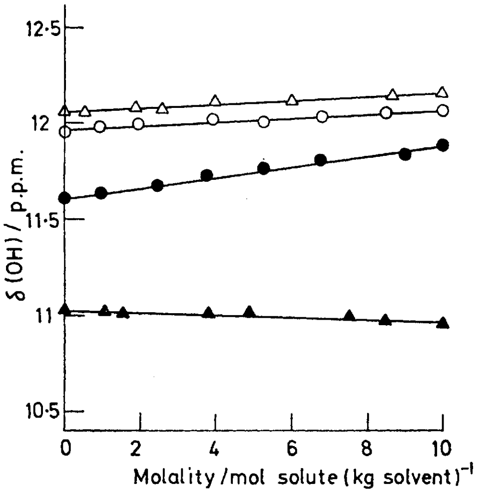


FIGURE 1 Effects of dilution on δ(OH) of carboxylic acids by inert solutes: (▲) $HCO_2H{-}CH_2Cl_2$; (●) $MeCO_2H{-}C_6H_{12}$; (○) $EtCO_2H{-}C_6H_{12}$; (△) $PrCO_2H{-}C_6H_{12}$

The values of δ(OH) of the protons of the hydrogen bond in $F^- \cdots H{-}O(O)CR$ are dependent on R. That of formic acid is the most deshielded while those of propionic and butyric acids are the same indicating a levelling off of the effect of R beyond a certain chain length. This situation is reflected in the changes in pK_a values of these acids: $pK_a(HCO_2H)$, 3.74; $pK_a(MeCO_2H)$, 4.76; $pK_a(EtCO_2H)$, 4.87; and $pK_a(PrCO_2H)$, 4.82. The stronger the acid, the higher the value of δ(OH), and the more deshielded is the acidic proton in the hydrogen-bonding situation. This relation between pK_a and δ(OH) of the acidic protons does not hold for the neat acids as Figures 1 and 2 show.

I.r. Studies.—Caesium fluoride dissolved in the four carboxylic acids at various concentrations showed very similar changes in all the solutions as the concentration of fluoride increased. The spectra of the saturated solutions were often more informative than the spectra of the di- or mono-solvates themselves. In the solvate spectra the hydrogen-bonding peak centred at *ca.* 1 550 cm^{-1} became so broad as to envelop the 1 400—1 800 cm^{-1} region and resolution was lost. On the other hand, with the saturated solution, or in the case of $CsF{-}HCO_2H$ with the solution of concentration 10 mol kg^{-1}, the other peaks in this region can be distinguished (Table 2).

The changes which occurred are as follows: the very broad hydrogen-bonding peak centred at *ca.* 3 000 cm^{-1} and due to the stretching vibration, $\nu_s(O{-}H \cdots O)$, of the solvent dimers gradually disappeared as the concentration of CsF increased. Three other peaks appeared in the spectra and these grew in intensity. The broad peak at *ca.* 3 380 cm^{-1} can be assigned to $\nu_s(O{-}H \cdots O)$ of a hydrogen bond formed between acid molecules of the type (I). The i.r. spectra of the disolvates showed this band clearly, but in the monosolvates it was absent. When a drop of saturated solution was evaporated on a

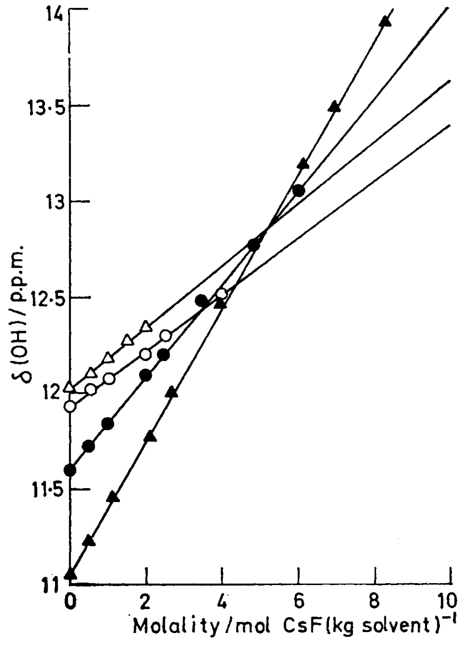
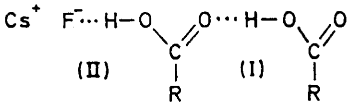


FIGURE 2 Effects of CsF on δ(OH) of carboxylic acids: (▲) HCO_2H; (●) $MeCO_2H$; (○) $EtCO_2H$; (△) $PrCO_2H$



$Cs^+\ F^- \cdots H{-}O{-}C(R){=}O \cdots H{-}O{-}C(R){=}O$

NaCl disc the intensity of this absorption diminished as the loosely bound acid molecules were lost and eventually disappeared when the film reached the monosolvate stage.

Two peaks appeared in the solution and solvate spectra at lower wavenumbers than the ν_s(O–H · · · O) of the original acid. These are broad bands at *ca.* 2 140 and *ca.* 1 550 cm^{-1}. We believe these arise from the F$^-$ · · · H–O bond (II). The band at *ca.* 1 550 cm^{-1} is assigned to ν_s(F$^-$ · · · H–O) on the grounds that it continues to grow in intensity with CsF concentration. The band at *ca.* 2 140 cm^{-1} remained small.

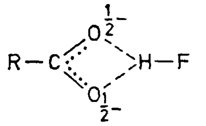
The i.r. spectra of compounds exhibiting very strong hydrogen bonding to an anion are characterized by a broad absorption below 1 800 cm^{-1} and there are several instances of this behaviour in such systems as $RCO_2^-\cdot HO_2CR$[11] and the hydrogen dihalide anions $[XHY]^-$,[12] where X and Y may be the same of different halogens. Joesten and Schaad[13] classified the spectra of hydrogen-bonding species as types (1) and (2). Type (1) have overlapping ν_s bands above 1 800 cm^{-1} and are typical of the asymmetric double-minimum-potential function kind of hydrogen bond. Type (2) spectra have broad bands below 1 800 cm^{-1} which represent a vibration of a very strong hydrogen bond characterized by a single-minimum-potential function. Reinterpretation[14] of the spectra of the hydrogen dihalide ions[12] has confirmed these to be of type (2). The work published here indicated that the spectra of CsF–RCO_2H solvates and of the fluoride species in solution were also of type (2). The hydrogen bond formed between F$^-$ and RCO_2H is therefore of the very strong kind.

The band in the CsF·RCO_2H spectra at *ca.* 2 140 cm^{-1} may be an overtone, a combination, or a proton-transfer band. Contributions from F–H · · · O$^-$ may be expected for these very strong hydrogen bonds which could well take the form of a bifurcated hydrogen bond (III).

TABLE 2

I.r. data (cm^{-1}) for CsF in carboxylic acids

HCO_2H	CsF–HCO_2H (10 mol kg^{-1})	$MeCO_2H$	CsF–$MeCO_2H$ (saturated)	$EtCO_2H$	CsF–$EtCO_2H$ (saturated)	$PrCO_2H$	CsF–$PrCO_2H$ (saturated)	Assignment
665m	670m							
	695m							
	770w					770w	770w	
800m, br				810w	810w			
				840w	840m			
		880w, br	885w			880w	880w	
		925w, br		930w, br		930m		
		1 000m	1 015w		1 000 (sh)			
1 060w	1 065w, br	1 050w	1 045w	1 080m	1 075s	1 090m	1 090m	
1 165s	1 175 (sh)							
1 200 (sh)	1 205vs		1 205vs	1 205vs	1 205vs	1 215vs	1 205vs	
		1 250 (sh)		1 240 (sh)				
		1 285s	1 270vbr	1 285w	1 280 (sh)	1 280s	1 275s	
						1 300 (sh)	1 300 (sh)	
				1 335w	1 335m			
1 355s, br	1 350s, br	1 360m	1 370m	1 380w	1 380m		1 360br (sh)	
	1 385 (sh)							
		1 400s, br		1 410m	1 400 (sh)	1 410s	1 405 (sh)	
				1 465m	1 460m	1 455m	1 460w	
	1 570vs, br		1 550vs br		1 550vs, br		1 550vs, br	ν-(F$^-$ · · · H–O) (II)
				1 660s	1 660vs, br	1 665s	1 660vs, br	ν(CO)
1 715vs	1 725vs, br	1 710vs	1 710vs, br	1 710vs	1 715vs, br	1 705vs	1 700vs, br	
	2 160s, vbr		2 140s, br		2 150s, br		2 120m, br	ν(O$^-$ · · · H–F) (III)
2 550 (sh)	2 515s, br	2 630ms		2 550br	2 440vbr			
	2 680s, br			2 600br	2 610vbr	2 650 (sh)	2 500w, br	
2 920s	2 930s			2 880 (sh)	2 900 (sh)	2 880 (sh)	2 870m	
				2 940 (sh)	2 940s	2 940 (sh)	2 940 (sh)	
				2 980s	2 980s	2 960s	2 960s	
3 040vs, br		3 050vs, br		3 050vs, br		3 050vs, br		ν(O–H · · · O) acid dimer
				3 270 (sh)	3 280 (sh)		3 280 (sh)	
	3 380s, br		3 380m, br	3 370s	3 370s, br	3 370s	3 370s	ν(O · · · H–O) (I)


(III)

The apparent anomaly of our results is that δ(OH) for F$^-$ · · · H–O varies widely whereas the value of ν_s(F$^-$ · · · H–O) remains constant. The problem is partly due to the types of picture of the hydrogen bond which n.m.r. and i.r. portray. The former is in essence a long exposure which blurs out the effects of the hydrogen bond in its different environments. The latter is a quick snap showing all the environments. Thus the i.r. picture shows all the possible hydrogen bonds while the n.m.r.

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picture enables one to calculate the time distribution, *i.e.* the time-averaged contribution which each bond makes to the system.

The results reported here suggest there are two environments of the proton of the hydrogen bond formed between the fluoride ion and the carboxylic acid proton. One of these is (II). The other is probably the proton-transfer hydrogen bond, $F-H\cdots O^-$. In this case, however, the anion is now the carboxylate anion in which both of the oxygen atoms are equivalent, with the negative charge shared between them. This suggests that the second environment may be that of a bifurcated hydrogen bond represented by (III), corresponding to the band at *ca.* 2 140 cm^{-1}. The contribution that (III) will make to the bonding situation should depend on the acid strength of RCO_2H, and our $\delta(OH)$ results seem to support this.

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