Solvent Isotope Effects on Chemical Shifts of Ions in Aqueous Solutions

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MEASUREMENTS of nuclear magnetic shieldings (chemical shifts) and nuclear spin relaxation times of ionic nuclei and solvent nuclei (^1H and ^{17}O) in aqueous solutions are contributing significantly to our understanding of ion–ion and ion–solvent interactions.[1] We report that the isotopic composition of the solvent has marked effects on the shieldings of nuclei in a number of ions in aqueous solution.[2] Our preliminary results for several alkali halides are given in the Table.‡

The isotope shift F^- in 0·5M-KF changes by less than 5% between 10° and 80°. Within experimental error it varies linearly with $D_2O:H_2O$ ratio.[2a] Concentration effects on the isotope shifts have also been observed and will be reported elsewhere. For all ions except $^{19}F^-$, they are within the present experimental uncertainties at concentrations below 1M.

We suggest that the isotope shifts arise because the interactions between ions and their hydration

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‡ Spectra were measured at 15·351, 25·142, 32·083, and 94·075 MHz with a Varian HR-100 n.m.r. spectrometer at 22—23°, and with a Varian DP-60 spectromete requipped with a 56·445 MHz fixed-frequency unit and a V4210A variable frequency unit.

TABLE

Solvent isotope effects on chemical shifts of ions in aqueous alkali halide solutions

Ion	Salt	Concentration (moles/l.)	$\sigma(D_2O) - \sigma(H_2O)$ (p.p.m.)[a]	$\sigma(H_2{}^{18}O) - \sigma(H_2{}^{16}O)$ (p.p.m.)[a]
$^{19}F^-$	NaF	0^b	3·02 ± 0·02	$<0{\cdot}05^{d,e}$
	KF	0^c	3·0 ± 0·06	
$^{35}Cl^-$	NaCl KCl	1—3	4·7 ± 0·3	
$^{79,81}Br^-$	RbBr	0·41—0·82	8·3 ± 0·3	
$^{127}I^-$	NaI	0·45—0·95	13·2 ± 2·5	
$^{7}Li^+$	LiCl	0·49—0·98	0·01 ± 0·02	
^{23}Na	NaBr	0·10—0·39	0·00 ± 0·01	
$^{87}Rb^+$	RbBr	0·25—1·00	0·29 ± 0·06	
$^{133}Cs^+$	CsCl	1·0	1·5 ± 0·2	$0{\cdot}8 \pm 0{\cdot}4^d$
		0·5	1·2 ± 0·2	

[a] All shifts are to higher magnetic fields in solvents containing heavier isotopes. Measurements were made by substitution method or with concentric tubes. Concentrations were closely matched and no susceptibility corrections were made.

[b] Extrapolated to infinite dilution from concentrations between 0·014 and 0·056M.

[c] Extrapolated to infinite dilution from concentrations up to 3M.

[d] Measured in water of natural deuterium content and 95% ^{18}O.

[e] Measured in 0·5M-KF.

spheres are altered by the changes in molecular vibrational amplitudes caused by isotopic substitution. The rather small temperature effect§ on F^- chemical shifts themselves indicates that differences in the bulk properties of the solvent (molar volume, dielectric constant, *etc.*) do not contribute significantly to the isotope effects. The small concentration and counter-ion dependence of the isotope shifts in dilute solutions demonstrate that solvent effects on ion–ion interactions are not responsible for the shifts.

The problem of calculating the isotope shifts can be broken down into two parts. The vibrational part of the calculation requires the assumption of a model (distances, angles, force constants) for the ion–water complex and the calculation of mass effects on its vibrational amplitudes. The results of such a calculation must then be combined with a theory of the chemical shift of the ion nucleus as a function of the internal co-ordinates of the complex. The development of a suitable theory for such calculations is as yet incomplete, but one can make reasonably simple calculations of the *fractional* isotope shift for a particular model and compare the results with the ratios of measured isotope shifts to various estimates of the total shift of an ion in aqueous solution relative to an isolated ion. Assumption of an inverse sixth-power dependence of the shift on the F^- to H distance in an $F^- \cdots H\text{–}O$ system, or the application of the "overlap" type of theory[3] can give results of about 1·5% for the fractional isotope shift. If there are no gross differences in the orientations of solvent molecules relative to different ions, the isotope shifts would be expected to be a nearly constant fraction of the total aqueous solution shifts. A number of rather tentative estimates of the nuclear magnetic shieldings of ions in aqueous solution relative to shieldings in the gas phase have been made[4] by combining various theoretical calculations and experimental results. The deuterium isotope shifts for halide ions seem to be about 1·5% of these estimated total shifts.

Two of us (P.C.L. and J.E.R.) are indebted to the Petroleum Research Fund of the American Chemical Society, The Research Foundation of State University of New York, and the National Science Foundation for financial support of this research.

(*Received, January 5th,* 1968; *Com.* 018.)

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§ Increasing 0·035 p.p.m./degree between 25 and 50° for 0·23M-KF in H_2O.

[1] See: H. G. Hertz, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 311, for a review, and C. Deverell and R. E. Richards, *Mol. Phys.*, 1966, **10**, 551, for recent work on shifts in ions.

[2] (a) A report on an application of the ^{19}F shift in D_2O–H_2O mixtures appeared after completion of this work (C. Deverell and K. Schaumburg, *Analyt. Chem.*, 1967, **39**, 1879). (b) An earlier report [P. M. Borodin, E. K. Legin, E. N. Sventitskii, M. B. Khusidman, and V. A. Shcherbakov, *J. Struct. Chem.* (*U.S.S.R.*), 1963, **4**, 240] on similar ^{19}F shifts contains data and interpretations in disagreement with ours.

[3] J. Kondo and J. Yamashita, *J. Phys. Chem. Solids*, 1959, **10**, 245.

[4] J. Itoh and Y. Yamagata, *J. Phys. Soc. Japan*, 1958, **13**, 1182; Y. Yamagata, *ibid.*, 1964, **19**, 10; D. Ikenberry and T. P. Das, *J. Chem. Phys.*, 1965, **43**, 2199; D. W. Hafemeister and W. H. Flygare, *ibid.*, 1966, **44**, 3584; S. J. Cawley and P. C. Lauterbur, to be published.