area ratio 1.17, and a singlet, 3.67 ppm, area ratio 1.00.

Crystalline 1:1 complexes of I have been prepared with, for example, LiI_3, $NaNO_2$, KI, KCNS, NH_4CNS, CN_3NH_3CNS, RbCNS, CsCNS, $CaCl_2$, $Ba(OH)_2$, $CdCl_2$, $HgCl_2$, and $Pb(OAc)_2$. The potassium thiocyanate complex can be obtained as long, glistening crystals melting at 248–249°, considerably higher than the melting points of the components (172° for potassium thiocyanate). The ammonium thiocyanate complex melts at 187–189° (149° for ammonium thiocyanate). The analytical data on the complexes are satisfactory.[1]

The solubility of I in polar solvents is increased by the addition of soluble complexable salts. For example, the solubility of I in methanol at 30° (1.1 mmoles/l.) is increased to the following values by the presence of the salts at 25 m*M*: NaCNS, 23.6 mmoles/l., KF, 24.7; RbCNS, 25.6; $AgNO_3$, 22.2; $SrCl_2$, 17.9; and $BaCl_2$, 26.6. The complexes tend to be more soluble in organic solvents of high dielectric constant, but most are decomposed by water. All soluble, ionic compounds of the complexable elements form complexes in solvents, such as methanol, regardless of the anion.

Compound II, being a mixture of isomers, forms solid complexes with not so well-defined melting points, but always higher than the melting point of II itself. Some of its complexes, such as that of potassium triiodide, are stable to water. II has the useful property of solubilizing ionic compounds in aprotic solvents including aromatic hydrocarbons. The following are a few examples. Crystals of potassium permanganate are insoluble in benzene, but they begin to dissolve immediately after the addition of II and continue to dissolve until the concentration of permanganate exceeds 0.02 *M*. Crystals of palladous chloride are insoluble in *o*-dichlorobenzene, but when crystals of potassium chloride and II are added, they go into solution as the complex of II with K_2PdCl_4. The salts of many other alkali, alkaline earth, and transition metals have been solubilized by these two methods. A most interesting and useful complex is that of II with potassium hydroxide, which is soluble in toluene to over 0.3 mole/l. This solution saponifies the hindered esters of 2,4,6-trimethylbenzoic acid by the normal acyl–oxygen fission.

Not all complexable salts, however, can be solubilized even in the better aprotic solvents. Salts of high crystal lattice energy, such as potassium fluoride, sulfate, nitrate, phosphate, and carbonate, do not form complexes in aprotic solvents, and neither can these complexes be isolated as solids from protic solvents, such as methanol.

A detailed paper on the cyclic polyethers and their complexes with metal salts is being prepared for publication.

[1] Crystalline etherates of the alkali metal salts have not been common heretofore. Two ($[Na(CH_3OCH_2CH_2OCH_2CH_2OCH_3)_2][Ta(CO)_6]$ and $[K(CH_3OCH_2CH_2OCH_2CH_2OCH_3)_3][Mo(CO)_5I]$) are mentioned by F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 318.

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Observation of Helix–Coil Transition Using Nuclear Magnetic Resonance Halogen Ion Probe Technique

Sir:

Recent work has shown that nuclear magnetic resonance of halide ions may be a valuable tool for investigating the gross physical characteristics and specific chemical reactivities of large biological molecules in solution.[1] This note reports an observation of the well-substantiated helix–coil transition in synthetic poly-L-glutamate using ^{35}Cl resonance, and thus illustrates a direct application of wide-line nmr to the study of macromolecular structure. The ^{35}Cl line width is usually determined by quadrupole relaxation so that in the extreme narrowing limit the line width for a nucleus of spin $^3/_2$ is given by eq 1, where $\Delta\nu$ is the

$$\Delta\nu = \frac{2\pi}{5}(e^2qQ)^2\tau_c \qquad (1)$$

full line width in cycles per second at half-height, q is the electric field gradient at the nucleus with quadrupole moment Q, τ_c is the correlation time for molecular rotation, and the asymmetry parameter has been neglected.[2] In aqueous sodium chloride solutions the chloride ion is symmetrically solvated producing a field gradient at the nucleus close to zero and a line width of about 16 cps. If, however, the quadrupolar chlorine nucleus can be found at environmentally different sites in solution, the line width will depend on the relative concentration of each site, the values of $(e^2qQ)^2$ and τ_c associated with each site, as well as the frequency with which the ^{35}Cl nucleus samples the various sites. In the case where exchange of the chloride is fast with respect to $1/\pi\Delta\nu$, a single composite line is observed with the line width given by

$$\Delta\nu = (\Delta\nu_a)P_a + (\Delta\nu_b)P_b \qquad (2)$$

where $\Delta\nu_a$ and $\Delta\nu_b$ are the contributions to the line width associated with sites a and b, while P_a and P_b are the probabilities that the chlorine is at site a and b, respectively.[3]

When a 2 *M* sodium chloride solution is made 10^{-3} *M* in mercuric chloride, the $^{35}Cl^-$ resonance is broadened to 34 cps. The effect is explained by the rapid exchange of chloride ions in solution with the covalent chlorine associated with the $HgCl_4^{2-}$ complex; thus, eq 2 correctly describes the line width. Since a similar effect is observed with species of the type RSHgCl in sodium chloride solutions, where R is almost any organic molecule, the mercury atom provides a convenient label for investigating changes in the correlation time of the molecule to which it is attached.[1]

In aqueous solutions of low pH, poly-L-glutamate acquires a helical structure while at higher pH the randomly coiled form predominates. The transition from the helical to the randomly coiled structure has been investigated as a function of pH using measurements of optical rotation, viscosity, per cent ionization, optical rotatory dispersion, and the infrared spectrum.[4,5] In solutions of low salt concentration the

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[1] T. R. Stengle and J. D. Baldeschwieler, *Proc. Natl. Acad. Sci. U. S.*, 55, 1020 (1966).

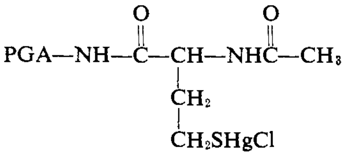
[2] A. Abragam, "The Principles of Nuclear Magnetism," The Clarendon Press, Oxford, 1961, p 314.

[3] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

transition is quite sharp at about pH 5.8, but in 0.2 *M* sodium chloride the transition is shifted to approximately pH 5.2.

Poly-L-glutamic acid (DP 530) as the sodium salt was purchased from Pilot Chemical Co. Sodium chloride, mercuric chloride, sodium hydroxide, and potassium hydrogen phthalate were purchased as analyzed reagents from the Baker Chemical Co. The N-acetyl-DL-homocysteine thiolactone was obtained from Professor L. Stryer of Stanford University. The ^{35}Cl line-width measurements were made on a Varian Model V-4300 nmr spectrometer at 4.3 Mc using 500-cycle modulation and lock-in-detection to stabilize the base line.

Poly-L-glutamate was labeled at the terminal amide function by reaction with N-acetyl-DL-homocysteine thiolactone using the method reported by Benesch and Benesch.[6] The solutions measured were made using a sodium hydroxide–potassium hydrogen phthalate buffer over a pH range from 4 to 8. All solutions were 1.00 *M* in sodium chloride, 1.0 × 10^{-4} *M* in mercuric chloride, and 0.18% poly-L-glutamate by weight. On mixing the labeled poly-L-glutamate with the mercury solution, the mercury adds to the -SH group so that the total molecule observed may be represented as



$$\mathrm{PGA{-}NH{-}\overset{\overset{\Large O}{\|}}{C}{-}\underset{\underset{\underset{CH_2SHgCl}{|}}{CH_2}}{\underset{|}{C}}H{-}NH\overset{\overset{\Large O}{\|}}{C}{-}CH_3}$$

Although the mercury(II) is in approximately a tenfold excess, the line broadening caused by 10^{-4} *M* mercury(II) in 1.0 *M* sodium chloride is less than 2 cps.[7] Under these conditions the probabilities of the chloride being at each site are a constant from one solution to the next so that any change in line width reflects only changes in the correlation time of the mercury site induced by the variations of pH. The experimental results are summarized in Figure 1.

The detailed features of the experimental curve are in excellent agreement with those reported by Idelson and Blout for optical rotation as a function of pH for a 0.2% solution of poly-L-glutamate in 0.2 *M* sodium chloride.[4] In that plot, however, there was a maximum at about pH 4.6 and the authors suggested that the decrease from the maximum rotation associated with the helical form could be caused by a contraction of the helix resulting from protonation of the carboxyl groups. While such a maximum is consistent with the data in Figure 1, the data are also consistent with a straight line of zero slope. This indicates that a change in the correlation time for the helix associated with such a contraction is on the order of the experimental error for this technique. These results demonstrate that the halogen ion probe is a sensitive technique for the investigation of structural properties and gross behavior of large molecules in solution.

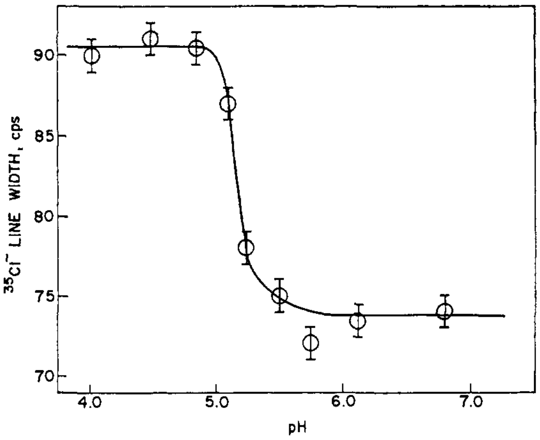


Figure 1. ^{35}Cl line width as a function of pH for 0.18% poly-L-glutamic acid in 1.0 *M* sodium chloride showing the poly-L-glutamic acid helix-coil transition at pH 5.2.

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(4) M. Idelson and E. R. Blout, *J. Am. Chem. Soc.*, **80**, 4631 (1958).

(5) P. Doty, A. Wada, J. T. Yang, and E. R. Blout, *J. Polymer Sci.*, **23**, 851 (1957).

(6) R. Benesch and R. E. Benesch, *Biochim. Biophys. Acta*, **63**, 166 (1962).

(7) At high pH the OH$^-$ ion interferes with the chloride exchange at the mercury site; however, below pH 9 the exchange is unaffected: R. Bryant, unpublished results.

Oxidation of Radon in Aqueous Solutions

Sir:

We have observed an apparent oxidation of radon in aqueous oxidizing solutions under certain conditions. Previously, Fields, Stein, and Zirin reported that a radon fluoride of low volatility was formed when radon and fluorine were heated to 400°,[1] but research on the chemistry of radon has been limited because of the short half-life and high specific activity of radon, a radioactive daughter of radium.

In our experiments, 10^{-7} *M* $RaBr_2$ solutions were allowed to remain in contact with various aqueous, oxidizing solutions for a period of 23 days or longer (six half-lives of radon). These solutions were then extracted with equal amounts of hexane. The relative amounts of radon in the two phases were determined by counting the 0.35-Mev α activity of a subsequent daughter, ^{214}Pb. The samples were counted after a 2-hr aging period which was sufficient time to essentially establish a state of secular equilibrium between the ^{222}Rn and the ^{214}Pb. The ratios of the ^{214}Pb counting rates in the two phases are given in Table I as the distribution ratio of radon between hexane and the various aqueous solutions. The error given is the standard deviation of the 6–12 trials run on each particular aqueous phase. A change from a nonpolar species in water to a polar or ionic species in oxidizing solutions is apparent. This behavior is not due to merely the influence of electrolyte in the aqueous phase. Tatsuya

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(1) P. R. Fields, L. Stein, and M. H. Zirin, "Noble Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago, Ill., 1963, pp 113–119; *J. Am. Chem. Soc.*, **84**, 4164 (1962).