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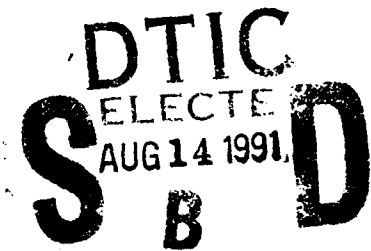
TECHNICAL REPORT 9110

The Effect of Changes in Acidity and Salinity on
the Octanol Water Partition Coefficient of Monomethylmercuric
Species Present in Aquatic Environments at High pE

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The octanol/water partition coefficient (K_{ow}) of methylmercury was determined at pH 7 in water and in aqueous solutions ranging from 0.0003 M to 0.6000 M in sodium chloride. It was also determined over a pH range of 2 to 10 with a fixed sodium chloride concentration of 0.0045 M. In these experiments, K_{ow} was seen to increase with increasing chloride concentrations in the range 0.0 to 0.075 M, with the sharpest increases in the range 0.00 to 0.01 M. K_{ow} was seen to decrease as the pH increased from 5 to 8. Results were similar whether low levels of methylmercuric chloride or methylmercuric hydroxide were used as the starting materials. Partitioning was not affected by changes in ionic strength in the range 0.01 to 0.6 M. Changes in partitioning behavior are attributed to an exchange of chloride and hydroxide anions on the methylmercuric cation. This equilibrium is predicted to produce a predominance of methylmercuric chloride at low pH and high salinity and methylmercuric hydroxide under the reverse					
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conditions. Because of its lower polarity, methylmercuric chloride would be predicted to have a higher K_{ow} than the hydroxide, and also a greater rate of uptake by aquatic organisms. A K_{ow} of $0.07 \pm .05$ is reported for methylmercuric hydroxide and $1.7 \pm .2$ for methylmercuric chloride.

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INTRODUCTION

Mercury has been released to the environment by a variety of military activities. Mercury fulminates are the primers of choice when optimal sensitivity and brisance are required. Prior to World War II fulminates of mercury were used as primer material in the majority of American-made ordnance (1). In addition, releases have been associated with use of the mercury cell process in manufacturing chlorine and with mercury used as a catalyst in the manufacture of vinyl chlorides such as lewisite. Mercury contamination is also generated by the burning of coal at military installations. Mercury is not removed from coal by modern washing methods. During the combustion of coal, mercury is converted to an uncharged metallic vapor which cannot be removed from exhaust gases by electrostatic precipitation.

The principal forms of mercury found in oxygenated (surface) waters are ion pairs and complexes with mercury in the +2 oxidation state (2). The reduction of mercury +2 to the metallic form has a higher standard potential (+0.789) than the majority of metals encountered in aqueous environments (3). This property results in significant acidity of the water molecules complexes to mercury I ions (3). Loss of protons from water complexed with electron withdrawing cations generates a mixture of compounds (3). In pure water, at very low pH, little dissociation occurs and Hg^{+2} predominates. At successively higher values of pH, increased amounts of HgOH^+ and Hg(OH)_2 are observed (4). In brackish water some hydroxyl groups are replaced by chloride and in sea water Hg(Cl)_2 , Hg(Cl)_3^- and Hg(Cl)_4^{2-} and sulfur containing species predominate (5).

Mercury in the +2 oxidation state can be methylated both by microorganisms and abiotically to form monomethylmercury cation, CH_3Hg^+ , and dimethylmercury $(\text{CH}_3)_2\text{Hg}$ (6). The latter form is usually generated only at pH values greater than 7 (3). Essentially all (>99%) of the mercury in edible fish tissue is methylmercury (7). Aqueous environmental monomethylmercury exists primarily as methylmercuric chloride and methylmercuric hydroxide. The carbon-mercury bond is stable in methylmercury compounds, whereas anions associated with the metal exchange easily; thus, the relative proportions of these compounds vary in response to changes in pH and salinity in a manner analogous to that described above for mercury +2 ions (5).

Determination of the coefficient of partition of a compound between 1-octanol and water (K_{ow}) is important to environmental research. Such values can be used in predictive models to estimate solubility, transport and bioconcentration of compounds in the environment (8). Because of its lower polarity, methylmercuric chloride would be predicted to have a higher K_{ow} (9) than the hydroxide, and also a greater rate of uptake by aquatic organisms (10).

Log K_{ow} values of 0.62 for mercury metal (11), and 2.26 for dimethylmercury (12) have been reported. In addition, a value for log K_{ow} of 0.6 has been found for the partition coefficient of methylmercuric chloride in the diethyl ether/water system (13). However, a search of the literature has failed to find K_{ow} values for either methylmercuric chloride or methylmercuric hydroxide.

Because of the importance of methylmercury as a pollutant and because of the pronounced effect of pH and salinity, it was concluded that an experimentally determined K_{ow} was required and that an understanding of the effects produced by changes in pH and chloride content was part of this. In this paper we present K_{ow} values for methylmercury (II) starting as the chloride and as the hydroxide. Values were determined at pH 7 in ultrapure water and at thirteen different salinities. They were also determined at fixed salinity at nine different pH values.

MATERIALS AND METHODS

1-Octanol was obtained from the Aldrich Chemical Company (guaranteed purity 99%) and fractionally redistilled. Ultrapure water was purchased from New England Reagent Laboratory; methylmercuric chloride and methylmercuric hydroxide were purchased from the Alfa Chemical Division of Morton Thiokol Corporation. Aqueous solutions of these two methylmercuries were prepared at 1000 ppm. Solutions of each of the two were checked for purity by HPLC with refractive index detection and diluted to 10 ppm with ultrapure water or with sodium chloride solutions of known concentration. The ultrapure water and the saline solutions that were used for all testing except the highest pH experiment were prepared with the appropriate buffer at a concentration of 0.01 M. The buffers used were: phosphate at pH 2, oxalate at pH 3, succinate at pH 4, acetate at pH 5, succinate at pH 6, phosphate at pH 7 and 8, and borate at pH 9 and 10. All partitions were carried out at ambient temperature (20-25 C°).

The ultrapure water and saline solutions for the high pH experiment were adjusted to pH 12 with NaOH and used without buffering. The effect of ionic strength on K_{ow} was tested by holding the salinity at 0.05 M and increasing the ionic strength with additions of NaClO₄. Perchlorate concentrations were 0.01 M, 0.05 M, 0.1 M and 0.6 M.

The concentration of mercury in octanol could not be assayed directly. To overcome this problem, the following procedure was used: Three aliquots of each aqueous test solution were removed for analysis and three additional aliquots were extracted with equal volumes of octanol by shaking for 20 min. The mixtures were allowed to separate for 10 h, the octanol removed, and the aqueous portions analyzed. The concentration of methylmercury in an octanol extract was calculated as the difference in concentration between the original and octanol-extracted aqueous samples.

To ensure that the mercuric compounds were partitioning as expected, and that adsorption or other phenomena were not producing erroneous results, the octanol fractions from these experiments were pooled and back-extracted with four successive additions of pure water.

Analyses of aqueous fractions and back-extracts were performed on a Beckman SpectraSpan V sequential plasma emission spectrometer. Calibration standards were prepared from stock solutions of mercuric chloride (Fischer Scientific) in water. The samples and standards were adjusted to 5000 ppm lithium to obscure sodium or other metal emissions. The emissions of the samples at 253.652 nm were recorded and mercury concentrations calculated by interpolation.

RESULTS

The values of K_{ow} for methylmercuric species as a function of chloride concentration are shown in Fig.1. Pairwise comparisons between the K_{ow} means, when either methylmercuric chloride or methylmercuric hydroxide were used as the source of methylmercury, show no statistically significant differences ($p > 0.10$) according to the Student's T-test. The mean K_{ow} was $0.07 \pm .05$ in ultrapure water and increased to $1.7 \pm .2$ at chloride levels above 0.075 M. Subsequent experiments with methylmercuric hydroxide, in the salinity range up to 0.037 M NaCl, reveal a zone of nearly linear increase in K_{ow} with salinity between 0.0000 M and 0.0047 M NaCl. At higher levels, increases in salinity produced smaller changes in K_{ow} (Fig 2).

Increase in pH of the system from pH 2 to pH 6 had little effect on K_{ow} , but further increases caused a sharp decrease in K_{ow} (Fig 3). Samples at pH 12 containing 0.001 M and 0.01 M NaCl had K_{ow} s statistically indistinguishable from those between pure water and octanol.

An additional experiment was designed to assess the effect of changes in ionic strength. Raising the ionic strength of a 0.0047 M chloride solution with potassium perchlorate at pH 7 in the ionic strength range of 0.01 M to 0.6 M did not affect the partitioning behavior.

Back-extractions of octanol pooled from these experiments confirmed that the octanol contained a quantity of mercury consistent with that lost from the water and salt solutions through partitioning.

DISCUSSION

The salinities chosen in this study approximate the range of chloride concentrations encountered in natural ecosystems. Altman and Dittmer (14) report a chloride level of 8 ppm (0.0002M) as a mean for North American river water, and sea water is approximately 19,000 ppm (0.54M) in chloride (15). Aquatic environments in the pH range of 6 to 8 are generally optimal for fish (16) and this is also the range in which methylmercury exhibits its greatest change in K_{ow} .

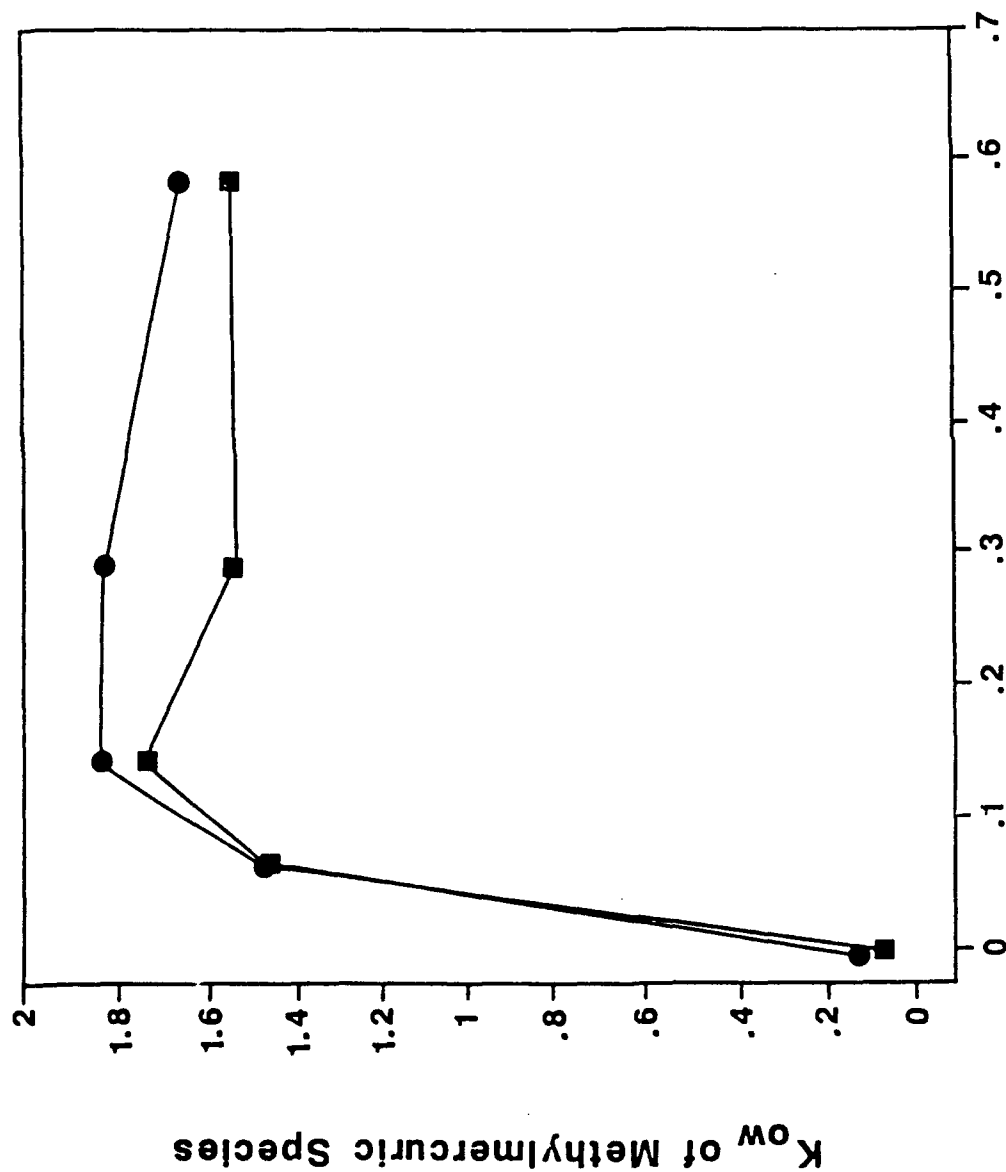
Observed increases in K_{ow} with increasing chloride concentration and decreasing pH are consistent with displacement of hydroxide by chloride on the methylmercuric cation. Similarly, the near zero K_{ow} of methylmercury in pure water and in saline solutions at high pH is attributed to a high proportion of methylmercuric hydroxide. From the behavior of the K_{ow} /salinity curve, we believe that the K_{ow} of methylmercury hydroxide is very nearly equal to the K_{ow} we observed with either species in ultrapure water and in test solutions at pH 12 ($0.07 \pm .05$). Conversely, the K_{ow} of methylmercuric chloride (1.7 ± 0.2) is equal to the K_{ow} of the methylmercury equilibrium mixture at high salinity.

The constancy of K_{ow} values for methylmercuric chloride in the ionic strength range 0.0047 to 0.6 at pH 7 may be attributed to the compound's high water solubility and small size.

The difference between the K_{ow} values for methylmercuric ion in pure water and in strong chloride solutions was $+1.6 \pm 0.2$. A difference of this magnitude should have some effect on bioconcentration. Bioconcentration factors of 0.03 and 0.84 were calculated for methylmercuric hydroxide and chloride in fish by means of the Arthur D. Little "CHEMEST" program (10). This program is useful in estimating environmental behavior of compounds from their physical/chemical properties. Thus, the absorption of methylmercury compounds by aquatic organisms should be enhanced by increased salinity and by decreased pH. However, current methods for estimation of bioconcentration were established with organic compounds that accumulate primarily in fat whereas mercury can also bind to sulfur. This property may provide additional sites of accumulation of mercury on sulfhydryls in protein and be a cause for inaccuracy in the estimation of bioconcentration factors.

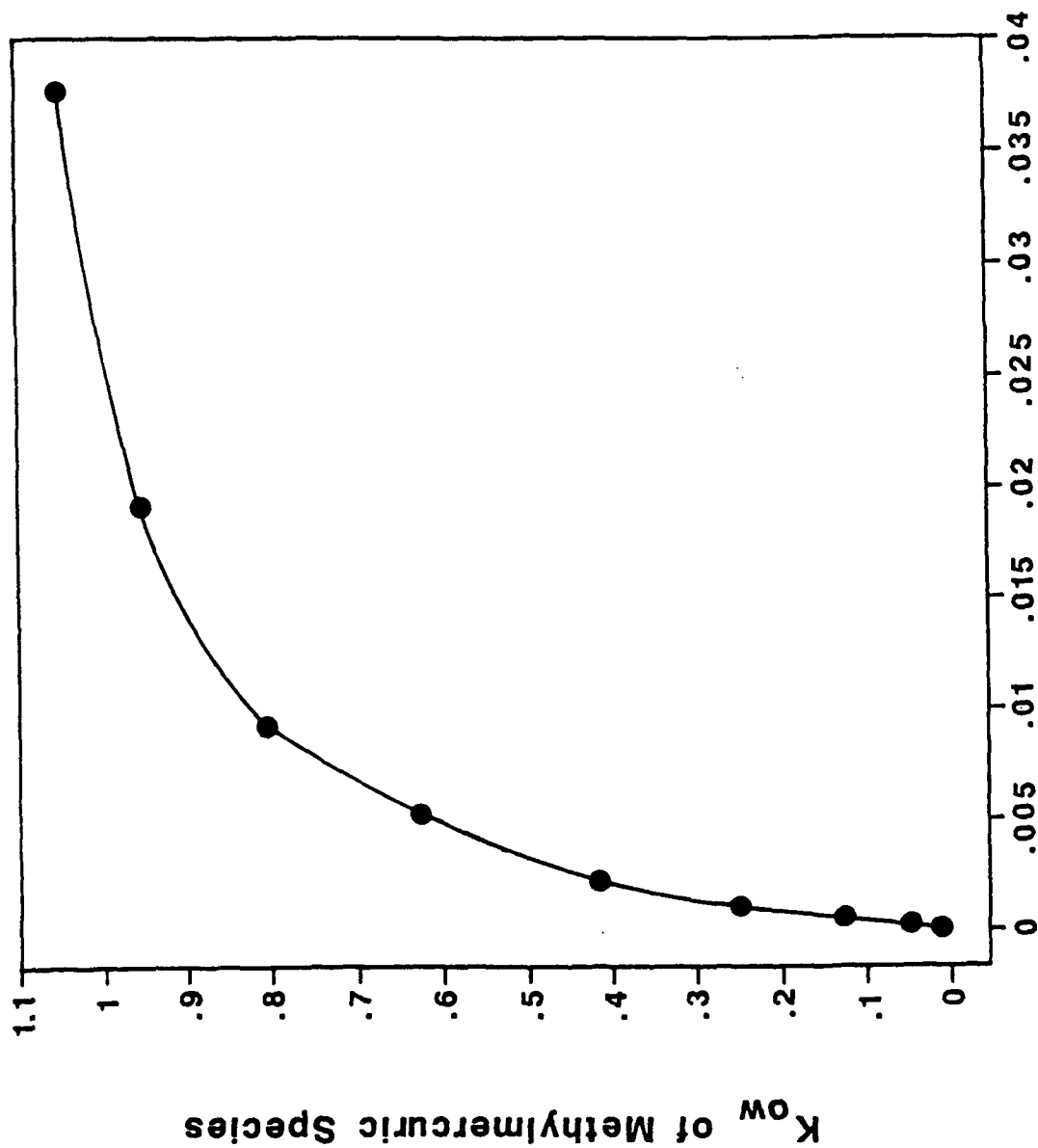
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Molar Concentration of NaCl

Fig. 1. The octanol/water partition coefficients of methylmercuric hydroxide and methylmercuric chloride in pure water and in 0.075M, 0.15M, 0.30M and 0.60M NaCl. The methylmercuric species was at 10 ppm.



Molar Concentration of NaCl

Fig. 2. The octanol/water partition coefficients of methylmercuric hydroxide in the salinity range 0.0000 to 0.0037M NaCl. The methylmercuric hydroxide was at 10 ppm.

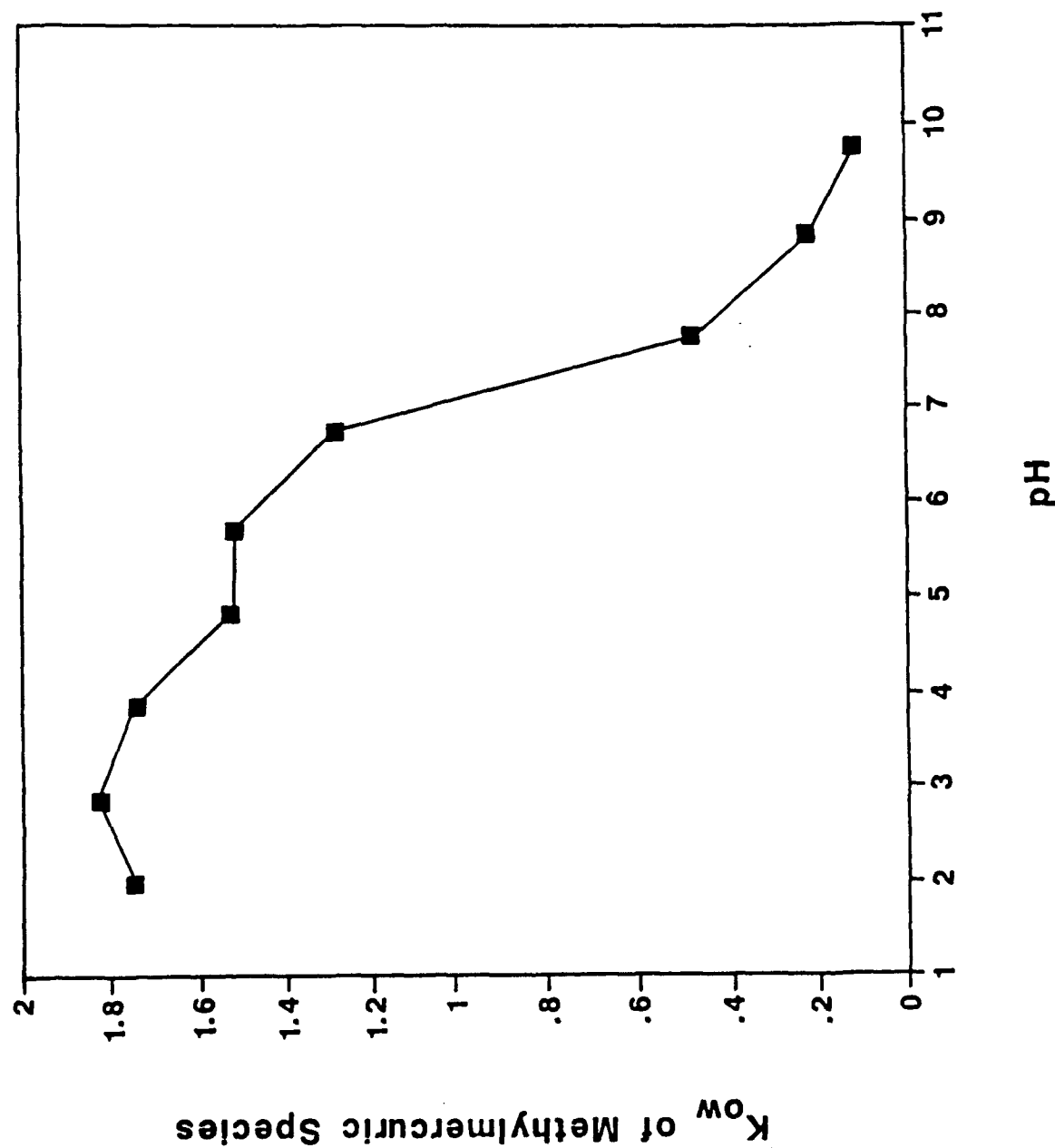


Fig. 3. The octanol/water partition coefficients of methylmercuric chloride in the pH range of 2 to 10 at a fixed salinity of 0.0045M NaCl. The methylmercuric chloride was at 10ppm.

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