ACKNOWLEDGMENT

Wilson Menashi and Gerald Clay helped prepare the sample; Ray Radebaugh and Merritt Hougen assisted in the operation of the calorimetric cryostat.

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RECEIVED for review August 8, 1962. Accepted November 23, 1962. This work was supported in part by the United States Air Force Aeronautical Systems Division under Contract AF 33(616)-7472.

The Solubility of Tetraethyllead in Water

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Tetraethyllead (I) vapor, water and air were equilibrated in all-glass apparatus. The phases were separated, the I extracted into pentane, and the pentane analyzed for lead. In the separated phases, no decomposition products of I were detected. Between 0.2 and 0.3 mg. of I saturate a liter of water at 0–38° C.

THE SOLUBILITY of tetraëthyllead (TEL) in water has been measured to aid in the understanding of the aqueous solubility of nonelectrolytes. The immiscibility of TEL and water is known, but no quantitative information has been published. Results are here reported that indicate the magnitude of the solubility of TEL in water saturated with air.

Two useful techniques of separation have been developed in this work, one for the separation of TEL from small volumes of air and the other for its separation from small volumes of water. These new techniques have been used in conjunction with an older method of equilibrating and separating gases and liquids (*6*) to obtain data on the distribution of TEL between air and water. From these data and data on the vapor pressure of TEL (*1*), the solubility of TEL in water has been calculated. A liquid phase of TEL has been avoided because of the uncertainty of complete separation of emulsions of TEL and water and because of the need to reach equilibrium before appreciable decomposition of TEL occurred. Both problems were encountered in preliminary experimentation.

RESULTS AND DISCUSSION

The concentrations of TEL in the aqueous and gaseous phases were calculated from the analytical data (Table I). From these concentrations and the following equation for the vapor pressure of TEL, the aqueous solubilities at saturation were calculated, assuming Henry's law:

$$\log_{10}P_{\text{TEL}} = 9.34286 - \frac{2908.43}{^\circ\text{K.}}$$

where P_{TEL} is the vapor pressure of TEL in mm. of mercury and 0° C. is taken as 273.16° K. This equation was obtained from a least squares fit of the data of Buckler and Norrish (*1*); it differs slightly from their equation. The aqueous solubility in the temperature range from 0° to 38° C. is between 0.2 and 0.3 mg. of TEL per liter of water.

Detailed thermodynamic calculations (*2*) on the results are unwarranted in view of the variability of the findings relating solubility to temperature. As usual with non-

Table I. Average Results from Duplicate Equilibrations

° C.	TEL Added to Each Syringe (Mg.)	TEL Not Found in Gas and Water From Each Syringe (Mg.)	TEL in Saturated Air (Mg./L.)	TEL in Equilibrated Gas Phase (Mg./L.)	TEL in Equilibrated Water Phase (Mg./L.)	Calculated Solubility of TEL in Water (Mg./L.)
0.0	0.02	0.008	0.94	0.39	0.081	0.20
24.7	0.13	0.017	6.60	3.60	0.155	0.29
26.6	0.15	0.022	7.56	4.10	0.116	0.21
31.5	0.25	0.018	10.65	4.60	0.095	0.22
31.5	0.13	0.017	10.65	6.40	0.102	0.27
37.5	0.17	0.015	15.97	5.01	0.078	0.25

electrolytes, the aqueous solubility of TEL per unit of its vapor pressure increases as temperature decreases.

EXPERIMENTAL

TEL, water and air were equilibrated by shaking them in 100 ml. glass syringes to which 12/1 ball joints had been sealed. The procedure was to introduce into a wet syringe 20 to 40 ml. of air partially saturated with TEL followed by 60 to 80 ml. of water distilled from glass (*3*). The capped syringe was vigorously shaken in a water bath in darkness for 2.5 hours at 0° C. or 0.5 to 1 hour at the higher temperatures. Then a 20-ml. aliquot of the gas phase was ejected through a glass capillary into about 80 ml. of chilled (−70° C.) *n*-pentane (redistilled in glass) in a 100-ml. volumetric flask. To ensure the transfer of any condensed TEL into the flask it was necessary to flush the contents of the capillary tube into the flask with warm pentane. After bringing the flask to room temperature, the contents were made up to volume and aliquots of 20 or 50 ml. were taken for bromination, evaporation and analysis for lead (*4*). From the syringe, after all the gas had been ejected, several grams of the aqueous phase were weighed out for direct reaction (i.e., without bromination) with dithizone. This was a test both for decomposition products (*5*) of TEL, and for contamination from the water of the bath. (The values found never exceeded those of the blank analyses.) Without further contact with any gas phase, most of the remaining aqueous phase was ejected under 25 ml. of pentane in a tared bottle. The bottle was weighed to determine the quantity of water. To extract the TEL from the water, the stoppered bottle was shaken for five minutes; it was then allowed to stand for half an hour for separation. A 20-ml. aliquot of the pentane extract was removed, brominated and analyzed for lead.

To test the entire procedure, all equilibrations were performed in duplicate. Thus, two aliquots of air containing TEL were charged into two wet 100-ml. syringes for equilibration. A third aliquot was then delivered into pentane at −70° C. for analysis for lead. Prior testing of this technique had shown that three successive aliquots of air delivered in this way contained 15.6, 14.8 and 15.0 micrograms of lead. From the syringes used in equilibrations, only 1 to 2 micrograms of TEL could be collected by rinsing with pentane, suggesting that no adsorption of TEL had occurred. An unaccountable loss of TEL did occur in every equilibration, as indicated in Table I. The aqueous solubilities from duplicate equilibrations differed on the average by 26 micrograms, at most by 65 micrograms, of TEL per liter of water.

A test of the recovery of 15.0 micrograms of TEL from a solution of a weighed quantity (30.0 mg.) of TEL in pentane (2 liters) gave recoveries of 100.3%, 101.4% and 102.4%; other aliquots, after shaking with water in bottles, gave recoveries of 97.6%, 99.8% and 102.4%. Blank analyses, whether including pentane and bromine or not, ranged from 0.03 to 0.05 micrograms of lead; the measured values were subtracted from all analyses for lead.

The purity of the TEL used in this work was evidenced by the finding of only a single peak in gas chromatograms, though chromatograms of "commercially pure" TEL showed between 1 and 2% of "impurities."

ACKNOWLEDGMENT

The authors are grateful for the courtesy of George W. Thomson of Ethyl Corp. in supplying naphthalene-free TEL.

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RECEIVED for review July 5, 1962. Accepted December 10, 1962.