gen atoms across the carbon–carbon single bond would be effective in lowering the heat of reaction.

Acknowledgment.—This work was made possible by a grant from the Research Corporation of New York.

Summary

The vapor phase heats of hydrobromination of tetrafluoroethylene, trifluorochloroethylene and 1,1-dichloro-2,2-difluoroethylene have been measured at 94°. The results are discussed.

BOULDER, COLO. RECEIVED NOVEMBER 10, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF DELAWARE]

The Solubility of Hydrogen Bromide in Normal Paraffin Hydrocarbons[1]

BY EDWARD R. BOEDEKER[2] AND CECIL C. LYNCH

Introduction

The measurement of the solubility behavior of hydrogen bromide has been carried out in only a few organic solvents. The majority of the publications report solubility measurements in solvents where polar effects and unsaturation obscure the true solubility behavior of hydrogen bromide. Only recently, Fontana and Herold[3] reported measurements of the solubility of hydrogen bromide in *n*-butane and in *n*-hexane, in which solvents the solute would be expected to exhibit its true solubility behavior since polar effects and unsaturation are absent. These authors measured the solubility of hydrogen bromide at partial pressures of hydrogen bromide up to about 35 lb. absolute. They did not analyze the liquid phase but calculated the hydrogen bromide solubility from the amount of hydrogen bromide added to the system and from the total pressure of the system and assumed Raoult's law to be valid.

The primary purpose of the present work was to obtain solubility data for several hydrogen bromide–*n*-paraffin hydrocarbon systems at several temperatures. It was hoped that these data could then be used in predicting the solubility of hydrogen bromide in other hydrocarbons within the temperature range studied. As a secondary objective, the results of the present study, wherein liquid phase analyses were made, can be compared with the results obtained by Fontana and Herold on the basis of vapor pressure measurements.

Experimental

The apparatus which was used is shown schematically in Fig. 1 and is a modification of the apparatus used by Howland, Miller and Willard.[4] The method consists in saturating the solvent in an absorption flask with the solute vapor under known partial pressure and then analyzing a weighed sample of the solution to determine the amount of dissolved gas.

The apparatus consists of three parts, (1) an hydrogen bromide purification and storage system, (2) the portion of the system wherein the solubility measurements are made, and (3) a sampling tube for withdrawing samples from the liquid phase for analysis.

The solubility flask is a 250-ml. round-bottom flask to which is attached a glass coil of 10-mm. Pyrex tubing. The glass coils are approximately two inches in diameter with the coils about one inch apart. The length of the coiled section is about fifteen inches. The solubility flask is attached to the vacuum system by means of a ground glass joint. The solubility flask also has sealed to it a female ground joint through which the liquid phase sampling tube passes.

The hydrogen bromide reservoir is a three-liter flask which has an eight-inch piece of 20 mm. tubing sealed to the bottom. The reservoir connects to an open end manometer. By means of a three-way stopcock sealed to the top of the flask, the reservoir can be connected either with the vacuum manifold or with the solubility flask.

The entire system is connected to a mercury diffusion pump and a mechanical pump.

Agitation of the solubility flask during the measurements was obtained by attaching the glass coil, by means of an elastic band, to an eccentric on a slow speed motor.

The solubility flask was immersed in a constant temperature bath during the solubility measurements. Temperatures were maintained constant within 0.05° and were read on a thermometer which was checked against a calibrated Bureau of Standards thermometer.

Experimental Procedure

Prior to the solubility measurements, the solubility flask with stopcocks S-2 and S-3 closed and stopcock S-1 open to line L-2 was evacuated to a pressure of less than 10^{-3} mm. for at least one hour. Stopcock S-1 was closed, and a female ball joint with a tube bent at right angles and drawn down to a fine capillary was attached to the ball joint sealed onto stopcock S-3. This capillary was immersed in the solvent to be used, and by opening stockcock S-3 the solvent was drawn into the solubility flask. Since a small amount of air was always drawn into the system during the introduction of the solvent, the solubility measuring system was evacuated by opening stopcock S-1 for short intervals of time. To remove the air completely the solvent was allowed to boil under reduced pressure.

The following sequence of operations was followed in making the solubility measurements. Stopcock S-6 was turned so that the hydrogen bromide reservoir, containing the purified hydrogen bromide, was opened to line L-1. A small amount of hydrogen bromide was admitted to the solubility system by slightly opening stopcock S-1. After the required amount of solute gas had been admitted to the system, stopcock S-1 was closed. Stopcock S-3 was opened very carefully and the draw-off tube almost emptied of solvent. The flask was then shaken and the agitation continued until the pressure in the system became constant.

After the pressure in the system had become constant, a sample was withdrawn in the following manner. A

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[1] Abstracted from a thesis submitted by Edward R. Boedeker in partial fulfillment of the requirements for the degree of Master of Science, University of Delaware, June, 1949.

[2] Houdry Process Corporation, Linwood, Pennsylvania.

[3] Fontana and Herold, THIS JOURNAL, **70**, 2881 (1948).

[4] Howland, Miller and Willard, *ibid.*, **63**, 2807 (1941).

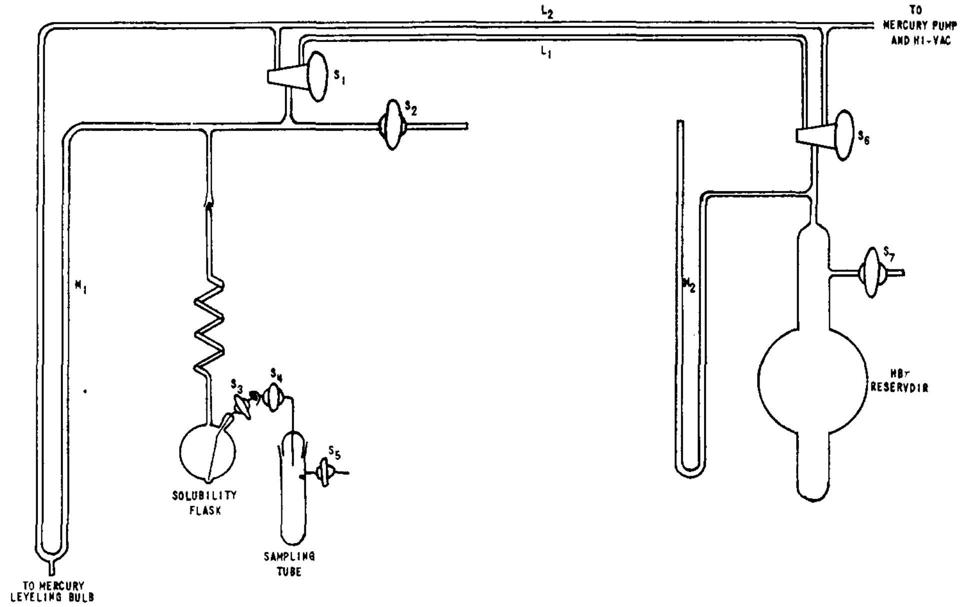

Fig. 1.—Solubility apparatus.

known volume of standard sodium hydroxide solution was measured into the sampling tube from a buret. The tube, with the male joint inserted, and containing the standard alkali solution was weighed and then attached to the solubility flask by means of the ball joint. Stopcock S-4 was closed and stopcock S-5 opened. The sampling tube was evacuated by momentarily opening stopcock S-5 to a vacuum line attached to the side arm. Stopcock S-3 was opened and a sample withdrawn into the sampling tube. Stopcocks S-3, S-4, and S-5 were closed and the sampling tube disconnected from the sampling withdrawal tube. The sampling tube was shaken vigorously to remove all of the hydrogen bromide from the hydrocarbon solution. The glass tubing external to stopcock S-4 was washed with acetone and dried, and after admitting air to the sampling tube the gross weight was determined. This weight was corrected for the small amount of water lost during the evacuation prior to obtaining the sample.

The contents of the sampling tube were emptied into a small separatory funnel and the aqueous layer withdrawn into an Erlenmeyer flask. The sampling tube was washed with water which was then added to the separatory funnel and, after vigorously shaking the contents of the separatory funnel and allowing the layers to separate, the water was withdrawn into the flask. This washing operation was repeated three times. The excess base was titrated with standard acid using phenolphthalein as indicator.

Before making the next solubility measurement, the glass external to stopcock S-3 was cleaned and dried. A further portion of hydrogen bromide was added to the system and the sequence of operations outlined above was followed to obtain a second sample. In this way it was possible to make as many as ten determinations starting with a solvent charge of 100 ml. and to cover a pressure range of about 500 mm.

Materials.—The *n*-hexane was obtained from the Phillips Petroleum Company and was used without further purification. The physical properties were: b. p. 68.8°, n^{25}D 1.3730; literature,[5] b. p. 68.7°, n^{25}D 1.3723. From the refractive index it was calculated that the *n*-hexane contained 2 mole % methylcyclohexane.

The *n*-octane and *n*-decane were obtained from the Connecticut Hard Rubber Company. These hydrocarbons were treated with concentrated sulfuric acid until the acid layer was no longer colored upon prolonged shaking. The hydrocarbon layer was water-washed, dried, and distilled. In each case a middle fraction was taken. The middle portion of the *n*-octane flat had the following physical properties: b. p. 125.0°, n^{25}D 1.3952; literature,[6] b. p. 125.7°, n^{25}D 1.3951. The distilled *n*-decane had the following physical properties: b. p. 174.0°, n^{25}D 1.4118; literature,[7] b. p. 174.0°, n^{20}D 1.4118-1.4120.

The hydrogen bromide was obtained from the Dow Chemical Company and was thoroughly degassed by alternate freezing and thawing before use.

Results

At each of the temperatures studied the systems were found to obey Henry's law quite well over the range of hydrogen bromide pressures studied (*ca.* 50–700 mm.). The values of the Henry's law constants were calculated by the method of least squares. The maximum deviation from these most probable values was of the order of 4%. The results are summarized in Table I.

TABLE I

HENRY'S LAW CONSTANTS FOR HYDROGEN BROMIDE-*n*-PARAFFIN SYSTEMS

Solvent	Henry's law constant × 10^{-3} at 25.0°	35.0°	45.0°
n-Hexane	1.64 ± 0.02	1.97 ± 0.08	2.20 ± 0.08
n-Octane	2.01 ± .05	2.33 ± .07	2.65 ± .09
n-Decane	2.15 ± .07	2.49 ± .07	2.75 ± .07

The units of the constant are mm. HBr/mole HBr/1000 g. solution.

In the calculation of the Henry's law constant for the *n*-octane–hydrogen bromide and *n*-decane–hydrogen bromide systems, the partial pressure of hydrogen bromide was obtained by subtracting

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(5) F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," Circular C 461, National Bureau of Standards, A. P. I. Research Project 44, p. 38.

(6) Rossini, *et al.*, ref. 5, p. 40.

(7) Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Co., New York, N. Y., 1939, Vol. I, p. 67.

from the total pressure in the system the vapor pressure of the liquid solvent[8] at the temperature under consideration. For the *n*-hexane–hydrogen bromide system the partial pressure was obtained by subtracting from the total pressure in the system the partial pressure of *n*-hexane as calculated by Raoult's law.

Figure 2 is a plot of the mole fraction of dissolved hydrogen bromide (at a partial pressure of one atmosphere) as a function of the reciprocal of the absolute temperature. Included in this plot are the data obtained by Fontana and Herold[3] for the *n*-hexane–hydrogen bromide system. The ideal solubility, $\log f_2/f_2^0$, was calculated from the Berthelot equation of state using the critical data as given by Pickering.[9] For comparison, $\log 1/p_2^0$, which does not allow for the deviations of hydrogen bromide from the perfect gas law, is also shown.

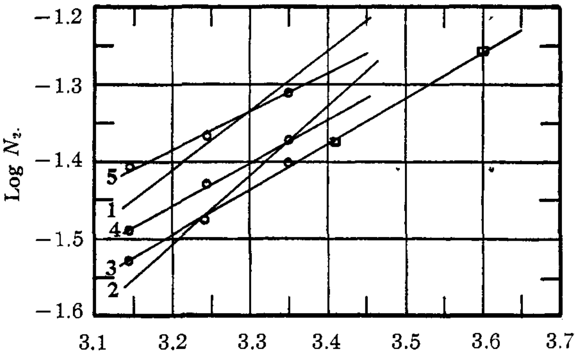

Fig. 2.—Solubility of hydrogen bromide: ●, this investigation; □, Fontana and Herold, ref. 3; 1, $\log f_2/f_2^0$; 2, $\log 1/P_2^0$; 3, *n*-hexane; 4, *n*-octane; 5, *n*-decane.

Figure 2 shows that the solubility of hydrogen bromide in *n*-hexane and *n*-octane is less than the ideal solubility but that at the higher temperatures the ideal solubility is rapidly approached, whereas the solubility of hydrogen bromide in *n*-decane is greater than the ideal solubility at temperatures above 30°. It is further evident that, at the same temperature, the solubility of hydrogen bromide increases with the molecular weight of the *n*-paraffin solvent. The present theory of solubility considers that the solubility is increased by disparity in molal volumes, which is the observed behavior for the solvents considered.

Figure 2 shows that the temperature coefficient is considerably less than the ideal for all of the solvents. The observed heats of solution are: *n*-hexane, 2620 cal./mole; *n*-octane, 2490 cal./mole; *n*-decane, 2340 cal./mole; from $\log f_2/f_2^0$, 3480 cal./mole. The discrepancy between the observed heats of solution and that calculated from the $\log f_2/f_2^0$ plot is assumed to be due to the entropy of mixing and is a function of v_1/v_2, where v is the molal volume and the subscripts 1 and 2 refer to the solvent and solute, respectively. Again, it is apparent that the observed variation of the heat of solution with the molal volume of the solvent is in qualitative agreement with theory.

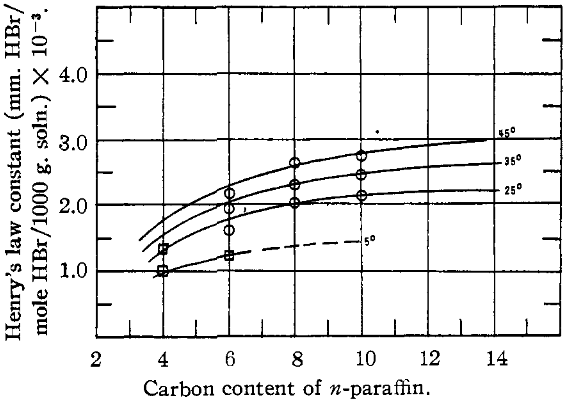

Fig. 3.—Henry's law constant *vs.* carbon content of solvent: ○, this investigation; □, Fontana and Herold, ref. 3.

By constructing isothermal plots (Fig. 3) of Henry's law constant as a function of the carbon content of the *n*-paraffin solvent, and including the data obtained by Fontana and Herold[3] for *n*-hexane and *n*-butane, it is possible to predict, over a limited range, the solubility of hydrogen bromide in other *n*-paraffin hydrocarbons. From this graph it can be concluded that at a constant temperature the value of the Henry's law constant approaches asymptotically a limiting value with an increase in the number of carbon atoms in the *n*-paraffin solvent.

Acknowledgment.—This work was carried out in the laboratories of the Houdry Process Corporation and their coöperation in making these facilities available is gratefully acknowledged.

Summary

The solubility of hydrogen bromide in *n*-hexane *n*-octane, and *n*-decane has been measured at 25, 35 and 45°. The heat of solution of hydrogen bromide in each of the solvents has been calculated.

From the experimental data predictions can be made, over a limited range, of the solubility of hydrogen bromide in *n*-paraffin solvents of varying carbon content. At a given temperature, the value of Henry's law constant approaches a limiting value as the number of carbon atoms in the *n*-paraffin solvent is increased.

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[8] Ref. 5, pp. 122, 124.

[9] Pickering, *J. Phys. Chem.*, **28**, 97 (1924).