[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

The Dissociation of Iodine Monobromide in Carbon Tetrachloride Solution

BY ALEXANDER I. POPOV, KEITH C. BRINKER, LOUIS CAMPANARO AND ROBERT W. RINEHART

Absorption curves of bromine, iodine and iodine monobromide solutions in carbon tetrachloride were measured with a Beckman DU spectrophotometer. The degree of dissociation of iodine monobromide determined from the absorption data was found to be 5.9 ± 1.5%. The method of calculation is given.

Introduction

The dissociation of iodine monobromide in carbon tetrachloride solution was first studied by Yost, Anderson and Skoog[1] by bubbling dry nitrogen through the solution and determining the composition of the vapor. From these data and from the previously obtained dissociation constant of iodine monobromide in the gas phase,[2] the degree of dissociation in solution was calculated to be 9.5%.

Gillam and Morton[3,4] have studied the absorption spectra of iodine and bromine mixtures in carbon tetrachloride solutions with the help of the Hilger photographic spectrophotometer. From the observations of the absorption curves the authors concluded that iodine monobromide dissociates to some extent in carbon tetrachloride, but that the degree of dissociation was small.

The work reported here is an attempt to obtain the dissociation of iodine monobromide from the absorption data.

Experimental Work

Carbon tetrachloride, bromine and iodine used in this work were carefully purified. Resublimed iodine monobromide was obtained through the courtesy of Dr. Jacob Cornog.

The solutions were prepared by adding appropriate amounts of the reagents to carbon tetrachloride, and titrating the resulting solution iodometrically. The absorbancy of the prepared solutions was determined with a Beckman DU spectrophotometer. Fresh solutions were prepared for each series of measurements. Calibrated Corex cells of optical path length 1.000 ± 0.001 cm. were used. The experiments were carried out at room temperature which was approximately 25°.

In general the shape of the absorption curves and the position of the absorption maxima for iodine, bromine and iodine monobromide agreed very well with the results of Gillam and Morton. Addition of the curves for 4 × 10^{-4} *M* iodine monobromide and 2 × 10^{-4} *M* iodine very nearly coincided with the curve for a single solution containing these substances at the same concentration. This indicates that the dissociation of iodine monobromide in the presence of a twofold excess of one of the reagents was extremely small. Absorption curves for iodine monobromide and iodine–bromine mixture of the same total concentration, were identical within the limit of experimental error.

From the absorption curves obtained in this work, as well as those of Gillam and Morton, it was found that the maximum difference between the addition curves of iodine and bromine, and the iodine monobromide curve occurs in the regions 390–400 mμ and 520–560 mμ. Solutions of desired concentrations were prepared and the absorbancy was measured in these wave length regions (Table I).

TABLE I

ABSORBANCIES OF BROMINE–IODINE MIXTURES

Wave length, mμ	Slit width, mm.	Concn., molarity Br_2	I_2	Absorbancy
390	0.04	5 × 10^{-3}	2.5 × 10^{-3}	0.453
390	.04	2.5 × 10^{-3}	5 × 10^{-3}	.106
390	.04	2.5 × 10^{-3}	2.5 × 10^{-3}	.111
400	.04	5 × 10^{-3}	2.5 × 10^{-3}	.637
400	.04	2.5 × 10^{-3}	5 × 10^{-3}	.202
400	.04	2.5 × 10^{-3}	2.5 × 10^{-3}	.200
520	.02	5 × 10^{-4}	1 × 10^{-3}	.755
520	.02	1 × 10^{-3}	5 × 10^{-4}	.326
520	.02	5 × 10^{-4}	5 × 10^{-4}	.308
540	.02	5 × 10^{-4}	1 × 10^{-3}	.590
540	.02	1 × 10^{-3}	5 × 10^{-4}	.210
540	.02	5 × 10^{-4}	5 × 10^{-4}	.208
560	.02	1 × 10^{-3}	5 × 10^{-4}	.116
560	.02	5 × 10^{-4}	5 × 10^{-4}	.117

Calculations

The reaction involved is

$$Br_2 + I_2 \rightleftarrows 2IBr$$

For the calculations the additivity of absorbancies was assumed

$$A_{s\lambda_1} = a_{Br\lambda_1} C_{Br} + a_{I\lambda_1} C_I + a_{IBr\lambda_1} C_{IBr} \qquad (1)$$

Where

$A_{S\lambda_1}$ = absorbancy at λ_1

$a_{Br\lambda_1}$, $a_{I\lambda_1}$, $a_{IBr\lambda_1}$ = molar absorbancy indices of bromine, iodine and iodine monobromide at λ_1

C_{Br}, C_I, C_{IBr} = molar concentrations of bromine, iodine and iodine monobromide

The calculations were based on the assumption that the twofold excess of iodine or bromine suppressed the dissociation of iodine monobromide. Absorbancy indices of bromine and iodine were obtained from their absorption curves.

For solution 1, *p* molar in bromine and 2*p* molar in iodine, equation (1) becomes

$${}_1A_{S\lambda_1} = a_{I\lambda_1}\, p + a_{IBr\lambda_1}\, 2p \qquad (2)$$

or

$$a_{IBr\lambda_1} = ({}_1A_{S\lambda_1} - a_{I\lambda_1}\, p)/2p \qquad (3)$$

The absorbancy at the same wave length for solution 2, *p* molar in bromine and *p* molar in iodine, is given by

$${}_2A_{S\lambda_1} = a_{Br\lambda_1}\, x + a_{I\lambda_1}\, x + a_{IBr\lambda_1}\, (2p - 2x) \qquad (4)$$

where *x* is the amount of free iodine or bromine, and indicates the approximate degree of dissociation.

As a second approximation the iodine in solution 1 is *p*/*x* times as concentrated as in solution 2.

TABLE II

MOLAR ABSORBANCY INDICES FOR BROMINE, IODINE AND IODINE MONOBROMIDE

λ, mμ	a_{Br}	a_I	a_{IBr}
390	144	5.2	18.2
400	179	5.6	37.4
520	64	910	293
540	36	776	201
560	20	510	105

---

[1] Yost, Anderson and Skoog, THIS JOURNAL, **55**, 552 (1933).

[2] McMorris and Yost, *ibid.*, **53**, 2625 (1931).

[3] Gillam and Morton, *Proc. Roy. Soc.* (*London*), **A124**, 604 (1929).

[4] Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).

Since the equilibrium constants for the two solutions are evidently equal, the concentration of bromine in solution 1 can be calculated. Applying this correction to equations (2) and (3), a better value for x and hence for the degree of dissociation can be calculated.

Mean value of the degree of dissociation obtained from the data given in Table I was 5.9% with the average deviation of 1.5%. This figure is somewhat lower than the one given by Yost, *et al.*,[1] but is of the same order of magnitude.

Due to the fact that the dissociation is small, and does not increase with dilution, and that at no wave length bromine or iodine absorb strongly while the remaining species absorb very little, one is forced to analyze for small quantities as differences of large quantities. It is thus quite difficult to decrease the experimental error.

Acknowledgment.—The authors wish to express their appreciation to Dr. Harold Boaz for helpful discussions on this problem.

IOWA CITY, IOWA RECEIVED JULY 13, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Electrical Conductance and Viscosity in the System Tetra-*n*-butylammonium Picrate–*n*-Butyl Alcohol at 91°

BY RALPH P. SEWARD

Densities, viscosities and conductances have been measured over the whole range of composition in the homogeneous liquid system tetra-*n*-butylammonium picrate–*n*-butyl alcohol at 91°. The limiting equivalent conductance has been evaluated. The product of the limiting equivalent conductance and viscosity is shown to be substantially equal to the equivalent conductance–viscosity product for the pure salt. At low concentrations the salt behaves like a weak electrolyte but appears to become a strong electrolyte at high salt concentrations.

Although the nature of dilute solutions of electrolytes in many solvents has been studied in a multitude of investigations, solutions of non-electrolytes in fused salts have been little explored. The high melting points of most salts, making experimental work more difficult, and perhaps a feeling that such solutions are intrinsically more complex, seems to account for their being neglected. In view of the lack of information in this field it was thought worth while to measure the electrical conductance in a binary system consisting of a non-electrolyte and a salt, over the whole range from zero to one hundred per cent. salt at a constant temperature. The results of the investigation are presented below.

The salt chosen was tetra-*n*-butylammonium picrate, because it is easily prepared and melts at about 90°. The non-electrolyte, *n*-butyl alcohol, was chosen on the basis of its showing complete miscibility with the salt and its relatively low volatility at the melting point of the salt. The temperature, 91°, was chosen as being just above the melting point. Viscosities in the system were measured since the viscosity is a major factor in determining electrical conductance. Densities were measured because they were required in calculating the viscosities and the equivalent conductances. Conductance measurements were made on a series of dilute solutions of the picrate in butanol in order to establish the limiting conductance and the nature of the salt in dilute solution.

Experimental

Tetra-*n*-butyl picrate was prepared by neutralization of aqueous tetra-*n*-butylammonium hydroxide with picric acid, recrystallization of the picrate several times from methanol, and drying at about 50°. Its m.p. was 89.4°.

A reagent grade of *n*-butyl alcohol was refluxed several hours with lime and distilled through a column equivalent to about six theoretical plates. Material boiling at 117.3–117.5° was used. Its specific conductance was 3.0×10^{-7} mho at 91°. Measurement of densities, viscosities and conductances were made in an oil filled constant temperature bath held at 91°. Although no effort was made to obtain an absolute value for the temperature to this accuracy, the temperature was held constant to ±0.02°. The various mixtures were made up by weight. The densities were determined with a Westphal balance. The viscosities were measured in Cannon and Fenske[1] type viscometers.

The conductances were measured in a cell, Fig. 1, of Pyrex glass with a mixing chamber of about 25-ml. capacity connected to a smaller chamber containing the electrodes into which the solutions were drawn for the resistance measurements. Solutions were made by adding known weights of material directly into the apparatus. The electrodes were platinized. The cell constant was determined with 0.015 *N* KCl at 25° as 2.00. It was assumed that no change in cell constant within the expected precision occurred on operation at 91°. For the dilute solutions (below 0.008 molar), a Freas type cell (Central Scientific Co. No. 70004) was used, having a cell constant of 0.356.

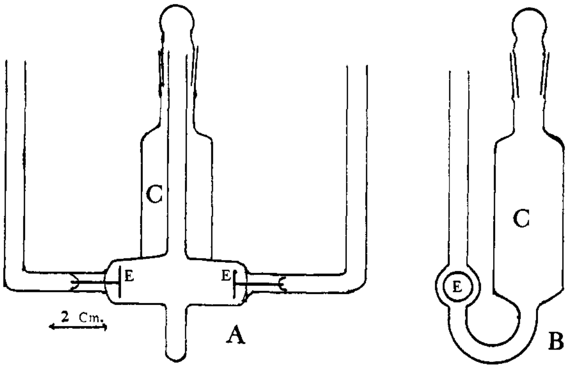

Fig. 1.—Conductance cells, A front, B side, E electrodes, C mixing chamber.

Resistances were measured with the use of an oscillator of variable frequency, a Leeds and Northrup Campbell-Shakelton ratio box, shielded a.c. resistance box and amplifier. An adjustable capacitance was connected in parallel with the resistance box.

Results

The density and viscosity measurements are shown in Table I; the viscosity is in poises, density

---

(1) M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).