The Partial Pressure of Hydrogen Chloride from its Solutions in β,β'-Dichloroethyl Ether and in Anisole and the Calculation of the Heat and Entropy of Solution[1]

By S. James O'Brien[2]

In a previous paper,[3] data were presented which suggested a linear relationship between the entropy of solution of hydrogen chloride and the shift produced in its 3.46 μ absorption band by the solvent. In an attempt to obtain additional facts concerning this relationship, vapor pressure studies were being made on a number of hydrogen chloride solutions. Since these studies have been temporarily interrupted, it seemed advisable to report at this time results obtained which are sufficiently complete for the purpose. These include measurements of the partial pressure of hydrogen chloride from its solutions in β,β'-dichloroethyl ether at 20, 25, 30 and 40°, and in anisole at 20, 30, 35 and 40°. These data were used, as in a previous paper,[3] to calculate the solubilities of hydrogen chloride at a pressure of 1 atm., from which are calculated the heat and entropy changes of the solute. The entropy values, in turn, are compared with the infrared absorption data of Gordy.[4]

Also, a discussion of the heat of solution of hydrogen chloride in carbon tetrachloride is included, since the value recently obtained for this quantity by Howland, Miller and Willard[5] would seem to eliminate the hydrogen chloride–carbon tetrachloride data from those which support the entropy change–infrared band shift relationship.

Experimental

The apparatus and method were the same as those employed in the previous study.[3,6] The ethers were Eastman Kodak Co. products which had been carefully dried and redistilled before using.

Results

The results of the experiments performed are given in Tables I and II in which the column headings have the same significance as in the earlier paper.[3]

(1) Part of the experimental work reported in this paper is included in the M. S. thesis of R. D. Gray, The Creighton University, 1941.

(2) Present address: Department of Chemistry, St. John's University, Brooklyn, N. Y.

(3) O'Brien, THIS JOURNAL, **63**, 2709 (1941).

(4) W. Gordy, *J. Chem. Phys.*, **9**, 218 (1941).

(5) J. J. Howland, Jr., D. R. Miller and J. E. Willard, THIS JOURNAL, **63**, 2807 (1941).

(6) J. Saylor, *ibid.*, **59**, 1712 (1937).

TABLE I

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS SOLUTIONS IN β,β'-DICHLOROETHYL ETHER

m	p, mm.	k	m	p, mm.	k
I. At 25.00 ± 0.02°			III. At 20.00 ± 0.05°		
0.571	418	0.96	0.794	533	0.88
.556	401	.95	.481	287	.79
.555	413	.98	.305	186	.80
.538	378	.93	.202	122	.80
.518	363	.92	.198	116	.78
.502	365	.96	.182	109	.79
.308	215	.92	.168	103	.81
.175	124	.94	.090	53	.78
.165	124	.99	.0419	23.7	.75
.140	94	.88		Mean	0.82 ± 0.03
.126	84	.88			
.103	68.3	.87	IV. At 40.00 ± 0.05°		
.0758	54.3	.94	0.291	307	1.37
.0572	38.1	.88	.265	307	1.52
.0091	6.6	.95	.166	177	1.41
	Mean	0.94 ± 0.03	.165	160	1.28
			.0711	70.9	1.31
II. At 30.00 ± 0.02°				Mean	1.40 ± 0.07
0.366	283	1.02			
.343	260	1.00			
.0292	25.6	1.15			
.0224	17.2	1.00			
	Mean	1.03 ± 0.05			

TABLE II

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS SOLUTIONS IN ANISOLE

m	p, mm.	k	m	p, mm.	k
I. At 20.00 ± 0.05°			III. At 35.00 ± 0.03°		
0.109	82.7	0.99	0.400	410	1.35
.100	70.7	.93	.253	264	1.37
.0926	66.7	.95	.250	250	1.31
.0378	30.3	1.05	.0764	77.8	1.34
	Mean	0.97 ± 0.04	.0720	72.0	1.31
			.0449	45.9	1.34
II. At 30.00 ± 0.02°				Mean	1.34 ± 0.02
0.448	408	1.20			
.200	181	1.19	IV. At 40.00 ± 0.05°		
.180	168	1.23	0.179	216	1.59
.092	85	1.22	.0929	106	1.61
.073	66	1.21	.0887	98.8	1.46
.059	52.7	1.18	.0735	82.3	1.48
	Mean	1.21 ± 0.02	.0463	61.8	1.56
				Mean	1.54 ± 0.05

Discussion

It was first necessary to determine whether hydrogen chloride would correspond with the law of Henry in such basic solvents as the ethers employed. Consequently, a considerable number of experiments were performed in β,β'-dichloroethyl ether at 25° over as wide a pressure range as possible with the method being used. It is evident from the results of these measurements that within the pressure range considered the solute does agree with the law of Henry at this

temperature, considering, of course, the limited accuracy of the experimental procedure. It is believed that sufficient data have been collected to indicate that this conclusion is valid for both ethers at all the temperatures investigated.

While the pressures obtained are in no case as high as 1 atm., there seems to be no indication that the assumption of the validity of the law of Henry up to this pressure is not correct. This assumption is made in calculating from the vapor pressure data, the mole fraction solubilities of hydrogen chloride under a partial pressure of 1 atm. as given in Table III.

TABLE III

THE MOLE FRACTION SOLUBILITY OF HYDROGEN CHLORIDE
AT 1 ATM. AND THE HEAT AND ENTROPY OF SOLUTION

Temp., °C.	In β,β'-dichloroethyl ether	In anisole
20	0.149	0.100
25	.131	
30	.122	.083
35		.074
40	.093	.066
$-\Delta H$ (cal.)	3850	3870
$-\Delta S$ (cal./deg.)	16.9 (16.9)	17.8 (17.7)

In Table III are also included the changes in heat content and in entropy of the solute in the solution process. These values were obtained by least square methods in fitting the solubility–temperature data to the straight line equation

$$-\log N = (\Delta H/2.303RT) - (\Delta S/2.303R) \quad (1)$$

considering ΔH and ΔS to be constants. The entropy values given in parentheses were obtained from the equation

$$\Delta S = 10.0\Delta\mu - 21.1 \quad (2)$$

which equation describes at least approximately the relationship between the change in entropy and the shift of the 3.46 μ absorption band of gaseous hydrogen chloride.[3] In this equation $\Delta\mu$ represents the shift in the wave length of the peak of this band which is[4] 0.42 μ in β,β'-dichloroethyl ether and 0.34 μ in anisole. The agreement between the entropy values obtained from this equation with those obtained from the solubility–temperature relationship is sufficiently good to be considered as additional support of the entropy–infrared absorption shift relationship although there is not yet available enough information to warrant an attempt to define this relationship with a more exact equation. For the present, it is only possible to repeat the conclusion that Eq. (2) is approximately true for those

hydrogen chloride solutions in which data are available, with the possible exception of carbon tetrachloride solutions.

From recent solubility measurements at 0, 20 and 25°, Willard and co-workers[5] obtain a value of 2670 cal. for the heat of solution of hydrogen chloride in carbon tetrachloride. This disagrees with the calorimetric value of 3680 cal. reported by Noyes and Tuley,[7] and with the value of 3610 cal. obtained[3] by means of Eqs. (1) and (2) combined with the solubility measurement of Bell[8] and the Raman spectra data of West and Arthur.[9] The agreement of the latter with the calorimetric value was taken as an indirect confirmation of Eq. (2). The value from the newer solubility measurements introduces, then, some doubt as to the suitability of this test of the equation. It is interesting, however, to compare the experimental solubilities of Willard and co-workers[5] with those calculated by means of the equation

$$2.303RT \log N = 3610 - 20.3T \quad (3)$$

derived from Eqs. (1) and (2) and the above-mentioned data[8,9] for hydrogen chloride solutions in carbon tetrachloride. This comparison is given in Table IV. Here it is seen that the experimental

TABLE IV

THE MOLE FRACTION SOLUBILITY OF HYDROGEN CHLORIDE
IN CARBON TETRACHLORIDE

Temp., °C.	N (Exptl.)[5]	N (Eq. 3)
25	0.0164	0.0163
20	.0178	(.0181)[8]
0	.0244	.0285

and calculated solubilities agree very well at 20 and 25°, but that there is a considerable deviation at 0°. Nevertheless, assuming that the entropy of solution is given correctly by the spectroscopic data through Eq. (2), the solubility measurement of 0° leads to a heat of solution of 3530 cal. which deviates from the calorimetric value by less than 5%. While these calculations do not remove the doubt concerning the applicability of the relationship between entropy and infrared absorption to this system, and while it appears impossible to give a satisfactory explanation of the discord in the heat of solution values without additional facts, it is believed that they do indicate that there is not yet sufficient reason for excluding the hydrogen chloride–carbon tetrachloride data from those which are in accord with Eq. (2).

(7) W. A. Noyes and W. F. Tuley, THIS JOURNAL, 47, 1338 (1925).
(8) R. P. Bell, J. Chem. Soc., 1371 (1931).
(9) W. West and P. Arthur, J. Chem. Phys., 2, 215 (1934).

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Summary

1. Measurements of the partial vapor pressure of hydrogen chloride from its solutions in β,β'-dichloroethyl ether and in anisole at four temperatures in the range of 20–40° are reported.

2. The vapor pressure measurements are used to calculate the mole fraction solubility of hydrogen chloride in these solvents at a partial pressure of 1 atm. These calculated solubilities, which fit an equation of the form $\log N = A/T + B$, are used to obtain the differential heat and entropy of solution. The entropy values so obtained are in agreement with those derived from pertinent infrared absorption data and an equation connecting the thermodynamic with the spectroscopic quantity.

3. The question of the applicability of this equation to hydrogen chloride solutions in carbon tetrachloride, arising from a value for the heat of solution obtained from recent solubility measurements in this system, is considered.

Contributions to the Chemistry of Indium. V.[1] Hydrolysis Constants for Indium Tribromide and Triiodide Solutions

BY THERALD MOELLER

In a previous communication,[2] the hydrolysis constant for indium trichloride solutions was evaluated from pH measurements at various concentrations upon the assumption that the governing hydrolytic reaction results in the formation of $[\text{In}(\text{H}_2\text{O})_5(\text{OH})]^{++}$ and H_3O^+ ions. Inasmuch as no similar literature data exist for solutions of the tribromide and triiodide, it has been of interest to extend such observations to these materials.

Experimental

Preparation of Anhydrous Indium Trihalides.—Anhydrous indium tribromide was prepared and purified by the method of Baxter and Alter.[3] The white crystalline product was preserved in dry nitrogen until used.

Although anhydrous indium triiodide has been obtained by heating the metal in a stream of dry carbon dioxide laden with iodine vapor,[4,5] a similar procedure using nitrogen instead of carbon dioxide proved to be less effective than a modification of the method of Meyer[6] in which indium metal was warmed with an excess of iodine in an atmosphere of dry nitrogen. The triiodide was obtained as a brown liquid which, after removal of the excess iodine by sublimation, was purified by slow distillation in a current of nitrogen. Upon cooling, the distillate solidified to a mass of bright yellow crystals containing none of the red monoiodide.

Experimental Procedure.—The procedure followed exactly duplicated that previously reported[2] and is, therefore, not included. The results obtained at 25 ± 0.05° with the glass electrode are summarized in Tables I and II for the bromide and iodide, respectively.

The indium tribromide solutions were unchanged upon standing, but the iodide solutions slowly turned yellow.

Results

Employing the assumption that the ions $[\text{In}(\text{H}_2\text{O})_5(\text{OH})]^{++}$ and H_3O^+ are formed in each instance, values for the degree of hydrolysis (x) and the hydrolysis constant (K_h) have been cal-

(1) For the fourth paper in this series see Moeller, *J. Phys. Chem.*, **45**, 1235 (1941).

(2) Moeller, THIS JOURNAL, **63**, 1206 (1941).

(3) Baxter and Alter, *ibid.*, **55**, 1943 (1933).

(4) Thiel, *Z. anorg. Chem.*, **40**, 280 (1904).

(5) Klemm, *Z. anorg. allgem. Chem.*, **152**, 252 (1926).

(6) Meyer, *Ann.*, **150**, 137 (1869).

TABLE I

HYDROLYSIS OF INDIUM TRIBROMIDE SOLUTIONS AT 25°

Moles of InBr₃ per liter	pH	Degree of hydrolysis x	Hydrolysis constant $K_\text{h} \times 10^5$
0.002500	3.42	0.152	6.8
.005000	3.33	.094	4.8
.01000	3.25	.056	3.3
.02000	3.18	.033	2.3
.04000	3.10	.020	1.6
.06000	3.03	.0155	1.5
.08000	2.98	.0130	1.4
.1000	2.94	.0115	1.3
.1500	2.86	.0092	1.3
.2000	2.80	.0079	1.3
.2500	2.74	.0073	1.3
.3000	2.69	.0068	1.4
.3500	2.64	.0065	1.5
.4000	2.59	.0064	1.6