[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

Activity of Cadmium Iodide in Deuterium Oxide

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Many salts have been found to be less soluble in deuterium oxide than in protium oxide. Provided the solid phase is not hydrated the activities of the electrolyte in both solvents must be identical at saturation, *i. e.*

$$m_H \gamma H = m'_D \gamma'_D \qquad \text{(A)}$$

In this expression m_H and m'_D represent the concentrations in terms of moles of salt per 55.507 moles of solvent, γ_H is the conventional stoichiometric mean ionic activity coefficient in water whose value is unity at infinite dilution, while γ'_D is a relative activity coefficient defined by the above equation. The value γ'_D at infinite dilution in D_2O is not unity; it combines the change in standard state in passing from H_2O to D_2O with the conventional activity coefficient in D_2O. Although γ'_D was termed an absolute activity coefficient by La Mer and Noonan[2] this designation is somewhat misleading since it is not referred to an absolute standard state. While the relative activity coefficient defined in this way could be used to describe the behavior of a given salt in any pair of solvents it is of particular value in the case of protium and deuterium oxides since the molecular volumes and dielectric constants of these solvents are nearly identical, and contributions to the change in standard state from these sources may usually be neglected. Any pronounced differences in activity effects between H_2O and D_2O can be directly compared, and are of interest since important factors of electrolytic behavior may be revealed which are not accounted for by present theories.

It has been suggested[3] that the macromolecular structure of water is responsible for solubility differences of salts in H_2O and D_2O. The greatest effects should therefore be observed at the highest dilutions, since the structure of the solution would then approach that of the undisturbed solvent. Only limited information is obtainable from solubility determinations in this region; activity data for salts in heavy water as a function of concentration are therefore desirable.

Eddy and Menzies[4] found that cadmium iodide was 26% less soluble in heavy water than in light water at 25°, indicating that further study of this salt might prove profitable. Bates[5] determined thermodynamic properties of cadmium iodide using the cell

$$\text{Cd-Hg(2 phase)/CdI}_2(m \text{ in } H_2O)\text{/AgI-Ag} \qquad \text{(B)}$$

Information obtained from measurements on a similar cell using H_2O–D_2O mixtures as the solvent is the subject of this paper.

Experimental

A. **Preparation of Materials: Deuterium oxide** was purified before each determination by consecutive vacuum distillation from alkaline permanganate and then from a crystal of potassium dichromate or chromic anhydride. Water treated in this manner was found to have a conductance of 2×10^{-6} mho or better.

Cadmium iodide was purified by the method of Baxter and Hartman for cadmium chloride.[6] A C.P. grade of cadmium iodide was fused in a glass vessel, cooled, dissolved in distilled water and filtered from an insoluble residue. The solution was then evaporated and the process repeated for a total of five times. The resulting salt was recrystallized twice.

Cadmium Amalgam.—An 800-g. sample of cadmium metal was distilled three times in vacuum using an all glass apparatus. The distillate amounted to 300 g. and carefully purified mercury was distilled upon it to give a saturated amalgam. During the course of the experiments, this amalgam was found to be awkward to use with the micro equipment involved and became contaminated with stopcock grease. It was then filtered through sintered glass and divided into two portions, one of which was diluted with mercury to yield a single phase amalgam. All these operations were carried out in vacuum or under an atmosphere of nitrogen.

Silver Iodide Electrodes.—These were made by the thermal method recommended by Bates.[5]

B. **Apparatus and Procedure.**—A 16-ml. pyrex pycnometer fitted with platinum electrodes was used to determine the density and conductivity of heavy water. Ground glass joints were used on the pycnometer, cell, weighing flasks and on all parts which came into contact with the heavy water solutions. All apparatus other than the pycnometer was carefully cleaned, steamed and dried before use. All parts of the apparatus were pyrex except the silver iodide electrode supports which were made of hard Jena glass.

Solutions for each cell were made up from 16 ml. of heavy water and the appropriate amount of dry salt. For the 0.1 molal solutions, the amount of water was adjusted with a 0.25-ml. hypodermic syringe calibrated to 0.01 ml. The three least concentrated solutions were made by diluting a stock solution. All solutions were evacuated to remove dissolved air and a nitrogen atmosphere substituted in the weighing flasks. The usual corrections were applied for the buoyancy of air.

The cell employed was equipped with two silver iodide and two cadmium-amalgam electrodes. Total volume of the cell was about 10 ml., and it was filled using vacuum technique. Voltage readings were taken over a six–twelve hour period with a suitably equipped Leeds and Northrup Type K potentiometer. Temperature was controlled at 25 ± 0.01° as measured with a B. S. calibrated thermometer.

A special cell was built to measure the e. m. f. of the 2-phase cadmium amalgam *versus* the dilute amalgam actually employed for the cadmium iodide cells. Two electrodes for each amalgam concentration were used, and the cell was filled with an aqueous solution of purified cadmium sulfate of undetermined concentration.

C. **Experimental Results.**—Deuterium contents of the heavy water mixtures were computed from the density increment over unity at

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(2) La Mer and Noonan, THIS JOURNAL, 61, 1489 (1939).

(3) Shearman and Menzies, *ibid.*, 59, 185 (1937).

(4) Eddy and Menzies, *J. Phys. Chem.*, 44, 207 (1940).

(5) Bates, THIS JOURNAL, 63, 399 (1941).

(6) Baxter and Hartman, *ibid.*, 37, 120 (1915).

25° and the $d^{25}{}_{25}$ value for heavy water of 1.10764 as determined by Stokland, Ronaess and Tronstad.[7] The total moles of water species were used to compute the molality which is uniformly expressed as moles of salt per 55.507 moles of water.

All cells were made using a single phase amalgam which was 0.00239 volt positive to a 2-phase cadmium amalgam at 25° and observed values were increased by this figure to give the e. m. f. of the cell

(C) Cd–Hg(2 phase)/CdI_2(m' in H_2O, D_2O)/AgI–Ag

Results of measurements of the e. m. f. of the above cell at 0.1 m' (moles of salt per 55.507 moles of total water species) as a function of deuterium content are presented in Table I. Values for light water were interpolated from the data of Bates[5] using large-scale plots of $-\log \gamma_H$ *vs.* $m'^{1/3}$ and the electromotive force equation at 25° given as (D).

$$\text{(D)} \qquad E = 0.18280 - 0.088716 \log \gamma_H m_H$$

Good agreement was obtained between the check runs in protium water and the original data of Bates. The voltage decrease of the cells made with deuterium water is nearly a linear effect of the deuterium content. Deviations from linear variation are given in the last column of Table I, and it appears that there may be a slight sag just beyond the experimental error. A slightly sagged curve was observed in a similar study of the thermodynamics of potassium chloride in protium and deuterium oxide.[2] For this work cells involving liquid junctions were employed and isotopic water species may have been transferred across the boundary. Apparently, whatever the nature of the solvation effects on cadmium iodide in protium-deuterium oxide mixtures, the amount of HDO present is not important. This is decidedly not true for the hydrochloric acid cell made in heavy water, for the value of $E_H - E_D$ passes through a maximum,[8] the effect being associated with the various isotopic hydronium ions formed.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL Cd–Hg(2 PHASE)/ CdI_2(0.1m')/AgI–Ag AT 25° AS A FUNCTION OF THE DEUTERIUM CONTENT OF THE SOLVENT

D_2O, %	m'	$E_{H_2O \cdot D_2O}$ obs., volts	$E_{H_2O} - E_{H_2O \cdot D_2O}$ volts	Deviation from linearity, millivolts
0.02	0.09989	0.35766	−0.00004	−0.01
0.02	.09996	.35765	− .00003	.00
18.76	.09991	.35620	.00142	− .17
44.15	.09971	.35391	.00372	− .07
89.33	.10000	.34994	.00768	− .02
89.46	.10003	.34989	.00773	+ .02

Discussion of Results

The data obtained in heavy water are not sufficiently comprehensive to permit the evaluation of the standard molal potential in pure D_2O nor the calculation of conventional activity coefficients in this solvent. However, the relative activity coefficient, γ'_D, defined in equation (A) may be obtained in the following manner. For the light water cell the e. m. f. is represented as

$$\text{(E)} \qquad E_H = E^0_H - RT/2F \ln 4(m_H\gamma_H)^3$$

(E) while for the deuterium oxide cell on the modified molal scale, m', (F) holds. If E^0_H is arbitrarily

$$\text{(F)} \qquad E_D = E'^0_D - RT/2F \ln 4(m'_D\gamma'_D)^3$$

set equal to E'^0_D and if $m_H = m'_D$ then equations (E) and (F) can be combined to give (G). At

$$\text{(G)} \qquad E_H - E_D = 3RT/2F \ln (\gamma'_D/\gamma_H)$$

25° this equation can be further simplified to (H).

$$\text{(H)} \quad (E_H - E_D)/0.0088716 + \log \gamma_H = \log \gamma'_D$$

Table II summarizes the results obtained at various concentrations, m', of cadmium iodide for cell (C). In all cases m' is given as the moles of salt per 55.507 moles of total water species. The observed potential of cell (C) is listed in the column headed $E_{H_2O.\ D_2O}$, obs. The heading $E_{H_2O} - E_{D_2O}$ refers to the difference between the e. m. f. of cell (B) in water (data of Bates) and the observed value of cell (C) extrapolated to pure deuterium oxide. Stoichiometric mean ionic activity coefficients, γ_H, taken from the data of Bates, were used to compute the listed values of γ'_D.

TABLE II

ELECTROMOTIVE FORCE OF THE CELL: Cd–Hg(2 PHASE)/ CdI_2(m')/AgI–Ag IN DEUTERIUM OXIDE AS A FUNCTION OF CONCENTRATION AT 25°

D_2O, %	m'	$E_{H_2O.D_2O}$, obs., volts	$E_{H_2O} - E_{D_2O}$, volts	γ_H	γ'_D
90.68	0.005729	0.39955	0.01247	0.469	0.649
90.82	.010008	.38697	.01139	.382	.513
90.48	.015542	.37823	.00998	.319	.413
90.33	.02836	.36767	.00926	.234	.298
90.78	.05961	.35669	.00878	.149	.188
90.34	.06019	.35674	.00862	.149	.186
89.33	.10000	.34994	.00860	.107	.134
89.46	.10003	.34989	.00864	.107	.134
89.46	.14385	.34511	.00860	.0843	.105
89.23	.50831	.32828	.00913	.0365	.0463
90.34	.83077	.32066	.00826	.0277	.0343
90.87	1.3593	.31186	.00796	.0214	.0263

Figure 1 is a plot of the activity ratio, a_D/a_H (which is equivalent to $(\gamma'_D)^3/(\gamma_H)^3$), *versus* the square root of molality, m'. It may be seen that there is a slight linear change with molality down to 0.06 m'; below that concentration the activity ratio rises sharply. Although the experimental error increases in this region the results indicate a very real trend. The most interesting area appears to be at dilutions beyond those reported in this paper (0.006 m').

At 0.1 m' the value for the partial molal free energy change when 1 mole of cadmium iodide

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(7) Stokland, Ronaess and Tronstad, *Trans. Faraday Soc.*, **35**, 312 (1938).

(8) Noonan and La Mer, *J. Phys. Chem.*, **43**, 247 (1939).

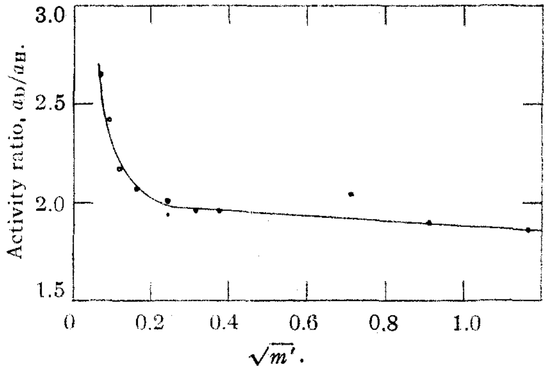

Fig. 1.—Activity ratio of cadmium iodide in heavy and light water at 25° as a function of concentration.

is transferred isothermally and reversibly from pure deuterium oxide solution to pure protium oxide solution is −398 cal. This may be compared with about −225 cal. for a similar transfer of potassium chloride.[2]

Correction for Differences in Molar Volume.—Because a mole of D_2O occupies 0.36% more volume than a mole of H_2O at 25° a correction should be applied for the electrical work obtained on isothermally and reversibly expanding the ionic assembly in light water to the volume it would occupy in heavy water. Using the appropriate e.m.f. equation for a cadmium iodide concentration cell, and assuming that the density and activity coefficients of the solutions do not change over a range of 0.36% variation in molality, it will be found that the value is 0.00014 volt. This correction should be added to the difference, $E_H - E_D$. It is about the order of the experimental error in measuring the most concentrated solutions and was neglected in treating the results.

Summary and Conclusions

1. The e.m.f. of cell (C) has been determined

(C) Cd-Hg(2 phase)/CdI_2(m' in H_2O, D_2O)/AgI-Ag

at 25° as a function of concentration, m', of cadmium iodide in terms of moles of salt per 55.507 moles of total water species. By combining the results with light water data, relative stoichiometric mean ionic acitivity coefficients, γ'_D, in deuterium oxide have been computed. The value of this activity coefficient is not unity at infinite dilution, but it affords a comparison of the activity behavior of cadmium iodide in the isotopic solvents.

2. At 0.1 m' the e.m.f. of cell (C) was found to be nearly a linear function of the deuterium content of the solvent.

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Adsorption of Gas Mixtures. Nitrogen–Oxygen on Anatase

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The data on multilayer adsorption of gas mixtures[2] are limited in quantity compared to those available on single gases. Moreover, the studies which have been made have employed chiefly charcoal and silica gel as adsorbents. These substances, while industrially important, are not suitable for fundamental studies, since the phenomena of multilayer adsorption and capillary condensation occur simultaneously on their surfaces. A further limitation of some of the studies[3] is the choice of pairs of adsorbates for which large deviations from additive properties, *e. g.*, Raoult's law, are to be expected. Such data are peculiar to the system studied, and cannot yield generally useful information.

Hill[4] has recently generalized the Brunauer–Emmett–Teller (BET) theory[2,5] to mixtures of gases, for which no or moderate deviations from Raoult's law occur. This extension brings out the important fact that any statistical theory of adsorption can be generalized to give adsorption isotherms for such mixtures. Since the added assumption involved in the generalization will not introduce a large error, for a well-chosen pair of gases, the degree of agreement obtained between gas mixture data and the extended theory will provide evidence for or against the original theory. It will be shown below that the present study provides strong evidence against at least one of the postulates of the BET theory, and indications in favor of a quite different model.

The system chosen for this study was the gas pair nitrogen–oxygen on the adsorbent anatase (TiO_2). The two gases have convenient vapor pressures at liquid nitrogen temperature, and their phase diagrams at this temperature show small deviations from Raoult's law. The analysis can be made readily by a direct method. The adsorbent is one which has been extensively studied,[6,7] and consists of single crystals, free from

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(2) Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, pp. 474–497.

(3) Rao, *J. Phys. Chem.*, **36**, 616 (1932); Tryhorn and Wyatt, *Trans. Far. Soc.*, **22**, 139 (1926).

(4) Hill, *J. Chem. Phys.*, **14**, 268 (1946).

(5) Hill, *ibid.*, **14**, 263 (1946).

(6) Jura and Harkins, THIS JOURNAL, **66**, 1356 (1944); Harkins and Jura, *ibid.*, **66**, 1362, 1366 (1944).

(7) Beebe, Beckwith and Honig, *ibid.*, **67**, 1557 (1945).