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STUDIES ON COORDINATION COMPOUNDS.
I. A METHOD FOR DETERMINING THERMODYNAMIC EQUILIBRIUM CONSTANTS IN MIXED SOLVENTS.

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by

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SUMMARY

In the past "pH" titrations in partially non-aqueous solvents have been made in order to determine the stability of coordination compounds. The interpretation of such data has been reconsidered with the object of obtaining thermodynamic stability constants. It is assumed that the activity coefficient of electrolytic solutes in these solvents is determined solely by the solvent composition and the ionic concentrations. Experimental substantiation of the assumption is given and the method of calculating thermodynamic stability constants is discussed.

INTRODUCTION

Several years ago J. Bjerrum introduced[1]

(1) Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase and Sons, Copenhagen, 1941.

the technique of determining the stability of metal ammines by a potentiometric titration in which a glass electrode was used to determine the hydrogen ion concentration during the formation reaction. The ease with which individual equilibrium constants for the n successive, reversible, step-reactions of the formation of a complex MA_n[2]

(2) M designates a metal ion; A, a complexing ligand.

could be determined led to the application of the method to other complexing agents. Jonassen and his students[3]

(3) Jonassen et al, J. Am. Chem. Soc., 72, 4968 (1950).

and Verhoek and coworkers[4]

(4) Carlson, McReynolds, and Verhoek, J. Am. Chem. Soc., 67, 1334 (1945).

have determined the stabilities of complexes with polydentate amines, as has Schwarzenbach and his school[5]

(5) Schwarzenbach et al, Helv. Chim. Acta., 33, 947-1005 (1950).

using a somewhat modified treatment of data obtained from similar pH titrations. Other investigators[6,7]

(6) Calvin and Wilson, J. Am. Chem. Soc., 67, 2003 (1945).
(7) Maley and Mellor, Australian J. Sci. Research, 2A, 92-110 (1949).

adapted the method for use with chelating agents which are weak acids, for example, beta-diketones and salicylaldehyde derivatives.

In all of the above cases the formation constants so determined have been concentration constants, which were valid only for a given set of conditions. Furthermore, the same conditions were not adopted by all investigators. Because of this and other facts that will be presented later, attention has been turned to the determination of activity constants.

In the present case the object is to determine thermodynamic constants for reactions of the type[8]

(8) Here Ch^- is used to designate the anion of a chelating agent which is a weak acid (HCh). This notation is adopted to replace the formerly-used Ke^- in order to avoid confusion with the conventional symbol for an equilibrium constant.

$$M^{++} + Ch^- \longrightarrow MCh^+ \qquad K_{f_1} \qquad (1)$$

$$MCh^+ + Ch^- \longrightarrow MCh_2 \qquad K_{f_2} \qquad (2)$$

The treatment of the experimental data further requires that the acid dissociation constant for the chelating agent be known; namely, that K_d be known for the reaction

$$HCh \rightleftharpoons H^+ + Ch^- \qquad (3)$$

The problem thus resolves itself into one of determining these three thermodynamic constants.

The situation is complicated by the fact that the species MCh_2 is frequently insoluble in water. The application of the Bjerrum method requires that the system be always in a single phase, in order that concentrations be calculable from the initial

composition. Consequently, the use of mixed water-dioxane solvents was introduced by Calvin and Wilson.[6]

The use of such solvents immediately raises the question of the interpretation of the potential obtained in a partially non-aqueous solvent from a cell containing a glass electrode and possessing a liquid junction error. It will be shown that in the solvents used the glass electrode behaves as a hydrogen electrode and that a standardization is possible, so that the potentials obtained can be converted to hydrogen ion concentrations. Once this behavior is characterized one can proceed to determine the necessary thermodynamic constants for chelation by the introduction of certain approximations.

The basic assumption which is to be made is that the activity coefficients in water-dioxane mixtures of electrolytes which are strong in water will be determined solely by the solvent composition and the ional concentration. That is, it is assumed that all strong electrolytes of the same charge type behave alike, where by "strong electrolyte" is understood "strong in water". This qualification is necessary since in solvents of greater than approximately 50% dioxane content all electrolytes are "weak" because of the extensive ionic association.

In essence the assumption is one of assuming the application of the principles of the interionic attraction theory, neglecting the difference in ion size (or the Debye-Hückel distance of closest approach). Such an assumption cannot be completely valid, but the important point is the magnitude of the errors which it introduces. In organic mixed solvents of low dielectric constant, the predictions of the interionic attraction theory will differ more from the observed behavior than in water by reason of the greater effect of the electrostatic interactions and the resulting ion association. Generally, as electrostatic forces increase, e.g., by an increased concentration of ionic charge, the failure of the Debye-Hückel treatment becomes more pronounced.

For the present determinations, however, one is concerned not with conformance to the Debye-Hückel behavior but with similarity of behavior of electrolytes of the

same charge type. Even though one might not be able to calculate accurately from the interionic attraction theory the activity coefficient of a given electrolyte, one might expect that the variations among the actual coefficients for similar electrolytes are small. It is assumed indeed that to a first approximation these differences are zero. It is important to recognize that the accuracy necessary in the study of the stability of chelate compounds is less than that which would be desirable for an exact thermodynamic treatment. The greatest accuracy possible of course is desirable, but much useful information can be obtained from stability constants which have an error of even a few tenths of a log unit.

EXPERIMENTAL

The techniques employed are those of Calvin and Wilson. A Beckman Model G pH meter was used as the measuring instrument. Beckman electrodes with extension leads were used for cell components, the reference electrode being a saturated calomel (Beckman No.1170) and the glass electrode a Beckman Type E (No.8990-75). This electrode, designed primarily for high pH use, functions well in acid solution, though probably with a shortened life. The hydrogen and Ag-AgCl electrodes used were prepared by the usual procedures.

All measurements were made at 30.0° ± 0.1°C. The pH meter was standardized against aqueous buffers prepared from NBS standard samples. The materials, with the exception of dioxane, were reagent grade used without further treatment. The dioxane was a commercial grade, purified by the method of Weissberger[9]

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(9) Weissberger and Proskauer, "Organic Solvents", Oxford, 1935, p. 139.

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and stored over activated alumina.

RESULTS

In order to avoid confusion over the use of the term "pH" this will be reserved for reference to aqueous solutions in which a pH scale has been standardized. The indication on the pH scale of the Beckman instrument obtained for nonaqueous solutions will be designated by the symbol B.

First it was necessary to verify the response of the glass electrode to hydrogen ions in water-dioxane solutions. Measurements were made on 75 volume % dioxane solutions over the B range of 2 to 11. Simultaneous measurements on the same solutions were made with a hydrogen, silver-silver chloride couple. The B values for the glass electrode cell and the corresponding EMF of the hydrogen electrode cell are recorded in Table 1 and represented graphically in Figure 1. The solid line is the Nernst slope for 30°C.

These data were obtained by the neutralization of an acetic acid solution containing NaCl at a concentration of 0.03 F with a dioxane solution of NaOH, followed by reacidification with HCl to obtain low B values. Because of the way in which the experiment was performed, there was a decrease in chloride ion concentration as base was added and then an increase as the acid was added. Corrections for the varying chloride ion concentration have been applied, assuming that the activity of the chloride ion is proportional to the concentration. The correction was negligible for all except the points at the extreme ends and here amounted to a maximum of 5 millivolts, or about twice the experimental error.

The results show that the glass-calomel cell measures hydrogen ion activity as defined by a hydrogen electrode; that is, an empirical calibration obtained at a given salt concentration and for a given solvent mixture is valid over a wide range of hydrogen ion concentrations. Other more extensive data not presented here in the B range of 1.6 to 3.3 confirm constancy of the calibration. These results are in agreement also with the findings of Calvin and Wilson for a 50% dioxane solution.

An empirical calibration by means of which the pH meter reading B could be converted to hydrogen ions concentration was made as follows. Readings were made on a

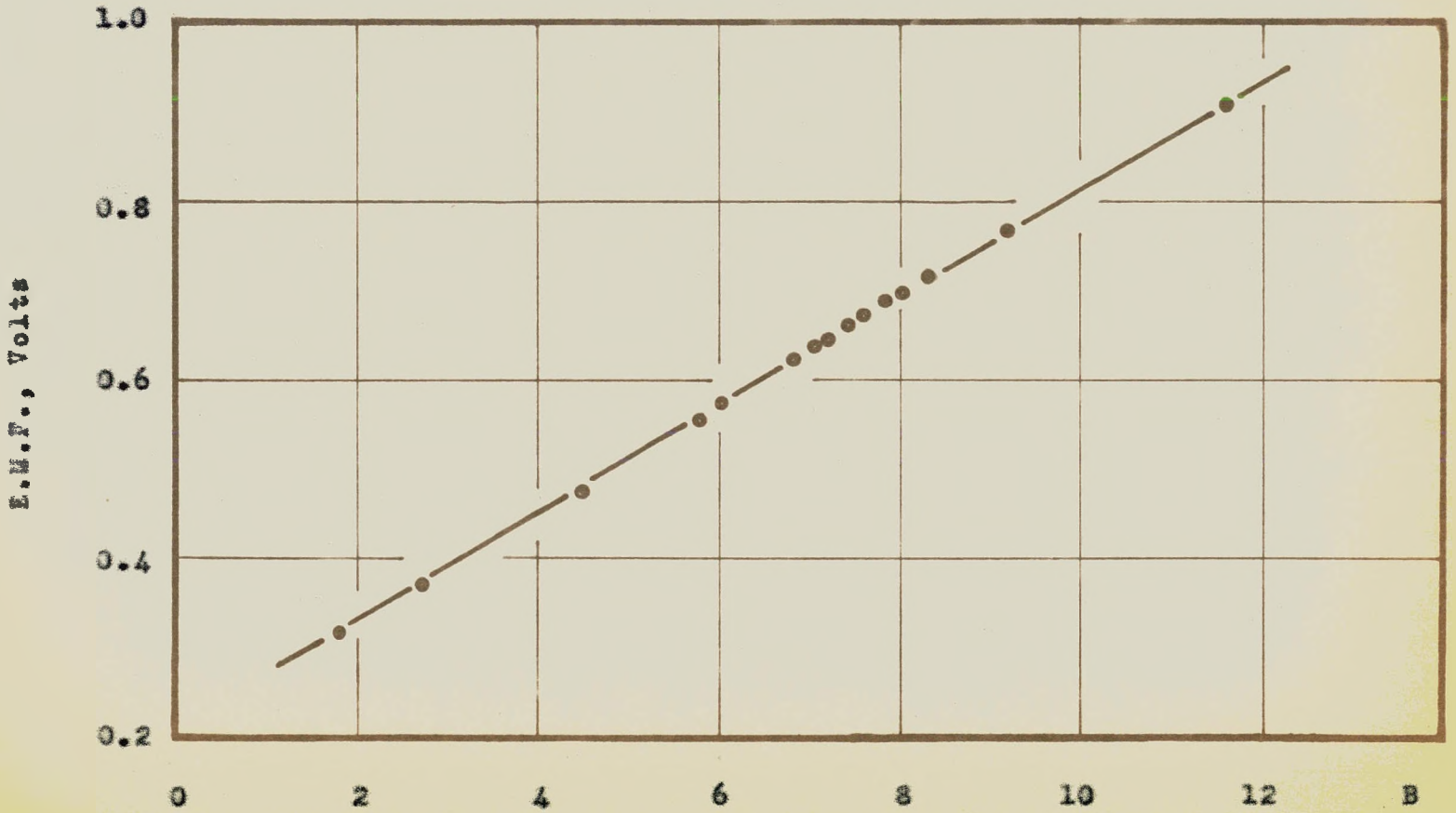

Fig. I. - The relation between the pH-meter readings (B) and the E.M.F. of the cell $H_2 \mid H^+, Cl^- \mid AgCl - Ag$ in 75 vol. % dioxane solution. The theoretical slope 0.0601 is drawn.

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series of solutions containing HCl and NaCl in various solvents ranging from pure water to 75 volume % dioxane. From the known stoichiometric hydrogen ion concentration $[H^+]$ a quantity U_H defined as

$$U_H \equiv \frac{\text{antilog } (-B)}{[H^+]} \qquad (4)$$

was calculated. U_H then is a conversion factor for obtaining the hydrogen ion concentration from the meter reading B:

$$-\log [H^+] = B + \log U_H \qquad (5)$$

and in general will be a function of solvent composition and ionic concentration.[10]

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(10) It should be noted that the hydrogen ion concentration calculated from equation (5) in the case of the calibration experiments is the stoichiometric concentration; the actual free hydrogen ion concentration will be less than this because of ion association. When the U_H determined as above is applied to a solution in dioxane of a weak acid (e.g., acetic acid or a beta-diketone) the hydrogen ion concentration calculated will not be the total stoichiometric concentration but will correspond to the concentration which would exist for the same solute in water as a solvent.

The values of log U_H obtained for solutions of varying solvent composition and of different salt and acid concentrations are given in Table 2 and represented by curves A, B, and C of Figure 2. It is seen that U_H is concentration dependent, as one would expect. If this dependence is primarily the result of change in the activity coefficient of hydrogen ion with total ionic concentration, one should be able to correct for the effect by using known activity coefficients and thus obtain a correction factor U_H° which is independent of ionic concentration; i.e., U_H° will correspond to the correction at zero ionic strength in the solvent under consideration.

For this purpose define

$$U_H^\circ \equiv U_H \cdot 1/\gamma \qquad (6)$$

where γ is the activity coefficient (mean) for the solvent composition and ionic concentration for which U_H was determined. If the assumption of equivalence of ions of the same charge type is valid, then one may use for γ any experimental activity coefficient, provided the coefficient for the appropriate solvent composition and

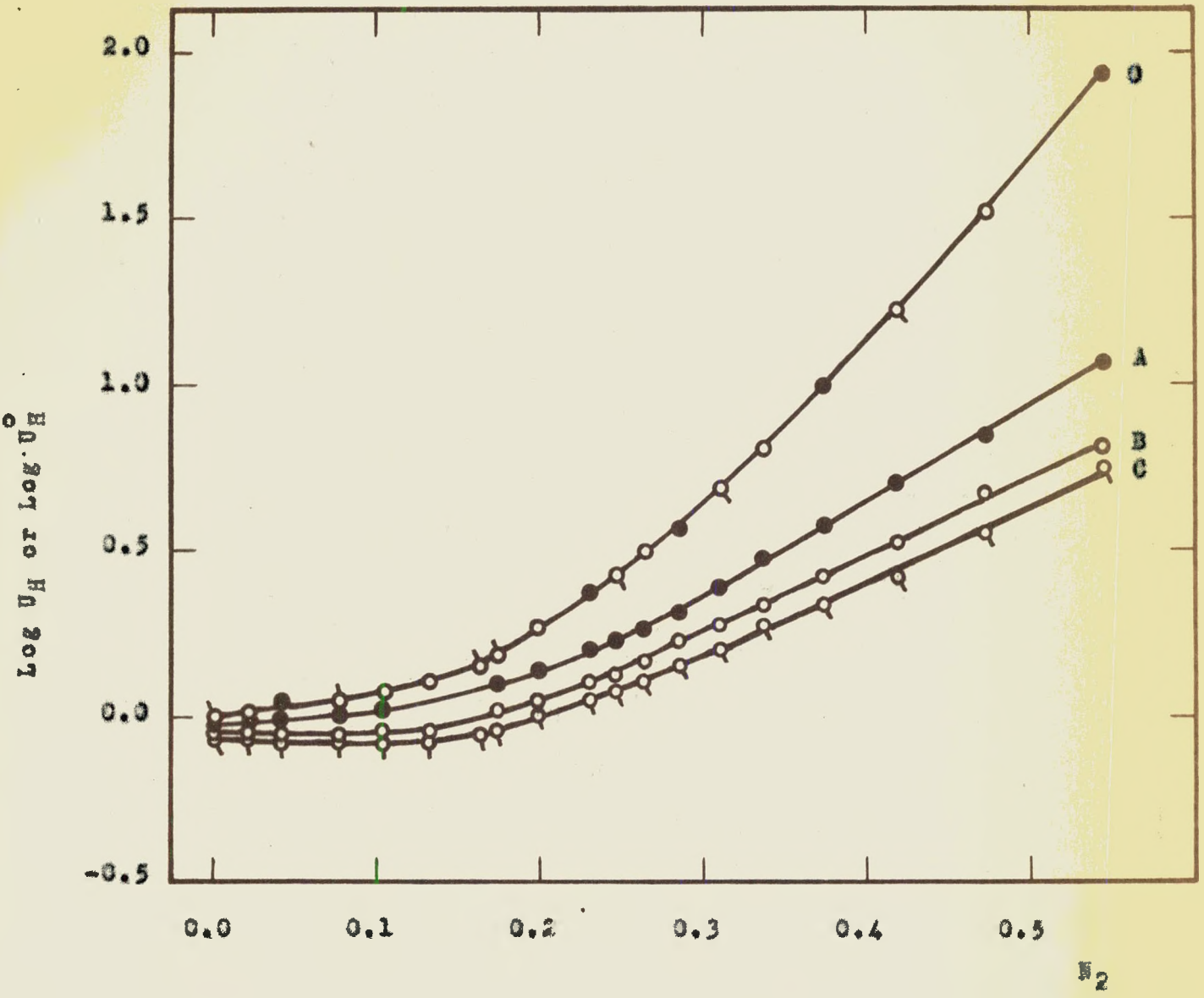

Fig. 2. - log U_H, for different salt concentrations, and log U_H^o as functions of N_2, the mole fraction of dioxane.

δ and ○, 0.0312 F.; ○, 0.0172 F.; ●, 0.00586 F.

Bolton Fig 2 paper I

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total ionic concentration is selected.

The result of the application of the activity coefficient correction as defined by equation (6) is indicated by column 5 in Table 2 and curve O of Figure 2. The activity coefficients used were obtained by interpolation from the data of Harned et al.[11]

(11) Harned and Owen, "Physical Chemistry of Electrolytic Solutions", 2nd Ed., Reinhold Publishing Company, 1950, p. 548.

The fact that one obtains the same function U_H° for different salt and acid concentrations furnishes the first substantiation of the basic assumption of equivalence of ions. With the exception of some of the data for curve C the average scattering of points is less than 0.02 log units.

The fact that the EMF of the cell

Glass electrode | HCl in organic solution | Sat'd KCl | Hg_2Cl_2-Hg (I)

varies with solvent composition (as reflected by the value of log U_H°) is attributable to two effects: (1) the partial molar free energy of the hydrogen ion (at infinite dilution) varies with solvent composition, the primary medium effect;[12]

(12) Ibid., p. 516.

and (2) the junction error at the solution — saturated KCl interface varies with solvent composition.

It should be possible to separate the two effects by measuring the EMF of the cell

Glass electrode | HCl in organic solution | AgCl-Ag (II)

In this case there is no liquid junction error and the correction term log U_{H° becomes equal to log γ_0, the primary medium effect, where γ_0 is the activity coefficient at zero electrolyte concentration in the organic solvent referred to unity in pure water.

Data from such measurements may be treated as follows. Designate the EMF of cell II as E. Then,

$$E = E^{o} - RT/F \ln a_{HCl} \quad (8)$$

$$= E^{o} - RT/F \ln C_{H^+} C_{Cl^-} - RT/F \ln \gamma_{\pm}^2 \quad (9)$$

For a given solute concentration, at 30°C.

$$\frac{E^{o} - \text{const}}{0.0601} = \frac{E}{0.0601} + \log \gamma_{\pm}^2 \quad (10)$$

Let X refer to some water-dioxane solvent and 1 refer to water.

Then

$$\frac{E_1^{o} - E_x^{o}}{0.0601} = \frac{E_1 - E_x}{0.0601} + \log \frac{\gamma_1^2}{\gamma_x^2} = \log \gamma_o^2 \quad (11)$$

where log γ_o is the primary medium effect.

The log γ_o values so calculated for HCl in water-dioxane mixtures are tabulated in Table 3 and are plotted as a function of mole fraction of dioxane in Figure 3. Also plotted are values of the same quantity obtained by Harned [13]

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(13) Ibid., p. 519.

---

from thermodynamic cell measurements. The agreement again indicates support of the basic assumption, since the activity coefficients used in the calculations were for HCl, whereas they are being applied to a mixed HCl-NaCl solute.

It can be shown that the difference between log γ_o and log U_H^{o} is the result of a liquid junction error at the junction

HCl in organic solution | Sat'd KCl

This point is established by comparing the EMF of cell (I) above with that of cell (II).

As an example of the use of the method one may determine the thermodynamic dissociation constant of a weak acid. One can measure B for a series of solutions in various solvents, each solution containing a weak acid HA at concentration C_1, the salt of that acid NaA also at C_1, and inert electrolyte, e.g. NaCl, at concentration C_2. From these measurements one can calculate the thermodynamic acid dissociation constant

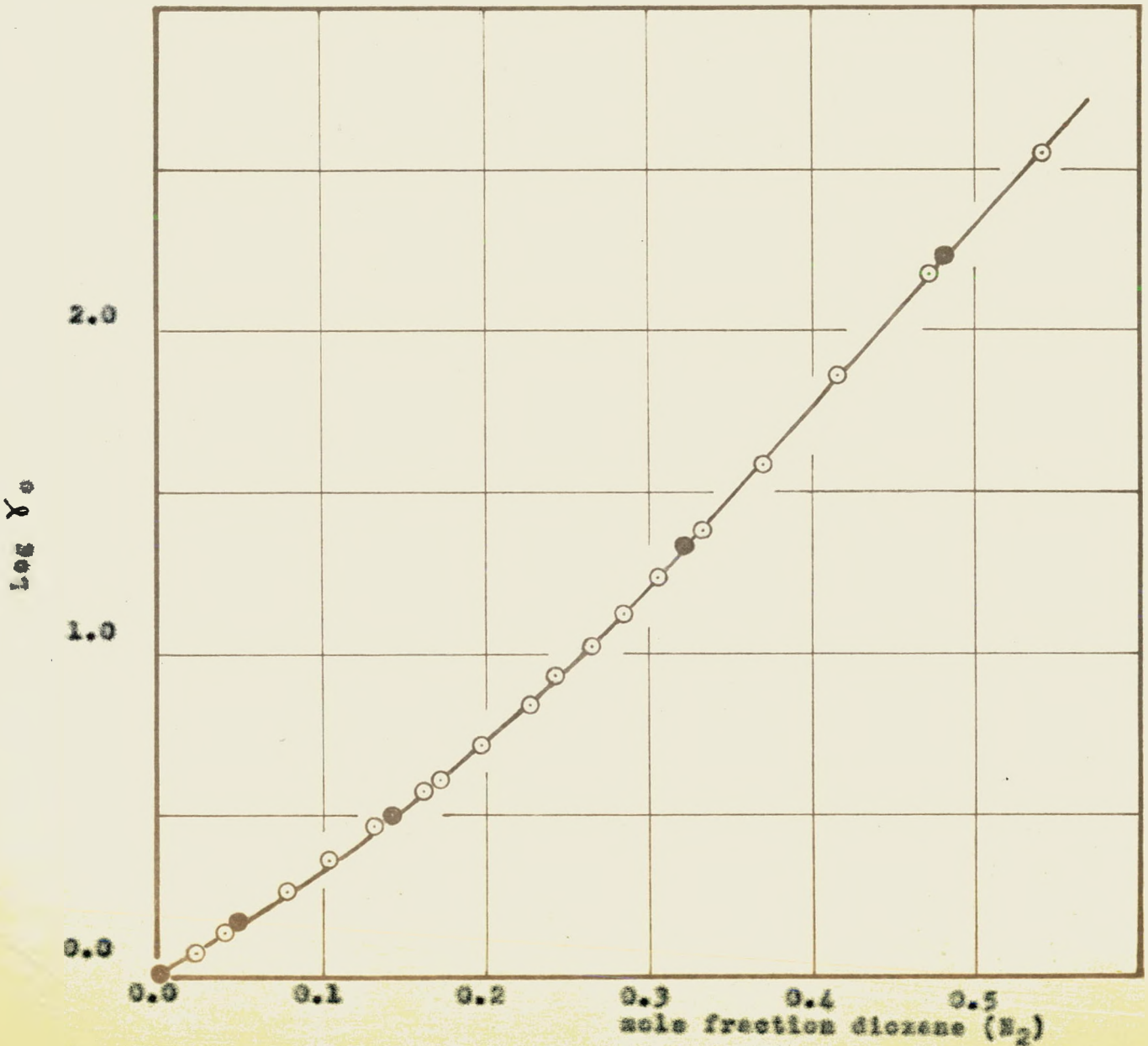

Fig. 3. - The primary medium function
● Data of harned using the cell H_2 | H^+, Cl^- | AgCl - Ag
○ Calculated data using the cell glass electrode | H^+, Cl^- | AgCl - Ag

$$K_D = \frac{[H^+]\ [A^-]}{[HA]} \cdot \frac{\gamma_{H^+}\ \gamma_{A^-}}{\gamma_{HA}} \qquad (12)$$

The stoichiometric concentrations are known experimentally and K_D may be calculated by the use of the following approximations.

1. Set γ_{HA} equal to unity. This is an approximation neglecting salt effects on the neutral molecule.
2. For $\gamma_{H^+}\ \gamma_{A^-}$ use $\gamma_{\pm}^2$ obtained for HCl in the same medium and at the same total ionic concentration.[11]

The values of the activity constant so calculated will vary with solvent and in general will decrease as the dielectric constant of the solvent decreases.

Measurements were made for acetic acid by this method, the data for which are given in Table 4. The dissociation constants calculated are represented in Figure 4, together with values for the same constant determined by Harned and coworkers[14]

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(14) Ibid., p. 581.

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from measurements made on galvanic cells without liquid junctions. The two measurements of Harned which are used (those to obtain $\gamma_{\pm}$ and those of K_D for comparison) are independent, so that the agreement exhibited by Figure 4 between the thermodynamic cell data and the pH data now determined is a reliable confirmation of the accuracy of the approximations made. It should be noted also that for the solvents of higher dioxane content the correction term for activity coefficients amounts to 1.5 log units; the slight scattering of points is no more than experimental error.

A second similar experiment to determine the dissociation constant of propionic acid was done, this time using $NaClO_4$ instead of NaCl. Again a comparison with data of Harned and coworkers (Fig. 4) illustrates the accuracy of the basic assumption, at least with respect to the ions involved in these two experiments.

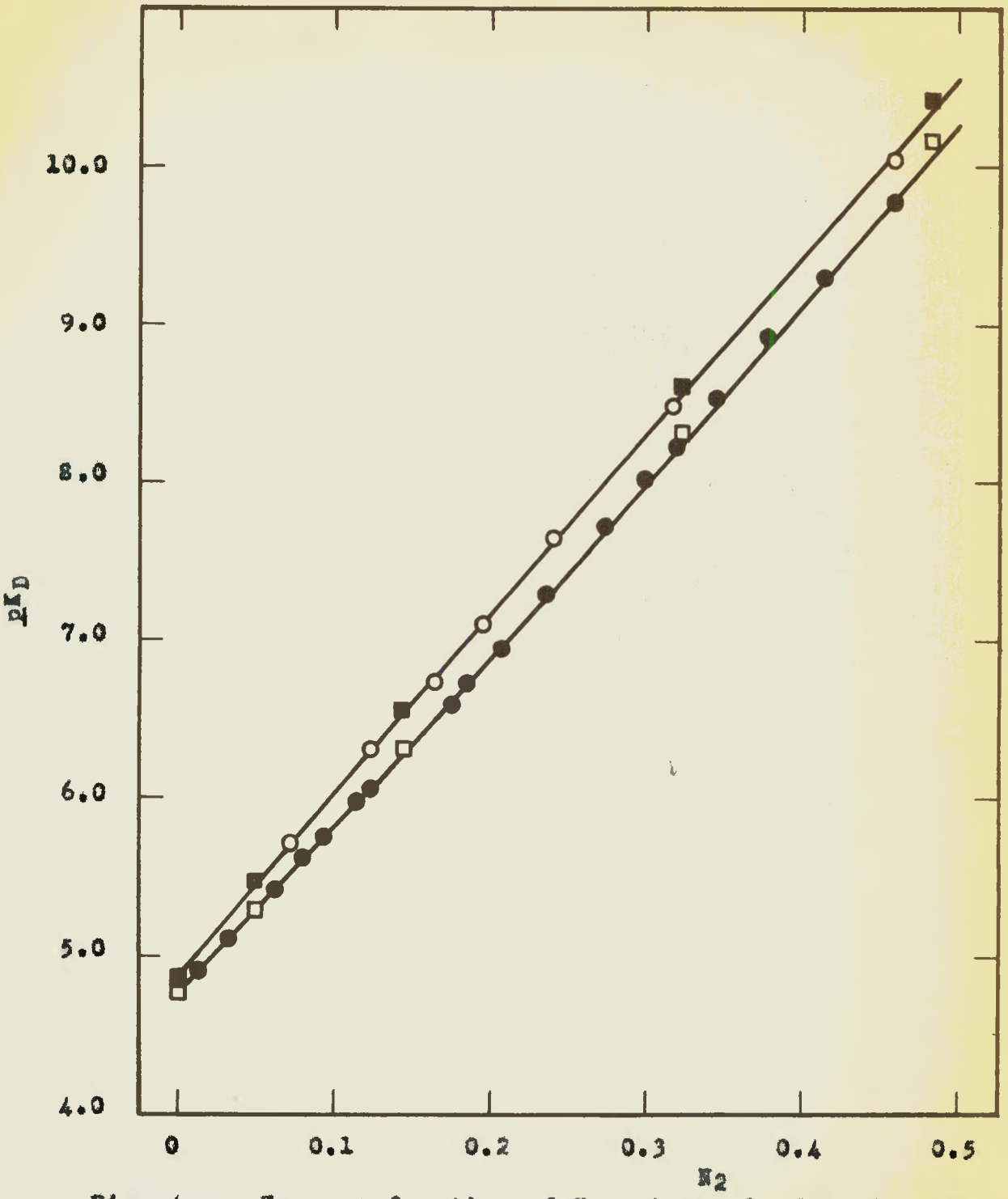

Fig. 4. - pK_D as a function of N_2, the mole fraction of dioxane (t = 30°C).

■ and □ are data of harned for propionic and acetic acids obtained using the hydrogen and AgCl - Ag electrodes.

O and ● are calculated data for propionic and acetic acids obtained using the glass and saturated calomel electrodes.

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Bottom Fig 4 page 1

DISCUSSION

It now remains to be shown how the determination of K_D, K_{f_1}, and K_{f_2} will be made.

The acid dissociation constant of a chelating agent HCh will be determined just as those of acetic and propionic acid were done.

The second chelation constant, for the reaction (2), can be treated as follows.

$$K_{f_2} \equiv \frac{[MCh_2]}{[MCh^+]\ [Ch^-]} \cdot \frac{\gamma_{MCh_2}}{\gamma_{MCh^+}\ \gamma_{Ch^-}} \qquad (13)$$

Multiplying by K_D, one obtains

$$K_{f_2} \cdot K_D = \frac{[MCh_2]}{[MCh^+]} \frac{[H^+]}{[HCh]} \cdot \frac{\gamma_{MCh_2}}{\gamma_{HCh}} \cdot \frac{\gamma_{H^+}}{\gamma_{MCh^+}} \qquad (14)$$

The point at which $[MCh_2] = [MCh^+]$ can be determined experimentally; in Bjerrum's notation,[1] here $\bar{n} = 3/2$. Making the assumption that $\gamma_{H^+} = \gamma_{MCh^+}$, one has at $\bar{n} = 3/2$

$$\log K_{f_2} = pK_D + \log \frac{[H^+]_{\bar{n}\,=\,3/2}}{[HCh]_{\bar{n}\,=\,3/2}} \qquad (15)$$

For convenience one may designate the log of the concentration ratio in (15) by C_2. The value of C_2 can be determined experimentally, the hydrogen ion concentration being obtained from a pH-meter reading and the concentration of unionized chelating agent being calculated from the amount of unbound chelating agent and the acid dissociation constant. From the measured value of pK_D, $\log K_{f_2}$ is then calculated.

In the above expression any specific interaction between MCh^+ and inorganic anions other than coulombic attraction has been implicitly assumed absent. That is, it is assumed that the activity coefficients of MCh^+ and H^+ are equal, or that MCh^+ behaves as the cation of a strong electrolyte. This also implies that solvent-ion interactions are the same as for the ion of a strong electrolyte of the same charge type.

In experimental work to be communicated later, it will be shown that for certain metals and certain chelating agents, C_2 is nearly independent of the inorganic anion

present and of the solvent in which the determination is made, whereas for certain other systems large variations are observed for both of the changes. The cases in which such variations are observed will be interpreted as examples of specific interactions of the two types mentioned.

The same type of treatment can be extended to the first chelation step (equation 1) for which we define

$$K_{f_1} \equiv \frac{[MCh^+]}{[M^{++}]\ [Ch^-]} \cdot \frac{\gamma_{MCh^+}}{\gamma_{M^{++}}\ \gamma_{Ch^-}} \qquad (16)$$

As before, multiplying by K_D one obtains

$$K_{f_1} \cdot K_D = \frac{[MCh^+]}{[M^{++}]} \cdot \frac{[H^+]}{[HCh]} \cdot \frac{\gamma_{MCh^+}\ \gamma_{H^+}}{\gamma_{M^{++}}\ \gamma_{HCh}} \qquad (17)$$

which can be written

$$\log K_{f_1} = pK_D + \log \frac{[MCh^+]}{[M^{++}]} + \log \frac{[H^+]}{[HCh]} + \log \frac{\gamma^2_{\pm\ 1\text{-}1}}{\gamma_{\pm\ 2\text{-}1}} \qquad (18)$$

where the subscripts on the activity coefficients signify 1-1 and 2-1 electrolytes. The activity coefficient term here causes uncertainty, since it can be approximated only in a rough manner. In the limiting case in which the Debye-Hückel limiting law applies, $\log \gamma_{\pm\ 2\text{-}1} = 2 \log \gamma_{\pm\ 1\text{-}1}$. Hence $\log \gamma^2_{\pm\ 1\text{-}1}/\gamma_{\pm\ 2\text{-}1} = 0$. This result is for ideal behavior and will not be completely valid at finite concentrations.

Again at the point at which $[MCh^+] = [M^{++}]$ (where Bjerrum's $\bar{n} = 1/2$) one obtains

$$\log K_{f_1} = pK_D + \log \frac{[H^+]_{\bar{n}\ =\ 1/2}}{(HCh]_{\bar{n}\ =\ 1/2}} = pK_D + C_1$$

the log of the concentration ratio being represented by C_1. C_1 has a significance analogous to that of C_2.

ACKNOWLEDGMENT

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Table 1

B	EMF[a]
6.02[b]	+ 0.570 volts
6.81	0.620
7.08	0.633
7.15	0.641
7.40	0.660
7.60	0.668
7.81	0.683
8.02	0.695
11.60	0.907
9.20	0.765
8.32	0.716
5.80	0.552
4.48	0.472
2.72	0.370
1.80	0.317

a. For the cell H_2/H^+, Cl^- / AgCl-Ag.

b. Not an equilibrium value.

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Table 2

A. [HCl] = 0.00116 F; [NaCl] = 0.0300 F; total 1-1 electrolyte = 0.0312 F.

$-\log [H^+] = 2.90$[a]

Mole fraction dioxane	B	$\log U_H$	$\log 1/\gamma$	$\log U_H^o$
0.000	2.97	-0.07	0.07	0.00
0.022	2.97	-0.07	0.08	0.01
0.041	2.98	-0.08	0.10	0.02
0.077	2.98	-0.08	0.12	0.04
0.104	2.98	-0.08	0.15	0.07
0.132	2.98	-0.08	0.18	0.10
0.163	2.96	-0.06	0.21	0.15
0.174	2.94	-0.04	0.22	0.18
0.199	2.90	-0.00	0.27	0.27
0.230	2.86	+0.04	0.32	0.36
0.246	2.83	0.07	0.35	0.42
0.264	2.80	0.10	0.39	0.49
0.285	2.76	0.14	0.43	0.57
0.310	2.71	0.19	0.49	0.68
0.336	2.63	0.27	0.56	0.83
0.374	2.57	0.33	0.67	1.00
0.418	2.48	0.42	0.80	1.22
0.473	2.35	0.55	0.98	1.53
0.545	2.15	0.75	1.19	1.94

a. The value for $-\log [H^+]$ was taken as equal the quality $(B - \log 1/\gamma)$ for the 100% water solution. Within experimental error this is the same as calculated from the composition of the solution.

Table 2 (continued)

B. [HCl] = 0.00116 F; [NaCl] = 0.0160 F; total 1-1 electrolyte = 0.0172 F.

$- \log [H^+] = 2.92^a$

Mole fraction dioxane	B	log U_H	log $1/\gamma$	log U_H°
0.000	2.97	-0.05	0.05	0.00
0.022	2.97	-0.05	0.06	0.01
0.041	2.98	-0.06	0.08	0.02
0.077	2.98	-0.06	0.10	0.04
0.104	2.97	-0.05	0.12	0.07
0.132	2.97	-0.05	0.15	0.10
0.174	2.90	+0.02	0.19	0.21
0.199	2.88	0.04	0.22	0.26
0.230	2.82	0.10	0.27	0.37
0.246	2.80	0.12	0.29	0.41
0.264	2.76	0.16	0.33	0.49
0.285	2.70	0.22	0.37	0.59
0.310	2.65	0.27	0.42	0.69
0.336	2.59	0.33	0.48	0.81
0.374	2.50	0.42	0.57	0.99
0.418	2.40	0.52	0.69	1.21
0.473	2.25	0.67	0.85	1.52
0.545	2.11	0.81	1.10	1.91

C. [HCl] = 0.00116 F; [NaCl] = 0.00470 F; total 1-1 electrolyte = 0.00586 F.

$- \log [H^+] = 2.93^a$

Mole fraction dioxane	B	log U_H	log $1/\gamma$	log U_H°
0.000	2.97	-0.04	0.04	0.00
0.022	2.94	-0.01	0.04	0.03
0.041	2.94	-0.01	0.05	0.04
0.077	2.93	0.00	0.06	0.06
0.104	2.91	+0.02	0.08	0.10
0.174	2.84	0.09	0.12	0.21
0.199	2.80	0.13	0.15	0.28
0.230	2.74	0.19	0.18	0.37
0.246	2.71	0.22	0.20	0.42
0.264	2.67	0.26	0.22	0.48
0.285	2.61	0.31	0.25	0.56
0.310	2.55	0.38	0.29	0.67
0.336	2.46	0.47	0.34	0.81
0.374	2.36	0.57	0.42	0.99
0.418	2.23	0.70	0.53	1.23
0.473	2.07	0.84	0.67	1.51
0.545	1.87	1.06	0.87	1.93

a. The value for - log $[H^+]$ was taken as equal the quantity (B - log $1/\gamma$) for the 100% water solution. Within experimental error this is the same as calculated from the composition of the solution.

Table 3

[HCl] = 0.00116 F; [NaCl] = 0.0300 F; total 1-1 electrolyte = 0.0312 F.

Mole fraction dioxane	EMF (Cell II)	$\frac{E_1-E_x}{.060}$	$\log 1/\gamma^2$	$\log \frac{\gamma_1^2}{\gamma_x^2}$	$\log \gamma_0$
0.000	-0.192 v.	0.00	0.14	0.00	0.00
0.022	0.200	0.11	0.16	0.02	0.06
0.041	0.205	0.22	0.20	0.06	0.14
0.077	0.217	0.42	0.24	0.10	0.26
0.104	0.225	0.55	0.30	0.16	0.35
0.132	0.234	0.70	0.36	0.22	0.46
0.163	0.242	0.83	0.42	0.28	0.55
0.174	0.247	0.92	0.44	0.30	0.61
0.199	0.254	1.03	0.54	0.40	0.71
0.230	0.263	1.18	0.64	0.50	0.84
0.246	0.270	1.30	0.70	0.56	0.93
0.264	0.276	1.40	0.78	0.64	1.02
0.285	0.283	1.52	0.86	0.72	1.12
0.310	0.290	1.63	0.98	0.84	1.23
0.336	0.300	1.80	1.12	0.98	1.39
0.374	0.311	1.98	1.34	1.20	1.59
0.418	0.325	2.22	1.60	1.46	1.84
0.473	0.340	2.47	1.96	1.82	2.14
0.545	0.361	2.82	2.38	2.24	2.53

Table 4

$[HC_2H_3O_2]$ = 0.0086 F; $[NaC_2H_3O_2]$ = 0.0086F; [NaCl] = 0.0086 F; total 1-1 electrolyte = 0.0172 F.

Mole fraction dioxane	B	log U^{o}_{H}	log $1/\gamma$	pK_D [a]
0.000	4.71	0.00	0.06	4.77
0.012	4.83	0.01	0.06	4.90
0.032	5.02	0.02	0.07	5.11
0.061	5.29	0.03	0.09	5.41
0.079	5.48	0.04	0.10	5.62
0.093	5.58	0.06	0.11	5.75
0.114	5.76	0.08	0.13	5.97
0.123	5.82	0.09	0.14	6.05
0.175	6.22	0.18	0.19	6.59
0.184	6.30	0.22	0.20	6.72
0.207	6.47	0.28	0.24	6.94
0.235	6.63	0.38	0.28	7.29
0.273	6.84	0.53	0.35	7.72
0.298	6.98	0.63	0.40	8.01
0.318	7.06	0.72	0.44	8.22
0.345	7.17	0.86	0.51	8.54
0.377	7.30	1.05	0.58	8.93
0.413	7.40	1.20	0.70	9.30
0.458	7.50	1.44	0.82	9.76

a. pK_D calculated as (B + log U^{o}_{H} - log γ).

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