[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Measurement and Correlation of Acid Dissociation Constants for Ammonium and Anilinium Salts in the System Dioxane–Water[1]

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We have measured thermodynamic pK_A values for the hydrochlorides of aniline, *p*-toluidine, *p*-anisidine, N-methylaniline, N-dimethylaniline, ammonia, and trimethylamine at 25.0° in dioxane–water mixtures containing 0.0, 20.0, 45.0, 70.0 and 82.0 weight % dioxane. The solvent dependence of the pK_A values is given according to the *activity postulate*[5] by the equation 4, $pK_A - pK_A^{HOH} = \log f_H + mY_0$, where m is a parameter characteristic of the acid and independent of the solvent composition, Y_0 is a function of the solvent and independent of the acid, and f_H is the Brønsted basicity constant of the solvent relative to water.[6b] The pK_A values are correlated by means of equation 4 with a probable error of 0.015 unit. The solvent dependence of the Y_0 values is approximated well by the expression $Y_0 = -(1 - w)^2$, where w is the weight fraction of water in the solvent. At equal values of w, the new Y_0 values for the system dioxane–water are equal, within experimental error, to the Y_0 values determined previously for the system ethanol–water.

The system dioxane–water has often been useful in studies of the effect of solvent on acid dissociation,[2,3] partly because it covers such a wide range of dielectric constant. The most recent pertinent K_A values for anilinium salts in this system are the conductometric values of James and Knox.[3] These values, however, are calculated using the principle of independent ionic mobilities at constant ionic strength—an assumption that may conceivably lead to erroneous values at low dielectric constant.

In the present article we report the potentiometric measurement of thermodynamic K_A values for a number of ammonium and anilinium salts at 25.0°, in dioxane–water mixtures containing up to 82.00 wt. % dioxane (D 10.56).[4] The effect of solvent on the K_A values has been examined with the aid of the *activity postulate* which we have used successfully on several previous occasions,[5,6a] and the pK_A values have been correlated on this basis with a probable error of 0.015 unit.

Measurement of pK_A Values.—Our new measurements are based on the e.m.f. of the cell

$$\text{Glass electrode/H}^+\ (c_H),\ \text{Cl}^-(c_{Cl}),\ \text{other solutes/AgCl–Ag} \quad (1)$$

at ionic strengths below 0.012 M. The e.m.f. of this cell affords an accurate measure of the activity product a_Ha_{Cl} even in 82% dioxane since the e.m.f. of the cell

$$\text{Pt–H}_2\ (\text{g, 1 atm.})/\text{HCl}\ (c)/\text{glass electrode} \quad (2)$$

is constant and independent of the acid concentration c.[7]

In order to derive values of c_H, and hence of K_A, from the e.m.f. data, one must know the mean ion activity coefficients, y, for hydrogen ion and chloride ion. We have assumed that the y values for the test solutions are equal to those obtained for HCl alone[7,8] in the same solvent and at the same ionic strength. That this approximation is satisfactory even in solutions containing 82% dioxane is shown by the results of e.m.f. measurements on a cell prepared by diluting 0.1017 meq. of *p*-toluidinium chloride and 0.0437 meq. of sodium hydroxide with varying amounts of solvent. The relevant data are listed in Table I, where it will be seen that the values of $E_0' = E' + \log a_Ha_{Cl}$, calculated from values assumed for y and with $pK_A = 4.13$, remain constant over the entire range of ionic strength from 0.003 to 0.001 M. Analogous results were obtained in two similar experiments which cover the range in ionic strength from 0.006 to 0.001 M, and also in one experiment in which anilinium chloride was the weak acid. The results indicate that the assumed y values are correct, at least up to a proportionality constant.

TABLE I

TEST OF ASSUMED VALUES OF ION ACTIVITY COEFFICIENTS[a]

82.00 wt. % dioxane, 25.0°

E' (pH scale reading)[b]	10^3c_{Cl}	10^5c_H	y[c]	E'_0
3.543	3.436	8.91	0.2165	−4.300
3.574	2.580	8.64	.2426	−4.308
3.610	2.061	8.40	.2663	−4.301
3.642	1.711	8.16	.2863	−4.299
3.668	1.463	7.94	.3041	−4.301
3.688	1.284	7.75	.3190	−4.306
3.754	0.976	7.33	.3528	−4.296

[a] Cells prepared from 0.1017 meq. of *p*-toluidinium chloride, 0.0437 meq. of sodium hydroxide, and the appropriate amount of 82.00 wt. % dioxane, pK_A of $p\text{-C}_7\text{H}_7\text{NH}_3^+ = 4.13$. [b] Average of two glass electrodes; E (mv.) $= -59.15(7.80 - E')$. [c] Ref. (7).

The validity of the assumed y values is confirmed further by the constancy of the calculated K_A values. For example, in the differential potentiometric measurement[9] of K_A, one may add to the aniline hydrochloride solution either some strong acid first and then strong base, or some strong base first and then strong acid. In the former method, c_{Cl} and

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(1) (a) The Effect of Solvent on Equilibrium and Rate Constants. III. Parts I and II of this series are given in ref. 5b and 6a. (b) Supported by the Office of Ordnance Research, U. S. Army.

(2) (a) H. S. Harned and G. L. Kazanjian, THIS JOURNAL, **58**, 1912 (1936); (b) H. S. Harned and L. D. Fallon, *ibid.*, **61**, 2377 (1939); (c) H. S. Harned and R. S. Done, *ibid.*, **63**, 2579 (1941); (d) H. S. Harned and T. R. Dedell, *ibid.*, **63**, 3308 (1941); (e) C. C. Lynch and V. K. La Mer, *ibid.*, **60**, 1252 (1938); (f) L. J. Minnick and M. Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939); (g) J. H. Eliott and M. Kilpatrick, *ibid.*, **45**, 485 (1941); (h) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).

(3) J. C. James and J. G. Knox, *Trans. Faraday Soc.*, **46**, 254 (1950).

(4) F. E. Critchfield, J. A. Gibson and J. L. Hall, THIS JOURNAL, **75**, 1991 (1953).

(5) (a) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); (b) E. Grunwald and B. J. Berkowitz, *ibid.*, **73**, 4939 (1951).

(6) (a) B. Gutbezahl and E. Grunwald, *ibid.*, **75**, 559 (1953); (b) **75**, 565 (1953).

(7) H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

(8) See, for example, H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943; (a) pp. 190 ff., (b) pp. 316–325.

(9) (a) S. Kilpi, THIS JOURNAL, **74**, 5296 (1952); (b) E. Grunwald, *ibid*., **73**, 4934 (1951).

μ change only slightly, but in the latter, they change considerably, and the K_A value is then quite sensitive to the method of predicting y. As is illustrated in Table II for anilinium chloride in 82% and 70% dioxane, the K_A values by these two methods are substantially equal and equally precise.

TABLE II

K_A VALUES FOR ANILINIUM CHLORIDE, 25.0°

82.00 wt. % dioxane			70.00 wt. % dioxane		
Method	$10^3\mu$ (av.)	10^4 K_A	Method	$10^3\mu$ (av.)	10^4 K_A
1, base; 2, acid	11.0	3.18	1, base; 2, acid	7.5	2.84
1, acid; 2, base	7.0	2.90	1, acid; 2, base	7.5	3.15
1, acid; 2, base	7.0	3.18	1, base; 2, acid	5.5	3.29
1, base; 2, acid	4.0	3.11	1, acid; 2, base	3.0	3.03

Our results are summarized in Table III. The values in water were obtained by a half-neutralization method[8b] relative to aqueous hydrochloric acid. In 45%, 70% and 82% dioxane, the values for anilinium and p-toluidinium ion were measured by a differential method,[9] and the values for the other acids were measured relative to these by a half-neutralization method. The values in 20% dioxane were measured relative to the pK_A values for anilinium and p-toluidinium ion reported by James and Knox.[3]

TABLE III

pK_A VALUES AND THEIR CORRELATION IN THE SYSTEM DIOXANE–WATER, 25.0°

	Dioxane by weight, %						
Acid	0.0	20.0	45.0	70.0	82.0	m_R	r
Anilinium	4.63	4.44	4.00	3.51	3.51	0.000	...
p-Toluidinium	5.11	4.92	4.53	4.11	4.13	−.189	0.01$_0$
N-Methylanilinium	4.86	4.62	4.01	3.31	3.27	.755	.02$_0$
N-Dimethylanilinium	5.15	4.89	4.21	3.33	3.20	1.318	.01$_0$
p-Anisidinium	5.31[6a]	....	4.86	4.57	4.60	−.662	.01$_5$
Ammonium	9.26	....	8.97	8.97	9.19	−1.650	.01$_5$
N-Trimethylammonium	9.81	....	9.31	8.90	8.96	−.402	.01$_5$
D (ref. 4)	78.48	61.86	40.25	19.07	10.56		
Y_0	0.000	−.052	−.230	−.522	−.635		

The pK_A values are based on 2–6 independent measurements, and their precision is within 0.04 pK unit as illustrated in Table II. The accuracy of the pK_A values is also within 0.04 pK unit except for p-anisidinium chloride where the error may amount to 0.1 unit since oxidation could not be completely prevented (see Experimental part).

Our results in water are in good agreement with those previously accepted[6] for all compounds except N-dimethylanilinium ion. Here our new value, 5.15, differs significantly from the value, 5.01, which we had used before,[10] but is in satisfactory agreement with the value, 5.17, calculated from the accurate conductance data of Ley and Grau,[11] and also with several other reported values.[12] Our results for anilinium and p-toluidinium ion are in excellent agreement with the conductometric values of James and Knox[3] in water and 45% dioxane, but deviate from the latter in 70% and 82% dioxane, possibly because of their assumption of independent ionic mobilities in these solvents of low dielectric constant. Our result for anilinium ion in water is also in acceptable agreement with the recent colorimetric value of Kilpatrick and Arenberg.[13]

Correlation of pK_A Values.—The solvent dependence of the pK_A values is given in terms of degenerate activity coefficients[5b] f by the expression

$$\Delta pK_A \equiv pK_A - pK_A^{HOH} = \log f_H + \log f_B/f_{BH} \quad (3)$$

where the subscripts B and BH refer to amine and conjugate acid, respectively, and f_H is the lyoniun ion degenerate activity coefficient.[6b] According to the *activity postulate*, the quantity $\log f_B/f_{BH}$ ought to be expressible as the product of two factors, a function m, characteristic of the organic radical of the acid and independent of the solvent, and a function Y_0 of solvent and independent of the acid.[6] Thus

$$\Delta pK_A = \log f_H + mY_0 \quad (4)$$

The experimental ΔpK_A values calculated from the data in Table III are thoroughly characteristic of the acid employed, but the family of ΔpK_A curves is described well by equation 4. Our method of demonstrating this fact is quite analogous to the one we described in detail for the system ethanol–water.[6a] Anilinium ion was again chosen as the reference acid, and it was convenient to define the *relative* dissociation constant for the acid BH$^+$ by $K_R(BH) = K_A(BH)/K_A(C_6H_5NH_3)$. It then follows from equation 4 that

$$\Delta pK_R \equiv pK_R - pK_R^{HOH} = m_R Y_0 \quad (5)$$

where $m_R = (m_{BH} - m_{C_6H_5NH_3})$. In agreement with equation 5, the ΔpK_R values for any two solvent compositions varied linearly, and the slopes were equal to the ratios of the corresponding Y_0 values which were thus determined. In order to define an absolute scale of Y_0 values, we set $Y_0 = 0.635$ for 82% dioxane, thus achieving optimum numerical agreement between Y_0 and $(1 - w)^2$ (see below).

The results of the correlation are included in Table III. The Y_0 values are given in the bottom row, and the m_R values and probable errors of fit, r, are given in the last two columns. The mean value of r for the entire table is only 0.015 unit, well within the experimental error of the pK_R values. Although the correlation involves relatively many adjustable parameters, there is little doubt that it is significant. The number of pK_R values correlated is almost three times the number of parameters.

The activity function Y has formerly been treated

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[10] This value was based on the work of M. Mizutani, *Z. physik. Chem.*, **116**, 350 (1925); **118**, 327 (1925).

[11] H. Ley and R. Grau, *Ber.*, **58B**, 1765 (1925).

[12] G. Bredig, quoted by H. Goldschmidt and H. Keller, *ibid.*, **35**, 3534 (1902); J. N. Pring, *Trans. Faraday Soc.*, **19**, 705 (1925).

[13] M. Kilpatrick and C. A. Arenberg, THIS JOURNAL, **75**, 3812 (1953).

as an unpredictable quantity that must be evaluated empirically. In the classical electrostatic treatment of the effect of solvent on acid dissociation,[14] ΔpK_R is given by the expression

$$\Delta pK_R = \frac{\epsilon^2}{2kT}\left\{\frac{1}{r_{BH}} - \frac{1}{r_{C_6H_5NH_3}}\right\} \times \Delta(1/D) \qquad (6)$$

where ϵ is the unit ionic charge, k is Boltzmann's constant, and r is the ionic radius. It will be noted that equation 6 is of a form consistent with our empirical relationships, since $\{(1/r_{BH}) - (1/r_{C_6H_5NH_3})\}$, like m_R, is independent of the solvent, and $\Delta(1/D)$, like Y_0, is independent of the acid. However, equation 6 does not fit beyond this formal resemblance since Y_0 is not proportional to $\Delta(1/D)$. As shown in Fig. 1, the plot of Y_0 *vs.* $\Delta(1/D)$ shows significant curvature, and the probable error of fit of the equation $Y_0 =$ *constant* $\times \Delta(1/D)$ is more than three times the probable error of the Y_0 values. One may therefore conclude that equation 6 is inadequate for data covering a wide range of dielectric constant, such as we have used, even in a single 2-component solvent system where the molecular structure of the two solvent components remains fixed.

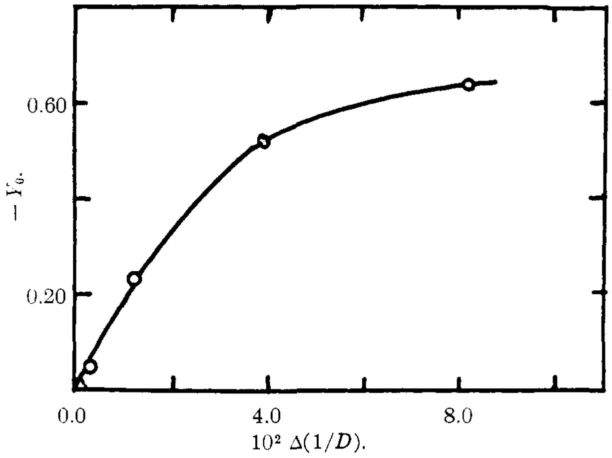

Fig. 1.—Plot of Y_0 *vs.* $\Delta(1/D)$, dioxane-water, 25.0°.

We have discovered the following empirical relationship (7) between Y_0 and w, the weight-fraction of water in the solvent medium

$$Y_0 = -(1 - w)^2 \qquad (7)$$

Equation 7 is adequate, as shown in Table IV, not only for the system dioxane–water, but also for the systems ethanol–water and methanol–water. The fit is in every case within the accuracy of ±0.05 unit estimated[6a] for the Y_0 values. Y_0 therefore depends only on the weight fraction of the aqueous component and is independent of the nature of the organic component, at least in these three systems.

TABLE IV

TEST OF EQUATION 7

Wt. % organic component	$(1 - w)^2$	$-Y_0$ Dioxane–HOH	$-Y_0$ Ethanol–HOH[a]	$-Y_0$ Methanol–HOH[b]
20	0.040	0.052	0.057	0.054
45	.202	.230	.220	.225
70	.490	.522	.445	.494
82	.672	.635	.605	.660
95	.902	...	.882	...

[a] Obtained by graphical interpolation from ref. 6a. [b] Tentative values calculated by Dr. B. Gutbezahl from the ΔpK_R values of Mizutani.[10]

While the Y_0 values are independent of the organic solvent component, the m_R values are not. In Fig. 2 there are plotted the m_R values for the system ethanol–water[6a] *vs.* those for the system dioxane–water. As shown in the figure, the m_R values for the anilines in the two solvent systems vary in a monotonic fashion but are not equal, and those for the amines fall very much off the curve described by the anilines. Similar relationships obtained when m_R values for the system methanol–water are used.[15]

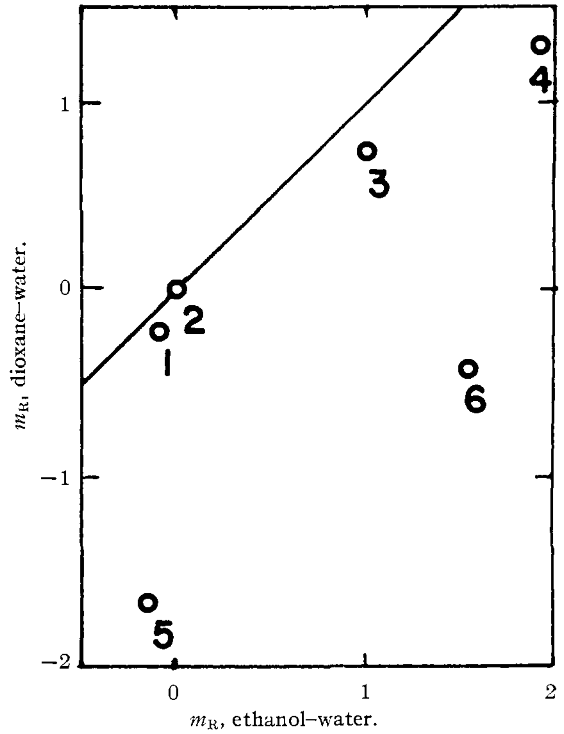

Fig. 2.—Comparison of m_R values in the systems ethanol–water and dioxane–water, 25°: 1, *p*-toluidine; 2, aniline; 3, N-methylaniline; 4, N-dimethylaniline; 5, ammonia; 6, trimethylamine; —, line of equal m_R.

The theoretical interpretation of the observed relationships is difficult. There is no doubt that ΔpK_R is partly due to electrostatic phenomena, and also that the acids and bases are strongly solvated in these polar media. In the classical electrostatic calculation of the effect of solvent on ΔpK_R, one treats the solvent as a homogeneous fluid of dielectric constant equal to the macroscopic dielectric constant. Since on a microscopic scale solvents such as 82% dioxane, or even water, are certainly not homogeneous, this assumption implies that the solute molecules are free to rotate and hence unsolvated. Evidently, the classical result is then only a first approximation, and it is often incon-

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(14) See, for example, W. F. K. Wynne-Jones, *Proc. Royal Soc. (London)*, **A140**, 440 (1933).

(15) E. Grunwald, B. Gutbezahl and H. P. Marshall, unpublished research.

sistent with experiment. For example, according to equation 6, which deals with the effect of ion size, ΔpK_R for a given acid pair is a function of dielectric constant only and independent of the nature of the solvent—a prediction which is at odds with observation. More successful are the calculations of the effect of polar groups within the acid molecule[16] since here a good part of the effect is due to the field within the molecule and hence independent of the external solvent. However, even here the results of the classical calculation are only in approximate agreement with observation. For example, the electrostatic effect on ΔpK_R has recently been calculated[13] for eight *m*- and *p*-substituted anilines, including the *m*- and *p*-NO_2 compounds, in the solvents methanol and ethanol. The calculated effect was consistently less than $^1/_5$ of the observed value of ΔpK_R.[13]

When the solutes are treated as solvated, the calculation of ΔpK_R must be modified in two ways. First, the electrostatic free energy must now be calculated for the solvated solutes, and a detailed knowledge of the structure of the solvation complex is required. Secondly, the effect of the preferred solvent–solute orientations on the values of the thermodynamic properties must be calculated. Although the estimation of this effect is difficult, one can conclude from the calculations that have already been made[17] that its magnitude may be appreciable.

The factor $(1 - w)^2$ is not completely unprecedented in the literature on degenerate activity coefficients for polar solutes. The solvent dependence of f values for amino acids in the system ethanol–water has been described by the equation[18]

$$\log f = K \times \Delta(1/D) + K'V(1 - w')^2 \qquad (8)$$

where V is the molar volume of the amino acid, w' is the volume fraction of water, and K, K' are constants. It is interesting to note that the term $K \times \Delta(1/D)$, which is thought to measure the electrostatic effect due to the zwitterion dipoles, is independent of the molar weight of the amino acid and, within limits, of the magnitude of the dipoles.[18] The term $K'V(1 - w')^2$ is analogous to $m_R(1 - w)^2$, which can be shown as follows.

Assume that values of f_B and f_{BH} are also represented by equations of the form 8, then

$$\log f_B/f_{BH} = (K_B - K_{BH}) \times \Delta(1/D) + (K'_B V_B - K'_{BH} V_{BH})(1 - w')^2 \qquad (9)$$

and

$$\Delta pK_R = (K'_B - K'_{BH}) V_R (1 - w')^2 \qquad (10)$$

where $V_R = (V_B - V_{C_6H_5NH_2})$. In deriving (10), V_R is also set equal to $(V_{BH} - V_{C_6H_5NH_3})$, which would be exact if the molar volume were strictly an additive property.[19]

Equation 10 is consistent with many features of our empirical relationships. The term $(1 - w')^2$ may represent Y_0 if the small difference between w and w' is neglected. The term $(K'_B - K'_{BH}) V_R$ may represent m_R if the interaction constant $(K'_B - K'_{BH})$ is characteristic of the organic solvent component and assumes different values for different homologous series, such as amines and anilines. Within a given homologous series, m_R is then expected to be proportional to V_R. Although this relationship is not rigorously observed, there is a definite trend for m_R to increase with V_R.

Experimental Part

Materials.—The aniline hydrochlorides were prepared from the purified amines and hydrogen chloride in dry ether. The precipitated solids were washed thoroughly with ether and dried over sodium hydroxide, first in the vacuum of a water aspirator and then of an oil pump. Reagent-grade ammonium chloride was recrystallized for us by Mr. C. F. Courtney of this Laboratory. A good commercial grade of trimethylamine hydrochloride was recrystallized from benzene–methanol and dried *in vacuo* over paraffin.

The solid aniline hydrochlorides generally turned colored on standing in air for much more than a week but could be stored for a longer period *in vacuo*. Nevertheless the compounds had to be freshly prepared several times during the course of this work. The acid equivalent weights of the aniline hydrochlorides and the chloride contents of the amine hydrochlorides were determined on each batch and were always within 0.5% of theory.

Trimethylamine hydrochloride and N-dimethylaniline hydrochloride proved to be hygroscopic and were handled with suitable precautions.

The best available commercial grade of 1,4-dioxane was further purified by refluxing for 48 hr. over a mixture of sodium hydroxide and silver oxide. The distillate obtained from this treatment was then placed in a 20-plate all-glass still and kept under gentle reflux in the presence of sodium metal until just before use in the K_A measurements. Water was redistilled from alkaline permanganate.

Hydrochloric acid solutions were prepared from constant boiling hydrochloric acid which served as primary acidimetric standard.[20] The equivalent weight of a standard sample of potassium acid phthalate was determined by comparison with the hydrochloric acid and agreed to 0.05% with the value furnished by the National Bureau of Standards. Acid–base titrations in the high-dioxane solvents were done in an atmosphere of nitrogen.

Technique of E.m.f. Measurement.—The cell was a stoppered 180-ml. electrolytic beaker fitted with two Beckmann #1190–42 glass electrodes, a Harned type 2 silver–silver chloride electrode,[21] and was provided with a hole for the loose insertion of a buret tip. The potentiometer was a Beckman model G *p*H meter which had been carefully calibrated against a Leeds and Northrop type K potentiometer.

The cell containing the solution to be measured was equilibrated to 25.0 ± 0.1° in a small, table-model thermostat, and e.m.f. readings were taken, using each electrode alternately, until an equilibrium value was reached. The e.m.f. readings for the two glass electrodes were not exactly equal since the values of E'_0 varied with the electrode, but their differences were constant and reproducible within ±0.005 *p*H scale unit. The stability of the glass electrodes was tested regularly by measuring comparable solutions in the solvent under study at the beginning and conclusion of each series of measurements and proved adequate even in 82% dioxane.

After the completion of a measurement, a new cell solution could often be prepared conveniently by adding a known volume of strong acid, base or solvent from a buret to the thermostated cell and stirring the contents with a magnetic stirrer. Since preliminary experiments on *p*-toluidinium chloride had shown that it was necessary to guard against oxidation of the anilines, each test solution

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(16) (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938); (b) F. H. Westheimer, THIS JOURNAL, **61**, 1977 (1939); (c) J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

(17) See, for example: (a) A. Münster, *Z. Elektrochem.*, **54**, 443 (1950); *Trans. Faraday Soc.*, **46**, 165 (1950); *Z. physik. Chem.*, **A195**, 67 (1950); **A196**, 106 (1950); (b) H. Tompa, *J. Chem. Phys.*, **21**, 250 (1953).

(18) (a) E. J. Cohn, T. L. McMeekin, J. T. Edsall and J. H. Weare, THIS JOURNAL, **56**, 2270 (1934); (b) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, chapter 9.

(19) Equation 9 is consistent with our previous work on acid dissociation in the system ethanol–water[0b] only if the term $(K_B - K_{BH}) \times \Delta(1/D)$ is small compared to the mY term.

(20) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 545.

(21) H. S. Harned, THIS JOURNAL, **51**, 416 (1929).

was prepared within one hour of any run. That this precaution was adequate was shown by the complete absence of characteristic colors in all solutions except those containing *p*-anisidinium chloride. To estimate the effect of oxidation on K_A, one solution of *p*-toluidinium chloride in 82% dioxane was allowed to stand for one week. The K_A value for this solution was 20% greater than for the freshly prepared solution.

Additional details have been described in previous publications from this Laboratory.[6a,7]

K_A Values by the Differential Method.—We used a two-point method quite similar to that used by Gutbezahl for 95% ethanol.[22] However, our method of calculating K_A was different. We used the expression

$$c'_H/c''_H = Z'/Z'' \qquad (11)$$

where c'_H/c''_H is the potentiometrically determined ratio of lyonium ion concentrations at the two experimental points where the degrees of neutralization are ϵ' and ϵ'' and the formal amine concentrations are c' $(= c'_B + c'_{BH})$ and c'' $(= c''_B + c''_{BH})$. The function Z is equal to

$$(\epsilon - 1)c - K_A + [(\epsilon - 1)^2c^2 + 2K_Ac(1 + \epsilon) + (K_A)^2]^{1/2} \qquad (12)$$

and is evaluated at the two experimental points for various assumed values of K_A. The correct value of K_A is that for which $c'_H/c''_H = Z'/Z''$.

Equations 3 and 4 are derived from the more fundamental expression[9b]

$$c_H[c_H - (\epsilon - 1)c]/[\epsilon c - c_H] = K_Ay_{BH}/y_By_H = K'_A \qquad (13)$$

on the assumption that $y_{BH}/y_By_H = 1.00$. At the ionic strengths and concentrations used in our experiments (<0.012 *M*), this assumption seemed to be justified in view of the charge type of the acid and was corroborated by the absence of significant drifts in the calculated K_A values.

K_A Values by the Half-Neutralization Method.—The standard *p*H scale reading $E'_0 = E' + \log a_Ha_{Cl}$ was evaluated for each solvent by means of acids of known K_A value and was then used to calculate c_H values of solutions containing the acids to be studied. For best accuracy, $\epsilon \approx 1/2$ and in our experiments ϵ was between $1/3$ and $2/3$. In the required calculations, the rigorous expression (13) was always used. The results were generally satisfactory except for ammonium and trimethylammonium ion in water. For these compounds the apparent pK_A values drifted downward by *ca.* 0.05 unit as sodium hydroxide was added to the cell and ϵ was varied from $2/3$ to $1/3$. Since calculation indicated that the amount of $Ag(NH_3)_2^+$ should be small and that silver chloride should be stable relative to silver oxide under the experimental conditions, the drifts could not be explained. Fortunately the drifts were small and disappeared, within the limit of experimental accuracy, in the high-dioxane media. In Table III we have listed the pK_A values obtained for these two compounds in the most acid solutions, at $\epsilon \approx 2/3$, where possible errors due to the use of a glass electrode should be at a minimum. Our pK_A value for ammonium ion is in good agreement with the value 9.246, reported recently by Bates and Pinching.[23]

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(22) Reference 6a, pp. 560–561.

(23) R. G. Bates and G. D. Pinching, THIS JOURNAL, **72**, 1393 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY]

Kinetics of Exchange and Disproportionation Reactions in Mercuric Cyanide Solutions[1]

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The exchange of radioactive mercury between mercuric and mercuric monocyanide ions has been measured and found to be slow. This is in agreement with mechanisms postulated in an earlier study for the exchange reactions between mercurous and mercuric species. The mercuric–mercuric monocyanide exchange proceeds by two paths: (1) A route consistent with a direct bimolecular mechanism, according to the rate law $R_3 = 4 \times 10^7\ e^{-11,800/RT}\ (Hg^{++})(HgCN^+)$ mole-liter^{-1}-min.$^{-1}$; (2) The reactions involved in the disproportionation equilibrium $2HgCN^+ \rightleftarrows Hg^{++} + Hg(CN)_2$. The above disproportionation system has also been studied directly. The equilibrium constant has been determined, $K = (Hg^{++})\cdot(Hg(CN)_2)/(HgCN^+)^2 = 5 \times 10^{-2}$ at 25°. The approach to equilibrium has been followed spectrophotometrically and obeys the rate law $R_{12} = 6 \times 10^{11}\ e^{-17,000/RT}\ (Hg^{++})(Hg(CN)_2) - 3 \times 10^{10}\ e^{-17,000/RT}\ (HgCN^+)^2$ mole-liter^{-1}-min.$^{-1}$. The value obtained for K has been used to explain the zero-time exchange found in the study of the mercurous–mercuric cyanide exchange. An explanation is offered for the unusual and perhaps unique non-lability of the mercuric mono- and dicyanide complexes.

Introduction

An earlier study[2] of the mercurous–mercuric cyanide exchange showed that this reaction proceeds at a measurable rate which is first order with respect to the mercurous concentration and first order with respect to the mercuric concentration. The results obtained were incompatible with a rapid exchange between mercuric ion and the mercuric monocyanide complex. The latter conclusion was received with some surprise[3] on the basis that *a priori* it seemed unlikely that a species such as $HgCN^+$ should not be in rapid equilibrium with Hg^{++} and CN^- ions.

The present work is a further study of the mercury–cyanide systems and attempts to present a more unified picture of the kinetics of the several interdependent reactions involved. It is interesting that the species $HgCN^+$, referred to above, is not in rapid equilibrium with its constituent ions; and it seemed worthwhile to inquire into the kinetics of its reactions somewhat more closely. Accordingly, the exchange of $HgCN^+$ with Hg^{++} has been directly studied, using a chemical separation of these ions. The conclusion on the slow dissociation of $HgCN^+$ has been confirmed and a more detailed reaction mechanism obtained.

The rate data obtained for the Hg^{++}–$HgCN^+$ exchange indicate that this exchange proceeds not only by a direct bimolecular mechanism

$$Hg^{*++} + HgCN^+ \longrightarrow Hg^{++} + Hg^*CN^+ \qquad (1)$$

but also indirectly by the reactions involved in the disproportionation equilibrium

$$\begin{gathered} Hg^{*++} + Hg(CN)_2 \longrightarrow Hg^*CN^+ + HgCN^+ \qquad (2) \\ Hg^*CN^+ + HgCN^+ \longrightarrow Hg^{++} + Hg^*(CN)_2 \end{gathered}$$

It was therefore desirable to check the kinetics of these disproportionation reactions directly, and it was found possible to do this spectrophotometric-

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(1) Research carried out under the auspices of the Atomic Energy Commission.

(2) R. L. Wolfgang and R. W. Dodson, *J. Phys. Chem.*, **56**, 872 (1952).

(3) A. W. Adamson, *ibid.*, **56**, 876 (1952).