in discussing kinetic effects of added "inert" electrolytes conclude that from kinetic data only the choice is difficult, if not impossible. The very effective catalysis by $Co(NH_3)_6^{+++}$ is analogous to the catalysis of the bromoacetate–thiosulfate reaction[26] by La^{+++} and is reasonable by either interpretation.

We believe the catalysis by $Fe(CN)_6^{---}$ involves the rapid reversible reaction[27]

$$MnO_4^- + Fe(CN)_6^{----} \underset{k_2}{\overset{k_1}{\rightleftarrows}} MnO_4^{--} + Fe(CN)_6^{---} \quad K' = \sim 200 \qquad (5)$$

The rate under the experimental conditions is given by

$$R = 1180(MnO_4^{--})(MnO_4^-) = 710(MnO_4^{--})(MnO_4^-) + k_2(MnO_4^{--})(Fe(CN)_6^{---})$$

$$k_2 = 470\,\frac{(MnO_4^-)}{(Fe(CN)_6^{---})} = 470\,\frac{(10^{-4})}{(10^{-3})} = 47$$

$$k_1 = K'k_2 = (\sim 200)(47) = \sim 10^4 M^{-1}\ \text{sec.}^{-1}$$

This value of k_1 is approximately the value we estimated from visual observations of the color changes that occur when MnO_4^- and $Fe(CN)_6^{----}$ are mixed in 0.1 *f* KOH at 5°.

Acknowledgment.—We wish to thank Professor E. L. King of the University of Wisconsin for reading the manuscript and making many valuable comments.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Activity Coefficients in Aqueous Zinc Chloride–Hydrochloric Acid Solutions, and their Application to Cation Exchange Data[1]

BY NORMAN J. MEYER, WILLIAM J. ARGERSINGER, JR., AND ARTHUR W. DAVIDSON

RECEIVED OCTOBER 4, 1956

The equilibrium quotient for the zinc–hydrogen exchange on Dowex 50 in aqueous chloride solutions has been determined as a function of resin composition at constant total solution ionic strengths of 0.5 and 1.0 *m*. Approximate values of the solution activity coefficient ratios, obtained from electromotive force measurements on mixed hydrochloric acid–zinc chloride solutions and the application of Harned's rule, are used to compute the thermodynamic equilibrium constant for the exchange process and the activity coefficients of the resin components. The values obtained for the equilibrium constant are 10.2 at 0.5 *m* ionic strength and 11.7 at 1.0 *m* ionic strength.

Introduction

Equilibrium in the process of cation exchange on a synthetic resin such as Dowex 50 may be formulated in terms of a thermodynamic equilibrium constant which includes the activity coefficients of the components of the resin phase. The method of calculation of these quantities which has been developed in several previous papers from this Laboratory[2–5] has been applied to a number of exchange systems involving two univalent cations[2–9] and to a smaller number of exchange systems involving either two bivalent ions or one bivalent ion and one univalent ion.[10] At least one earlier study[11] was made of systems involving the exchange of bivalent ions on Dowex 50, but in this instance approximate methods were used for the computation of the exchange equilibrium constant, and resin activity coefficients were ignored.

The computation of the exchange equilibrium constant requires, in addition to the exchange data themselves, a knowledge of the activity coefficients of the electrolyte solutes in the aqueous phase—or, more precisely, of the appropriate ratio of these coefficients. If the aqueous solutions are sufficiently dilute, this ratio may be taken as unity[6,7]; in somewhat more concentrated solutions, the ratio may be estimated from a modified form of the ionic strength principle.[8] In general, however, it seems preferable to use experimentally determined values of the activity coefficient ratios if such are available. Thus in the case of the silver–hydrogen exchange on Dowex 50, the values of the ratios of activity coefficients of silver nitrate and nitric acid were obtained from independent electromotive force measurements.[12]

The direct determination of the activity coefficients of both electrolyte solutes in a mixed aqueous solution is extremely difficult; it has been ac-

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complished by Harned and Cook[13] for hydroxide–chloride mixtures by means of electromotive force measurements on suitably contrived cells. Somewhat less directly the coefficients may be determined from vapor pressure data for the mixed solutions, as suggested by McKay[14] and by McKay and Perring,[15] and accomplished by Bonner and Holland[16] for aqueous solutions of *p*-toluenesulfonic acid and its sodium salt, and by McCoy and Wallace[17] for aqueous solutions of potassium chloride and bromide. In a few instances it is possible to determine directly the activity coefficient ratios from electromotive force measurements on cells containing electrodes reversible with respect to the two different cations,[12,18,19] and to compute therefrom the activity coefficients of the two solutes.[20]

It has been shown by Harned and his co-workers that in many aqueous mixtures of hydrochloric acid with a metal chloride at constant total ionic strength, the activity coefficient of the acid is a linear function of its ionic strength.[21] It has been inferred that in such cases the activity coefficient of the metal chloride is also a linear function of its ionic strength at constant total ionic strength, and experimental results by Harned and Gary[22] seem to justify this assumption at least for higher concentrations in systems containing barium, strontium, aluminum or cerium chloride. Thus for those cation-exchange systems involving hydrogen ion and the ion of a metal more reactive than hydrogen, in chloride solution, the requisite activity coefficient ratios may be obtained from electromotive force measurements designed to yield the activity coefficient of the acid, and the assumption that Harned's rule holds for both electrolyte solutes.

In this paper data are presented for the exchange of zinc and hydrogen ions on Dowex 50 at 25°

$$Zn^{++} + 2HR \longrightarrow ZnR_2 + 2H^+ \qquad (1)$$

for which the equilibrium constant K is defined as

$$K = \frac{a^2{}_{H^+}}{a_{Zn^{++}}} \times \frac{a_{ZnR_2}}{a^2{}_{HR}} = \frac{m^2{}_{H^+}}{m_{Zn^{++}}} \times \frac{\gamma^4{}_{HCl}}{\gamma^3{}_{ZnCl_2}} \times \frac{N_{ZnR_2}}{N^2{}_{HR}} \times \frac{f_{ZnR_2}}{f^2{}_{HR}} \qquad (2)$$

in which a represents activity, m molality and γ mean molal activity coefficient in the aqueous solution; N represents mole fraction in the resin and f resin activity coefficient on a mole fraction basis. It is convenient also to define the equilibrium quotient K_m and the apparent equilibrium constant K_a

$$K_m = \frac{m^2{}_{H^+}}{m_{Zn^{++}}} \times \frac{N_{ZnR_2}}{N^2{}_{HR}};\ K_a = K_m \frac{\gamma^4{}_{HCl}}{\gamma^3{}_{ZnCl_2}} \qquad (3)$$

so that

$$K = K_a \frac{f_{ZnR_2}}{f^2{}_{HR}} \qquad (4)$$

This paper presents also data for the determination of approximate values of γ_{HCl} from electromotive force measurements on the cell

$H_2(1\ \text{atm.})/HCl\,(m = \mu x),\ ZnCl_2\,(m = {}^1/_3\mu(1 - x))/AgCl\text{–}Ag$

in which μ is the total ionic strength and x the ionic strength fraction of hydrochloric acid. The electromotive force of such a cell is given by

$$E = E^0 - \frac{RT}{F} \ln \mu^2 \frac{x(2 + x)}{3} \gamma_1{}^2 \qquad (5)$$

where $\gamma_1 \equiv \gamma_{HCl}$ and the other symbols have their usual meanings.

Experimental Methods

Ion-exchange Measurements.—The sodium form of Dowex 50 containing 8% DVB was completely converted to either the hydrogen or the zinc form by treatment with concentrated hydrochloric acid or concentrated zinc chloride solution; the products were thoroughly washed with water and then air-dried. Stock solutions of zinc chloride and of hydrochloric acid were prepared with conductivity water and Bakers Analyzed Reagent grade or Mallinckrodt Analytical Reagent grade chemicals. The acid solution was analyzed by standard methods, and the zinc chloride solution was analyzed for both zinc and chloride, the former both gravimetrically by the sulfate method[23] and volumetrically by the ferrocyanide method,[24] the latter gravimetrically as silver chloride. The stock solutions were mixed in predetermined proportions, diluted with conductivity water, and stored in glass-stoppered bottles.

Triplicate samples of pure hydrogen or zinc resin weighing approximately two grams were shaken for one to two hours with portions of a selected mixed electrolyte solution. The process was twice repeated and then the resin was transferred to a small exchange column, approximately 1 cm. in diameter, placed in a thermostat maintained at 25 ± 0.1°. After thermal equilibrium had been reached, fresh mixed solution of the same composition as that earlier used was allowed to percolate through the resin in the column. Although analyses showed only a negligible change in composition of the solution after the passage of about 100 ml. of solution, 200–300 ml. more was passed through to ensure the attainment of equilibrium. In this manner it was possible to obtain equilibrium data at constant total ionic strength and specified solute composition of the equilibrium aqueous solution.

The analysis of the equilibrium resin was inevitably complicated by the interference of zinc ion with the accurate determination of hydrogen ion by titration. In practice, the difficulty could be overcome only by the application of empirical corrections determined from the analysis of mixtures of known compositions. The equilibrium resin was rapidly but thoroughly washed with water and then exhaustively exchanged with a concentrated solution of an eluting electrolyte. Attempts were made to analyze the resin by elution with magnesium sulfate solution followed by analysis of the eluate for both hydrogen and zinc ions, but by this method the requisite accuracy could not be attained for either ion, primarily because of the high concentration of magnesium sulfate. The method finally adopted involved the determination of one ion and of the total number of equivalents of resin, the number of equivalents of the second ion being obtained as the difference. In a few cases, the equilibrium resin was completely eluted with hydrochloric acid, the eluate was analyzed for zinc by the ferrocyanide method, and the exchanged resin was washed and then eluted with sodium chloride or nitrate solution to yield an eluate which was titrated to give the total number of equivalents of exchanged ions. Most commonly, however, because the resin so strongly prefers zinc over hydrogen, the equilibrium resin was completely eluted with sodium

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chloride solution and the eluate titrated with standard base to give the number of equivalents of hydrogen; the exchanged resin was converted to the hydrogen form by treatment with hydrochloric acid, thoroughly washed, and then again eluted with sodium chloride solution. This second eluate was titrated with standard base to give the total number of equivalents of equilibrium resin. The methods were tested on known samples; only very small corrections to the titrations were required because of the added electrolyte present.

Electromotive Force Measurements.—The materials and stock solutions were the same as those used for the ion-exchange investigation. Silver-silver chloride electrodes were prepared as recommended by Rule and LaMer[25] or by Shedlovsky and MacInnes.[26] The potentials of these electrodes were compared in 0.1 *M* hydrochloric acid solution and found to agree within 0.05 mv. The electrodes were stored in 0.1 *M* hydrochloric acid. Hydrogen electrodes were prepared as recommended by Popoff, Kunz and Snow.[27] The various combinations of hydrogen and silver-silver chloride electrodes used in the study of mixed solutions were always checked before such use, and usually afterwards as well, in dilute hydrochloric acid solutions; they were considered satisfactory if the potentials were sensibly constant and within 0.05 mv. of the appropriate values of Harned and Ehlers[28] for the acid solution. The electrodes in pairs and the solutions were placed in an all-glass cell which was immersed in a thermostat at 25 ± 0.1°. The solution was freed of oxygen by means of nitrogen gas previously saturated with water vapor from a solution of the same composition. and was maintained oxygen-free through the special design of the cell. After thermal equilibrium had been attained, potential measurements were made with a Leeds and Northrup Type K2 potentiometer and a Leeds and Northrup No. 2430 galvanometer. The measured potentials were corrected to a hydrogen pressure of one atmosphere by means of the usual (approximate) corrections.[29] At least three independent measurements were made for each solution; the maximum difference between results for a given solution was 0.1 mv., and the average deviation from the mean was about 0.05 mv.

Results and Calculations

Activity Coefficients.—Table I contains the values of log γ_1 calculated by means of eq. 5 from e.m.f. measurements on mixed solutions at constant total ionic strengths of 0.2, 0.5 and 1.0 *m*. At 25° E^0 is taken as 0.22246 v. and RT/F as 0.05914 v. The final figure in each tabulated value of log γ_1 is uncertain but is included for the sake of completeness.

TABLE I

ACTIVITY COEFFICIENTS OF HCl IN HCl–ZnCl$_2$ SOLUTIONS

	log γ_1		
x	$\mu = 0.2$	$\mu = 0.5$	$\mu = 1.0$
0.087	−0.1242	−0.1484	−0.1569
.182	.1239	.1406	.1491
.286	.1206	.1372	.1407
.400	.1197	.1372	.1373
.526	.1177	.1285	.1268
.667	.1166	.1273	.1147
.824	.1148	.1247	.1087
.927	.1153	.1210	.0999
1.000	.1154^a	.1208^a	.0920^a

^{a} Values of Harned and Ehlers (ref. 28).

These values conform approximately to the linear Harned relations

$$\log \gamma_1 = \log_{1(0)} - \alpha_{12}\,\mu(1 - x) = \begin{cases} -0.1143 - 0.0495\,(0.2)\,(1 - x) \\ -0.1194 - 0.0547\,(0.5)\,(1 - x) \\ -0.0935 - 0.0689\,(1.0)\,(1 - x) \end{cases} \qquad (6)$$

Although Harned's rule is known not to hold exactly at low ionic strengths, we shall nevertheless apply it here to the second solute, zinc chloride, in order to obtain approximate values of the activity coefficient for use in ion-exchange calculations. Harned and Gary[22] have shown that if

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}\mu x \qquad (7)$$

then for the present case

$$\alpha_{21} = 2\alpha_{12} - \frac{2}{2.3\mu}\,[2\phi_1 - \phi_2 - 1] \qquad (8)$$

in which ϕ_1 and ϕ_2 are the osmotic coefficients of hydrochloric acid and zinc chloride, respectively, in their own pure solutions at the same ionic strength as the mixed solution. The values of α_{21} so computed are shown in Table II, together with values of the osmotic and activity coefficients of the two solutes obtained by interpolation from the data compiled by Robinson and Stokes,[30] and also the value of $2\alpha_{12} + \alpha_{21}$, which should be constant at all ionic strengths if Harned's rule holds precisely. The several values of $2\alpha_{12} + \alpha_{12}$ are, it is true, only roughly in agreement; it is believed, however, that the constancy of this quantity constitutes an extremely sensitive test of the validity of Harned's rule. The degree of divergence here observed would scarcely justify the discarding of this rule as a means of obtaining approximate results for γ_2.

TABLE II

DATA FOR EQ. 6, 7, 8

μ	log $\gamma_{1(0)}$	α_{12}	ϕ_1	ϕ_2	α_{21}	log $\gamma_{2(0)}$	$2\alpha_{12} + \alpha_{21}$
0.2	−0.1154	0.0495	0.945	0.850	−0.075	−0.259	0.024
0.5	− .1208	.0547	.974	.846	− .068	− .323	.042
1.0	− .0920	.0689	1.039	.841	− .068	− .372	.070

Ion-Exchange Equilibrium.—The results of the zinc–hydrogen exchange study are given in Table III, which includes the values of x, the ionic strength fraction of hydrochloric acid in the aqueous phase, E_q, the equivalent fraction of zinc resin, and K_m, the equilibrium quotient defined by eq. 3. Table III includes also the values of log γ_1^4/γ_2^3 computed from eq. 6 and 7 and the data of Table II, and finally the values of log K_a and K_a calculated by means of eq. 3 modified to the form

$$\begin{aligned} \log K_a &= \log K_m + 0.382 + 0.008\,x,\ \mu = 0.5 \\ \log K_a &= \log K_m + 0.466 + 0.072\,x,\ \mu = 1.0 \end{aligned} \qquad (9)$$

Each value of K_m is the mean of at least three and often of four or five independent results.

It has been shown previously[2,4] that the thermodynamic equilibrium constant K and the resin activity coefficients f may be computed from the exchange data by use of the equations

$$\log K = \int_0^1 \log K_a\,\mathrm{d}E_q$$

$$\log f_{\mathrm{ZnR}_2} = -(1 - E_q)\log K_a + \int_{E_q}^{1} \log K_a\,\mathrm{d}E_q \qquad (10)$$

$$\log f_{\mathrm{HR}} = {}^1\!/_2 E_q \log K_a - {}^1\!/_2 \int_0^{E_q} \log K_a\,\mathrm{d}E_q$$

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TABLE III

ZINC–HYDROGEN EXCHANGE ON DOWEX 50

	$\mu = 0.5$					$\mu = 1.0$				
x	E_q	K_m	$\log \gamma_1^4/\gamma_2^3$	$\log K_a$	K_a	E_q	K_m	$\log \gamma_1^4/\gamma_2^3$	$\log K_a$	K_a
0.927	0.303	4.65	0.389	1.056	11.38	0.165	3.82	0.533	1.115	13.03
.824	.498	4.29	.388	1.020	10.47	.336	3.66	.525	1.088	12.25
.667	.663	3.91	.387	0.979	9.53	.525	3.43	.514	1.049	11.19
.526	.761	3.61	.386	.944	8.79	.660	3.36	.504	1.030	10.72
.400	.828	3.29	.385	.902	7.98	.758	3.22	.495	1.003	10.07
.286	.885	3.23	.384	.893	7.82	.837	3.15	.487	0.985	9.66
.182	.933	3.33	.383	.905	8.04	.905	3.30	.479	0.998	9.95
.118	.959	3.47	.383	.923	8.38	.944	3.75	.474	1.048	11.17
.073	.977	4.13	.383	.999	9.98	.968	4.24	.471	1.098	12.53
.053	.984	4.29	.382	1.014	10.33	.979	4.94	.470	1.164	14.59
.034	.990	4.59	.382	1.044	11.07	.988	6.35	.468	1.271	18.66

The values of $\log K_a$ given in Table III were plotted against E_q as in Fig. 1, and values of $\log K$, $\log f_{\mathrm{ZnR_2}}$ and $\log f_{\mathrm{HR}}$ were obtained by graphical integration. The results for the two ionic strengths studied are given in Table IV as a function of N, the mole fraction of zinc in the equilibrium resin.

TABLE IV

EQUILIBRIUM CONSTANTS AND RESIN ACTIVITY COEFFICIENTS

	$\mu = 0.5$		$\mu = 1.0$	
N	$f_{\mathrm{ZnR_2}}$	f_{HR}	$f_{\mathrm{ZnR_2}}$	f_{HR}
0	0.818	1.000	0.855	1.000
0.1	.855	0.998	.897	0.998
.2	.891	.991	.933	.991
.3	.921	.980	.962	.981
.4	.947	.965	.985	.969
.5	.968	.947	1.003	.954
.6	.989	.924	1.017	.939
.7	1.008	.891	1.025	.924
.8	1.013	.881	1.025	.927
.9	1.009	.901	1.015	.987
1.0	1.000	1.110	1.000	1.47
	$K = 10.2$		$K = 11.7$	

Discussion

While no great accuracy can be claimed for the individual measurements of the activity coefficients of hydrochloric acid, it is believed that the linear variation is established, and that the reported values of α_{12} are correct to within 5% at $\mu = 1.0$ m and 15–20% at $\mu = 0.2$ m. The values of $\gamma_{1(0)}$ obtained from the straight lines are in fair agreement with accepted values. The use of Harned's rule for zinc chloride must indeed be viewed as a rough approximation, particularly at the lower ionic strength. The activity coefficient ratios thus obtained, however, are probably rather better approximations than those which would result from the use of the ionic strength principle in any simple form.

The ion-exchange curves of Fig. 1 exhibit a form similar to that observed for the silver–hydrogen exchange on the same resin exchanger. The minimum in the curves implies a large deviation from ideal behavior in the resin, which is also quite evident in the calculated values of the resin activity coefficients as listed in Table IV. Because of the extrapolation required, the values of the latter coefficients for mixtures which are dilute in the particular component are rather uncertain, especially in the case of the hydrogen form of the resin. In addition, the experimental errors in the determination of the exchange curve, apparently arising particularly from exchange during the washing process, become quite large for values of $E_q \geqslant 0.95$; although this factor does not markedly affect the value of K, its effect on f_{HR} may be profound.

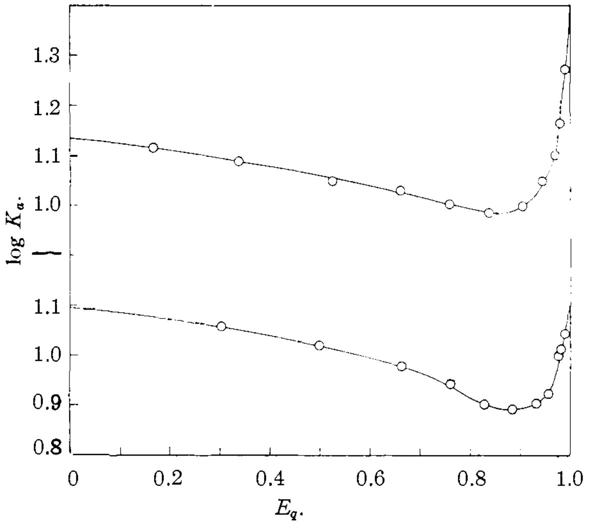

Fig. 1.—Zinc–hydrogen exchange on Dowex 50: top curve, $\mu = 1.0$ m; bottom curve, $\mu = 0.5$ m.

The calculated values of K at the two ionic strengths should be expected to agree provided the assumptions inherent in eq. 10 are valid. In particular, the presence of water and of "adsorbed" electrolyte in the equilibrium resin has been ignored in these equations; since it is easily demonstrated experimentally that both are actually present in amounts determined by the solution ionic strength, the apparent values of K at different ionic strengths may be expected to vary. It has been shown[5,9] that for other systems the detailed consideration of these factors reconciles the results at various ionic strengths. In the present instance, insufficient data are available for such additional calculations.

No previous extensive study has been made of the zinc–hydrogen exchange on a polystyrenesulfonic acid type of resin. Kressman and Kitchener[31] found a K_m value of 5.2 for the zinc–hydrogen exchange on a phenolsulfonic acid resin at an ionic

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(31) T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, 1190 (1949).

strength of 0.1 *N*. This value and those obtained in the present investigation are in qualitative agreement with values found for other uni-bivalent exchanges.[10]

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LAWRENCE, KANSAS

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

Molarity Quotients of Some Metal Complexes of Pyrazolone Dyes[1]

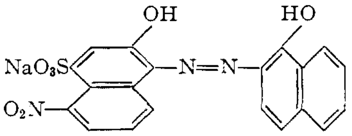
BY FRED A. SNAVELY,[2] W. CONARD FERNELIUS AND B. P. BLOCK

RECEIVED JULY 30, 1956

The relative stabilities of the metal derivatives of simple azo pyrazolone compounds have been measured potentiometrically in 75 volume % dioxane. The order of decreasing stability of the metal derivatives, Cu > Ni > Co > Zn, agrees with the orders already reported for other bidentate groups. The log *Q* values for the compounds of a given metal ion are proportional to the *p*QD values for the chelating agents. Three new metal derivatives of the azo compounds were prepared.

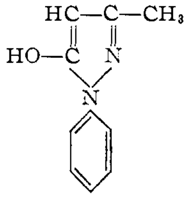
Introduction

Aryl azo compounds which contain an acidic or basic group *ortho* to the azo linkage are well known for their ability to form coördination compounds with metal ions. In spite of the many applications of these compounds in the dyeing of fabrics[3] and in the preparation of organic pigments,[4] almost no measurements have been made on the inherent stability of these metal derivatives toward dissociation into their constituent ions. The only measurements of this type recorded are those of Schwarzenbach and Biederman[5] for the magnesium and calcium derivatives of dyes of the type of Eriochrome Black T.[6]



The work reported here was part of a general study undertaken to determine (1) the adaptability of the Bjerrum[7]–Calvin[8] techniques to the study of the metal derivatives and (2) the order of stability among a series of metals with a given azo compound and among a series of azo compounds with a given metal ion.

The study of the simple azo derivatives of 1-phenyl-3-methyl-5-pyrazolon is reported here.



Experimental

Preparation of Materials.—The azo compounds were prepared by coupling the appropriate diazotized amines to 1-phenyl-3-methyl-5-pyrazolone. They were recrystallized from hot dioxane.

I. **1-Phenyl-3-methyl-4-(phenylazo)-5-pyrazolone:** orange needles, m.p. 155°, reported[9] 155°.

II. **1-Phenyl-3-methyl-4-(4-methylphenylazo)-5-pyrazolone:** orange needles, m.p. 138–140°, reported[10] 136–37°.

III. **1-Phenyl-3-methyl-4-(4-chlorophenylazo)-5-pyrazolone:** long, bright orange needles (like colored glass wool), m.p. 141–142°, reported[10] 141–142°.

IV. **1-Phenyl-3-methyl-4-(4-nitrophenylazo)-5-pyrazolone:** red-orange platelets, m.p. 198–200°, reported[11] 198–99°.

Each of the azo compounds was tested for purity by use of a chromatographic column packed with 100/200 mesh Florisil.[12] Development of the chromatogram using dioxane showed only one band in each case. Determination of the neutral equivalents by potentiometric titration gave the values in Table I.

TABLE I

Dye	Wt. of	Milliequiv. NaOH	Exptl. neut. equiv.	Theor. neut. equiv.
I	0.2781	1.00	278	278.3
II	.2923	1.00	292	292.3
III	.3137	1.00	314	312.8
IV	.3234	1.00	323	323.3

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.[13]

Titrations with iron(II) and cobalt(II) were carried out under a nitrogen atmosphere; all other titrations at *p*H values above 9 were made under a nitrogen atmosphere. The solutions were so adjusted that in 100 ml. of solution there was 1.00 mmole of dye, 1.482 mmoles of nitric acid and 0.210 mmole of metal nitrate. In general, no more electrolyte could be added without salting out the azo compounds or their metal derivatives. A 0.9983 *N* solution of sodium hydroxide was added in increments of about 0.05 to 0.10 ml., and readings were taken on the *p*H meter after each addition until a constant value was obtained. With this procedure, results were found to be reproducible. The average time per titration was about 2 to 2.5 hr.

In 75 volume % dioxane it was necessary to calibrate the *p*H meter. Van Uitert and Haas[14] have shown that a cell containing a glass electrode measures hydrogen ion activity in dioxane–water solutions as defined by the hydrogen electrode and that at a given salt concentration an empirical

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[1] From a portion of a thesis presented by Fred A. Snavely in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1952.

[2] Franklin and Marshall College, Lancaster, Pa.

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[11] P. Karrer and E. B. Hershberg, *Helv. Chim. Acta*, **17**, 1014 (1934).

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