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## Salt Effects and Medium Effects on Indicator Acid-Base Equilibria in a Methanol-Water Solvent

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The thermodynamic dissociation constants of four acid-base indicators have been determined at 25° by spectrophotometric measurements in solutions of hydrochloric acid in 33.4 wt. % methanol. The indicators and their charge types were: *p*-nitroaniline, A<sup>+</sup>B<sup>0</sup>; methylpicric acid, A<sup>0</sup>B<sup>-</sup>; dimethylpicric acid, A<sup>0</sup>B<sup>-</sup>; and *m*-cresolsulfonphthalein, A<sup>±</sup>B<sup>±</sup>. Salt effects and medium effects on the acid-base dissociation have been determined and correlated with the charge type. The results suggest that the salt effects for indicators of the same charge type display a considerably greater uniformity than do the medium effects. Salt effect terms for *p*-nitroaniline and methylpicric acid were determined in mixtures of hydrochloric acid and sodium chloride of constant total ionic strengths 0.559 and 1.13 in 33.4 wt. % methanol. The logarithm of the salt effect varies linearly with the composition of the mixture of electrolytes in accordance with the "Harned rule." Hammett acidity functions were determined but are thought to be of doubtful validity in this solvent medium.

### Introduction

The behavior of the activity coefficients of the colored forms of acid-base indicators when (a) the ionic strength of the solution is altered (*concentration effect* or *salt effect*) and (b) the composition of the solvent medium is changed (*medium effect*) have an important bearing on the usefulness of the indicator in acid-base measurements. If the salt effect is sufficiently regular, the salt errors in test solutions can be matched with those of colorimetric standards.<sup>2</sup> Moreover, a considerable uniformity in the medium effects of a series of different indicators of the same charge type is the *sine qua non* for the establishment of an acidity scale in a partially aqueous medium on the basis of the Hammett acidity function.<sup>3</sup>

In dilute aqueous solutions, useful predictions of the behavior of the ratio of activity coefficients of the colored indicator forms can be made if the charge type of the indicator is known. In concentrated salt solutions of fixed composition containing buffer substances in amounts that are small with respect to the concentration of the salt medium, the activity coefficients of ions are substantially constant and the formal dissociation constants of indicators are substantially independent of the nature and concentration of the buffer solutes.<sup>4</sup>

Data for the activity coefficients of indicators in mixed solvents, however, are not numerous. In particular, it is not known what regularities, if any, exist in the medium effect. However, Gutbezahl and Grunwald<sup>5</sup> have evaluated, by a semiempirical method, the "degenerate activity coefficient" of hydrogen ion in ethanol-water solvents. With this value it is possible to obtain the medium effects on the ratio of the activity coefficients,  $\gamma_{\text{In}}/\gamma_{\text{HIn}}$ , of the base and acid forms of certain indicators. Their results suggest that this ratio is quite different for indicators of different structures.

In this investigation, the dissociation constants of four indicators of three charge types have been determined in hydrochloric acid solutions at 25°, in 33.4 wt. % methanol as solvent. The indicators were *p*-nitroaniline, charge type A<sup>+</sup>B<sup>0</sup> (the reference indicator of the Hammett  $H_0$  scale); methylpicric acid and dimethylpicric acid, charge type A<sup>0</sup>B<sup>-</sup>; and *m*-cresolsulfonphthalein (acid range), charge type A<sup>±</sup>B<sup>-</sup> or A<sup>±</sup>B<sup>±</sup>. Charge types are identified by

indicating the charges borne by the acid form (A) and the base form (B). Salt effects of hydrochloric acid and sodium chloride on the activity coefficient quotients of the indicators in 33.4% methanol and the free energies and medium effects for the transfer of each indicator from water to 33.4% methanol have been obtained.

The logarithms of the activity coefficient quotients  $\gamma_{\text{HIn}}/\gamma_{\text{In}}$  for two indicators (*p*-nitroaniline and methylpicric acid) in methanolic solutions of hydrochloric acid and sodium chloride have been shown to vary linearly with composition at constant ionic strength. This behavior is consistent with the "Harned rule," which has been well established for many binary electrolyte mixtures in aqueous media<sup>6</sup> and for certain binary mixtures of hydrochloric acid and sodium chloride in methanol-water solvents.<sup>7,8</sup>

### Experimental

A reagent grade preparation of *p*-nitroaniline was recrystallized twice from 95% ethanol and once from water. *m*-Cresolsulfonphthalein (*m*-cresol purple) was a specially purified commercial sample. The preparation and purification of the methylpicric acid and the dimethylpicric acid have been described elsewhere.<sup>9</sup> The solutions for study were prepared in 100-ml. amounts from 40 ml. of Spectro grade methanol and aqueous solutions of the indicators and of hydrochloric acid and sodium chloride of known concentrations. The weights of methanol and of each of the aqueous solutions were determined, permitting the calculation of the molalities of the solutes and the weight composition of the solvent. The observed spectral absorbance was corrected to correspond with a solvent composition of exactly 33.4 wt. % methanol in each case.

The spectral absorption was determined with a Beckman Model DU quartz spectrophotometer, the cell compartment of which was controlled within 0.1° of 25°. The absorbance was measured in 1-cm. cells at two or more wave lengths near those at which the spectral absorptions of the two picrate ions, the basic form of *p*-nitroaniline, or the acid form of *m*-cresol purple are at their maxima.

The limiting absorptions of the acid and base forms of *p*-nitroaniline, methylpicric acid, and dimethylpicric acid were determined in solutions of hydrochloric acid (6 *M*) and sodium hydroxide (0.0009 *M*) in 33.4 wt. % methanol. The absorption of the acid form of *m*-cresolsulfonphthalein was also determined in 6 *M* hydrochloric acid, but that of the base form was measured in the methanolic solvent without addition of alkali.<sup>10</sup> The fraction,  $\alpha$ , of the indicator present in the base form was calculated by  $\alpha = (D - D_1)/(D_2 - D_1)$  where  $D_1$ ,  $D_2$ , and  $D$  are, respectively, the optical densities (spectral absorbances) of the acid form, the base

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, Chapter 14; R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London, 1959, Chapter 15. This linear relationship is often termed the "Harned rule."

(7) G. Åkerlöf, J. W. Teare, and H. Turck, *J. Am. Chem. Soc.*, **59**, 1916 (1937).

(8) R. G. Bates and D. Rosenthal, *J. Phys. Chem.*, **67**, 1088 (1963).

(9) M. M. Davis, M. Paabo, and R. A. Robinson, *J. Research Natl. Bur. Standards*, **64A**, 531 (1960); M. M. Davis and M. Paabo, *ibid.*, **64A**, 533 (1960). The authors are indebted to Dr. Davis for samples of these two acids.

(10) E. E. Sager, H. J. Keegan, and S. F. Acree, *J. Research Natl. Bur. Standards*, **31**, 323 (1943).

(1) On leave from Clarkson College of Technology, Potsdam, N. Y., summer, 1961.

(2) See, for example, I. M. Kolthoff and C. Rosenblum, "Acid-Base Indicators," The Macmillan Co., New York, N. Y., 1937.

(3) (a) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932); (b) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(4) D. Rosenthal and J. S. Dwyer, *Anal. Chem.*, **35**, 161 (1963).

(5) B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, **75**, 559, 565 (1953).

form, and the mixture of the two forms, all measured in the same cells at equal total concentrations of the indicator.

**Methods. Dissociation Constants.**—The protonated forms of all four indicators are relatively strong acids in water, with  $pK_a$  ranging from 0.8 to 1.7. It is possible to achieve a considerable range of transformation in 33.4 wt. % methanol by varying the concentration of added strong acid. One can therefore determine the thermodynamic dissociation constants without recourse to buffer solutions and acidity functions whose validity in mixed solvents has not yet been well established.

The value of  $p(sK_{HI_{1+}})$  for *p*-nitroanilinium ion ( $HI_{1+}$ ) was determined from the known molality of hydrogen ion and the ratio of the concentrations of the base and acid forms of the indicator, determined spectrophotometrically<sup>11</sup>

$$p(sK_{HI_{1+}}) = -\log m_H - \log \frac{m_{In}}{m_{HI_{1+}}} - \log_s \left( \frac{\gamma_H \gamma_{In}}{\gamma_{HI_{1+}}} \right) \quad (1)$$

where  $\gamma_i$  is an activity coefficient on the molal scale.

As in aqueous solutions of hydrochloric acid,<sup>12</sup> the last term of eq. 1 was found to vary linearly with  $m_H$  up to molalities of hydrochloric acid exceeding 1. The extrapolation to  $m_H = 0$  was therefore easily carried out.

The dissociation constants of the other three indicators were determined by the method proposed by Bates and Schwarzenbach,<sup>13</sup> which combines spectrophotometric data with the acidity function  $p(a_{H\gamma Cl})$  in such a way as to yield a linear extrapolation function

$$p(sK_{HI_n}) = p(a_{H\gamma Cl}) - \log \frac{m_{In^-}}{m_{HI_n}} - \log_s \left( \frac{\gamma_{In^-}}{\gamma_{HI_n} \gamma_{Cl^-}} \right) \quad (2)$$

The values of  $p(a_{H\gamma Cl})$  are readily obtained from the activity coefficients of hydrochloric acid in 33.4 wt. % methanol reported recently.<sup>3</sup>

The extrapolation plot according to eq. 2 showed that the activity coefficient quotient term is a linear function of ionic strength for *m*-cresol purple as well as for the two substituted picric acids. It seems very likely that the acid form of the indicator is a hybrid  $A^\pm$ , but it is not yet clear how the activity coefficient of such a species changes with ionic strength.<sup>14</sup> The behavior of the activity coefficient function cannot therefore lend support to one of three possible structures  $A^+B^-$ ,  $A^\pm B^-$ , or  $A^\pm B^{\pm-}$ .

**Salt Effects.**—The salt effect or concentration effect is regarded as the change in the activity coefficients (referred to the standard state in 33.4% methanol) produced by a change in the ionic strength. The salt effect on the equilibrium between the forms  $HI_n$  and  $In$  (charges not specified) is therefore characterized by the quantity  $s\Gamma_{HI_n}$

$$s\Gamma_{HI_n} \equiv \log_s \left( \frac{\gamma_H \gamma_{In}}{\gamma_{HI_n}} \right) \quad (3)$$

**Medium Effects.**—The medium effect on the species *i*, namely  $m\gamma_i$ , is the ratio of the activity coefficient of *i* referred to the aqueous standard state to that referred to the standard state in the particular medium in question.<sup>15</sup> Thus

$$m\gamma_i \equiv w\gamma_i/s\gamma_i \quad (4)$$

For the acidic dissociation of the indicator  $HI_n$

$$m\Gamma_{HI_n} \equiv \log_m \left( \frac{\gamma_H \gamma_{In}}{\gamma_{HI_n}} \right) \quad (5)$$

where  $m\Gamma_{HI_n}$  is the medium effect on the acid-base equilibrium  $HI_n \rightleftharpoons H^+ + In$ . This quantity is directly related to the standard free energy of transfer,  $\Delta G_{tr}^\circ$ , of  $HI_n$  from the standard state *s* to the aqueous standard state (*w*)

$$\begin{aligned} \Delta G_{tr}^\circ &\equiv \Delta G_s^\circ - \Delta G_w^\circ = RT \ln ({}_wK/{}_sK) \\ &= 2.3026RT [p({}_sK_{HI_n}) - p({}_wK_{HI_n})] \\ &= 2.3026RT \log m\Gamma_{HI_n} \end{aligned} \quad (6)$$

(11) The subscript *s* indicates that the standard state is the aqueous methanolic solvent rather than pure water. Dissociation constants are expressed on the scale of molality, where the molality is the number of moles per 1000 g. of solvent (water or methanol-water). For simplicity, the + charge is omitted from the symbol for hydrogen ion ( $H^+$ ) in subscripts.

(12) M. A. Paul, *J. Am. Chem. Soc.*, **76**, 3236 (1954). Molar concentrations were used, and a linear dependence on  $CHCl$  was demonstrated.

(13) R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **37**, 1089 (1954);  $p(a_{H\gamma Cl})$  is a conventional abbreviation for  $-\log(a_{H\gamma Cl})$ .

(14) There is support for the belief that the hybrid behaves like an uncharged species  $A^0$  in very dilute solutions; see, for example, E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, Chapter 4, Chapter 12 (by J. G. Kirkwood). However, I. M. Kolthoff and L. S. Guss, *J. Am. Chem. Soc.*, **60**, 2516 (1938), have expressed the view that, at all but the lowest concentrations, the hybrid ion behaves as two independent univalent ions.

(15) The medium effect defined here is identical with the "primary medium effect" of B. B. Owen, *ibid.*, **54**, 1758 (1932).

TABLE I

DISSOCIATION CONSTANTS OF FOUR INDICATORS IN 33.4 WT. % METHANOL FROM SPECTROPHOTOMETRIC MEASUREMENTS IN HYDROCHLORIC ACID SOLUTIONS (MOLALITY *m*) AT 25°

<i>m</i>	$p(a_{H\gamma Cl})$	$\alpha$	$\log (m_{In}/m_{HI_n})$	$p({}_sK_{HI_n})'$	$p({}_sK_{HI_n})$
<i>p</i> -Nitroaniline ( $6.12 \times 10^{-5}$ and $1.22 \times 10^{-4}$ <i>M</i> ; measurements at 385 m $\mu$ )					
0.1274		0.745	0.465	0.430	0.403
.1593		.694	.355	.443	.409
.3200		.510	.018	.477	.408
.5595		.346	— .277	.529	.409
.6434		.306	— .356	.548	.410
.9743		.198	— .607	.618	.408
1.1394		.161	— .716	.659	.414
1.3077		.137	— .798	.681	.400
				Av.	0.408
				S.d.	0.004
Methylpicric acid ( $7.00 \times 10^{-5}$ and $1.00 \times 10^{-4}$ <i>M</i> ; measurements at 350, 355, and 380 m $\mu$ )					
0.06354	1.430	0.739	0.453	0.977	0.980
.1274	1.179	.616	.205	.974	.980
.1593	1.098	.573	.127	.971	.979
.3199	0.833	.426	— .130	.963	.978
.5595	.597	.309	— .350	.947	.974
1.1321	.235	.169	— .692	.927	.981
				Av.	0.979
				S.d.	0.002
Dimethylpicric acid ( $3.00 \times 10^{-4}$ <i>M</i> ; measurements at 385, 390, 400, and 410 m $\mu$ )					
0.01610	1.937	0.627	0.226	1.711	1.716
.03191	1.677	.484	— .028	1.705	1.713
.06354	1.430	.354	— .261	1.691	1.706
.09560	1.284	.283	— .404	1.688	1.711
.1274	1.179	.238	— .505	1.684	1.715
				Av.	1.712
				S.d.	0.004
<i>m</i> -Cresolsulfonphthalein, acid range ( $3.08 \times 10^{-5}$ <i>M</i> ; measurements at 532 m $\mu$ )					
0.01590	1.939	0.688	0.343	1.596	1.599
.03176	1.678	.549	.085	1.593	1.600
.06354	1.430	.411	— .157	1.587	1.600
.09560	1.284	.335	— .298	1.582	1.602
.1274	1.179	.288	— .393	1.572	1.599
.1593	1.098	.253	— .468	1.566	1.600
				Av.	1.600
				S.d.	0.001

The quantities  $\Delta G^\circ$ , and  $\Delta G_w^\circ$  in eq. 6 are the free energies of dissociation of the acid  $HI_n$  in the standard states indicated by the subscripts.

## Results

The data for the determination of the dissociation constants of the four indicators in 33.4 wt. % methanol are summarized in Table I. The values of  $p({}_sK_{HI_n})'$  represent the sums of the first two terms on the right of eq. 1 and 2, the activity coefficient terms being omitted. In each instance,  $p({}_sK_{HI_n})'$  is a linear function of ionic strength. The numbers identified as "s.d." are the estimates of the standard deviations of a single value from the least-squares line. The slopes of the lines indicate the values of the activity coefficient terms, which were found to be as follows in solutions of hydrochloric acid (*m*) in 33.4% methanol

$$p\text{-nitroaniline, } 0 < m < 1.3; \log_s (\gamma_H \gamma_{In} / \gamma_{HI_{1+}}) = 0.215m \quad (7)$$

$$\text{methylpicric acid, } 0 < m < 1.1; \log_s (\gamma_{In^-} / \gamma_{HI_n} \gamma_{Cl^-}) = -0.048m \quad (8)$$

$$\text{dimethylpicric acid, } 0 < m < 0.13; \log_s (\gamma_{In^-} / \gamma_{HI_n} \gamma_{Cl^-}) = -0.243m \quad (9)$$

*m*-cresolsulfonphthalein,  $0 < m < 0.16$ ;

$$\log s(\gamma_{\text{In}^{\pm}}/\gamma_{\text{HIIn}}\gamma_{\text{Cl}^-}) = -0.211m \quad (10)$$

The values of  $p(sK_{\text{HIIn}})$  given in the last column of Table I were obtained by eq. 1 and 2 from  $p(sK_{\text{HIIn}})'$  and the activity coefficient terms of eq. 7-10.

The dissociation constants in 33.4% methanol are summarized in Table II and compared with the corresponding dissociation constants in water, taken from the literature. The fourth column gives the medium effect term  $\log m\Gamma_{\text{HIIn}}$ , and the last column gives the standard free energy of transfer (compare eq. 5 and 6). The value of  $2.3026RT$  is 1364.2 thermochemical cal. mole<sup>-1</sup> at 25° (1 cal. = 4.1840 joules).

TABLE II

DISSOCIATION CONSTANTS, MEDIUM EFFECTS, AND FREE ENERGIES OF TRANSFER FOR FOUR INDICATORS IN 33.4 WT. % METHANOL AT 25°

Indicator	$p(wK_{\text{HIIn}})$	$p(sK_{\text{HIIn}})$	$\log m\Gamma_{\text{HIIn}}$	$\Delta G^{\circ}_{\text{tr}}$ , cal. mole <sup>-1</sup>
<i>p</i> -Nitroaniline	1.003 <sup>8</sup>	0.408	-0.595	-812
Methylpicric acid	0.808 <sup>9</sup>	0.979	.171	233
Dimethylpicric acid	1.376 <sup>9</sup>	1.712	.336	458
<i>m</i> -Cresol purple	1.703 <sup>10</sup>	1.600	-.103	-141

It is evident from a consideration of the dissociation equilibria and eq. 3 that

$$sK_{\text{HIIn}} = (m_{\text{HIIn}}/m_{\text{HIIn}}) s\Gamma_{\text{HIIn}} \quad (11)$$

where  $s\Gamma_{\text{HIIn}}$  is the salt effect on the dissociation of the indicator. The salt effect on *p*-nitroaniline in solutions of hydrochloric acid in 33.4% methanol is expressed by eq. 7. For the other three indicators it can be obtained by combining the experimental values of  $s[\gamma_{\text{In}}/(\gamma_{\text{HIIn}}\gamma_{\text{Cl}^-})]$  given by eq. 8, 9, and 10 with the mean activity coefficient ( $\gamma_{\pm}$ ) of hydrochloric acid<sup>8</sup> in the same solutions

$$\log s\Gamma_{\text{HIIn}} = \log s(\gamma_{\text{In}}/\gamma_{\text{HIIn}}\gamma_{\text{Cl}^-}) + 2 \log \gamma_{\pm} \quad (12)$$

Salt effects for the four indicators in solutions of hydrochloric acid in 33.4% methanol are summarized in Table III.

TABLE III

SALT EFFECTS FOR FOUR INDICATORS IN SOLUTIONS OF HYDROCHLORIC ACID (MOLALITY *m*); SOLVENT: 33.4 WT. % METHANOL

<i>m</i>	$-\log s\Gamma_{\text{HIIn}} \equiv \log s(\gamma_{\text{HIIn}}/\gamma_{\text{HIIn}})$ for			
	<i>p</i> -Nitroaniline	Methylpicric acid	Dimethylpicric acid	<i>m</i> -Cresol purple
0.005	0.001	-0.086	-0.087	-0.087
.01	.002	-.117	-.118	-.118
.02	.004	-.155	-.160	-.159
.05	.011	-.218	-.228	-.226
.1	.022	-.272	-.292	-.289
.2	.043	-.325		
.3	.065	-.350		
.4	.086	-.364		
.5	.108	-.370		
1.0	.215	-.354		
1.2	.258			

These values were calculated by the equation (compare eq. 12 and ref. 8)

$$\log s\Gamma_{\text{HIIn}} = \frac{-1.345\sqrt{m}}{1 + 1.521\sqrt{m}} + 2[\text{ext.}] - 2 \log(1 + 0.0422m) + (0.264 + B)m \quad (13)$$

where *B* is the coefficient of *m* in eq. 8, 9, and 10 for methylpicric acid, dimethylpicric acid, and *m*-cresol purple, respectively. For *p*-nitroaniline, eq. 7 was employed.

The behavior of the salt effect term,  $\log s\Gamma_{\text{HIIn}}$ , for *p*-nitroaniline (*p*NNA, charge type A<sup>+</sup>B<sup>0</sup>) and methylpic-

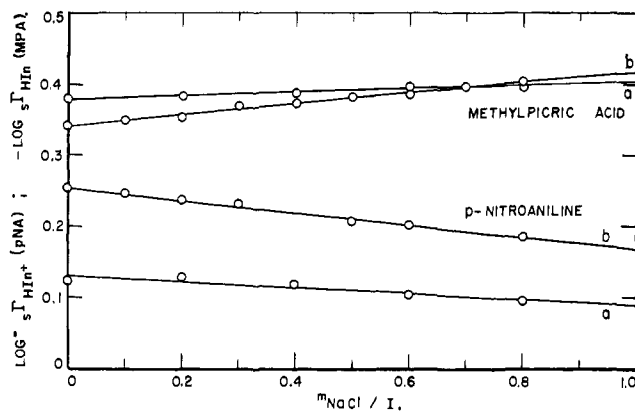


Fig. 1.—Salt effects on the dissociation of *p*-nitroaniline (*p*NA) and methylpicric acid (MPA) in HCl-NaCl mixtures of constant ionic strength in 33.4 wt. % methanol: a, *I* = 0.559; b, *I* = 1.13.

ric acid (MPA, charge type A<sup>0</sup>B<sup>-</sup>) was examined further in mixtures of hydrochloric acid and sodium chloride of constant total ionic strength in 33.4 wt. % methanol. Two ionic strengths, 0.559 and 1.13, were chosen for study. The data are collected in Tables IV and V, and the salt effect terms for the two indicators are plotted in Fig. 1 as a function of the fractional contribution of sodium chloride to the ionic strength.

TABLE IV

ACTIVITY COEFFICIENTS OF *p*-NITROANILINE IN MIXTURES OF HYDROCHLORIC ACID AND SODIUM CHLORIDE OF CONSTANT IONIC STRENGTH IN 33.4 WT. % METHANOL

<i>m</i> <sub>1</sub> (HCl)	<i>m</i> <sub>2</sub> (NaCl)	$\alpha$	$\log (m_{\text{In}}/m_{\text{HIIn}^+})$	$\log s\Gamma_{\text{HIIn}^+}$
Ionic strength = 0.559				
0.5595	...	0.346	-0.277	0.123
.4470	0.1118	.396	-.183	.127
.3357	.2236	.471	-.050	.118
.2239	.3357	.580	.141	.103
.1120	.4473	.738	.450	.095
...	.5595			(.089)

Ionic strength = 1.133

1.139	...	0.161	-0.716	0.253
1.023	0.1137	.178	-.663	.247
0.9050	.2262	.201	-.599	.236
.7935	.3399	.225	-.538	.232
.5653	.5655	.302	-.364	.206
.4521	.6783	.353	-.263	.202
.2262	.9041	.532	.055	.185
...	1.139			(.166)

It is clear that  $\log s\Gamma_{\text{HIIn}}$  for both indicators varies linearly with the composition of the acid-salt mixture at constant total ionic strength.<sup>16</sup> The equations for the lines and the standard deviations of a point from the line are

$$I = 0.559: \text{p-nitroaniline, } \log s\Gamma_{\text{HIIn}^+} = 0.1292 - 0.0715m_{\text{NaCl}}; \text{ s.d. } 0.005 \quad (14)$$

$$\text{methylpicric acid, } -\log s\Gamma_{\text{HIIn}} = 0.3786 + 0.0474m_{\text{NaCl}}; \text{ s.d. } 0.002 \quad (15)$$

$$I = 1.13: \text{p-nitroaniline, } \log s\Gamma_{\text{HIIn}^+} = 0.2545 - 0.0780m_{\text{NaCl}}; \text{ s.d. } 0.003 \quad (16)$$

$$\text{methylpicric acid, } -\log s\Gamma_{\text{HIIn}} = 0.3425 + 0.0687m_{\text{NaCl}}; \text{ s.d. } 0.003 \quad (17)$$

The limiting values of  $\log s\Gamma_{\text{HIIn}}$  in solutions of sodium chloride in 33.4% methanol containing no hydrochloric acid are enclosed in parentheses in Tables IV and V.

(16) The concentration of indicator was so small that its contribution to the ionic strength could be ignored.

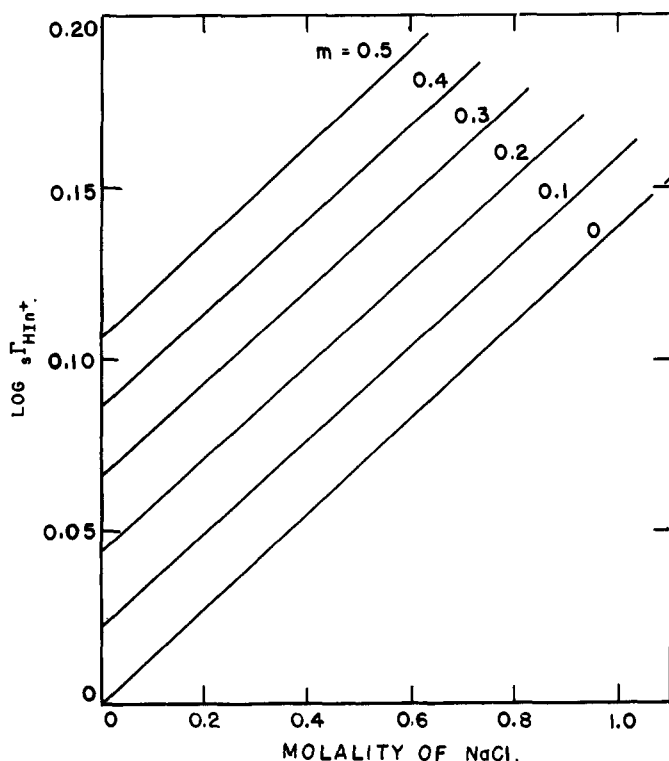


Fig. 2.—Effect of added sodium chloride on the salt effect term  $\log_s \Gamma_{HIa^+}$  for *p*-nitroaniline in solutions of hydrochloric acid (molality  $m$ ); solvent = 33.4% methanol.

The linear variation of the logarithms of the activity coefficients of two electrolytes in a binary aqueous mixture of constant total ionic strength has, of course, been demonstrated repeatedly.<sup>6</sup> There is also ample evidence that a concentrated salt medium “swamps out”

TABLE V

ACTIVITY COEFFICIENTS OF METHYLPICRIC ACID IN MIXTURES OF HYDROCHLORIC ACID AND SODIUM CHLORIDE OF CONSTANT IONIC STRENGTH IN 33.4 WT. % METHANOL

Methylpicric acid,  $7.00 \times 10^{-5} M$ ; measurements at  $380 m\mu$

$m_1$ (HCl)	$m_2$ (NaCl)	$\alpha$	$\log (m_{Ia^-}/m_{HIa})$	$\log_s \Gamma_{HIa}$
Ionic strength = 0.559				
0.5595	....	0.309	-0.350	-0.379
.4478	0.1120	.361	-.248	-.384
.3356	.2236	.431	-.120	-.387
.2236	.3356	.538	.066	-.397
.1119	.4476	.701	.369	-.399
....	.5595			(-.405)
Ionic strength = 1.131				
1.132	....	0.169	-0.692	-0.343
1.017	0.1133	.186	-.640	-.349
0.9051	.2262	.207	-.584	-.354
.7920	.3397	.237	-.509	-.371
.6775	.4525	.267	-.438	-.374
.5649	.5658	.309	-.350	-.383
.4519	.6781	.360	-.250	-.386
.3397	.7915	.435	-.113	-.399
.2266	.9048	.539	.067	-.403
....	1.132			(-.420)

variations in the activity coefficients of substances present in relatively small concentration, and that the value of  $\Gamma_{HIa}$  for indicators and other weak acids and bases in media of this sort is fixed by the composition of the salt medium.<sup>4,17</sup> It now appears that the activity coefficient of an indicator or other substance present in

(17) See D. Rosenthal and J. S. Dwyer, *J. Phys. Chem.*, **66**, 2687 (1962); J. S. Dwyer and D. Rosenthal, *ibid.*, **67**, 779 (1963).

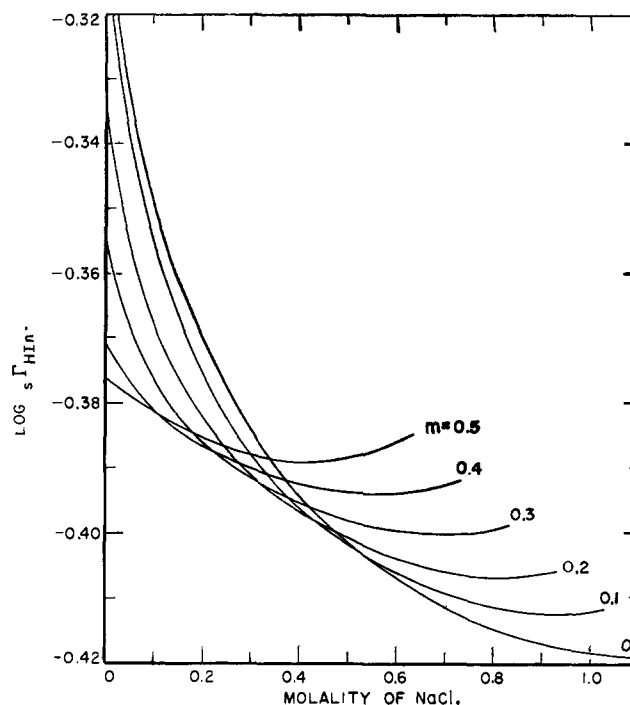


Fig. 3.—Effect of added sodium chloride on the salt effect term  $\log_s \Gamma_{HIa}$  for methylpicric acid in solutions of hydrochloric acid (molality  $m$ ); solvent = 33.4% methanol.

small concentration in a binary mixture of electrolytes of changing composition but constant ionic strength varies in a simple fashion with the composition of the mixture.<sup>18</sup>

### Discussion

**Salt Effects.**—It is of interest to compare the variation of the salt effect terms,  $\log_s \Gamma_{HIa}$ , for indicators of two charge types in hydrochloric acid as sodium chloride is added. The salt effect in solutions of hydrochloric acid has been determined for all four indicators (compare Table III) and for *p*-nitroaniline (charge type  $A^+B^0$ ) and methylpicric acid (charge type  $A^0B^-$ ) in HCl–NaCl mixtures of two different ionic strengths. The salt effects calculated for five molalities of hydrochloric acid containing varying amounts of sodium chloride, and for acid-free solutions of sodium chloride, are plotted in Fig. 2 and 3.

The salt effects for the two indicators are widely different in form, sign, and magnitude, as is to be expected from the difference in the charge types of the two dissociation processes. Nevertheless, it may be seen from Table III that the salt effect terms for indicators of the same charge type are strikingly similar in dilute solutions.

The linear variation of  $\log_s \Gamma_{HIa}$  for *p*-nitroaniline and methylpicric acid in HCl–NaCl mixtures of constant total ionic strength suggests that the magnitude of each of the activity coefficient terms in eq. 7 to 10 is determined by two parameters  $B$  and  $B'$ . Hence for *p*-nitroaniline

$$\begin{aligned} \log_s \Gamma_{HIa^+} &= B m_{HCl} + B' m_{NaCl} \\ &= B I + (B' - B) m_{NaCl} \end{aligned} \quad (18)$$

and for the other three indicators

$$\log_s (\gamma_{Ia^-} / \gamma_{HIa} \gamma_{Cl^-}) = B m_{HCl} + B' m_{NaCl} \quad (19)$$

(18) After the completion of this work, it was reported by C. H. Brubaker, Jr., P. G. Rasmussen, and D. C. Luehrs, *J. Chem. Eng. Data*, **7**, Pt. 2, 563 (1962), that  $H_0 + \log m_H$  (where  $H_0$  is the Hammett acidity function) in aqueous mixtures of hydrochloric acid with  $KCl$ ,  $SrCl_2$ ,  $AlCl_3$ , or  $BiCl_3$  varies linearly with  $m_{HCl}$  at a constant ionic strength. It will be noted that  $H_0 + \log m_H$  is equal to  $-\log (m \Gamma_s \Gamma)$  for the Hammett indicators used.

It remains to examine the constancy of  $B$  and  $B'$  for different ionic strengths in the experimental range. Data are available for two ionic strengths, 0.559 and 1.13. From the values of  $\log {}_s\Gamma_{\text{HIn}^+}$  for  $p$ -nitroaniline (Table IV) one obtains by the method of least squares

$$I = 0.559; B = 0.231, B' = 0.160 (0.170)$$

$$I = 1.13; B = 0.225, B' = 0.147 (0.154)$$

With the use of eq. 12 and 19 we find for methylpicric acid

$$\begin{aligned} \log {}_s\Gamma_{\text{HIn}} &= Bm_{\text{HCl}} + B'_{\text{NaCl}} + 2 \log \gamma_{1(0)} - 2\alpha_{12}m_{\text{NaCl}} \\ &= BI + (B' - B - 2\alpha_{12})m_{\text{NaCl}} + 2 \log \gamma_{1(0)} \quad (20) \end{aligned}$$

In eq. 20,  $\gamma_{1(0)}$  is the mean ionic activity coefficient of hydrochloric acid at  $m = I$  in the absence of sodium chloride. This activity coefficient and the corresponding "Harned rule" coefficient  $\alpha_{12}$  have been given in an earlier publication.<sup>8</sup> The latter has the value 0.035 and is affected little, if at all, by changes in ionic strength. From  $\log {}_s\Gamma_{\text{HIn}}$  given in Table V we find by least-squares methods

$$I = 0.559; B = -0.060, B' = -0.038 (-0.046)$$

$$I = 1.13; B = -0.047, B' = -0.046 (-0.046)$$

A practical assessment of the experimental uncertainties in these values of  $B$  and  $B'$  can be made as follows. From the data in hydrochloric acid solutions,  $B$  for  $p$ -nitroaniline was found to be 0.215 (eq. 7) and for methylpicric acid was found to be  $-0.048$  (eq. 8). The values of  $B'$  corresponding to these values of  $B$  are given in parentheses above. It may therefore be judged that the differences in the values of  $B'$  found at the two ionic strengths 0.559 and 1.13 are not significant. It is likewise of interest to note that  $\log {}_s\Gamma_{\text{HIn}}$  for methylpicric acid decreases at about the same rate as  $\log {}_s\gamma_{\pm}$  for hydrochloric acid when HCl is replaced by NaCl. At  $I = 1.13$ , for example,  $(d \log {}_s\Gamma / dm_{\text{NaCl}})_I$  is  $-0.069$  (see eq. 17) or very nearly  $2\alpha_{12}$ , as expected from the charge types of the respective activity coefficient terms. The agreement is less satisfactory at the lower ionic strengths where the uncertainty in establishing the slope is considerably enhanced.

**Medium Effects.**—Medium effect terms  $\log {}_m\Gamma_{\text{HIn}}$  for indicator equilibria of the charge types  $\text{A}^0\text{B}^-$  and  $\text{A}^+\text{B}^0$  in 33.4 wt. % methanol are collected in Table VI. It is evident that the medium effects for individual indicators of the same charge type do not show as high a degree of uniformity as do the corresponding salt effects. deLigny, Loriaux, and Ruiter<sup>19</sup> noted a similar irregularity in methanol-water solvents, both for primary aliphatic amines and for a series of azo indicators. Whereas the salt effects for  $m$ -cresol purple resemble closely those for methylpicric acid and dimethylpicric acid, the medium effect is of opposite sign.

**Hammert Acidity Functions.**—The Hammert acidity functions ( $H$ ) in 33.4 wt. % methanol are given by the equations

$$\begin{aligned} H &= -\log m_{\text{H}} - \log {}_w(\gamma_{\text{H}}\gamma_{1\text{n}}/\gamma_{\text{HIn}^+}) \\ &= -\log m_{\text{H}} - \log {}_m\Gamma_{\text{HIn}} - \log {}_s\Gamma_{\text{HIn}} \quad (21) \end{aligned}$$

For indicators of the types  $\text{A}^+\text{B}^0$  and  $\text{A}^0\text{B}^-$ , these functions are designated  $H_0$  and  $H_-$ , respectively.<sup>3</sup> Their values in certain mixtures of hydrochloric acid and sodium chloride (in 33.4% MeOH) have been evaluated from the salt and medium effects for  $p$ -nitroaniline and methylpicric acid found in this investigation. The results are summarized in Table VII.

The salt effects on  $p$ -nitroaniline in 33.4 wt. % methanol are very similar to those observed by Paul<sup>12</sup> in aqueous solutions of hydrochloric acid upon addition of

(19) C. L. deLigny, H. Loriaux, and A. Ruiter, *Rec. trav. chim.*, **80**, 725 (1961).

TABLE VI  
COMPARISON OF MEDIUM EFFECTS FOR INDICATOR ACIDS OF TWO CHARGE TYPES IN 33.4 WT. % METHANOL

Indicator acid	$p({}_wK_{\text{HIn}})$	$p({}_sK_{\text{HIn}})$	$\log {}_m\Gamma_{\text{HIn}}$
	(water)	(MeOH-H <sub>2</sub> O)	
Charge type $\text{A}^0\text{B}^-$			
$p$ -Nitrophenol	7.15	7.51 <sup>19</sup>	0.36
4-Chloro-2,6-dinitrophenol	2.97	3.18 <sup>20</sup>	.21
2,6-Dinitrophenol	3.69	4.19 <sup>21</sup>	.50
Methylpicric acid	0.81	0.98	.17
Dimethylpicric acid	1.38	1.71	.33
Charge type $\text{A}^+\text{B}^0$			
$m$ -Nitroanilinium ion	2.46	1.94 <sup>20</sup>	-0.52
$p$ -Nitroanilinium ion	1.00	0.41	-.59
$p$ -Chloroanilinium ion	2.62	2.22 <sup>20</sup>	-.40

<sup>a</sup> Molarity scale.

TABLE VII  
SALT EFFECTS OF NaCl ON HAMMETT ACIDITY FUNCTIONS FOR SOLUTIONS OF HYDROCHLORIC ACID IN 33.4 WT. % METHANOL  
 $H_0$  indicator =  $p$ -nitroaniline;  $H_-$  indicator = methylpicric acid

$m_{\text{HCl}}$	$m_{\text{NaCl}}$	$H_0$	$H_-$
0.1	0	1.575	1.100
	0.1	1.557	1.182
	.2	1.541	1.202
	.4	1.509	1.223
	.6	1.480	1.233
	0.2	0	1.253
0.5	0.1	1.234	.893
	.2	1.217	.908
	.4	1.186	.923
	.6	1.158	.930
	0	0.789	.504
	0.1	.765	.510
0.2	.2	.747	.513
	.4	.717	.517
	.6	.696	.514

neutral salts.<sup>22</sup> In 0.01 and 0.1  $M$  aqueous solutions of hydrochloric acid, Paul found the salt effect to be accurately linear with the salt concentration, the apparent acidity increasing as salt was added. The plots shown in Fig. 2 are likewise straight lines. By solubility measurements, Paul was able to show that a considerable part of the salt effect is attributable to changes in the activity coefficient ( $\gamma_{\text{In}}$ ) of the uncharged indicator molecules, the rest being a contribution from  $\gamma_{\text{H}^+}/\gamma_{\text{HIn}^+}$ .

The utility of the  $H_0$  function in aqueous solutions, particularly those of high acidity, has been amply demonstrated.<sup>3,23</sup> A useful  $H_0$  scale covering a wide range of acidities requires a series of indicators of the  $\text{A}^+\text{B}^0$  charge type, for all of which  ${}_w(\gamma_{\text{H}}\gamma_{\text{In}}/\gamma_{\text{HIn}^+})$  has a single value in a given solution. A series of indicators meeting this requirement in strongly acidic media has been selected.<sup>3,24</sup> It appears that indicators of the type  $\text{A}^0\text{B}^-$  displaying the regularities necessary for a practical scale of  $H_-$  are less easy to find.

To demonstrate that a useful scale of  $H_0$  or  $H_-$  exists in 33.4 wt. % methanol, it would be necessary to find a series of indicators of a single charge type, for which both  ${}_s\Gamma_{\text{HIn}}$  and  ${}_m\Gamma_{\text{HIn}}$  are independent of the indicator structure and acid strength when present in a given

(20) E. E. Sager, R. A. Robinson, and R. G. Bates, *J. Research Natl. Bur. Standards*, in press.

(21) G. Kortüm and M. Buck, *Z. Elektrochem.*, **62**, 1083 (1958).

(22) See also the study of the effect of ionic strength on  $H_0$  by I. I. Moiseev and R. M. Flid, *Zh. Prikl. Khim.*, **27**, 1110 (1954).

(23) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(24) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963), have recently demonstrated the usefulness of a new set of uniform Hammett indicators consisting entirely of primary anilines.

medium. The results of this investigation suggest (but do not prove) that the necessary regularity in the salt effect term may well exist. However, the rather large variation in the medium effect for monosubstituted anilines of closely similar structures (see Table VI) makes it seem doubtful that a suitable series of indi-

cators can be found. This conclusion, which applies with equal force to the  $H_-$  function in 33.4% methanol, substantiates the earlier finding of deLigny, *et al.*<sup>19</sup> It is likewise consistent with the view of Gutbezahl and Grunwald<sup>5</sup> that useful scales of  $H_0$  and  $H_-$  do not exist in ethanol-water mixtures.

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC SYNTHESIS, POLISH ACADEMY OF SCIENCES, WARSZAWA 10, POLAND]

## Proton Magnetic Resonance Study of Nitroalkanes

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An attempt was made to explain chemical shifts (at 60 Mc.) of protons in nitroalkanes in terms of the inductive effect of the  $\text{NO}_2$  group and the effect of diamagnetic anisotropy of the C-C bonds. The inductive effect was shown to operate as far as the fourth carbon atom in the chain. Some correlations were observed between bond polarization and the diamagnetic anisotropy effect. Rather narrow ranges of chemical shifts of various types of protons in nitroalkanes were found. Analysis of the multiplet pattern and position of the methine signal of nitrocyclohexane showed that the chair form with an equatorial nitro group is the only species of the compound at room temperature. The effect of internal rotation on the chemical shifts of the protons at C-1 is discussed.

Very little literature data are known on the position of n.m.r. signals of protons in alkyl groups bonded to one or more nitro groups. The only substances which have been examined so far are nitromethane,<sup>1-3</sup> nitroethane,<sup>1b,3</sup> nitropropanes,<sup>3</sup> nitrocyclohexane,<sup>4</sup> and some rather complicated alicyclic nitro compounds.<sup>5,6</sup>

We have been interested in the possibility of qualitative and, eventually, quantitative predictions of the chemical shifts, particularly those of  $\alpha$ -hydrogen signals in proton resonance spectra of nitroalkanes.

This work presents a discussion of the problem in terms of the inductive effect of the nitro group and the effect of diamagnetic anisotropy of the C-C bonds. The latter seems to be particularly valuable in structural assignments and conformational analysis based on n.m.r. data.

### Experimental

The following compounds were examined: nitromethane (I), nitroethane (II), 1-nitropropane (III), 1-nitrobutane (IV), 1-nitropentane (V), 1-nitrohexane (VI), dinitromethane (VII), trinitromethane (VIII), 2-nitropropane (IX), nitrocyclohexane (X), 2-chloro-2-nitropropane (XI), 1,1-dinitroethane (XII), 1,1-dinitropropane (XIII), 2-methyl-2-nitropropane (XIV), and 2,2-dinitropropane (XV).

Compounds I-VI, IX, XI, and XV were commercial C.P. grade products, distilled under reduced pressure. Dinitromethane (VII) was prepared from dibromodinitromethane after Duden.<sup>7</sup> Trinitromethane (VIII) was obtained from its potassium salt made by the action of aqueous solution of  $\text{K}_2\text{Fe}(\text{CN})_6$  on tetranitromethane.<sup>8</sup> Nitrocyclohexane (X) and 2-methyl-2-nitropropane (XIV) were made by the Meyer reaction from the corresponding iodide<sup>9a</sup> and chloride,<sup>9b</sup> respectively. The dinitroalkanes XII<sup>10</sup> and XIII<sup>10</sup> were prepared from the corresponding sodium salts of mononitro compounds according to Shechter and Kaplan.<sup>11</sup> All compounds were vacuum distilled; their purity, tested by the integration of their n.m.r. peaks, was found to be higher than 98%.

The n.m.r. spectra were measured at 60 Mc./sec. using a Varian HR-60 spectrometer with a flux stabilizer, a field homo-

geneity control unit, and a spinning sample insert. The temperature was maintained at  $26 \pm 0.3^\circ$ . Calibration of the spectra was carried out by the side-band superposition method with accuracy of  $\pm 0.3$  c.p.s. within the 20-100 c.p.s. range and  $\pm 0.5$  c.p.s. within the 100-500 c.p.s. range, measured from tetramethylsilane internal standard. Peak positions were reported in  $\tau$ -units =  $10.00 - (\nu_{\text{TMS}} - \nu_x)/\nu_{\text{TMS}} \times 10^6$ . The chemical shifts of multiplets were determined at the frequencies of the "first moments"

$$\langle \nu \rangle = \sum \nu_i L_i / \sum L_i$$

( $\nu_i$  is the component frequency,  $L_i$  the corresponding integral intensity). The coupling constants were measured by the wobble-beat method with an error of  $\pm 0.2$  c.p.s. The spectra are presented together with their integral curves in Fig. 1 and 2.

### Discussion

**Local Diamagnetic Deshielding by Inductive Effect of Nitro Group.**—The nitro group, being strongly electron-attracting, decreases local electron density around alkyl protons in nitroalkanes, thus shifting their resonance signals to lower magnetic fields. The effect depends both on the number of nitro groups and on the number of intervening bonds between the proton and the nitro group. This may be seen in the series

	$\text{CH}_3$	$\text{CH}_2\text{NO}_2$	$\text{CH}_2(\text{NO}_2)_2$	$\text{CH}(\text{NO}_2)_3$
$\tau$ , p.p.m.	9.767	5.72	3.90	2.48

and in the spectra of primary, straight-chain nitroalkanes II-VI. The negative inductive effect of the  $\text{NO}_2$  group operates significantly as far as to the fourth carbon atom in the chain, permitting the observation of resolved signals of individual methylene groups up to 1-nitrobutane (IV); the first two  $\text{CH}_2$  multiplets are clearly distinguished in the whole series.

The same conclusion may be drawn if the chemical shifts of the terminal methyl groups are considered (Fig. 3).

The  $\text{CH}_3$  shifts presented on the above diagram may be considered as a measure of the decrease in local electron density around successive carbon atoms in the chain, since the effect of diamagnetic anisotropy of the  $\text{NO}_2$  group and additional C-C bonds should not be significant (except in nitromethane) because of the averaging effect of internal rotation. This diagram will be used in the next part of this work for some quantitative predictions regarding polarization of the C-C bonds in nitroalkanes.

The  $\tau$ -values of the  $\text{CH}_3$  peaks of branched-chain nitroalkanes (IX, XIV) lie rather in line with those of straight-chain ones. Positions of the methyl signals

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(10) Kindly supplied by Dr. Z. Buczkowski.

(11) H. Shechter and R. B. Kaplan, *J. Am. Chem. Soc.*, **83**, 3535 (1961).