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Strong Acid–Weak Base Reactions in the Binary Solvent, Acetic Acid–Nitromethane

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Proton exchange between perchloric acid and weak bases in the two-component solvent, acetic acid–nitromethane, was studied spectrophotometrically by the Kolthoff–Bruckenstein method. The dielectric constant range considered was from 6.2 to 24.8 at 25°. The apparent strength of the base increases with increasing nitromethane content up to 0.20 in mole fraction; however, a slight decrease in basicity occurs at higher nitromethane compositions. The initial increase in the basicity constant in the presence of small amounts of the more polar solvent reflects the influence of increasing dielectric constant upon the dissociation of the base perchlorate ion pair and higher ionic aggregates.

Introduction

Nitromethane has been used as a representative aprotic solvent for the comparison of the influences exerted by different solvent types upon the vibrational and electronic spectra and oxidation–reduction behavior of metal complexes in solutions. The characteristics of strong electrolytes in this solvent of intermediate range dielectric constant have been reported recently by Schiff and co-workers.[1] However, relatively little fundamental information concerning acid–base behavior in nitromethane is available.[2,3] In the study reported herein the role of nitromethane in the neutralization reaction of a strong acid with a weak base was investigated by employing a two-component solvent of the protonic–aprotic type. Anhydrous acetic acid is a nearly ideal protonic solvent component for this purpose, because of its low dielectric constant and strong tendency to solvate acids and uncharged bases.

The proton-transfer reaction between perchloric acid and two high molecular weight weakly basic indicators, thioflavine T and neutral red, was studied spectrophotometrically within the nitromethane mole fraction range from 0.0 to 0.614 for the solvent composition. The dielectric constant of the medium at 25° was used as the solvent parameter for correlation to the apparent basicity of the indicator expressed by the formation constant, K_f, for the perchlorate salt. All symbols used are those employed by Kolthoff and Bruckenstein[4] and Hummelstedt and Hume.[5]

Experimental

Solvents and Solutions.—Reagent grade glacial acetic acid was made anhydrous by adding the stoichiometric amount of acetic anhydride to consume the water present. Nitromethane was dried for 1 week over anhydrous calcium sulfate followed by alumina column chromatographic purification, according to the method of Larson and Iwamoto.[6] The water contents of the solvents, as determined by Karl Fischer titration, were 0.001% for acetic acid and 0.0005% for nitromethane.

Standard solutions of 0.1 *M* perchloric acid, 0.1–0.2 *M* sodium acetate, and the indicator bases were made in anhydrous acetic acid as reported previously.[7] Sodium perchlorate in anhydrous acetic acid was prepared by careful neutralization of the parent acid and base to give a stock solution that was 0.0645 *M* in the salt.

Methods of Measurement.—Absorbance values at 25° were determined for the base form of the indicator, using a Bausch and Lomb Spectronic 20 spectrophotometer. The wave lengths used were 535 mμ for neutral red and 420 mμ for thioflavine T. It was verified that $\lambda_{\max}$ of the base form did not shift with solvent composition within the limits of resolution of the instrument. Solution compositions were adjusted so that absorbance values were between 0.100 and 0.450 unit.

Volumes of standard solutions were measured from microburets at 25° into 50-ml. volumetric flasks. The indicator color ratio *R* (and its reciprocal) was calculated from eq. 1 in which C_B is the real concentration of the base form and C_T is the total concentration of the dye added. Since the value of C_T was in

$$R = \frac{C_B}{C_T - C_B} \tag{1}$$

the range of 10^{-5} to 10^{-6} *M* and the stoichiometric concentration of the added perchloric acid was varied between 10^{-3} and 10^{-4} *M*, all calculations involving C_{HClO_4} required the application of the correction noted by Hummelstedt and Hume[5] in eq. 2. Indica-

$$C_{HClO_4} = [HClO_4]_{added} - \Sigma[IH^+] \tag{2}$$

tor constants were computed as reported earlier[8] from a minimum of five different C_{HClO_4} values on each solvent composition. Quadruplicate measurements were made at each acidity and for each salt concentration.

Results

The spectrophotometric method developed by Kolthoff and Bruckenstein[4] for the study of acid–base equilibria in glacial acetic acid includes a suitable criterion for distinguishing between strong and weak acids in media of low dielectric constant. If the sum of the protonated species of an indicator base is denoted by $\Sigma[IH^+]$ and the base form is [I], a plot of $\Sigma[IH^+]/[I]\sqrt{C_{HX}}$ *vs.* $\sqrt{C_{HX}}$ yields a single straight line that is independent of the C_T (total) of the indicator base for HX acting as a strong acid. On the other hand,

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(1) A. Unni, L. Elias, and H. Schiff, *J. Phys. Chem.*, **67**, 1216 (1963); S. Blum and H. Schiff, *ibid.*, **67**, 1220 (1963); R. Kay, S. Blum, and H. Schiff, *ibid.*, **67**, 1223 (1963).

(2) H. VanLooy and L. Hammett, *J. Am. Chem. Soc.*, **81**, 3872 (1959).

(3) C. A. Streuli, *Anal. Chem.*, **31**, 1652 (1959); **32**, 985 (1960).

(4) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956); **79**, 1 (1957).

(5) L. Hummelstedt and D. Hume, *J. Am. Chem. Soc.*, **83**, 1564 (1961).

(6) R. Larson and R. Iwamoto, *Inorg. Chem.*, **1**, 316 (1962).

(7) O. Kolling and T. Stevens, *Anal. Chem.*, **34**, 1653 (1962).

(8) O. Kolling and M. Smith, *ibid.*, **31**, 1876 (1959).

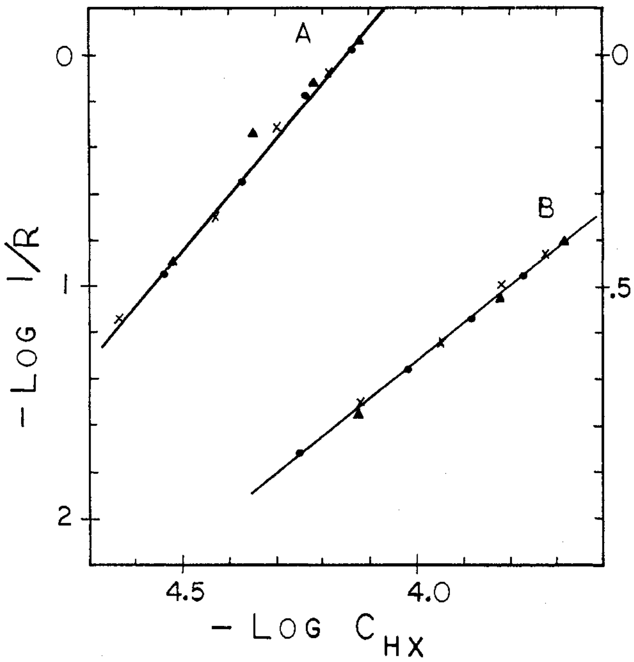

Figure 1.—The reaction of perchloric acid (HX) with the indicator bases in the binary solvent having a dielectric constant of 14.8 at 25°. The total concentration of base was varied as follows: curve A (ordinate 0.0–0.5), thioflavine T, ● = 4.00 × 10^{-5}, × = 6.00 × 10^{-5}, and ▲ = 3.00 × 10^{-5} *M;* curve B (ordinate 0–2.0), neutral red, × = 6.0 × 10^{-6}, ● = 1.0 × 10^{-5}, and ▲ = 1.40 × 10^{-5} *M*. The concentration of $NaClO_4$ was 4 × 10^{-3} *M*.

if HX is weak, a family of straight lines will be obtained upon varying C_T. Similarly, the plot of log $\Sigma[IH^+]/[I]$ *vs.* log C_{HX} will be linear and independent of the total indicator concentration for a strong acid and will give a series of parallel lines for a weak acid with changes in C_T. Graphs of the log–log type for strong acids form the basis for empirical acidity functions in acetic acid.[9]

Hummelstedt and Hume[5] applied the Kolthoff–Bruckenstein method to acid–indicator base reactions in a few aprotic hydrocarbon solvents and found that the above criteria gave nonlinear plots in several cases, although a family of curves was obtained for weak acids. They concluded that the method is not quantitatively valid in nonaqueous media other than acetic acid nor in the one binary solvent composed of *o*-dichlorobenzene and acetonitrile. The dielectric constant of the latter mixture was about 15.

Initially, we tested the suitability of the Kolthoff–Bruckenstein method for the perchloric acid–indicator base equilibrium in a single acetic acid–nitromethane solvent mixture, having a nitromethane mole fraction of 0.209 and a dielectric constant of 14.8 at 25°. In Figure 1 the logarithm $1/R$ *vs.* the logarithm C_{HClO_4} is linear for each indicator base and independent of C_T, thereby demonstrating that perchloric acid functions as a strong acid in the presence of nitromethane. The related graphs of $1/R\sqrt{C_{HClO_4}}$ *vs.* $\sqrt{C_{HClO_4}}$ were made, and single linear plots were obtained for each dye; however, these graphs are not included here. The slopes of the lines in Figure 1 are 1.15 ± 0.07 for thioflavine T and 1.57 ± 0.05 for neutral red. The values greater than unity show that higher ionic aggregates than ion pairs are present in appreciable quantities at very low indicator–perchlorate concentrations[4] and that more extensive association into higher ionic aggregates occurs for perchlorate salts derived from weak bases than for those derived from stronger bases in nitromethane.

The indicator perchlorate formation constant for each base was determined as a function of the composition of the binary solvent, and these results are summarized in Table I. The K_f values in pure acetic acid were redetermined with sodium acetate as the reference base, since the earlier experimental expedient[10] using a saturated potassium perchlorate solution could not be continued in the binary solvent. To maintain a constant electrolyte composition, a fixed concentration of 3.98 × 10^{-3} *M* sodium perchlorate was substituted. An increase in the apparent basicity of the indicator is observed as the mole fraction of nitromethane increases from 0.0 to about 0.2; however, the magnitude of the increase is dependent upon the dye and is greater for the stronger base. Beyond a mole fraction of 0.2, there is a small, though real, decrease in the indicator constant with increasing nitromethane content.

TABLE I

EFFECT OF SOLVENT COMPOSITION UPON THE INDICATOR CONSTANT

Mole fraction (X_2) of CH_3NO_2	D^a	Indicator perchlorate formation constant (pK_f)	
		Neutral red[b]	Thioflavine T[c]
0.000	6.2	−2.68 ± 0.04	−4.04 ± 0.07
0.011	7.3	−2.72 ± 0.11	−4.14 ± 0.06
0.021	8.0	−2.74 ± 0.06	−4.27 ± 0.08
0.063	9.9	−2.78 ± 0.03	...
0.106	11.4	−2.73 ± 0.02	−4.36 ± 0.04
0.209	14.8	−2.70 ± 0.10	−4.45 ± 0.07
0.313	17.7	−2.70 ± 0.03	−4.43 ± 0.06
0.414	20.1	−2.69 ± 0.02	−4.42 ± 0.11
0.515	22.3	−2.65 ± 0.02	−4.40 ± 0.04
0.614	24.8	−2.60 ± 0.03	−4.40 ± 0.04

[a] Dielectric constant values listed are those published separately in ref. 12. [b] Indicator concentration, C_T, was 1.00 × 10^{-5} *M*. [c] Indicator concentration, C_T, was 2.00 × 10^{-5} *M*.

Although the Fuoss–Onsager theory describing solvent influences upon strong electrolytes has been shown to be inexact in some two-component solvents of low dielectric constant,[11] the plot of the logarithm of the association constant of the electrolyte *vs.* the reciprocal of the dielectric constant of the medium is helpful in detecting specific solvent effects upon ion pair and multiple ion association. In the acetic acid–acetic anhydride solvent system it was found that a simple ion-pair equilibrium model predicts that the indicator constant will be a linear function of $1/D$ in the absence of competing salt–solvent and solvent–solvent interactions.[12] The corresponding graphs (not included

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(9) S. Bruckenstein, *J. Am. Chem. Soc.*, **82**, 307 (1960); O. W. Kolling, *J. Chem. Educ.*, **35**, 452 (1958).

(10) O. Kolling and T. Stevens, *Anal. Chem.*, **33**, 1384 (1961).

(11) J. B. Hyne, *J. Am. Chem. Soc.*, **85**, 304 (1963); H. Bodenseh and J. Ramsey, *J. Phys. Chem.*, **67**, 140 (1963).

(12) O. Kolling, K. O'Hara, and T. Stevens, *Trans. Kans. Acad. Sci.*, **66**, 435 (1963).

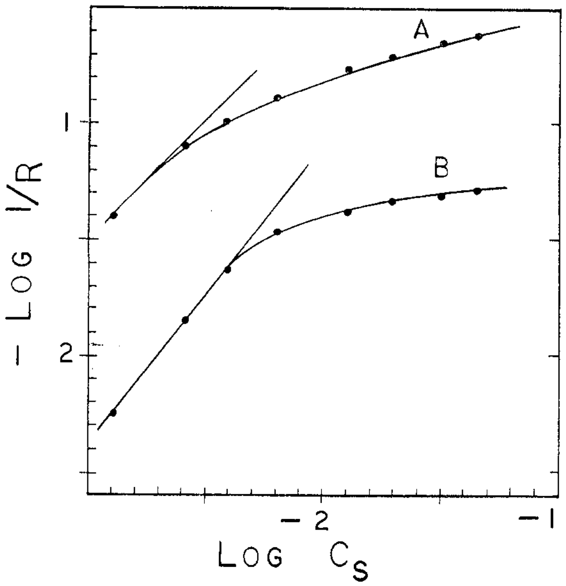

Figure 2.—The effect of the total concentration of sodium perchlorate upon the indicator color ratio in the binary solvent having a dielectric constant of 14.8 at 25°. Curve A is thioflavine T and curve B is neutral red.

Table II

Influence of Sodium Perchlorate upon the Indicator in the Binary Solvent Having X_2 of 0.21 in Nitromethane[a]

Molarity of $NaClO_4$ (C_S)	Color ratio[b] 1/R for— Neutral red	Thioflavine T
0.00129	0.00571	0.0396
0.00258	0.0140	0.0798
0.00387	0.0232	0.1010
0.00645	0.0342	0.1286
0.0129	0.0403	0.1730
0.0194	0.0462	0.192
0.0322	0.0462	0.224
0.0452	0.0524	0.241

[a] The corresponding dielectric constant is 14.8 at 25°. [b] C_T for each dye was 1.00 × 10^{-5} M, and no $HClO_4$ was added.

here) for the data in Table I are nonlinear and exhibit a maximum.

Absorbance measurements were made on a series of solutions in which the C_T of the indicator was constant and the concentration of the sodium perchlorate was varied. The solvent composition was the same as that used for the results in Figure 1. The data recorded in Table II were used to construct the curves in Figure 2. In pure acetic acid the same plot is linear and has a slope of 0.5 for low concentrations of salt.[4,13] For the acetic acid–nitromethane solvent in Figure 2, the log 1/R *vs.* log C_S plot approaches linearity and a limiting slope of unity within the salt concentration (C_S) range from 0.0 to 0.004 M. The actual slopes are 1.06 for thioflavine T and 1.15 for neutral red, indicating that the reaction between the indicator base and the salt has only approximately 1:1 stoichiometry. The lower slope for thioflavine T confirms the results of Figure 1 that the stronger indicator base perchlorate is less extensively associated into higher ionic aggregates than is the perchlorate of the weaker base. At contrations greater than 0.004 M sodium perchlorate the influence of the added salt upon the indicator base equilibrium is diminished by self-association of the salt into multiple ion aggregates.

Discussion

Any set of concomitant chemical equilibria that might be formulated from the above results must be compatible with the following observations on pure nitromethane made by other investigators.

(1) The electrical conductances of quaternary ammonium chlorides and bromides indicate that these salts are strong electrolytes and that the salts are largely unassociated in nitromethane.[1] The chlorides appear to be more associated than bromides as a result of solvation of the anion through weak ion–dipole interactions.

(2) Nitromethane may be involved in solvent–solute interactions with coordination complexes. Alterations in the absorption spectrum of cobalt(II) chloride were assigned to a disolvated species.[14] However, the polarographic and spectrophotometric study of aquo–copper(II) complexes by Larson and Iwamoto[6] demonstrated that trace amounts of water will hydrate the metallic ion preferentially. The large diffusion coefficient of iron(III) chloride in nitromethane seems to reflect a weak interaction with the solvent.[15]

(3) For proton-transfer reactions between inorganic acids and nitrogen bases, nitromethane is a nonleveling, very weakly acidic, solvent.[3] In the spectrophotometric study of VanLooy and Hammett[2] the reaction of nitroaniline-type indicators with a monoprotic acid consumed 2 equivalents of acid, and with a diprotic acid 3 equivalents of acid per mole of base is required.

(4) The resonance structures of the nitro group contain a formal charge separation (positive nitrogen and negative oxygen), making nitromethane an electron-attracting molecule.[16] The proton shift from the methyl group to an oxygen atom to give the *aci* form tends to enhance the acidic character of nitromethane, although in its solvent function it would be classified as a soft (class b) Lewis acid.[17]

Although the macro dielectric constant for the acetic acid–nitromethane solvent system shows a systematic increase with increasing content of the more polar component,[12] it is clear that the perchloric acid–weak base reaction cannot be treated exclusively as a change of electrolyte association with a change in dielectric constant. For the solvent system itself the region of greatest increase in the total polarization as a function of mole fraction occurs between 0.0 and 0.35 in nitromethane.[12] The solvent composition of 0.209 (D = 14.8) used in applying the Kolthoff–Bruckenstein method here is well within the changing polarization region. Since the results from Figure 1 indicate that the major increase in base strength of the indicator at D = 14.8 involves ion pair and multiple ion disso-

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(14) S. Buffagni and T. Dunn, *J. Chem. Soc.*, 5105 (1961).

(15) J. Voorhies and E. Schurdak, *Anal. Chem.*, **34**, 939 (1962).

(16) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 128.

(17) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

ciation, eq. 3 and 4 are the most probable processes for the lower nitromethane mole fractions. As the

$$\begin{array}{l}\mathrm{I(HOAc) + HClO_4 \rightleftharpoons IH^+ClO_4^- + HOAc}\\ \hspace{9em}\upharpoonleft\!\downharpoonright \hspace{6em}(3)\\ \hspace{8em}\mathrm{IH^+ + ClO_4^-}\end{array}$$

$$\begin{array}{l}\mathrm{I(CH_3NO_2) + HClO_4 \rightleftharpoons IH^+ClO_4^- + CH_3NO_2}\\ \hspace{10em}\upharpoonleft\!\downharpoonright \hspace{6em}(4)\\ \hspace{9em}\mathrm{IH^+ + ClO_4^-}\end{array}$$

activity of the HOAc decreases with increasing $\mathrm{CH_3NO_2}$, the competitive solvate in eq. 4 will become more significant even though acetic acid is a stronger acid than nitromethane. Since proton transfer to each of the solvated forms of the base gives the same acidic species, one would expect an increase in D to shift these equilibria toward the right in the same manner as occurs in acetic acid–acetic anhydride.[12] However, the results in Table I indicate this is not true for the higher mole fraction range in nitromethane.

The effect of the salt upon the indicator color ratio in pure acetic acid has been described by Higuchi, Feldman, and Rehm[18] as an anion exchange between the salt and the solvated base form of the indicator. However, the limiting slope of unity in the presence of nitromethane (Figure 2) instead of the slope of 0.5 found in pure acetic acid[13] results from the appearance of invalid approximations when the same mechanism is applied to the binary solvent of higher dielectric constant. The acetolysis of the salt in the presence of the indicator base (for simplicity written as the unsolvated base) may be represented by eq. 5a, 5b, and 5c. The proportionality between $1/R$ and $\sqrt{C_{\mathrm{NaClO_4}}}$

$$\mathrm{I + HOAc + Na^+ClO_4^- \rightleftharpoons IH^+ClO_4^- + NaOAc} \qquad (5a)$$

$$\mathrm{IH^+ClO_4^- + CH_3NO_2 \rightleftharpoons IH^+ClO_4^-\cdot CH_3NO_2 \rightleftharpoons IH^+ + CH_3NO_2\cdot ClO_4^-} \qquad (5b)$$

$$\mathrm{Na^+ClO_4^- + CH_3NO_2 \rightleftharpoons Na^+ClO_4^-\cdot CH_3NO_2 \rightleftharpoons Na^+ + CH_3NO_2\cdot ClO_4^-} \qquad (5c)$$

was obtained from the assumptions that the indicator perchlorate ion pair (and multiple ion aggregate) dissociations can be ignored in acetic acid and that the concentration of NaOAc equals that of the dissociated $\mathrm{HClO_4}$. For the binary solvent, the only approximate relationship that is suitable for very low concentrations of sodium perchlorate is eq. 6, obtained from eq. 5a, in which the proportionality between $1/R$ and $C_{\mathrm{NaClO_4}}$

$$\frac{[\mathrm{IH^+ClO_4^-}]}{[\mathrm{I}]} = C_{\mathrm{NaClO_4}}K_{\mathrm{eq}}\frac{[\mathrm{HOAc}]}{[\mathrm{NaOAc}]} \qquad (6)$$

is a lower limiting condition. As the sodium perchlorate concentration increases, the fraction of the total $C_{\mathrm{NaClO_4}}$ available for acetolysis becomes smaller as self-association of the salt takes place in addition to solvation of sodium perchlorate in eq. 5c. The curves in Figure 2 are consistent with these trends and indicate that eq. 5a proceeds more extensively to the right for the more basic indicator.

Even though the quantitative validity of the Kolthoff–Bruckenstein method may be questionable when applied to proton exchange between a weak acid and weak base in a binary solvent of low dielectric constant,[5] the experimental distinction between strong and weak protonic acids can be made in such solvent systems. Semiquantitative evidence for ion pair and multiple ion aggregates can be deduced from the application of graphical parts of the Kolthoff–Bruckenstein method to a protonic–aprotic solvent pair in the dielectric constant range from 6.2 to 24.8 at 25°.

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The Induction Period of the Chloride-Catalyzed Decomposition of Ammonium Nitrate

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A novel procedure of flushing with inert gas at reaction temperature to establish a zero time enables accurate measurements of induction periods to be made in ammonium nitrate melts containing chloride. The resulting data together with pH measurements are interpreted to indicate that the mechanism of the induction period consists of an acid-autocatalyzed adjustment of the melt acidity from one steady-state level to another. The data also support the mechanism previously published for the chloride-catalyzed thermal decomposition of ammonium nitrate.

Introduction

A detailed mechanism[1] proposed for the chloride-catalyzed thermal decomposition of ammonium nitrate has recently received strong support[2] from mass spectral analyses of the product gases from the isotopically-labeled reagent. The published mechanism pertains

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[1] A. G. Keenan and B. Dimitriades, *J. Chem. Phys.*, **37**, 1583 (1962).

[2] C. I. Colvin, A. G. Keenan, and J. B. Hunt, *ibid.*, **38**, 3033 (1963).