U.D.C. 543.257.1; 547.173.2

Acid-Base Equilibria in Amphiprotic Solvents and Potentiometric Titration

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Modern ideas about acid-base equilibria in amphiprotic solvents (acetonitrile, dimethylformamide, ketones, and others) are discussed. Data are presented for the homoconjugation constants of phenol and benzoic acid derivatives in these solvents and the calculation of acid-base titration curves is described. The question of the solvent acidity scales and their relative positions on a unique acidity scale are discussed. Factors limiting the solvent acidity scale calculated from its autoprotolysis constant are considered. Data are presented for the measured relative (practical) acidity scales for non-aqueous solvents and their mixtures in potentiometric titration. The optimal conditions chosen for acid-base titration are justified. The bibliography includes 180 references.

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1. INTRODUCTION

During recent years considerable advances have been achieved in the physical and analytical chemistry of non-aqueous solutions[1-17]. This has assisted a quantitative assessment of the effect of the properties of the solvent on those of the solute and a further development of the theory of acid — base potentiometric titration in non-aqueous solutions.

The study of acid — base interaction in amphiprotic solvents with weak acid and basic properties showed that the overall scheme of equilibria in electrolyte solutions (acids, bases, and salts) includes a large number of intermediate stages. Therefore a quantitative interpretation of these interactions is very much more complicated than in an aqueous medium or in solvents with properties similar to those of water (lower alcohols, glycols). Progress in this field of science involved measurements by different methods (spectrophotometric, conductimetric, and potentiometric) not only of the dissociation constants of acids and bases in amphiprotic solvents but also of equilibrium constants characterising individual stages of the acid — base interaction. The effect of water and other hydrogen bond donors and acceptors on the conditions governing acid — base interactions in amphiprotic solvents has been characterised quantitatively. The equations derived by Kolthoff make it possible to calculate the pH of buffer solutions and also potentiometric titration curves in solvents such as acetonitrile, dimethylformamide (DMF), and dimethyl sulphoxide.

Since acid — base interaction in any solvent is due primarily to the acid and basic properties of the solvent itself, it is necessary to consider the question of solvent acidity scales. The studies in this field have yielded many new data for autoprotolysis constants and the unique null proton activity coefficients which can be used to construct a unique solvent acidity scale. Factors limiting solvent acidity scales merit special attention, since under real conditions solvents usually contain admixtures of water and other solvents which distort their acid — base properties. This necessitates the study of the physicochemical properties of mixed solvents.

The present review considers the latest data on acid — base interaction in amphiprotic solvents and solvent acidity scales. The large volume of information in this field necessitates continual review and critical assessment of the published work.

In conclusion the choice of the optimal conditions for potentiometric acid — base titration is justified. New studies on the theory and practice of potentiometric acid — base titration have shown that the potentialities of this method are far from being exhausted[18].

2. ACID — BASE EQUILIBRIA AND CALCULATION OF TITRATION CURVES

When an acid HA interacts with a base B in a protolytic solvent SH, a number of reactions take place; the main processes are as follows[8,19-21]:

intrinsic ionisation of the solvent:

$$2SH \rightleftarrows SH_2^+ + S^- ; \quad (1)$$

interaction of the acid with the solvent:

$$HA + SH \rightleftarrows HS \cdots HA \rightleftarrows SH_2^+ \cdot A^- \rightleftarrows SH_2^+ + A^- ; \quad (2)$$

interaction of the base with the solvent:

$$B + SH \rightleftarrows B \cdots SH \rightleftarrows BH^+ \cdot S^- \rightleftarrows BH^+ + S^- ; \quad (3)$$

interaction of the acid with the base:

$$HA + B \rightleftarrows BH^+ \cdot A^- \rightleftarrows BH^+ + A^- . \quad (4)$$

Depending on the properties of the solvent, the acid and the base, a definite relation is established between these equilibria.

When an acid HA is titrated in a solvent SH with a standard solution of a base B, reaction (4) predominates[19]. However, there is the possibility of a simultaneous side reaction (3) in which the solvent interacts as an acid with the titrant. The extent of reaction (4) depends on the relative acid properties of the acid HA and the solvent SH. The stronger the acid HA and the weaker the acid SH, the higher the extent of reaction (4) and the interaction of the HA acid being determined with the titrant B is quantitative. The weaker the acid HA and the stronger the acid SH the less complete is reaction (4).

When a base B is titrated in a solvent SH with a standard solution of an acid HA, the main reaction (4) is accompanied by a side reaction (2). The extent of reaction (4) depends on the relative basic properties of the

base B being determined and the solvent SH. The more basic the properties of the solvent SH and the weaker those of B the less complete is reaction (4) because the side reaction (2) occurs to a considerable degree.

Since in aqueous solutions salts are fully dissociated and strong acid and base solutions may be employed as titrants, for the calculation of titration curves in water it is necessary to know the concentration of the acid HA or the base B being titrated, their dissociation constants K_A or K_B, and the autoprotolysis constant of water K_S.[22,23]

Calculation of acid — base equilibria in water-like solvents such as ethanol and methanol resembles the calculation of titration curves in water, since the formation of ion pairs takes place to only a slight extent and salts behave as strong electrolytes. Compared with water, the activity coefficients in these solvents are appreciably reduced (at the same ionic strength). The Debye — Hückel law may be employed at ionic strengths less than 0.01.[19]

In other alcohols, the dielectric constants of which are less than 24, calculations of titration curves are complicated, since ion pairs are formed. In this case it is also necessary to consider the dissociation constants of the titrant electrolyte and of the salt formed. Such calculations of titration curves have been performed by Kolthoff and Bruckenstein[19] for acetic acid. They studied the acid — base equilibria in acetic acid and measured the dissociation constants of electrolytes and the autoprotolysis constant of the solvent[22]. The titration curves calculated from these data agree satisfactorily with experiment. The lack of data for the dissociation constants of electrolytes and sometimes also the autoprotolysis constants of the solvents precludes the use of the Kolthoff equation for the calculation of titration curves in alcohols with low dielectric constants.

Table 1. The dissociation (K_{HA}) and homoconjugation ($K_{HA_2^-}$) constants of substituted phenols and benzoic acids in acetonitrile.

No.	Compound	pK_{HA}[28,30,32—34]	$\lg K_{HA_2^-}$[27,28,30,32,33]
1	*o*-Nitrophenol	22.0; 22.1; 21.2	2.0; 2.2
2	*p*-Nitrophenol	20.0 20.7; 21.0; 20.9	3.66; 3.15; 3.48; 3.67
3	*m*-Nitrophenol	22.6	3.48
4	2,4-Dinitrophenol	16.0	3.08
5	3,5-Dinitrophenol	20.5; 20.8; 20.9	4.64
6	2,6-Dinitrophenol	16.0; 15.34	2.08
7	4-Chloro-2,6-dinitrophenol	15.0	1.00
8	3-Chloro-4-nitrophenol	19.95	3.62
9	2,4,6-Trinitrophenol	11.0	0.30
10	*p*-Hydroxybenzoic acid	20.8	3.05
11	Benzoic acid	20.7	3.60
12	*m*-Bromobenzoic acid	19.5	3.75
13	3,4-Dichlorobenzoic acid	19.04	—
14	*m*-Nitrobenzoic acid	19.29	4.03
15	*p*-Nitrobenzoic acid	18.7	3.85
16	4-Chloro-3-nitrobenzoic acid	18.55	3.97
17	*o*-Nitrobenzoic acid	18.24	3.98
18	3,5-Dinitrobenzoic acid	16.9	4.0;4.22
19	2,4-Dinitrobenzoic acid	16.19	4.29

Considerable advances have been achieved recently in the study and interpretation of the acid — base interaction in aprotic dipolar solvents (acetonitrile, dimethyl sulphoxide, dimethylformamide, and others). In these solvents, the molecules of which are incapable of forming hydrogen bonds with the acid anions and base molecules, hydrogen-bonded complexes of the type HA_2^- and B_2H^+ are formed.

Much credit is due to Kolthoff, Coetzee, and coworkers[24-26] for their investigation of acid — base interactions in acetonitrile. The formation of complexes via hydrogen bonding between the acid (HA or BH^+) and the conjugate base (A^- or B) was called homoconjugation. Homoconjugation in acetonitrile has been studied comprehensively for the dissociation of phenol and benzoic acid derivatives, amines, and other organic bases[21,24-30].

The existence in solution of species of the type HA_2^- was predicted theoretically[31]. In the first place homoconjugation is determined by the relative basicities of the solvent molecule and the acid anion and the amphoteric properties of the solvent molecule. The capacity of the acid molecule HA for the formation of the complex HA_2^- increases as the proton-donating properties of the acid and the proton-accepting properties of its anions become more pronounced. The possibility of forming an intramolecular hydrogen bond lowers the capacity of the acid for interaction with the anion. Thus *ortho*-substituted phenols and benzoic acids are less involved in the homoconjugation process than the *meta*- and *para*-substituted derivatives. Homoconjugation does not occur when acid anions are additionally stabilised by intramolecular hydrogen bonding or by resonance (the anions of picric acid, 2,4-dinitrophenol, and 2,6-dihydroxybenzoic acid) and also as a result of steric blocking of the ionic group (2,6-di-t-butylphenol)[32,33].

Kolthoff[25] showed that, in the calculation of the concentration of hydrogen ions in a solution of a weak acid, it is necessary to begin with the overall constant $K_{2(HA)}$ which includes the acid dissociation constant K_{HA} and the homoconjugation constant $K_{HA_2^-}$:

$$HA \rightleftarrows H^+ + A^-; \quad K_{HA} = \frac{[H^+][A^-]\, f^2}{[HA]},$$

$$HA + A^- \rightleftarrows HA_2^-; \quad K_{HA_2^-} = \frac{[HA_2^-]}{[HA]\,[A^-]},$$

$$2HA \rightleftarrows H^+ + HA_2^-; \quad K_{2(HA)} = \frac{[H^+]\,[HA_2^-]\, f^2}{[HA]^2} = K_{HA}\, K_{HA_2^-},$$

The data in Table 1 show that the homoconjugation constants $K_{HA_2^-}$ for phenol and benzoic acid derivatives are usually fairly high. The acid strength of phenol and benzoic acid derivatives in acetonitrile increases on introduction of electron-accepting substituents. It was found that the relations between pK_{HA} and the σ constants for the substituents in phenols and benzoic acids are linear[32,33]. For benzoic acids, the relations between $\lg K_{HA_2^-}$ and σ are also linear[33]. Fig. 1 shows the variation of pK_{HA} and $\lg K_{HA_2^-}$ with the σ constants of the substituents in benzoic acids (lines I and II respectively). The different forms of these relations are due to the fact that the capacity for homoconjugation is less sensitive to changes in the structure of the compound.

To characterise quantitatively the proton-donating capacity of benzoic acid molecules and the proton-accepting capacity of their anions, Kolthoff and Chantooni[33] measured the heteroconjugation constants of acid molecules in relation to the base Cl^- and of acid anions in relation to the acid *p*-bromophenol (HR):

$$HA + Cl^- \rightleftarrows HACl^-; \quad K_{HACl^-} = \frac{[HACl^-]}{[HA]\,[Cl^-]},$$

$$HR + A^- \rightleftarrows HRA^-; \quad K_{HRA^-} = \frac{[HRA^-]}{[HR]\,[A^-]}.$$

Fig. 1 shows (lines III and IV) that the proton-donating capacity of the molecules increases and the proton-accepting capacity of the corresponding anions falls with increase of the σ constants of the substituents. The overall effect of these changes due to the σ constants is reflected in the relation between $\lg K_{HA_2^-}$ and $\Sigma\sigma$ (line II). Similar relations have been found for phenol derivatives[32].

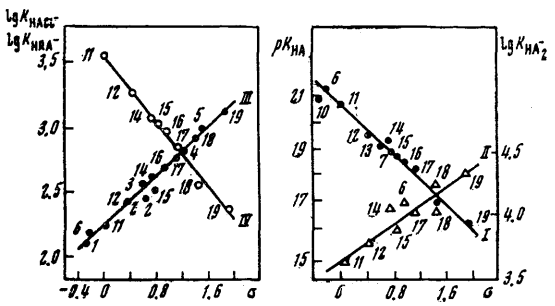


Figure 1. Variation of pK_{HA} (line I), $\lg K_{HA_2^-}$ (line II), $\lg K_{HACl^-}$ (line III), and $\lg K_{HRA^-}$ (line IV) for substituted benzoic acids with the σ constants of the substituents: 1) *p*-methoxy-; 2) *o*-iodo-; 3) *o*-chloro-; 4) 2,6-dichloro-; 5) 5-chloro-2-nitro-; 6) 3,4-dimethyl-; 7) 3,5-dichloro-; numbers 10—19 correspond to the ordinal numbers in Table 1.

It has been established that homoconjugation has a significant influence on the shape of the titration curves of acids and bases in acetonitrile. Kolthoff[25] derived an equation relating the activity of hydrogen ions in a solution of a weak acid and its salt, the acid dissociation and homoconjugation constants, and the analytical concentrations of the acid (C_A) and the salt (C_S):

$$a_{H^+}^2 f^2 C_s - a_{H^+} f K_{HA}\{(C_s + C_A) + K_{HA_2^-}(C_s - C_A)^2\} + K_{HA}^2 C_A = 0. \quad (5)$$

In the derivation of Eqn. (5), it was assumed that (1) the salt R_4NA formed in the interaction between the acid HA and the base R_4NOH is fully dissociated, (2) the salt R_4NHA_2 is also a strong electrolyte, and (3) the concentration of hydrogen ions in solution is much lower than the concentration of the salt ($C_{H^+} \ll C_S$). Eqn. (5) is applicable only to a thoroughly purified solvent free from impurities capable of behaving as hydrogen bond donors or acceptors (water, methanol).

Examination of Eqn. (5) shows that, at the instant of half-neutralisation, $a_{H^+} = K_{HA}/f$, i.e. the pH of the solution is determined by the pK for the dissociation of the acid. The shape of the titration curve in the buffer region is determined by the product $K_{HA_2^-}(C_S + C_A)$ or $K_{HA_2^-}C_A^0$, where C_A^0 is the initial analytical concentration of the acid titrated. The higher this value the higher the slope of the buffer section of the titration curve, the smaller the pH jump at the end of the titration, and the less satisfactory the conditions for the differential titration of a mixture of acids[35].

Calculation of the pH for the buffer section of the titration curve by Eqn. (5) shows that, when $K_{HA_2^-}C_A^0 \geqslant 10^2$, an inflection is observed in the titration curve at the half-neutralisation point[25]. Since $K_{HA_2^-}$ for acetonitrile is of the order of $10^3 - 10^4$ (Table 1), the shape of the titration curves is hardly distorted for $C_A^0 \leqslant 10^{-3}$. In the absence of homoconjugation, the pH in the course of titration from 1% to 99% neutralisation increases by 4 units. In the presence of homoconjugation the pH change is $\Delta pH = -\lg[10^{-4}/(K_{HA_2^-}C_A^0)^2]$. Thus, when $K_{HA_2^-}C_A^0 = 10^3$, ΔpH is as much as 10 units.

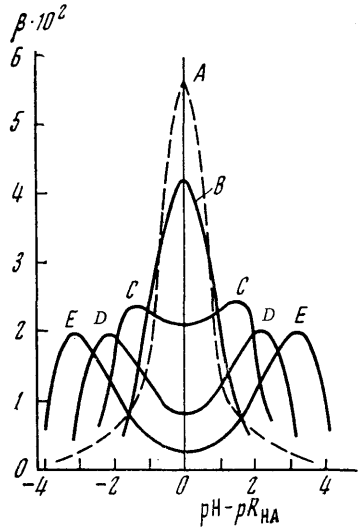


Figure 2. Dependence of the buffer capacity β on the pH of a mixed solution of HA and $(C_2H_5)_4NA$: *A*) dissociation without homoconjugation; *B*) $K_{HA_2^-}C_0 = 1$; *C*) $K_{HA_2^-}C_0 = 10$; *D*) $K_{HA_2^-}C_0 = 100$; *E*) $K_{HA_2^-}C_0 = 1000$.

Kolthoff and Chantooni[25] studied the buffer capacity of solutions of acids and their tetraethylammonium salts as a function of $K_{HA_2^-}C_A^0$. The authors derived from Eqn. (5) an expression for a quantitative characteristic of the buffer capacity of the solution (β):

$$\beta = -2.303\left[\frac{K_{HA}\,K_{HA_2^-}(C_A^0 - 2C_s)^2 + K_{HA}\,C_A^0 - 2C_s[H^+]}{[H^+] + 4K_{HA}\,K_{HA_2^-}(C_A^0 - 2C_s) - K_{HA}^2/[H^+]}\right], \quad (6)$$

which is applicable to the calculation of β almost over the entire section of the neutralisation curve corresponding to the buffer region. Fig. 2 presents relations between the buffer capacity β and the pH of the solution in mixtures of HA and $(C_2H_5)_4NA$ for different values of $K_{HA_2^-}C_A^0$. Calculation of the buffer capacity by Eqn. (6) at the instant of half-neutralisation when $K_{HA_2^-}C_0 \gg 1$ leads to the expression

$$\beta_{1/2} = -\frac{2.303}{2}\sqrt{\frac{C_0}{2K_{HA_2^-}}},$$

which shows that $\beta_{1/2}$ depends on the ratio $C_0/K_{HA_2^-}$ and is smaller the smaller the value of the ratio.

If homoconjugation takes place to a considerable extent and $K_{HA_2^-}C_0 \geq 10$, the buffer capacity has two maxima which are displaced with increase of $K_{HA_2^-}C_0$ towards more acid and alkaline regions, in accordance with $pH_{1/2}$.

Water and alcohols can behave as hydrogen bond donors and acceptors in aprotic dipolar solvents[32,33,36-41]. Kolthoff and Chantooni[37] made a quantitative study of the effect of these impurities on the acidity of solutions of mixtures of weak acids and their salts in acetonitrile. They showed that, in the presence of a hydrogen bond donor HR, it is necessary to take into account the following equilibria involving the formation of complexes:

$$A^- + HR \rightleftarrows AHR^-; \quad K_{AHR^-} = \frac{[AHR^-]}{[A^-][HR]},$$

$$A^- + 2HR \rightleftarrows A(HR)_2^-; \quad K_{A(HR)_2^-} = \frac{[A(HR)_2^-]}{[A^-][HR]^2}.$$

If the substance is amphoteric, then, owing to its acceptor properties in relation to the hydrogen bond, we have the equilibria (heteroconjugation)

$$HA + B \rightleftarrows AHB; \quad K_{BHA} = \frac{[BHA]}{[B][HA]},$$

$$HA + 2B \rightleftarrows AHB_2; \quad K_{B_2HA} = \frac{[B_2HA]}{[B]^2[HA]}.$$

An equation has been derived for the calculation of a_{H^+} in a buffer solution taking into account heteroconjugation. Apart from the assumptions made in the derivation of Eqn. (5), it was postulated that (1) K_{HA} and $K_{HA_2^-}$ do not change when HR and B are introduced into the solution, (2) HA_2^- is not involved in heteroconjugation, and (3) the $A^-...HR$ and $AH...B$ interactions take place without proton transfer owing to the extremely weak acid and basic properties of HR and B. The equation relating a_{H^+} to the analytical concentrations of the acid and the salt, the equilibrium concentrations of the hydrogen bond donor HR and acceptor B, the acid dissociation constant, and the homoconjugation and heteroconjugation constants is

$$a_{H^+}^2 f^2 W^2 C_s - a_{H^+} f K_{HA} V W \left[(C_s + C_A) + \frac{K_{HA_2^-}}{V W}(C_s - C_A)^2\right] + K_{HA}^2 V^2 C_s = 0, \quad (7)$$

where

$$V = 1 + K_{AHR^-}[HR] + K_{A(HR)_2^-}^2[HR]^2 + \ldots$$
$$W = 1 + K_{BHA}[B] + K_{B_2HA}^2[B]^2 + \ldots$$

The pH values of buffer solutions of methanesulphonic, picric, 3,5-dinitrobenzoic, salicylic, and benzoic acids and their tetraalkylammonium salts in acetonitrile in the presence of added water, calculated by Eqn. (7), agree well with measurements up to a water concentration of 0.7 M. Fig. 3 shows the effect of water and other hydrogen bond donors and acceptors on the pH of a benzoate buffer solution in the presence of an excess of the acid or salt. It demonstrates that, in the presence of excess salt in the buffer solution, the addition of a hydrogen bond acceptor (dimethyl sulphoxide) causes almost no change in the pH of the buffer solution, but the addition of hydrogen bond donors greatly reduces the pH. In the presence of an excess of acid in the buffer solution, water, methanol, and n-butyl alcohol hardly change the pH, while more powerful hydrogen bond donors and acceptors reduce or increase the pH respectively.

It follows from Eqn. (7) that, when the concentrations of the acid and salt are equal, the activity of hydrogen ions is defined by the relation

$$(a_{H^+})_{1/2} = \frac{V}{W} \cdot \frac{K_{HA}}{f}.$$

Consequently $pH_{1/2}$ is in this case smaller by $\lg(V/W)$ than the $pH_{1/2}$ for a buffer solution in which only a homoconjugation process takes place.

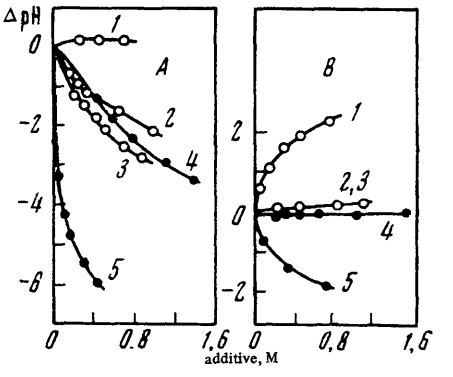


Figure 3. Effect of impurities on the pH of a benzoate buffer solution: *A*) $C_A = 3.6 \times 10^{-3}$ M, $C_S = 3.05 \times 10^{-2}$ M, pH_0 23.40; *B*) $C_A = 6.5 \times 10^{-2}$ M, $C_S = 2.18 \times 10^{-3}$ M, pH_0 16.80; 1) $(CH_3)_2SO$; 2($n\text{-}C_4H_9OH$; 3) CH_3OH; 4) H_2O; 5) $p\text{-}BrC_6H_4OH$;

It follows from the foregoing that heteroconjugation can have a significant influence on the shape of the titration curve in the buffer region[37,42]. According to Eqn. (7) the shape of the curve is determined by the factor[25,37]

$$\frac{C_0 K_{HA_2^-}}{V W}.$$

The study of the effect of methanol added to the solution during the titration is of particular practical interest for acid — base titration in acetonitrile, since standard solutions of quaternary ammonium hydroxides are usually prepared in a benzene — methanol mixture. Fig. 4 presents curves for the potentiometric titration of a 0.02 M solution of 3,5-dinitrobenzoic acid in acetonitrile with tetra-alkyl ammonium hydroxide calculated by Eqns. (5) and (7). The calculations were performed in the range from 0.5% to 99% neutralisation. Fig. 4 shows that methanol has a significant effect only after the point of half-neutralisation. In the presence of *p*-bromophenol, which shows a greater tendency towards heteroconjugation, the titration curve has the shape identical with that for a weak acid in water. The pK_A for 3,5-dinitrobenzoic acid is reduced by 3 units compared with the value in the pure solvent.

Homoconjugation and heteroconjugation in acetonitrile are less characteristic of bases than acids, since acetonitrile has a greater solvating capacity in relation to cations than in relation to anions. These processes have

almost no effect at a base concentration of 10^{-3} M. However, certain hydrogen-bonded complexes B_2H^+ are fairly stable, and their formation must be taken into account in a quantitative interpretation of acid — base equilibria in acetonitrile[12,24,26,29,43]. It has been shown[24] that nitrogenous bases form in acetonitrile not only 1 : 1 hydrogen-bonded complexes B_2H^+ but also more complicated species:

$$B + BH^+ \rightleftarrows BHB^+; \quad K_{BHB^+} = \frac{[BHB^+]}{[B][BH^+]},$$

$$B + BHB^+ \rightleftarrows B_2HB^+; \quad K_{B_2HB^+} = \frac{[B_2HB^+]}{[B][BHB^+]}.$$

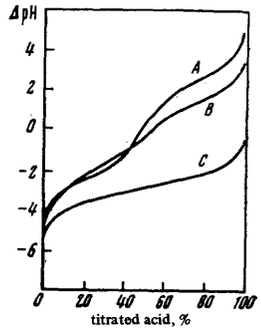


Figure 4. Curves for the potentiometric titration of 0.02 M solution of 3,5-dinitrobenzoic acid calculated by Eqn. (7): *A*) in the absence of impurities; *B*) with 0.1 M R_4NOH solution containing 10% of methanol; *C*) in the presence of 0.5 M solution of *p*-bromophenol.

Table 2. The negative exponents of the dissociation constants (pK_{BH^+}) of the conjugate acids of bases and the logarithms of the homoconjugation constants in acetonitrile[24,29].

Base	pK_{BH^+}	$\lg K_{BHB^+}$	$\lg K_{B_2HB^+}$
Ammonia	16.46	1.04	0.3
Methylamine	18.37	1.54	0.3
Dimethylamine	18.73	1.49	—0.3
Trimethylamine	17.61	0.78	—
Ethylamine	18.40	1.40	0.3
Diethylamine	18.75	0.3	—
Triethylamine	18.46	—	—
n-Propylamine	18.22	1.28	0.3
Tri-n-propylamine	18.10	—	—
n-Butylamine	18.26	1.42	0.4
Di-n-butylamine	18.31	—	—
Tri-n-butylamine	18.09	—	—
t-Butylamine	18.14	1.30	0
Isobutylamine	17.92	—	—
Di-isobutylamine	17.88	—	—
Tri-isobutylamine	18.04	—	—
Piperidine	18.92	1.42	—
Pyrrolidine	19.58	1.51	0.3
Pyridine	12.33	0.6	—
Aniline	10.56	—	—
p-Toluidine	11.25	—	—
Benzylamine	16.76	1.18	—
Monoethanolamine	17.53	1.38	0.18
Morpholine	16.61	1.00	—
1,3-Diphenylguanidine	17.90	—	—

Homoconjugation increases with the strength of the base and the number of hydrogen atoms at the nitrogen atom of the conjugate acid and depends on steric factors (Table 2).

It follows from the pK_{BH^+} data that in acetonitrile all protonated amines are weaker acids than in water owing to the low basicity of acetonitrile[24]. Although on average ΔpK_{BH^+} for bases in acetonitrile and water is 7.6 units, there is a fairly complex quantitative relation between $pK_{BH^+}(CH_3CN)$ and $pK_{BH^+}(H_2O)$. Thus in acetonitrile steric factors play a more important role than in water[29].

Table 2 shows that the formation constants of the complexes BHB^+ in acetonitrile are approximately 100 times smaller than those of the complexes HA_2^-. The tendency of aliphatic amines towards homoconjugation increases in the sequence $R_3N < R_2NH < RNH_2$. Aromatic amines, which are weaker bases, are less capable of homoconjugation than aliphatic amines. For diamines, the formation of BHB^+ decreases with increase of the number of methylene groups owing to the stabilisation of the cation by an intramolecular hydrogen bond[29].

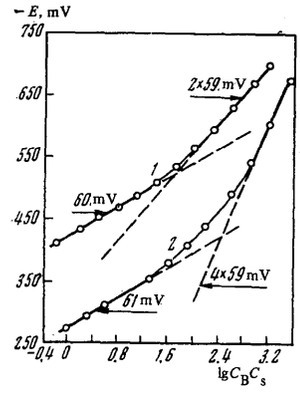


Figure 5. Variation of the glass electrode potential in buffer solutions: 1) piperidine and piperidinium picrate at constant $C_S = 5 \times 10^{-4}$ M; 2) hydrazine and hydrazinium perchlorate at constant $C_S = 5 \times 10^{-4}$ M.

Examination of the effect of homoconjugation on the shape of neutralisation curves for bases showed that, as for acids, the formation of hydrogen-bonded complexes leads to a decrease of the buffer capacity of the solution and a decrease of the pH near the end point of the titration[24]. The main effect of homoconjugation is shown at the beginning of the titration and before the equivalence point where either the base or the salt is present in a large excess. Fig. 5 illustrates the effect of homoconjugation on the change of the glass electrode potential in buffer solutions where the concentration of the salt was kept constant and that of the base was varied. In the absence of homoconjugation, the $E = f(\lg \frac{[B]}{[BH^+]})$ relation is linear with a slope of 59 mV (at 25°C) in accordance with the Nernst equation. When BHB^+ complexes are formed, the equilibrium concentrations [B] and $[BH^+]$ are not equal to the analytical concentrations, because

$$[B] = C_B - [BHB^+] \text{ и } [BH^+] = C_s - [BHB^+]$$

and the relation between E and $\lg(C_B/C_S)$ deviates from linearity. In the presence of a large excess of the base

the relation $E = f(\lg \frac{C_B}{C_{BH^+}})$ is again linear but with a slope of 118 mV (Fig. 5, curve 1). The formation of large complexes leads to a slope $n \times 59$ mV, where n is the number of base molecules bound to the protonated base, i.e. the complex may be represented by B_nHB^+. Fig. 5 (curve 2) illustrates this type of relation for a buffer solution consisting of hydrazine and its perchlorate. It shows that the effect of homoconjugation for bases in acetonitrile occurs for fairly high ratios $C_B/C_{BH^+} \geq 100$.

Table 3. The negative exponents of the dissociation constants (pK_{HA}) and the logarithms of the formation constants ($\lg K_{HA_2^-}$) of the complexes of certain acids in dimethyl sulphoxide[41].

Acid	pK_{HA}	$\lg K_{HA_2^-}$
Picric	—1.0	—
2,6-Dihydroxybenzoic	3.1	—
4-Chloro-2,6-dinitrophenol	3.5	—
2,6-Dinitrophenol	4.9	—
Salicylic	6.8	0.48
3,5-Dinitrobenzoic	7.4	0.36
2,6-Di-t-butyl-4-nitrophenol	7.6	—
3,5-Dinitrophenol	10.6	0.48
p-Nitrophenol	11.0	0.60
o-Nitrophenol	11.0	0.78
Benzoic	11.1	0.78
Acetic	12.6	0.48
5-5-Diethylbarbituric	13.0	—
Phenol	16.4	1.60

In the absence of homoconjugation or when the concentration of the titrated base is less than 10^{-3} M, the neutralisation curves for bases in acetonitrile resemble those in aqueous solution[26].

Table 4. The negative exponents of the acid dissociation constants (pK_{HA}) and the logarithms of the homoconjugation constants ($\lg K_{HA_2^-}$) in dimethylformamide[50].

Acid	pK_{HA}	$\lg K_{HA_2^-}$
Picric	1.4	—
Hydrochloric	3.2	2.2
2,6-Dihydroxybenzoic	3.56	—
4-Chloro-2,6-dinitrophenol	4.7	—
2,6-Dinitrophenol	5.9	—
2,4-Dinitrophenol	6.3	—
Salicylic	8.23	1.7
3,5-Dinitrobenzoic	8.9	3.2
p-Nitrobenzoic	10.6	2.6
3,5-Dinitrophenol	11.3	3.2
p-Nitrophenol	12.5	2.3
Benzoic	12.25	2.4
Acetic	13.4	2.6

Homoconjugation and heteroconjugation phenomena also are observed in other aprotic dipolar solvents such as dimethyl sulphoxide[44,45], dimethylformamide[46-50], sulpholane[51], and acetone[52].

Dimethyl sulphoxide is a more basic solvent than acetonitrile. Therefore dimethyl sulphoxide molecules enter into a reaction with the anion which competes with the homoconjugation process:

$$A^-...HA + SH \rightleftharpoons A^-...HS + HA.$$

As a result, phenols and benzoic acids show a smaller tendency towards the formation of HA complexes in dimethyl sulphoxide (Table 3).

Table 3 shows that the formation constants of the complexes HA_2^- in dimethyl sulphoxide are smaller approximately by a factor of 100 than in acetonitrile (Table 1). In consequence, the potentiometric titration curves in dimethyl sulphoxide have a more pronounced buffer region and a correspondingly sharper change of the pH at the end point of the titration.

Dimethylformamide is somewhat less basic than dimethyl sulphoxide and therefore homoconjugation of acids in this solvent takes place to a greater extent than in dimethyl sulphoxide but to a lesser extent than in acetonitrile[46-50]. The homoconjugation constants in dimethylformamide are approximately ten times smaller than in acetonitrile (Table 4).

The buffer regions on the titration curves of acids and bases in dimethylformamide and dimethyl sulphoxide can be calculated as in acetonitrile. Similar calculations cannot be made for cations because one cannot make the assumptions used in the derivation of Eqn. (5) for the pH in acetonitrile.

3. SOLVENT ACIDITY SCALES

Acid—base equilibria in any solvent are due primarily to the acid—base properties of the solvent itself. Therefore the question of acid—base interaction is closely related to the question of solvent acidity scales. The extent of acidity scale is determined by the autoprotolysis constant of the solvents and their relative positions on the pH scale are determined by the relative trans-solvation energies of the protons in the different solvents (see Izmailov[8], Chapter X, and Bates[53], Chapters VII and VIII).

Izmailov[54,55] proposed unique zero-concentration proton activity coefficients γ_{0H^+} which are determined by the change in the solvation energy of protons when they are transferred from an infinitely dilute non-aqueous solution to an infinitely dilute aqueous solution. The activity coefficient γ_{0H^+} enabled Izmailov[54,56] to establish a unique solvent acidity scale:

$$pA = pH_s - \lg \gamma_{0_{H^+}},$$

where pH_S assumes values ranging from 0 to pK_S for the solvent and $\lg \gamma_{0H^+}$ indicates the shift of the acid limit of the scale in the non-aqueous solvent relative to the acid limit of the scale in water.

A rigorous thermodynamic approach to the determination of the activity coefficients of individual ions is difficult to achieve, since the accuracy of the theoretical calculations of solvation energy is less than that of the differences between the solvation energies in different solvents; experimental methods do not yield an unambiguous answer in those cases where the diffusion potential is high. Therefore several methods have been proposed for the determination of $\lg \gamma_0$ for ions, each of which involves certain non-thermodynamic assumptions[14,53-64]. The problem of the estimation of the γ_0 for ions has engaged the attention of many investigators. They were called "degenerate activity coefficients" by Grunwald,

"medium effects" by Bates, "solvent activity coefficients" by Parker, and "partition coefficients" by Kolthoff.

Izmailov, Aleksandrov, and other investigators of the Kharkov school of physical chemistry have made a major contribution to the theory of unique zero-concentration ionic activity coefficients, in the first place those of hydrogen ions, and their experimental determination in practice[54-56,65-68]. Studies in recent years showed that interest in unique zero-concentration activity coefficients of protons has increased in connection with the further development of methods for the measurements of pH in non-aqueous solutions and the development of the theory of acid — base interaction[69-76]. However, there are few $\lg \gamma_{0H^+}$ data for solvents employed in acid — base titrations and they are contradictory[44,56,73,74].

On the basis of the pK_s and $\lg \gamma_{0H^+}$ data then available, Izmailov[56] included only five solvents in his unique acidity scale (pA). At the present time the unique acidity scale already includes thirteen solvents[77]. The solvent autoprotolysis constants have been determined by various methods[78-89]. A critical assessment of the pK_s values available in the literature for amphiprotic solvents has been made by the authors of the review[77]. Table 5 lists the pK_s and $\lg \gamma_{0H^+}$ values for certain solvents widely employed in analytical practice.

Table 5. The negative exponents of the autoprotolysis constants (pK_s) of certain solvents at 25°C and the values of $\lg \gamma_{0H^+}$.

Solvent	pK_s [77—85]	$\lg \gamma_{0H^+}$ [44,56,67]
Formic acid	6.2	10.0
Acetic acid	14.5	—
Ethylene glycol	15.6	—
Water	14.0	0
Methyl alcohol	16.7	3.1
Ethyl alcohol	19.5	3.9
Isopropyl alcohol	22.0	4.2
t-Butyl alcohol	26.8	—
Acetone	32.5	4.7
Ethyl methyl ketone	31.0	—
Acetonitrile	33.3	7.9
Dimethylformamide	29.4	—
Dimethyl sulphoxide	33.3	—1.5

Acidity in non-aqueous solvents is measured and acidity scales are established also on the basis of the H_0, H_-, and $R(H)$ functions[90-98]. Izmailov (see Ref. 8, Chapter X) showed that the H_0 and H_- functions cannot reflect the activity of hydrogen ions in a non-aqueous solution owing to the different effects of the medium on the activity coefficients of indicator ions and molecules. Other acidity functions (H_R, H_0, H_+, H_{2+}) proposed subsequently suffer from the same disadvantages[99,100].

Cells with transport are mainly used in potentiometric titration in non-aqueous solutions[1,2,4]. The glass electrode, the advantages of which are well known, is employed as the indicator electrode and the reference electrodes are calomel or silver|silver chloride half-cells. The behaviour of the glass electrode in non-aqueous and mixed solvents has been described in a number of studies[101-116]. It has been shown that in many non-aqueous media the glass electrode retains its response to hydrogen ions. However, the applicability of the glass electrode in non-aqueous solutions may be limited in highly acid and highly basic media. The use of reference electrodes in non-aqueous solutions has been described[117-122].

In cells with transport, there is a liquid junction between two solutions where a diffusion potential arises, which leads to an indeterminacy in the measurement of proton activities (see Izmailov[8], Chapter X, and Bates[53], Chapters VII and VIII). However, it has been suggested that the error due to the liquid junction in cells with transport is constant in a given solvent and depends little on the nature of the electrolyte and the activity of protons (see Bates[53], Chapter VIII). Experimental studies have confirmed this hypothesis[67,68,123,124].

A direct measurement of the diffusion potential E_j is impossible and its estimation is extremely difficult. E_j may be determined only when the proton activity coefficients are known (see Bates[53], Chapter VIII). However, since the $\lg \gamma_{0H^+}$ are contradictory, the values of E_j cannot always be estimated unambiguously either[60-62,67,69]. The values of E_j for measurements with an aqueous calomel electrode have been quoted in a number of studies for methyl, ethyl, and isopropyl alcohols, acetonitrile, dimethylformamide, and dimethyl sulphoxide and it has been shown that the E_j can reach several pH units[57,69,125-127]. There are data showing that when the aqueous potassium chloride solutions in the reference electrode is replaced by a methanol solution, E_j decreases[60,112]. When a liquid junction is formed between two aprotic dipolar solvents, E_j does not exceed 20 mV.[60]

The problem of the estimation of the E_j and $\lg \gamma_{0H^+}$ has been recently solved successfully with the aid of the quantity δ proposed by Bates (see Ref. 53, Chapter VIII and Ref. 124), which is defined as the difference

$$\delta = \bar{E}_j - \lg \gamma_{0H^+},$$

where $\bar{E}_j$ is the diffusion potential in pH units.

Measurements of δ in aqueous alcoholic media have shown that in mixed solvents δ is small up to 80 wt.% of the alcohol (see Izmailov[54], Chapter VIII). It is suggested that in this composition range there is a mutual cancellation of E_j and $\lg \gamma_{0H^+}$. A further increase of the content of alcohol in the mixture leads to a sharp increase of δ to 2 — 2.5 pH units. The values of δ have been measured for mixtures of water with alcohols, acetone, dioxan, dimethylformamide, dimethyl sulphoxide, and other solvents[67,68,128-130]. The variation of δ with mixture compositions is explained by changes in the structure and acid — base properties of the mixed solvent.

Together with the question of the extent of solvent acidity scales and their relative positions, the question relating to factors which limit the solvent acidity scale is very important for acid — base titration. The pH range corresponding to the theoretical pK_s solvent acidity scale calculated from the autoprotolysis constant can be by no means always fully employed in acid — base titration in the given solvent. The theoretical solvent acidity scale is limited by the influence of the following factors. In the first place the alkaline titrants employed are usually solutions of bases without the solvent lyate ions, since it is often impossible to obtain the latter. Many solvents have low dielectric constants and therefore acids and bases with strengths equal to those of the lyonium and lyate ions of the solvent cannot exist in them. The concentrations of the compounds titrated and of the titrants are as a rule 0.01 — 0.1 M, which also reduces the pH jump in the titration. Finally the employment of the entire solvent acidity scale in the titration is hindered

also by the loss of sensitivity of the indicator and particularly glass electrodes in highly acid or highly basic regions.

A particularly marked limitation of acidity scales for solvents with weak acid or basic properties is caused by the presence in them of admixtures of water, alcohols, glycols and other solvents with fairly pronounced acid or basic properties[131,132]. The available literature data for the autoprotolysis constants of mixed solvents show that the addition of the first portions of water to isopropyl alcohol, acetone or dimethyl sulphoxide leads to a sharp increase of the autoprotolysis constant and a corresponding contraction of the solvent acidity scale[96,97,114,133-135].

In a mixture of two protolytic solvents SH and MH there are four main inter-related equilibria which determine protolysis in the mixed solvent[132,136-141]:

$$SH + SH \rightleftarrows SH_2^+ + S^-, \quad (I)$$

$$MH + MH \rightleftarrows MH_2^+ + M^-, \quad (II)$$

$$MH + SH \rightleftarrows MH_2^+ + S^-, \quad (III)$$

$$SH + MH \rightleftarrows SH_2^+ + M^-. \quad (IV)$$

To a first approximation, the autoprotolysis constant for the mixed solvent can be regarded as the product of the equilibrium concentrations of the lyonium and lyate ions of the mixed solvent:

$$K_s = (C_{SH_2^+} + C_{MH_2^+})(C_{S^-} + C_{M^-}).$$

Depending on the acid and basic properties of the components of the mixed solvent and its composition, definite relations are established in each specific case between the activities of the individual ions in solution. If the acidities and basicities of the mixture components are similar, then protolysis in the mixed solvent is determined by all four equilibria. Only for mixture compositions close to those of the pure solvents does protolysis correspond mainly to the autoprotolysis of the pure solvents. Examples of mixtures of this kind are those of water and ethylene glycol.

When the acidity and basicity of the solvent MH are higher than those of the solvent SH, the autoprotolysis of SH may be neglected in the mixed solvent (acetone — water mixtures):

$$K_s = C_{MH_2^+} C_{M^-}.$$

For mixtures of two solvents one of which has more pronounced acid properties (SH) and the other more pronounced basic properties (MH), protolysis is determined mainly by equilibrium (III) (mixtures of water and amines):

$$K_s = C_{MH_2^+} C_{S^-}.$$

If the basicities of the solvents constituting the mixture are similar and the acidity of the solvent MH is higher than that of SH (dimethylformamide — water mixtures), the autoprotolysis constant of the mixed solvent may be represented by the following expression [equilibria (II) and (IV)]:

$$K_s = (C_{MH_2^+} + C_{SH_2^+})\, C_{M^-}.$$

If the acid properties of the mixture components are similar and the basic properties of the solvent MH are more pronounced than those of SH (water — methanol mixtures), the expression for the autoprotolysis constant of the mixed solvent is [equilibria (II) and (III)]:

$$K_s = C_{MH_2^+} (C_{M^-} + C_{S^-}).$$

The addition of a solvent MH with a basicity higher than that of the solvent SH leads to a decrease of the acid limit of the acidity scale for the mixed solvent owing to the reaction

$$SH_2^+ + MH \rightleftarrows MH_2^+ + SH.$$

If the acidity of the solvent MH is higher than that of SH, the addition of MH to SH leads to a decrease of the basic limit of the acidity scale for the mixed solvent; this involves the following reaction:

$$S^- + MH \rightleftarrows M^- + SH.$$

Fig. 6 presents as an example three cases of the decrease of the limits of the acidity scales for non-aqueous solvents with weak acid or basic properties in the presence of added water.

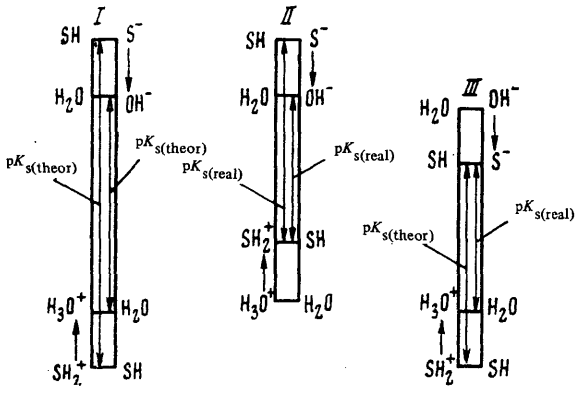


Figure 6. Effect of water on the acidity scales for non-aqueous solvents: I) acidity and basicity of water higher than the corresponding properties of the solvent; II) acidity of water higher and its basicity lower than the corresponding properties of the solvent; III) basicity of water higher and its acidity lower than the corresponding properties of the solvent.

In choosing the conditions for acid — base titration, it is necessary to know the effect of added solvents on each limit of the solvent acidity scale. Since, as stated above, the determination of individual ionic activities involves considerable difficulties, the determination of the variation of the acidity scale limits for mixed solvents on the basis of a rigorous thermodynamic approach is difficult to achieve. There are literature data for $\lg \gamma_{OH^+}$, which determine the variation of the acid limit of the acidity scale for mixtures of water with methyl, ethyl, and isopropyl alcohols and with acetone[57,67,68,74]. These results demonstrate that the addition of water leads to a decrease of the acid limit of the acidity scale for alcohols and acetone since these solvents are less basic than water. The data described above, referring to the acidity scales of non-aqueous solvents and their relative positions on the unique acidity scale, show that at present the physicochemical data necessary for the construction of practical (real) acidity scales for the majority of solvents and their mixtures, which might be used in potentiometric acid — base titration, are not available. It is therefore of interest to obtain practical solvent acidity scales taking into account all the factors which determine the titration conditions.

Real (empirical) solvent acidity scales were first obtained by van der Heijde and Dahmen[142,143]. However, these workers did not give a physicochemical interpretation of their acidity scales. Probably this is why van der Heijde and Dahmen's studies were not developed further in the following decade.

Later a simple and rapid method was proposed for the measurement of real acidity solvent scales, which were called relative acidity scales (E_S).[144] The method of measurement of the relative acidity scales was used successfully to investigate real acid base titration conditions[145-148]. The relative acidity scale is the range of values in millivolts (E_S) or in pH units (E'_S) which may be used in acid — base titration in the given solvent under specified conditions (titrant system, presence of other solvents, etc.). The limits of the E_S scale are measured as the half-neutralisation potentials of $HClO_4$ and R_4NOH solutions which are widely used as the strongest titrants in non-aqueous media[4]. The relation between the negative exponent of the autoprotolysis constant of the solvent and the extent of the relative acidity scale may be represented by the equation

$$pK_s \geqslant E'_s - \lg (a_{H^+}\, a_{OH^-}). \qquad (8)$$

The sign of equality refers to the case where K_S is the autoprotolysis constant of the solvent containing water and the "greater than" sign refers to the case where K_S is the autoprotolysis constant of the pure solvent. It follows from Eqn. (8) that the relative (real or practical) solvent acidity scale in terms of pH units is part of the pK_S acidity scale and depends on the system of titrants employed. Fig. 7 presents the relative acidity scales for water and non-aqueous solvents. Evidently the E_S scales for non-aqueous solvents have different lengths and occupy different positions relative to the acidity scale for water.

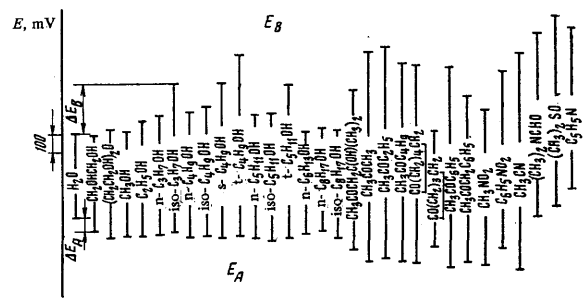


Figure 7. Relative acidity scales for certain solvents.

It has been shown that one of the main factors determining the position of the limits of the relative solvent acidity scale relative to the limits of the scale for water is the acid and basic properties of the solvent[149]. Comparison of the limits of the relative acidity scales with parameters characterising the basic and acid properties of solvents showed that, with decrease of the basic properties of the solvent, the acid limit E_A of the scale shift towards the region of higher proton activities, and with decrease of the acid properties of the solvent, there is a shift of the basic limit E_B of the scale towards the region of lower proton acitivities. Thus, the highest values of the acid limits of relative acidity scales obtain in ketones, acetonitrile, nitrobenzene, and nitromethane, which are least basic; the highest values of the basic limits of relative acidity scales are in ketones, acetonitrile, dimethylformamide, dimethyl sulphoxide, and pyridine, which are characterised by the smallest acidity.

The lengths of the E'_S and pK_S solvent acidity scales are compared in Fig. 8.[83] The values of E'_S and pK_S were taken from the literature[80,81,84,85,88,112,144,150-153]. With the exception of the points referring to acetonitrile and dimethyl sulphoxide, there is a linear relation between E'_S and pK_S. The points lying below the straight line drawn according to the equation

$$E'_s = pK_s + \lg (C_{HClO_4}\, C_{R_4NOH}) \qquad (9)$$

(C_{HClO_4} and C_{R_4NOH} are the $HClO_4$ and R_4NOH concentrations employed in the measurement of the limits of the E'_S scale) are readily explained by the incomplete dissociation of $HClO_4$ and R_4NOH in certain solvents and also by the presence of water and methanol impurities in the solvents, since the R_4NOH solutions were prepared in a benzene — methanol mixture and those of $HClO_4$ were obtained from 70% aqueous solution.

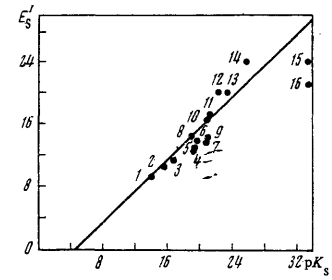


Figure 8. Comparison of the negative exponents of the autoprotolysis constants (pK_S) and the E'_S parameters of relative acidity scales: 1) water; 2) ethylene glycol; 3) methyl alcohol; 4) ethyl alcohol; 5) n-propyl alcohol; 6) n-butyl alcohol; 7) n-pentyl alcohol; 8) isobutyl alcohol; 9) isopentyl alcohol; 10) isopropyl alcohol; 11) s-butyl alcohol; 12) t-butyl alcohol; 13) dimethylformamide; 14) ethyl methyl ketone; 15) acetonitrile; 16) dimethyl sulphoxide.

Since the method of measurement of relative solvent acidity scales and Eqn. (9) yields values of pK_S which are lower than the true values, the points above the straight lines can only be due to incorrect autoprotolysis constants for a number of solvents (t-butyl alcohol, ethyl methyl ketone, dimethylformamide) in the literature. Consequently, comparison of the E'_S and pK_S solvent acidity scales yields information about the reliability of the experimental K_S for solvents, as shown by the authors of the review[83].

The relative positions of the E'_S and pK_S relative solvent acidity scales on Izmailov's pA unique acidity scale are compared in Fig. 9.[83] The filled regions correspond to those parts of the pK_S scale which for one reason or another cannot be used in titration. As already stated, one of such reasons is the incomplete dissociation of $HClO_4$ and R_4NOH in certain solvents. The filled regions can also reflect the

effect of the diffusion potential of the cell used to measure the limits of the E'_S scale.

In the measurement of the limits of the E'_S scale, R_4NOH solutions were prepared in a 1 : 5 benzene — methanol mixture and therefore the solvents investigated contained a certain amount of methanol and benzene and also water. Water and methanol have more pronounced acid or basic properties than many amphiprotic and aprotic dipolar solvents (ketones, acetonitrile, dimethyl sulphoxide, etc.). Therefore one of the factors restricting the limits of the acidity scales for solvents with weak acid or basic properties is of course the presence of water, methanol, and similar solvent impurities.

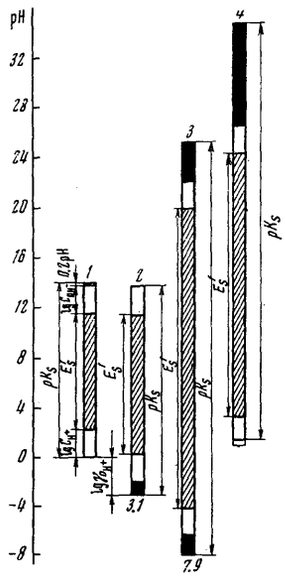


Figure 9. Comparison of the E'_S and pK_S acidity scales in terms of the pA unique acidity scale: 1) water; 2) methyl alcohol; 3) acetonitrile; 4) dimethyl sulphoxide.

The method of measurement of relative acidity scales proved to be effective not only in the study of the chemical-analytical properties of individual solvents but also in the study of the properties of their various mixtures widely used in titration[154-158]. The general laws governing the variation of the limits of the relative acidity scales for mixed solvents have been established. It has been shown that the length and position of the acidity scale for a mixed solvent depend mainly on the lengths and positions of the scales for the mixture components (Fig. 10). If the limits of the acidity scales for the individual solvents differ greatly, the limits of the acidity scale for the mixed solvent vary with composition non-additively. The most marked change in the limits of the acidity scale is observed following the addition of the initial portions of a second solvent with lower values of acidity scale limits. The variation of the limits of the E_S scales for mixed solvents can be explained by the variation of the acid and basic properties of the mixture in relation to those of the individual components, since the acid and basic properties of the mixed solvent vary non-additively with composition (see Izmailov[8], Chapter VII).

Measurements of relative acidity scales for mixtures of protolytic and aprotic solvents showed that the addition of 40 — 50% of the aprotic solvent has almost no influence on the limits of the acidity scale for the protolytic solvent[150]. The variation of the limits of the acidity scales for mixtures is not related to changes in the dielectric constant provided that the latter is not too low ($\epsilon > 10 - 15$).[156]

Comparison of the extents of the E_S scales and solvent polarities on the E_T scale reveals a definite relation between these quantities[151]. For protolytic solvents a decrease of polarity corresponds as a rule to an increase of the extent of the relative acidity scale. If one of the solvents has a higher acid limit and the other a higher basic limit of the E_S scale, then, on passing from solvent to solvent, the change in acid or basic properties may not correspond to the change in the polarity of the mixtures. Under these conditions, the curve relating the limit to mixture composition shows a minimum (mixtures of pyridine with water, methanol, and ethylene glycol and mixtures of nitromethane with alcohols) (Fig. 10).

Comparison of the extents of relative acidity scales for mixed solvents in terms of pH units with published negative exponents of the autoprotolysis constants (pK_S) showed that the variation of these quantities is the same. Consequently the variation of the extents of E'_S scales for mixed solvents reflects correctly the variation of the pK_S for the mixed solvents, as shown for a mixture of water and dimethyl sulphoxide (Fig. 11).

Comparison of the changes in the acid limits ΔE_A of E_S acidity scales for mixture of water with methyl, ethyl, and isopropyl alcohols and actone with the δ values[67,68,128,129] showed that the variation of ΔE_A for the mixtures parallels that of δ (Fig. 12). This confirms the conclusion that the position of the acid limit of the E_S scale on the unique acidity scale is determined mainly by the change in the

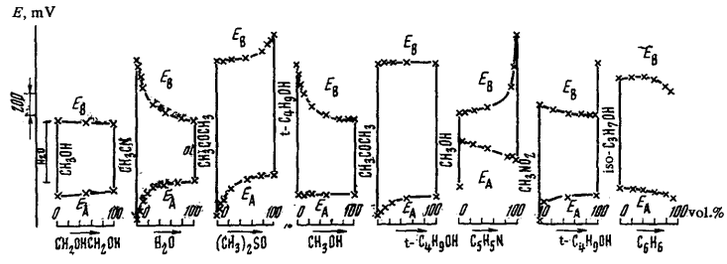


Figure 10. Relative acidity scales for mixed solvents corresponding to different component ratios.

basicity of the solvent and the diffusion potential of the cell used to measure the limits of the E_S scale.

The similarity in the variation of the limits of the E_S scales for mixed solvents made it possible to derive empirical equations for the calculation of the acid and basic limits of the acidity scales for mixtures as a function of mixture composition. With the aid of these equations, the limits and extents of the acidity scales were extrapolated and their values for pure solvents evaluated. This is particularly important for solvents with weak acid and basic properties[159]. On the basis of the E_S scales for pure solvents, it is possible to determine their pK_S values[77].

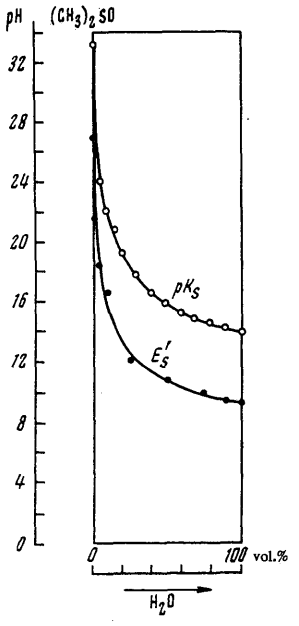


Figure 11. Comparison of the pK_S and E'_S acidity scales for a mixture of dimethyl sulphoxide and water.

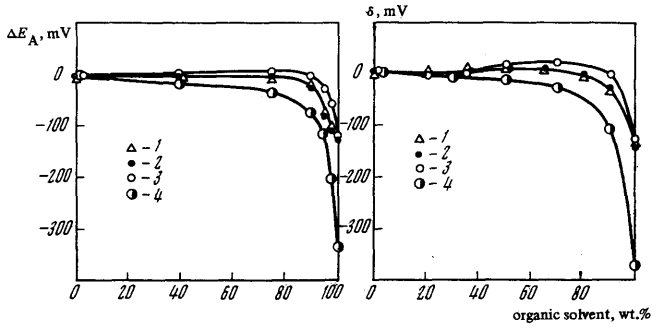


Figure 12. Comparison with δ of the differences ΔE_A between the acid limits of the acidity scales for water and its mixtures with different solvents: 1) methyl alcohol; 2) ethyl alcohol; 3) isopropyl alcohol; 4) actone.

It follows from the foregoing that study of the chemical-analytical properties of mixed solvents by measuring their relative acidity scales has made it possible (a) to establish the main factors determining the practical solvent acidity scale in potentiometric titration, (b) to establish the general characteristics of the variation of the limits of the acidity scales for mixed solvents, (c) to elucidate the role of water and similar added solvents (alcohols, glycols) in acid – base titration, and (d) to propose a simple method for the estimation of the autoprotolysis constants of solvents with insignificant acid or basic properties.

4. CHOICE OF OPTIMAL CONDITIONS FOR POTENTIOMETRIC ACID – BASE TITRATION

In connection with the extensive development of methods for acid – base titration, the problem of a soundly based choice of optimal titration conditions is becoming increasingly urgent. The scientific principles for the employment of non-aqueous solvents in acid – base titration have been developed by Izmailov (see Ref. 8, Chapter XI, and Refs. 160 and 161). Starting with the theory of titration errors developed by Roller, Izmailov specified the principal ways for the improvement of acid – base titration conditions. The choice of conditions for the titration of acids, bases, mixtures of acids, or mixtures of bases is made by comparing the solvent autoprotolysis constants K_S and the acid (K_A) or basic (K_B) dissociation constants. On the assumption of complete dissociation of the titrant and of the salt formed and of the absence of a salt effect, the titration conditions are characterised by the titration constant K_T (C_A and C_B are the concentrations of the acid and base):

$$\text{for acids } K_T = \frac{K_S}{K_A C_A}; \qquad \text{for bases } K_T = \frac{K_S}{K_B C_B},$$

$$\text{for mixtures of bases } K_T = \frac{K_{A_1} C_{A_1}}{K_{A_2} C_{A_2}} (K_{A_1} < K_{A_2}), \text{ and}$$

$$\text{for mixtures of bases } K_T = \frac{K_{B_1} C_{B_1}}{K_{B_2} C_{B_2}} (K_{B_1} < K_{B_2}).$$

On passing from water to non-aqueous solvents, an improvement in the conditions for the titration of weak acids and bases and also of mixtures of acids and mixtures of bases is achieved when the titration constant is appreciably reduced.

When he considered methods for the improvement of titration conditions, Izmailov had at his disposal the autoprotolysis constant of solvents such as alcohols, acetic and formic acids, liquid ammonia and hydrazine. Calculation of the pK_T values for acids and bases from these data led to general agreement between theory and experiment. However, the use of later data for the autoprotolysis constants of acetonitrile, dimethylformamide, and dimethyl sulphoxide to estimate pK_T for phenol and its mononitro-derivatives failed to reflect the improvement in the conditions governing the titration of weak acids which is known to occur on passing from water to these solvents[150]. The apparent conflict between theory and experimental acid – base titration can be resolved if the literature values of the autoprotolysis constants of the solvents are incorrect. The use of the latest K_S data for acetonitrile and dimethyl sulphoxide in the calculation of pK_T indicates a much greater improvement in the conditions for the titration of phenols in these solvents compared with water.

A critical examination of the published data for the solvent autoprotolysis constants and the dissociation constants of the compounds titrated shows that the choice of titration conditions on the basis of the known values of K_S and K_{diss} is impossible for the majority of solvents important in practice. Firstly, few values of K_S for solvents and K_{diss} for electrolytes are available and their reliability is in many cases poor[77]. Secondly, titrations are not usually performed in pure solvents and there are almost no K_S and K_{diss} data for mixed solvents. Thirdly, the choice of titration conditions on the basis of K_S and K_{diss} includes a number of assumptions which are inapplicable to solvents with a low ionising capacity. Fourthly, for aprotic dipolar solvents, where acid — base interaction involves a large number of intermediate stages, the titration conditions cannot be determined by comparing the autoprotolysis constants of the solvents and the dissociation constants of the electrolytes.

In his paper, Charlot[162] states the principles of acid — base titration in non-aqueous media and begins with the same basic postulates as Izmailov. The titration curve is predicted by comparing the pK_S solvent acidity scales with the pH values for various acid — base pairs corresponding to the instant of half neutralisation of the acid (pH = pK). However, the author points out that, owing to the lack of data for the relative positions of the non-aqueous solvent acidity scales, this method is applicable to the assessment of titration conditions in a single solvent only.

The half-neutralisation potential $E_{1/2}$ is frequently used as a chemical-analytical characteristic of the compound determined in a non-aqueous solution[1,2,4,163-179]. Owing to the complete dissociation of the salt formed and its high solubility, the pH of an aqueous solution at the half-neutralisation point is equal to pK_{diss} and therefore the half-neutralisation potential is a function of the dissociation constants only. In most cases $E_{1/2}$ in a non-aqueous solution, employed as a measure of the relative acidity of electrolytes, reflects correctly the variation of their dissociation constants, which is confirmed by the linear relation between $E_{1/2}$ and $pK_{A(ns)}$.[112] Therefore the half-neutralisation potential for the electrolyte in a non-aqueous solvent is largely determined by the same factors as the dissociation constant.

If the electrolyte is a stronger acid than the solvent lyonium ions, the half-neutralisation potential of the electrolyte is reduced to the level of the half-neutralisation potential of SH_2^+; the half-neutralisation potential of a base stronger than the solvent lyate ions is reduced to the level of the half-neutralisation potential of S^-. If the acid or base is a weaker electrolyte than the solvent (considered as an acid or base respectively), its half-neutralisation potential is outside the limits of the acidity scale for the solvent and such electrolytes cannot be titrated as acids or bases in the solvent.

The position of $E_{1/2}$ for the electrolyte on the unique solvent acidity scale depends mainly on the strength of the electrolyte in the given solvent and on the activity of protons in the form of lyonium ions. The half-neutralisation potential for the electrolyte in a non-aqueous solvent depends not only on factors determining the dissociation constant of the electrolyte but also on those which determine the shape of the titration curve in the buffer region. Thus the half-neutralisation potential of the electrolyte has a number of advantages over the dissociation constant in the selection of conditions for potentiometric titration. On the other hand, it is necessary in many cases to know not only the half-neutralisation potential but also the shape of the titration curve for the electrolyte in the buffer region[35].

Van der Heijde and Dahmen[143] attempted to find a theoretical basis for the choice of titration conditions. However, they compared for this purpose the half-neutralisation potentials of acids with the acid limits of empirical solvent acidity scales, which depend on the basicity of the solvents, while the titration conditions for acids are determined by the acid properties of the solvent. This led them to the incorrect conclusion that there is no definite relation between the change in the half-neutralisation potentials of acids on passing from solvent to solvent and the limits of the acidity scales. As a result, the solvent — titrant combinations proposed by van der Heijde for acids and bases of different groups lack a rigorous theoretical basis and the method of selection of titration conditions involving them is complicated and inefficient.

Further studies in this field showed that the basic limit E_B of the relative solvent acidity scale determines the possibility of the titration in the solvent of weak acids and the acid limit E_A determines the possibility of the titration of weak bases, since the half-neutralisation potentials of weak acids are located close to the basic limit and those of weak bases are close to the acid limit of the E_S solvent scale. The higher the basic and acid limits of the E_S scale compared with the limits of the water scale the greater the possibility of titrating in the given solvent weak acids and bases which cannot be titrated in an aqueous solution[144,150,156]. The potential jumps in the titration of electrolytes in the given solvent can be determined approximately as the differences between the basic (for acids) or acid (for bases) limits of the solvent scale on the one hand and the half-neutralisation potential of the electrolyte on the other.

The length of the relative solvent acidity scale characterises the possibility of differential titration of acids or bases in the solvent. A shift of the relative solvent acidity scale to the basic region creates favourable conditions for the differential titration of mixtures of weak and moderately strong acids. A shift of the acidity scale to the acid region improves the conditions for the separate titration of mixtures of strong acids.

In considering the conditions for differential titration of mixtures of bases, one should bear in mind that the position of the acid limit of the scale determines the conditions for the titration of mixtures of weak bases and that of the basic limit determines the conditions for the titration of mixtures of strong bases.

The differentiating effect of solvents is shown to varying extents for acids and bases of different strengths and types. The use of relations between half-neutralisation potentials for acids and bases on the one hand and their pK values in water and Hammett's σ constants on the other makes it possible to predict the half-neutralisation potentials for electrolytes in non-aqueous solvents on the basis of $pK_A(H_2O)$ and σ:[165-179]

$$\Delta E_{1/2} = A\ pK_A\ (H_2O) + B, \qquad (10)$$

$$\Delta E_{1/2} = A'\ \Sigma\sigma + B', \qquad (11)$$

where $\Delta E_{1/2}$ is the half-neutralisation potential of the electrolyte in relation to a standard.

To assess the possibility of the differential titration of a mixture of electrolytes on the basis of $pK_A(H_2O)$ or the σ constants and Eqns. (10) and (11), the values of their half-neutralisation potentials in non-aqueous solutions are found and their differences are determined. For a fairly distinct buffer region on the titration curves for the

individual compounds, a difference between the $E_{1/2}$ for two electrolytes of 150 — 200 mV is usually enough to ensure their separate titration in the mixture[163]. When the potential changes more markedly in the buffer region, the required difference may increase to 300 mV.

On passing from water to non-aqueous solvents, electrolytes belonging to a different reaction series give rise to individual relations between $\Delta E_{1/2}$ on the one hand and $pK_A(H_2O)$ or σ constants on the other[150]. As a result, in some cases there is an improvement in non-aqueous solvents (relative to water) of the conditions for the separate titration of mixtures of electrolytes with similar values of $pK_A(H_2O)$ and in others there is a worsening of the conditions for the separate titration of mixtures of electrolytes with different values of $pK_A(H_2O)$.

Measurements of the relative acidity scales for mixed solvents yield conclusions as to the influence of added solvents on the titration conditions in the given solvent and the use of mixed solvents to improve the conditions for the titration of individual compounds and their mixtures. It was established that the addition of water, methanol, glycols, and similar solvents impairs the titration conditions for weak acids and bases and also for mixtures of electrolytes in solvents with weak acid or basic properties, since it restricts the acidity scales for such solvents[156].

As for individual solvents, the choice of titration conditions in mixed solvents is made by comparing the half-neutralisation potentials of electrolytes with the limits of the acidity scale for the mixtures. If another solvent is added to improve the solvent power of the medium and an attempt is made at the same time to preserve the properties of the main solvent, the permissible content of the added solvent is determined from the dependence of ΔE_A and ΔE_B on mixture composition (Fig. 10). If the second solvent is added to improve the titration conditions, one should bear in mind that a significant improvement of such conditions can be achieved only after adding more than 90 vol. % of the second solvent.

When the use of solvents for acid — base titration is considered, one must take into account the effect of the solvent added together with the titrant to the solution analysed[180]. This applies particularly to R_4NOH solutions, which are usually prepared in alcohol — benzene mixtures. The permissible contents of various alcohols in mixtures used to prepare titrant solutions have been established. However, the choice of the alcohol and its content in the mixture are frequently limited also by the solubility of R_4NOH, the stability of solutions, and the method of their preparation.

The above method of choosing the optimal conditions for acid — base potentiometric titration based on E_S solvent acidity scales and half-neutralisation potentials $E_{1/2}$ of the compounds being titrated has the following advantages. Firstly, account is taken of the effect of many factors determining the titration conditions (the amount and properties of added solvents, the strength and concentration of titrants, the formation of salt precipitates during their titration, etc.) and secondly it is possible to select the conditions for titration in mixed solvents.

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The above discussion of the acid — base equilibria in amphiprotic solvents showed that Izmailov's scheme for acid — base interaction (Ref. 8, Chapter VIII), which includes a number of related processes involving the formation of products of the addition of solvent molecules to those of the electrolyte and the formation of solvated ions and ion pairs, must be supplemented by new equilibria. Kolthoff demonstrated convincingly in the case of acetonitrile, dimethyl sulphoxide, and dimethylformamide that for solvents with weak acid properties these additional equilibria involve homo- and hetero-conjugation processes. Factors determining the degree of homo- and hetero-conjugation have been established and it has been shown that, for a quantitative interpretation of acid — base interaction and the calculation of the pH of electrolyte solutions, it is necessary to take into account the constants characterising these equilibria.

The latest determinations of the autoprotolysis constant of solvents have shown that many amphiprotic solvents (acetonitrile, dimethylformamide, dimethyl sulphoxide, and ketones) have extensive acidity scales. Factors which reduce the limits of solvent acidity scales have been discovered and relations governing the variation of the limits of the acidity scales for mixed protolytic solvents have been established. The importance of water (and similar solvents) for the explanation of protolysis in mixed solvents has been demonstrated.

Studies on acid — base interaction in amphiprotic solvents have promoted the development of the theory of potentiometric acid — base titration. The use of electrolyte dissociation constants and homo- and hetero-conjugation constants permits the calculation of titration curves in the buffer region. The conversion from theoretical solvent acidity scales, calculated from the autoprotolysis constants, into real scales is possible on the basis of the δ values taking into account the overall effect of the zero-concentration proton activity coefficient and the diffusion potential in measurements in cells with transport. The effect of numerous factors which determine the conditions governing acid — base titration is reflected in the extent of the relative (real) E_S solvent acidity scale and the electrolyte half-neutralisation potential $E_{1/2}$. The knowledge of these chemical-analytical characteristics permits a choice of the optimal titration conditions.

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