

ACID–BASE TITRATIONS IN SOLVENTS OF RELATIVELY LOW DIELECTRIC CONSTANT

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The importance of titrations in nonaqueous solvents as an analytical method is increasing; not only has more sophisticated instrumentation become available, but theoretical knowledge about the physicochemical processes which govern titrations in nonaqueous solvents has extended very much in recent years. Especially the titrations of Brønsted acids and bases have been the subject of numerous studies^{1,2}, and most applications relate to these particular titrations.

It is of great importance to make a proper choice of the solvent and the titrant when such titrations are applied to the analysis of a given compound, *i.e.* knowledge about acid–base strengths in the various solvents is an absolute necessity. Only when all equilibria occurring during a neutralization and their corresponding equilibrium constants are known, can one calculate whether this neutralization can be successfully used in an analytical titration. For the more common acids and bases in a number of solvents like acetonitrile³, dimethylsulfoxide⁴, dimethylformamide⁵ such is indeed the case.

Empirically it has been found that solvents with a relatively low dielectric constant such as acetic acid⁶, 1,2-dichloroethane⁷ and pyridine⁸, can also be effectively used as a medium for acid–base titrations. Some rules with regard to the choice of a solvent for a particular titration can be found from the classification of the solvent according to Brønsted^{9,10}. Here the solvents with a relatively low dielectric constant are classified as numbers 5–8 (*cf.* Table I).

TABLE I
SOLVENT CLASSES ACCORDING TO BRØNSTED^{9,10}

<i>Class no.</i>	<i>Acidity</i>	<i>Basicity</i>	<i>Dielectric constant</i>
1	High	High	High
2	High	Low	High
3	Low	High	High
4	Low	Low	High
5	High	High	Low
6	High	Low	Low
7	Low	High	Low
8	Low	Low	Low

It is to be expected that the behaviour during titration of a compound in solvents belonging to the same Brønsted class will not be too different, so that from pK_a determinations in representatives of each of the Brønsted classes, one can obtain an impression of the usefulness of these solvent classes in acid-base titrations. With that purpose acid-base strengths were determined in the solvents pyridine^{11,12} (class 7), *m*-cresol¹³ (class 5) and 1,2-dichloroethane¹⁴ (class 8). In the evaluation of the results obtained, the following *theoretical* considerations may serve. The acidity of a compound in a particular solvent can best be expressed as its pK_a value, the negative logarithm of the equilibrium constant of the overall dissociation:



where SH is the solvent and HX an acid. The equilibrium constant is given by

$$K_{\text{HX}} = (a_{\text{SH}_2^+} \cdot a_{\text{X}^-})/a_{\text{HX}} \quad (2)$$

hence

$$pK_a^{\text{HX}} = -\log (a_{\text{SH}_2^+} \cdot a_{\text{X}^-})/a_{\text{HX}} \quad (3)$$

One can also write

$$-RT \ln K_{\text{HX}} = \Delta G^0 \quad (4)$$

with

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

The difference in pK_a value of compound HX in the solvent I and the solvent II now becomes:

$$(pK_a^{\text{HX}})_I - (pK_a^{\text{HX}})_{II} = (0.43/RT) \{ \Delta G_I^0 - \Delta G_{II}^0 \} \quad (6)$$

Combination of eqns. (5) and (6) gives:

$$(pK_a^{\text{HX}})_I - (pK_a^{\text{HX}})_{II} = (0.43/RT) \{ \Delta H_I^0 - T\Delta S_I^0 - \Delta H_{II}^0 + T\Delta S_{II}^0 \} \quad (7)$$

As an approximation the entropy part is neglected in relation to the enthalpy part. The enthalpy contains an electrical part, because in the dissociation a separation of charges occurs. The electric energy of an ion is given by:

$$E_{\text{elec}} = \varepsilon^2 z^2 / 2Dr \quad (8)$$

where ε is the unit charge, z the valency of the ion, D the dielectric constant of the solvent, and r the radius of the ion in solution. For reaction (1) eqn. (8) gives:

$$\Delta E_{\text{elec}} = N \left\{ \frac{\varepsilon^2 z_{\text{SH}_2^+}^2}{2Dr_{\text{SH}_2^+}} + \frac{\varepsilon^2 z_{\text{X}^-}^2}{2Dr_{\text{X}^-}} - \frac{\varepsilon^2 z_{\text{HX}}^2}{2Dr_{\text{HX}}} \right\} \quad (9)$$

In the comparison of pK_a values in solvents with the same dielectric constant, the electric energy part can be omitted if it is assumed that the ionic radii remain constant with change of solvent. The difference in pK_a values of compound HX in solvent I and solvent II then reduces to:

$$(\text{p}K_{\text{a}}^{\text{HX}})_{\text{I}} - (\text{p}K_{\text{a}}^{\text{HX}})_{\text{II}} = (0.43/RT) \{ (E_{\text{SH}_2^+}^0)_{\text{I}} + (E_{\text{X}^-}^0)_{\text{I}} - (E_{\text{HX}}^0)_{\text{I}} - (E_{\text{SH}_2^+}^0)_{\text{II}} - (E_{\text{X}^-}^0)_{\text{II}} + (E_{\text{HX}}^0)_{\text{II}} \} \quad (10)$$

If the differences of solvation of the compounds X^- as well as HX between the solvents I and II are neglected, one gets:

$$(\text{p}K_{\text{a}}^{\text{HX}})_{\text{I}} - (\text{p}K_{\text{a}}^{\text{HX}})_{\text{II}} = (0.43/RT) \{ (E_{\text{SH}_2^+}^0)_{\text{I}} - (E_{\text{SH}_2^+}^0)_{\text{II}} \} \quad (11)$$

In this case with the approximations stated, the difference of $\text{p}K_{\text{a}}$ of compound HX in the two solvents is completely determined by the difference in proton affinity of the two solvents. Thus it is possible to find the difference in basicity of these solvents under these conditions.

On the other hand, quantitative information about differences in basicity of solvents together with dielectric constant data and eqn. (9), can be used to predict the $\text{p}K_{\text{a}}$ values which are of analytical interest.

$\text{p}K_{\text{a}}$ VALUES IN SOLVENTS WITH A RELATIVELY LOW DIELECTRIC CONSTANT

A comparison of the $\text{p}K_{\text{a}}$ values of various compounds in the solvents acetic acid, pyridine, *m*-cresol and 1,2-dichloroethane is given in Table II. From the Table it can be seen that for a particular compound, the difference in $\text{p}K_{\text{a}}$ value in two solvents depends on the charge type, even if the dielectric constant of the two

TABLE II

COMPARISON OF $\text{p}K_{\text{a}}$ VALUES IN ACETIC ACID, PYRIDINE, *m*-CRESOL, 1,2-DICHLOROETHANE AND WATER

Compound	$\text{p}K_{\text{a}}$ values				
	Dichloroethane ($D=10.23$)	<i>m</i> -Cresol ($D=12.3$)	Acetic acid ($D=6.13$)	Pyridine ($D=12.3$)	Water ($D=78.5$)
Perchloric acid			4.87 ^a	3 ^b	
Hydriodic acid	7.9 ^d	4.4 ^c		3.2 ^c	
Hydrobromic acid	8.7 ^d	4.4 ^c		4.4 ^c	
Hydrochloric acid	10.8 ^d	6.4 ^c	8.55 ^a	6.1 ^c	
Benzenesulfonic acid	12.1 ^d	6.3 ^c			
Picric acid	13.7 ^d	12.0 ^c	a	3.0 ^b	0.38 ^f
Iodoacetic acid	17.6 ^d	13.0 ^c			3.12 ^f
Benzoic acid	20.0 ^d	15.0 ^c		11.0 ^g	4.19 ^f
Acetic acid		16.0 ^c		12.0 ^g	4.75 ^f
DMAABH ⁺		11.0 ^c	8.13 ^a		3.3 ^j
Methyl orange H ⁺		11.0 ^c	7.60 ^k		3.5 ^j
Strychnine H ⁺	16.0 ^d	13.0 ^c			8.0 ^f
Morpholine H ⁺	15.0 ^d	12.1 ^c		3.5 ^b	9.6 ^f
<i>n</i> -Butylamine H ⁺	17.0 ^d	13.9 ^c	8.59 ^h	5.5 ^b	10.6 ^f
Triethylamine H ⁺	17.7 ^d	14.2 ^c	9.45 ^h	3.8 ^b	10.8 ^f
Tetramethylguanidine H ⁺	21.5 ^d	14.5 ^c		9.6 ^b	12.3 ^k
Bromophenol blue (2)	23.8 ^d			5.3 ^b	4.1 ^j
Bromocresol green (2)	22.2 ^d			5.5 ^b	4.9 ^j
Bromocresol purple (2)	24.7 ^d			7.5 ^b	6.4 ^j

^a Ref. 15. ^b Ref. 11. ^c Ref. 16. ^d Ref. 14. ^e Ref. 13. ^f Ref. 17. ^g Ref. 12. ^h Ref. 18. ^j Ref. 19. ^k Present work.

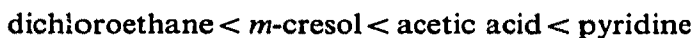
solvents is the same. This means that the assumption that ionic radii remain constant going from one solvent to another is not entirely justified. The influence of a changing ionic radius upon the pK_a difference is smallest for acids of the cation-type (see eqn. 9), so that in the determination of basicity differences of solvents, the best thing to do is to take into account the pK_a values of these cationic acids. For these compounds the following relationships are valid in approximation:

$$(pK_a)_{\text{dichloroethane}} = (pK_a)_{m\text{-cresol}} + 3$$

$$(pK_a)_{m\text{-cresol}} = (pK_a)_{\text{acetic acid}} + 4$$

$$(pK_a)_{\text{acetic acid}} = (pK_a)_{\text{pyridine}} + 4$$

The basicity of these solvents thus increases in the order



If it is assumed that the basicity of dichloroethane is 0 pK units, the basicity of m -cresol, acetic acid and pyridine becomes 3, 7 and 11 pK units, respectively.

From Table II, it can also be seen that for hydriodic acid, hydrobromic acid and hydrochloric acid, levelling occurs in pyridine and m -cresol. For tetramethylguanidine in m -cresol there is a basicity levelling.

Comparison of the pK_a values of an electrically uncharged acid in two solvents with the same dielectric constant, shows that the difference between the pK_a values is not equal to the difference in basicity of the two solvents. The same holds for anion-type acids. Equation (9) explains this behaviour, especially on the basis of differences in ionic radii.

In order to estimate the pK_a value of a compound in one of the solvents of the Brønsted classes 5–8, which is necessary to find a suitable titration, the following procedure can be used.

(a) Check if a pK_a value of the compound, or a related one, is known in one of the solvents belonging to the Brønsted classes 5–8.

(b) If necessary, extrapolate the value found in step *a* to the pK_a value in the solvent to be used. Here it is necessary to take into account the difference in basicity between the various Brønsted classes as well as the influences of difference in dielectric constant and the influence of the charge type of the compound. Care should also be taken to deal with any levelling.

(c) Should the pK_a value of neither the compound nor a related one be known in any of the solvents belonging to the Brønsted classes 5–8, then the pK_a value of the compound in water must be extrapolated in the same way as given in step *b*.

ACCURACY OF TITRATIONS IN SOLVENTS WITH A RELATIVELY LOW DIELECTRIC CONSTANT

In all the cases investigated, the glass electrode behaves in the solvents belonging to the Brønsted classes 5–8, according to the Nernst equation. Potentiometry with the glass electrode is therefore very useful as an indication method for

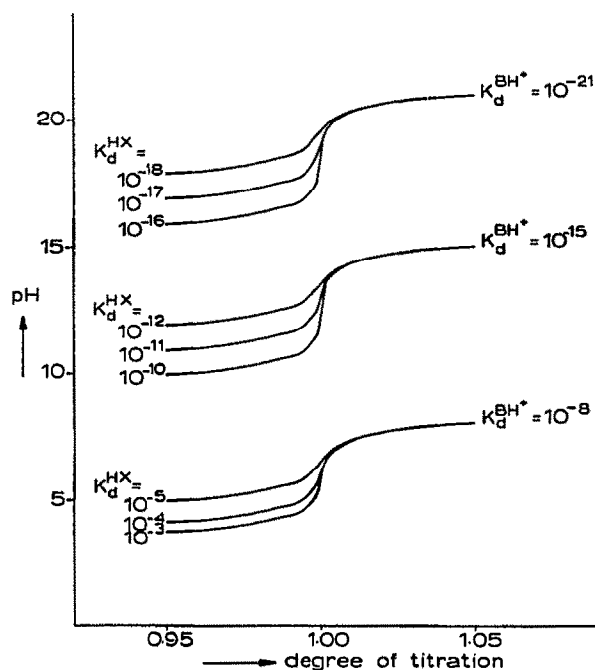


Fig. 1. Simple dissociation. Titration of 0.01 M HX with 0.01 M B.

TABLE III

ACCURACY OF THE TITRATION OF 0.0100 M HX WITH 0.0100 M B FOR DIFFERENT COMBINATIONS OF K_d^{HX} AND $K_d^{BH^+}$ IN THE CASE OF SIMPLE DISSOCIATION OF HX AND BH^+ AND FORMATION OF THE ION-PAIR BHX

($K_d^{BHX} = 10^{-5}$)

K_d^{HX}	$K_d^{BH^+}$	Accuracy (%)	$\Delta pH (\lambda = 0.99-1.01)$
10^{-18}	10^{-21}	± 0.15	1.74
10^{-17}	10^{-21}	$< \pm 0.10$	2.72
10^{-16}	10^{-21}	$\ll \pm 0.10$	3.72
10^{-12}	10^{-15}	± 0.15	1.74
10^{-11}	10^{-15}	$< \pm 0.10$	2.72
10^{-10}	10^{-15}	$\ll \pm 0.10$	3.72
10^{-5}	10^{-8}	± 0.15	1.72
10^{-4}	10^{-8}	$< \pm 0.10$	2.55
10^{-3}	10^{-8}	$\ll \pm 0.10$	2.97

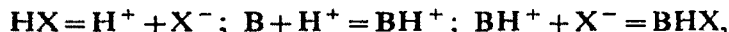
acid-base titrations in these solvents, especially as the results are more easily interpreted than with any other indication method.

If it is assumed that the end-point of the titration can be taken as the point of the curve with maximal slope, this end-point can be detected experimentally with an accuracy of ± 0.2 pH unit. From theoretical curves, calculated with the computer program EQUIL²⁰, the corresponding accuracy of the titration can be found as a

function of the various equilibrium constants of the reactions that take part in the titration. This is done for a few cases below.

Simple dissociation

For the simple case that the titration can be fully described by the equilibria



the theoretically calculated curves for various combinations of $K_d^{\text{BH}^+}$ and K_d^{HX} with $K_d^{\text{BHX}} = 10^{-5}$ are given in Fig. 1. Table III shows the accuracy of the titration as a function of K_d^{HX} and $K_d^{\text{BH}^+}$.

The influence of the ion-pair dissociation constant K_d^{BHX} in this case can be seen from Fig. 2; Table IV shows the accuracy of the titration as a function of this K_d^{BHX} .

Differential titration of two acids

Sometimes, if differences in acidity are great enough, it is possible to determine the separate components in a mixture of acids with different strengths in

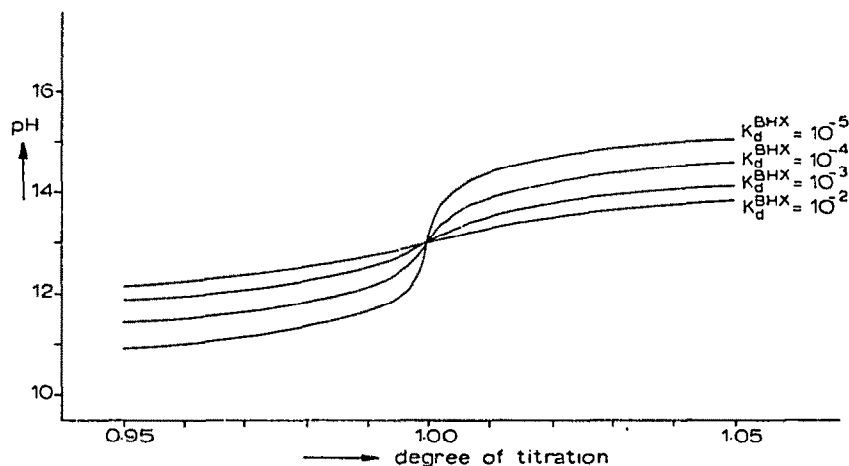


Fig. 2. Titration of 0.00100 *M* HX with 0.0100 *M* B in the case of simple dissociation for various values of K_d^{BHX} .

TABLE IV

ACCURACY OF THE TITRATION OF 0.0100 *M* HX WITH 0.0100 *M* B AS A FUNCTION OF THE DISSOCIATION CONSTANT OF THE ION-PAIR BHX IN THE CASE OF SIMPLE DISSOCIATION OF HX AND BH⁺

(The difference of $\text{p}K_d^{\text{HX}}$ and $\text{p}K_d^{\text{BH}^+}$ is 4 *pK* units)

K_d^{BHX}	Accuracy (%)	ΔpH ($\lambda = 0.99-1.01$)
10^{-5}	$< \pm 0.10$	2.72
10^{-4}	± 0.15	1.77
10^{-3}	± 0.35	0.99
10^{-2}	± 0.7	0.56

a single titration. In the case of the titration of two acids, HX and HY, with the base B, the titration curve can be calculated with the use of the equilibria:

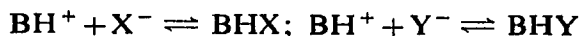


Figure 3 shows theoretically calculated curves for this titration with various combinations of K_d^{HX} and K_d^{HY} . The ion-pair dissociation constants K_d^{BHX} and K_d^{BHY} were taken to be 10^{-5} ; for $K_d^{\text{BH}^+}$ the value 10^{-21} was taken. In Table V the accuracy of the titration as a function of the difference in $\text{p}K_a$ value between HX and HY is given. With greater values for K_d^{BHX} and K_d^{BHY} (still equal to each other), the accuracy of the second end-point decreases (see Fig. 4 and Table VI).

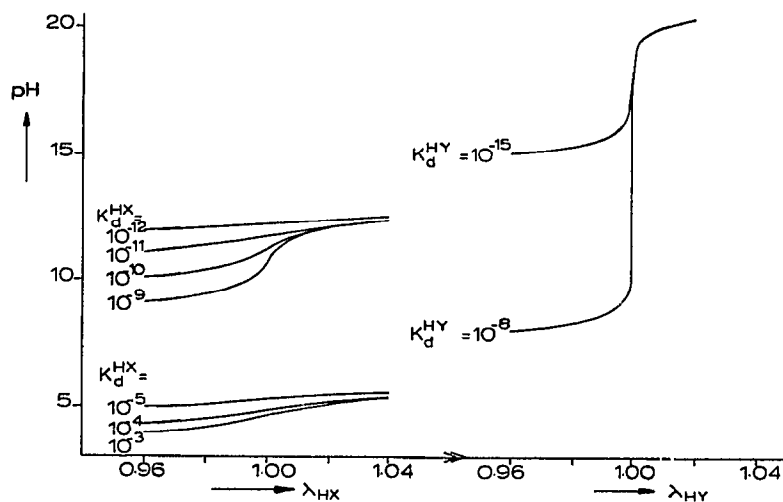


Fig. 3. Titration of 0.005 M HX and 0.005 M HY with 0.010 M B as a function of K_d^{HX} and K_d^{HY} . $K_d^{\text{BHX}} = K_d^{\text{BHY}} = 10^{-5}$, $K_d^{\text{BH}^+} = 10^{-21}$.

TABLE V

ACCURACY OF THE TITRATION OF A SOLUTION WITH 0.005 M HX AND 0.005 M HY WITH 0.010 M B AS A FUNCTION OF K_d^{HX} AND K_d^{HY}

($K_d^{\text{BHX}} = K_d^{\text{BHY}} = 10^{-5}$, $K_d^{\text{BH}^+} = 10^{-21}$. Simple dissociation of HX, HY and BH^+)

K_d^{HX}	K_d^{HY}	Accuracy, 1st e.p. (%)	ΔpH ($\lambda=0.99-1.01$) 1st e.p.	Accuracy 2nd e.p. (%)	ΔpH ($\lambda=0.99-1.01$) 2nd e.p.
10^{-9}	10^{-15}	± 0.10	2.01	$\ll \pm 0.10$	5.03
10^{-10}	10^{-15}	± 0.3	1.08	$\ll \pm 0.10$	5.03
10^{-11}	10^{-15}	± 0.9	0.43	$\ll \pm 0.10$	5.03
10^{-12}	10^{-15}	e.p. indetectable	0.14	$\ll \pm 0.10$	5.03
10^{-2}	10^{-8}	± 0.7	0.54	$\ll \pm 0.10$	12.03
10^{-3}	10^{-8}	± 0.8	0.50	$\ll \pm 0.10$	12.03
10^{-4}	10^{-8}	± 1.5	0.34	$\ll \pm 0.10$	12.03
10^{-5}	10^{-8}	c.p. indetectable	0.13	$\ll \pm 0.10$	12.03

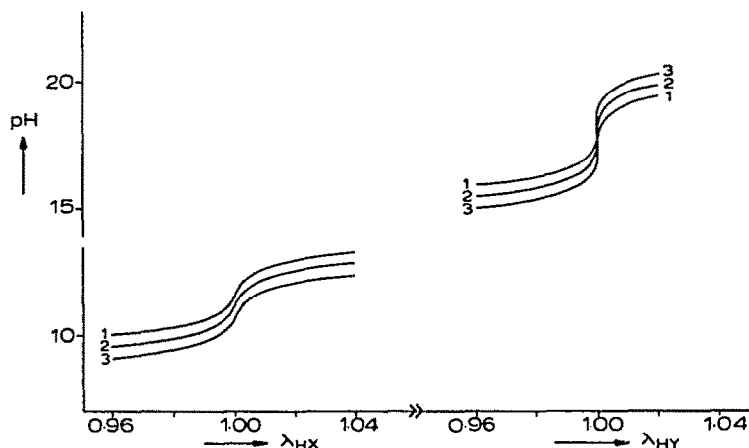


Fig. 4. Titrations of a mixture of 0.005 M HX and 0.005 M HY with 0.010 M B as a function of ion-pair dissociation constants ($K_d^{\text{BH}^{\text{X}}} = K_d^{\text{BH}^{\text{Y}}}$). $K_d^{\text{HX}} = 10^{-9}$, $K_d^{\text{HY}} = 10^{-15}$, $K_d^{\text{BH}^{\text{H}^{\text{X}}}} = 10^{-21}$. (1) $K_d^{\text{BH}^{\text{X}}} = K_d^{\text{BH}^{\text{Y}}} = 10^{-3}$; (2) $K_d^{\text{BH}^{\text{X}}} = K_d^{\text{BH}^{\text{Y}}} = 10^{-4}$; (3) $K_d^{\text{BH}^{\text{X}}} = K_d^{\text{BH}^{\text{Y}}} = 10^{-5}$.

TABLE VI

ACCURACY OF THE TITRATION OF A SOLUTION 0.005 M HX AND 0.005 M HY WITH 0.010 M B AS A FUNCTION OF THE ION-PAIR DISSOCIATION CONSTANTS

($K_d^{\text{BH}^{\text{X}}} = K_d^{\text{BH}^{\text{Y}}}$, $K_d^{\text{HX}} = 10^{-9}$, $K_d^{\text{HY}} = 10^{-15}$, $K_d^{\text{BH}^{\text{H}^{\text{X}}}} = 10^{-21}$)

$K_d^{\text{BH}^{\text{X}}} = K_d^{\text{BH}^{\text{Y}}}$	Accuracy 1st e.p. (%)	ΔpH ($\lambda=0.99-1.01$) 1st e.p.	Accuracy 2nd e.p. (%)	ΔpH ($\lambda=0.99-1.01$) 2nd e.p.
10^{-5}	± 0.10	2.01	$\ll \pm 0.10$	5.03
10^{-4}	± 0.10	2.02	$\ll \pm 0.10$	4.07
10^{-3}	± 0.10	2.02	$\ll \pm 0.10$	3.21

When the dissociation constant of the salt of the weakest acid ($K_d^{\text{BH}^{\text{Y}}}$) is smaller than that of the strongest acid ($K_d^{\text{BH}^{\text{X}}}$), the accuracy of the determination of the first end-point is less than in the case of equal salt dissociation constants. This happens because the weaker acid starts to react with the base before the first equivalence point. Quantitative data about this are given in Table VII and Fig. 5.

In the case of greater dissociation constants of the salt of the strongest acid ($K_d^{\text{BH}^{\text{X}}}$), the first end-point can be detected less accurately. Although the position of the second equivalence point is dependent upon this dissociation constant, the height of the break in the curve is not; hence the accuracy of the determination of the second end-point does not depend on the value of $K_d^{\text{BH}^{\text{X}}}$ (see Table VIII and Fig. 6).

Acid dimerization

The accuracy of the titration is influenced unfavourably by dimerization of the acid during titration. The titration curve can in this case be calculated with the use of the equilibria:

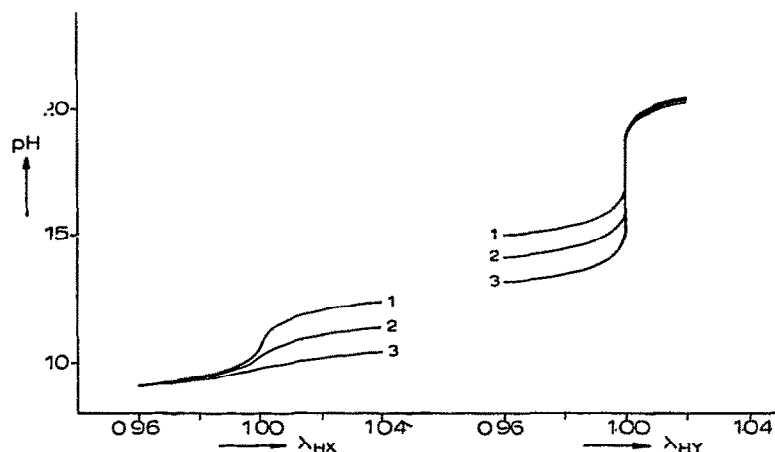


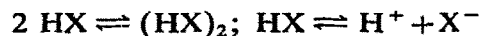
Fig. 5. Titration of a mixture of 0.005 *M* HX and 0.005 *M* HY with 0.0100 *M* B for various values of K_d^{BHY} . $K_d^{HX} = 10^{-9}$, $K_d^{HY} = 10^{-15}$, $K_d^{BH^+} = 10^{-21}$, $K_d^{BHX} = 10^{-5}$. (1) $K_d^{BHY} = 10^{-5}$; (2) $K_d^{BHY} = 10^{-6}$; (3) $K_d^{BHY} = 10^{-7}$.

TABLE VII

ACCURACY OF THE TITRATION OF A MIXTURE OF 0.005 *M* HX AND 0.005 *M* HY WITH 0.010 *M* B AS A FUNCTION OF K_d^{BHY}

($K_d^{HX} = 10^{-9}$, $K_d^{HY} = 10^{-15}$, $K_d^{BH^+} = 10^{-21}$, $K_d^{BHX} = 10^{-5}$)

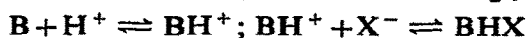
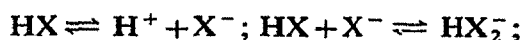
K_d^{BHY}	Accuracy 1st e.p. (%)	ΔpH ($\lambda = 0.99-1.01$) 1st e.p.	Accuracy 2nd e.p. (%)	ΔpH ($\lambda = 0.99-1.01$) 2nd e.p.
10^{-5}	± 0.10	2.01	$\ll \pm 0.10$	5.03
10^{-6}	± 0.3	1.10	$\ll \pm 0.10$	6.01
10^{-7}	± 0.9	0.44	$\ll \pm 0.10$	7.01



In the titration curve dimerization shows by a higher start and a smaller slope up to the end-point (see Fig. 7). The effect of the dimerization constant $K_f^{(\text{HX})_2}$ on the accuracy of the titration is very small. Only in the case $K_f^{(\text{HX})_2} > 10^4$, the determination of the end-point becomes less accurate, while owing to curve asymmetry, a systematic error occurs (Table IX).

Homoconjugation and triple ion formation

Homoconjugation and triple ion formation of the acid lessen the accuracy of the end-point determination of the acid-base titration. Moreover, there is the possibility of an extra inflection point at half-neutralization. The system of equilibria:



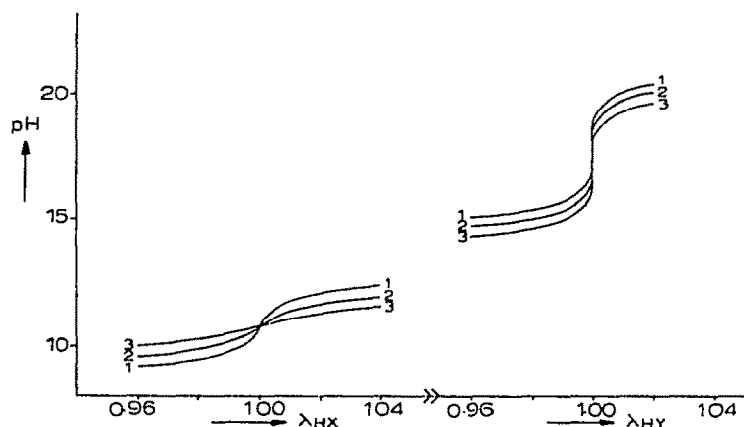


Fig. 6. Titration of a mixture of 0.005 *M* HX and 0.005 *M* HY with 0.010 *M* B for various values of $K_d^{BH^X}$, $K_d^{HX} = 10^{-9}$, $K_d^{HY} = 10^{-15}$, $K_d^{BH^Y} = 10^{-21}$ and $K_d^{HY} = 10^{-5}$. (1) $K_d^{BH^X} = 10^{-5}$; (2) $K_d^{BH^X} = 10^{-4}$; (3) $K_d^{BH^X} = 10^{-3}$.

TABLE VIII

ACCURACY OF THE END-POINT DETERMINATION IN THE TITRATION OF A MIXTURE OF 0.005 *M* HX AND 0.005 *M* HY WITH 0.010 *M* B AS A FUNCTION OF $K_d^{BH^X}$

($K_d^{HX} = 10^{-9}$, $K_d^{HY} = 10^{-15}$, $K_d^{BH^Y} = 10^{-21}$, $K_d^{HY} = 10^{-5}$)

$K_d^{BH^X}$	Accuracy 1st e.p. (%)	ΔpH ($\lambda = 0.99-1.01$) 1st e.p.	Accuracy 2nd e.p. (%)	ΔpH ($\lambda = 0.99-1.01$) 2nd e.p.
10^{-5}	± 0.10	2.01	$\ll \pm 0.10$	5.03
10^{-4}	± 0.3	1.15	$\ll \pm 0.10$	5.02
10^{-3}	± 0.7	0.54	$\ll \pm 0.10$	5.01

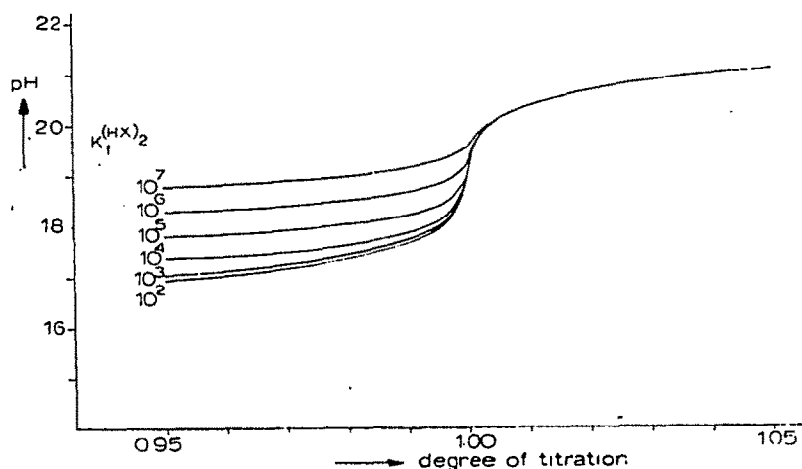


Fig. 7. Influence of $K_1^{(HX)_2}$ on the titration of 0.01 *M* HX with 0.01 *M* B. $K_d^{HX} = 10^{-17}$, $K_d^{BH^X} = 10^{-21}$, $K_d^{BH^X} = 10^{-5}$.

TABLE IX

INFLUENCE OF THE DIMERIZATION CONSTANT IN THE TITRATION OF 0.01 M HX WITH 0.01 M B

($K_d^{\text{HX}} = 10^{-17}$, $K_d^{\text{BH}^+} = 10^{-21}$, $K_d^{\text{BH}^+} = 10^{-5}$)

$K_f^{\text{HX}_2}$	Accuracy (%)	ΔpH ($\lambda=0.99-1.01$)	Systematic error (%)
10^2	$< \pm 0.1$	2.72	Negligible
10^3	$< \pm 0.1$	2.69	Negligible
10^4	$< \pm 0.1$	2.51	Negligible
10^5	± 0.1	2.15	+0.05
10^6	± 0.15	1.70	+0.10
10^7	± 0.20	1.23	+0.20

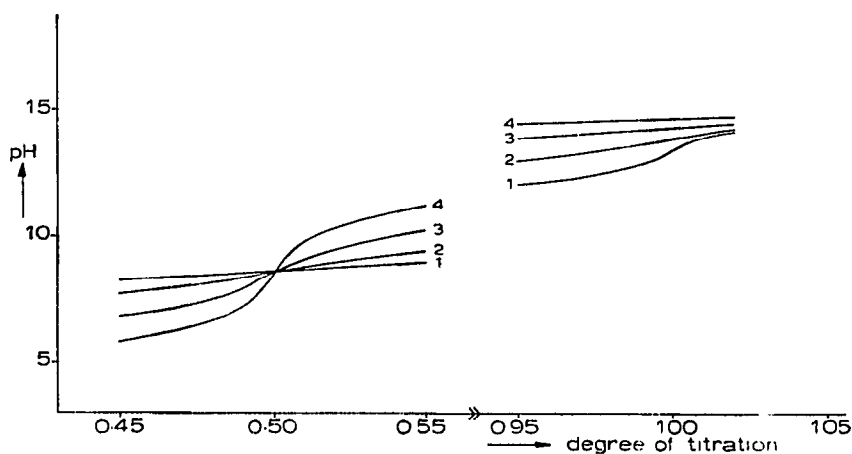


Fig. 8. Influence of $K_f^{\text{HX}_2}$ on the titration of 0.01 M HX with 0.01 M B. $K_d^{\text{HX}} = 10^{-4}$, $K_d^{\text{HX}} = 10^{-10}$, $K_d^{\text{BH}^+} = 10^{-15}$. (1) $K_f^{\text{HX}_2} = 10^5$; (2) $K_f^{\text{HX}_2} = 10^6$; (3) $K_f^{\text{HX}_2} = 10^7$; (4) $K_f^{\text{HX}_2} = 10^8$.

TABLE X

ACCURACY OF THE TITRATION OF 0.01 M HX WITH 0.01 M B AS A FUNCTION OF THE HOMOCONJUGATION CONSTANT $K_f^{\text{HX}_2}$

($K_d^{\text{HX}} = 10^{-4}$, $K_d^{\text{HX}} = 10^{-10}$, $K_d^{\text{BH}^+} = 10^{-15}$)

$pK_f^{\text{HX}_2}$	Accuracy (%)	ΔpH ($\lambda=0.99-1.01$)
-3	$< \pm 0.1$	2.56
-4	± 0.1	1.92
-5	± 0.3	1.06
-6	± 1	0.43
-7	End-point indetectable	0.17
-8	End-point indetectable	0.08

TABLE XI

ACCURACY OF THE TITRATION OF 0.01 M HX WITH 0.01 M B IN THE CASE OF HOMOCONJUGATION ($K_r^{HX_2} = 10^5$) COMPARED WITH THE ACCURACY OF THE SAME TITRATION IN CASE OF SIMPLE DISSOCIATION FOR VARIOUS VALUES OF K_d^{BHX}

($K_d^{HX} = 10^{-10}$, $K_d^{BH'} = 10^{-15}$)

pK_d^{BHX}	Accuracy (%)		$\Delta pH (\lambda = 0.99-1.01)$	
	Homoconj. $K_r^{HX_2} = 10^5$	Simple dissociation	Homoconj. $K_r^{HX_2} = 10^5$	Simple dissociation
4	± 0.3	$< \pm 0.1$	1.06	2.76
5	$< \pm 0.1$	$< \pm 0.1$	2.46	3.72
6	$\ll \pm 0.1$	$\ll \pm 0.1$	4.04	4.71
7	$\ll \pm 0.1$	$\ll \pm 0.1$	5.61	5.70
8	$\ll \pm 0.1$	$\ll \pm 0.1$	6.92	6.70

TABLE XII

ACCURACY OF THE TITRATION OF 0.01 M HX WITH 0.01 M B AS A FUNCTION OF $K_r^{B(HX)_2}$ FOR DIFFERENT COMBINATIONS OF $pK_d^{BH'}$ AND pK_a^{HX}

($K_d^{BHX} = 10^{-5}$)

$pK_a^{BH'}$	pK_a^{HX}	$pK_r^{B(HX)_2}$	Accuracy (%)	$\Delta pH (\lambda = 0.99-1.01)$
21	17	-2	$< \pm 0.10$	2.56
21	17	-3	± 0.10	1.97
21	17	-4	± 0.30	1.11
21	17	-5	± 1.0	0.45
21	17	-6	$> \pm 2$	0.15
21	15	-5	± 0.10	2.05
21	15	-6	± 0.30	1.12
21	15	-7	± 1.0	0.44

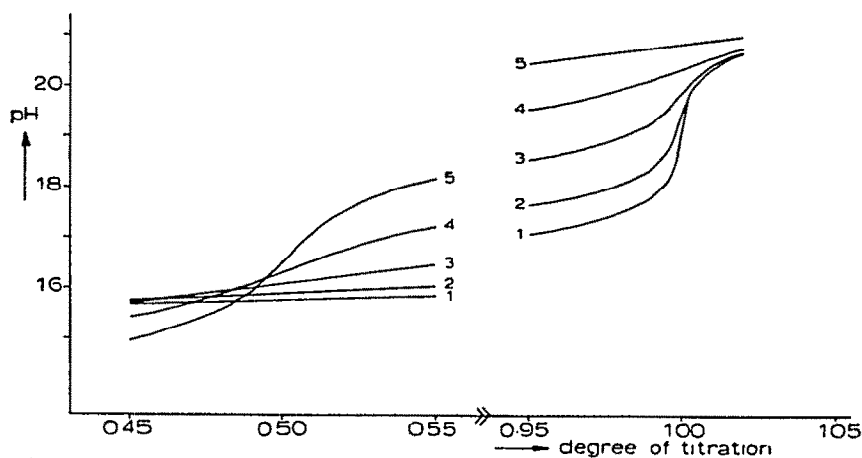
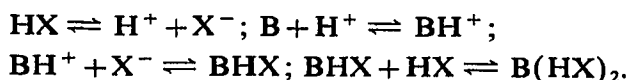


Fig. 9. Influence of $K_r^{B(HX)_2}$ on the titration of 0.01 M HX with 0.01 M B. $K_d^{BHX} = 10^{-5}$, $K_d^{BH'} = 10^{-21}$, $K_a^{HX} = 10^{-17}$. (1) $K_r^{B(HX)_2} = 10^2$; (2) $K_r^{B(HX)_2} = 10^3$; (3) $K_r^{B(HX)_2} = 10^4$; (4) $K_r^{B(HX)_2} = 10^5$; (5) $K_r^{B(HX)_2} = 10^6$.

gives the titration curves represented in Fig. 8. The accuracy of the end-point determination for various values of $K_f^{HX_2^-}$ is given in Table X. Homoconjugation has a smaller effect when the dissociation constants of the acid and the salt BHX are small (Table XI).

Formation of 2:1 acid-base complex

In inert solvents during acid-base titrations, a 2:1 acid-base complex is sometimes formed (*e.g.* carboxylic acids in 1,2-dichloroethane). This makes the detection of the end-point more difficult. In this case the titration can be described by the equilibria:



Theoretical curves for various values of $K_f^{B(HX)_2}$ are given in Fig. 9. Here an extra inflection point at half-neutralization is also possible. The accuracy of the end-point determination for this titration is shown in Table XII.

DISCUSSION

The specifications which the equilibrium constants should meet in the different cases for a titration accuracy of $\pm 0.1\%$ are summarized in Table XIII. It should be noted, however, that for many purposes less accurate results are sufficient, and for titrations with solutions with concentrations higher than 0.01 *M* the requirements for the equilibrium constants are less severe. Complex formation, like homoconjugation, etc. has an unfavourable influence on the accuracy of a titration. It is clear that to find a suitable solvent for a particular titrimetric analysis, one always has to take into account the chance of the occurrence of such complexes and the effect of these phenomena on the accuracy of the titration. Generally complications of this kind are rare in solvents with a high H-bond formation capacity. However, in such a solvent triple ion formation may occur.

TABLE XIII

CONDITIONS WITH REGARD TO THE CONSTANTS OF ACID-BASE EQUILIBRIA IN SOLVENTS WITH A RELATIVELY LOW DIELECTRIC CONSTANT FOR A TITRATION ACCURACY OF $\pm 0.1\%$

Type of equilibrium reactions	Conditions for accuracy $\pm 0.1\%$
Simple dissociation of acid and protonated base	$\text{p}K_a^{\text{BH}^+} - \text{p}K_a^{\text{HX}} + \text{p}K_d^{\text{BHX}} \geq 9$
Differential titration of two acids HX and HY $\text{p}K_a^{\text{HX}} < \text{p}K_a^{\text{HY}}$	$\text{p}K_a^{\text{HY}} - \text{p}K_a^{\text{HX}} + \text{p}K_d^{\text{BHX}} - \text{p}K_d^{\text{BHY}} \geq 6$ and $\text{p}K_a^{\text{BH}^+} - \text{p}K_a^{\text{HY}} + \text{p}K_d^{\text{BHY}} \geq 9$
Homoconjugation of the acid (formation of HX_2^-)	$\text{p}K_a^{\text{BH}^+} - \text{p}K_a^{\text{HX}} + 2\text{p}K_d^{\text{BHX}} + \text{p}K_f^{\text{HX}_2^-} \geq 10$ if $\text{p}K_d^{\text{BHX}} + \text{p}K_f^{\text{HX}_2^-} \leq 1$, otherwise $\text{p}K_a^{\text{BH}^+} - \text{p}K_a^{\text{HX}} + \text{p}K_d^{\text{BHX}} \geq 9$
2:1 Acid-base complex formation ($\text{B}(\text{HX})_2$)	$\text{p}K_a^{\text{BH}^+} - \text{p}K_a^{\text{HX}} + \text{p}K_f^{\text{B}(\text{HX})_2} \geq 1$, and $\text{p}K_a^{\text{BH}^+} - \text{p}K_a^{\text{HX}} + \text{p}K_d^{\text{BHX}} \geq 9$
Dimerization of the acid (formation of $(\text{HX})_2$)	$\text{p}K_a^{\text{BH}^+} - \text{p}K_a^{\text{HX}} + \text{p}K_d^{\text{BHX}} \geq 9$ and $K_f^{(\text{HX})_2} < 10^5$

In comparison to solvents with higher dielectric constants, the solvents belonging to the Brønsted classes 5–8 offer some special advantages in acid–base titrations. For the same titration accuracy, the difference between the pK_a values of the acid and the protonated base can be much smaller, which makes it possible to use mild stable titrants. Homoconjugation as well as triple ion formation does not much affect the accuracy of the titrations.

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SUMMARY

From a comparison of the pK_a values of various compounds in the solvents 1,2-dichloroethane, *m*-cresol, acetic acid and pyridine, the differences in basicity of these solvents could be determined. If the basicity of 1,2-dichloroethane is taken as 0 pK units, the basicities of *m*-cresol, acetic acid and pyridine were found to be 3, 7 and 11 pK units, respectively. It is shown how these differences in basicity can serve to predict pK_a values in solvents belonging to the Brønsted classes 5–8. Theoretical titration curve calculations gave the conditions for the equilibrium constants under which the acid–base titration accuracy is $\pm 0.10\%$:

(a) simple dissociation:

$$pK_a^{BH^+} - pK_a^{HX} + pK_d^{BH^+X} \geq 9$$

(b) differential titration of two acids HX and HY:

$$pK_a^{HY} - pK_a^{HX} + |pK_d^{BH^+X} - pK_d^{BH^+Y}| \geq 6 \text{ and } pK_a^{BH^+} - pK_a^{HY} + pK_d^{BH^+Y} \geq 9$$

RÉSUMÉ

Une étude est effectuée sur des titrages acide–base dans des solvants, de constante diélectrique relativement faible. Des calculs basés sur une courbe de titrage théorique ont donné les conditions pour des constantes d'équilibre, offrant $\pm 0.10\%$ d'exactitude, de titrage acide–base:

dissociation simple:

$$pK_a^{BH^+} - pK_a^{HX} + pK_d^{BH^+X} \geq 9;$$

titrage différentiel de deux acides HX et HY:

$$pK_a^{HY} - pK_a^{HX} + |pK_d^{BH^+X} - pK_d^{BH^+Y}| \geq 6 \text{ and } pK_a^{BH^+} - pK_a^{HY} + pK_d^{BH^+Y} \geq 9$$

ZUSAMMENFASSUNG

Durch Vergleich der pK_a -Werte verschiedener Verbindungen in den Lösungsmitteln 1,2-Dichloräthan, *m*-Kresol, Essigsäure und Pyridin konnten die Differenzen in der Basizität dieser Lösungsmittel bestimmt werden. Wenn die Basizität von 1,2-Dichloräthan gleich 0 pK-Einheiten gesetzt wird, ergeben sich für *m*-Kresol, Essigsäure und Pyridin die Basizitäten 3, 7 und 11 pK-Einheiten. Es wird gezeigt,

wie diese Basizitätsunterschiede dazu dienen können, die pK_a -Werte in Lösungsmitteln vorherzusagen, die den Brønsted-Klassen 5–8 angehören.

Theoretische Berechnungen der Titrationskurven ergaben die Bedingungen für die Gleichgewichtskonstanten, unter denen die Genauigkeit der Säure-Base-Titration $\pm 0.10\%$ ist:

einfache Dissoziation:

$$pK_a^{BH^+} - pK_a^{HX} + pK_d^{BHX} \geq 9;$$

differentielle Titration zweier Säuren HX und HY:

$$pK_a^{HY} - pK_a^{HX} + |pK_d^{BHX} - pK_d^{BHY}| \geq 6 \text{ und } pK_a^{BH^+} - pK_a^{HY} + pK_d^{BHY} \geq 9.$$

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