

Determination and strength of bases in methyl isobutyl ketone

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The equilibrium constants (dissociation and relative basicity constants) of the derivatives of benzo(*a*)phenoxazone in methyl isobutyl ketone were determined. The investigated compounds were used as indicators in visual and photometric titrations of weak bases (comparable to *p*-nitroaniline as regards basicity) in methyl isobutyl ketone. The results have been confronted with some data obtained by potentiometric titrations.

Были определены равновесные константы диссоциации и относительной основности производных бензо(*a*)феноксазона в метилизобутилкетоне. Изученные соединения были использованы в качестве индикаторов визуального и фотометрического титрования слабых оснований (сравнимых с основностью *p*-нитроанилина) в метилизобутилкетоне. Результаты были сравнены с данными потенциометрического титрования.

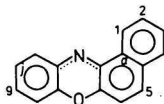
Methyl isobutyl ketone (4-methylpentanone-2; MIBK) was already twenty years ago recommended as an outstanding differentiating solvent [1]. But only the further basic study of this solvent [2] enabled the authors to calibrate a cell with liquid junction in operational acidity scale and laid the foundation for investigating acid-base equilibria in MIBK. The use of the solvent for neutralization titrations involves for the present the determination of several acids though the situation is complicated by homoconjugation. The determination of bases in MIBK is, to a certain extent, described in the introductory paper [1] (derivatives of pyridine) and moreover, some alkaloids [3], aliphatic amines [4—6], aromatic and heterocyclic amines, and derivatives of urea [7] were titrated. On the whole, the determinations were carried out potentiometrically. The convenient indicators were almost not tested.

The aim of this study was to determine the equilibrium constants of some indicators and propose their practical test for the determination of some model bases by visual and photometric titrations.

Experimental

Chemicals, agents, and instruments

The indicators were prepared [8—11] in laboratory and all of them were derived from benzo(*a*)phenoxazine skeleton



DEABP	9-diethylamino-5-benzo(<i>a</i>)phenoxazine [8]
HBP	2-hydroxy-9-benzo(<i>a</i>)phenoxazine [9]
MBP	2-methoxy-9-benzo(<i>a</i>)phenoxazine [9]
ABP	2-acetoxy-9-benzo(<i>a</i>)phenoxazine [9]
BP	9-benzo(<i>a</i>)phenoxazine [10]
DBP	5-dibenzo(<i>a,j</i>)phenoxazine [11]

The titrated bases were products of Lachema, BDH; Fluka; Koch-Light and mostly anal. grade chemicals or products of pharmacopoeial quality.

Antipyrine, used as standard, was recrystallized from ethanol, dried and kept over P_2O_5 . 2,4-Dibromoaniline (Koch-Light), chemically pure, used as standard base for the determination of relative basicity constants was not more purified and its content was determined by repeated potentiometric titration.

MIBK was purified as described earlier [12].

The 0.1 and 0.01 mol dm^{-3} solutions of $HClO_4$ in acetic acid were prepared in anhydrous form by adding the calculated amount of acetic acid anhydride [13].

The buffer solution used for calibration of the electrode system was obtained by mixing equal parts of the 10^{-2} mol dm^{-3} solution of picric acid and 2×10^{-2} mol dm^{-3} solution of tetraethylammonium picrate. The value $pH^* = 10.56$ was calculated from the dissociation constants given in literature [2]. In contrast to preceding authors, the equimolar mixture which does not have the ideal buffer capacity because of incomplete salt dissociation was not used.

The spectrophotometric measurements were performed with a spectrophotometer Unicam SP 1800 adapted for simultaneous measurement of absorbance and pH [14] in nonbuffered solutions. The cells of 3.5 cm width (content 100 cm^3) were thermostatted (25°C) and equipped with a teflon cap through which a glass electrode (Beckman No. 40495), calomel electrode (Laboratorní přístroje, Prague) filled with a saturated solution of KCl in methanol, tip of an automatic burette Radiometer ABU 12 (2.5 cm^3), and teflon inlet of nitrogen were inserted. The mixing was accomplished by an intensive stream of nitrogen after each addition of agent. The potentials were measured with a pH-meter Radiometer PHM-26 using an expanded scale.

The potentiometric titrations were carried out automatically either with a digital system Radiometer (ABU 13, pH-meter PHM-64, printer) or with a recording system (ABU 12, PHM-26, recorder SBR-2, titration unit TTT 11).

A burette ABU 12 was used for titrations with indicators.

Absorption spectra

The spectra of both coloured forms of indicators were measured against a pure solvent in the region 370—710 nm in an inert nitrogen atmosphere. The absorption curve of the neutral form was recorded in pure solvent while the absorption curve of the protonated form was recorded after such an addition of $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ that the value of absorbance in the maximum did not change. The basic data are given in Table 1.

Dissociation constants of indicators

100 cm^3 of the approximately $10^{-5} \text{ mol dm}^{-3}$ solution of indicator in MIBK were put into the measuring cell and the electrode system (calibrated immediately before and after measurement by means of the picrate buffer solution) was inserted. The solution was washed and stirred with CO_2 and H_2O free nitrogen. Then the solution of $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$ was added in small doses. After each addition, the solution was stirred and the potential and absorbance were read. The absorbance was corrected for volume change by usual method. The obtained values of potentials were corrected by the difference between $E(S)$ and the mean of the values of the picrate buffer solution before and after one set of measurements \bar{E}_{pi}

$$E(X) = E - \Delta E = E + E(S) - \bar{E}_{\text{pi}} \quad (1)$$

The values of pH^* , HNP, and $\text{p}K_{\text{IH}^+}$ were calculated from the data thus obtained according to eqns (2—4)

$$\text{pH}^* = 10.56 + \frac{E(S) - E(X)}{59.16} = 10.56 + \frac{324 - E(X)}{59.16} \quad (2)$$

$$\text{HNP} = E(X) - 59.16 \log \frac{|A - A_2|}{|A_1 - A|} \quad (3)$$

$$\text{p}K_{\text{IH}^+} = \text{pH}^* + \log \frac{|A - A_2|}{|A_1 - A|} = \text{pH}^* + \frac{E(X) - \text{HNP}}{59.16} \quad (4)$$

where 10.56 is the pH^* value of the picrate buffer solution and $E(S)$ is the value of electromotive force of the cell corresponding to this pH^* . The symbols $E(X)$, HNP, A , A_1 , and A_2 stand for corrected value of electromotive force measured in a given solution, potential of half neutralization, absorbance of the investigated solution at a certain analytical wavelength (AWL), absorbance of the pure acid form of indicator, and absorbance of the pure basic form of indicator at equal overall concentration and equal AWL, respectively. In the course of measurements of the whole series, the values of \bar{E}_{pi} varied in the range $324 \pm 2 \text{ mV}$. A set of absorption curves of the indicator ABP is represented in Fig. 1.

The measured and calculated values were used for calculating the dissociation constants for each addition of $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$ and each selected AWL. The set of the values of K_{IH^+} found for particular indicators was subjected to statistical evaluation [15], some stray

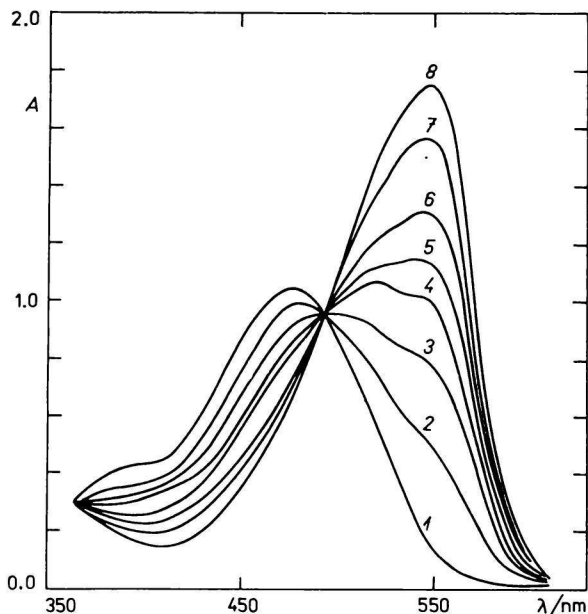


Fig. 1. Absorption curves of the indicator ABP as a function of pH*.

1. pH* = 15.55 (neutral form I); 2. pH* = 5.93; 3. pH* = 5.61; 4. pH* = 5.44; 5. pH* = 5.39; 6, 7, 8. pH* cannot be reliably determined; 8. acid form IH*.

results were eliminated by the *T* criterion and the arithmetic mean as well as the estimation of the standard deviation was calculated.

The dissociation constants of benzo(*a*)phenoxazones thus obtained, the selected AWL, and the colour changes accompanying protonation are given in Table 2.

Relative basicity constants

The determination of these constants was performed analogously, *i.e.* spectrophotometrically with the described equipment. In contrast to the measurements of dissociation constants, the buffer systems were used without potentiometric checking. Antipyrine—antipyrine perchlorate and 2,4-dibromoaniline—2,4-dibromoaniline perchlorate were used as buffer systems.

100 cm³ of the approximately 10⁻⁵ mol dm⁻³ solution of indicator prepared in 5 × 10⁻³ mol dm⁻³ solution of free base (antipyrine or 2,4-dibromoaniline) in MIBK were spectrophotometrically titrated with 0.1 mol dm⁻³ HClO₄. The absorbances were corrected with respect to volume changes which were significant. Antipyrine is a relatively strong base and was applied only to determination of the relative basicity constant of DEABP (0.14 ± 0.03).

The relative basicity constants for selected AWL were calculated from the following equation

$$K_{\text{rel}} = \frac{|A - A_2| c_B}{|A_1 - A| c_S} \quad (5)$$

where the instantaneous concentrations of free base c_B and formed salt c_S were calculated for each point from the consumption of titrating agent s , its molarity and titre, initial concentration of base c_B^0 , initial volume (100 cm^3), and instantaneous volume V by means of the equation

$$c_S = \frac{sMf}{V}; \quad c_B = \frac{c_B^0 100}{V} - c_S \quad (6)$$

A few absorption curves of the indicator HBP are presented in Fig. 2 and Table 3 contains the values of relative basicity constants of indicators with respect to 2,4-dibromoaniline.

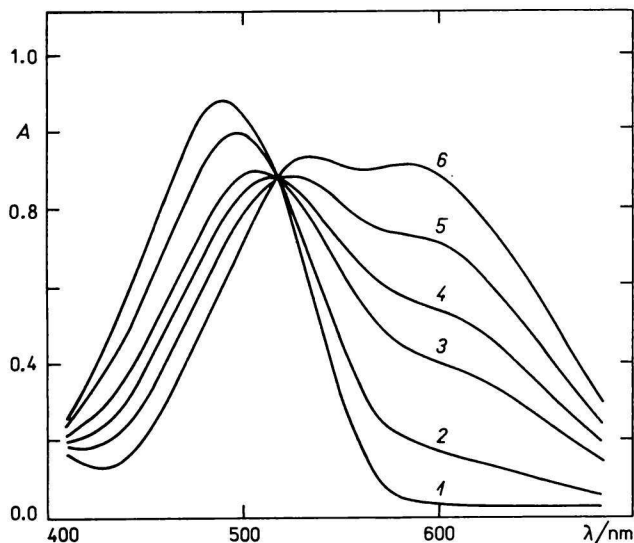


Fig. 2. Absorption curves of the indicator HBP as a function of c_B/c_S .

c_B — concentration of 2,4-dibromoaniline; c_S — concentration of the perchlorate of 2,4-dibromoaniline.

c_B/c_S : 1. $\gg 1$; 2. 2.30; 3. 0.32; 4. 0.14; 5. 0.03; 6. 0.0.

Determination of model bases

The amount of 5×10^{-5} — 2×10^{-4} moles of base was dissolved in 25 cm^3 of MIBK and titrated with the 0.1 mol dm^{-3} solution of HClO_4 (in anhydrous acetic acid) either

potentiometrically or with indicator. The blank experiment with individual indicators and 25 cm³ of solvent varied in the range 0.001—0.003 cm³. These values were always subtracted. The indicators were selected according to the equivalence potentials found potentiometrically and the HNP values of indicators. The titrations were carried out in an inert nitrogen atmosphere. The couple of electrodes, glass electrode (Radiometer G 202 B)—calomel electrode (filled with the saturated solution of KCl in methanol), was used for potentiometric determinations. Before each series of titrations, the electrode system was again calibrated with the picrate buffer (pH* = 10.56) the electromotive force of which varied within the range 340 ± 10 mV during all titrations (the glass electrode used for titrations was different from that used for the determination of p*K*_{TH}⁺). The strength (p*K*_A) of the titrated bases was estimated from the values of HNP read from the printer or graph by means of the equation

$$\text{p}K_A = 10.56 + \frac{340 - \text{HNP}}{59.16} \quad (7)$$

The calculated values of p*K*_{AA} and the obtained values of HNP are listed in Table 4. Table 5 contains the results of visual and potentiometric titrations of some bases in MIBK. The potentiometric titration curves are presented in Fig. 3.

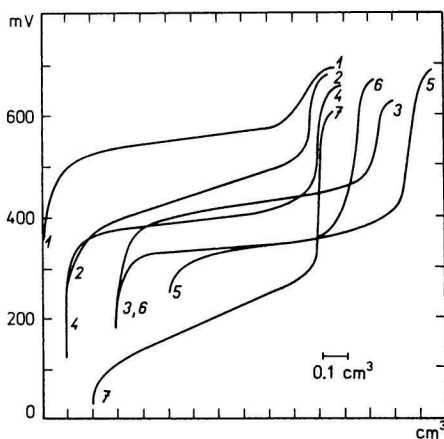


Fig. 3. Titration curves of bases in MIBK.

1. 2-Chloroaniline; 2. antipyrine;
3. amide of nicotinic acid; 4. aniline;
5. acridine; 6. 4-methoxyaniline;
7. brucine.

For the determination of very weak bases (e.g. 2,4-dibromoaniline) we used photometric titrations. In this case, the weighed amount of base (approximately 1×10^{-4} moles) was dissolved in 100 cm³ of a solution of indicator in MIBK. On each addition of titrating agent, the absorbance at a selected AWL was ascertained. The indicators used, their concentrations and selected AWL are quoted in Tables 1 and 3. The results were graphically evaluated and are together with the values of relative basicity constants determined graphically and numerically from these photometric titrations given in Table 6.

Results and discussion

By comparing the spectra of benzo(*a*)phenoxazine and its derivatives (Table 1), we may draw some conclusions about the influence of structure of these substances on the shift in absorption bands. The condensation of another benzene ring with the fundamental skeleton results in a hypsochromic shift and splitting of the long-wave band of the neutral form of 5-dibenzo(*a,j*)phenoxazine while

Table 1

Absorption characteristics of benzo(*a*)phenoxazines in MIBK

Indicator	$c \cdot 10^5$ mol dm ⁻³	I λ_{\max} nm	($\epsilon \cdot 10^{-3}$)	$\lambda_{\text{isob.}}$ nm	IH ⁺ λ_{\max} nm	($\epsilon \cdot 10^{-3}$)
DEABP	0.60	530	(42.5)	560	596 637	(45.2) (49.2)
HBP	1.00	492	(18.2)	514	530 586	(16.8) (15.1)
MBP	1.70	485	(18.4)	506	545	(19.4)
ABP	1.85	476	(16.2)	494	547	(28.2)
BP	1.45	480	(14.2)	500	516 sh 550	(18.5) (26.2)
DBP	1.48	457 sh 475	(15.4) (16.6)	490	534 sh 565	(22.7) (26.2)

a bathochromic shift appears in the spectrum of the acid form. This effect brings about a separation of the absorption maxima of both coloured forms and an improvement in the indicator properties of DBP when compared with BP. In the series of derivatives with different substituents in position 2, the least change is to be observed in position of the absorption bands of ABP (in comparison with BP) because only a very small hypsochromic shift in the long-wave band of the spectra of both forms appears. More conspicuous changes are exhibited by both coloured forms of MBP and HBP. As for HBP, an extension and disintegration of the long-wave band of the acid form appears, which brings about an improvement of the indicator properties of this derivative. From the view-point of contrast of the colour changes, the most convenient indicator is DEABP which manifests a distinct separation of absorption bands of the neutral and acid form.

The reliability of determination of dissociation constant decreases with decreasing basicity of indicator (Table 2). In the presence of very weak bases, the potential surpasses the value of 770 mV and does not change any more. After a certain period of time, the potential starts to decrease. It means that the glass electrode

Table 2

Dissociation constants of benzo(*a*)phenoxazones in MIBK (25°C)

Indicator	Colour change	AWL nm	HNP mV	pK_{IH^+}
DEABP	Red—blue	530, 596, 637	517	7.30 ± 0.07
HBP	Orange—blue violet	492, 530, 586	615	5.64 ± 0.11
MBP	Yellow orange—red violet	485, 545	685	4.46 ± 0.32
ABP	Orange—violet	476, 547	(632) ^a	$(5.35 \pm 0.04)^a$
BP	Orange—red violet	—	>700	—
DBP	Yellow—blue violet	—	>700	—

a) Unreliable data.

loses response. We do not think that the solvent decomposes because it remains clear. That is also confirmed by the “spectrophotometrically pure” equilibrium of ABP (Fig. 1). The obtained low mean value of HNP due to instability of the potential during measurement could suggest that the 2-acetoxy derivative should be more basic than the 2-methoxy derivative of 9-benzo(*a*)phenoxazone. That is, however, in contradiction with the idea of the effect of two functional groups upon acidity. The acetoxy group has a positive Hammett constant σ for both *m* and *p* substitution in the benzene ring which, in a measure, means that the inductive contribution as well as the sum of inductive and mesomeric contribution causes a decrease in electron density in the reaction centre. ABP ought to be a weaker base than the nonsubstituted BP in contrast to HBP and MBP in which the substituents have opposite effect (they raise electron density). The value of pK_{IH^+} found for ABP (5.35 ± 0.04) must be regarded as unreliable.

The values of pK_{IH^+} were not determined for BP and DBP and the comparison of basicities was founded on the relative basicity constants in the sense put forward by Higuchi [13, 16, 18, 19]. Table 3 shows that the basicity of indicators, in this case,

Table 3

Relative basicity constants of benzo(*a*)phenoxazones with respect to 2,4-dibromoaniline in MIBK (25°C)

Indicator	AWL nm	K_{rel}
DEABP	530, 596, 637	31.4 ± 9.6
HBP	492, 564, 582	0.42 ± 0.05
MBP	544	0.32 ± 0.09
ABP	546	0.04 ± 0.01
BP	550	0.07 ± 0.03
DBP	475, 534, 565	<0.01

decreases in the expected order. For the indicators ABP, BP, and DBP, it would be more convenient to use a weaker reference base than 2,4-dibromoaniline. However, the experiments were not successful because the basicity of MIBK was comparable with the basicity of the reference base and a portion of reagent was consumed owing to protonation of solvent. In this case, the amount of the salt formed and the amount of the added HClO_4 cannot be considered identical.

The values of $\text{p}K_{\text{A}}$ given in Table 4 are evidently somewhat higher than the real ones because of incomplete dissociation of the salts in MIBK. The value found for the anilinium ion is, however, in good agreement with literature [2] and the dissociation constants of all salts in the series of the substituted anilines may be almost equal because the linearity of the Hammett equation in MIBK is not impaired

$$\log K_{\text{A}} = 3.08 \sigma - 9.63 \quad (8)$$

(the value of regression coefficient $r_k = 0.995$, deviation of the slope $s_b = 0.150$, deviation of the point of intersection $s_a = 0.082$).

The slope $\rho = 3.08$ in MIBK is only a little greater than in water ($\rho = 2.77$) and thus shows that the differentiating effect of MIBK in the series of substituted

Table 4

Strength of bases in MIBK (25°C)

Compound	HNP mV	$\text{p}K_{\text{A}}$	$\text{p}K_{\text{a}}(\text{H}_2\text{O})^a$	$\Delta\text{p}K$
Brucine	196	12.9	7.96	5.0
Acridine	359	10.2	4.11	6.1
Amide of nicotinic acid	429	8.9	—	—
Antipyrine	420	9.2	—	—
4-Methoxyaniline	332	10.7	5.34	5.3
4-methylthylaniline	354	10.2	5.07	5.1
Aniline	391	9.63 ^b	4.60	5.0
4-Fluoroaniline	407	9.4	4.65	4.8
4-Bromoaniline	458	8.6	3.88	4.7
3-Chloroaniline	469	8.4	3.52	4.9
3-Nitroaniline	526	7.4	2.45	5.0
4-Nitroaniline	612	5.9	1.00	4.8
2-Chloroaniline	543	7.1	3.64	4.5
2,4-Dibromoaniline	568	6.6	—	—

a) Values for the substituted anilines taken from Ref. [17]; b) the value quoted in Ref. [2] is 9.60.

Concentrations of the titrated substances varied in the range 1×10^{-3} — 8×10^{-3} mol dm⁻³.

Number of parallel determinations is 10 for antipyrine and 3 for other substances.

anilines is by far not so distinct as it is in the series of noncharged acids of the type HA [12]. The difference between the pK_A values of the type BH^+ in MIBK and water is in agreement with literature in the range of 5–6 units. The substitution in *ortho* position raises the acidity more than it is in water which is made evident not only by ΔpK found for 2-chloroaniline but also by the difference calculated according to literature [2] for 2-nitroaniline ($\Delta pK = 3.56$). The linear relationship between HNP (MIBK) and $pK_{BH^+}(H_2O)$ values in the group of the derivatives of aniline is represented in Fig. 4.

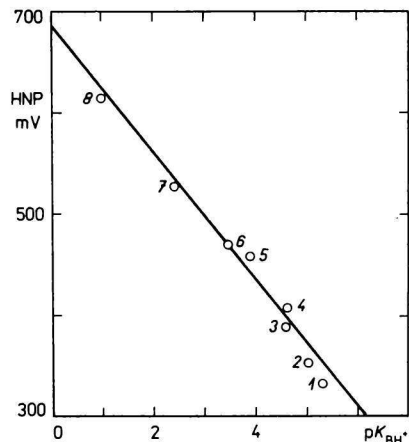


Fig. 4. Dependence of HNP (MIBK) on $pK_{BH^+}(H_2O)$ for the derivatives of aniline.

1. 4-Methoxyaniline; 2. 4-methylaniline;
3. aniline; 4. 4-fluoroaniline;
5. 4-bromoaniline; 6. 3-chloroaniline;
7. 3-nitroaniline; 8. 4-nitroaniline.

$$\text{HNP (MIBK)} = -62.8 pK_{BH^+}(H_2O) + 683.3$$

$$(r_k = -0.991).$$

The value of K_{rel} corresponding to a certain couple indicator—base was calculated from the course of photometric titrations by means of eqn (5) and the method of graphical evaluation [20, 21] was chosen according to the magnitude of that quantity. Provided $K_{rel} > 0.05$, the ratio $[I]/[IH^+]$ was plotted against reciprocal value of the consumption of titrating agent. The section on the axis of ordinates corresponds to $-1/K_{rel}$. For instance, the determination of 2,4-dibromoaniline by means of the indicator HBP (Fig. 5) was evaluated in this way. If the indicator ABP

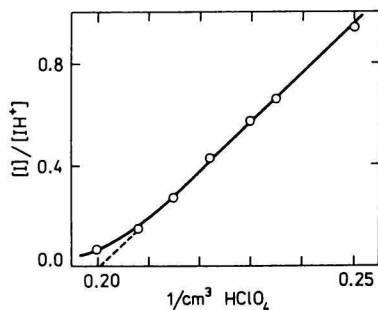


Fig. 5. Photometric titration of 2,4-dibromoaniline to HBP ($K_{rel} = 0.29$).

is applied to equal aim, it holds $K_{rel} < 0.05$ and we may immediately represent the dependence of $[I]/[IH^+]$ on the consumption of titrating agent. The section on the axis of ordinates gives $1/K_{rel}$. The indicator DBP is much weaker than the titrated 2,4-dibromoaniline and the linear change in concentration ratio of its coloured forms sets in behind the point of equivalence. In graphical processing, we must plot the indicator ratio $[IH^+]/[I]$ against consumption of acid titrant.

The results of potentiometric determination of model bases in MIBK are compared with titrations by means of indicators in Table 5. The results evaluated by the t test show that HBP is the most convenient indicator for the determination of antipyrine, amide of nicotinic acid, *p*-toluidine, and aniline, DEABP for brucine, amidopyrine, and acridine, and MBP for 4-bromoaniline. Even the indicator ABP is a too strong base for the determination of 3-nitroaniline and 2,4-dibromoaniline. Other bases which were weaker than 3-nitroaniline gave very low potential jumps even in potentiometric titrations in MIBK. For this reason,

Table 5

Results of determination of bases in MIBK

Compound	Weighed amount mg	Found ^a %	Found ^b %	Indicator ^c
Antipyrine	10—40	100 ^d	99.84 ± 0.35	HBP
			100.95 ± 0.57	MBP
			100.77 ± 0.17	ABP
Brucine 2H ₂ O	15—60	—	100.23 ± 0.13	DEABP
Acridine	7—35	98.32 ± 2.12	99.06 ± 1.58	DEABP
			100.44	MBP
Amide of nicotinic acid	6—20	98.95 ± 0.95	99.02 ± 1.33	HBP
Amidopyrine	10—40	—	100.76 ± 0.78	DEABP
4-Methoxyaniline	6—20	96.27 ± 0.36	96.17 ± 0.50	DEABP
4-Methylaniline	7—20	99.83 ± 1.14	99.08 ± 0.46	DEABP
			99.53 ± 0.66	HBP
Aniline	5—20	98.73 ± 0.12	99.46 ± 0.19	HBP
			99.99 ± 0.38	MBP
4-Fluoroaniline	5—20	97.75 ± 0.72	—	—
4-Bromoaniline	10—35	91.73 ± 0.20	91.80 ± 0.91	MBP
3-Chloroaniline	6—20	97.42 ± 1.35	—	—
3-Nitroaniline	7—25	98.50 ± 1.08	96.90 ± 2.34	ABP
4-Nitroaniline	7—25	98.36 ± 1.44	—	—
2-Chloroaniline	6—20	100.40 ± 1.43	—	—
2,4-Dibromoaniline	15—50	100.05 ± 1.16	94.77	ABP

a) Potentiometric titration; b) titration to indicator marked with c; c) colour changes of indicators see in Table 2; d) standard for determination of the titre of reagent.

Number of parallel determinations 3—6; interval of reliability from variation range.

2,4-dibromoaniline was determined by photometric titration. The results thus obtained have shown (Table 6) that the precision of determination is considerably dependent on the choice of indicator and method of evaluation. The graphical representations have usually "sigmoid" form, the linear sections are short and a correct putting of the extrapolating straight line is not easy. Therefore we did not succeed in finding convenient conditions for the photometric titration of 4-nitroaniline in MIBK. DBP appears to be the best indicator for the photometric titration of 2,4-dibromoaniline. It is a so weak base that the colour change turns up as far as behind the point of equivalence.

Table 6

Determination of 2,4-dibromoaniline by photometric titration in MIBK

Indicator	Found. %	K_{rel}	
		calc	graph
HBP	100.82	0.29	0.26
MBP	104.03	0.27	0.26
BP	101.69	0.065	0.06
ABP	101.92	0.045	0.04
DBP	100.06	—	—

The values of K_{rel} obtained from equilibrium measurements (Table 3) and photometric titrations (Table 6) are different, which is caused by different concentrations of the reference base (2,4-dibromoaniline). But the order of indicators according to basicity and the relations between them remain preserved.

In conclusion, we may state that MIBK is a convenient solvent for potentiometric and visual titration of weak bases. The bounds for successful determination are roughly given by the basicity of *p*-nitroaniline. The resolution power is only a little greater than in water but substantially weaker bases, *e.g.* 2,4-dibromoaniline can be determined by photometric titration in MIBK. But such weak bases as diphenylamine and amides cannot be determined even by this method.

These conclusions are valid for the determination of bases without electric charge. Much more favourable is the situation if anion bases are to be determined because the relative permittivity of solvent plays a more important part in this case. The determination of these substances, present even in mixtures, will be the topic of further study.

References

1. Bruss, B. D. and Wyld, G. E. A., *Anal. Chem.* 29, 232 (1957).
2. Juillard, J. and Kolthoff, I. M., *J. Phys. Chem.* 75, 2496 (1971).
3. Sakurai, H., *J. Pharm. Soc. Jap.* 81, 155 (1961).
4. Miller, M. and Keyworth, D. A., *Talanta* 10, 1131 (1963).
5. Dubois, J. E. and Lacaze, P. C., *C. R. Acad. Sci., Ser. C* 252, 748 (1961).
6. Uhlar, L. and Polievka, M., *Petrochémia* 14, 8 (1974).
7. Schertz, W. L. and Christian, G. D., *Anal. Chem.* 44, 755 (1972).
8. Thorpe, J. F., *J. Chem. Soc.* 91, 324 (1907).
9. Dostál, V. and Ružička, E., *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.* 45, 129 (1974).
10. Fischer, O. and Hepp, E., *Ber.* 36, 1807 (1903).
11. Ružička, E. and Dostál, V., *Monatsh. Chem.* 99, 1915 (1968).
12. Dostál, V., Stránský, Z., and Slouka, J., *Collect. Czech. Chem. Commun.*, in press.
13. Kucharský, J. and Šafařík, L., *Titrace v nevodných prostředích.* (Titrations in Nonaqueous Media.) Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1961.
14. Karliček, R., *Collect. Czech. Chem. Commun.* 40, 3825 (1975).
15. Eckschlager, K., *Chyby chemických rozborů.* (Errors in Chemical Analyses.) Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1961.
16. Higuchi, T. and Connors, K. A., *J. Phys. Chem.* 64, 179 (1960).
17. Larson, J. W. and Hepler, L. G., in *Solute-Solvent Interactions.* (Coetze, J. F. and Ritchie, C. D., Editors.) P. 14. M. Dekker, New York, 1969.
18. Higuchi, T., Rehm, C., and Barnstein, C., *Anal. Chem.* 28, 1506 (1956).
19. Higuchi, T., Feldman, J. A., and Rehm, C., *Anal. Chem.* 28, 1120 (1956).
20. Connors, K. A. and Higuchi, T., *Anal. Chim. Acta* 25, 509 (1961).
21. Rehm, C. and Higuchi, T., *Anal. Chem.* 29, 367 (1957).

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