

Differential Titration of Bases in Glacial Acetic Acid

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Abstract □ A study of bases in acetic acid and their differential titration was carried out. The overall basicity constants for 20 bases were measured in acetic acid, and the differential titration of five binary mixtures of variable ΔpK_b values in acetic acid was followed using a glass electrode-modified calomel electrode system. Agreement with literature values was good. A leveling diagram was constructed that indicated that bases stronger than aqueous pK_b 10 are leveled to an acetous pK_b 5.69, whereas weaker bases are not leveled but instead exhibit their own intrinsic basicity, with the acetous pK_b to aqueous pK_b values being linearly related (slope 1.18, correlation coefficient 0.962). A minimum acetous ΔpK_b of four units is required for the satisfactory differential titration of two bases in acetic acid.

Keyphrases □ Bases—differential titration in glacial acetic acid □ Differential titration—bases in glacial acetic acid

Glacial acetic acid is generally considered to be a leveling solvent for bases, but some weak bases are not leveled in acetic acid. Hall (1) used a chloranil electrode system to obtain acetous half-neutralization potentials and reported a leveling diagram that was a plot of aqueous pK_b values versus acetous base strengths calculated from half-neutralization potentials. Critchfield (2) reported a similar leveling diagram, which was a plot of aqueous pK_a values versus acetous half-neutralization potentials, and stated that a mixture of bases may be differentially titrated if $\Delta pK_{\text{acetous}}$ is 4; however, he provided no data. Fritz (3) stated that a mixture of an aliphatic amine and an aromatic amine cannot be differentially titrated in glacial acetic acid and recommended using dioxane or acetonitrile as the solvent.

More recent work has shown that studies in glacial acetic acid are valid theoretically. Kolthoff and Bruckenstein (4) showed that accurate acetous pK_b values may be calculated from neutralization potentials. These potentials can be measured with a glass electrode-modified calomel electrode system, which has been shown to function theoretically (5). This paper presents studies from which an accurate leveling diagram was constructed and from which a reliable $\Delta pK_{\text{acetous}}$ value for the differential titration of mixtures of bases in glacial acetic acid was established.

EXPERIMENTAL

Chemicals—All chemicals were reagent grade and were used without further purification.

Solutions—Acetous perchloric acid (~0.1 N) was prepared according to the method of Fritz (6) and standardized against potassium biphthalate¹.

Apparatus—The potentials of the cells were measured using a pH meter² equipped with a 20-ohm ($\pm 0.05\%$) resistor across the output resistor terminals. A recorder³ was set at 10 mv full scale and at a chart drive of 5 cm/min. The ground terminals of the pH meter, recorder, automatic constant-rate buret⁴ chassis, and magnetic stirrer⁵ chassis were connected

Table I—Comparison of Aqueous and Acetous Basicity

Compound	Aqueous pK_b^a	Acetous pK_b	ΔpK	Sharpness Index ^b
1 Urea	13.90	— ^c , 10.24 ^d	3.66	—
2 Theophylline	>13	— ^c	—	—
3 2,5-Dichloroaniline	12.43	9.22, 9.17 ^e 9.48 ^d	3.36	0.38
4 <i>p</i> -Aminosalicylic acid	12.22	8.75	3.47	2.18
5 <i>p</i> -Aminobenzoic acid	11.50	8.04	3.46	4.58
6 Benzocaine	11.22	7.53, 7.60 ^e	3.69	6.92
7 Nicotinic acid	10.87	7.01	3.86	4.58
8 Isonicotinic acid	10.74	6.86	3.88	7.35
9 β -Alanine	10.39	5.72	4.67	6.63
10 Triphenylguanidine	9.10	5.55, 5.57 ^e	3.55	12.24
11 Phenanthroline	9.08	4.86	4.22	11.84
12 Asparagine	8.90	6.57	2.33	7.76
13 Pyridine	8.79	6.21, 6.10 ^d	2.58	9.67
14 <i>N,N</i> -Diethylaniline	7.39	5.56 ^e	1.83	—
15 Triethanolamine	6.23	5.00	1.23	10.76
16 Tris(hydroxymethyl)-aminomethane	5.97	6.06 ^e	-0.09	—
17 Benzylamine	4.67	5.95	-1.18	12.24
18 Atropine	4.15	5.93 ^e	-1.78	—
19 Tribenzylamine	—	4.87 ^e , 5.40 ^d	—	14.86
20 Triethylamine	3.25	5.35	-2.10	9.59

^a Data of Perrin (9). ^b Magnitude of the slope of the titration curve (10). ^c Compounds are not titratable in glacial acetic acid. ^d Data of Bruckenstein and Kolthoff (11). ^e Data of Medwick *et al.* (5).

to a common ground. The cell consisted of a 400-ml beaker with a ground-glass cover with openings for the electrodes and buret. The electrodes used were a glass electrode⁶ (stored in distilled water) and a fiber calomel electrode⁷ (stored in glacial acetic acid) modified by replacing the aqueous salt bridge solution with 0.1 M acetous lithium perchlorate.

Procedures and Calculations—The titrations were performed by dissolving ~0.6 mEq of base in 50.00 ml of glacial acetic acid. The electrodes were blotted dry and inserted into the beaker. The initial and final potentials were read from the pH meter, and the end-point potentials were taken from the acetous perchloric acid titration curve described by Medwick and Kirschner (7). The E^0 value for the glass electrode, using

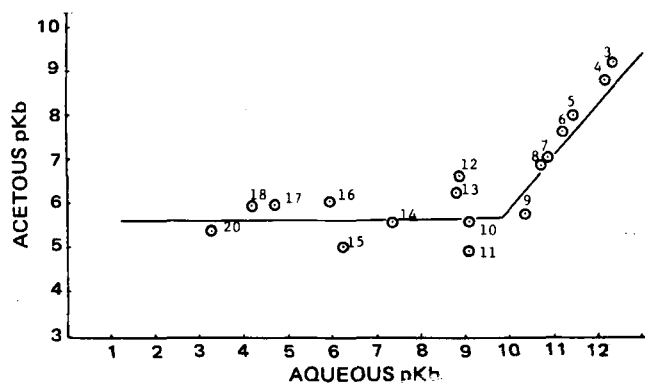


Figure 1—Leveling diagram of bases showing aqueous versus acetous pK_b values. Numbers used for each compound correspond to the numbers in Table I.

⁶ Beckman 39099 E3.

⁷ Corning 476002.

¹ Thorn Smith, Troy, Mich.
² Leeds & Northrup model 7401.
³ Leeds & Northrup Speedomax.
⁴ Sargent model C.
⁵ SGA Magne stir.

Table II—Analytical Results of Study of Differentiation of Bases in Glacial Acetic Acid

Mixture	Component, Purity ^a	pKb _{acetous}	ΔpK	Sharpness Index	Recovery ^a , %
1	Triethanolamine	5.00	1.06	—	— ^b
	Tris(hydroxymethyl)aminomethane	6.06		—	— ^b
2	1,10-Phenanthroline	4.86	2.00	—	— ^b
	Isonicotinic acid	6.86		—	— ^b
3	1,10-Phenanthroline, 102.36 ± 0.63%	4.86	3.18	0.47	107.51 ± 1.06
	p-Aminobenzoic acid, 100.93 ± 0.63%	8.04		4.99	93.14 ± 0.63
4	Tribenzylamine, 101.14 ± 0.19%	5.03	4.14	3.47	101.65 ± 1.05
	2,5-Dichloroaniline, 99.17 ± 0.48%	9.17		1.01	100.34 ± 0.40
5	1,10-Phenanthroline, 102.36 ± 0.63%	4.86	4.31	3.65	100.84 ± 0.39
	2,5-Dichloroaniline, 99.17 ± 0.48%	9.17		1.02	101.11 ± 1.15

^a The mean and standard deviation are given for a group of three analyses. ^b Individual analysis is not possible.

tribenzylamine⁸ as the standard, and the conversions of the end-point potentials to pKb values were calculated as detailed by Medwick *et al.* (5).

RESULTS AND DISCUSSION

Table I compares the aqueous and acetous basicity of the compounds studied. The acetous pKb values were calculated from the mean millivoltage value of three titrations. The variations in the millivoltage values ranged from 2 mv (ΔpKb = 0.04) to 13 mv (ΔpKb = 0.22). In this study, the two weakest bases, urea and theophylline, were not titratable, contrary to the report of Hall (1). Medwick and Scheisswohl (12) showed that theophylline cannot be titrated in glacial acetic acid.

The acetous pKb for urea reported by Bruckenstein and Kolthoff (11) must be considered erroneous since the titration behavior indicates that it is a weaker base than had been reported. Comparisons of other values determined by Bruckenstein and Kolthoff (11) are, with the exception of pyridine, weaker than those reported here. Comparisons of values reported by Medwick *et al.* (5) for three compounds agree very well with the results of this study, as the pK differences indicate: 2,5-dichlo-

roaniline, ΔpK 0.05; benzocaine, ΔpK 0.07; and triphenylguanidine, ΔpK 0.02. This agreement demonstrates the excellent reproducibility of the glass electrode-modified calomel electrode system and shows its superiority to the chloranil electrode system since chloranil is subject to decomposition, precipitation, and the formation of hemiperchlorates (1).

The leveling diagram (Fig. 1) consists of three parts: the horizontal or leveling line, representing the value (pKb_{acetous} 5.69) to which strong bases are leveled; the inflection point (9.67), theoretically 9.24, the aqueous pKb value of acetate; and the line with a slope of 1.180 (correlation coefficient 0.962). Theoretically, the slope of the line is exactly 1.00 since there is no interaction of weaker bases with either solvent, water or acetic acid, and the intrinsic basicity of each compound is observed. The scatter of points may be due to the varied sources for the aqueous pKb values.

To determine the ΔpKb_{acetous} value necessary for differential titration of bases in glacial acetic acid, five binary mixtures with differing ΔpKb values were prepared (Table II). The individual titration curves for each mixture are given in Fig. 2. When the ΔpK is two units or less, only one titration break is seen. At a ΔpK of three units, two breaks are observed, but the quality of the end-point is not very good, as seen from the sharpness index (the magnitude of the slope of the titration curve) (10), and the analytical results show overlap. When the ΔpK is greater than four units, better resolution of components and satisfactory analytical results are obtained since each titration break is sharper.

On the basis of this work, it is concluded that the minimum acetous ΔpKb for satisfactory differential titration of bases in glacial acetic acid is four units. This conclusion agrees with the statement of Critchfield (2).

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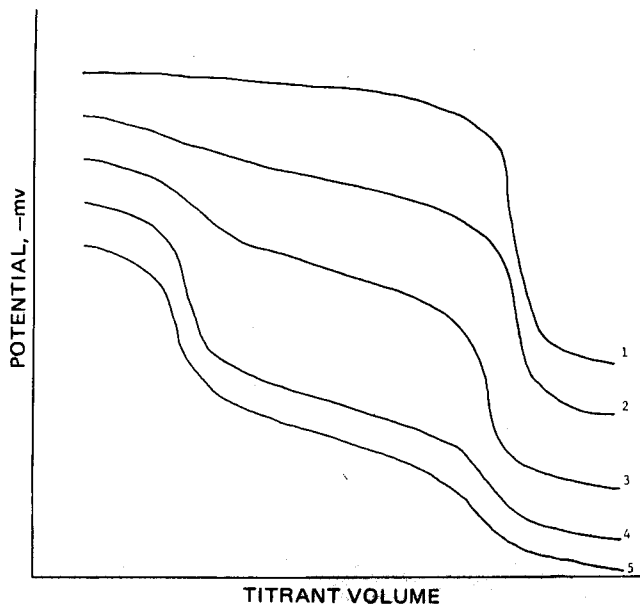


Figure 2—Titrations of five different mixtures of two bases in glacial acetic acid. The individual curves are numbered to identify the mixture titrated using the same numbers as in Table II.

⁸ The melting point (uncorrected) was 93° [lit. (8) mp 92°].