TITRATION OF ORGANIC CATIONS WITH SODIUM TETRAPHENYLBORATE INDICATED BY K^+ ION SELECTIVE ELECTRODE CRYTUR

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Univalent nitrogen-containing organic cations and ammonium salts have been determined by potentiometric titration with volumetric solution of sodium tetraphenylborate. K^+-selective Crytur electrode type 19—15 with polyvinyl chloride membrane and valinomycin as the active compound has proved suitable for indication. In most cases, especially in those of titrations of bulky cations, the potentiometric titration curves show a marked change in the equilibrium voltage and are sufficiently steep towards the titration end. Shape of the titration curves is determined by the electrode selectivity for the given ion and solubility of the respective tetraphenylborate, the symmetry in the charge distribution being significant, too. The investigated titration determination can be classified as a precise analytical method.

Organic compounds containing nitrogen atoms able of protonation form precipitates with tetraphenylborate ion, water solubility of them being very limited. The titration methods based on this behaviour of nitrogen bases used indirect determination of excess tetraphenylborate in most cases (especially the argentometric determination with silver electrode[1,2]). Also a doubly indirect method was suggested[3], the excess of tetraphenylborate being precipitated by a known excess of silver nitrate in aqueous-alcoholic medium, and the excess of silver salt was determined by titration with volumetric solution of sodium chloride. Siska and Pungor[4] suggest, besides silver electrode, also a halogenide ion sensitive electrode for titrimetric determination of excess tetraphenylborate. The first mention of direct titrations of organic bases with sodium tetraphenylborate is perhaps that by Kirsten and coworkers[5]. The authors studied determination of Oxaditon (3-oxapentamethylene-1-triethylammonium-5-ethyldimethylammonium ditartrate) with combined silver and calomel electrodes or combined silver and glass or a second silver electrodes. For determination of the other organic and inorganic ions they recommend an indirect titration consisting in titration of excess tetraphenylborate by Oxaditon reagent. Higuchi, Illian and Tossounian[6] checked experimentally the titrimetric determination of benadryl and dextromethorphan using an electrode with PVC membrane plasticized with N,N-dimethyloleamide. Fukumachi and coworkers[7] published the titration curve of methylephedrine obtained with a ion-selective electrode containing methylephedrine tetraphenylborate as the active component in membrane.

It was found that titrations of inorganic ions[8] (K^+, Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+) and alkaloid cations[9] with volumetric solutions of sodium tetraphenylborate can be indicated by K^+-selective electrode Crytur with PVC membrane containing valinomycin[10] as the active component. Preliminary experiments have shown that this elect-

rode depends also on the concentration changes of univalent ions of protonated organic bases. This paper gives the titration results of a compound set chosen at random.

EXPERIMENTAL

Solutions, Apparatus and Measurement Procedures

Volumetric solution of sodium tetraphenylborate was prepared by dissolving 25 g of the substance (*p.a.*, Lachema) in 500 ml redistilled water. After dissolution, about 5 g alumina (for chromatography) was added, and the bottle content was shaken several times. Next day the solution was filtered and its volume adjusted at 1000 ml. The solution was standardized with thallium nitrate solution using K^+-selective electrode[8].

Stock solutions of the substances to be titrated were prepared from available chemicals, the final concentrations being about 0·1M or 0·01M. The organic bases were transformed into the respective hydrochlorides by addition of hydrochloric acid, the substances available as salts of organic bases were dissolved directly. The used chemicals were from Lachema (ammonium chloride, 1-naphthylamine, phenyltrimethylammonium iodide, hexamethylenetetramine, pyridine and 8-hydroxyquinoline, all of *p.a.* purity grade; Dimethyl Yellow, PAR and Methylene Blue of „indicator" purity grade; Methylene Green and Crystal Violet of „for microscopy" quality), from Fluka (isobutylamine pure, S-benzylthiuronium chloride pract.) and from Kepec (Acridine Orange for microscopy).

The potentiometric cell titration consisted of the ion-selective electrode Crytur type 19—15 and the saturated calomel electrode. Changes in equilibrium voltage of the cell were read from the Precision pH Meter OP-205 (Radelkis, Budapest).

The respective volumes of the solutions of the compounds to be titrated (*i.e.* 5 ml 0·1M or 50 ml 0·01M) were diluted with water to about 70 ml in a 150 ml beaker. The solutions were titrated with 2·5% sodium tetraphenylborate solution added from a burette or from a micro-dose pump type 335A (Unipan, Warszawa).

RESULTS AND DISCUSSION

The ion-selective electrode Crytur with membrane containing valinomycin proved suitable as a universal electrode for titrations of organic cations. However, the potentiometric titration curve does not always have a suitable course for evaluation of the titration end-point. This is the case especially for the titrations of low-molecular aliphatic amines the tetraphenylborates of which are more soluble (for the solubility data see ref.[1]). Table I gives the values of the overall change of equilibrium voltage along with the slope values of the titration curve near its point of inflexion. With increasing mass of the cation the solubility of the corresponding tetraphenylborate decreases, and, consequently, both the steepness and the overall change of the equilibrium voltage increase (see also the examples of titration curves in Figs 1 to 4). Symmetry of charge distribution is significant, too. This point clearly follows from comparison of potentiometric titration curves of Methylene Blue and Methylene Green (Fig. 4). The both dyestuffs are of thiazine type differring only in that the green dyestuff contains one more nitro group (in *o*-position to one of the dimethyl-

amino groups). In the case of titration of Methylene Blue (in which the positive charge distribution is symmetrical) the overall change of the equilibrium voltage is 320 to 340 mV, the slope near the point of inflexion being 70 to 80 mV per 0·1 ml tetraphenylborate. In the case of Methylene Green, where the symmetry of the cation is disturbed by the present nitro group, both the overall change of the equilibrium voltage and the slope near the point of inflexion of the titration curve are smaller.

The titrations of some bulkier ions have a drawback in that the equilibrium voltage is established slowly (especially so near the point of inflexion), which makes the titration longer (up to 45 minutes for Crystal Violet).

On the other hand, in the case of titrations of phenyltrimethylammonium iodide, 8-hydroxyquinoline, S-benzylthiuronium chloride and Acridine Orange it is necessary to wait (about 3 minutes) for the equilibrium voltage only in the region of the point of equivalence, otherwise the voltage is established almost immediately after addition of tetraphenylborate.

TABLE I

Slope and Range of the Potential Jump of the Titration Curves

Titrated substance	Overall change of equilibrium voltage ΔE, mV	Slope[a] near the point of inflexion $\Delta E/\Delta V$, mV/0·1 ml
Ammonium chloride	80	3
Isobutylamine	70	1,4
1-Naphthylamine	150—70	7
Dimethyl Yellow[b]	130	5
Phenyltrimethylammonium iodide	160—70	30
Hexamethylenetetramine	120	4
S-Benzylthiuronium chloride	160	12
Pyridine	120—30	7
8-Hydroxyquinoline	120—40	11
4-(2-Pyridylazo)resorcinol	200—20	5
Acridine Orange[c]	360	70
Methylene Blue[d]	320—40	70—80
Methylene Green[e]	240—80	20—30
Crystal Violet[f]	380	30—40

[a] For 2·5% (*i.e.* about 0·07M) sodium tetraphenylborate solution; [b] 4-dimethylaminoazobenzene, C. I. 11020; [c] N,N,N′,N′-tetramethyl-2,8-diaminoacridine hydrochloride, C. I. 46005; [d] 3,7-bis-(dimethylamino)phenazthionium chloride, C. I. 52015; [e] 3,7-bis-(dimethylamino)-4-nitrophenazthionium chloride, C. I. 52020; [f] hexamethyl-*p*-rosaniline hydrochloride, C. I. 42555.

Titration curves of hexamethylenetetramine (urotropine) showed slight indication of two subsequent jumps, the second one being at the reading corresponding to the weighed amount of the substance. These deformations of the titration curve are

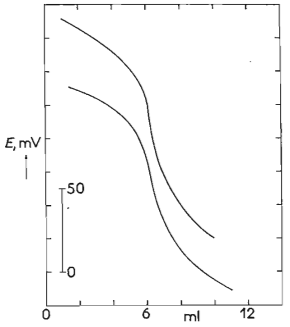

FIG. 1

Potentiometric Titration Curves of c. 0·01M Pyridine with Sodium Tetraphenylborate

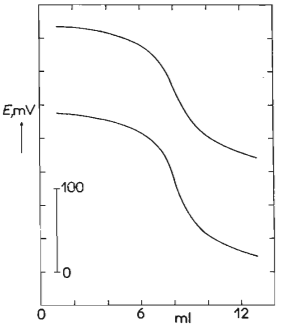

FIG. 2

Potentiometric Titration Curves of c. 0·01M 1-Naphthylamine with Sodium Tetraphenylborate

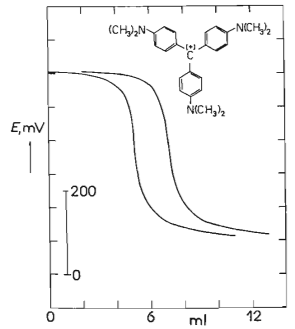

FIG. 3

Potentiometric Titration Curves of c. 0·01M Crystal Violet

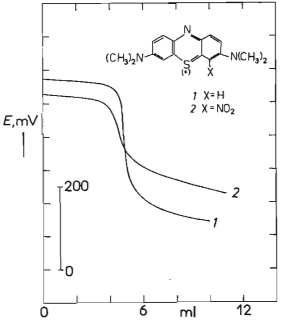

FIG. 4

Potentiometric Titration Curves of c. 0·01M Solutions of *1* Methylene Blue *2* Methylene Green

observed also in those cases when a sufficient excess of hydrochloric acid (to transform hexamethylenetetramine to its cation) was added.

Table II gives a random set of nitrogen substances and their statistical evaluation of titrations of them. From the table it is obvious to see that the titrations with sodium tetraphenylborate using the ion-selective electrode are sufficiently precise, the relative standard deviation being mostly about 1%. However, comparison of the added and the found amounts by means of the Lord test u_0 shows that the differences are statistically insignificant only in the case of two of the titrated compounds. Several other compounds (pyridine, 8-hydroxyquinoline, S-benzylthiuronium chloride, phenyltrimethylammonium iodide) have a higher calculated u_0 value than the respective tabulated one, although the difference between the added and the found amounts is not very large. Even when the weighing was corrected with respect to the substance content declared by the manufacturer (*e.g.* min 99·0% in the case of 8-hydroxyquinoline and phenyltrimethylammonium iodide), the amount calculated from the potentiometric titrations is slightly lower than the weighing. Especially significant diffe-

TABLE II

Statistical Evaluation of Titration Determinations[a]

Titrated substance	Given mg	Found			s_r %	Lord test	
		n	$\bar{x}$ mg	s_R mg		u_0	u_0^{crit}
Ammonium chloride	9·06	4	9·12	0·13	1·47	0·187	0·717
Isobutylamine	25·76	3	19·78	0·44	2·22	7·973	1·304
1-Naphthylamine	77·96	4	73·47	0·98	1·33	2·223	0·717
Dimethyl Yellow	112·65	3	94·17	1·93	2·05	5·657	1·304
Phenyltrimethylammonium iodide	116·61	4	113·37	0·41	0·36	3·839	0·717
Hexamethylenetetramine	64·34	3	63·47	1·12	1·76	0·461	1·304
S-Benzylthiuronium chloride	92·90	5	90·57	0·67	0·74	1·494	0·507
Pyridine	31·85	6	31·14	0·38	1·22	0·737	0·399
8-Hydroxyquinoline	72·22	5	70·07	0·64	0·91	1·444	0·507
4-(2-Pyridylazo)resorcinol	131·35	4	65·68	1·59	2·43	20·060	0·717
Acridine Orange	127·06	3	75·42	0·57	0·75	53·347	1·304
Methylene Blue	125·83	3	97·75	0·49	0·50	33·856	1·304
Methylene Green	182·22	4	97·65	3·30	3·39	12·447	0·717
Crystal Violet	148·90	3	132·91	0·62	0·47	15·232	1·304

[a] n Number of measurements, $\bar{x}$ arithmetic mean, s_R standard deviation calculated from the range R, s_r relative standard deviation; the significance level $\alpha = 0{\cdot}05$ was taken for the Lord's u_0 test (ref.[12]).

rences are observed in titrations of organic dyestuffs, which is obviously due to the technological procedures during their isolation. Content of substances is not declared by the manufacturers, and it is different in substances of various origin or even in various batches of the same manufacturer. A sufficiently reliable reference determination using another independent method (*e.g.* photometry) is then highly influenced by the choice of the standard substance, which is, of course, directly connected with the problem of accuracy of results. However, potentiometric titration curves of organic dyestuffs have the most suitable course in most cases, and, as far as relative standard deviations are concerned, the determinations of *e.g.* Crystal Violet, Methylene Blue or Acridine Orange can be classified as the best reproducible.

The ion-selective electrode Crytur with valinomycin membrane has a great advantage in its low value of the selectivity constant towards the proton, which makes it possible to measure the samples without previous pH adjustment[10]. However, its application for solutions of organic nitrogen bases necessitates a complete transformation of the base into the respective cation (usually addition of hydrochloric acid). This transformation provides also complete dissolution of high-molecular bases in aqueous medium.

Incomplete protonation of the organic base affects (besides its own solubility) the value of the conditional solubility product of the respective tetraphenylborate. Some information about the pH effect on the shape of the potentiometric titration curves can be obtained from titrations of ammonium salts (Fig. 5) with different additions of sodium hydroxide. At higher pH values NH_4^+ ions are partially dissociated, the overall change of the equilibrium voltage decreases, the slope of the curves decreases, and the titration end-point shifts towards lower readings of tetraphenylborate. A similar pH effect was observed also in titrations of pyridylazoresorcinol.

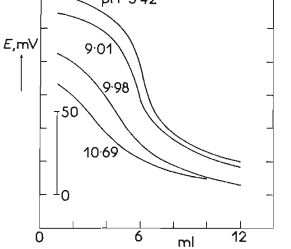

FIG. 5
Effect of pH on Shape of Potentiometric Titration Curves of c. 0·01M Ammonium Chloride with Sodium Tetraphenylborate

If there is a great difference in solubilities of tetraphenylborates of the titrated compounds, their simultaneous determination in one titration becomes possible. *E.g.* titration curves were recorded for a mixture of Dimethyl Yellow and Methylene Blue, the titration end-points corresponded to the readings in the separate determinations. It would be, of course, possible to try titrations of various mixtures, but it is the matter of practical use.

Direct titration of numerous organic nitrogen compounds can be useful in analytical control of starting substances, intermediates and products of organic syntheses. We have done some experiments in this area, too[11]. Titrations with tetraphenylborate indicated with the electrode Crytur 19–15 can also help to solve the problems of determination of contents of basic dyestuffs in commercial products which, besides other, affects unfavourably the studies of their complex formation equilibria in solutions *etc.*

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