

## POTENTIOMETRIC ION-PAIR FORMATION TITRATIONS OF N-ALKYL-N-ETHYLPYRROLIDINIUM CATIONS USING PLASTIC MEMBRANE ELECTRODES

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Cations of the homologous series of N-alkyl-N-ethylpyrrolidinium salts were determined with a good precision by a titration using sodium tetraphenylborate titrant and potentiometric indication with a simple PVC membrane coated-wire electrode. The value of the potentiometric titration break depended on the number of carbon atoms in the alkyl chain. To explain the role of the equilibria involved, the values of both the distribution ratios and the extraction constants as well as the solubility products of N-alkyl-N-ethylpyrrolidinium tetraphenylborates were determined. The value of the titration break could readily be correlated with the logarithmic values of the extraction parameters.

Correlations between the terms of ion-selective electrode potentiometry and the extraction parameters of the ion-pairs used as the electroactive materials in liquid and/or plastic membrane electrodes were studied by numerous authors. For example, Scholer and Simon<sup>1</sup> developed a sensor exhibiting a nernstian response towards "onium" salts, and its selectivity was explained in terms of its extraction properties. In summarizing the selectivity of their dinonylnaphthalene sulfonate electrode, Martin and Freiser<sup>2</sup> have shown the role of solvent extraction in determining the selectivity sequence. In a related series of aliphatic ammonium ions, they observed a regular change of selectivity with the number of carbon atoms in the ion and when they plotted the logarithm of the selectivity coefficient,  $k_{i,j}^{pot}$ , vs the number of carbon atoms in the interfering ion, they obtained a straight line with a slope of  $0.55 \pm 0.10$ , which agreed well with the slope of 0.5 to 0.6 observed for an analogous linear relationship between the logarithm of the extraction constant for quaternary ammonium ion-containing ion-pairs vs the carbon number<sup>3,4</sup>.

In liquid-liquid extraction studies of various anions using methyltricaprylammo-

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nium (Aliquat 336S) salts, values of extraction constants were obtained that showed a one-to-one correspondence between these constants and the electrode selectivity coefficients<sup>5</sup>. In this fashion, systematic selectivity studies of dinonylnaphthalene sulfonate-based coated-wire electrodes were done using tributylammonium as a primary ion<sup>6</sup>. The plots of  $\log k_{i,j}^{\text{pot}}$  vs the carbon number in homologous series of alkylammonium salts were linear, as well as the plots of  $\log k_{i,j}^{\text{pot}}$  vs  $\log D$  (where  $D$  is the distribution ratio of the appropriate ion-pair)<sup>7</sup>. Similarly, Selinger and Staroscik<sup>8</sup> stated the relationship between electrode selectivity and the extraction constant in their extensive study of the electrodes based on strongly associated ion-pairs. Similar studies were recently presented by other authors<sup>9,10</sup>.

When the liquid and/or plastic membrane electrodes are used to monitor the titrations based on ion-pair formation, the magnitude of both the potential break and sharpness at the inflexion point of the titration curve is predetermined by the solubility of the corresponding ion-pair compound and connected also with the extractability of the ion-pair into the membrane solvent. In titrations of organic cations, the solubility of the corresponding ion-pair decreases and consequently both the steepness and the overall change of the potentiometric cell voltage increase with increasing mass of the cation<sup>11</sup>. For example, Smolyakov and coworkers<sup>12</sup> have demonstrated these influences in the titrations of the cations of homologous series of tetraalkylammonium salts. Having used various plasticizers, Haláček et al.<sup>13</sup> have recently shown the correlations between the magnitude of the potentiometric break and the  $\log D$  values in titrations of brucine or atropine with tetraphenylborate. In this paper we report the results obtained in titrations of the cations of the homologous series of N-alkyl-N-ethylpyrrolidinium salts.

## EXPERIMENTAL

### Apparatus

The potentiometric titrations were performed using both manual and automatic procedures. For the manual procedure, an OP-208/1 pH meter (Radelkis, Budapest) was used. The automatic titrations were performed using a titration assembly consisting of the 10-cm<sup>3</sup> automatic burette OP-930/1 and an universal recording titrator OH-407 (both from Radelkis) with a constant rate of the titrant delivery, 0.8 cm<sup>3</sup> min<sup>-1</sup>, and a constant recorder chart speed, 1 cm min<sup>-1</sup>.

The measuring cells consisted of a sensing and a calomel electrode. The sensors of the coated-wire type were prepared as described previously, using either an aluminium conductor<sup>14</sup> or a glass electrode<sup>15</sup> as the support for the membrane, which was obtained from a solution of poly(vinyl chloride) (0.09 g) and a plasticizer (0.2 cm<sup>3</sup>) in tetrahydrofuran (3 cm<sup>3</sup>); 2,4-dinitrophenyl octyl ether (DNPOE), dibutyl phthalate (DBP), or bis(2-ethylhexyl) phthalate (BEHP) were used as the plasticizers. An RCE-102 double-junction calomel electrode (Crytur, Turnov), filled with 0.1M sodium nitrate, was used as the reference half-cell.

The spectrophotometric measurements were performed using a Specord M40 UV-VIS recording spectrophotometer (Zeiss, Jena), equipped with 1-cm quartz cuvettes.

### Solutions

The sodium tetraphenylborate stock solution (approx.  $0.05 \text{ mol dm}^{-3}$ ) was prepared by dissolving about 17 g of the substance (VEB Jenapharm Laborchemie, Apolda) in  $500 \text{ cm}^3$  of distilled water and by adding approx. 5 g of an adsorbent (alumina for chromatography, Lachema, Brno). The solution was allowed to stand, filtered, its pH was adjusted to 8.5 with sodium hydroxide and it was diluted to  $1 \text{ dm}^3$  with water. Before routine use, the stock solution was diluted to obtain an  $0.01 \text{ M-NaBPh}_4$  titrant, which was standardized potentiometrically against standard  $0.01 \text{ M}$  thallium(I) nitrate.

The aqueous solutions of N-alkyl-N-ethylpyrrolidinium salts ( $0.01 \text{ mol dm}^{-3}$ ) were prepared from their bromides; the alkyl chains were hexyl, octyl, nonyl, decyl, undecyl, dodecyl, pentadecyl, hexadecyl and octadecyl. The salts were synthesized by nucleophilic reaction of N-ethylpyrrolidine with the respective 1-bromoalkane<sup>16,17</sup>.

### Preparation of Saturated Ion-Pair Solutions

Saturated aqueous solutions of N-alkyl-N-ethylpyrrolidinium tetraphenylborates were prepared by mixing equimolar ( $0.01 \text{ mol dm}^{-3}$ ) solutions of a particular pyrrolidinium bromide and sodium tetraphenylborate and heating the mixture to  $80^\circ\text{C}$ . After slow cooling, the precipitate was filtered off and washed several times with water to remove any residue of free pyrrolidinium salt or  $\text{NaBPh}_4$ . The precipitate was then dissolved in water on heating to  $80^\circ\text{C}$ , allowed to stand overnight, tempered to  $20^\circ\text{C}$ , and the precipitate filtered off again. The filtrate represented a saturated ion-pair solution.

### Determination of the Solubility Products

The solubility products of the N-alkyl-N-ethylpyrrolidinium tetraphenylborate ion-pairs (QX) were determined by measuring the absorbance values of their saturated aqueous solutions at 266 nm. As only tetraphenylborate ion absorbed at the above wavelength ( $\epsilon_{\text{X}} = 3.19 \cdot 10^2 \text{ m}^2 \cdot \text{mol}^{-1}$ ), the concentration solubility products could simply be obtained from the spectrophotometric measurements. The values determined are listed in Table I.

### Determination of the Distribution Ratios and the Extraction Constants

The distribution ratios were determined by the procedure described earlier<sup>13</sup>, by spectrophotometric evaluation of the distribution equilibrium for the mixture of a saturated ion-pair aqueous solution ( $5 \text{ cm}^3$ ) and an organic phase (the plasticizer of the PVC membranes,  $0.1 \text{ cm}^3$ ). To eliminate the blank (absorbing species dissolved from the organic solvents), the same volumes of the phases were mixed, but distilled water was used instead of the saturated ion-pair solution. All the extractions were carried out in a thermostat at  $20^\circ\text{C}$ . The values of the distribution coefficients as well as the extraction constants were evaluated and calculated from the difference spectrophotometric measurements in the aqueous phase at 266 nm. The results are listed in Tables II and III.

## RESULTS AND DISCUSSION

As expected, the precipitation of substituted pyrrolidinium salts by  $\text{NaBPh}_4$  gives rise to titration curves with well defined end-point potential breaks. The shape of the curves remains approximately the same, but the value of the end-point potential

break increases significantly with increasing number of carbon atoms of the alkyl chain (Fig. 1). Manual and automatic titrations yielded the curves of identical

TABLE I

Mean values of the concentration solubility products (20°C) of N-alkyl-N-ethylpyrrolidinium tetraphenylborates

$n_C^a$	Solubility product, $K_s(QX) \cdot 10^{9b}$
6	3.90 ± 0.18
8	3.39 ± 0.33
9	3.19 ± 0.17
10	2.66 ± 0.08
11	2.58 ± 0.24
12	2.53 ± 0.02
15	2.40 ± 0.20
16	2.27 ± 0.09
18	2.12 ± 0.09

<sup>a</sup> Number of carbon atoms in the N-alkyl chain; <sup>b</sup> given as an interval  $\bar{x} \pm s$  for 5 measurements.

TABLE II

Mean values of the distribution ratios  $D(Q^+)$  of N-alkyl-N-ethylpyrrolidinium ions into different plasticizers

$n_C$	$D(Q^+)$ for organic phases <sup>a,b</sup>		
	DNPOE	DBP	BEHP
6	21.5 ± 2.5	13.5 ± 2.5	13.0 ± 2.0
8	40.2 ± 4.4	26.6 ± 3.2	17.0 ± 1.0
9	40.6 ± 6.2	34.0 ± 3.6	18.4 ± 1.1
10	63.1 ± 7.2	34.9 ± 3.4	25.3 ± 1.2
11	88.8 ± 4.0	42.8 ± 3.0	27.8 ± 1.7
12	116.7 ± 11.8	58.4 ± 5.4	36.8 ± 1.8
15	173.4 ± 12.3	108.3 ± 8.9	70.7 ± 6.0
16	177.9 ± 27.9	122.0 ± 13.2	90.6 ± 11.0
18	199.6 ± 14.2	144.7 ± 15.3	99.5 ± 6.1

<sup>a</sup> DNPOE 2,4-dinitrophenyl octyl ether, DBP dibutyl phthalate, BEHP bis(ethylhexyl) phthalate;

<sup>b</sup> values for 20°C, given as an interval  $\bar{x} \pm s$  for 5 measurements

shape (Fig. 2). In titrations of this homologous series, the increase of the potential break was proportional to the number of carbon atoms of the alkyl chain up to  $n_C = 15$  (Fig. 3).

TABLE III

Mean values of the extraction constants  $K_{ex}(QX)$  of N-alkyl-N-ethylpyrrolidinium tetraphenylborates into different plasticizers

$n_C$	$K_{ex}(QX) \cdot 10^{-6}$ for organic phases <sup>a</sup>		
	DNPOE	DBP	BEHP
6	0.49 ± 0.20	0.27 ± 0.19	0.26 ± 0.15
8	1.25 ± 0.26	0.70 ± 0.19	0.39 ± 0.06
9	1.30 ± 0.54	1.01 ± 0.30	0.44 ± 0.08
10	2.77 ± 0.91	1.15 ± 0.40	0.74 ± 0.13
11	4.85 ± 0.28	1.56 ± 0.20	0.85 ± 0.11
12	7.73 ± 3.67	2.52 ± 1.51	1.27 ± 0.45
15	15.80 ± 1.10	7.00 ± 0.75	3.48 ± 0.48
16	17.03 ± 4.61	8.81 ± 0.18	5.34 ± 1.42
18	21.64 ± 1.91	12.23 ± 2.10	6.46 ± 0.72

<sup>a</sup> See the footnotes in Table II.

TABLE IV

Mean values of the potential titration break ( $\Delta E$ ) in titrations of N-alkyl-N-ethylpyrrolidinium salts with sodium tetraphenylborate

$n_C$	$\Delta E(\text{mV})$ for electrode membrane plasticizers <sup>a</sup>		
	DNPOE	DBP	BEHP
6	296 ± 7	251 ± 4	246 ± 6
8	369 ± 9	332 ± 4	323 ± 11
9	398 ± 10	361 ± 6	350 ± 7
10	429 ± 8	387 ± 7	374 ± 9
11	461 ± 8	415 ± 7	402 ± 4
12	490 ± 3	443 ± 7	426 ± 4
15	581 ± 4	527 ± 9	501 ± 7
16	610 ± 8	547 ± 10	518 ± 11
18	641 ± 6	569 ± 11	542 ± 6

<sup>a</sup> See the footnotes in Table II; support: a glass electrode.

The precision of the titrations was tested using samples of N-octyl-, N-decyl-, N-dodecyl-, and N-hexadecyl-N-ethylpyrrolidinium bromides (a 5-cm<sup>3</sup> portion of a 0.01M solution of a salt and a 45-cm<sup>3</sup> of distilled water was taken to each titration). Except for the N-octyl-derivative, which was highly hygroscopic (the content determined was 96.2 ± 0.6%), the assay values were nearly 99%, with relative standard deviations not higher than ±1% (based on 5 measurements).

In precipitation titrations, it is well known that the magnitude of the potentiometric break is governed predominantly by the solubility product of the precipitate formed. However, when the precipitate is extractable into the membrane mediator, the role of the extraction parameters must also be taken into account (see the differences in the ΔE values for various plasticizers, summarized in Table IV).

A quantitative expression for the precipitation equilibrium is given by the solubility

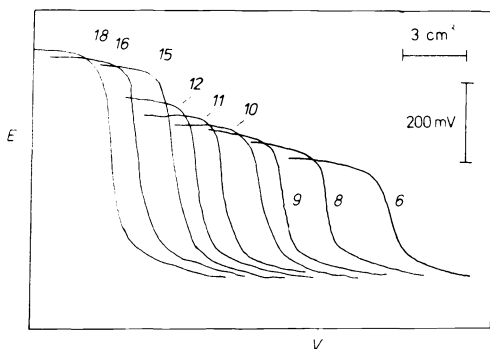


FIG. 1

Automatic potentiometric titrations of N-alkyl-N-ethylpyrrolidinium bromides (c. 0.05 mmol) using sodium tetraphenylborate (9.68 mmol dm<sup>-3</sup>) as the titrant. Volume of solution titrated, 50 cm<sup>3</sup>. The indication coated-wire electrode: PVC membrane plasticized with DNPOE on an aluminium support. The curves are denoted with the number of carbon atoms in the N-alkyl chain

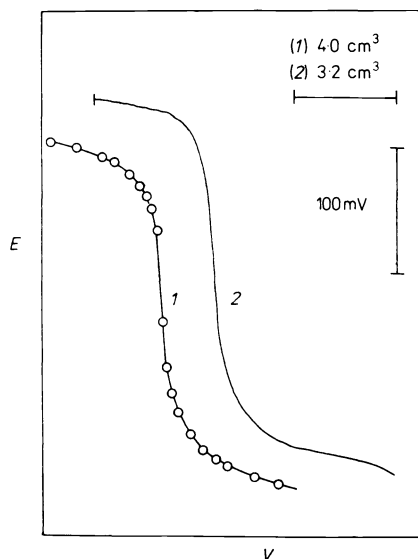


FIG. 2

A comparison of the titration curves for titrations of N-octyl-N-ethylpyrrolidinium bromide (c. 0.05 mmol) with NaBPh<sub>4</sub> (9.68 mmol dm<sup>-3</sup>). The volume of the solution titrated and the indication electrode are the same as in Fig. 1. Titration mode: 1 manual; 2 automatic

product,  $K_s(QX)$ , which is defined by

$$K_s(QX) = [Q^+][X^-]. \quad (1)$$

In the presence of another, immiscible organic solvent, another equilibrium is attained, because the two ions will form an associated ion-pair in a phase of lower polarity<sup>18</sup>



which is characterized by the extraction constant,  $K_{\text{ex}}(QX)$ ,

$$K_{\text{ex}}(QX) = [QX]_{\text{org}} [Q^+]_{\text{aq}}^{-1} [X^-]_{\text{aq}}^{-1}. \quad (3)$$

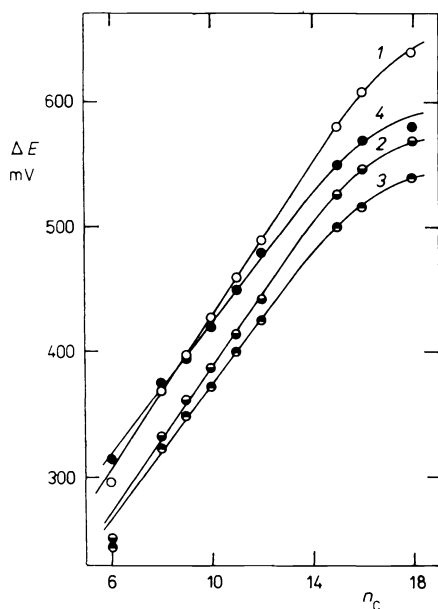


FIG. 3

Dependence of the potential break on the length of the N-alkyl chain in titrations of N-alkyl-N-ethylpyrrolidinium salts. Titration mode: 1, 2, 3 manual; 4 automatic; the support of the indication electrode: 1, 2, 3 glass; 4 aluminium; plasticizer: 1, 4 DNPOE; 2 DBP; 3 BEHP

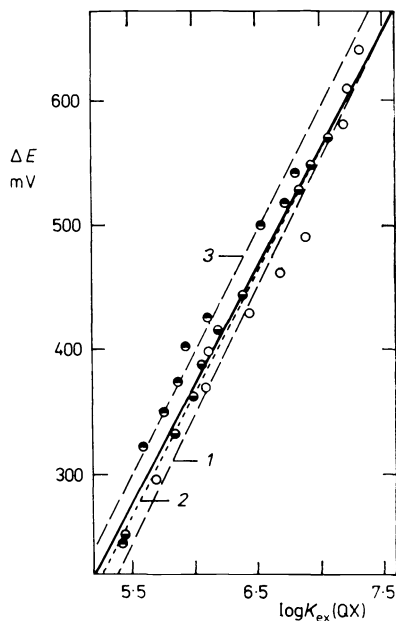


FIG. 4

Relationship between the value of the potential break and the logarithm of the extraction constant of N-alkyl-N-ethylpyrrolidinium tetraphenylborates in titrations monitored with coated-glass electrodes. Plasticizer: 1, ○ DNPOE; 2, ● DBP; 3, ● BEHP; the full line is the regression line for all the plasticizers

The distribution ratio of ion  $Q^+$ ,  $D(Q^+)$ , can be expressed by

$$D(Q^+) = [QX]_{\text{org}} [Q^+]_{\text{aq}}^{-1} = K_{\text{ex}}(QX) [X^-]_{\text{aq}} \quad (4)$$

In the absence of side reactions, the ion-pair concentration in the organic phase (plasticizer) which is in contact with an aqueous suspension of the same ion-pair

TABLE V  
Statistical evaluation of the parameters of the regression lines  $\log K_{\text{ex}}(QX) = a + b \Delta E$

Support	Plasticizer	$a$	$b(V^{-1})$	$r^a$	No.
glass	DNPOE	4.298	4.913	0.983	1
glass	DBP	4.109	5.178	0.998	2
glass	BEHP	3.976	5.120	0.982	3
glass	all 1 to 3	4.038	5.270	0.976	—
aluminium	DNPOE	3.783	6.201	0.989	4
both 1 and 4	DNPOE	4.117	5.381	0.977	—

<sup>a</sup> Correlation coefficient.

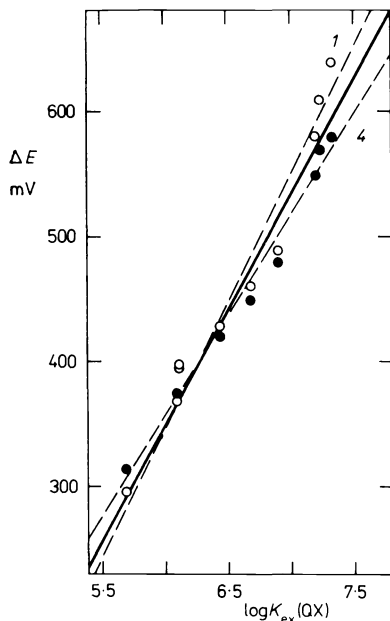


FIG. 5  
Relationship between the value of the potential break and the logarithm of the extraction constant in titrations monitored with DNPOE-plasticized membrane electrodes. Support and the titration mode: 1,  $\circ$  glass, manual titrations; 4,  $\bullet$  aluminium, automatic titration. The curve designation agrees with the data in Table V, the full line is the regression line for both the electrodes



is determined by the two above constants,

$$[\text{QX}]_{\text{org}} = K_{\text{ex}}(\text{QX}) K_{\text{s}}(\text{QX}). \quad (5)$$

This concentration can be considered as that of ion-exchanging sites in the membrane of such a  $\text{Q}^+$ -selective electrode. It follows that this concentration increases with increasing values of both the extraction constant and the solubility product of the ion-pair studied.

The above parameters  $D$  and  $K_{\text{ex}}$  increase with increasing length of the alkyl chain and the dependence is analogous to that for the potential break within a homologous series. Plotting of the  $\Delta E$  values against  $D$  or  $K_{\text{ex}}$  on logarithmic scale yields a linear relationship. In addition, the correlation coefficients for the  $\log K_{\text{ex}}$  vs  $\Delta E$  plot are somewhat higher than those for the  $\log D$  vs  $\Delta E$  plot. These dependences are shown in Fig. 4 for various plasticizers. It is also shown in Fig. 5 that the differences between manual and automatic titration (or for the same electrode membrane coated on different supports) are not significant, taking into account the standard deviations for both the  $\Delta E$  and  $\log K_{\text{ex}}$  values. The parameters of these regression lines are given in Table V.

The correlations between the value of the potential break and the  $\log D$  or  $\log K_{\text{ex}}$  values confirm that the cation titratability depends predominantly on the extraction parameters of the ion-pair formed. It is known that highly hydrophilic substituents, e.g., hydroxyl, carboxyl and amino groups, decrease the extraction constants and, subsequently, the titratability of the organic ion. This negative influence is compensated for by the presence of other substituents lipophilic in their character, bound in neighbouring positions to a hydrophilic group; it should be mentioned that such steric effect have also been evaluated<sup>19</sup>.

Organic ammonium salts are known for their marked antimicrobial effect. As the relationships between their structure and antimicrobial activity, the critical micelle concentrations, etc., were also described<sup>20,21</sup>, it is suggested to use the correlations obtained in ion-pair formation titrations for predicting this behaviour in homologous series of the cations.

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