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RESPONSE AND SELECTIVITY CHARACTERISTICS OF ALKYLAMMONIUM ION-S--ETC(U)

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20. Abstract

→ increase in $\log k_{pot}$ with carbon number was observed in each series. Two additional sets of electrodes selective to dodecylammonium ion and to di-n-hexylammonium ion were evaluated for response to other C-12 amines. It was observed that electrodes for primary amines show little or no response to secondary and tertiary amines, while electrodes for tertiary amines respond strongly to primary amines and less strongly to secondary amines. The effect of structural modifications was evaluated in a study of N-substituted cyclohexylamines. The dependence of the magnitude of k_{pot} on interferent concentration was determined for both strong and weak interfering species. For strong interferences, k_{pot} was observed to increase to a maximum value of characteristic concentration. For weak interferences, the k_{pot} variation with interferent concentration was markedly less. Guides for estimating the response to an interfering species based on its structure and molecular weight were obtained from these studies. The results are compared to analogous solvent extraction systems. The significance of these results is discussed in terms of quantitative different components in binary mixtures using several electrodes simultaneously.

* Selectivity coefficient

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L. Cunningham and H. Freiser

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RESPONSE AND SELECTIVITY CHARACTERISTICS
OF ALKYLAMMONIUM ION SELECTIVE ELECTRODES

by

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SUMMARY

A series of polyvinyl chloride matrix coated-wire electrodes (c.w.e.) based on dinonylnaphthalene sulfonic acid (DNNS) selective to various alkylammonium ions was prepared and selectivity characteristics were evaluated. Using a set of tributylammonium c.w.e., the interference by homologous series of alkylammonium ions were studied. It was found that selectivity coefficient ($k_{1,j}^{pot}$) values for alkylammonium ions at a given carbon number decrease in the order primary, secondary, tertiary, quaternary. A linear increase in $\log k_{1,j}^{pot}$ with carbon number was observed in each series. Two additional sets of electrodes selective to dodecylammonium ion and to di-n-hexylammonium ion were evaluated for response to other C-12 amines. It was observed that electrodes for primary amines show little or no response to secondary and tertiary amines, while electrodes for tertiary amines respond strongly to primary amines and less strongly to secondary amines. The effect of structural modifications was evaluated in a study of N-substituted cyclohexylamines. The dependence of the magnitude of $k_{1,j}^{pot}$ on interferent concentration was determined for both strong and weak interfering species.

For strong interferences, $k_{i,j}^{pot}$ was observed to increase to a maximum value of characteristic concentration. For weak interferences, the $k_{i,j}^{pot}$ variation with interferent concentration was markedly less. Guides for estimating the response to an interfering species based on its structure and molecular weight were obtained from these studies. The results are compared to analogous solvent extraction systems. The significance of these results is discussed in terms of quantitative different components in binary mixtures using several electrodes simultaneously.

Previous work in this laboratory has demonstrated that polyvinyl chloride matrix membrane electrodes incorporating dinonylnaphthalene sulfonic acid (DNNS) are selective for large organic cations such as dodecyltrimethylammonium (1), phencyclidine (2) and propranolol (3). Since interference from compounds of structure similar to that of the primary ion is encountered when applying these electrodes, a thorough understanding of their response characteristics in complex mixtures is necessary. Such characteristics include not only values of $k_{i,j}^{pot}$ for different ionic species, but also the long and short term effects on electrode response on samples containing high interferent levels. Some puzzles that still remain unanswered include the way in which $k_{i,j}^{pot}$ varies with the activity of the interfering ions.

Earlier studies were conducted to examine the selectivity of DNNS electrodes with respect to a variety of singly charged cations. It was found that alkali and alkaline earth metal ions and organic ions much smaller than the primary ion showed no appreciable interference.

In this work, a systematic approach to the interference problem was undertaken using electrodes selective to tertiary, secondary and primary ammonium ions. A complete study of the response of tributylammonium (TBA^+) electrodes to homologous series of amines was used to establish a relationship between selectivity and structure. Tributylammonium (TBA^+) was chosen as the primary ion since its molecular weight (185.4) was nearest the average molecular weight (181.7) in the range of ions considered. In this way, interference from both smaller and larger ions could be observed.

Since selectivity is not only a function of molecular weight but also of the types of substituents in a molecule, responses of the TBA electrodes to solutions of TBA^+Cl^- containing N-ethyl, N-(2-cyanoethyl), N-(2-hydroxyethyl), and N-(3-aminopropyl)-cyclohexyl ammonium chlorides were measured. With these compounds the carbon number and the degree of nitrogen substitution were constant in order to isolate the substituent effect.

Variations in the nature of the primary ion were also of interest. In addition to tributylammonium electrodes, others selective for dodecylammonium (DOA^+), di-n-hexylammonium (DHA^+) and tripropylammonium (TPA^+) were prepared as described below. Response of these electrodes to various alkyl ammonium ions was then evaluated.

EXPERIMENTAL SECTION

Reagents:

Amines were obtained from Eastman (Rochester, New York) and further purified by vacuum distillation. Amines obtained as hydrochlorides were

dried over CaCl_2 , while others were converted to hydrochlorides by dissolving in a minimum of 0.1M HCl. Acetate (10^{-2}M) buffer pH 4.00 was the main diluent for all solutions. Dioctylphthalate was used as obtained from Eastman and chromatographic grade polyvinylchloride from Polysciences (Warrington, Pennsylvania).

Potentiometric measurement system.

A double junction of Ag/AgCl reference electrode containing 0.1M NH_4NO_3 in the external junction was used for all experiments. Potentiometric measurements were performed using a microcomputer controlled system described earlier (4) as well as a Nova 2/10-based system.

Electrode preparation and handling.

Both conventional polymeric membrane and coated wire electrodes (c.w.e.) were evaluated for their response to TBA^+ . c.w.e. were used for all remaining studies after having shown that they are equal to, and in most cases better than, the conventional electrodes employing a Ag/AgCl internal reference.

The solution used to cast membranes was made as described previously (5). To this solution, pure amine was added in stoichiometric relation to DNNS. It was then possible to cast membranes (6) or coat copper wires (7). Both types of electrodes were then soaked in a 10^{-3}M alkylammonium ion solution for several days in order to stabilize, during which time the membranes became opaque (probably due to hydration). Electrodes were then repeatedly calibrated during the course of the selectivity studies.

Selectivity coefficients.

Values of $k_{1,j}^{pot}$ were calculated using the mixed-solution method (8). In a typical selectivity determination, a set of five electrodes was calibrated using the NOVA 2/10 system. Immediately after the calibration, a standard solution of an interfering ion was titrated into the calibration vessel containing the final concentration of primary ion. In this fashion, the value of $k_{1,j}^{pot}$ at specified levels of interferences was calculated from the responses of electrodes in each solution tested. The accuracy of this approach is also increased by using the slope of the electrode response calculated by the computer immediately after the calibration run. An entire calibration curve and selectivity determination of one compound required about thirty to forty-five minutes, depending upon the number of solutions desired.

RESULTS AND DISCUSSION

Shown in Table 2 are response characteristics for both conventional and coated-wire ion selective electrodes. Nearly Nernstian responses were obtained for both types. Detection limits were also virtually identical. Electrodes in use over five months are still functional.

Selectivity coefficients for TBA^+ c.w.e. are plotted against the number of ^{carbon} atoms in the ion in Figure 1. The linear increase in $\log k_{1,j}^{pot}$ with carbon number for each series, expected from the corresponding increase of lipophilicity of the ion, facilitates estimation of $k_{1,j}^{pot}$ values for amines of known molecular weight and degree of N substitution.

A plot of $\log k_{1,j}^{pot}$ vs. carbon number for tributylammonium c.w.e. shows that the selectivity order is primary > secondary > tertiary > quaternary. At low carbon numbers, secondary alkyl-ammonium ions and tertiary alkylammonium ions have approximately equal $k_{1,j}^{pot}$ values.

In Table 2, $\log k_{i,j}^{\text{pot}}$ values are given for substituted cyclohexylamines. It is interesting to note that the compounds gave lower $k_{i,j}^{\text{pot}}$ values than dibutylamine, an aliphatic amine of the same carbon number. As expected, the most hydrophilic compound was the least interfering: ($\log k_{i,j}^{\text{pot}} = -2.35$ for N-(2-hydroxyethyl)-cyclohexylamine).

The dependence of selectivity behavior on degree of N-substitution

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of the primary ion was evaluated using c.w.e. of three isomeric ions: - dodecylamine, di-n-hexylamine and tributylamine. Responses of each electrode to the other C-12 amines resulted in $k_{1,j}^{pot}$ values shown in Table III. It is clear that electrodes selective to primary amines show greatest selectivity in this series and tertiary amine electrodes are least selective.

Memory effects are ascribed to changes in electrode response after exposure to strong interferences. It was observed that the TBA^+ c.w.e. calibration curve would shift by as much as +20 mV after exposure to interferences having six carbon atoms or less, and by +100 mV after exposure to very strong interferences such as trihexylammonium ion. The magnitude and duration of this temporary shift increases with the magnitude of $k_{1,j}^{pot}$ for the interfering specie which causes it. It also depends upon how long the electrodes are exposed to the interference and on its concentration. For this reason, exposure times are usually kept below fifteen minutes. To restore electrode response, soaking in $10^{-3}M$ TBA for fifteen minutes was necessary after exposure to the more weakly interfering species. In extreme cases, such as prolonged (overnight) soaking in $10^{-3}M$ trihexylammonium ion (THA), TBA c.w.e. required three hours soaking in the TBA bathing solution before TBA response returned. In this latter case, absolutely no TBA response was attainable prior to the three hour soaking period.

It is important to note that the change in $k_{1,j}^{pot}$ observed was not due to the electrode being chemically altered during the titration. This

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was proven by observing the electrode response at five minute intervals while soaking in $10^{-4}M$ TBA⁺ which was $10^{-4}M$ in THA⁺, during which time (~ 1 hr.) it did not fluctuate more than 2 mv. The presence of primary ion helps to prevent temporary loss of electrode response, which occurred when they were soaked overnight in $10^{-3}M$ THA⁺.

The dependence of $k_{i,j}^{pot}$ on concentration is shown in Figures 2 (DOA = j) and 3 (THA = j). The range where there was a Nernstian response to the primary ion (TPA⁺) was chosen as the region of interest since it is here where these devices are most commonly used. Above $10^{-4}M$, $k_{i,j}^{pot}$ is seen to increase only gradually, whereas below this level it is a very sensitive function of interferent concentration. At low interferent concentrations, the effect on the potential is small, however, reducing the reliability of the calculation of $k_{i,j}^{pot}$. Still, the absence of scatter in this region is surprising.

CONCLUSIONS

It is apparent that polyvinylchloride matrix membrane electrodes can be made selective to a wide variety of organic cations. The coated-wire type electrode is sufficiently well behaved to continue to provide an extremely convenient method for studying membrane processes. The small size of the c.w.e. enables one to do multiple calibrations in a relatively small solution volume.

The selectivity characteristics of the TBA⁺ electrodes towards the other amines studied show that $k_{i,j}^{pot}$ is closely related to carbon number.

The importance of degree of N-substitution is indicated by the ten-fold decrease in $k_{1,j}^{pot}$ values at a given carbon number as additional alkyl groups are added. This effect is possibly due to the greater degree of H-bonding in the membrane for compounds having a less sterically hindered nitrogen. The overlap of the plots for secondary and tertiary alkylammonium ions at low carbon numbers indicates that these compounds have about the same degree of H-bonding. As carbon number increases in these series, the steric effect of the tertiary alkylammonium ions becomes much greater than for secondary alkylammonium ions. Quarternary alkylammonium ions, having no H-bonding, have the lowest $k_{1,j}^{pot}$ values, about 100 fold lower than those of the primary ammonium ions.

The significance of these results is best appreciated by comparison to solvent extraction systems. In a study of the ion pair extraction of amines via picrate ion in various organic solvents (9), Gustavii pointed out that the ion pair formation constant (K_{IP}) as well as the distribution constant (K_D) determine the overall K_{ex} . When methylene chloride, a low dielectric solvent, was employed the order of extraction was tertiary > secondary > primary = quaternary. One reason given for this was the greater degree of hydrogen bonding experienced in aqueous media by the less substituted amines. In the electrode system, however, it would seem likely that hydrogen bonding occurs in the membrane as well as the aqueous phase. Otherwise, the selectivity order would be expected to be similar to that found in the extraction system.

For primary alkylammonium ion electrodes, a large degree of selectivity is observed over higher analogs. This also points out

the importance of steric hindrance at the nitrogen. Apparently, the DNNS-dodecylamine ion pair is stronger than the DNNS tributylamine ion pair; otherwise, it is expected that tributylamine would interfere with the dodecylammonium ion e.w.e. response.

Though the exact value for $k_{i,j}^{pot}$ must be determined by experiment,

the relative interference between two compounds can also be estimated by distribution constants. Such values for amine hydrochlorides between octanol and H₂O, as calculated by the correlation technique of Hansch (10), are plotted against carbon number in Figure 4. Comparison to the $\log k_{i,j}^{pot}$ vs. carbon number plots indicates that hydrogen bonding, though dominant in the aqueous phase, must also occur to an appreciable extent in the membrane phase. This behavior is expected for media of high dielectric constant, as is the case when sufficient amounts of dioctylphthalate are added to polyvinylchloride. This was also the case for picrate ion-pair extraction into methylene chloride as described previously, where it was shown that the partition coefficients^{of neutral amines} decrease in the order $1^0 > 2^0 > 3^0 > 4^0$. Since the slightly transparent polymer becomes opaque after soaking in aqueous solution and becomes clear again after drying in air, the concentration of water in the membrane probably is significant.

The importance of the partition coefficients is indicated by the relative magnitude of $k_{i,j}^{pot}$ values calculated for substituted N ethylcyclohexylamines. The selectivity order corresponds to the relative solubility of the cyclohexylamines between octanol and water. In addition, the $k_{i,j}^{pot}$ value for di-isobutylamine ($\log k_{i,j}^{pot} = -1.56$) was less than that of dibutylamine ($\log k_{i,j}^{pot} = -1.27$) which is also expected of their distribution constants. It is apparent that the selectivity coefficient for a given compound can be reasonably estimated if a known value for a compound of the same family is available.

It has been shown that memory effects become significant when electrodes are exposed to powerful interferents for long time periods. Even so, electrode response can be restored by soaking in sufficiently concentrated solutions of the primary ion. This behavior is consistent with an ion-exchange process occurring in the outer layer of the membrane exposed to the solution.

During the time scale of the selectivity coefficient measurement (15 min.), the shifts in electrode response were slight, indicating that some interfering specie was displacing the primary ion in the outer portion of the membrane. After long exposure times with strong, lipophilic interferences, this displacement was sufficient to nullify electrode response to the primary ion, probably resulting from more complete exchange of primary ion by interfering ion.

As demonstrated by this study, it is possible to measure binary mixtures using the c.w.e. Of course, in the presence of strongly interfering species, significant and (in the time scale of our measurement technique) irreversible errors occur. Even so, provided their presence is suspected, it would be possible to minimize electrode contamination by measuring the concentration of the ions with their respective electrodes in the following sequence: - 1^o, 2^o, 3^o, 4^o. From analysis of samples where the interferences do not change drastically in their nature and/or concentrations, this approach could prove efficacious in that it involves minimum sample preparation, rapid equilibration of electrodes and direct readout of concentrations.

C.C.

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Legend for Figures

LEGEND FOR FIGURES

- Figure 1. Dependence of $\text{Log } k_{i,j}^{\text{pot}}$ on the carbon number of interfering ammonium ions for typical tributylammonium coated wire electrodes.
- Figure 2. Dependence of $\text{Log } k_{i,j}^{\text{pot}}$ on the concentration of dodecylammonium for typical tripropylammonium coated wire electrodes.
 $[\text{TPA}^+] = 1 \times 10^{-3} \text{ M}$
- Figure 3. Dependence of $\text{log } k_{i,j}^{\text{pot}}$ on the concentration of trihexylammonium ions for typical tripropylammonium coated wire electrodes.
 $[\text{TPA}^+] = 1 \times 10^{-3} \text{ M}$
- Figure 4. Dependence of partition coefficient (P), as $\text{Log } P$ for the octanol/water system on the carbon number of various alkyl ammonium chlorides (10). $\square$ = primary, $\triangle$ = secondary, $\times$ = tertiary, and $\odot$ = quaternary ammonium ions, respectively.

Table 1. Response characteristics of DNNS-based ion selective electrodes at 25° C

	<u>Conventional TBA⁺</u>	<u>c.w.e. TBA⁺</u>
Slope (MV/LOG[TBA]):	58.59 ± 0.50 ^a	59.53 ± 0.67 ^a
Std. deviation (MV):	0.30 ^b	1.10 ^b
Intercept (mv):	306 ± 10 ^a	333 ± 12 ^a
Std. deviation:	8.7 ^b	8.3 ^b
Detection limit:	4.0 x 10 ⁻⁶ <u>M</u>	4.0 x 10 ⁻⁶ <u>M</u>
Logarithmic range:	-2.0 to -5.0	-2.0 to -5.0

a. standard deviation for individual electrodes

b. standard deviation among several electrodes

Table 2. Log $k_{i,j}^{pot}$ and log P values for cyclohexylamines at 25° C.

Compound	Log $k_{i,j}^{pot}$ (TBA ⁺ c.w.e.)	Log P (Hansch)
N-ethyl cyclohexylamine	-1.97	-1.36
N-2 hydroxyethyl cyclohexylamine	-2.35	-3.98
N-2 cyanoethyl cyclohexylamine	-2.12	-2.16
N-3 aminopropyl cyclohexylamine	-2.22	-3.52

a - Interferent concentration was $10^{-2}M$ with a background level of $10^{-4}M$ TBA.

Table 3. Values of $k_{i,j}^{pot^a}$ C-12 coated wire electrodes

<u>Primary Ions:</u>			
Interfering Ions:	<u>DOA</u>	<u>DNH</u>	<u>TBA</u>
DOA	-	$2.36 \pm .6^b$	50.1 ± 3.0
DNH	$0.4 \pm .2$	-	$3.8 \pm .4$
TBA	Not measurable	$0.6 \pm .5$	

a - Average values for thirty-five electrodes

b - Standard deviation of $k_{i,j}^{pot}$ values among above electrodes

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