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ION-PAIR EXTRACTION CONSTANTS OF SOME ANIONS AND SELECTIVITY OF LIQUID MEMBRANE ELECTRODES BASED ON CRYSTAL VIOLET AND BRILLIANT GREEN

Negussie Negash, Bhagwan Singh Chandravanshi* and Ghirma Moges

Department of Chemistry, Addis Ababa University, P.O. Box 1176,
Addis Ababa, Ethiopia

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ABSTRACT. Extraction constants of the ion-pairs of perchlorate, iodide, saccharin, and hydrogen phthalate with Crystal Violet and Brilliant Green have been determined in nitrobenzene and 1,2-dichloroethane. The extraction constants of the ion-pairs are correlated with the selectivities of liquid membrane electrodes based on Crystal Violet-perchlorate and Brilliant Green-hydrogen phthalate. A very high selectivity of Crystal Violet-perchlorate and Brilliant Green-hydrogen phthalate ion-selective electrodes towards perchlorate, relative to iodide, saccharin, and hydrogen phthalate, is found to be associated with relatively higher extraction constants of the Crystal Violet-perchlorate and Brilliant Green-perchlorate ion-pairs in the liquid membrane solvent (nitrobenzene).

INTRODUCTION

Since 1973, triphenylmethane dyes have been employed in liquid and polymer membrane ion-selective electrodes. Based on ion-association salts of triphenylmethane dyes several anion-selective liquid and polymer membrane electrodes have been reported [1-13]. Recently Crystal Violet and Brilliant Green have been used for the preparation of liquid and PVC membrane electrodes for tetrathiocyanatozincate(II) [14], saccharin [15], perchlorate [16], hydrogen phthalate [17], tetrachloroferrate(III) [18], and hexafluorotantalate(V) [19-21].

The use of the triphenylmethane dyes as ion-exchangers in ion-selective liquid membrane and PVC membrane electrodes is based on the formation of ion-pairs with anions extractable into water immiscible organic solvents.

Electrodes based on Brilliant Green-saccharin PVC membrane [15], Crystal Violet-perchlorate and Brilliant Green-perchlorate liquid membranes [16], and Brilliant Green-hydrogen phthalate liquid membrane [17] respond to perchlorate, iodide, saccharin, and hydrogen phthalate. The selectivity order of all the four electrodes are: perchlorate >> iodide ≈ saccharin ≈ hydrogen phthalate. All the four electrodes exhibit much higher selectivity (about two orders of magnitude) to perchlorate than to the other three anions (iodide, saccharin, and hydrogen phthalate) [15-17].

The selectivity of liquid membrane electrodes is a function of extraction constant of the ion-pairs in the membrane [22]. However, no attempt has been made to determine extraction constants of the ion-pairs of Crystal Violet and Brilliant Green in the liquid membrane solvents used in ion-selective electrodes. Hence it is worthwhile to undertake the determination of the extraction constants of the ion-pairs of perchlorate, hydrogen phthalate, saccharin, and iodide with Crystal Violet and Brilliant Green and to establish a relationship between extraction constant and selectivity of the electrodes.

The present investigation deal with the determination of the extraction constants of the ion-pairs of perchlorate, hydrogen phthalate, saccharin, and iodide with Crystal Violet and Brilliant

Green in nitrobenzene and 1,2-dichloroethane, which are used as liquid membranes in ion-selective electrodes, and correlation of this parameter with selectivity coefficients of Crystal Violet-perchlorate and Brilliant Green-hydrogen phthalate liquid membrane electrodes.

EXPERIMENTAL

Reagents and chemicals. Double distilled water and analytical reagent-grade chemicals were used unless stated otherwise. Stock solutions (0.1 M) of sodium perchlorate monohydrate, potassium hydrogen phthalate, potassium iodide, and saccharin sodium dihydrate (pharmaceutical grade) were prepared by dissolving known amounts of the salts in water. Aqueous solutions (1.0 x 10^{-3} M) of Crystal Violet and Brilliant Green (both from Hopkins and Williams, 95%) were used to prepare ion-association salts of perchlorate, iodide, hydrogen phthalate, and saccharin. Nitrobenzene (Reidel-de Haen) and 1,2-dichloroethane (BDH) were used without further purification.

Preparation of ion-association salts of basic dyes. Crystal Violet and Brilliant Green salts of each of the anions (perchlorate, iodide, hydrogen phthalate, and saccharin) were prepared by shaking the solution of the anion (20 mL, 1.0 x 10^{-2} M) with the solution of the basic dye (100 mL, 1.0 x 10^{-3} M) for 5-10 min. The resulting mixture was saturated with sodium chloride to promote precipitation of the ion-association salt and allowed to stand overnight. Each product was separated by centrifugation, washed twice with water and dried at 50-60 °C for 5-6 h. Stock solutions (1.0 x 10^{-3} M) of each of the salts were then prepared in nitrobenzene and 1,2-dichloroethane for the desired investigation [15-17].

Instrumentation. Absorbance measurements of the dye salts in the two organic solvents were made in 1-cm cuvettes with a Beckman Model 24 UV-Visible spectrophotometer.

Determination of the extraction constant, K_{ex}

An extraction system in which a monovalent cation (C^+) reacts with a monovalent anion (A^-) to form only one kind of ion-pair (C^+A^-) in the aqueous phase, and in which the extracted ion-pair does not dissociate or aggregate, involves the following equilibria.

The ion-association constant in aqueous solution, K_A, refers to the reaction

$$C^+ + A^- \rightleftharpoons C^+A^- ; \; K_A = [C^+A^-]/[C^+][A^-] \tag{1}$$

The distribution coefficient of the ion-pair (C^+A^-) between the aqueous and organic phases, refers to the equilibrium

$$C^+A^- \rightleftharpoons (C^+A^-)_{org} ; \; K_D = [C^+A^-]_{org}/[C^+A^-] \tag{2}$$

where the subscript org refers to the organic phase and the aqueous concentrations are unmarked.

The distribution ratio of C^+ between the aqueous and organic phases, D, and the extraction constant, K_{ex}, are described by

$$D = [C^+A^-]_{org}/([C^+] + [C^+A^-] \tag{3}$$

$$K_{ex} = [C^+A^-]_{org}/[C^+][A^-] = K_D \times K_A \quad (4)$$

From equations (1-4), the following equation can be derived

$$D^{-1} = K_D^{-1} + (K_{ex}[A^-])^{-1} \quad (5)$$

The plot of D^{-1} against $[A^-]^{-1}$ must be linear; from the intercept of the y-axis and the slope, K_D and K_{ex} can be calculated [23].

Procedure. The distribution ratio of each of the basic dye salts of perchlorate, hydrogen phthalate, saccharin, and iodide between water and the water-immiscible organic solvents were determined spectrophotometrically. 10 mL of 10^{-5} M solutions of each of the dye salts in nitrobenzene or 1,2-dichloroethane were shaken with 10 mL of water for 5 min. The organic phase was separated, dried over anhydrous sodium sulphate and used for spectrophotometric determination. The absorbance of each of the salts in the organic phase before extraction and the remaining dye in the organic phase after extraction with water were measured at 585 nm for Crystal Violet and at 624 nm for Brilliant Green. The concentration of each salt in the organic phase was determined from calibration plots of absorbance *vs* concentration of the standard ion-association salt solution in the organic solvent. The difference between the initial concentration of the salt and the concentration after partition gave the dye concentration in the aqueous phase. The concentrations of the ion-association salt in the organic and the aqueous phases were used to evaluate the extraction constant [23].

RESULTS AND DISCUSSION

Selection of membrane solvents. The selectivity of a membrane electrode is governed by both the mobility of the ions in the membrane and the equilibrium that exists at the membrane-solution interface, i.e. extraction and ion-exchange equilibrium constants [22]. In the case of liquid membrane electrodes these selectivity parameters are dependent on the nature of the solvents.

Nitrobenzene, chlorobenzene, 1,2-chloroethane, and chloroform were considered as membrane solvents. The solvents with low dielectric constants [24], namely, chlorobenzene and chloroform, did not appreciably dissolve the dye salts and hence could not be employed as membrane solvents. Nitrobenzene and 1,2-dichloroethane were employed as membrane solvents in the Crystal Violet-perchlorate and Brilliant Green-perchlorate liquid membrane electrodes [16], and the Brilliant Green-hydrogen phthalate liquid membrane electrode [17]. Hence, nitrobenzene and 1,2-dichloroethane were selected as membrane solvents for the present study.

Extraction constant. The extraction constants of ion-association salts provide useful information for selecting the proper ion-association salts and membrane solvents in the preparation of liquid membrane electrodes with better performance [22].

The extraction constants of the salts for the partition equilibria between water and nitrobenzene and water and 1,2-dichloroethane were determined spectrophotometrically [23]. The results are given in Table 1. The extraction constants of the ion-pairs of Brilliant Green and Crystal Violet in nitrobenzene are comparable, while those of the ion-pairs of Crystal Violet salts in 1,2-dichloroethane are slightly smaller than those of in nitrobenzene. The large K_{ex} values in both solvents show that both nitrobenzene and 1,2-dichloroethane can be used as membrane solvents for ion-pairs of perchlorate, saccharin, iodide, and hydrogen phthalate with Brilliant

Table 1. Extraction constants of Crystal Violet and Brilliant Green ion-association salts.

Anions associated	log K_{ex}*		
	Crystal Violet		Brilliant Green
	in nitrobenzene	in 1,2-dichloroethane	in nitrobenzene
ClO_4^-	8.4	7.8	7.6
I^-	7.0	6.6	7.2
$Sacc^-$	7.6	6.7	7.0
HP^-	7.4	5.7	7.3

*log of the mean K_{ex} of three measurements. $Sacc^-$ = saccharin and HP^- = hydrogen phthalate ion.

Green and Crystal Violet. The comparison of the extraction constants of the ion-pairs of perchlorate, iodide, saccharin, and hydrogen phthalate with Crystal Violet and Brilliant Green also show that the Crystal Violet-perchlorate and Brilliant Green-perchlorate have higher values in both the solvents than the ion-pairs of iodide, saccharin, and hydrogen phthalate. This explains as to why the reported electrodes based on Crystal Violet and Brilliant Green ion-pairs of these anions have very high selectivity towards perchlorate than to iodide, saccharin, and hydrogen phthalate [15-17].

Relationship between K_{ex} and k_{ij}^{pot}. The relationship between the selectivity coefficient, k_{ij}^{pot}, of the membrane electrode to the various physicochemical parameters are summarized by Wuhrmann and coworkers [25], from which it is seen that the selectivity of the membrane electrode is governed by both the mobility of the ions in the membrane and the equilibrium that exists at the membrane-solution interfaces (e.g. partition coefficient, ion-exchange equilibrium constants).

Though the relative ionic mobility, a non-equilibrium factor, should be taken into account for more quantitative description of selectivity, an attempt has been made to relate the chemical factors, such as extraction constants to the selectivity of the electrodes.

The relative K_{ex} values of Crystal Violet salts (C^+A^-) and $_{ij}k^{pot}$ values of Crystal Violet-perchlorate electrode are given in Table 2. The relative K_{ex} values of Brilliant Green salts (B^+A^-) and k_{ij}^{pot} values of Brilliant Green-hydrogen phthalate electrode are given in Table 3. The plots of log k_{ij}^{pot} values as a function of log relative K_{ex} values are shown in Figure 1 and 2. From Table 2 and 3 and Figure 1 and 2, it is possible to note the relation between the extraction constants of the ion-association salts into nitrobenzene and the selectivity coefficients of the liquid membrane electrodes. This correlation indicates that the extraction constants determine the selectivity characteristics of the liquid membrane electrodes. Thus, as shown in Table 2 and 3 and Figure 1 and 2, the perchlorate ion is highly selected by both the perchlorate and the hydrogen phthalate electrodes owing to its higher extractability in the liquid membrane (nitrobenzene) relative to the other anions. The other three ions, namely, iodide, saccharin, and hydrogen phthalate, have practically the same selectivity to both the electrodes even though the iodide as Crystal Violet salt and saccharin as Brilliant Green salt have relatively somewhat smaller extraction constants than that of the corresponding other two salts, respectively. However, they have generally similar extractability, i.e. same order of magnitude of K_{ex}, in the liquid membrane (nitrobenzene). Similar

Table 2. Comparison of logarithmic ratios of K_{ex} of Crystal Violet salts (C^+A^-) of the ion, j, to that of the ion of interest, i, (ClO_4^-) and k_{ij}^{pot} (potentiometric selectivity coefficient of the ion, j, with respect to the ion of interest, i, ClO_4^-) of Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent).

Crystal Violet salt	log [(K_{ex}, C^+j^-)/(K_{ex},C^+i^-)]	log k_{ij}^{pot} [16]*
$C^+ClO_4^-$	0.0	0.0
C^+I^-	-1.4	-1.8
C^+Sacc^-	-0.8	-1.8
C^+HP^-	-1.0	-1.9

* k_{ij}^{pot} values by separate solution method.

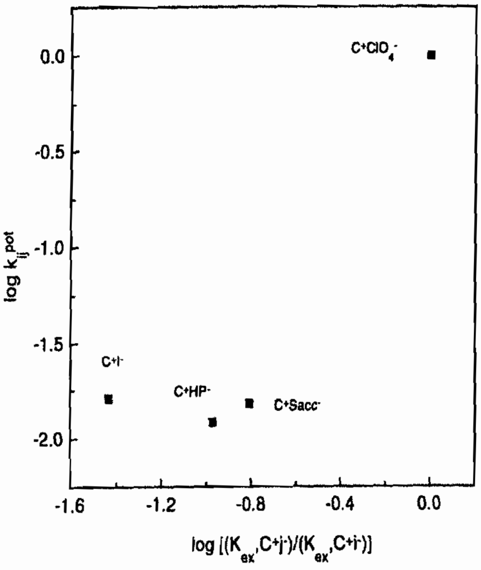
relations have been shown in an earlier study [26] for various amino acids (anionic forms) and organic anion-responsive electrodes based on tetrahexylammonium salts.

It should also be of interest to note that selectivity of the liquid membrane electrodes is related not only to the extraction constant of the ion-pairs but also to the hydration energy and ionic radius. The order of selectivity of the Crystal Violet-perchlorate and Brilliant Green-hydrogen phthalate liquid membrane electrodes showed that selectivity decreases with increasing standard free energy of hydration of ions and with decreasing ionic radius [16, 17]. This is explained by the lipophilicity of the ions [17]. Thus the ions with lower hydration energies and larger ionic radii are lipophilic and hence are easily extractable into liquid membrane solvents of lower permittivity.

Table 3. Comparison of logarithmic ratios of K_{ex} of Brilliant Green salts (B^+A^-) of the ion, j, to that of the ion of interest, i, (ClO_4^-) and k_{ij}^{pot} (potentiometric selectivity coefficient of the ion, j, with respect to the ion of interest, i, HP^-) of Brilliant Green-hydrogen phthalate electrode (nitrobenzene as membrane solvent).

Brilliant Green salt	log [(K_{ex}, B^+j^-)/(K_{ex},B^+i^-)]	log k_{ij}^{pot} [17]*
$B^+ClO_4^-$	0.0	2.0
B^+I^-	-0.4	0.1
B^+Sacc^-	-0.6	0.1
B^+HP^-	-0.3	0.0

* k_{ij}^{pot} values by separate solution method.



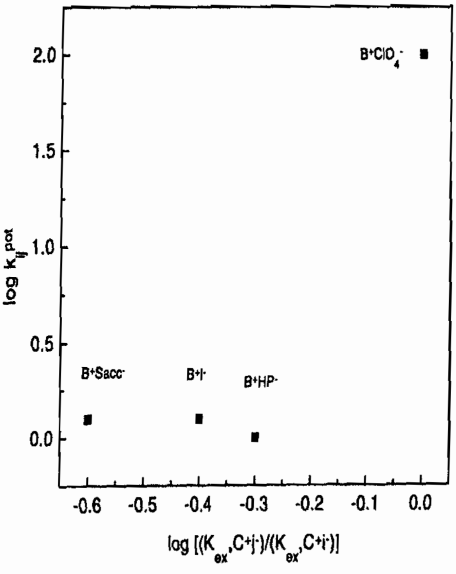


Figure 1. Plot of log k_{ij}^{pot} (potentiometric selectivity coefficient of the ion, j, with respect to the ion of interest, i, ClO_4^-) of Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent) as a function of logarithmic ratios of K_{ex} of Crystal Violet salts (C^+A^-) of the ion, j, to that of the ion of interest, i, (ClO_4^-) in nitrobenzene.

Figure 2. Plot of log k_{ij}^{pot} (potentiometric selectivity coefficient of the ion, j, with respect to the ion of interest, i, HP^-) of Brilliant Green-hydrogen phthalate electrode (nitrobenzene as membrane solvent) as a function of logarithmic ratios of K_{ex} of Brilliant Green salts (B^+A^-) of the ion, j, to that of the ion of interest, i, (ClO_4^-) in nitrobenzene.

CONCLUSION

A very high selectivity of Crystal Violet-perchlorate and Brilliant Green-hydrogen phthalate ion-selective electrodes towards perchlorate, relative to iodide, saccharin, and hydrogen phthalate which have about the same selectivity order, is found to be associated with relatively high extraction constants of the Crystal Violet-perchlorate and Brilliant Green-hydrogen phthalate ion-pairs. A major strategy to obtain high selectivity in liquid membrane electrodes is therefore to choose membrane solvents with higher extractability for the ions of interest.

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