Use of PVC Plasticized Membranes for Uptake of Radioactive Cesium and Strontium

J. Rais[a]; C. V. Mason[b]; K. D. Abney[b]

[a] NUCLEAR RESEARCH INSTITUTE, ŘEŽ, CZECH REPUBLIC [b] LOS ALAMOS NATIONAL LABORATORY LOS, ALAMOS, NEW MEXICO, USA

PLEASE SCROLL DOWN FOR ARTICLE

Use of PVC Plasticized Membranes for Uptake of Radioactive Cesium and Strontium

J. RAIS*
NUCLEAR RESEARCH INSTITUTE, ŘEŽ
25068 ŘEŽ, CZECH REPUBLIC

C. V. MASON and K. D. ABNEY
LOS ALAMOS NATIONAL LABORATORY
LOS ALAMOS, NEW MEXICO 87545, USA

ABSTRACT

A new type of sorbent for the selective uptake of elements based on the use of PVC plasticized membranes, commonly used in electrochemistry as ion selective (ISE) membranes, is described. It is theoretically derived that the material acting as a selective ion sensor of ISE must be also effective as a sorbent. In experimental verification of the hypothesis, the cobalt dicarbollide and sodium tetraphenylborate with the addition of a synergist of the polyethyleneglycol type were dissolved in several solvents mixed with a tetrahydrofurane solution of 5% PVC and evaporated to produce a membrane used for the sorption experiments. It was found that PVC, besides functioning as a solid support, does not influence significantly the behavior of the prepared materials; however, the kinetics are slower than for the analogous solvent extraction techniques. Practical applications of such membranes for the isolation of radioactive cesium and strontium from acidic and alkaline solutions with a high of Na^+ ions content are shown, with emphasis on nontoxic solvents as substitutes for the toxic nitrobenzene.

INTRODUCTION

The isolation of radioactive ^{137}Cs and ^{90}Sr from nuclear wastes is important from the point of view of their biotoxicity. Various methods are available for this task, e.g., precipitation methods of ^{137}Cs with sodium tetra-

* To whom correspondence should be addressed.

951

phenylborate (1), sorption on various inorganic sorbents (2), and extraction methods from Purex raffinate by cobalt dicarbollide (3). Each of the methods has it own limitations. Precipitation methods have generally been abandoned in the nuclear industry due to the difficulties with handling radioactive solid phases. Sorption on inorganic ion exchangers is often irreversible, i.e., the sorbent is used only in the once-through mode, the capacity of the sorbent may be low, and release of solid particles from the sorbent may complicate the separation. Extraction methods, which are usually highly effective and for which extraction–backextraction can be done continuously, demand high capital costs for the construction of extraction equipment and for its maintenance. Further, extraction methods are usually not as flexible, i.e., the flow sheet is only convenient for a given feed composition, e.g., of Purex raffinate. Moreover, the organic liquid phase in the extraction process cannot be immediately disposed of or stored if an immediate need arises, and generally the process is more dangerous from the point of view of possible radioactive spills.

Therefore, a more advanced separation technique is desirable which will conserve the reversibility and capacity of extraction methods but remove their drawbacks.

In this work we concentrated our effort mainly on the possibility of separation of cesium and strontium from solutions of high ionic strength. Both acidic [e.g., mixed effluents of Purex waste of medium activity, dissolved parts of sludge of highly active wastes (HAW) of nuclear waste repositories] and basic (neutralized HAW) aqueous solutions were used.

Some nontoxic variants of nitrobenzene were tested both as plasticizers and extracting solvents for cobalt dicarbollide. In the latter sense, the original dicarbollide process for the isolation of radioactive cesium and strontium invented in the Czech Republic and developed to the technological stage after 15 years of Czech–Russian cooperation (4) is here broadened.

ION SELECTIVE PVC-BASED MEMBRANES

The systems used in electrochemistry often resemble the extraction systems used for the separation of univalent and bivalent cations. For example, the sodium salt of TPB, which is an extraction agent for heavy alkali metals (5, 6), is also used as a reagent for the determination of these same alkali metals in ion selective (ISE) membranes (7). o-Nitrophenyl octylether, which is often used in electrochemistry, (7) is a nonvolatile and nontoxic variant of previously used nitrobenzene in ion pair extraction systems (5, 6, 8). This similarity is not fortutious, as will be shown below.

In ISE membranes the polymer of preference is high molecular weight PVC. The polymer matrix exerts little influence on the behavior of the

TABLE 1
Some Corresponding Terms and Components in Electrochemistry of ISE Membranes
and in Extraction Chemistry

ISE	Extraction
Polymer matrix (PVC, . . .)	None
Plasticizer (o-nitrophenyl octyl ether, . . .)	*Solvent* (nitrobenzene, . . .)
Anion blocker (hydrophobic anion like tetraphenylborate, . . .)	*Extraction agent* (hydrophobic anion like tetraphenylborate, ...)
Ionophore (crown ether, ...)	*Synergist* (crown ether, . . .)

separation agent within the membrane except for lower diffusion coeffi-
cients compared to liquid–liquid extractions (9). Therefore, even on an
empirical basis, the materials of ISE membranes are worth examining in
terms of their separation properties for the same cations which are mea-
sured electrochemically. However, the suitability of such membranes for
the uptake of the cations may also be derived theoretically (vide infra).
Some similarities and corresponding terms in electrochemistry and in ex-
traction chemistry are given in Table 1.

A review of the literature shows there have been several attempts to
use plasticized PVC membranes for actinides and rare earth elements as
summarized in the recent review article of Kopunec and Th. Ngo Manh
(10). Initial applications involved the transfer of neutral complexes of the
cations across PVC membranes plasticized with tributylphosphate, dibu-
tyl cresyl phosphate, and dicresyl butyl phosphate (11). More recently,
membranes using o-nitrophenyl octyl ether (a solvent well known from
elecrochemical studies) and with cellulose triacetate as the polymer sup-
port were studied for their ability to transfer rare earth elements using
complexants such as several substituted acetones and isopropyltropolone
(12). The intent of studies was not to understand the transfer of charged
ions. Quite recently a number of methods for the uptake of various sub-
stances by the use of plasticized membranes was applied for as a patent
by Bauer et al. (13). However, electrochemical membranes containing
PVC as the polymer and the uptake of alkali and alkali metal cations are
not the subject of this patent application.

THEORETICAL

The potential of an ion selective electrode can be expressed in several
ways. The simplest treatment applicable to any kind of cation selective
electrode regards the electrode as a kind of junction with transference

numbers of cation $t_+ = 1$ and anion $t_- = 0$ (7). Under this condition it can used to determine the difference of the inner potentials of the phases, $\Delta\varphi_m$:

$$\Delta\varphi_m = (RT/zF) \ln[a_i(S)/a_i(I)] \tag{1}$$

where $a_i(S)$ is the activity of the univalent ion in the sample solution, $a_i(I)$ is its activity in the internal electrode compartment, T is the absolute temperature expressed in Kelvins, R is the molar gas constant (8.31441 $J\cdot mol^{-1}\cdot K^{-1}$), z is charge of the ion, and F is the Faraday constant ($96,484.6$ $C\cdot mol^{-1}$).

If $a_i(I)$ remains constant for various samples, which is the normal case, then ΔE is directly proportional to the activity of the ion in question in the sample solution (7).

A more detailed treatment should take into account the electrochemical equilibria of the sample solution and membrane as well as the actual transference numbers through the membrane (the electrochemical potential between the inner solution and the membrane may be considered constant). If a partial electrochemical equilibrium is established between the sample solution near the interface of the membrane and some adjacent layer of membrane material (or the bulk of the membrane if the membrane is sufficiently thin) during the measurement of the sample, and if for simplicity the transference numbers effect is neglected, then $\Delta\varphi_m$ can be calculated from the equality of electrochemical potentials in the aqueous phase, μ_S^{el}, and the membrane phase, μ_M^{el}:

$$\mu_M^{el} = \mu_S^{el} \tag{2}$$

Hence there are for two equilibrium polar phases for a univalent cation:

$$\mu_0^{i,S} + RT \ln a_i^S + F\varphi^S = \mu_0^{i,M} + RT \ln a_i^M + F\varphi^M \tag{3}$$

where $\mu_0^{i,S}$ and $\mu_0^{i,M}$ are the standard chemical potentials of the ion i in the solution and membrane phases, respectively; the a_is are their respective activities there, F is the Faraday constant, and φ^S and φ^M are respectively the inner potentials of the two phases.

From Eq. (3) the same relation as of Eq. (1) results. Again the potential difference is given by the aqueous concentration of the sample ion i under the condition that a_i^M is constant during use of the electrode. The latter can be maintained only if the concentration of i in the membrane phase does not change during the measurement of various samples. Relation (3) is important for our purpose since it illustrates that an equilibrium is established, at least at the surface layer of the membrane adjacent to the sample solution. Complete equilibrium between the sample solution and the bulk of the membrane is assumed in cases when the membrane is sufficiently thin (14).

Equation (3) is exactly the relation for Donnan equilibrium for the case when the membrane is permeable only for cations, hence the equilibria for ISE are often considered to be a kind of Donnan equilibrium. In classical Donnan equilibrium at least one counteranion, for which an equation analogous to Relation (3) could be written, is fully confined to one compartment. Hence, its electrochemical equilibrium is not operational, and Relation (3) applies only for cations.

However, the condition of semipermeability is assured for all ISEs in a different way than in Donnan equilibrium. For example, for an ISE sensitive to cations, a sufficiently bulky anion like tetraphenylborate is usually used, and it prevents the transfer of any other inorganic anion into the membrane phase. The "blocking" function of the bulky and hydrophobic anion is generally due to its much higher affinity (as compared to any simple inorganic anions possibly present in the sample solution, like Cl^-, NO_3^-, etc.) toward the organic liquid phase used in the membrane, i.e., toward the "plasticizer" in the terminology of ISE. The same is true for the opposite case of an anion-sensitive ISE with the difference that a suitable cation is used as a "blocker."

As a matter of fact, some hydrophobic and bulky ion is used as a reagent for the extraction of ion pairs in extraction chemistry. This is so in the case of the already-mentioned dicarbollide process (3, 4) where the anion of bis(dicarbollyl)cobaltate$^-$ is extremely hydrophobic. Such a bulky ion is used in this case to minimize the loss of reagent in the outgoing aqueous phase and thereby improve the economic parameters of the process. While the purpose of the two approaches is different, the requirements for the "blocker" or "extraction agent" are practically the same. The same class of compounds with the same properties is used in both disciplines.

For the sake of completeness it must be noted here that the equilibria involved in the extraction of electrolytes by polar solvents, ISEs, and in electrochemical studies of the interface of two immiscible electrolyte solutions (ITIES) are more complicated than simple Donnan equilibrium. In fact, Relation (3) must be considered for all ions present in the system, i.e., also for the "blocker" or "reagent" B^- ion. We can see easily from Eq. (3) than even if B^- is practically fully contained in the organic membrane or solvent phase, the potential may still vary for a given concentration of the sample ion i in the aqueous phase. This is so because its value depends, according to Eq. (3), not on the absolute concentration of B^- in the organic phase but rather on the *ratio* of a_B^M/a_B^S or a_i^o/a_i^a (the latter two values designate the activities of i in the organic and aqueous phases, respectively). The first mathematical solution of the complex equilibria on ITIES was given by Hung (15). The studies were subsequently broadened by Vanýsek (16) and Kakiuchi (17). Mathematical treatment of the complex equilibria during the extraction of electrolytes was given before

(3). The basic idea of the equality of the electrochemical potentials of each ion present in two equilibrium polar phases is the starting point of all the disciplines given above, viz., ITIES, ISEs, and electrolyte extraction. Also, the presence of a "synergistic agent" in extraction terminology or an "ionophore" in ISE terminology leads to the same effects in both disciplines. These are connected with the selectivity of the ligand to a particular ion in such a manner that the selectivity of the system is controlled.

WORKING HYPOTHESIS AND AIMS

On the basis of foregoing discussion a following working hypothesis can be made: *Electrochemical membranes containing PVC, plasticizer, and hydrophobic anion (cation) must also behave as sorbents of the ion under question, i.e., of the cation (anion).* Or in other words and in equivalent form: *The properties of ISE membrane phases, as far as they concern the exchange of ions, are analogous to pure extractants not containing polymer material.* An experimental test of this hypothesis is the main goal of this work. We studied systems with a hydrophobic anion.

Experimental verification requires: 1) determination of the degree of sorption of individual elements by ISE membrane materials, and 2) elucidation of the role of the polymer in the sense of whether it can be considered as only an inert support not influencing the partition characteristics.

As written in the Introduction, the practical aim was to discover sorption materials suitable for the separation of Cs^+ and Sr^{2+} from solutions of high salinity. Therefore, higher concentrations of the reagent than are usual in ISE studies were used. In fact, the concentrations were the same as those appropriate for extractions (3). In order to verify Point 2), the full dependence of sorption on PVC content was examined.

As seen from the model given above, ISE theory automatically takes into account the exchange of ions but not of the uncharged particles. Hence, any proof of the identity of ISE materials with extraction systems is additional evidence for the deep involvement of ionic processes in the systems studied. The ionic character was proved in a number of studies (8, 14, 18), but opposite views (and incorrect, in our opinion) of the essentially molecular mechanism of extraction in the presence of dicarbollides and in polar solvents like nitrobenzene are encountered (19).

There is an urgent need to substitute highly toxic nitrobenzene by some nontoxic solvent (19). Surprisingly, nontoxic halogenated derivatives of nitrobenzene and nitrotoluene can be easily found in commercial catalogs. It was aim of this work to show the good properties of new solvents in both the extraction and sorption modes. It is hoped that these new solvents will be more broadly used in both basic studies and in technology.

EXPERIMENTAL

Reagents and Radioisotopes

Chlorinated cobalt dicarbollide, H^+ form, hydrate, of the same origin and of the same purity as in Ref. 20 was used (HBCl). The compound produced by Katchem, Ltd., Czech Republic, is in fact chloroprotected cobalt dicarbollide with homologues containing 5–7 molecules of Cl per 1 dicarbollide anion. A 0.1 M solution was prepared by dissolving 0.7 g of HBCl in 10 mL of solvent. Polyvinyl chlorides of low and high molecular weight (LMW PVC with an inherent viscosity of 0.68 and an average molecular weight of 56,000; HMW PVC with 1.02 and 94,000 respective values; catalog numbers # 18,958-8 and #34,675-6) were products of Aldrich, as was Triton X 114 (p-octylphenyl octaethylene glycol, #36,934-9) and polyethylene glycol of mean molecular weight 400 (PEG 400, #20,239-8). The solvents used in this work were used as supplied from Aldrich (purity 95.2–99%). Dodecyl sebacate was obtained from Jansen (95% purity). All other chemicals were of analytical grade and used without purification. The following abbreviations are used for the solvents: o-NPOE for o-nitrophenyl octyl ether, C1NT for 4-chloro-3-nitrotoluene, FNT for 2-fluoro-6-nitrotoluene, F2NB for 1-fluoro-2-nitrobenzene, F3NB for 1-fluoro-3-nitrobenzene. DOS for dioctyl sebacate, DBPht for dibutyl phtalate, and DDB for dodecyl benzene.

^{137}Cs and ^{85}Sr were used as radioactive tracers. Their radiochemical purity was checked by γ-spectrometry using a Ge-Li detector.

Preparation of the Membranes

The plasticized PVC membranes were prepared as follows. The extractant was first prepared: 0.2 M cobalt dicarbollide in o-NPOE was dissolved and shaken twice with equal volumes of 3 M HNO_3. After the addition of PEG the organic phase typically became nontransparent and required two additional nitric acid contacts. All aqueous phases were discarded. Five milliliters of the prepared extractant were mixed with 70 mL of 5% (wt) of PVC (mostly high molecular weight HMW PVC) in tetrahydrofuran. After vigorous shaking the solution was poured into three Petri dishes of 9.7 cm internal diameter and left to stand overnight. The peeled membrane was allowed to dry for an additional 2 hours at room temperature before use. For sorption experiments the membrane was cut into pieces of about 1 × 1 cm, placed into a test bottle, and the tracer radioactive solution was added.

Procedures and Measurement

The distribution coefficients were determined from a known amount of the sorbent and the specific radioactivity before sorption and the measured

specific radioactivity of the solution after sorption. For sorption experiments the reported K_d values are defined as $K_d = (a_s/a_a)(V/g)$ [mL/g], where a_s and a_a are radioactivities of the sorbent and aqueous phase, respectively, V is the volume of the aqueous phase, and g is the mass of the sorbent. The ratio V/g was usually around 10. The value a_s was determined from the radioactivity of the aqueous phase before and after sorption. Varying times of shaking with a circular shaker of 1000 min^{-1} were allowed for, as specified in the text. Aliquots of both the organic and aqueous phases were withdrawn for radioactivity measurement at the end of the extraction experiments. The extraction distribution ratio was determined as $D = a_o/a_a$, where a_o and a_a are the specific radioactivities of the organic and aquous phases. Equal volumes of the phases were used, and D was determined from measuring samples of both phases. The time of extraction contact under shaking was 30 minutes which, according to previous results, is sufficient for attaining extraction equilibrium. All experiments were done at room temperature (23 ± 2°C).

In most experiments a synergist for Sr uptake (Triton X 114 or PEG 400) was used. According to previous findings (21), the maximum distribution ratio of Sr (Ba) in mixtures of PEG with dicarbollide is attained more or less independently of the PEG type and an overall concentration of reagents at a ratio of 0.06 mol/L of dicarbollide anion: 1% (wt) PEG. Since there may be an abrupt decrease of D_{Sr} at higher concentrations when using substituted PEGs (like Triton X 114), we used a more conservative ratio of the above two components equal to 0.2 mol/L:3% (wt).

RESULTS AND DISCUSSION

Toxicity

Particular attention was paid to nontoxicity when choosing solvents for this study. Highly toxic substances according to Aldrich and to their respective material safety data sheets supplied by the manufacturer, like nitrobenzene, nitrotoluene, 3-nitro-α,α,α-trifluorotoluene, and 1-chloro-2-nitrobenzene, were omitted. o-NPOE is harmless. F2NB and F3NB are harmful according to data from Aldrich, and C1NT and FNT are irritants, but none of them belongs to the category "toxic" or "highly toxic." DBPht, although only an irritant, according to Aldrich, may have possible teratogenic effects (as stated on the received bottle). DOS, now currently used as an ISE material, is "harmful" (Jansen). We found no data on the possible toxicity of DDB.

Slightly Hardened Membranes

Contrary to common practice in the preparation of electrochemical sensors, we first investigated materials containing as little as 10% PVC in

relation to the extractant (plasticizer). It was expected that such materials would most closely resemble a pure extractant. The results of sorption of microamounts of Cs are given in Table 2 and show that the sorption of Cs is very high (sorption of Sr was small since no synergist for Sr was added). The resulting K_d values are approximatively 2 times higher from 0.5 M HNO_3 than from 1.0 M HNO_3, which compares well with the supposed mechanism of ion competition of H^+ and Cs^+ ions. No substantial influence of the kind of PVC on the K_d values was observed. These preliminary results justify further experiments. However, the materials with approximately 10% PVC had a gel consistency, were difficult to handle, and were not further studied.

Influence of PVC Content on Sorption

Membranes with PVC contents of 20–100% (relative to the plasticizer) were prepared. A synergist for Sr was added in order to determine whether the synergist functions under the solidified conditions in the same way as during extraction. Comparison of the results presented in Table 3 with those in Table 2 confirms the dramatic increase of Sr sorption upon addition of the Triton synergist.

The model used here indicates that the PVC in the membrane lowers the resulting K_d value only by its "dilution" effect on the active mass of the sorbent, i.e., by increasing the g value in the expression $K_d = (a_s/a_a)(V/g)$. Theoretical values of $K_d(Cs)^*$ in which only the effect of dilution is taken into account can be compared with experimental values. Calculated values of $K_d(Cs)^*$ at the point at which the PVC content is 20% are

TABLE 2

Sorption of ^{137}Cs and ^{85}Sr on Slightly Hardened Cobalt Dicarbollide Membranes[a]

PVC	PVC content[b]	c(HNO_3) (M)	$K_d(Cs)$	$K_d(Sr)$
LMW	12.5	0.5	163.5	2.2
	12.5	1.0	60.6	0.2
	8.3	0.5	100.8	1.0
	8.3	1.0	45.0	—
HMW	12.5	0.5	194.1	2.1
	12.5	1.0	103.2	0.6
	8.3	0.5	90.8	0.4
	8.3	1.0	39.3	—

[a] Membranes: 0.4 or 0.6 mL of 0.2 M HBCl in o-NPOE mixed with 0.5 mL of 10% PVC in THF was poured into a Petri dish of 0.5 cm internal diameter. Dried membranes were conditioned for 48 hours in 2.5 M HNO_3; 3 hours contact.

[b] Relative to extractant in percent.

given at the last column of Table 3. These were calculated as $K_d(Cs)^*$ = $[K_d(Cs, 20\%)g^*)/(0.83\ g)]$, where g^* denotes the weight of the active extractant (plasticizer), g is the total weight of the sorbent in the experiment, and the numerical factor 0.83 corresponds to the reference point. As seen from the table, the dilution model of sorbent mass by PVC correlates well with the exception of high concentrations of high molecular PVC, where the $K_d(Cs)$ value decreased to 70% of the expected value at the highest relative content of PVC. Still, even here, this decrease may be kinetic (vide infra).

Kinetics of Sorption and Solvent Evaporation

The diffusion coefficients in the PVC membranes are approximately 2 orders of magnitude lower than in a corresponding liquid phase [Mikhelson gives a typical value of about $D_i = 10^{-8}\ cm^2 \cdot s^{-1}$ (22)]. Extended time periods in comparison with classical extraction systems are therefore to be expected for attaining the equilibrium state. Some results are depicted on Fig. 1. It is seen from the figure that at particular conditions of the sorption of microamounts of Cs^+ and Sr^{2+} from 1 M HNO_3, equilibrium was established after more than 1 day of contact. However, an increase by more than half of that value was attained within 3 hours of shaking. Subsequently, for convenience, 3 hours of contact time were used when

TABLE 3
Sorption of ^{137}Cs and ^{85}Sr on Cobalt Dicarbollide Membranes with Various
PVC Content[a]

PVC	PVC content[b]	$K_d(Cs)$	$K_d(Sr)$	$K_d(Cs)^{*,c}$
LMW	20	165.4	780	—
	40	139.2	—	141.5
	60	121.4	—	123.5
	80	91.9	880	109.6
HMW	20	116.2	—	—
	40	103.7	—	99.4
	60	97.6	—	86.8
	80	52.8	675	77.0
	100	47.9	401	70.0

[a] Membranes: 10 mL of 0.2 M HBCl in o-NPOE with 0.3 mL of Triton X 114 were shaken two times with fresh portions of 2.5 M HNO_3. Extractant (0.5 mL) was mixed with an appropriate volume of 10% PVC in THF and poured into a 5-cm Petri dish; 3 hours contact.
[b] Relative to extractant in percent.
[c] Theoretical value for dilution effect related to the experimental data for 20% PVC content.
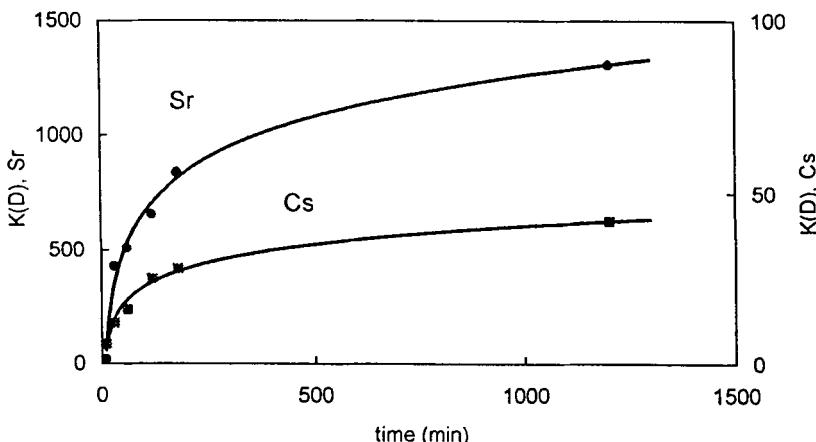
FIG. 1   Kinetics of sorption of ^{137}Cs and [85]Sr. Kinetics refers to sorption of ^{137}Cs and [85]Sr on a membrane composed from 0.2 M chlorinated cobalt dicarbollide and 3% Triton X 112 with o-NPOE as a plasticizer (weight ratio of solvent to HMW PVC 1:1) from aqueous medium of 1 M HNO₃.

measuring batch distribution coefficients. Moreover, it appears from the results given below that the kinetics are dependent on the ionic strength of the aqueous phase and are faster for sorption from higher values of the latter.

For practical applications of the PVC plasticized materials as sorbents, the durability of the material over time is important. This has been extensively studied in plasticized polymeric materials from the point of view of their extended practical use (23). It has been argued that after the initial period of evaporation of relatively freely surface-bound solvent, a state is reached where the evaporation significantly slows down and is intrisically given by the volatility of the plasticizer (23). However, for high molecular solvents with very low volatility, problems of mutual solubility may arise and some compromise is needed (23). From ISE studies it is known that membranes with o-NPOE plasticizer may be stable for more than 2 years (24).

We studied the losses of plasticizer for two solvents, and the results expressed as cumulative losses in dependence on time are given in Fig. 2. The membranes were placed in a room with good ventilation but without direct air currents around the samples. A distinct slowing down of the differential losses with time was observed. The losses of the solvent for o-NPOE are very small, indicating long term durability of the material.
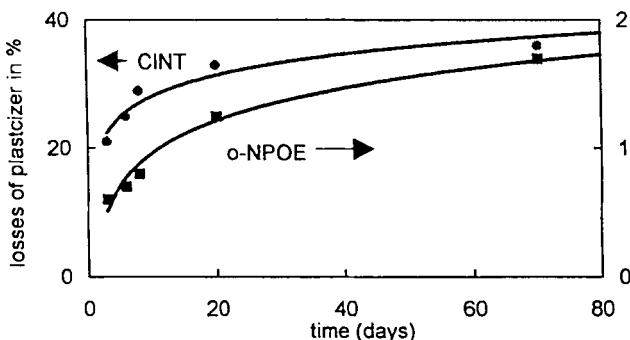
FIG. 2   Kinetics of plasticizer losses. Cumulative losses of plasticizer from the membrane
are given for two plasticizers. See details in text.

But even for CINT a significant increase of the compactness of the membrane was observed after 30 days.

Screening Tests of Use of the Membranes for Highly Salinic Media

This work was oriented toward the possible use of membranes for the separation of ^{137}Cs and ^{90}Sr from United States high-level radioactive wastes from national defense programs. Consequently, the following study concerns the possible use of PVC plasticized sorbents for isolation of these two radioisotopes from both acidic and alkaline media with a relatively high $NaNO_3$ content. We used chlorinated dicarbollylcobaltatate and tetraphenylborate anions as reagents.

The results for dicarbollide anion are given in Table 4. It is seen that sufficiently high K_d's are measured for cesium, even from media containing 4 M $NaNO_3$. However, for solutions containing 0.5 M NaOH, decomposition of chlorinated dicarbollide is observed. Strontium was poorly sorbed under all conditions. Hence, we tried to use a strontium synergist more powerful than Triton X 114. It may be noted here that Triton X 114 of Slovak production (Slovafol 909, nonylphenol nonylethylene glycol) was proposed in Czech-Russian dicarbollide technology for the isolation of the two isotopes in question from Purex waste by Czech scientists (3, 4). However, its use as a Sr synergist for media with high $NaNO_3$ was never successful, so its failure here is not surprising. Also, the poor distribution coefficients of Sr when using this synergist for media of high salinity, as it probably is in the "Russian" dicarbollide process (25), are not unexpected.

TABLE 4

Sorption of ^{137}Cs and ^{85}Sr on Cobalt Dicarbollide–Triton X 114 Membranes
from Acid and Base and Varying Amounts of NaNO₃[a]

Acid/base	NaNO₃ (M)	K_d(Cs)	K_d(Sr)
0.5 M HNO₃	1	19.50	2.00
	2	11.34	1.54
	3	7.54	1.30
	4	5.84	1.08
0.5 M NaOH[b]	1	32.69	4.49
	2	17.20	2.91
	3	10.43	1.99
	4	7.56	2.09

[a] Membranes: Membranes of the same composition as in Table 3 and with a HMW PVC ratio to extractant equal to 100% were cast. Shaking time: 4 hours.

[b] Strong yellow coloration of the aqueous phase due to the dissolved chlorinated cobalt dicarbollide.

Substitution of HMW PVC by LMW did not lead to any improvement. In another series, a crown ether (dibenzo-18-crown-6) was used in concentrations of 0.062–0.163 M (for 0.2 M HBCl in *o*-NPOE and 1 M HNO₃ + 2 M NaNO₃ in the aqueous phase) instead of Triton X 114. Practically no sorption of strontium occurred for the membranes with DB-18-C-6, and K_d(Cs) slightly decreased from 9.89 to 3.49 with an increasing concentration of the crown ether. Further, we tried to change the solvent phase to very hydrophobic by using 2,5-di-*tert*-butylnitrobenzene (preparing the membrane by its dissolution as a solid at room temperature, together with HBCl in PVC–THF solution, and evaporating the THF). However, at these conditions crystallization in the membrane occurred, accompanied by practically no sorption. The effect of crystallization of compounds with melting points higher than room temperature in the membrane phases is known and was thoroughly discussed by Eugster et al. (9).

Systems with Dicarbollide and PEG 400

According to our previous experience, the use of simple nonsubstituted polyethylene glycols, such as PEG 400, may be particularly effective for increasing the distribution ratio of Sr from media with a high Na⁺ ions content. This effect is ascribed to steric hindrance of full coordination of etheric oxygens to Sr²⁺ for alkylphenol-substituted PEGs (4). Hence, we used PEG 400 synergist. Further, we changed the toxic nitrobenzene to two nontoxic solvents, *o*-NPOE and ClNT. Experiments with dicarbollide

were done in both the extraction and sorption modes in order to 1) com-
pare the results in the two modes and (2) possibly improve the dicarbollide
extraction process with a new solvent and synergist for Sr. The results
are given in Fig. 3.

Each element and solvent is depicted in four bars. The first three bars
correspond to sorption on the membrane containing about 70% HMW
PVC relative to the extractant, and the fourth bar is the extraction experi-
ment (0% PVC). Because of the quick establishment of equilibrium in
the extraction experiments, the latter value is considered to represent

a) Cs^+
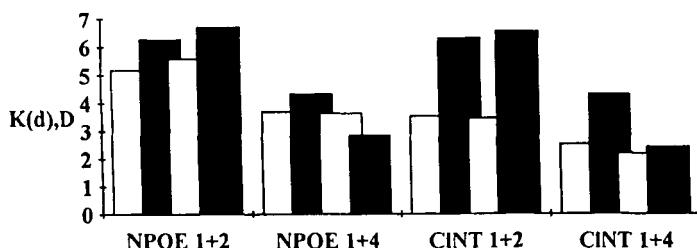
b) Sr^{2+}
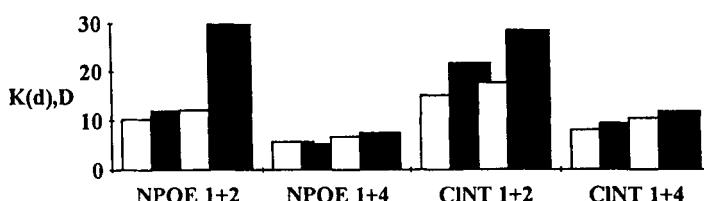
FIG. 3   Comparison of data for sorption, sorption on pretreated membranes, and extraction
distribution ratio with the same system without PVC. In each series of four columns, the
first column is sorption during 4 hours, the second column is sorption during 4 hours on a
pretreated membrane, the third column is sorption on a nonpretreated membrane after 24
hours, and the fourth column is the distribution ratio of elements at equilibrium for the
respective extraction systems. Membranes contained 0.2 M chlorinated cobalt dicarbollide
+ 3% PEG 400 in the respective solvent with a solvent to PVC ratio of 5 mL to 3.5 g (HMW
PVC). Pretreatment was done by keeping the material for 72 hours in 2.5 M HNO_3. The
extraction time for the distribution ratio (at PVC = 0) was 30 minutes. In "1 + x" in the
legend, 1 stands for 1 M HNO_3 and x is the molar concentration of $NaNO_3$. See the experi-
mental Section for the abbreviations of solvents.

approximatively the equilibrium state for membrane sorption. (In fact, the effect of "dilution" by PVC applies to membrane experiments, see the Fig. 3 legend. For strict comparison, the density of the membrane should be known as defined by K_d and D in the Procedures and Measurement Section. For a simple comparison, the density of the membrane may be approximated as $g/V = 1$ g/mL.)

The three first entries correspond to sorption on a nonpretreated membrane for 4 hours and on a pretreated membrane for 4 and 24 hours, respectively. Pretreatment of membranes by washing them for a given time in a solution of specific composition is a common practice in electrochemical sensor fabrication.

It can be seen from the figure that equilibrium for cesium is nearly established for a membrane system with a contact time of 4 hours. For strontium, the D values are higher than the respective K_d values for a lower $NaNO_3$ content at higher ionic strengths of the aqueous phase; however, the differences are small.

An interesting feature of Fig. 3 is the effect of pretreatment of the membrane for 72 hours with 2.5 M HNO_3 (second bar for each set of four data). This seems to be particularly pronounced for ClNT solvent and cesium. In two data sets in Fig. 3, the distribution values of Cs were even higher for pretreated membranes than for extraction. A tentative explanation may be that in both solvents some impurities which decrease the distribution of cesium (but not that of strontium) are removed during pretreatment.

Acceptable distribution coefficients for strontium, even from solutions of 1 M HNO_3 + 4 M $NaNO_3$, were obtained. Materials with D or K_d = 5–10 may be successfully used both in countercurrent extraction and sorption modes.

We tried to prepare membranes with dicarbollide and PEG 400 for fluorinated nitro solvents. During evaporation of THF, high proportions of FNT, F2NB, and F3NB were lost, and the membranes with F2NB and F3NB became brittle. These materials were not tested for sorption. Nevertheless, the fluorinated nitro solvents, being nontoxic, may be used in the dicarbollide extraction process as substitutes for toxic nitrobenzene, and data on the distribution of cesium and strontium in the liquid–liquid extraction mode are given in Table 5.

Technologically acceptable distribution ratios of Sr (7.9–11.5) were obtained from a mixture of 1 M HNO_3 + 4 M $NaNO_3$. The fourth solvent in the table is a mixture of o-NPOE with DDB. It is seen from a comparison of the table and Fig. 3 that this mixture gives a slight increase to the distribution ratios in comparison with pure o-NPOE. Also, the hydrodynamic characteristics are better than for pure o-NPOE. The last solvent

TABLE 5

Extraction of ^{137}Cs and ^{85}Sr by 0.2 M Chloroprotected Cobalt Dicarbollide and 3% PEG 400 into Various Solvents

Solvent	FNT	F2NB	F3NB	o-NPOE + DDB[c]	DBuPht
D_{Cs} (1 + 2)[a]	18.5	23.1	19.1	11.4	0.510
D_{Sr} (1 + 2)[a]	20.9	31.7	14.3	26.9	1.36
D_{Cs} (1 + 4)[b]	9.52	9.89	7.97	5.93	0.214
D_{Sr} (1 + 4)[b]	11.5	7.87	8.44	10.3	0.300

[a] Extraction from a mixture of 1 M HNO$_3$ + 2 M NaNO$_3$.

[b] From a mixture of 1 M HNO$_3$ + 4 M NaNO$_3$.

[c] By a solvent of 45 vol% of o-NPOE + 55% DDB; extraction time 30 minutes in all cases.

in Table 5 DBPht, is ineffective for extraction, probably because of its partial protonization in acidic media.

Systems with Sodium Tetraphenylborate and PEG 400

We investigated the tetraphenylborate reagent for use in highly alkaline solutions since it is reported to be more stable than halogenated dicarbollides in alkaline solutions. The membranes were prepared in the same manner as with dicarbollides and the same concentrations of reagents (i.e., 0.2 M reagent and 3% PEG 400) were used. The sorption results for Cs and Sr ions and mixtures of NaOH and NaNO$_3$ are given in Table 6.

It is seen that generally and rather unexpectedly high K_d values are obtained. This is still more apparent when comparing dicarbollide and the same concentrations of reagents in the organic phase and same total content of Na$^+$ in the aqueous phase. The sorption of cesium strongly increases with NaOH content but decreases with NaNO$_3$ content. Sorption of strontium is more regular in the sense that K_d decreases with increasing Na$^+$ content. There may be an influence of activity coefficients for high ionic strengths, or perhaps the formation of undissociated ion pairs in the PVC layer, but the effect should be studied.

We have also performed preliminary extraction experiments with the above systems, but these are not reported in detail here. The distribution ratios were in good accord with data from Table 6 for both Cs and Sr when the solvent was ClNT. If FNT was used instead of ClNT, a white precipitation which contained the main portion of radioactivity (samples of both centrifugated liquid phases have shown radioactivity below the detection limit of measurement for both Cs and Sr) occurred at the inter-

TABLE 6
Sorption of ^{137}Cs and ^{85}Sr on the Membrane Composed from Sodium
Tetraphenylborate–PEG 400–ClNT in PVC[a]

(a) From NaOH Solutions			
NaOH (M)	1	1.90	3.04	3.93
K_d(Cs)	373	21.2	141	467
K_d(Sr)	27.7	29.7	8.47	4.12

(b) From 1 M NaOH + NaNO$_3$ Solutions		
NaNO$_3$ (M)	2.05	3.15	4.12
K_d(Cs)	234	201	92.1
K_d(Sr)	62.5	22.5	12.3

[a] 0.2 M solution of NaTPhB + 3% PEG 400 was prepared in 4-chloro-3-nitrobenzene (the solid which formed after addition of PEG 400 dissolved after shaking the organic phase with a solution of aqueous 1 M NaNO$_3$ two times). A ratio of 3 mL solution:2.35 g of HMW PVC was used for the preparation of membranes. The time of contact with the radioactive solution was 24 hours.

face. When DBPht was the solvent, the distribution ratios of Cs were higher than 10 and distribution ratios of Sr were close to 1–2 for mixtures of 1 M NaOH + 2 M NaNO$_3$ and 1 M NaOH + 4 M NaNO$_3$. Other variants of solvents and solvent mixtures are currently under investigation.

CONCLUSIONS

On the basis of compositional similarity of the materials used as ion selective electrodes and extraction systems for the extraction of ions, a hypothesis of the possible use of ISE materials as sorbents of ions was formulated. The hypothesis was experimentally verified in this work.

For practical use, membranes containing as extracting agent anions of chlorinated dicarbollylcobaltate and tetraphenylborate were prepared and tested. From synergestic agents for Sr, the best one studied was polyethylene glycol of MW 400. The studied materials can be used for the efficient separation of ^{137}Cs and ^{90}Sr from solutions containing 1 M HNO$_3$ or 1 M NaOH and NaNO$_3$ up to a concentration of 4 M.

A second main result of this study is the possibility of substituting some nontoxic nitroaromatic solvent for toxic nitrobenzene in extraction technology for the preparation of the membrane materials and in electrochemi-

cal studies. The extraction characteristics of these new solvents are nearly the same as those of nitrobenzene.

All examined properties except the kinetics were the same for the extraction systems and derived membrane phases. Hence, although not studied in this work, it may be reasonably supposed that the capacity of the membranes toward the studied ions will also be the same. In practice, this means that the membranes prepared here (0.2 M solution of reagent in 5 mL of solvent mixed with 3.5 g of PVC) possess a cation exchange capacity of the order of 0.12 mmol of Cs^+/g. This value is sufficient for most use during the treatment of nuclear wastes.

A practical use of the studied materials would be whenever the separation properties of the extraction system are to be maintained but the presence of a liquid phase is not desirable, e.g., use of membrane sheets in the dip-in mode or as separators. Classical use as a separating membrane in a two-compartment arrangement is possible. As a practical application, we tried forming the membrane directly on the measuring window of a radiometric device for the purpose of preconcentrating the radioisotope to be measured. The possibility to preparing PVC—plasticizer materials in the form of spherical particles is also envisaged.

ACKNOWLEDGMENTS

REFERENCES

1. D. J. McCabe, *WSRC-RP-93-1325*, 1993.
2. S. F. Marsh, Z. V. Svitra, and S. M. Bowen, *LA-12654, Rev.*, 1994.
3. J. Rais, P. Selucký, and L. Kadlecová, *ÚJV-7956-Ch*, 1986.
4. J. Rais, P. Selucký, and M. Kyrš, *J. Inorg. Nucl. Chem.*, *38*, 1376 (1976); J. Rais, E. Šebestová, P. Selucký, and M. Kyrš, *Ibid.*, *38*, 1742 (1976); J. Rais, M. Kyrš, and S. Heřmánek, Czechoslovak Patent 153,933 (1973); M. Kyrš, S. Heřmánek, J. Rais, and J. Plešek, USSR Patent 508,476 (1976); M. Kyrš, S. Heřmánek, J. Rais, and J. Plešek, Czechoslovak Patent 182,913 (1980); M. Kyrš, J. Rais, P. Selucký, V. Škarda, S. Heřmánek, J. Plešek, J. Koryta, and H. Gáncheová, *Symposium IMEBORON III*, Etal, Germany, 1976; E. Makrlík, P. Selucký, P. Vaňura, J. Rais, M. Kyrš, and I. Podzimek, *Proc. ISEC'83, Int. Solv. Extr. Conf.*, Denver, USA, 1983; etc.
5. J. Krtil, M. Fojtík, and M. Kyrš, *Collect. Czech. Chem. Commun.*, *27*, 2096 (1962).
6. T. Sekine and D. Dyrssen, *Anal. Chim. Acta*, *45*, 133 (1969).
7. D. M. Pranitis, M. Telting-Diaz, and M. E. Meyerhoff, *Crit. Rev. Anal. Chem.*, *23*, 163 (1992).
8. J. Rais, *Collect. Czech. Chem. Commun.*, *36*, 3080 (1971).

9. R. Eugster, T. Rosatzin, B. Rusterholz, B. Aebersold, U. Pedrazza, D. Rüegg, A. Schmid, U. E. Spichiger, and W. Simon, *Anal. Chim. Acta*, *289*, 1 (1994).
10. R. Kopunec and Th. Ngo Manh, *J. Radioanal. Nucl. Chem.*, *Articles*, *183*, 181 (1994).
11. E.g., R. Block, O. Kedem, and D. Vofsi in *Proc. Int. Conf. Solv. Extr. Chem.*, Gothenburg 1966, North-Holland, Amsterdam, 1967, p. 605.
12. M. Sugiura, M. Kikkawa, and S. Urita, *J. Membr. Sci.*, *42*, 47 (1989); M. Sugiura, *Sep. Sci. Technol.*, *25*, 1189 (1990); *Ibid.*, *27*, 269 (1992).
13. B. Bauer, H. Strathmann, and H. Schulenberg-Schell, European Patent Application 93117131.8 (1993).
14. E. Bakker, M. Willer, M. Lerchi, and E. Pretsch, *Anal. Chem.*, *66*, 516 (1994).
15. L. Q. Hung, *J. Electroanal. Chem.*, *115*, 159 (1980).
16. P. Vanýsek in *Biomembrane Electrochemistry* (M. Blank and I. Vodyanoy, Eds.), American Chemical Society, Washington, D.C., 1994, p. 55.
17. T. Kakiuchi, *Electrochim. Acta*, *40*, 2999 (1995).
18. H. H. Girault, in *Modern Aspects of Electrochemistry* (J. O'M. Bockris, B. E. Conway, and R. E. White, Eds.), Plenum Press, New York, NY, 1993, p. 1.
19. V. V. Korolev, M. A. Afonin, A. A. Kopyrin, V. V. Proyaev, V. V. Romanovskii, A. N. Viznyi, V. N. Romanovskii, and L. N. Lazarev, *Radiokhimiya*, *3*, 97 (1990); V. V. Proyaev and V. N. Romanovskii, *The Treatment of Liquid HLW by Liquid Extraction* (in Russian), St. Petersburg Technology Institute, St. Petersburg, 1992.
20. J. Rais and S. Tachimori, *Sep. Sci. Technol.*, *29*, 1347 (1994).
21. P. Vaňura, J. Rais, P. Selucký, and M. Kyrš, *Collect. Czech. Chem. Commun.*, *44*, 157 (1979).
22. K. N. Mikhelson, *Sensors Actuators B*, *11*, 1 (1993).
23. T. H. Durrans, *Solvents*, Chapman & Hall, London, 1957.
24. E. Pretsch, R. Büchi, D. Amman, and W. Simon, in *Essays on Analytical Chemistry* (E. Wänninen, Ed.), Pergamon Press, Oxford, 1977.
25. T. A. Todd, K. N. Brewer, R. S. Herbst, T. J. Tranter, V. N. Romanovskii, L. N. Lazarev, B. N. Zaitsev, V. M. Esimantovskii, and I. V. Smirnov, *Proceedings of The Fifth International Conference on Radioactive Waste Management and Environmental Remediation*, September 3–8, 1995, Berlin, Germany, p. 463.