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THE USE OF LIQUID ION EXCHANGERS IN EXTRACTION CHROMATOGRAPHY

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SUMMARY

   A new development in separation science is the application of liquid ion exchangers. For the separation of metal ions, additional complexing in the aqueous phase can be favourable in some instances. The best method for increasing the efficiency of a separation is to impregnate an inert support with the exchanger.
   A number of analytical problems can be solved, and reversed-phase chromatography is useful especially in the separation of rare earth elements. From the chromatographic data, conclusions on the behaviour of ion-exchange resins, extractants and reactions in the aqueous phase can be drawn.

   In the development of ion-exchange technology, new fields of application have been discovered that require ion-exchange materials which differ from conventional materials not only in their functional groups but also in physical form. The use of water-insoluble acidic and basic reagents as liquid ion exchangers was first proposed by Smith and Page[1] in a paper entitled "The acid-binding properties of long-chain aliphatic amines". Since then, increasing interest has been shown in the use of high-molecular-weight bases and acids as extractants.
   The operation of liquid ion exchangers involves the selective transfer of electrolytes between two immiscible phases. In this process, the electrolytes undergo reactions that influence this distribution. In the aqueous phase, hydration (ion–dipole interaction), complex formation (covalent interaction) and ion association (electrovalent interaction) occur. In the organic phase, in addition to solvation, complex formation and ion association also occur. In general, ion associates are considered to be aggregates in which the different ions are separated by solvent molecules, while ion pairs, in which the ions are not separated by solvent molecules, are often referred to as complexes, even if the charges are still located on their original sites[2].
   Of course, liquid cation exchangers effect extraction by exchanging protons for cations originally present in the aqueous phase and liquid anion exchangers effect extraction by exchanging their original anion with an anionic species in the aqueous phase. However, a number of additional effects must also be considered.
   One of the most recent applications of liquid ion exchange is the recovery of

copper by the so called LIX reagents (LIX = liquid ion exchanger). These are hydroxyoximes:
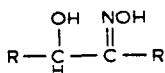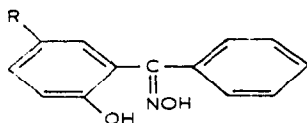
LIX 63   LIX 64N

which extract copper very selectively, and it is reported[3] that the recovery of copper from low-grade ores is possible. This is not, of course, a pure ion-exchange reaction. The high selectivity is a consequence of complex formation.

As a first example of reversed-phase extraction chromatography, the application of LIX 64 will be mentioned. Cerrai and Ghersini[4] treated paper or cellulose powder with LIX 64 and were able to separate copper from cobalt, nickel, manganese, chromium, molybdenum, tungsten, vanadium and iron (after aqueous phase complexing with fluoride).

In his Plenary Lecture, Prof. Laskorin[5] pointed out the advantages and disadvantages of liquid ion exchangers. For analytical chemists, separation problems in which elements with very similar chemical properties are to be separated are mainly of interest. In some instances, the high selectivity of liquid ion exchangers is sufficient. Here the amine extraction of coloured anionic species (extraction photometry) can be mentioned. But in other instances, one requires better separation factors, and one possibility for obtaining them is by aqueous phase complexing. Here use is made from the different stabilities of coordination compounds in the aqueous phase. However, only in a few instances is a really good separation possible.

Another possibility for improving the separation is to combine liquid ion exchange with a chromatographic process, permitting an elementary separation step to be repeated many times. An inert support is treated with the liquid ion exchanger and a thin-layer or paper chromatographic or column operation is carried out. Because the organic phase is the stationary phase, the process is called reversed-phase extraction chromatography. An excellent review of the theory and applications of this technique was given by Cerrai and Ghersini[6], and at this conference the most active workers in this field, Ghersini[7], Testa and Delle Site[8], and Brinkman *et al.*[9], reported their latest results.

In liquid ion exchange, the ratio of the concentrations of a given element in the two phases at equilibrium is called the distribution coefficient. In the thin-layer or paper chromatographic application of reversed-phase chromatography, a relationship with the R_F value exists:

$$D = \frac{A_L}{A_S} \cdot \left(\frac{1}{R_F} - 1 \right)$$

$$R_M = \log \left(\frac{1}{R_F} - 1 \right)$$

where D is the distribution coefficient and A_L and A_S are the cross-sectional areas of the liquid (aqueous) and stationary (organic) phases, respectively.

In Table I, a list of liquid anion exchangers is given, based on primary, sec-
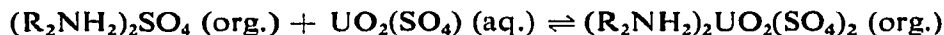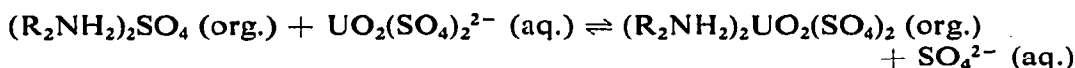
TABLE I

LIQUID ANION EXCHANGERS

Type	Composition	Name/abbreviation
Primary amine	Trialkylmethylamine	Primene JM-T
Secondary amine	N-Dodecenyltrialkylmethylamine	Amberlite LA-1
	N-Lauryltrialkylmethylamine	Amberlite LA-2
Tertiary amine	Tri-n-octylamine	TnOA
	Triisooctylamine	TiOA
	Tri-n-octylamine + tri-n-decylamine	Alamine 336
Quaternary ammonium salt	Methyltri-n-(octyl + decyl)ammonium chloride	Aliquat 336

ondary, tertiary and quaternary amines. In the following discussion, the different types of amines are not considered, but rather the different types of aqueous systems involved.

As an example of hydrochloric acid systems, the results of Neef and Grosse-Ruyken[10] who separated trace concentrations of manganese, iron, cobalt, copper, nickel, zinc and cadmium, can be mentioned. Such a separation is possible only by use of a chromatographic procedure. Using TnOA on silica gel and by a gradient elution column technique, a complete separation of all these elements was possible, when the elution conditions were determined from liquid ion-exchange experiments.

The nitric acid system is often used in the separation of rare earths. In liquid ion exchange with TOA, the distribution coefficients of the rare earth elements decrease with atomic number[11]. Hence it should be possible to increase the separation factors by aqueous phase complexing, because of the better extraction of the lanthanum which forms the less stable complexes with EDTA. However, little success was achieved[11]. On the other hand, the R_F differences obtained in reversed-phase chromatography by Testa[12] using the same system are large enough for some separations to be obtained.

In liquid anion exchange, it is not clear whether real anion exchange or adduct formation occurs. In an investigation by Coleman and McDowell[13], the amine extraction of uranium from acidic sulphate solutions was examined by interfacial tension measurements and by studying the transfer of ^{35}S-labelled sulphate between the two phases. In the system in question, in the aqueous phase the species UO_2SO_4 and $UO_2(SO_4)_2^{2-}$ exist and so two reactions are possible:

$$(R_2NH_2)_2SO_4 \text{ (org.)} + UO_2(SO_4)_2^{2-} \text{ (aq.)} \rightleftharpoons (R_2NH_2)_2UO_2(SO_4)_2 \text{ (org.)}$$
$$+ SO_4^{2-} \text{ (aq.)}$$

$$(R_2NH_2)_2SO_4 \text{ (org.)} + UO_2(SO_4) \text{ (aq.)} \rightleftharpoons (R_2NH_2)_2UO_2(SO_4)_2 \text{ (org.)}$$

The difference is that if an anion is exchanged, a sulphate ion from the organic phase is transferred to the aqueous phase, which does not occur in neutral uranyl sulphate transfer. It was found that uranyl amine extraction from sulphate solutions proceeds by both anion exchange and neutral transfer, the proportion shifting according to the proportion of anionic uranium present, probably with some bias towards anion exchange.

TABLE II

LIQUID CATION EXCHANGERS

Composition	Abbreviation
Dinonylnaphthalenesulphonic acid	HDNS
Di-(2-ethylhexyl)orthophosphoric acid	HDEHP
Di-n-butylorthophosphoric acid	HDBP
2,6,8-Trimethylnonyl-4-phosphoric acid	H_2MiDP

In Table II, some liquid cation exchangers are listed. In addition to the compounds listed, carbonic acids must also be considered. Gindin *et al.*[14] introduced liquid ion-exchange extraction, in which not only an exchange with hydrogen ions occurs but also an exchange between different metals. In the reversed-phase technique, phosphoric acids and dinonylnaphthalenesulphonic acid were mainly used as stationary phases. Extraction by dialkylphosphoric acids, for instance for a rare earth element, occurs according to the reaction

$$M^{3+} \text{ (aq.)} + 3[(RO)_2PO(OH)]_2 \text{ (org.)} \rightleftharpoons M\{[(RO)_2POO]_2H\}_3 \text{ (org.)} + 3H^+ \text{ (aq.)}$$
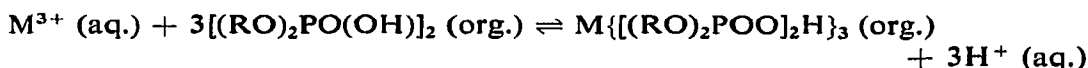
We obtained thin-layer chromatographic separations of the rare earth elements on silica gel impregnated with HDEHP[15,16], and it was shown that the anions in the aqueous phase have some influence on the exchange kinetics.

With organophosphorus liquid cation exchangers, in the rare earth series an increase in distribution coefficients usually occurs with increasing atomic number. In general, the separation of rare earths by liquid–liquid extraction is not very good, and we would therefore like to use the double effect of extraction and aqueous phase complexing. However, almost invariably the two effects tend to neutralize each other. The aqueous phase complexing favours the higher atomic numbers, and one will therefore have a partially nullifying effect rather than an enhancing effect. It is not very likely that there will be ligands in the aqueous phase that form less stable complexes with the heavier rare earth elements. Therefore, we looked for liquid cation exchangers that have the desired property. By analogy with sulphonic acid ion-exchange resins, dinonylnaphthalenesulphonic acid could be used[17]. According to Eisenman's theory, the reversal of selectivity between phosphoric or carbonic acid exchangers and sulphonic acid exchangers can be explained. In the first case, the gain in free energy

$$\Delta G_{1/2}^0 = \left(\frac{e^2}{r_A + r_2} - \frac{e^2}{r_A + r_1} \right) - (\Delta G_2 - \Delta G_1)$$

(where 1 and 2 are the exchanging ions, e is the charge, r_A and r_i are the radii of the fixed group and of the ions 1 and 2, and ΔG_1 and ΔG_2 are the standard free energies of hydration of the counter ions) is determined by the first terms in the equation because r_A is small. Hence the exchanger will prefer the ion with the smaller radius. In the case of sulphonic acids, where r_A is relatively large, the second terms are important. Because of the lanthanide contraction, the lighter elements are now pre-

ferred. Therefore, the addition of complex-forming agents to the aqueous phase is useful[18]. The effect is not very large but, in the separation of the alkaline earth elements, a separation factor for Sr/Ca of 120 was found[19].

In the case of HDNS also, the reversed-phase technique in chromatography gives better results. With α-hydroxyisobutyric acid as eluent, a separation of the rare earth elements on paper impregnated with HDNS is possible[20]. However, it must be mentioned that reproducible results can be achieved only if real elution chromatography is effected, *i.e.*, the paper strip must be in equilibrium with the eluent before the elements are spotted. The usual R_F and R_M values then cannot be obtained but, by introducing the velocity of the element and the velocity of the eluent, which can be determined, an analogous value is found. By this method, a complete separation of the rare earth ions was possible[21]. The chromatographic data can also be used to calculate the composition and stability of complexes between the metal ions and the eluent in the aqueous and stationary phases[22]. From the results, a very close analogy between reversed-phase liquid ion exchange and resinous ion exchange was obtained, and we obtained the same separation factors as on ion-exchange resins. Therefore, liquid ion exchangers fixed on an inert support can be used as models for ion-exchange resins and for solvent extraction, and are thus an invaluable analytical tool.

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