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SOME ASPECTS OF ION-EXCHANGE IN NON-AQUEOUS AND MIXED SOLVENTS

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SUMMARY

The author's published work has been used to illustrate certain aspects of ion-exchange resin stability and sorption behaviour in non-aqueous and mixed solvent media. Solvent and thermal stability studies have confirmed that even strong-base ion-exchange resins are sufficiently stable in methanol and heptane media at ambient temperature to permit their use in analytical separations. The enhanced selectivity differences of ion-exchange resins for inorganic ions in mixed media is illustrated by the sorption of alkali metal ions on Zeo-Karb 225 (hydrogen form) from aqueous methanol, aqueous ethanol, and aqueous acetone. Finally, on the organic side, the discussion of work on the separation principles of phenols from methanolic media with De-Acidite FF (acetate form) is extended to the wider context of ion-exchange fractionation of peat and petroleum constituents.

INTRODUCTION

It has long been known that water is by no means the only solvent from which sorption by ion-exchange resins can take place; over a quarter of a century ago some of the general principles of ion exchange in mixed solvents had been established¹. For example, Na⁺, K⁺, Ba²⁺, and Ca²⁺ ions were claimed to show greater affinity for a cation exchanger in aqueous solutions of increasing ethanol or acetone content¹. Enhanced sorption and selectivity trends have since been confirmed and recent reviews²⁻⁴ summarise the several systematic investigations demonstrating the versatility of non-aqueous solvents and aqueous-organic solvent mixtures for metal separations.

Rather more striking is the fact that many organic compounds can ionize sufficiently or are sufficiently polar to permit sorption by ion exchangers. This phenomenon even extends to the sorption by orthodox ion-exchange resins of naphthenic acids, alkylphenols and certain non-basic and basic nitrogen compounds present in non-ionising petroleum fractions⁵.

The use of non-aqueous and mixed solvent media therefore offer a greatly extended scope for ion-exchange resins and illustrations of the sorption principles of inorganic and organic materials and of ion-exchange resin stability are centred on the author's published work.

STABILITY AND SWELLING CONSTRAINTS

Stabilities of ion-exchange resins have recently been reviewed from the mechanical⁶, chemical⁶, radiation⁷, solvent⁸, and thermal⁸ standpoints. Solvent and thermal stabilities are of special interest in the present context and observations in aqueous systems that salt forms of the resins are more able to withstand high temperatures than are free-base and free-acid forms^{8,9} also apply to basic resins in non-aqueous media like methanol and heptane⁸. This pattern presumably extends to acidic resins in non-aqueous media as might also be the trend for free-base resins less resistant to capacity loss than the free-acid types. Weak-base and weak-acid resins are generally more stable thermally than their strong-base and strong-acid counterparts⁹.

Just as in water, ion-exchange resins are degraded in non-aqueous solvents by normal erosive forces, but in organic solvent media the hydrocarbon resin matrix might be expected to be especially sensitive to erosion. This could account for the tendency to particle attrition and emulsification at higher temperature ($>50^{\circ}$) in methanol and heptane¹⁰. The greater incidence of this feature in macroreticular resins lends support to this susceptibility of the hydrocarbon matrix¹⁰. Nevertheless, stability studies at ambient temperature indicate that resins have adequate stability in non-aqueous media¹⁰ for a wide range of studies and applications.

Provided the desired separation objective is achieved, the relatively slow exchange rate imposed by low swelling characteristics in non-aqueous media can be tolerated and in this respect it is now appreciated that considerable ion-exchange capacity is possible without resin swelling¹¹. Thus, even the microporous or gel-type resins are sufficiently porous to permit ready access of solvents and polar species. Here, the studies of Inczédy and Pásztlér¹² with strongly acidic and strongly basic resins in seven water-miscible solvents are interesting. They confirm earlier reports that swelling is at a maximum with water, with alcohols and glycols also producing significant swelling. However, there is a surprising difference between solvent sorption by the hydrogen and sodium forms of cation exchangers in ethanol with a lesser difference in methanol¹². This is significant, and in the low swelling of the sodium form in ethanol (0.3 for Dowex 50-X8 in sodium form compared with 2.5 for the hydrogen form) there may well be a clue to pronounced selectivity patterns in non-aqueous over aqueous media. Similar swelling patterns were observed for macroporous or macroreticular resins¹³.

SELECTIVE SORPTION OF INORGANIC MATERIALS

Much of the work on ion exchange from non-aqueous and mixed solvent media has been aimed at developing new and improved methods for separating and purifying lanthanides and actinides, mostly by anion exchange in mixed solvents containing water^{14,15}. Experimental studies undertaken to learn more of the ion-exchange process have been mainly based on straightforward cation exchange, especially of univalent cations, and useful data on ion selectivities for cation exchangers have been accumulated. Recent studies¹⁶ demonstrate that while selectivity differences of Zeo-Karb 225 (8% divinylbenzene) in the hydrogen form were not very marked for alkali metal ions in water, there were strikingly different extents of increase in resin affinity

TABLE I

SELECTIVITY COEFFICIENTS, K_H^M , FOR HYDROGEN FORM OF ZEO-KARB 225 (8% DVB) IN WATER AND ORGANIC SOLVENT-WATER AT 30°¹⁶

Volume fraction water	Organic solvent	K_H^M					
		Li-H	Na-H	K-H	Rb-H	Cs-H	NH ₄ -H
1.0*	Methanol	0.92	1.61	2.34	2.12	2.29	1.86
	Ethanol	0.83	1.62	2.29	1.64	1.71	1.13
	Acetone	1.03	1.50	1.89	1.89	2.06	1.89
0.1	Methanol	2.08	33.5	978	147	79	15.6
	Ethanol	7.5	83	183	99	67	8.5
	Acetone	15.2	53	15.2**	173	21.4**	16.3**

* Three sets of figures arise for water because the preliminary resin treatment involves washing with organic solvent.

** These figures may be low because of poor solubility.

for the alkali metal ions with increasing organic solvent (Table I). This leads to increasing and very substantial selectivity differences between one ion and another, as is illustrated by the data of Table I, in passing from purely aqueous media to 90% by volume of methanol, ethanol or acetone in water.

Although polarity of the medium as expressed by the dielectric constant is an important factor, the breakdown of the linear relation between $\log K_H^M$ and $1/D$ through the tendency of selectivities to maximise suggests that several factors may be responsible for selectivities. These include solvation, hydrogen bonding, ion-pair formation, and the coordinating abilities of the solvent. Also meriting consideration are the standard molar free energies of transfer for single cations between various media¹⁷. As seen from the data of Table II, such free energies of transfer between water and water-methanol media become increasingly lower with increasing methanol content of the medium. This pattern is relevant in the light of the observation¹⁸ that the medium associated with the resin phase is predominantly aqueous. Thus, the fact that the alkali metal ions, Li⁺, Na⁺, and K⁺, are sequentially in a higher (more positive) free energy state than hydrogen (Table II) has been used¹⁶ to suggest that hydrogen ions prefer the more organic liquid medium. This leads to an increase in K_H^M with increasing organic solvent content of the medium and to increasingly higher K_H^M in the series Li⁺, Na⁺, K⁺ as the free energy of the ion relative to hydrogen becomes more positive.

TABLE II

STANDARD FREE ENERGY OF TRANSFER (J/mole) AT 25° OF SINGLE CATIONS FROM WATER TO WATER-METHANOL MEDIA¹⁷

Ion	Water-10% (w/v) methanol	Water-43.12% (w/v) methanol
H ⁺	-2060	-11 760
Li ⁺	-1390	-8 400
Na ⁺	-920	-5 900
K ⁺	-800	-5 000
	(±250 J/mole)	(±2 500 J/mole)

No amount of theoretical explanation will disguise the feature of potential analytical interest, namely, that mixed organic solvent-water media are capable of creating large differences in selectivity coefficients with the effect of also bringing about changes in the order of selectivities with consequent interesting separation possibilities (Table III).

TABLE III

AFFINITY ORDER OF HYDROGEN FORM OF ZEO-KARB 225 (8% DVB) FOR ALKALI METAL/AMMONIUM IONS IN VARIOUS ORGANIC SOLVENT-WATER MEDIA AT 30° (REF. 16)

<i>Solvent composition</i> (% organic solvent)	<i>Affinity (decreasing) →</i>					
Methanol						
0	K	Cs	Rb	NH ₄	Na	Li
10	K	Cs =	NH ₄	Rb	Na	Li
30	K	Rb	Cs =	NH ₄	Na	Li
50	K	Rb	Na	Cs	NH ₄	Li
70	K =	Rb	Cs	Na	NH ₄	Li
90	K	Rb	Cs	Na	NH ₄	Li
Ethanol						
0	K	Cs	Rb	Na	NH ₄	Li
10	K	Cs	Rb	Na	NH ₄	Li
30	K	Na	Rb	Cs	NH ₄	Li
50	K	Na	Rb	Cs	NH ₄	Li
70	K	Na	Rb	Cs	NH ₄	Li
90	K	Rb	Na	Cs	NH ₄	Li
Acetone						
0	Cs	Rb =	K =	NH ₄	Na	Li
10	Cs =	Rb =	K	N ₄ H	Na	Li
30	Rb	K	Cs	Na	NH ₄	Li
50	Rb	K =	Na	Cs	NH ₄	Li
70	Rb	K	Na	Cs	NH ₄	Li
90	Rb	Na	Cs	NH ₄	K =	Li

SEPARATION OF ORGANIC MATERIALS

An important area of application of ion-exchange resins in non-aqueous solvent media is in the separation of organic acids and bases¹⁹. One reason for this is the facility in overcoming the insolubility problems frequently characteristic of aqueous systems as exemplified by precipitation trapping free phenols on columns of free-base resins during an attempted desorption stage with aqueous hydrochloric acid²⁰.

The principles of separations using ion-exchange resins in non-aqueous media may be illustrated with reference to phenols, where elution of a mixture of phenols from an anion-exchange resin column with amine-acetic acid buffer solutions leads to a separation pattern parallel to the aqueous pK_a values of the weakly acidic phenols. Thus, according to the pattern shown in Table IV, Logic²⁰ isolated the constituents of crude 2,4-dichlorophenol with a column of De-Acidite FF (acetate form) from a solution of 0.2% by volume of triethylamine in methanol (pH 9.2). By sequential elution with various methanol-triethylamine-acetic acid systems of decreasing pH (arbitrary only for these non-aqueous systems) *p*-chlorophenol (pK_a 9.38), 2,4-di-

TABLE IV

SEPARATION OF CONSTITUENTS OF CRUDE 2,4-DICHLOROPHENOL ON DE-ACIDITE FF (ACETATE FORM)²⁰

Sorption medium: 0.2% triethylamine in methanol (pH 9.2).

<i>Elution order and phenol eluted</i>	<i>Eluent</i>
1. <i>p</i> -Chloro- ($pK_a = 9.38$)	200 ml of 0.2% triethylamine acetate in methanol per litre of 0.2% triethylamine in methanol (pH 8.6)
2. 2,4-Dichloro- ($pK_a = 7.51$)	0.2% triethylamine acetate in methanol (pH 8.0)
3. 2,6-Dichloro- ($pK_a = 6.79$)	0.2% acetic acid in methanol (pH 3.5)
4. 2,4,6-Trichloro- ($pK_a = 6.41$)	5% acetic acid in methanol

chlorophenol (pK_a 7.51), 2,6-dichlorophenol (pK_a 6.79) and 2,4,6-trichlorophenol (pK_a 6.41) were eluted²⁰ in the order of decreasing pK_a (Table IV).

The separation illustrated by Table IV may also be effected with a longer ion-exchange resin column using gradient elution²¹. The gradient is effected by replenishing an eluent reservoir initially of pure methanol, with 0.2% acetic acid in methanol. This releases *p*-chlorophenol, 2,4-dichlorophenol and 2,6-dichlorophenol according to the order of their pK_a values, while 2,4,6-trichlorophenol may be released with a final elution with 5% acetic acid in methanol²¹.

When the pK_a values of the phenols are close, fixed concentration elution is ruled out because of the amount of experimentation required. A more effective solution is a rigorous combination of the use of amine-acetic acid buffer solutions in methanol combined with gradient elution²². Thus, *m*, *o* and *p*-nitrophenols of pK_a 8.39, 7.22 and 7.15, respectively, may be loaded on to a column of De-Acidite FF (acetate form) in 4% triethylamine in methanol and sequentially eluted during gradient elution involving replenishment of a reservoir of 4% triethylamine in methanol with 4% of 1 *M* triethylamine acetate in methanol together with 80 ml 1 *M* triethylamine in methanol plus 10 ml acetic acid per litre.

The same principles of ion-exchange separation by gradient elution combined with judicious use of amine-acetic acid buffer systems can be extended²² to the very weakly acidic cresols (pK_a 10.1 to 10.33) and xyenols (pK_a 10.20 to 10.62). The buffer systems must now include the more basic diethylamine instead of triethylamine. The xyenols must represent the limit to which the method can extend, that is, to a phenol pK_a of about 10.5, for 2,3-xylenol (pK_a 10.54), 2,4-xylenol (pK_a 10.60) and 2,6-xylenol (pK_a 10.62) defy sorption on the acetate form of De-Acidite FF—even from 25% of diethylamine in methanol²².

Application of the above principles to technological situations is interesting. For example, IR analysis suggests that a methanolic extract of peat bitumen fractionated on the acetate form of De-Acidite FF gives ethers, aliphatic esters, and other weakly ionised substances on elution with methanol; aromatic esters on elution with methanol-acetic acid (3:1); and evidence of phenolic type materials in the fraction eluted with glacial acetic acid^{23,24}.

A fractionation scheme (Table V) of petroleum constituents using macro-

TABLE V

FRACTIONATION OF PETROLEUM CONSTITUENTS USING MACRO-RETICULAR ANION-EXCHANGE RESINS²⁵

Stage	Resin form	Step	Directions	Fraction eluted
A.	CO ₃ ²⁻	1	Add mixture of naphthenic acids, alkylphenols, pyrrolic compounds and nitrogen bases dissolved in toluene to column.	Nitrogen bases (not adsorbed)
		2	Elute with methanol.	Alkylphenols Pyrrolic compounds
		3	Elute with methanol-CO ₂ .	Naphthenic acids
B.	OH ⁻	1	Add fraction A.2 to column and elute with methanol.	Pyrrolic compounds (not adsorbed)
		2	Elute with methanol-CO ₂ .	Alkylphenols

reticular anion-exchange resin²⁵ can have an important role in the petroleum field and it is pertinent to mention here that, apart from the strict ion-exchange mechanism which is probably characteristic of the phenol separations described above, sorption can also be effected by a more physical mechanism through the polar site facilities on the resin phase. The separation shown in Table V is potentially capable of refinement¹⁹ and an elution immediately following stage A.1 with methanol-ammonia could well provide a sub-fraction of the alkylphenols/pyrrolic compounds fraction of A.2. Also, a gradient elution with methanol-carbon dioxide immediately after stage B.1 might sub-fractionate the alkylphenols.

CONCLUSION

The possibilities of enhancing and reversing selectivities of ion-exchange resins by the addition or exclusive use of organic solvents can clearly extend the application of ion-exchange resins as a separation tool. In this a quantitative knowledge of the forces of solvation and sorption, the polar effects of substituent atoms and groups in organic molecules, and other physical phenomena can be of considerable value in establishing practical principles.

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