Asian Journal of Chemistry Vol. 3, No. 4 (1991), 391-397

Anion-Exchange Selectivity Trends in Aqueous Acetone Media

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Equilibrium exchange studies have been performed for Cl^-/NO_3^-, Br^-/NO_3^-, I^-/NO_3^-, I^-/NO_3^- and CNS^-/NO_3^- exchanges on Amberlite IRA-400 (NO_3^-) in acetone-water media. The corrected selectivity constants were evaluated by graphical integration. Corrected selectivities have been found to vary with the acetone concentration. The free energies of exchange, $\Delta F°$, have also been calculated to show the selectivity differences in mixed acetone-water media. The effect of increasing acetone in the mixed solvent systems on the exchange of anions and selectivity reversal for CNS^- ion at higher acetone percentages (v/v) have been explained.

INTRODUCTION

The theories putforth to explain the cation exchange selectivities[1] have failed to explain many of the observed trends in anion-exchange selectivities. Explanations based on polarizability of anions[2,3], clustered ion-pairing[3] and disturbances in the water structure[4] have been putforth for anion exchange in aqueous medium. Similar studies in non-aqueous and mixed solvent media are comparatively fewer in number[5-8]. The selectivity trends in such solvents have been explained in different ways by different workers. Hence, many conflicting views prevail regarding anion-exchange selectivities in mixed solvent media[9]. Attempts have been made in this communication to provide data and explanation to throw light on the exchange of halide and thiocyanate ions against nitrate ion using a strongly basic anion-exchanger in aqueous-acetone media.

EXPERIMENTAL

Anion solutions were prepared by dissolving chloride, bromide, iodide and thiocyanate as their potassium salts (BDH, A. R.) in deionised water to give 0·25M stock solutions, Analytical grade acetone (BDH) was used to prepare mixed aqueous acetone solutions. Amberlite IRA-400 (A. R. 20-40, mesh was used as a strongly basic exchanger in its nitrate form. The exchange capacity determined experimentally was 4·5 meq/gm of the air dried (*ca* 20°C) resin. Selectivity studies were carried out by batch technique at room temperature (*ca* 20°C). Always 1.00 gm of the exchanger was equilibrated with 50 ml of the electrolyte solution (aqueous or mixed with acetone). The electrolyte concentrations were varied from 0.1M to 0·2M in different batch studies. The mixed solvents contained 10, 20, 40 or 60% (v/v) of acetone in deionised water. Batches were equilibrated for *ca* 24 hrs. The anion concentrations after exchange were obtained by titrating aliquots (5 ml) from these batches.

Apparent selectivity coefficients (K_a) were evaluated as under :

$$K_a = \frac{X(x^-)_R}{X(NO_3^-)_R} \cdot \frac{C(NO_3^-)_S}{C(x^-)_S}$$

In this relationship X term represent equivalent fraction of the two counter ions in the resin phase; while C term represent their ionic concentration in the solution phase. The K_a varied with $X(x^-)_R$; and hence method of graphical integration was adopted to get corrected selectivity coefficients, K′. The following relationship was used (Table 1)

$$\ln K^1 = \int_0^1 \ln K_a \cdot dX(x^-)_R$$

TABLE 1

SELECTIVITY CONSTANTS (CORRECTED) AT DIFFERENT ACETONE CONCENTRATIONS

Acetone,	K′			
% v/v	Cl^-/NO_3^-	Br^-/NO_3^-	I^-/NO_3^-	CNS^-/NO_3^-
0	0.20	0.50	2.11	1.96
10	0.21	0.53	1.93	1.57
20	0.22	0.54	1.70	1.34
40	0.25	0.58	1.42	0.92
60	0.30	0.68	1.15	0.57

Free energies, ΔF° for the exchange reaction under study (Table 2) have also been calculated using the expression.

$$\Delta F^\circ = - RT \ln K'$$

TABLE II

FREE ENERGIES OF ANION EXCHANGE IN ACETONE-WATER MEDIA AT 30°C

Acetone,	ΔF°				Selectivity Sequence for
% v/v	Cl^-/NO_3^-	Br^-/NO_2^-	$1^-/NO_3^-$	CNS^-/NO_3^-	Cl^-, Br^-, NO_3^-, CNS^-, I^-
0	985	414	−448	−404	$Cl^- < Br^- < NO_3^- < CNS^- < I^-$
10	927	384	−394	−272	$Cl^- < Br^- < NO_3^- < CNS^- < I^-$
20	926	379	−318	−191	$Cl^- < Br^- < NO_3^- < CNS^- < 1^-$
40	845	322	−211	+ 49	$Cl^- < Br^- < CNS^- < NO_3^- < 1^-$
60	721	230	− 85	+336	$Cl^- < CNS^- < Br^- < NO_3^- < Cl^-$

RESULTS AND DISCUSSION

The results in (Table 1) for halide/nitrate and CNS^-/NO_3^- exchanges in different acetone containing solvents show preference of the nitrate form of Amberlite IRA–400 for iodide and CNS^- while chloride and bromide ions were not the preferred ion for it. Thus the sequence of affinity for the halides in aqueous and mixed acetone-water media with respect to nitrate ion is uniformally.

$$Cl^- < Br^- < NO_3^- < I^-$$

However, the preference for thiocyanate ion changed with acetone concentration in mixed solvents. Though CNS^- was preferred ion in aqueous and mixed solvents containing acetone upto *ca* 20% (v/v), it lost its position as a preferred ion in solutions containing 40 and 60% (v/v) acetone showing affinity variations with dielectric constant of the aqueous solvents. Thus the sequence of ions in aqueous and 20% acetone-$Cl^- < Br^- < NO_3^- < CNS^- < I^-$ changed to $Cl^- < Br^- < CNS^- < NO_3^- < I^-$ in 40% v/v acetone and $Cl^- < CNS^- < Br^- < NO_3^- < I^-$ in 60% v/v acetone solutions.

The position of CNS^- in aqueous solution has been shown after NO_3^- by Gartner[10]. Its position after Cl^- in aqueous soiution is more or less undisputed; however, nothing has been shown regarding the position with respect to other halide ions as the reported selectivity data is only with respect to the chloride ion.

The conclusions as given above in queous and aqueous acetone solvents can also be drawn from the ΔF° data (Table 2) also. The positive ΔF° values indicated less preference for the exchanged ion, while the negative values indicated greater preference of ions for the nitrate form of the exchanger.

Apart from the affinity sequences other points of interest can also be brought to light. The K′ values changed with changing acetone percentages in mixed solvents. Plots of K′ *vs* acetone concentration (Fig. 1) pointed out that the selectivities for Cl^- and Br^- ions for NO_3^- form of the resin increased with increasing acetone concentration, while those of I^- and CNS^- ions decreased. The plots were linear for Cl^-/NO_3^-, Br^-/NO_3^-, and I^-/NO_3^- exchanges but were curvilinear for CNS^-/NO_3^- exchange. Thus the seleetivity sequence values for halides showed lesser separation with increase in acetone concentration or decreasc in dielectric constant of the medium (Fig 2). The K′ values which were showing a relative separation of about 1.0 : 2.6 : 11.0 for Cl^-, Br^- and I^- gave a decreased separation of 1.0 : 2.3 : 3.8 for these ions. Thus iodide was brought more closer to Br^- than Br^- to Cl^- by solutions having higher percentages of acetone.

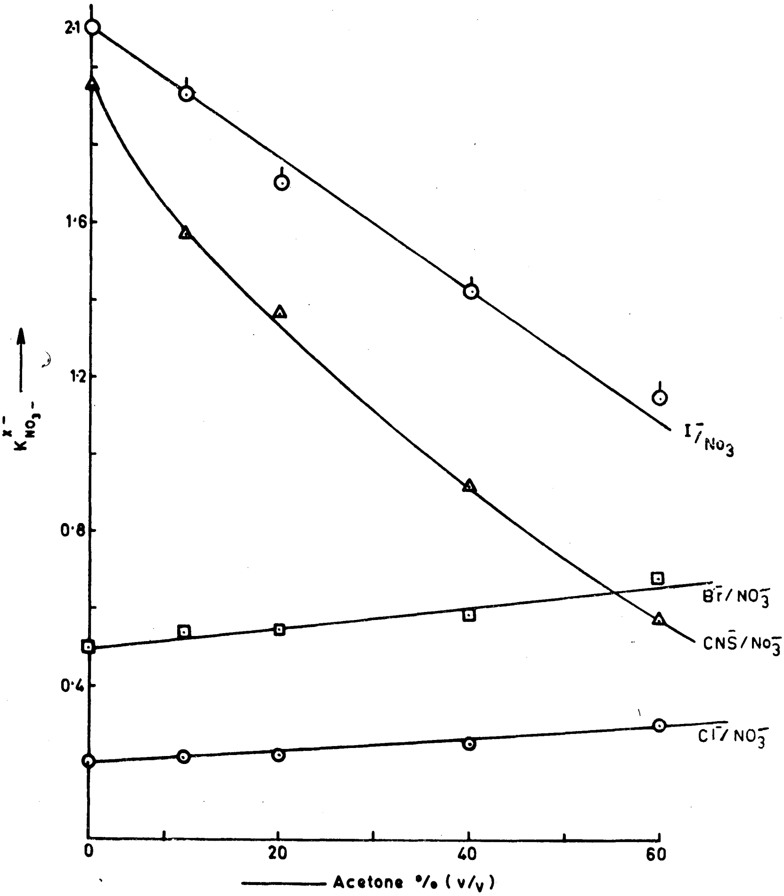

Fig. 1—Variation of selectivity constants (K°) with acetone concentration (% v/v)

A similar change in the selectivity was shown by Jansen and Diamond[11] in their tracer studies with tertiary amine base (weak base) resin, Thus anions in mixed solvents at higher percentage of the organic solvents (dielectric of the solvent less) behaved similar to the a weak-base exchangers. The increase of an organic solvent in mixed aqueous systems either provide some sort of hinderance in the dissociation of the salts used in the solution phase or influences their ion-pair formations in the resin phase.

The observed sequence for halides can be well explained on the basis of the effect of the water structure on the solute ions as suggested by Diamond[4]. The ion pair interaction for Cl^-, Br^- and I^- decreased with increasing size of the ion. Thus I^- has weakest interactions with water. As the resin phase contained a much less structured imbibed water the halide ions of bigger size preferred the less structured and much broken framework of the resin phase than the well structured water phase. Hence the ion like I^- is more preferred by the resin than Br^- or Cl^- ions. Now, if acetone is a solvent present with water in the system, then the usual structure of water is partially broken to accommodate the less polar but hydrogen bondable solvent molecules. The resin, which as a rule prefers water over organic solvents imbibes less of organic solvent than water when mixed solvents are used. With increasing concentration of acetone in the outside solution, the solution phase becomes less structured, while one inside the resin is not so. Comparatively in each mixed solvent systems I^- is expected to stay on in the less structured out side solution rather than in the more structure pore liquid (resin phase, liquid). This is the reason why the exchange of chloride and bromide ions increases wlth increasing acetone percentage while that of iodide decreases.

The increase in selectivity of Cl^- and Br^- ions is influenced by ion pairing which is increased by increasing acetone in the media. The primary hydration shells of these halide ions are influenced considerable making ions as less preferred by the solvent phase. Iodide on the other hand finds the much broken water structure of the outside solution more suitable than the better structured pore liquid. Its exchange thus decreases with increasing acetone in the outside solution.

The reversals shown by CNS^- vis-a-vis nitrate ion in higher % (v/v) of acetone can be explained only due to lesser degree of the ionization of its potassium salt used. This polyatomic anion has a hydrogen bondable linear structure, hence its preference for the aqueous phase as compared to iodide can be understood. But even after increasing the acetone of the outside liquid, no increase in exchange is observed. On the other hand it decreases, hence the above suggestion.

Some authors [8,12] have emphasised the importance of dielectric constant of the solvent media in predicting the selectivity of ions for the exchanges. The generalised notion as per paulys model[12] that the selectivity constants show an increase with decrease in dielectric constant of the medium does not appear to hold good for anions of all types. Results (shown graphically in fig. 2) for the present studies point out an increase of K' for Cl^-/NO_3^- and Br^-/NO_3^- exchanges but decrease for I^-/NO_3^- and CNS^-/NO_3^- exchanges. Therefore, authors like some earlier workers[12–14] also confirm that the concept of dielectric constant is not a convincing one for anion exchange in aqueous acetone also. The water structure enforced processes appear to govern the anion exchange selectivities in this media[15]. Morover, flate statements regarding the increase of ion selectivities with increase in organic solvent content [13,17] or decrease with its increase[6] are not justified. The trends appear to be dependent also on the resin form and type apart from the concentration of the organic solvent in the mixed systems. Looking to the trend of the linear plots (Fig. 1) the complete reversal of selectivity sequences for all halides can be anticipated in perfectly non-aqueous systems as shown by Phipps [16,17] in DMSO.

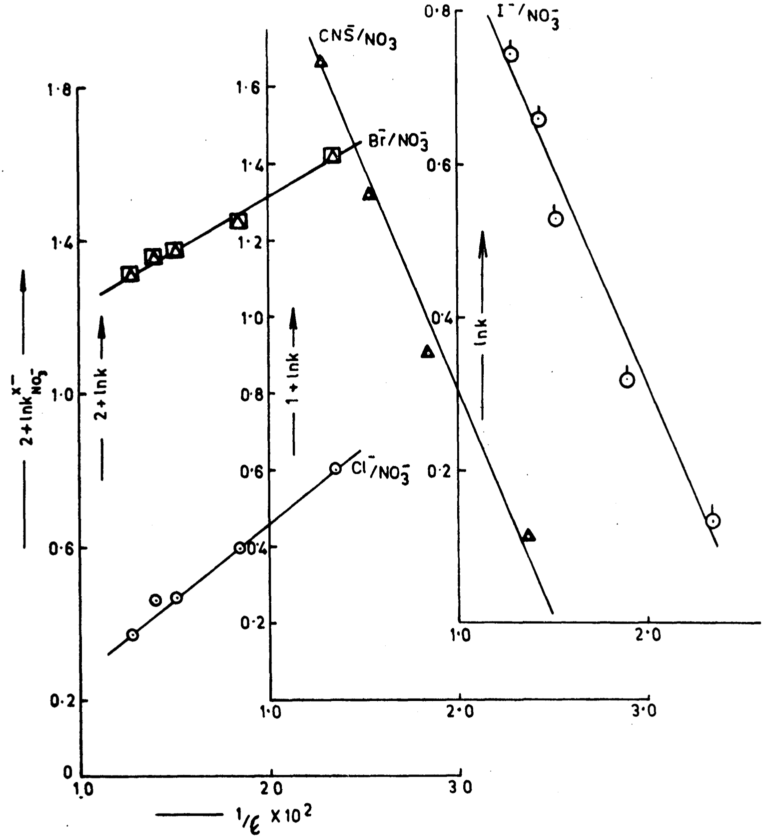

Fig. 2. Variation of selectivity constants (K°) with the dielectric constant (ε)

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(*Recevied* : 15 January 1990, *Accepted* : 5 July 1990) AJC–204