

EFFECT OF THE ANION HYDRATION STATE ON THE SELECTIVITY COEFFICIENTS ( $K_{Y/X}^{sel}$ ) OF QUATERNARY ONIUM SALTS UNDER PHASE-TRANSFER CATALYSIS CONDITIONS.

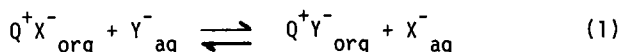
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Abstract. A study of how specific hydration affects anion selectivity coefficients ( $K_{Y/X}^{sel}$ ) was made for a series of tetrahexylammonium salts (1a-o) under phase-transfer catalysis (PTC) conditions in a chlorobenzene-aqueous NaOH (15 or 50%) two-phase system. The dehydration of the anion always produced a change of  $K_{Y/X}^{sel}$  values, particularly noticeable in the case of F<sup>-</sup>, OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>

The efficiency of the catalyst in a typical anion-promoted reaction carried out under phase-transfer catalysis (PTC) conditions depends on the concentration in the organic phase of the reactive anion Y<sup>-</sup> associated with a quaternary cation Q<sup>+</sup> in the ion pair Q<sup>+</sup>Y<sup>-</sup> (Scheme I).<sup>1</sup> Such a concentration is, in turn, related to the distribution of the anions Y<sup>-</sup> and X<sup>-</sup> competing for the cation Q<sup>+</sup> in the aqueous-organic two-phase system. This distribution is expressed by the equilibrium constant of the exchange reaction (1), defined as selectivity coefficient  $K_{Y/X}^{sel}$  (2).<sup>1a-d,2</sup>

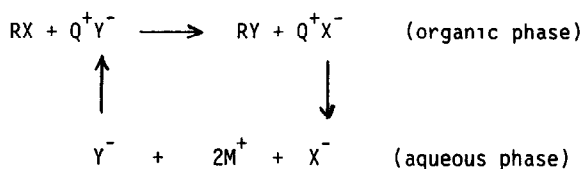


$$K_{Y/X}^{sel} = \frac{[Q^+Y^-]_{org}[X^-]_{aq}}{[Q^+X^-]_{org}[Y^-]_{aq}} \quad (2)$$

$K_{Y/X}^{sel}$  values have been found to depend mainly on the nature of the anions (X<sup>-</sup> and Y<sup>-</sup>), and, to a lesser extent, on the structure of the cation Q<sup>+</sup> and on the

solvent. 1a-d,2-5

In the case of  $\text{OH}^-$ , we recently pointed out the importance also of the hydration state of the anions involved in the partitioning equilibrium (1).<sup>6</sup> In fact the variation of this parameter can noticeably modify the anion extractability, especially in solvents of low polarity.<sup>6</sup> In order to establish whether this phenomenon is general we undertook a systematic study of how the specific hydration affects the selectivity coefficients ( $K_{Y/X}^{\text{sel}}$ ) of a series of representative inorganic and organic anions like tetrahexylammonium salts  $\text{Q}^+\text{Y}^-$  1 in a chlorobenzene-aqueous NaOH (15 or 50%) two-phase system.<sup>7</sup> Scheme I.



### Results and Discussion.

Selectivity coefficients  $K_{Y/X}^{\text{sel}}$  for a variety of inorganic a-c, f, h, k, n, o and organic e, g, i, j, l, m  $\text{Y}^-$  anions were determined in the above two-phase systems, at 25°C, taking the chloride d as a reference anion (Table 1). Measurements were carried out by stirring a chlorobenzene solution (0.02-0.04 M) of tetrahexylammonium chloride 1d with an aqueous NaOH solution (15% or 50%) containing comparable amounts of the inorganic salts  $\text{M}^+\text{Y}^-$  and  $\text{M}^+\text{Cl}^-$  (where  $\text{M}^+ = \text{Na}^+$  or  $\text{K}^+$ ) (0.02-0.1 M). The quantity of  $\text{Y}^-$  extracted in the organic phase as  $\text{Q}^+\text{Y}^-$  by the quaternary cation  $\text{Q}^+$  was evaluated by the potentiometric titration of the anion. In parallel the amount of  $\text{Cl}^-$  remaining associated with  $\text{Q}^+$  was determined, as well as the total  $\text{Q}^+$  concentration (see Experimental Section). For anions with  $K_{Y/\text{Cl}}^{\text{sel}} \geq 10^3$  the partition measurements were performed with  $\text{Br}^-$  or  $\text{I}^-$ , as the reference anions, instead of  $\text{Cl}^-$ , due to their much higher extractability. The selectivity coefficients  $K_{Y/\text{Cl}}^{\text{sel}}$  are obtained in this case by the equation  $K_{Y/\text{Cl}}^{\text{sel}} = (K_{Y/X}^{\text{sel}})/(K_{X/\text{Cl}}^{\text{sel}})$ , where  $X = \text{Br}$  or  $\text{I}$ . If  $\text{Y}^-$  is  $\text{F}^-$  b or  $\text{SO}_4^{--}$  c, a certain amount of  $\text{OH}^-$  (10-15%) is extracted in the organic phase as quaternary hydroxide  $\text{Q}^+\text{OH}^-$  1a together with  $\text{Q}^+\text{Cl}^-$  1d. For this reason partition measurements for b and c were performed taking  $\text{OH}^-$  instead of  $\text{Cl}^-$  as the reference anion (see Experimental Section). The selectivity coefficients  $K_{Y/\text{Cl}}^{\text{sel}}$  are in turn obtained by the equation  $K_{Y/\text{Cl}}^{\text{sel}} =$

$= (K_{Y/OH}^{sel}) (K_{OH/Cl}^{sel})$ , where  $Y = F, SO_4$  (Table 1).

The hydration states of Hexyl $_4N^+Y^-$  **1a-o**, expressed as moles of  $H_2O$  per mole of  $Q^+Y^-$ , were determined in parallel in chlorobenzene-15% aq.NaOH and chlorobenzene-50% aq.NaOH (Table 1).

The sequence of the  $K_{Y/Cl}^{sel}$  values is similar for both systems and is comparable with sequences reported in the literature for the same anions by other authors.<sup>1a-d,2,3,5</sup>

Table 1. Hydration States and Selectivity Coefficients  $K_{Y/Cl}^{sel}$  of Quaternary Onium Salts, Hexyl $_4N^+Y^-$  **1a-o**, in a Chlorobenzene-Aqueous NaOH (15 and 50%) Two-Phase System, at 25°C.

$Y^-$	$C_6H_5Cl$ -15% aq.NaOH		$C_6H_5Cl$ -50% aq. NaOH	
	Hydration State $n$ of Hexyl $_4N^+Y^- \cdot nH_2O$ <sup>b</sup>	$K_{Y/Cl}^{sel}$ <sup>c</sup>	Hydration State $n$ of Hexyl $_4N^+Y^- \cdot nH_2O$ <sup>b</sup>	$K_{Y/Cl}^{sel}$ <sup>c</sup>
a $OH^-$	11.0	$2.5 \times 10^{-4}$	3.5	$4.7 \times 10^{-6}$
b $F^-$ <sup>d</sup>	8.5 <sup>e</sup>	$4.1 \times 10^{-4}$	-- <sup>f</sup>	$6.6 \times 10^{-6}$
c $SO_4^{--}$	12.0	$4.9 \times 10^{-1}$	-- <sup>f</sup>	$2.3 \times 10^{-2}$
d $Cl^-$	3.4	1.0	0.4	1.0
e $MeSO_3^-$	2.5	1.7	0.4	6.5
f $N_3^-$	3.0	$3.0 \times 10$	0.3	$5.1 \times 10$
g $C_6H_5CH_2COO^-$	4.0	$4.3 \times 10$	1.4	$2.7 \times 10^2$
h $Br^-$	2.0	$5.8 \times 10$	0.4	$2.0 \times 10^2$
i $C_6H_5COO^-$	4.0	$1.1 \times 10^2$	1.0	$8.2 \times 10^2$
j $pNO_2C_6H_4COO^-$	3.0	$1.8 \times 10^3$	0.7	$1.3 \times 10^4$
k $I^-$	1.1	$8.2 \times 10^3$	0.2	$4.5 \times 10^4$
l $oNO_2C_6H_4O^-$	3.4	$1.6 \times 10^4$	1.0	$2.1 \times 10^4$
m $pNO_2C_6H_4O^-$	2.8	$2.0 \times 10^4$	0.5	$1.2 \times 10^5$
n $SCN^-$	2.0	$3.3 \times 10^4$	0.2	$1.2 \times 10^5$
o $ClO_4^-$	1.1	$5.8 \times 10^5$	0.0	$1.5 \times 10^6$

<sup>a</sup> 30 mL of a chlorobenzene solution (0.02-0.04M) of Hexyl $_4N^+Hal^-$  (**1d**, **1h**, **1k**) and 30 mL of an aqueous NaOH solution (15 or 50%) of comparable amounts of NaHal and NaY (0.02-0.1M),  
<sup>b</sup> Average of at least four determinations. The error in this field is estimated to be 10%,  
<sup>c</sup> Average of at least three runs. The error in these values is estimated to be 15%,  
<sup>d</sup> KF was used instead of NaF,  
<sup>e</sup> Hydration value for Hexyl $_4N^+F^-$  **1b** under classical liquid-liquid PTC conditions,  
<sup>f</sup> Hydration state determination was impossible due to the relevant coextraction in the organic phase of  $OH^-$  as  $Q^+OH^-$  **1a**.

As shown in Table 1 the selectivity coefficients  $K_{Y/Cl}^{sel}$  of a-c, e-o are affected, noticeably, by their specific hydration. The increase of the concentration of NaOH aqueous phase (from 15% to 50%) leads to the almost complete dehydration<sup>7</sup> of the anion and always produces a change in the extractability value in the organic phase. In part at the highest base concentration (50% aq. NaOH) the anions with  $K_{Y/Cl}^{sel} > 1$  (e-o) are better extracted than chloride d. The enhancements of the selectivity coefficients from 1.3 for  $oNO_2C_6H_4O^-$  l to 7.5 for  $C_6H_5COO^-$  i.

On the contrary anions with  $K_{Y/Cl}^{sel} < 1$ , such as  $F^-$  b,  $OH^-$  a and  $SO_4^{--}$  c, are less extracted than chloride d. Table 1 shows how in the passage from 15% to 50% the selectivity coefficients  $K_{Y/Cl}^{sel}$  diminish by 62, 53 and 21 times for b, a respectively. This effect seems to be related to the charge distribution of the anion, increasing the electronegativity increases the effect. A typical example is represented by the series  $F^-$ ,  $OH^-$ ,  $SO_4^{--}$  where the lower stabilization, due to the dehydration of the anion, is the main reason for its reduced extractability in the organic phase.

In previous papers we pointed out the fundamental role played by the specific hydration of the anions on their reactivity under liquid-liquid PTC conditions.<sup>1</sup> The present data highlight the effect of the hydration extent also in determining the extractability of the anions in the organic phase.<sup>17</sup> As a consequence we can conclude that the reactions of the anions with  $K_{Y/X}^{sel} > 1$  are those most favoured by concentrated alkaline solutions (50% aq. NaOH) because their better extractability is combined with increased reactivity. On the other hand the dramatic increase in reactivity found<sup>6</sup> under these conditions for the anions with  $K_{Y/X}^{sel} < 1$  largely overcomes their diminished extractability.

### Experimental Section.

Potentiometric titrations were performed with a Metrohm 670 Titroprocessor by silver, fluoride or glass, together with calomel, electrodes, this last isolated by a potassium sulphate bridge.

### Materials and Solvents.

Inorganic sodium and potassium salts  $M^+Y^-$  (except  $MeSO_3K$ ) as well as benzoic, p-nitrobenzoic and phenylacetic acids, o-nitrophenol and p-nitrophenol were Analar commercial products, used without further purification.  $MeSO_3K$  was prepared by neutralizing an aqueous solution of methanesulphonic acid with KOH and then evaporating the water under vacuum.

Tetrahexylammonium chloride (1d), bromide (1h) and iodide (1k) were Analar

commercial products used without further purification. Tetrahexylammonium salts **1c**, **1e-g**, **1i,j**, **1l-o** were generated in situ from the commercially available tetrahexylammonium chloride (**1d**) or hydrogen sulphate  $\text{Hexyl}_4\text{N}^+\text{HSO}_4^-$  (**1p**) by exchange with the appropriate anion, according to the ion-pair extraction technique.<sup>19</sup> Tetrahexylammonium fluoride (**1b**) was prepared from the corresponding hydrogen sulphate **1p** by exchange with the  $\text{F}^-$  anion.<sup>20</sup> Chlorobenzene was Analar grade used without further purification.

#### Partition Measurements.

In a typical procedure, a 100 mL flask was thermostatted at  $25 \pm 0.1^\circ\text{C}$  and charged with 30 mL of a standardized chlorobenzene solution (0.02-0.04 M) of tetrahexylammonium halide (**1d**, **1h**, **1k**) and 30 mL of an aqueous NaOH solution (15% or 50%) containing comparable amounts of the inorganic salts NaY and NaHal (0.02-0.1M). The mixture was magnetically stirred for 10-30 min, then, three portions (2-5 mL) of the organic phase were withdrawn and analyzed as follows (1) the extraction of the anion  $\text{Y}^-$  was checked by acid-base or argentometric titration with 0.01N HCl or 0.01N  $\text{AgNO}_3$  (potentiometric titration in 50 mL of MeOH), (2) the quantity of halide  $\text{Hal}^-$  remained in the organic phase associated with quaternary cation  $\text{Hexyl}_4\text{N}^+$  was potentiometrically evaluated with 0.01N  $\text{AgNO}_3$ , (3) the total amount of quaternary cation  $\text{Q}^+$  in the organic phase was potentiometrically determined with 0.01N  $\text{AgNO}_3$  after shaking the organic sample (5 mL) with 2 mL of a saturated aqueous solution of NaBr in order to completely convert  $\text{Q}^+\text{Y}^-$  to  $\text{Q}^+\text{Br}^-$ . In the case of  $\text{F}^-$  (**b**), 30 mL of a chlorobenzene solution (0.02-0.04 M) of tetrahexylammonium fluoride **1b** were equilibrated with 30 mL of an aqueous KOH solution (20 or 63%) containing 30 molar equiv. of KF instead of NaF due to the low solubility of the latter. The quaternary fluoride **1b** was determined by potentiometric titration of  $\text{F}^-$  anion with 0.01 N lanthanum nitrate in 50 mL of 40% methanol in a water solution.<sup>16</sup> In the case of  $\text{SO}_4^{--}$  (**c**), 30 mL of a standardized chlorobenzene solution (0.02-0.04M) of  $\text{Hexyl}_4\text{N}^+\text{HSO}_4^-$  (**1p**) were equilibrated with 30 mL of an aqueous NaOH solution (15 or 50%).

#### Hydration State of Quaternary Salts.

The hydration state of quaternary salts **1a-o** was determined by Karl-Fischer titration of the organic phase according to a known procedure.<sup>6a,13</sup>

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