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SEPARATION OF MIXTURE OF *m*-CRESOL AND *p*-CRESOL BY DISSOCIATION EXTRACTION

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The separation of closely boiling organic acid is discussed using dissociation extraction techniques. A mathematical model is developed to calculate the separation factor in dissociation extraction process showing good agreement with experimental data. Important system variables are the concentration of the solutes, ratios of solutes in the organic phase and the solvent used. Experimental data is presented to show the affect of these parameters on the extraction of cresols.

Key words: Dissociation extraction, Cresol separation, Organic solvents.

Introduction

Dissociation extraction is a separation technique for mixture of organic acids or bases that takes advantage of chemical (rather than physical) properties of compounds. It exploits the difference in the dissociation constants of the constituents so as to effect a separation. Application of this technique is particularly useful for the separation of closely similar phenols, amines and organic acids (Wadekar and Sharma 1981; Arif *et al* 1995) because the separation of these chemicals by common techniques such as distillation or fractional crystallisation (Pratt 1983; Shaheen 1978) is quite difficult. Liquid-liquid extraction process (Pratt 1983; Wadekar and Sharma 1981) commonly used to separate mixtures of close boiling liquids has proved difficult to develop in this case because of close chemical similarity of the components.

The application of dissociation extraction can be traced as early as 1924 when Warnes (1924) applied it to separate phenolic substances. The commercial application for the separation of organic acids and bases occurring in coal tar industry particularly of m-cresol, p-cresol, 3-picoline and 4-picoline systems (Modak *et al* 1999; Wadekar and Sharma 1981) on a large scale was suppressed by the continuous consumption of strong alkali or strong acid. The consumption of large quantities of acids or bases was no longer acceptable which were difficult to recover. Therefore, new technique are being explored for more productive alternatives.

The detailed treatment of theoretical analysis was discussed by Wise and Williams (1964) who also considered multistage operation. However, Anwar *et al* (1979) made some necessary adjustment to their theory.

In this paper, the use of weak Base, instead of strong alkalis has been described. The reagents are regenerated and can be used again. A number of organic solvents were also used to study their influence on the distribution of cresols.

A theoretical analysis of the technique is also discussed.

Materials and Methods

Most isomers have an appreciable difference in strength as acids. If a solution of the two isomer acids in an organic solvent are equilibrated with an aqueous phase containing stoichiometric defficiency of base. The two acids compete for the reaction with the available base. The stronger acid will react preferentially with the base to form an ionized salt, insoluble in the organic solvent. The weak acid remains in its undissociated form (Anwar *et al* 1979) in the organic phase.

Consider the separation of a mixture of weak organic acids HX_1 and HX_2. The overall distribution coefficients of the individual acids are given by:

$$D'_1 = \frac{[HX_1]_s}{[HX_1]_a + [X_1^-]_a} \qquad (1)$$

$$D'_2 = \frac{[HX_2]_s}{[HX_2]_a + [X_2^-]_a} \qquad (2)$$

The separation factor $\propto_{12}$ for the separation of two weak acids was defined in an analogous way to relative volatility in distillation as:

$$\propto_{12} = \frac{D'_1}{D'_2}$$

$$\propto_{12} = \frac{[HX_1]_s}{[HX_2]_s} \times \frac{[HX_2]_a + [X_2^-]_a}{[HX_1]_a + [X_1]_a} \qquad (3)$$

The distribution coefficients for the undissociated acids will be:

$$D_1 = \frac{[HX_1]_s}{[HX_1]_a}$$

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$$D_2 = \frac{[HX_2]_s}{[HX_2]_a} \tag{4}$$

D_1 and D_2 can be expected to be functions of the concentrations of the dissociated and undissociated acids. The weak acids will dissociate partially in the aqueous phase and their dissociation constants, neglecting activity coefficients, are given by:

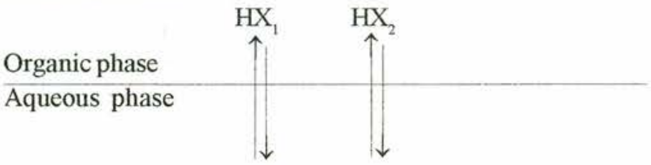
$$K_1 = \frac{[H^+]\ [X_1^-]}{[HX_1]} \tag{5}$$

$$K_2 = \frac{[H^+]\ [X_2^-]}{[HX_2]} \tag{6}$$

One of the organic acids dissociated in the aqueous phase will react to form salt with the stoichiometric deficient weak base BX_3 because of its higher affinity for the acid. This is analogous to solvent extraction of metals (Ahmad *et al* 1989, 1994). The salt formed HX_3 is insoluble in organic phase and its dissociation constant is given by:

$$K_3 = \frac{[H^+]\ [X_3^-]}{[HX_3]} \tag{7}$$

The equilibria established in the aqueous phase is illustrated as follows:



$$HX_2 \rightleftarrows H + X_2^-$$
$$HX_1 \rightleftarrows H^+ + X_1$$
$$HX_3 \rightleftarrows B^+ + X_3^-$$
$$H^+ + X_3^- \rightleftarrows HX_3$$

The extent of reaction depends on the relative dissociation constants of acids HX_1, HX_2 and HX_3. The equilibrium constants for reactions in the aqueous phase are:-

$$K_{e1} = \frac{[HX_3]\ [X_1^-]}{[HX_1]\ [X_3^-]} \tag{8}$$

$$K_{e2} = \frac{[HX_3]\ [X_2^-]}{[HX_2]\ [X_3^-]} \tag{9}$$

and clearly

$$K_{e1} = \frac{K_1}{K_3}$$

$$K_{e2} = \frac{K_2}{K_3}$$

Suppose sodium hydroxide is used in the aqueous phase to neutralize partially the mixture of organic acids. The electrical neutrality of the process in the aqueous phase requires that:

$$[X_1^-] + [X_2^-) + [X_3^-] = N \tag{10}$$

N is an initial concentration of X_3^- ions in the aqueous phase.

If K_1 and K_2 are large compared to K_3, then $[X_3^-]$ at equilibrium will be comparatively very small hence $[X_1^-] + [X_2^-] = N$.

The above relationships may be combined to find $\propto_{12}$:

$$\propto_{12} = \frac{K_1}{D_2} \text{ x } \frac{D_2N + [HX_2]_s + \frac{K_1}{K_2}\frac{D_2}{D_1}[HX_1]_s}{D_2N \text{ x } \frac{K_1}{K_2} + [HX_2]_s + \frac{K_1}{K_2}\frac{D_2}{D_1}[HX_1]_s} \tag{11}$$

From equation (11), it is clear that we can increase the amount of $[X_1^-]$ in the aqueous phase by keeping the anions in stoichiometric deficiency. The above equation also shows the control of pH in a practical dissociation extraction process is an unnecessary complication and it does not provide an effective method of controlling the separation. The relationship (11) expresses separation factor in terms of ratio of the two acids, and their dissociation constants and distribution coefficients. The values of D_1 and D_2 can be obtained from experimental data and so can the values of undissociated acids Wadekar *et al* 1981) Litrature values (Shaheen 1978) for the dissociation constants at 25°C are 6.7×10^{-11} for p-cresol and 9.8×10^{-11} for m-cresol. Experimental work was conducted to assess the equation and its application for the separation of close boiling mixture of isomers.

Experimental

A first series of experiments was performed to determine the distribution of the individual cresols between toluene and aqueous sodium hydroxide. A 50ml sample of a solution of an individual cresol in toluene of known concentration was equilibrated with 50ml of aqueous sodium hydroxide of known normality. The equilibrated mixture was allowed to settle at 25°C in a thermostatically controlled bath. After separating the organic and aqueous phases, exactly 0.5 g of o-cresol was added to organic phase as an internal standard and solution thus obtained was analysed in Gas Liquid Chromatograph of Vega Series Carlo Erba. The sample solution passed through the 5-foot coiled-shape column of 3mm internal diameter packed with chromosorb G AW DMCS of about 90 mesh as support material and matexil as a stationery phase. The operating temperature was maintained at 195°C. High purity nitrogen was used as a carrier gas in the column. Hydrogen and air were used as fuel for the flame ionisation detector. The nitrogen gas flow rates through the column was 60ml/min. whereas hydrogen and air flow rates were maintained at 60ml/min and 360ml/min respectively. The column residence time was 20 minutes for the *p*-cresol peak. Successive samples were injected after the previous sample peak was recorded. The residence time of the cresols in the column became smaller with continuous use which was rectified by flushing the column with 0.5 μl acetone at intervals. From the peak area ratios recorded by a Kent 'chromolog' integrator,the known weight of o-cresol added and the standard charts previously prepared, the concentration of cresol in the organic phase was calculated as follows:

$$\text{Let T} = \frac{\text{integrated area of } m\text{-cresol peak}}{\text{integrated area of } o\text{-cresol peak}}$$

From the calibration chart, let the weight ratio of m-cresol and o-cresol appropriate to a peak area ratio T be L.

Then

$$L = \frac{\text{Weight of } m\text{-cresol}}{\text{Weight of } o\text{-cresol}}$$

Weight of *m*-cresol = 0.5 x L

The weight of m-cresol in the aqueous phase was calculated by difference.

Similar procedure was adopted to calculate distribution of *p*-cresol in the conjugate phases.

A second series of experiments was carried out to determine the separation factors directly from the analytical results. The effect of cresol ratio and the concentration of aqueous sodium hydroxide were studied. These experiments include cresol weight ratios from 10% to 90% with an organic phase concentration of 3.0 g/l of total cresols and a variety of aqueous phase concentrations ranging from 0.5 to 2 N sodium hydroxide in distilled water. The experimental procedure was the same as for the individual isomers, except the two phases were analysed without the addition of *o*-cresol as an internal standard.

The amount of cresols in each of the two phases and the separation factor were calculated from the concentration ratios in each phase and the known total amount present. Separation factors were always expressed as the ratio of mole fraction of total acids in each phase; i.e. on a solvent free basis.

$$\frac{(p\text{-cresol in the organic phase}) \times (m\text{-cresol in the aqueous phase})}{(p\text{-cresol in the aqueous phase}) \times (m\text{-cresol in the organic phase})}$$

The concentration of each organic acid was determine with a maximum error if ± 0.5% in reproducibility.

Exactly the same experimental and analytical procedure was adopted to calculate the effect of temperature on the distribution of both isomers in the conjugate phase. The temperature studied was 50°C.

A third series of experiments was carried out to study the effect of different organic solvents on the distribution of cresols between the conjugate phases. The solvent studied were chloroform, carbon tetrachloride n-hexane, benzene, toluene, and octan-1-01. The analytical and experimental procedure adopted were same as above.

The chemicals used were of Analar grade and obtained from BDH. All the experiments were carried out at 25°C except where it is stated.

Results and Discussion

To understand fully whether the reaction in the aqueous phase proceeds to completion or not, individual distribution of solution of *m*-cresol and *p*-cresol between toluene and aqueous sodium hydroxide was studied. These results given in Fig 1 show that the concentration of the acid in the organic phase remains very low until an amount of the acid close to molar equivalence of sodium hydroxide present in the aqueous phase has been added. However, the presence of the acid in the organic phase is never zero when equal molar concentration

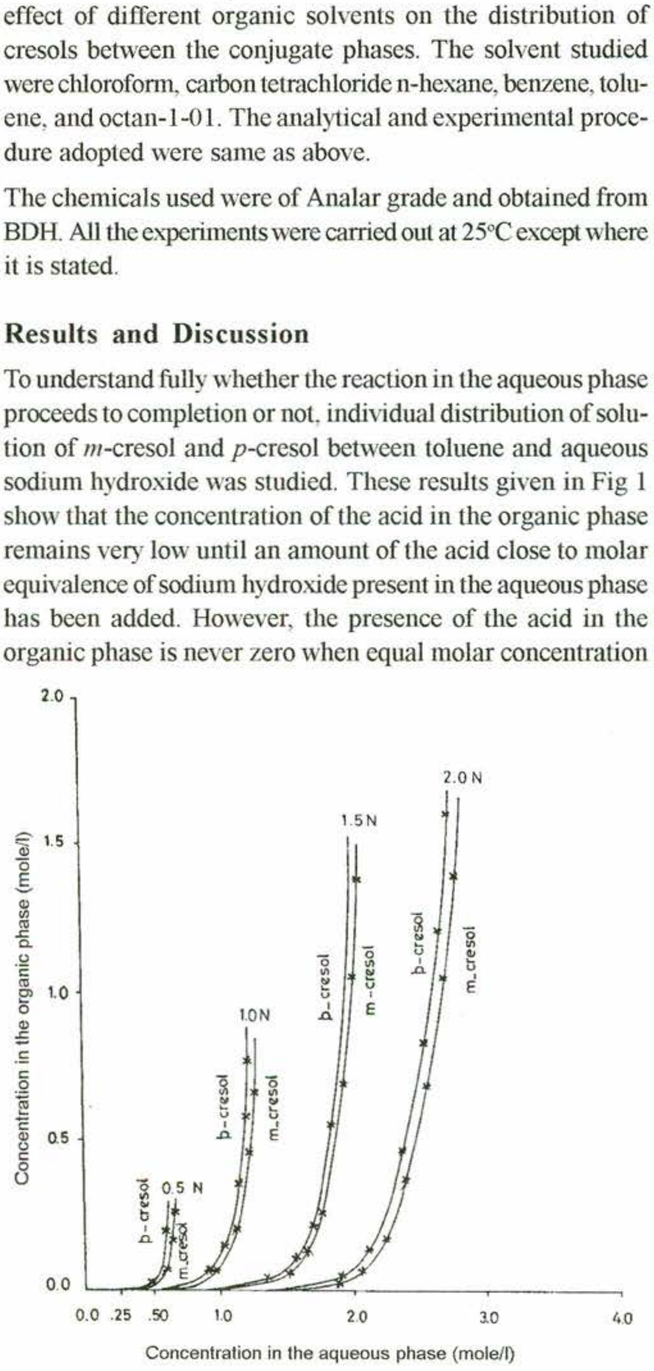


Fig 1. Equilibrium distribution of cresols between NaOH and Toluene.

of the acid and that of sodium hydroxide are present in the system. Moreover, the lines in Fig 1 show that as the cresol is added to the system, initially most of the cresol forms a salt in the aqueous phase but some is also present in the organic phase. At the stoichiometric equivalent concentration of aqueous sodium hydroxide, an appreciable quantity of the cresol is present in the organic phase. Above this concentration, the aqueous phase concentration still increases and contrary to an earlier (Shaheen 1978) report all the cresol does not pass to the organic phase.

So, if the molar concentration difference of the strong alkali is much greater than the cresol added to the system, most of the organic acid is transferred to the aqueous phase.

The results shown in Table 1 indicate that the separation factor decreases to the value of 1.40 as the concentration of isomers increases in the organic phase. This confirmed the analysis presented in equation (11) that the concentration of isomers in the organic phase is close to zero until sufficient organic acid has been added to neutralize completely the aqueous base. The concentration of dissociated acids in the aqueous phase then becomes virtually constant Modak *et al* 1999; Arif *et al* 1995). This explains the low separation factor with increase in concentration of isomers.

Separation factors were also evaluated for 3 g of cresols in different ratios using the above procedure. The results obtained are given in Tables 2 and 3 showing the variation of separation factor with total base concentration in the organic phase. General conclusions can be drawn from a consideration of equation (11). N approaches O because of total separation of *p*-cresol in the aqueous phase and the $[X_1^-]$ and $[X_2^-]$ are all in the organic phase to satisfy the electrical neutrality of the phases. Hence, it can easily be seen that when N → O, the equation (11) reduces to:

$$\propto_{12} = \frac{D_1}{D_2} \tag{12}$$

This represents minimum value of the separation factor and is the separation factor which would be derived from distribution of the undissociated acids. All practical values of separation factor obviously must be around the limits set by equation (12). The separation factor calculated using equation (11) in each case increases in favour of *p*-cresol as the proportion of that isomer increases in the mixture. The value of separation factor decreases from 1.61 to 1.544 (Table 2). Such variations in the value of the separation factors have been reported before (Shaheen 1978; Wise and Williams 1964; Pratt and Spoke 1979). However, the total concentration of the cresols in the aqueous phase remains approximately constant and its average value is 0.64 moles/l which is 0.14 moles/l greater than stoichiometric equivalence of 0.5 N sodium hydroxide present in the aqueous phase. Similar trend can be observed in Table 3 with 2 N sodium hydroxide.

Table 1

Separation factors of isomers in organic phase

NaOH = 0.5 N	
Equimolar *m*- and *p*-cresols (g)	Separation factor
1.0	1.58
2.0	1.52
2.5	1.48
3.0	1.47
4.0	1.40

Tables 2 and 3 show a small variation in the separation factor but it is very important from separation point of view.

Table 2

The distribution of *p*-cresol and *m*-cresol mixture between 50 ml toluene and 50 ml of 0.5 N NaOH

% *p*-cresol	Organic phase		Aqueous phase		Separation factor	
m-cresol	*p*-cresol	*m*-cresol	*p*-cresol	*m*-cresol	Experimental	Calculated
10 : 90	0.249	2.106	0.049	0.596	1.438	1.544
20 : 80	0.501	1.857	0.101	0.541	1.445	1.551
30 : 70	0.748	1.609	0.157	0.486	1.439	1.560
40 : 60	0.989	1.374	0.210	0.427	1.464	1.570
50 : 50	1.231	1.136	0.267	0.362	1.469	1.580
60 : 40	1.466	0.899	0.333	0.302	1.478	1.580
70 : 30	1.699	0.669	0.399	0.233	1.483	1.596
80 : 20	1.926	0.441	0.472	0.161	1.490	1.600
90 : 10	2.150	0.219	0.547	0.084	1.508	1.610

Total cresol concentration = 3g

Table 3

The distribution of *p*-cresol and *m*-cresol mixture between 50 ml toluene and 50 ml of 2 N NaOH

% *p*-cresol	Organic phase		Aqueous phase		Separation factor	
m-cresol	*p*-cresol	*m*-cresol	*p*-cresol	*m*-cresol	Experimental	Calculated
10 : 90	0.097	0.685	0.202	2.016	1.400	1.503
20 : 80	0.190	0.594	0.409	1.807	1.410	1.514
30 : 70	0.280	0.505	0.620	1.595	1.420	1.526
40 : 60	0.365	0.422	0.833	1.380	1.433	1.540
50 : 50	0.449	0.343	1.051	1.157	1.441	1.550
60 : 40	0.526	0.266	1.273	0.935	1.452	1.563
70 : 30	0.598	0.193	1.500	0.709	1.465	1.577
80 : 20	0.672	0.126	1.729	0.476	1.468	1.582
90 : 10	0.734	0.062	1.960	0.244	1.474	1.589

Total cresol concentration = 3g

Table 4

The distribution of *p*-cresol and *m*-cresol mixture at high temperature between 50 ml toluene and 50 ml of 0.5 N NaOH

%*p*-cresol	Organic phase		Aqueous phase		Separation factor
m-cresol	*p*-cresol	*m*-cresol	*p*-cresol	*m*-cresol	experimental
10 : 90	0.201	1.611	0.096	1.092	1.420
30 : 70	0.600	1.220	0.300	0.881	1.444
50 : 50	0.978	0.843	0.522	0.657	1.460
70 : 30	1.337	0.497	0.754	0.412	1.470
90 : 10	1.664	0.157	1.034	0.145	1.486

Total cresol concentration = 3g, Temperature = 50°C

Actually, the difference between the percentage amount of the cresol extracted in the aqueous phase and that initially added in the feed decreases as the ratio increases.

$$\frac{\text{Concentration of aqueous sodium hydroxide}}{\text{Concentration of the cresols in the feed mixture}}$$

Similarly percentage difference of cresol in the organic phase and that in the feed mixture increases. For example in Table 2 and 3, when the concentration ratios (50:50) of the feed cresols are similar and sodium hydroxide concentration is 0.5 N and 2 N, the *m*-cresol in the aqueous phase on percentage basis decreases from 57.65 (0.362g)) to 52.44 (1.157g). The respective quantities of *m*-cresol in the organic phase are 48.06 (1.136g) and 43.28 (0.343g), as compared with the feed mixture ratio of 50:50. Therefore, the separation factor alone provides no means to judge the success of the separation process.

To study the effect of temperature on the extraction, equal volumes of the organic phase and the aqueous phase were treated separately in water bath at 50°C and then equilibrated for 15 minutes at the same temperature. The analysis given in Table 4 virtually show the same composition and experimental separation factor varies between 1.43 and 1.49, showing that increased temperature brings about no material benefit in the *m*-cresol and *p*-cresol separation (Wadekar and Sharma 1981; Anwar *et al* 1979). There was, however, an improved phase separation under these conditions. No trace of emulsion appeared in either phase.

To assess the effect of organic solvents on completion of reaction in the aqueous phase and to assess the possibility of reversal of the aqueous phase reaction, *m*-cresols and *p*-cresols were individually distributed between 1 N sodium hydroxide and various organic solvents.

The experimental results showed that benzene, carbon tetrachloride and chloroform produced the same results as toluene. The major share of the distributed acids remains in the aqueous phase until the stoichiometric equivalence is reached, after which the acid accumulates in the organic phase.

Octan 1-01 as solvent indicated that the extraction of cresols is lower compared to other solvents which shows an affinity of octan 1-01 for the cresols.

Hexane as solvent produced a third phase on equilibrium with aqueous phase. Most of the organic acid added to this system went initially into the aqueous phase. With successive addition of *m*-cresol, the concentration of the aqueous phase increased continuously until a third phase appeared. *p*-cresol did not produce a third phase even if the concentration of it in the aqueous phase was increased to 272 g. This indicated that n-hexane (Arif *et al* 1995) does not have much affinity for the cresols and is a poor solvent for them.

These results are shown in Fig. 2 indicating that the distribution of cresols between the conjugate phases is strongly influenced by the nature of the organic solvent. Therefore, the choice of the solvent has strong bearing on the successful extraction of closely boiling isomers.

Nomenclature

B^+ = base cation D = distribution coefficient of undissociated acids. D' = overall distribution coefficient of acids. $[H^+]$ = concentration of cations. [HX] = concentration of cresols in the organic phase. K = dissociation constant of the species.

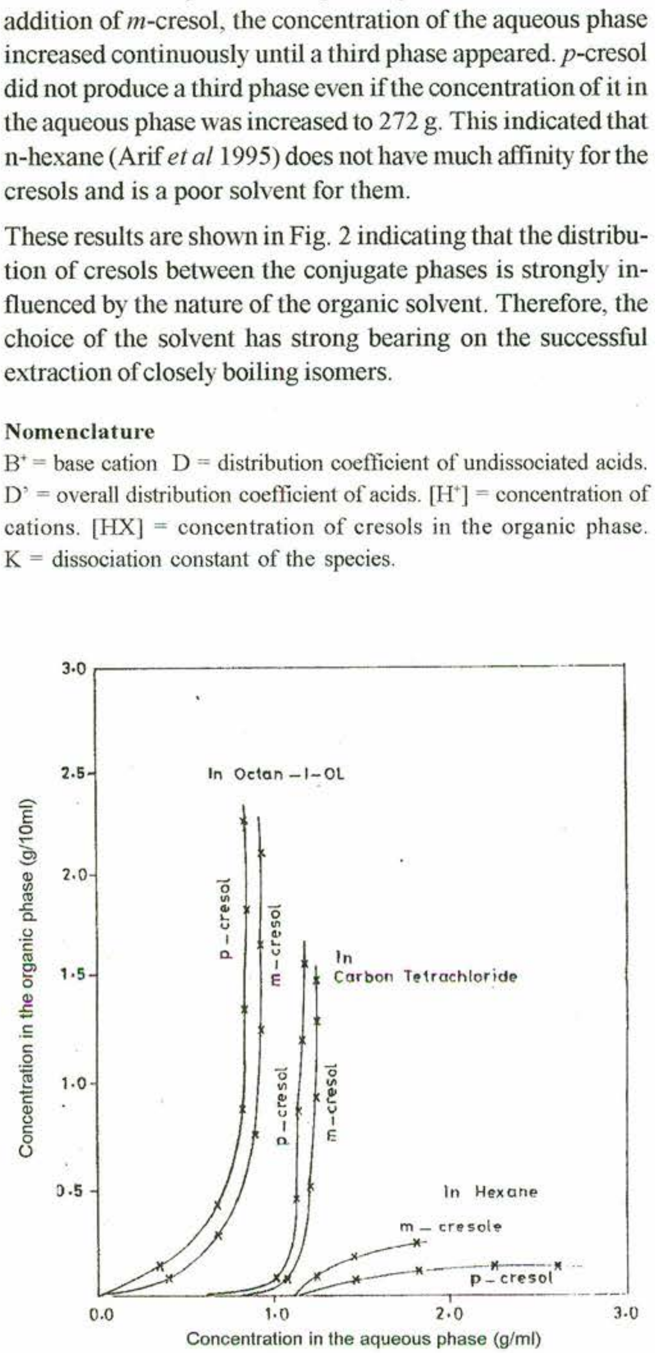


Fig 2. Equilibrium distribution of cresols in different solvents.

K_e = equilibrium constant. N = total concentration of anions in the aqueous phase at equilibrium. $[X^-]$ = concentration of dissociated acids in aqueous phase. $\propto$ = separation factor for acids HX_1 and HX_2.

Subscript

a = aqueous phase

s = organic phase

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