Pak. J. Sci. Ind. Res. 2005 **48**(4) 240-246

Separation of Close Boiling Acidic Isomers by Dissociation Extraction

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(recived March 18, 2004; revised January 27, 2005; accepted January 30, 2005)

Abstract. The separation of *m*-cresol and *p*-cresol was studied using dissociation extraction technique. The separation factors obtained for cresols-carbon tetrachloride-caustic soda system were in the range of 1.40 to 1.52, whereas for cresols-carbon tetrachloride-monoethanolamine system were in the range of 1.297 to 1.417. Isomer ratios, concentration of cresols and the strength of aqueous extractant have a significant influence on the separation of cresols. The organic acid (*m*-cresol) was successfully back-extracted from aqueous caustic soda with a non-polar organic solvent, octanol. pH of the aqueous phase and the choice of organic solvent have an important role in the back-extraction of *m*-cresol.

Keywords: dissociation extraction, cresols, monoethanolamine, isomer separation, close-boiling isomers

Introduction

The coal-tar produced in steel industries on carbonization of coal contains industrially important phenolic compounds (Micheal and Muder, 1974). These are used as intermediates, or starting compounds, for the production of dyes, herbicides, pesticides, medicines, and several other useful chemicals (Hutton *et al.,* 2000; Lo and Baird, 1996; Anwar *et al.,* 1995). These phenolic compounds cannot be separated by the well established unit operations, as they exhibit normal boiling points, differing by only a fraction of a degree and having similar solubilities in most solvents. However, the difference in molecular arrangements of the isomers does result in an appreciable difference in their strength as acids or bases, as shown by their relative dissociation constants, which are 9.8×10^{-11} for *m*-cresol, 6.7×10^{-11} for *p*-cresol, 4.54×10^{-9} for 3-picoline and 10.62×10^{-9} for 4-picoline. This difference is being exploited as the basis of practicable separation by the less known process of dissociation extraction. The basic principles of dissociation extraction were reported by Warnes (1924), long before the term "dissociation extraction" was suggested (Twigg, 1949). The commercial applications of dissociation extraction technique, based on the earlier studies (Pratt, 1967; Wise and Williams, 1964), were impeded by the continuous consumption of strong bases or strong acids for the recovery of phenolic compounds. This was due to the difficulty in reversing the reaction in order to free the purified isomer, as well as to regenerate the extractant. Ideally, there should only be a weak interaction between the extractant and the desired isomer, yet sufficiently strong to achieve the separation but weak enough to be broken-down without using excessive chemicals, or thermal energy. Considering this, weak acids and bases (organic and inorganic) in water were successfully used as extractants (Anwar *et al.,* 1979; 1971). These studies also provided the theorctical basis for such applications. The findings reported in these studies prompted Sharma and coworkers (Pahari and Sharma, 1992; Gaikar and Sharma, 1987; Wadekar and Sharma, 1981) to study other weak acids and bases for the separation of close boiling substances using the dissociation extraction technique.

In the dissociation extraction process, the weakly acidic or basic organic or inorganic compounds may be used as extractants as long as they are preferentially soluble in the aqueous phase (Ahmed *et al.,* 2002; Anwar *et al.,* 1979), and insoluble in the organic solvent. Earlier work (Ahmed *et al.,* 2003) established that aqueous sodium dihydrogen phosphate, a weak acid, could be used successfully to separate the mixture of 4-picoline and 3-picoline. Although experimental results confirmed the viability of the process, the low separation factors and aqueous phase loadings of picoline implied that a liquid-liquid extraction contactor, with a large number of stages, is required for the desired results.

To illustrate the principles of dissociation extraction, let us consider a mixture of weak organic acids, *m*-cresol and *p*-cresol obtained from the coal-tar distillate. These, in the organic diluent, are partially neutralized by an aqueous weak organic base, such as monoethanolamine, $C_2H_4(NH_2)OH$. There will thus be a competition between the two organic acids to react preferentially with the aqueous organic base. The organic acid (*m*-cresol), having higher dissociation constant, will react preferentially with the base to form an ionized salt in the aqueous phase, insoluble in the organic phase. The other organic acids (*p*-cresol), having a lower dissociation constant, will remain predominantly in its un-

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dissociated form, soluble in the organic phase. Due to the weakly basic nature and stoichiometric deficiency of monoethanolamine (MEA) in the aqueous phase, as compared with total cresols, the reaction does not proceed to completion in the aqueous phase. Therefore, the isomers are partially separated and high degree of separation and purification may be achieved by contacting aqueous MEA containing cresols with a fresh feed of cresols in a number of similar contacts. The loaded aqueous phase is contacted with a suitable organic solvent to extract-back *m*-cresol from the aqueous MEA and consequently regenerate MEA to recycle in the process. The cresol is recovered from the organic solvent by distillation.

The theory described above was applied to separate *m*-cresol from the mixture of *m*-cresol and *p*-cresol present in carbon tetrachloride. The effect of various parameters, such as isomer ratios, concentration of feed, and the organic and aqueous phase loadings on the separation factors was studied. It was shown that separation of cresols could be achieved by MEA, and consequently *m*-cresol can easily be back-extracted from aqueous MEA by a secondary solvent, toluene.

The present work also combined with the earlier work (Anwar *et al.,* 1979; 1971; Pratt, 1967; Wise and Williams, 1964) to describe another approach to the dissociation extraction process. This process employs a strong aqueous base, aqueous caustic soda, for the extraction of *m*-cresol from the mixture of cresols according to the dissociation extraction theory. Then, the reaction was reversed by using an organic reagent, having a higher affinity for the dissociated *m*-cresol, to extract-back *m*-cresol from the aqueous caustic soda. This process produced higher aqueous phase loadings of cresols and as a result higher separation factors were realized. The use of organic solvent to extract-back *m*-cresol from the aqueous caustic soda gave the advantage of separation, without continuous consumption, of bases or acids for the recovery of the desired product. Hence, the reagents were regenerated and recycled to economise the process.

The influencing factors on the back-extraction of cresols were found to be the organic solvent, as discussed earlier (Ahmed *et al.,* 2003; 2002), the aqueous phase pH, and the concentration of *m*-cresol in the aqueous phase. Therefore, the variation of pH of the aqueous phase with different concentrations of *m*-cresol was studied to find its effect on the back-extraction by the chosen secondary solvent. Although the aqueous phase remained alkaline, the back-extraction of *m*-cresol from the aqueous caustic soda was successfully achieved by using octan-1-ol as the solvent.

Materials and Methods

The equilibrium concentrations of *m*-cresol and *p*-cresol were determined for (a) aqueous MEA and carbon tetrachloride system, and (b) aqueous caustic soda and carbon tetrachloride system.

Aqueous MEA-carbon tetrachloride system. For the MEA-carbon tetrachloride system, a 20 ml mixture of known concentration of *m*-cresol and *p*-cresol, dissolved in carbon tetrachloride, was equilibrated with 20 ml of aqueous MEA. The two phases were shaken vigorously for 5 min and then kept in a thermostat at $25\pm1^{\circ}$C for 20 min. These conditions were shown to be fully adequate for the equilibrium distribution of cresols in the conjugate phases. After equilibration, the two phases were separated and the isomer ratios of cresols in the organic phase were found by gas liquid chromatography (GLC). The concentration of cresol isomers in the aqueous phase could then be calculated by mass balance, since the total quantity of each isomer in the feed was known. The concentration of isomer ratios of cresols could be verified by direct injection of aqueous phase into the GLC column. The GLC column was a coil-shaped glass column having 3 mm dia and 1.5 m length. The column was filled with chromosorb GAW DMCS of 80-100 mesh as support material and 8% w/w matexil as the stationary phase. A high resolution of *m*-cresol and *p*-cresol, with 30 min retention time, was achieved at the column temperature of 195 °C. The GLC was calibrated with standard solutions of *m*-cresol and *p*-cresol in carbon tetrachloride. The reproducibility of analytical results was $\pm$0.1%.

Aqueous NaOH-carbon tetrachloride system. For the caustic soda-carbon tetrachloride system, equilibrium distribution of *m*-cresol and *p*-cresol between carbon tetrachloride and aqueous caustic soda was determined using different cresol ratios and different aqueous caustic soda concentrations. 10 ml of each solution was equilibrated according to the experimental procedure described for the aqueous MEA-carbon tetrachloride system. After equilibration, phases were separated and samples of the organic phase were analysed by GLC as described previously. The aqueous phase samples were neutralized with dilute hydrochloric acid and made homogeneous by the addition of methanol before injecting into the GLC glass column, since direct injections of aqueous caustic soda seemed to deteriorate the column, resulting in merged peaks of both cresols on the chromolog integrator. All the chemicals used were of Analar grade (Merck).

Results and Discussion

Separation of *m*-cresol and *p*-cresol by aqueous MEA. The equilibrium distribution of an equimolar mixture of *m*-cresol and *p*-cresol between 20 ml carbon tetrachloride and 20 ml

aqueous MEA of concentrations ranging from 2-10% (w/w) is given in Table 1. The total weight of cresol added to the system, equilibrium weights of both the isomers in each phase, and the separation factors have been listed (Table 1). The expression for the separation factors is defined as:

$$[m\text{-cresol}]_a [p\text{-cresol}]_o / [m\text{-cresol}]_o [p\text{-cresol}]_a$$

where:

terms in square brackets = concentrations

subscripts a and o = the aqueous and organic phases, respectively

For 100 g/l MEA, the cresol feed concentration was 50 to 150 g/l. The separation factors varied only between 1.28 to 1.37. These results showed that although separation factor increased with the increase in cresol feed concentration, it was virtually insensitive to MEA concentration. The GLC analysis indicated slight solubility of cresol-MEA salt in the organic phase at 100 g/l MEA feed concentration. Therefore, higher MEA concentrations were not used for the cresols-MEA- carbon tetrachloride system.

The concentration of total cresols in the aqueous phase (dissociated plus undissociated) increased with the increase in cresol loading in the system, but reached an almost constant level for a given MEA concentration: 24, 31, 38, 45 and 53 g/l, respectively, for the MEA strengths of 20, 40, 60, 80 and 100 g/l. The limiting concentration of cresols in the aqueous phase, therefore, increased linearly with the increase in MEA concentration, but was not directly proportional to it, as also reported earlier (Pratt, 1967).

The effect of cresol isomer ratios on the separation factor is shown in Fig. 1. The same-phase volumes were used

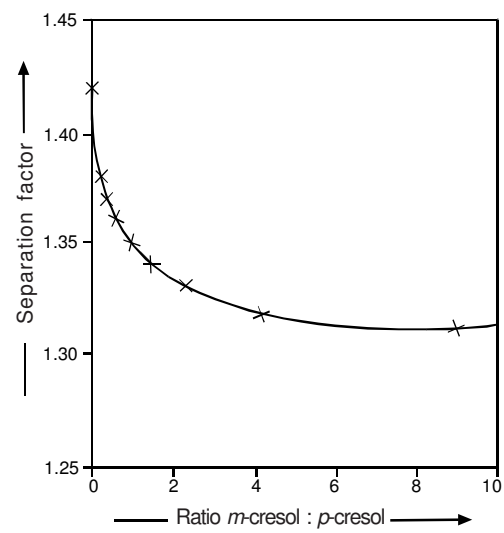

Fig. 1. The effect of cresol isomer ratios (*m*-cresol : *p*-cresol) on their separation, using 4% monoethanolamine (MEA) as the aqueous phase and 150 g/l total cresols in carbon tetrachloride as the organic phase.

Table 1. Distribution of the cresol mixture (equimolar) between 20 ml carbon tetrachloride (organic phase) and 20 ml aqueous monoethanolamine (MEA) (aqueous phase) system

Aqueous MEA concentration (w/w, %)	Total cresols (g)	Equilibrium distribution of cresols (g)				Separation factor
		Organic phase		Aqueous phase		
		m-cresol	*p*-cresol	*m*-cresol	*p*-cresol	
2	1.0	0.244	0.280	0.256	0.220	1.34
	2.0	0.733	0.788	0.267	0.212	1.35
	3.0	1.229	1.292	0.271	0.208	1.37
4	1.0	0.184	0.218	0.316	0.282	1.33
	2.0	0.661	0.725	0.339	0.275	1.35
	3.0	1.153	1.230	0.347	0.270	1.37
6	1.0	0.136	0.165	0.364	0.335	1.32
	2.0	0.587	0.658	0.413	0.342	1.35
	3.0	1.076	1.165	0.424	0.335	1.37
8	1.0	0.142	0.169	0.358	0.331	1.29
	2.0	0.536	0.605	0.464	0.395	1.33
	3.0	0.996	1.096	0.504	0.404	1.37
10	1.0	0.023	0.029	0.477	0.471	1.28
	2.0	0.951	1.046	0.549	0.454	1.33
	3.0	0.921	1.028	0.579	0.472	1.37

with 4% MEA in the aqueous phase and 150 g/l total cresols (in different ratios) initially present in carbon tetrachloride. The separation factor increased from 1.309 to 1.414 as the ratio of *m*-cresol / *p*-cresol in the system decreased from 90 : 10 to 10 : 90. The variation in separation factors was virtually the same with other MEA concentrations in the range from 20 g/l to 100 g/l. In all cases, the total cresols loading in the aqueous phase was not significantly affected by the change in isomer ratios (Table 2). Niewoudt (1997), using boric acid in the aqueous phase, separated phenolic compounds and neutral oil and reported a similar finding for his system. These results show that the separation of *m*-cresol and *p*-cresol with the weak organic base MEA is practicable using the dissociation extraction technique. The separation factors ranging from 1.28 to 1.37 (Table 1) implied that the number of equilibrium stages necessary to achieve a high degree of separation should not be small. Recovery of *m*-cresol from the aqueous MEA was easily achieved by contacting it with toluene.

Separation of *m*-cresol and *p*-cresol by aqueous caustic soda. The equilibrium distribution of the mixture of *m*-cresol and *p*-cresol, between carbon tetrachloride and various concentrations of caustic soda, is given in Table 3. The volume of each phase was 10 ml and the total weight of cresols in the system was 3 g. The data given in Table 3 include isomer ratios of the total cresols, the normality of caustic soda in the aqueous phase, the equilibrium contents of each isomer in each phase, and the separation factors. Separation factors were greater for caustic soda than those for the MEA reagent. The separation factors ranged from 1.40 to 1.52 as the total cresols isomer ratio of *m*-cresol / *p*-cresol decreased from 9 to 0.11 (90 : 10 to 10 : 90) for 0.5 N caustic soda.

Table 2. Distribution of the cresol mixture (3 g) between 20 ml carbon tetrachloride (organic phase) and 20 ml aqueous monoethanolamine (MEA) (aqueous phase) system

Aqueous MEA concentration (w/w, %)	Cresol ratio (%)		Organic phase (g)		Aqueous phase (g)		Separation factor
	m-cresol	*p*-cresol	*m*-cresol	*p*-cresol	*m*-cresol	*p*-cresol	
2	90	10	2.260	0.261	0.440	0.039	1.303
	70	30	1.762	0.786	0.338	0.114	1.323
	50	50	1.228	1.292	0.272	0.208	1.370
	30	70	0.73	1.798	0.170	0.302	1.386
	10	90	0.250	2.366	0.050	0.334	1.417
4	90	10	2.108	0.247	0.592	0.053	1.309
	70	30	1.631	0.740	0.469	0.160	1.330
	50	50	1.152	1.230	0.348	0.271	1.371
	30	70	0.682	1.708	0.218	0.392	1.393
	10	90	0.223	2.170	0.077	0.530	1.414
6	90	10	1.989	0.236	0.711	0.064	1.318
	70	30	1.531	0.704	0.569	0.196	1.335
	50	50	1.076	1.165	0.424	0.335	1.370
	30	70	0.636	1.616	0.264	0.484	1.386
	10	90	0.208	2.057	0.092	0.643	1.415
8	90	10	1.865	0.223	0.835	0.077	1.297
	70	30	1.381	0.646	0.719	0.254	1.324
	50	50	0.996	1.096	0.504	0.404	1.373
	30	70	0.589	1.519	0.311	0.581	1.380
	10	90	0.197	1.920	0.113	0.780	1.412
10	90	10	1.690	0.206	1.010	0.094	1.310
	70	30	1.297	0.614	0.803	0.286	1.329
	50	50	0.92	1.030	0.580	0.470	1.382
	30	70	0.546	1.454	0.344	0.656	1.396
	10	90	0.173	1.777	0.127	0.923	1.413

Table 3. Distribution of the cresol mixture (3 g) between 10 ml carbon tetrachloride (organic phase) and 10 ml aqueous caustic soda (aqueous phase)

NaOH	Cresol ratio (%)		Organic phase (g)		Aqueous phase (g)		Separation
(normality)	*m*-cresol	*p*-cresol	*m*-cresol	*p*-cresol	*m*-cresol	*p*-cresol	factor
0.5	90	10	2.103	0.250	0.597	0.050	1.42
	70	30	1.613	0.745	0.487	0.155	1.45
	50	50	1.136	1.231	0.364	0.269	1.47
	30	70	0.667	1.702	0.233	0.398	1.49
	10	90	0.217	2.156	0.083	0.544	1.52
1.0	90	10	1.612	0.203	1.088	0.097	1.43
	70	30	1.220	0.600	0.880	0.300	1.44
	50	50	0.843	0.978	0.657	0.522	1.46
	30	70	0.501	1.340	0.399	0.760	1.47
	10	90	0.159	1.667	0.141	1.033	1.49
1.5	90	10	1.123	0.151	1.577	0.149	1.42
	70	30	0.839	0.440	1.264	0.460	1.44
	50	50	0.574	0.712	0.926	0.788	1.46
	30	70	0.327	0.962	0.573	1.138	1.48
	10	90	0.104	1.192	0.196	1.509	1.49
2.0	90	10	0.681	0.096	2.019	0.204	1.40
	70	30	0.505	0.280	1.595	0.620	1.43
	50	50	0.343	0.449	1.157	1.051	1.44
	30	70	0.193	0.599	0.707	1.501	1.46
	10	90	0.061	0.738	0.239	1.962	1.47

Separation factors were not much affected by the caustic soda normality. The total cresol concentration in the aqueous phase remaind approximately constant for a particular normality of caustic soda, 0.6 molar (64.7 g) for 0.5 N, 1.1 molar (117.4 g) for 1 N, and 2.0 molar (220.1 g) for 2 N. The loading of total cresols in the aqueous phase was thus slightly greater than the stoichiometric equivalence of the caustic soda and the total cresol loading in the caustic soda was also greater than that of the weak basic reagent MEA. The separation of *m*-cresol and *p*-cresol with 2 N caustic soda, as the reagent, is shown in Fig. 2.

It was established in the previous studies that carbon tetrachloride, toluene and benzene were good solvents for this system, whereas octan-1-ol had higher affinity for cresols (Ahmed *et al.,* 2003; 2002) . Therefore, octan-1-ol was selected as the secondary solvent to exploit the extraction of *m*-cresol from caustic soda and to regenerate caustic soda for recycling. The most important influencing factor on the back-extraction of *m*-cresol from the aqueous caustic soda was found to be pH of the aqueous phase. Therefore, variation of pH of the aqueous phase, along with the concentration of *m*-cresol in the aqueous phase, concentration of cresol in each phase,

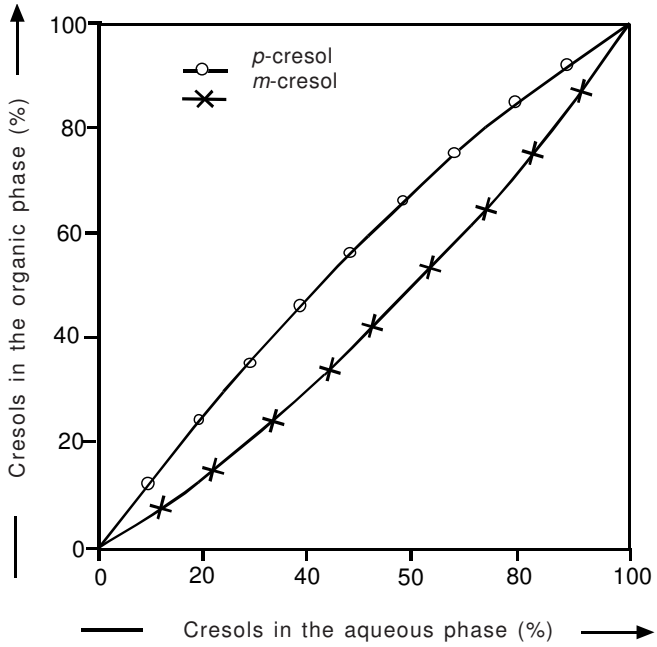

Fig. 2. Equilibrium distribution of the cresol mixture between 2 N NaOH (aqueous phase) and carbon tetrachloride (organic phase).

Table 4. The effect of pH on the back-extraction of *m*-cresol from the aqueous phase caustic soda with octan-1-ol

Concentration of *m*-cresol in the aqueous phase (g/l)	pH of the aqueous phase	Equilibrium concentration of *m*-cresol in conjugate phases (g/l)		Percentage extraction
		Aqueous phase	Organic phase	
12.5	13.23	12.5	-	-
25.0	13.20	22.905	2.095	8.38
37.50	13.18	33.261	4.239	11.30
50.00	13.15	40.755	9.245	18.49
63.00	13.12	50.850	12.150	19.29
75.00	13.06	58.754	16.246	21.66
87.00	12.98	63.753	23.247	26.72
108.50	12.27	74.431	34.069	31.40
125.00	11.53	75.500	49.500	39.60
221.00	11.18	76.453	144.547	65.41

and percentage extraction of cresol was also investigated (Table 4). The results of this study show that aqueous phase was still alkaline even when *m*-cresol concentration was more than twice the stoichiometric equivalence of caustic soda. Moreover, a reduction in pH proved supportive to the extraction of *m*-cresol by octan-1-ol and the percentage extraction improved in favour of the organic phase. At the equivalence point of *m*-cresol (108 g/l), the pH was 12.3 and the extraction was 31.4%. These results also indicate that there was a lower limit on the proportion of *m*-cresol per mole of caustic soda, about 25 g/l *m*-cresol, below which the extraction was not practicable because the aqueous phase was too alkaline.

Conclusions

The process described is capable of separating *m*-cresol and *p*-cresol with aqueous caustic soda as the reagent giving high values of separation factors and also showing subsequent recovery of *m*-cresol from the aqueous phase by contacting it with the organic solvent, octanol. The process avoids the continuous consumption of chemicals and still benefits from the maximum phase loading associated with strong aqueous reagents. The weak organic acids or bases may be employed as extractants for the separation of close boiling tar distillates. The monoethanolamine (MEA), a weak organic base, employed in this study as the extractant was noted to be capable of separating cresol isomers. The separation factors were, however, rather low as compared to caustic soda. It has been also shown that the separation factor was a function of the concentration of solutes and their ratios in the organic phase and the concentration of the extractant in the aqueous phase.

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