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Experimental Study on Effect of Addition of Different Salts on Distribution of Aniline between Water and Toluene

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***Abstract* - The aim of this experimental work was to know the effect of addition of certain inorganic salts on removal of aniline from water by using toluene as the extracting solvent. The inorganic salts used were NaCl, KI, and $MgCl_2 \cdot 6H_2O$. The influence of factors such as amount of salt, phase volume ratio, initial aniline concentration in feed-water solution, and temperature on the distribution of aniline was investigated. It was found that addition of 5% NaCl shows an appreciable salting-out effect on distribution of aniline. It was also found that the distribution of aniline was favoured at low aniline concentrations, and a phase volume ratio of toluene to water of little above 1.0. It is also found that the dissociation of salt added plays an important role in aniline extraction and the effect of cation and/or anion as predicted by the Hofmeister series may not be always followed in all cases. The distribution of aniline between water and toluene is found to be endothermic in nature.**

***Keywords:* Aniline, Toluene, Extraction, Salting-Out Effect**

I. INTRODUCTION

Amine compounds, such as aniline, are important organic chemical materials and also are generally harmful to human health and aquatic species because of their toxicity and carcinogenicity. Aniline is a hazardous substance that readily dissolves in water up to 3.5%, and is an essential reagent used as an intermediate in the manufacture of many dyes, pesticides and pharmaceuticals, and as chemical feedstock for rubber making and in many chemical syntheses [1]. Therefore, liquid effluents from these industries inevitably contain aniline and/or amine compounds in water at dangerous levels even after various treatment processes have been employed for their removal.

The typical chemical engineering methods of purification such as, distillation, liquid extraction and absorption can be used for removal of organic contaminants from wastewater. However, due to aniline's high boiling point (183°C), and generally low concentration, usually about 1% or lower in wastewater, distillation operation needs a large amount of energy to vaporize the high boiling material. The other option of conventional liquid extraction process can be attractive [2]. Liquid-liquid equilibria have been studied for several systems with and without salt addition to understand the effect of various parameters, such as percentage of salt added, extraction time, initial aqueous aniline concentration, phase volume ratio, temperature, nature of extracting solvent, and effect of pH [2, 3, 4, 5, 6, 7, 9, 10, 11, 13, 15, 16, 19, 20]. Also, enhancement in mass transfer rate by addition of salt solution has been studied [12]. Recent methods, such as dispersive Liquid Phase Micro Extraction (LPME), have been studied for determination of five aromatic amines in water samples [17]. The effect of salt addition on extraction of an aqueous phase organic solute is quite complex, and various experimental works have recorded different and divergent views like repulsive effects of salt addition [18].

In this work, the conventional liquid-liquid extraction method was employed with addition of certain inorganic salts - NaCl, KI, and $MgCl_2 \cdot 6H_2O$ - to separate and concentrate aniline in toluene from water samples, and also to verify the cation and anion effect enunciated by the Hofmeister series [23]. This process is simple, easily scalable, and effective. Toluene has been used as an extractive solvent because of its low toxicity and low cost as compared to many other solvents such as, benzene, cyclohexanol, 2-Ethylhexanoletc [7, 13, 14]. The present work also gives certain pointers towards finding the optimum operating conditions for concentrating aniline from aqueous samples in the pre-treatment process.

II. EXPERIMENTAL SECTION

A. Materials

The chemicals used in this work were obtained from the local vendor and used as supplied. Table I lists the chemicals employed and their purity.

TABLE I CHEMICALS USED AND THEIR PURITY

Aniline	**Toluene**	**NaCl**	**KI**	**$MgCl_2.6H_2O$**
99.5%	99.0%	99.9%	99.8%	97%

B. Experimental Procedure

Aqueous aniline solutions were prepared gravimetrically by dissolving known amounts aniline in distilled water using an electronic balance (Shimadzu). The initial aniline concentrations in aqueous solution were in the range 12,000 to 33,000 ppm. A mixture with a known weight was held in a stopper conical flask. The inorganic solid salt, when used, was first added to the mixture. After the aqueous solution was completely mixed, a known volume of toluene was added to form the organic and aqueous phases starting the extraction process. The added salt and toluene were weighed beforehand. The liquid-liquid extraction experiments were performed in a mechanical shaker (G K Technologies) with a frequency of 115 to 130 rpm in which the stoppered conical flask filled with the water + aniline + toluene or water + aniline + toluene + salt mixtures were placed. The shaking of solutions was performed for sufficient time to allow the equilibrium to be attained; this time was pre-determined by separate experiments to be 1 h. Each sample system was maintained in the equilibrium state for about 1-2 h and then separated in a separating funnel. The equilibrium temperature was maintained constant with an uncertainty of 1°C. The equilibrium experiments with and without salt were performed at 33 ± 1^0C. All the experiments and their analyses were done in duplicate sets.

C. Analysis

The concentration of aniline in the organic phase was determined by a gas chromatograph (Shimadzu). As majority of components were organic substances in the organic phase and water was almost negligible, we could utilize a gas chromatograph (AOC 5000 Auto injector) equipped with a flame ionization detector (FID). The chromatographic column (100 m × 0.25 µm) was a DB-5 capillary column. The carrier gas was nitrogen flowing at 4 kg/cm^2. The operating conditions were as follows: hydrogen (H_2), 3 kg/cm^2; air, 4 kg/cm^2; detector and injector temperatures, 180°C and 130°C. The injection volume was 5.0μL. The gas chromatograph was calibrated using mixtures of known compositions of reagents. The maximum uncertainty in the mass fractions of the components was 0.001. Each analysis was done at least twice to ensure repeatability.

III. RESULTS AND DISCUSSION

Distribution coefficient, % recovery of the solute, and selectivity are important values from the standpoint of selection, efficiency of a solvent used for extraction, and economy of operation. These are defined as

$$D = \frac{c_o}{c_a}$$

Where,

D = distribution coefficient

c_o= concentration of aniline in organic phase at equilibrium

c_a=concentration of aniline in aqueous phase at equilibrium

$$\%\ \text{recovery of aniline} = \frac{c - c_a}{c} \times 100$$

Where,

c = initial concentration of aniline in water

Selectivity (β) = {(Y_C/Y_A)/ (X_C/X_A)}

Where,

Y_C = molar concentration of aniline in organic phase

Y_A = molar concentration of water in organic phase

X_C = molar concentration of aniline in aqueous phase

X_A = molar concentration of water in aqueous phase

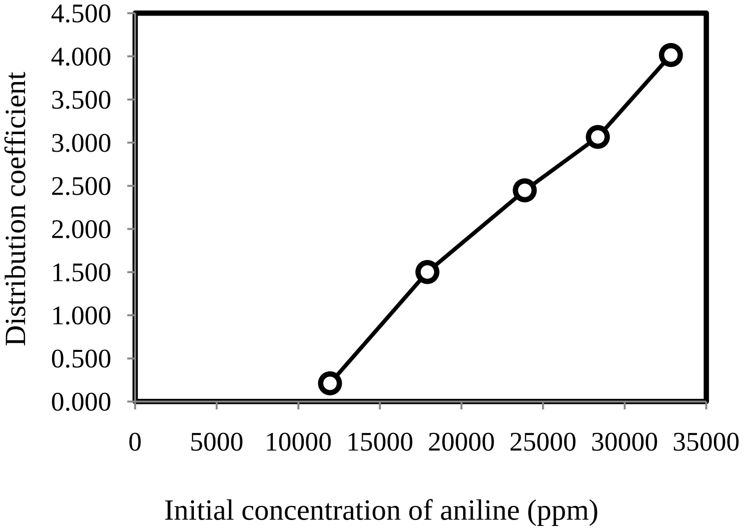

Fig.1 Distribution of aniline without salt addition

Fig. 1 shows the variation of distribution coefficient of aniline in toluene-water system without salt-addition. The coefficient monotonically increases with the aqueous aniline concentration. The solubility of aniline in toluene (5.774g/100 ml) is more than that in water (3.6g/100 ml), therefore for the same amount of water and toluene, aniline partitions more in toluene. Similar trend is depicted by a plot of selectivity versus aqueous aniline concentration (not shown here).

A. Effect of Salt Addition on Extraction Process

Addition of salt is known to influence distribution of solute by salting out or salting in effect in liquid-liquid systems.

The Setchenow's constant [24] is a direct quantitative measure of the effect of salt addition. In the present work, three inorganic salts were selected to understand the effect of salt addition on distribution of aniline in toluene-water system. The salts are NaCl, KI, and $MgCl_2 \cdot 6H_2O$ in amounts 1%, 3%, and 5% each by weight of water. These salts are selected with a definite purpose of studying the cation and anion effect on the distribution as envisaged by Hofmeister series [23]. Tables II, III and IV show the variation of distribution coefficient against the initial concentration of aniline in aqueous phase at particular NaCl concentrations used in this work.

TABLE II VARIATION OF DISTRIBUTION COEFFICIENT (1 % NACL)

Initial Concentration of Aniline in aqueous phase (ppm)	Distribution Coefficient	Remarks
33000	0.025	As the initial aniline aqueous phase concentration increases, the distribution coefficient increases because aniline solubility in toluene is more than that in water. The effect is more pronounced at lower initial concentration because of salt addition.
28000	0.034	
24000	0.035	
18000	0.046	
12000	0.066	

TABLE III VARIATION OF DISTRIBUTION COEFFICIENT (3 % NACL)

Initial Concentration of Aniline in aqueous phase (ppm)	Distribution Coefficient	Remarks
33000	0.046	As the initial aniline aqueous phase concentration increases, the distribution coefficient increases because aniline solubility in toluene is more than that in water. The effect is more pronounced at lower initial concentration because of salt addition.
28000	0.053	
24000	0.064	
18000	0.088	
12000	0.121	

TABLE IV VARIATION OF DISTRIBUTION COEFFICIENT (5 % NACL)

Initial Concentration of Aniline in aqueous phase (ppm)	Distribution Coefficient	Remarks
33000	1.794	As the initial aniline aqueous phase concentration increases, the distribution coefficient increases because aniline solubility in toluene is more than that in water. The effect is more pronounced at lower initial concentration because of salt addition.
28000	2.123	
24000	2.708	
18000	4.267	
12000	8.068	

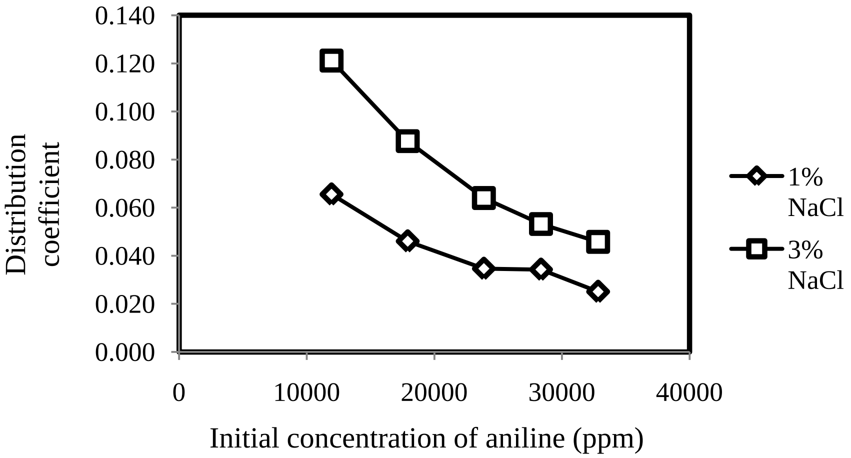

Fig. 2(a) Effect of addition of NaCl(1% and 3% by weight) on the recovery of aniline

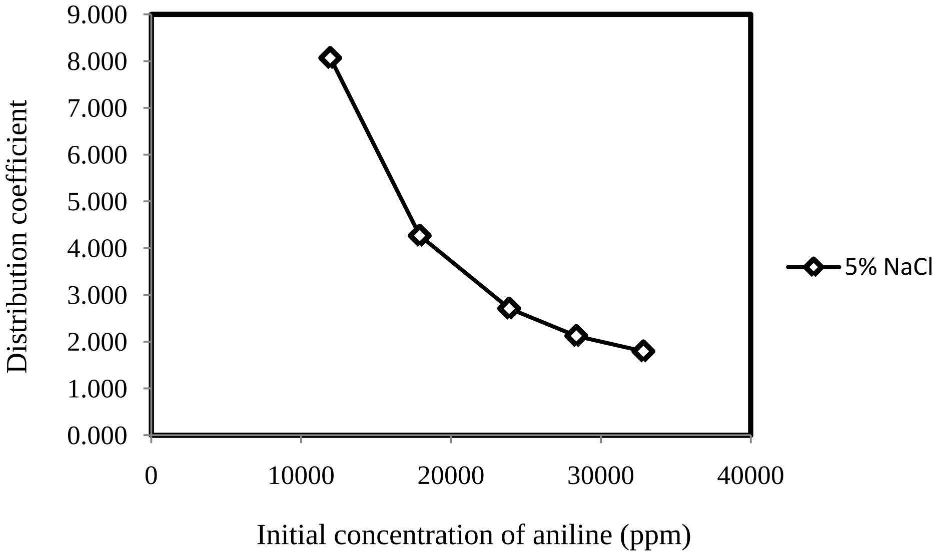

Fig. 2 (b) Effect of addition of NaCl (5% by weight) on the recovery of aniline

Fig. 2 (a) and 2 (b) show the effect of NaCl addition on aniline distribution. The change in amount of salt has profound effect on distribution. It shows that with increase in amount of NaCl the aniline partitioning in toluene increases. This is a clear indication of salting out effect created by NaCl, because with increase in salt concentration, the water molecules are increasingly surrounded by the salt molecules which ultimately increase aniline partitioning in toluene. Similar trend is shown by Fig. 3 in which Setchenow's constant is plotted on the Y-axis against aqueous aniline concentration in ppm. The slope increases with amount of salt showing positive effect when the amount goes to 5%.

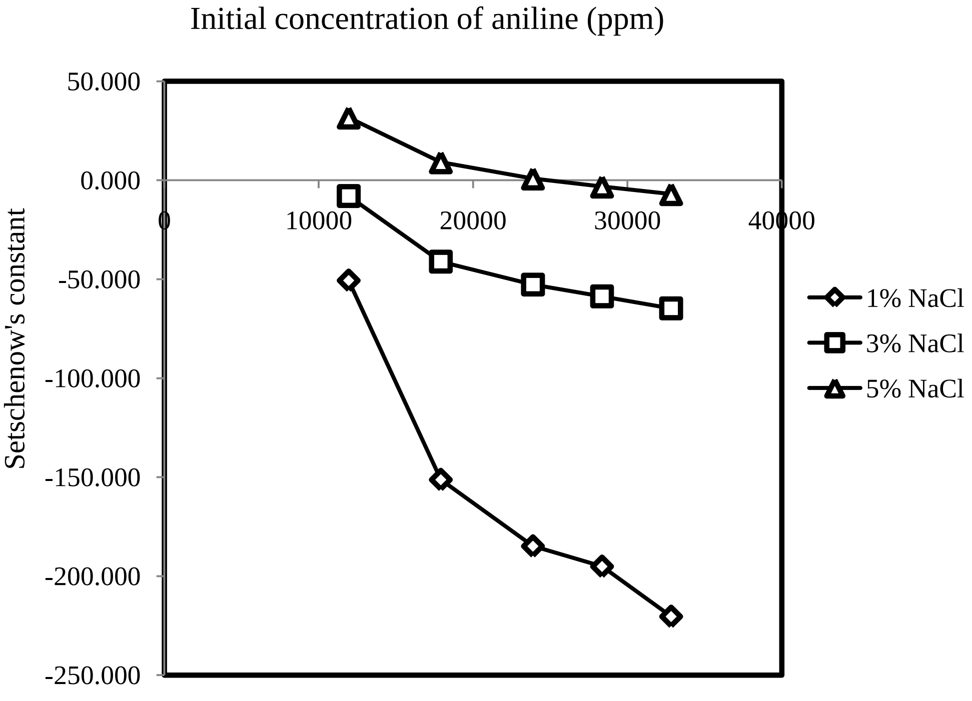

Fig. 3 Effect of addition of NaCl on the recovery of aniline in terms of Setchenow's constant

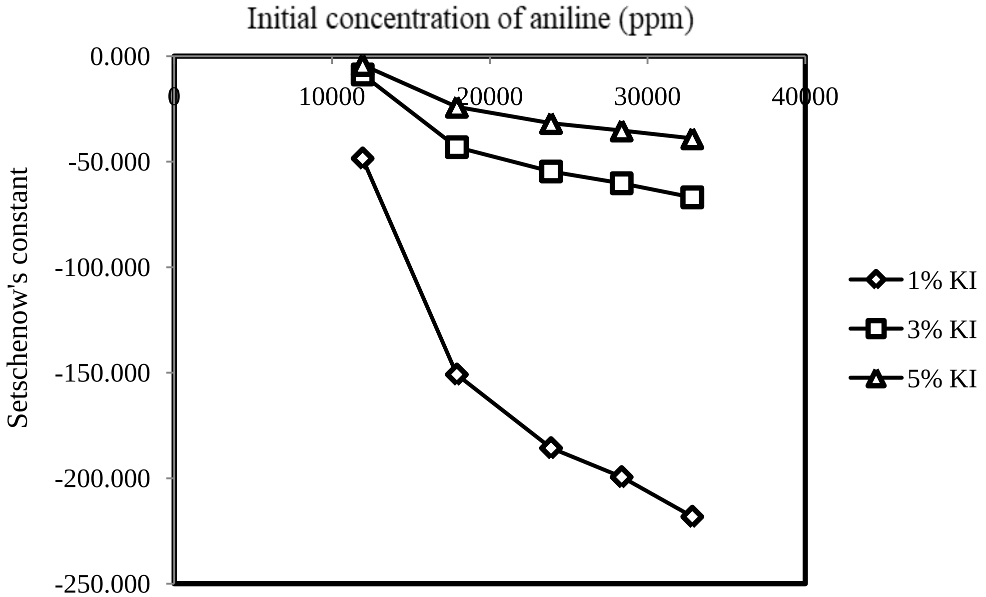

Fig. 4 Effect of addition of KI on the recovery of aniline in terms of Setchenow's constant

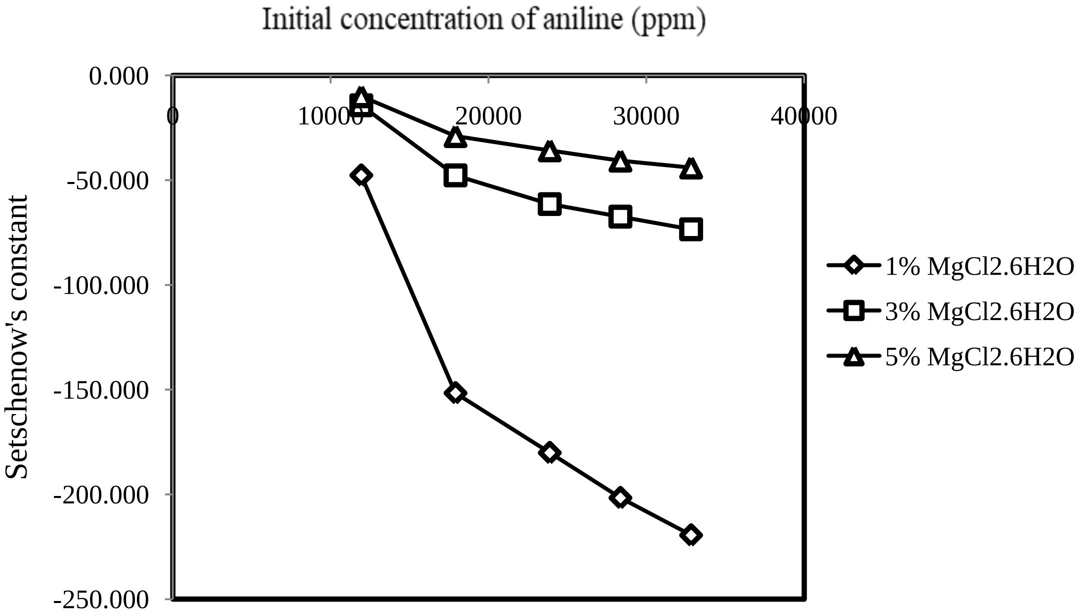

Fig. 5 Effect of addition of$MgCl_2.6H_2O$ on the recovery of aniline in terms of Setchenow's constant

Fig. 4 and 5 shows the effect of addition of KI and $MgCl_2.6H_2O$ on the recovery of aniline in terms of Setchenow's constant. Although the trends are similar to that of NaCl, in terms of values,NaCl is seen to be much more effective than KI and $MgCl_2.6H_2O$. The effect of KI and $MgCl_2.6H_2O$is quite small in comparison with NaCl. The salting out effect is in the order NaCl>KI>$MgCl_2.6H_2O$, whereas the solubility of these salts in water is in the order NaCl<KI<$MgCl_2.6H_2O$. Therefore, the water molecules engaged in caging effect of the salt molecules will also be in the same order as that of solubility, which facilitates aniline partitioning in toluene.

Fig. 6 shows comparison of performance of addition of salts with no-salt condition. It shows that in general 5% NaCl is more effective than other salts, but the effectiveness of NaCl is more pronounced at lower initial aniline concentration in water. This is a fortuitous effect as far as removal/extraction of aniline is concerned.

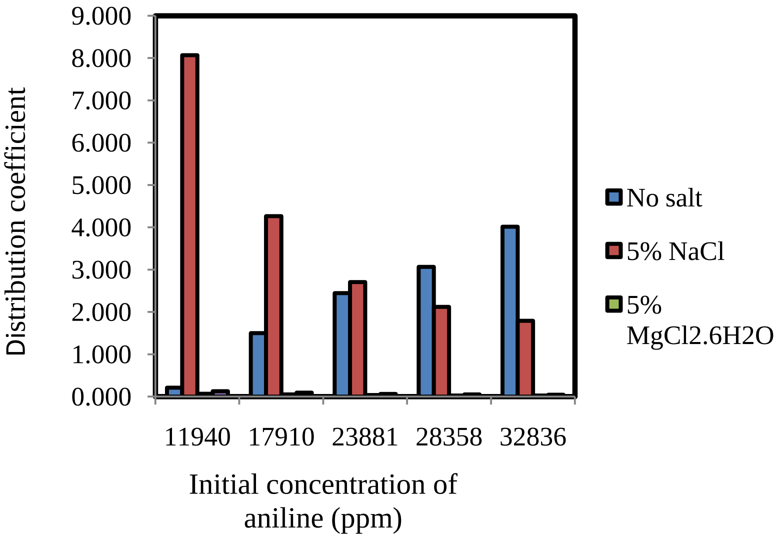

Fig. 6 Comparison of performance of all salts with no-salt condition

From above discussion, it can also be noted that the sodium salt is more effective than the potassium salt in increasing the aniline partitioning in the organic phase. This exactly conforms to the well-known Hofmeister series [23]. According to the Hofmeister series, the salting-out effect for the order of cations is Mg^{2+} > Na^+ >K^+ whereas, anions follow the order Cl^-> I^-. In this case, the salting-out effect of NaCl is higher than that of KI and $MgCl_2{\cdot}6H_2O$. In dissolution of inorganic salts in water, their dissociation plays an important role. Hence, dissociation constant was calculated from pH of the aqueous solution and the known amount of salt added. It is found that the dissociation constant for NaCl increases appreciably with increase in its amount, but that for KI and $MgCl_2{\cdot}6H_2O$ appreciably decreases; the decrease being more in magnitude for KI than for $MgCl_2{\cdot}6H_2O$. Thus, it can be concluded that dissociation of salt added plays an important role in aniline extraction.

B. Effect of Phase Volume Ratio and Initial Aqueous Aniline Concentration on Extraction Process

From the point of view of economic operation and concentration of solute in feed water to be treated, phase volume ratio is an important parameter in its own right. Therefore, a suitable phase volume ratio should be determined for the extraction process. In this work, different phase volume ratios (V_o/V_a) between the aqueous phase volume (V_a) and organic phase volume (V_o) were investigated for no salt condition. Figure 7 shows the change of phase volume ratio with change of percentage recovery of aniline. It shows that as the phase volume ratio increases, the aniline concentration in the organic phase also increases, but an economic phase volume ration is little above 1.0.

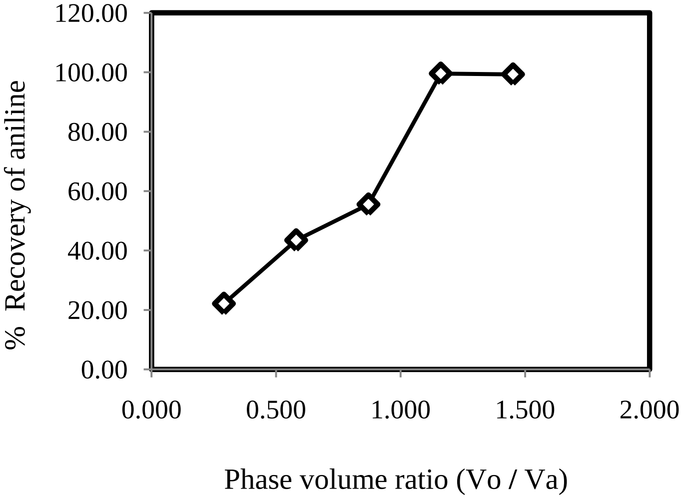

Fig. 7 Effect of phase volume ratio (V_o/V_a) on the percentage recovery of aniline (initial concentration of aniline in the aqueous phase is 32000 ppm)

The experiments were also conducted with different initial concentrations of aniline in the aqueous phase. As shown in Fig. 8, there is a linear relationship between the initial aqueous aniline concentration and percentage recovery of aniline with toluene as the separating agent. This indicates that the initial aqueous aniline concentration can be deduced from the concentration of aniline in the organic phase after extraction in sample analysis. The % recovery corresponding to phase volume ratios of 1.161 and 1.451 are respectively 99.57 and 99.30 though they are seen to be 100% because of auto-truncation by Microsoft Excel.

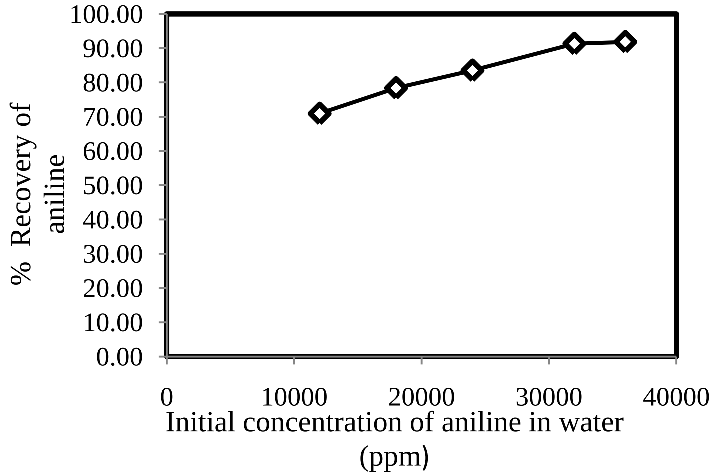

Fig. 8 Effect of initial aqueous aniline concentration on the percentage recovery of aniline

C. Effect of Temperature on Aniline Extraction

Fig. 9 shows the effect of temperature of extraction (*T*) on distribution coefficient (*K*). Experiments were carried out at 296, 302, and 307 K with no salt addition. The enthalpy change of extraction and distribution coefficient can be correlated by a linear relation [2] between *lnK* and *1/T*. In this case, the enthalpy change of the extraction process, Δ*H*, is deduced to be positive which means that the extraction process with toluene as the separating agent is endothermic.

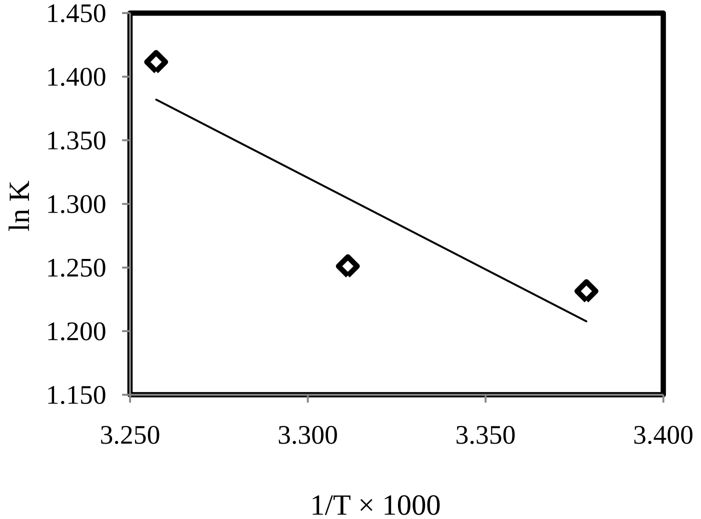

Fig. 9 Logarithmic distribution coefficient as a linear function of inverse temperature with toluene as a separating agent

IV. CONCLUSION

In the present work, extraction of aniline from aqueous phase was carried out in toluene phase through usual liquid extraction experiments. The experiments were planned to study the effect of addition of inorganic salts, phase volume ratio, initial aniline concentration in the feed solution, and temperature on distribution of aniline. Apart from the above, our experiments have also revealed certain interesting observations towards the trend of cations and anions given by the Hofmeister series and the trend of effectiveness of salt as given by the Setschenow's constant. Based on our experimental readings and observations, the following conclusions are drawn.

1. Aniline distribution and selectivity in toluene increases with increase in its initial concentration in water (feed solution), thus toluene is a good solvent for aniline from the standpoint of extraction / removal efficiency. 5 % NaCl addition shows a high degree of extraction / removal of aniline as compared to KI and $MgCl_2 \cdot 6H_2O$ and NaCl addition favors lower initial aniline concentration. Also, 5 % NaCl addition is more effective at lower concentration of aniline in feed water.
2. The effect of 5 % addition of $MgCl_2 \cdot 6H_2O$ and KI is not according to the Hofmeister series but shows exactly reverse trend as far as the cation and anion of the two salts are considered. According to the series prediction, $MgCl_2 \cdot 6H_2O$ should show higher extraction / removal of aniline than KI. But, $MgCl_2 \cdot 6H_2O$ shows lower performance than KI. It means that there is some other influence at work than that predicted by the series. The effect is due to higher dissociation of NaCl as compared to that of KI and $MgCl_2 \cdot 6H_2O$.
3. Roughly, the phase volume ratio of 1:1 or little above is reasonably effective. Higher the initial concentration, higher is the % extraction of aniline at the given temperature. It is an expected result since solubility of aniline in toluene is greater than in water at given temperature. The plot of lnK versus $1/T$ shows that, in general, this extraction process is endothermic in nature. As expected, the endothermicity is lower at higher temperature and higher at lower temperature.
4. The salting out effect of NaCl on aniline and water is the highest among all of the salts investigated. In addition, the aniline concentration in the aqueous phase decreases as the amount of NaCl increases. Therefore, the salting-out effect of NaCl plays an important role in concentrating aniline, and the aniline concentration in the organic phase is much higher with a mixture of toluene and NaCl than with pure toluene as the separating agent. However, formerly, only pure toluene was recommended as the separating agent.

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