



THE DISTRIBUTION COEFFICIENTS OF ACETIC ACID BETWEEN WATER AND SOLVENT SYSTEMS

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ABSTRACT

Distribution coefficients of acetic acid between aqueous phase and solvents (water-C₆-C₁₀ alcohols, butyl acetate, ether and benzene) were studied. Synergetic effect was obtained for alcohol and ester systems. A slightly positive deviation was obtained for benzene-ester mixtures. The best distribution coefficient was obtained for hexanol-butyl acetate systems. The coefficients of Redlich-Kister equation were obtained for the deviations.

Key Words : Acetic acid, Distribution coefficient, Solvent mixtures, Alcohols, Esters

ASETİK ASİDİN SU VE SOLVENT SİSTEMLERİ ARASINDA DAĞILIM KATSAYILARI

ÖZET

Asetik asidin sulu çözelti ve solvent sistemleri (C₆-C₁₀ alkolleri-butil asetat, eter-benzen) arasında dağılım katsayısı incelendi. Alkol ester sistemleri için sinerjik etki elde edildi. Benzen-eter sistemleri için hafif pozitif sapma görüldü. En iyi dağılım katsayısı hegzanol-ester karışımı için elde edildi. Sapmalar için Redlich-Kister eşitliği katsayıları elde edildi.

Anahtar Kelimeler : Asetik asit, Dağılım katsayısı, Solvent karışımları, Alkoller, Esterler

1. INTRODUCTION

Acetic acid is one of the most important organic substances in industry and presents in concentrations ranging from 0.1 to 5 % in effluents depending on the source (Helsel, 1977). Waste water contained acetic acid must be treated to meet quality standarts. In addition to treatment requirements, the discharge of acetic acid wastes represents the loss of a valuable resource. Removal and recovery of acetic acid from effluents is desirable from the pollution control as well as the product recovery point of view. The seperation of acetic acid from water has been industrially important for more than a century. There are many methods such as degradation, extraction, adsorption and stripping for treating waste waters (Earhart et al., 1977; Takatsuji and Yoshida, 1997). In degradation method, pollutants

are converted into substances that are satisfactory for release to the environment. But it is desired that the product in the effluent is not converted into other substances when valuable substances such as acetic acid are present in the effluents.

Liquid-liquid extraction, commonly known today as solvent extraction, has played a vital and powerful role in seperation technology (Naylor, 1992; Bora et al., 2000). Solvent extraction can be considered as an alternative to other methods and the key to suitable application to the treatment process lies in the selection and availability of a solvent with a suitable characteristics.

In solvent extraction processes, it is desired that the solvents used in the process has a high distribution coefficient to decrease the solvent circulation rate. In

addition, a high distribution coefficient lessens the extent of solute removal required during the regeneration of the solvent. It is also desired to minimize lost solvent and water contamination since the higher the concentration of solvent in water the greater the cost for recovering the solvent for recycle (Earhart et al., 1977; Kaullos et al., 1999) It is known that alcohols have high distribution coefficient for many organic acids since they have the dual nature of their hydrogen-bonding process. The low molecular weight alcohols have high solubilities in water as a result of hydrogen bonding with water molecules. In methanol, the hydroxyl group accounts for almost half of weight of the molecule and it is miscible with water in all proportions. As the size of hydrocarbon group of an alcohol increases, the hydroxyl group accounts for progressively less of the molecular weight, and hence water solubility decreases. Therefore hexanol, heptanol, octanol, nonanol and decanol were chosen as the solvent to remove acetic acid from aqueous solutions, whereas butyl acetate was chosen to prepare mixed solvent with alcohol. In addition benzene and ether were chosen to make a comparison with alcohols. There are some data reported that mixed solvent systems may be effective and indeed may be superior to the individual solvents (Mahramanlioğlu, 1997a).

The aim of this study is to calculate the distribution coefficient of acetic acid between water and solvent systems and to investigate the synergetic effect for solvent systems.

2. MATERIAL AND METHOD

The distribution coefficient was determined between water and the following solvents: hexanol, heptanol, octanol, nonanol, decanol, benzene, ether and butyl acetate. The solvent systems used were butyl acetate-hexanol, butyl acetate-heptanol, butyl acetate-octanol, butyl acetate-nonanol, butyl acetate-decanol and benzene-ether.

All the solvents and acetic acid, sodium hydroxide were obtained from Merck and were used without purification.

The distribution coefficient can be defined as

$$K_d = \frac{C_o}{C_w} \quad (1)$$

Where C_o is the concentration of solute in the organic phase, C_w is the concentration of the solute in aqueous phase. Several methods have been used to determine the distribution coefficient

(Haelst et al., 1994; Wu et al., 1998; Wang and Liug, 1998; Treszczanowicz et al., 1999). In our study, in order to determine the distribution coefficient of acetic acid between water and solvents and solvent mixtures, the following procedure was carried out (Mahramanlioğlu et al., 1997a). 25 mL of aqueous acetic acid solution and solvent or binary solvents was shaken in a 250 mL erlenmeyer flasks on a water bath at 25 °C. After equilibration the samples were allowed to stand for two hours to allow phase separation at the same temperature. The acetic acid concentration in aqueous phase was determined using alkali titration. The concentration of acetic acid in the organic phase was found from the difference of the initial concentration of acetic acid and the concentration in the aqueous phase after equilibration.

3. RESULT AND DISCUSSION

Figures 1a, b, c, d, e show that the distribution coefficients of acetic acid vs volume percent of alcohol in alcohol-ester systems. It is seen that the highest distribution coefficient obtained is for hexanol-butyl acetate systems

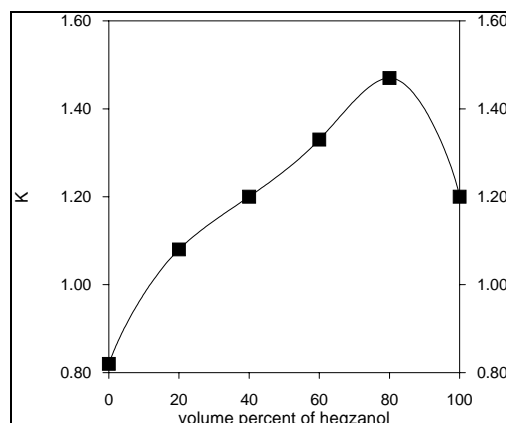


Figure 1.a

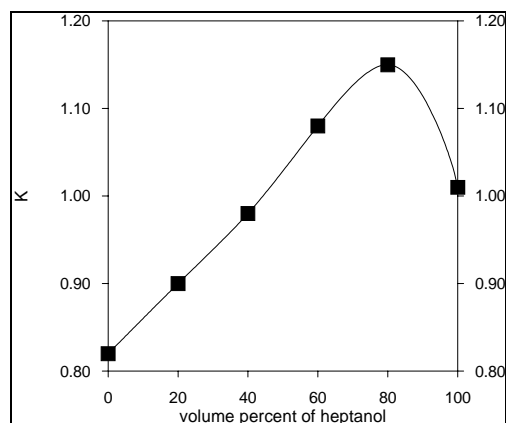


Figure 1. b

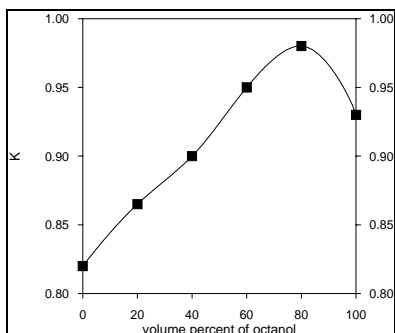


Figure 1. c

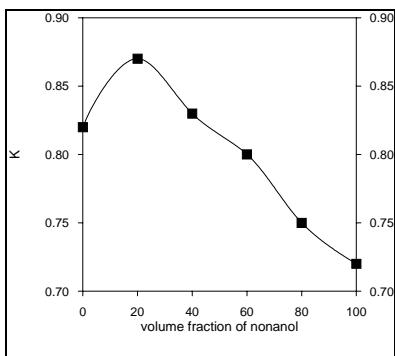


Figure 1. d

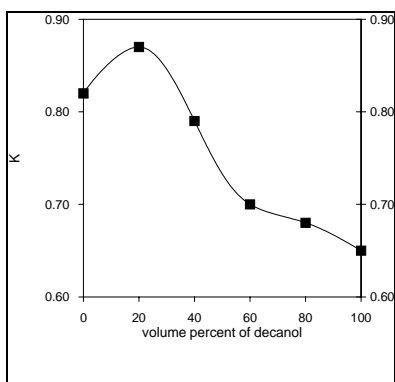


Figure 1. e

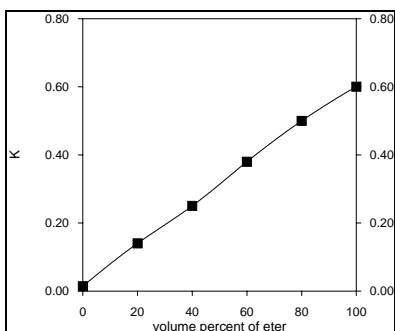


Figure 1. f

Figure 1. Distribution coefficient of acetic acid between water and a) butyl acetate-hexanol, b) butyl acetate-heptanol, c) butyl acetate-octanol, d) butyl acetate-nonanol, f) butyl acetate-decanol g) benzene- ether systems

This value decreases when the carbon number of alcohol increases. It is known that butyl acetate has the great capacity to reduce the self association of the alcohol and the increases the concentration of free hydroxyl groups (Medir and Mackay, 1974). Therefore synergetic effect was seen in alcohol-ester mixtures.

The value of distribution coefficient for individual solvents decreased with the increase in carbon number. This can be explained by the physical properties of higher molecular weight alcohols are very similar to hydrocarbons (Mahramanlioğlu, 1997b).

Figure 1. f shows the distribution of acetic acid for benzene-ether systems. It is seen that a slightly positive deviation but, there is not a synergetic effect.

The distribution coefficient of acetic acid for toluene, carbon tetrachloride and chloroform was also obtained in another study (Mahramanlioğlu, 1997b). When the distribution coefficient obtained in this study was compared with another study the distribution coefficient of acetic acid for alcohols, butyl acetate and ether is greater than toluene, carbon tetrachloride and chloroform since alcohols, esters and ethers are the hydrogen bonding solvents. The highest distribution coefficient in the study was obtained for hexanol-butylacetate system ($K=1.47$). In the literature there are also some data on the distribution coefficient of acetic acid, between water and alamine-sorbent systems. However, although the temperature was the same, the experiments were performed under different conditions (Şenol, 2001). The values of distribution coefficient from this study is as follows : $K = 0.017$ for Xylene, $K = 0.048$ for Xylene + Alamine 336, $K = 0.925$ for methylcyclohexanol, $K = 1.957$ for methylcyclohexanol + Alamine. It is seen that when a long-chain, aliphatic tertiary amine such as Alamine 336 was dissolved in organic solvent it causes to increase the distribution coefficient of acetic acid since it forms acid-amine complex with acetic acid. On the other hand, in our system acetic acid does not form a complex. Therefore it is more suitable to recover acetic acid.

It is known that excess values for the systems are very useful in design calculations. Therefore Redlich-Kister type equation was used to calculate excess distribution coefficients. The deviations were expressed as a function of volume percent of solvents (Fermeglia and Torriano, 1999; Weng et al., 1999). Redlich-Kister type equation can be expressed as follows:

$$\Delta K = \frac{x_1 \cdot x_2 \cdot \sum_{j=0}^{n-1} a_j (x_1 - x_2)^j}{j=0} \quad (2)$$

Where the a_j are the adjustable parameters, n is the order of the polynomial, and x_1 and x_2 are the volume percent of components 1 and 2 and ΔK is

the deviation of distribution coefficient. The values of the parameters of Redlich-Kister type equation were calculated for all the systems except benzene-ether system since it showed a rather slightly deviation. The values of the parameters are shown in Table 1.

Table 1. Redlich-Kister Parameters for Acetic Acid

Organic phase	a_0	a_1	a_2	a_3
hexanol-butyl acetate	0.988	0.245	0.170	0.024
heptanol-butyl acetate	0.453	0.637	0.655	0.191
octanol-butyl acetate	0.198	0.297	0.276	-0.118
nonanol-butyl acetate	0.187	-0.192	0.002	-0.323
decanol-butyl acetate	0.027	-0.618	0.358	0.879

4. CONCLUSION

Distribution coefficients of acetic acid for individual solvents and solvent systems were studied. In alcohol-butyl acetate system, synergetic effect was obtained. Synergetic effect was not seen in ether-benzene systems. The highest distribution coefficient was obtained for the lowest carbon number of alcohol (hexanol). However, the decrease in the carbon number causes the increase in the water solubility of alcohols. It is seen that the highest distribution coefficient is obtained at the expense of greater solubilities in water and toxicity. The results obtained from this study present useful data for recovering process in chemical industry.

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