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Extraction of Glycolic Acid from Aqueous Solutions by Amberlite LA-2 in Different Diluent Solvents

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In this work, extraction of glycolic acid was investigated from aqueous solutions by different organic solutions containing Amberlite LA-2, a secondary amine mixture. The extraction of glycolic acid with Amberlite LA-2 dissolved in six individual solvents has been measured at 298.15 K. The solvents used were 1-octanol, cyclohexane, isooctane, toluene, 2-octanone, and methyl isobutyl ketone (MIBK). The effect of different parameters on recovery of glycolic acid has been investigated. The investigated parameters were selected as solvent type, amine concentration, and initial acid concentration. To show the effect of these parameters, distribution coefficients (D), loading factors (Z), and extraction efficiency (E) are calculated. The maximum removal of glycolic acid is 79.43 % with MIBK and 0.93 mol·L⁻¹ initial concentration of Amberlite LA-2.

Introduction

In recent years, hydroxycarboxylic acids have received much attention for their important medical and pharmaceutical applications. Besides their use as cleaners in the household, in industry, and for electronic elements, they are also used as automotive oil additives, oil and water well flow enhancers, pH control, cosmetics, and intermediates in chemical manufacture. Currently, these substances are widely used as inhibitors of harmful oxidation in biochemical processes.^{1–3}

Glycolic acid is the simplest kind of hydroxycarboxylic compound, which is now produced from fermentation broth⁴ or from glycolonitrile hydrolysis by mineral acids, such as sulfuric acid.^{5,6} Both processes produce multicomponent solutions with the acid concentration typically less than 10 % by mass for fermentation technologies and less than 40 % by mass for glycolonitrile hydrolysate. Subsequent purification of carboxylic acids from these products presents a challenging separation difficulty because water is distilled from the dilute, nonvolatile, heat sensitive acid solutions which involves a large amount of energy consumption. Furthermore, distillation cannot fractionate the nonvolatile acids, as well as the mixture of hydroxy carboxylic acids and inorganic sulfate. The strong aqueous activity of carboxylic acids results in a low distribution coefficient of the acids into conventional solvents.^{7,8}

Because of their hydrophilic nature, hydroxycarboxylic acids are not easily extracted by common organic solvents; so, for their recovery from aqueous solutions, reactive liquid–liquid extraction has been considered. Aliphatic secondary and tertiary amines, with C₇–C₁₀/C₁₂ alkyl groups (TAA), have been proposed as suitable extractants for carboxylic and hydroxycarboxylic acids.^{9–11} The amine extractants are dissolved in a diluent that dilutes the extractant to the desired concentration and controls the viscosity and density of the solvent phase. It has been found that, in systems with the same acid and the same

amine, the type of diluent and the composition of the extraction mixture influence the extraction equilibrium.^{12–15}

Polar diluents have been shown to be more convenient than inert ones (nonpolar), due to their higher distribution. However, active polar and proton-donating diluents such as alcohols have been shown to be the most suitable diluents for amines because they give the highest distributions resulting from the formation of solvates through specific hydrogen bonding between the proton of the diluent and the acid–amine complex.^{16,17}

Some authors suggest the formation of acid–amine complexes of only one type (1,1) or (1,2), depending on the diluent, while others suggest the formation of at least two.^{13,16}

It has been found that diluents, especially those with functional groups, can affect the extraction behavior of amines significantly. The stoichiometry of the solute:amine complex, loading of the amine, as well as a third phase formation are influenced by the diluent. The effect of the diluent can be understood in terms of the ability to solvate organic phase species, therefore it is necessary to distinguish between general solvation from electrostatic, dispersion, or other forces and specific solvation due to hydrogen bonding.¹⁷ The resulting acid:amine complexes are supposed to be stabilized due to the hydrogen bonding with the diluent.^{14,18}

Wasewar et al. have investigated the removal of a lot of carboxylic acids by different extractants.^{19–21} Aljundi has investigated the removal of lactic acid using an adsorption column.²² Also, Mahfud has made a comprehensive investigation on the extraction of some carboxylic acids.^{23,24} Uslu has studied the extraction of tartaric acid with a mixture of tertiary amines named Alamine 336.²⁵ There are not any data on glycolic acid and Amberlite LA-2/diluent systems. In the present work, the extraction of glycolic acid from aqueous solutions by Amberlite LA-2 in different diluent solvents was examined over a wide range of amine concentration [(0.19 to 0.93) mol·L⁻¹].

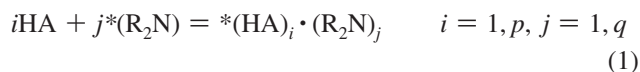
Extraction experiments were carried out with Amberlite LA-2 dissolved in the diluents of various types—ketone (MIBK,

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2-octanon), different alkanes (isooctane, cyclohexane, hexane), alcohol (1-octanol), and aromatic hydrocarbon (toluene). As a result of batch extraction experiments, distribution coefficients were calculated. In addition to distribution coefficients, extraction efficiency and variation of loading factors were obtained. Furthermore, they were used to obtain conclusions about the stoichiometry of complex formation.

Theoretical

The extraction of glycolic acid (HA) with Amberlite LA-2 (R_2NH) can be shown by the reaction



where HA represents the nondissociated part of the acid present in the aqueous phase and organic phase species are marked with *. As no overloading of the amine has been observed, it is expected to be lesser than or equal to j for any p and q . Reaction 1 can be characterized by the overall thermodynamic extraction efficiency.

$$*K_{ij} = \frac{[(HA)_i \cdot (R_2N)_j]}{[HA]^i [R_2N]^j} \quad (2)$$

where square brackets denote activities.

The loading of the extractant, Z , is defined as the total concentration of acid in the organic phase, divided by the total concentration of amine in the organic phase.⁷ The expression for the loading, Z , can be written in the form

$$Z = C_{a,org}/C_{e,org} \quad (3)$$

Distribution coefficients for glycolic acid extracted from water into the organic phase were determined as

$$D = C_{a,org}/C_a \quad (4)$$

The efficiency of extraction, E , is expressed as

$$E = (1 - (C_a/C_{a0})) \cdot 100 \quad (5)$$

where C_a is the concentration of acid in the aqueous phase after extraction and C_{a0} is the initial concentration of acid in the aqueous phase. An E value of 100 % means that all of the acid in the aqueous phase has been removed and is present in the organic phase.²⁷

Experimental Section

Amberlite LA-2, glycolic acid, and the solvents were purchased from Merck. The Amberlite LA-2 used was a straight-chain secondary amine mixture ($M = 374 \text{ g} \cdot \text{mol}^{-1}$). Glycolic acid (Merck, > 99 %), cyclohexane (Merck, > 99 %), toluene (Carlo Erba, > 99 %), isooctane (Merck, > 99 %), MIBK (Merck, > 99 %), 2-octanone (Merck, > 99 %), and 1-octanol (Merck, > 99 %) were used without further purification.

Glycolic acid was dissolved in water to prepare the solutions with initial concentrations of acid of 10.81 % w/w ($1.56 \text{ mol} \cdot \text{L}^{-1}$). The initial organic phases were prepared by the dissolution of Amberlite LA-2 in the diluents to produce solutions with approximately constant concentrations ($0.93 \text{ mol} \cdot \text{L}^{-1}$, $0.74 \text{ mol} \cdot \text{L}^{-1}$, $0.56 \text{ mol} \cdot \text{L}^{-1}$, $0.37 \text{ mol} \cdot \text{L}^{-1}$, $0.19 \text{ mol} \cdot \text{L}^{-1}$).

For distribution experiments, equal volumes of an aqueous glycolic acid solution and an organic solution of amine were mixed in flasks in a shaker bath at 25°C for 4 h. Preliminary tests demonstrated 4 h to be a sufficient amount of time for equilibration. Later the mixture was kept in a bath for another 10–12 h to achieve full separation of phases.

Table 1. Experimental Results of the Extraction of Glycolic Acid ($C_{a0} = 1.56 \text{ mol} \cdot \text{L}^{-1}$) with Amberlite LA-2/Individual Diluting Solvents

diluent	$C_{e,org}$ ($\text{mol} \cdot \text{L}^{-1}$)	C_a ($\text{mol} \cdot \text{L}^{-1}$)	$C_{a,org}$ ($\text{mol} \cdot \text{L}^{-1}$)	D	Z	E (%)
cyclohexane	0.19	1.36	0.20	0.14	1.06	12.59
	0.37	1.13	0.43	0.38	1.16	27.45
	0.56	0.94	0.62	0.66	1.12	39.63
	0.74	0.73	0.83	1.12	1.11	52.89
	0.93	0.63	0.93	1.49	1.01	59.89
isooctane	0.19	1.26	0.30	0.24	1.61	19.12
	0.37	1.07	0.49	0.46	1.33	31.51
	0.56	0.76	0.80	1.07	1.46	51.57
	0.74	0.66	0.90	1.36	1.22	57.66
	0.93	0.55	1.01	1.82	1.09	64.49
MIBK	0.19	1.16	0.40	0.34	2.15	25.56
	0.37	0.90	0.66	0.74	1.79	42.45
	0.56	0.68	0.88	1.28	1.59	56.17
	0.74	0.52	1.04	2.03	1.41	66.96
	0.93	0.32	1.24	3.86	1.34	79.44
1-octanol	0.19	1.23	0.33	0.27	1.77	21.04
	0.37	1.00	0.56	0.56	1.52	36.03
	0.56	0.81	0.75	0.93	1.37	48.16
	0.74	0.57	0.99	1.73	1.33	63.30
	0.93	0.39	1.17	2.98	1.26	74.90
2-octanone	0.19	1.20	0.36	0.30	1.93	22.96
	0.37	0.98	0.58	0.60	1.56	37.10
	0.56	0.73	0.83	1.15	1.52	53.45
	0.74	0.55	1.01	1.86	1.37	65.04
	0.93	0.34	1.22	3.61	1.32	78.29
toluene	0.19	1.30	0.26	0.20	1.39	16.48
	0.37	1.03	0.53	0.52	1.43	33.97
	0.56	0.86	0.70	0.82	1.28	45.11
	0.74	0.60	0.96	1.61	1.30	61.64
	0.93	0.52	1.04	2.02	1.13	66.87

The concentration of acid in the aqueous phase was determined by titration with Schott titroline easy modul-2 automatic titrator and aqueous 0.1 N sodium hydroxide (relative uncertainty: 1 %). Acid analysis was checked against a material balance.¹⁴

Results and Discussion

Table 1 shows the results of the experimental investigation. The concentrations of Amberlite LA-2 in solvents were between $0.19 \text{ mol} \cdot \text{L}^{-1}$ and $0.93 \text{ mol} \cdot \text{L}^{-1}$. The glycolic acid concentration in the initial aqueous phase was $1.56 \text{ mol} \cdot \text{L}^{-1}$ (= 10 % w/w).

The equilibrium data on the distribution of glycolic acid between water and Amberlite LA-2 dissolved in 1-octanol, cyclohexane, isooctane, toluene, methyl isobutyl ketone (MIBK), and 2-octanone is given in Table 1. It can be seen from Table 1 that (60 to 80) % by mass of glycolic acid is recovered by $0.93 \text{ mol} \cdot \text{L}^{-1}$ Amberlite LA-2 from initial aqueous solutions. The amount of acid recovered depends on the amount of amine and type of diluting solvent. The maximum removal of glycolic acid was 79.43 % with MIBK with $0.93 \text{ mol} \cdot \text{L}^{-1}$ initial concentration of Amberlite LA-2. The acid concentration in water at equilibrium (C_a) decreases from $1.16 \text{ mol} \cdot \text{L}^{-1}$ to $0.32 \text{ mol} \cdot \text{L}^{-1}$ when increasing the amount of Amberlite LA-2 from $0.19 \text{ mol} \cdot \text{L}^{-1}$ to $0.93 \text{ mol} \cdot \text{L}^{-1}$. The distribution coefficient increases from 0.34 to 3.86 when increasing the amount of Amberlite LA-2 from $0.19 \text{ mol} \cdot \text{L}^{-1}$ to $0.93 \text{ mol} \cdot \text{L}^{-1}$ for MIBK.

Extraction of carboxylic acids with a secondary amine mixture–solvent system can be understood by the formation of acid:amine complexes, which are effected by the diluents in different ways. Solvation of the complex by the diluent is the most important factor in the extraction of acid. The mutual interactions between the complex and diluent can be divided into two concepts. These are general solvation and specific interactions of the diluent with the complex. It is explained in

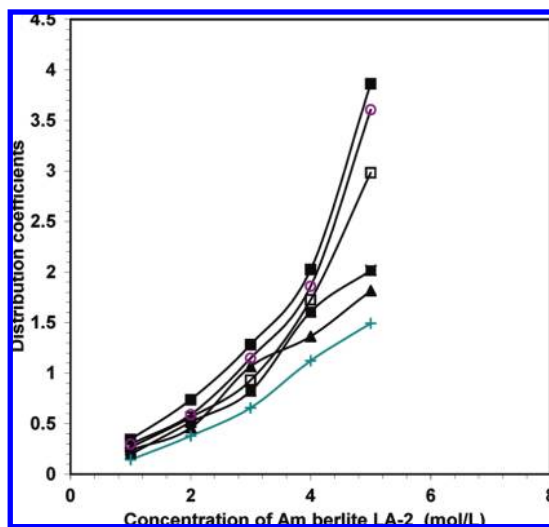


Figure 1. Variation of distribution coefficients with concentration of Amberlite LA-2 in different individual diluting solvents: ■, toluene; ▲, isooctane; □, 1-octanol; ○, 2-octanone; +, cyclohexane; ■, MIBK.

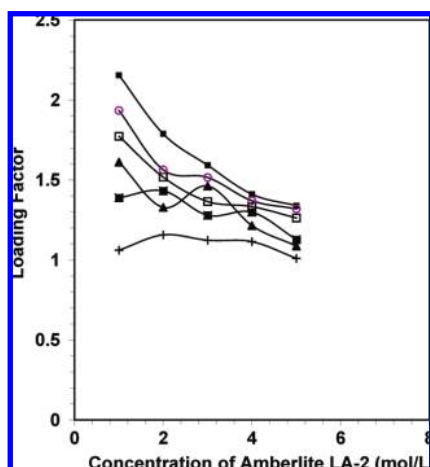


Figure 2. Variation of loading factors with concentration of Amberlite LA-2 in different diluting solvents: ■, toluene; ▲, isooctane; □, 1-octanol; ○, 2-octanone; +, cyclohexane; ■, MIBK.

the literature that polar diluents have been shown to be more convenient diluents than inert ones (nonpolar), due to their higher distribution.^{20,27} However, the extraction of glycolic acid by the secondary amine mixture used in this investigation has not found such an effect. It has been found that the polarity of the diluent is not important in the extraction of glycolic acid by the secondary amine mixture.

The effect of organic solvents on the extraction of glycolic acid from aqueous solutions can be seen Figure 1. It shows that MIBK shows the best results in terms of the distribution coefficient value, followed by 2-octanone and 1-octanol. The extraction power of Amberlite LA-2–diluent mixtures increases with increasing concentration of Amberlite LA-2 in the organic phase. The effects of MIBK, 2-octanone, and 1-octanol are more prominent with Amberlite LA-2 than with other solvents.

In Figure 2, the effect of the Amberlite LA-2 concentration on loading is presented. The loading curve is a plot of Z vs amine concentration. Overloading (loading greater than unity) shows that complexes with more than one acid per amine have been formed. With all of the solvents, overloading can be observed.

For systems with only one amine per complex, there is no effect of total amine concentration on the loading. In this work, only cyclohexane shows this type of loading.

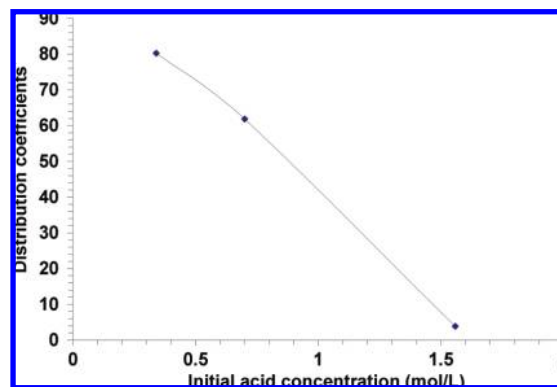


Figure 3. Effect of the initial acid concentration on glycolic acid distribution between water and Amberlite LA-2.

Table 2. Effect of Initial Acid Concentration on the Extraction of Glycolic Acid

initial acid concentration (mol·L ⁻¹)	$C_{e,org}$ (mol·L ⁻¹)	C_a (mol·L ⁻¹)	$C_{a,org}$ (mol·L ⁻¹)	D	Z	E
0.34	0.93	0.004	0.34	80.25	0.18	99.73
0.70	0.93	0.011	0.69	61.84	0.36	99.28
1.55	0.93	0.032	1.23	3.86	0.76	79.43

Table 3. Distribution of Glycolic Acid between Solvents and Water

diluent	C_a (mol·L ⁻¹)	$C_{a,org}$ (mol·L ⁻¹)	D	E (%)
cyclohexane	1.54	0.02	0.01	1.15
isooctane	1.48	0.08	0.06	5.35
MIBK	1.46	0.10	0.07	6.39
1-octanol	1.46	0.10	0.07	6.60
2-octanone	1.53	0.03	0.02	2.10
toluene	1.53	0.03	0.02	2.21

In this work, most of the solvents (isooctane, hexane, MIBK, 1-octanol, toluene) show a decrease in loading with increasing amine concentration, indicating that complexes include the diluent, specifically complexes that include more than one amine per complex.^{25,26}

Figure 3 and Table 2 present the effect of the initial concentration of glycolic acid on the distribution coefficient. As the concentration increases, the distribution coefficient decreases. It can be seen that the extraction power of Amberlite LA-2 decreases with an increase in the initial concentration of glycolic acid in the aqueous phase. In this experiment, we use the MIBK as a diluent.

The distribution data of glycolic acid between water and the solvents used in this study (1-octanol, cyclohexane, isooctane, hexane, methyl isobutyl ketone (MIBK)) are presented in Table 3 and shown in Figure 4. The results show that the extractions

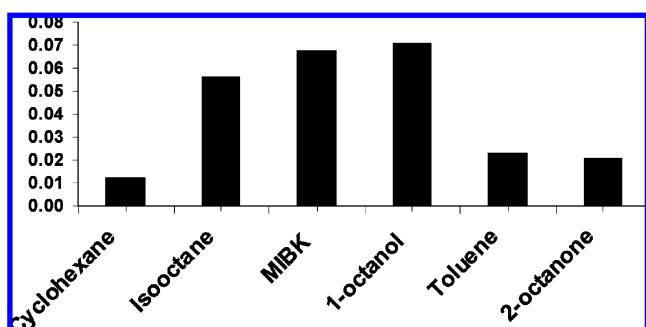


Figure 4. Distribution coefficients of glycolic acid between water and solvents used in this study.

in water have a very low efficiency for all of the solvents employed.

Conclusions

Extraction data for glycolic acid from aqueous solutions by Amberlite LA-2 and six individual solvent systems were determined. As a result of this study, it can be said that the extractability of glycolic acid with Amberlite LA-2 is high especially in the case of polar solvents. It can be said that, for example, of these solvents MIBK and 2-octanone are the best. The maximum extractability of glycolic acid is 79.44 % with MIBK and 0.93 mol·L⁻¹ initial concentration of Amberlite LA-2. The maximum extraction efficiencies for solvents used at maximum Amberlite LA-2 concentration are determined as

MIBK > 2-octanone > 1-octanol > toluene > isooctane > cyclohexane

SYMBOLS AND ABBREVIATIONS

C_a = Molar concentration of acid in the aqueous phase, mol·L⁻¹

C_{ao} = Initial molar concentration of acid in the aqueous phase, mol·L⁻¹

$C_{a,org}$ = Molar concentration of acid in the organic phase, mol·L⁻¹

$C_{e,org}$ = Molar concentration of amine in the organic phase, mol·L⁻¹

D = Distribution coefficient

E = Extraction efficiency

HA = Glycolic acid

MIBK = Methyl isobutyl ketone

R2N = Amberlite LA-2

Z = Loading factor

* = Organic phase

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