Extraction of Gluconic Acid with Organic Solutions of Alamine 336

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Gluconic acid is used for a large number of different industrial applications due to some exceptionally useful properties. It is normally obtained in its pure state by extraction processes using amines. The aim of this study is to investigate the extraction of gluconic acid from aqueous solutions by Alamine 336 dissolved in a variety of diluents in a wide range of amine concentrations (0.23 – 1.72 mol L^{-1}). Diluting solvents used in this study are hexane, cyclohexane, toluene, methyl isobutyl ketone (MIBK), and propanol. Using Bizek's approach, two acid : amine *complexes*, (HO) : (R$_3$N) and (HO) : (R$_3$N)$_2$, are assumed to exist in the organic phase in the case of proton – donating diluents, while the complexes (HO) : (R$_3$N) and (HO)$_2$: (R$_3$N)$_3$ are suggested in the case of non-proton-donating diluents. As a result of batch extraction experiments, valuable engineering data, such as distribution coefficients (D), loading factors (Z), and overall extraction constants (K_{11}, K_{12}, K_{23}), are calculated. No similar data were published previously for the investigated systems.

Key words:
Extraction, Gluconic acid, Alamine 336

Introduction

Gluconic acid has a large number of different industrial usages due to some exceptionally useful properties. These include its extremely low toxicity and corrosiveness, and its ability to form water-soluble complexes with different metal ions, and to plastify concrete and retard the setting process.

As shown by *Kertes* and *King*, the extractability of most organic acids by common solvents is very low, and reactive extraction must be considered. High-molecular-mass amines seem to be promising extractants for this purpose. Long-chain aliphatic tertiary amines with seven to nine carbon atoms in each alkyl group are effective extractants for carboxylic acids. Amines are used with suitable organic diluents, and these diluents may modify the extraction power of amine. The stoichiometry of solute : amine complex, loading of amine as well as the third phase formation are influenced by the diluent. The effect of diluent can be understood in terms of ability to solvate to 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.[1]

The effect of diluents is usually presented in a qualitative way as a sequence of diluents corresponding to increasing or decreasing solute distribution. An important study on the influence of diluents on amine extraction of carboxylic acids was carried out by *Tamada* and *King*.[2–3]

The resulting acid : amine complexes are supposed to be stabilised due to the hydrogen bonding with the diluent.[4–5] The structures of acid: amine *complexes* in diluents were determined by *Barrow* and *Yerger*.[6] They propose that the first acid interacts directly with the amine to form an ion pair and the OH of the carboxyl of the second acid forms a hydrogen bonding with the conjugated CO of the carboxylate of the first acid to form a complex.[7]

Several workers have investigated the extraction of different carboxylic acids by amines dissolved in organic solvents.[8–14] However, no data were presented considering the gluconic acid and Alamine 336 / diluent system. In present work the extraction of gluconic acid from aqueous solutions by a tri-n-octylamine extractant in a variety of diluents was examined in a wide range of amine concentrations (0.23 – 1.72 mol L^{-1}).

Batch extraction experiments were performed with Alamine 336 dissolved in the diluents of various types – ketone (MIBK), aromatic (toluene), different alkanes (hexane, cyclohexane), and alcohol (propanol). As a result of batch extraction experiments, distribution coefficients were calculated. In addition, overall extraction constants and loading factors were obtained. Furthermore, they were used to draw conclusions about the stoichiometry of complex formation.

Theoretical

The extraction of gluconic acid (HA) with amine (R_3N) can be described by the set of reactions:

$$i(HA)^R + j(R_3N)^E \rightleftarrows ((H_3A)_i \cdot (R_3N)_j)^E \tag{1}$$
$$i = 1, p; \ j = 1, q$$
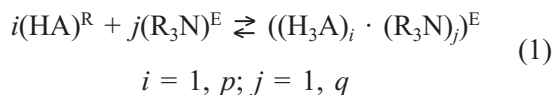
where HA represents the undissociated part of the acid present in the raffinate or aqueous phase (^{R}) and extract (organic) phase species are marked with asterisk (^{E}). As no overloading of amine has been observed i is expected to be lesser than or equal to j for any p and q. Reactions 1 can be characterised by the overall thermodynamic extraction constants:

$$(K_{ij})^E = [(HA)_i \cdot (R_3N)_j]^E / ([HA^i]^R ([R_3N]^j)^E \tag{2}$$

where square brackets denote activities.

Equations 1 could be written in terms of dissociated species – hydrogen ions and acetate anions – as it is used in the literature on amine extraction of acids.[15] Taking into account the dissociation equilibrium, one can derive that both concepts are equivalent, the only difference being in the values of equilibrium constants. Replacing the activities by the products of molalities (mol/kg of solvent) and molal activity coefficients, equation 2 takes the form:

$$(K_{ij})^E = (b_{ij})^E \cdot a_{ij} / (b_a a_a)^{iE} (b_e a_e)^{jE} \tag{3}$$

where water and diluent are understood as solvents for the aqueous or organic phases, respectively.

As presented by Levien, the activity coefficients of undissociated gluconic acid in water can be neglected in the first approximation.[16] Moreover, supposing the ratio of the activity coefficients of organic phase species being constant, it can be incorporated into the equilibrium constants. The conditional overall extraction constants are given by expressions:

$$K_{ij} = (b_{ij})^E / (b_a^i)^R (b_e^j)^E \tag{4}$$
$$i = 1, p; \ j = 1, q$$

Combining equation (4) with the balance equations of acid and amine in the organic phase, the mathematical model of equilibrium is obtained in the form:

$$(b_a)^E = \Sigma \ \Sigma \ i \ K_{ij} \ (b_a^i)^R \ (b_e^j)^E \tag{5}$$
$$i = 1, p; \ j = 1, q$$

where the molality of free amine is given by equation:

$$(b_e)^E + \Sigma \ \Sigma \ j \ K_{ij} \ (b_a^i)^R \ (b_e^j - b_e^0)^E = 0 \tag{6}$$
$$i = 1, p; \ j = 1, q$$

where b_e^0 is the total molality of amine in organic phase. Equation 6 has a unique solution between zero and the aqueous phase molalities of undissociated acid, according to the dissociation equilibrium. As can be seen from the results by *Vanura* and *Kuca*[17] and *Sato* et al.[18], all possible (i, j) combinations for $i = 1, p$ and $j = 1, q$ need not to be taken into account. It could be possible to study the extraction of acid by pure diluent in order to obtain the distribution coefficient, but there is no evidence of the true value of this coefficient in the presence of amine and its complexes with the acid. The changes of K_{ij} with amine concentration can be caused by both the conditional character of this constant and the stoichiometry of complex formation. 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 organic phase.[18] The expression for the loading, Z, can be derived from equations 5 and 6 in the form:

$$Z = (b_a)^E / (b_e^0)^E \rightleftarrows [\Sigma i K_{i1} (b_a^i)^R] / [1 + \Sigma K_{i1} (b_a^i)^R] \tag{7}$$
$$i = 1, p; \ j = 1, q$$

Distribution coefficients for gluconic acid extracted from water into organic phase were determined as:

$$D = (b_a)^E / (b_a)^R \tag{8}$$

Experimental

Alamine 336, a commercial product (Henkel Co.) was used – a mixture of straight-chain tertiary amines with seven to nine carbon atoms per chain containing 2.75 mol kg^{-1} of active amines ($M = 363.3$ g mol^{-1}). Gluconic acid (Merck, > 99 %), hexane (Merck, > 99 %), cyclohexane (Merck, > 99 %), toluene (Carlo Erba, > 99 %), MIBK (Merck, > 99 %) and propanol (Merck, > 99 %) were used without further purification.

The appropriate amounts of gluconic acid were dissolved in water to prepare the solutions with initial concentrations of acid of 2.10 mol L^{-1} ($w = 4.8$ %). The initial organic phases were prepared by the dissolution of amine in the diluents to produce solutions with approximately constant concentrations (1.72 mol L^{-1}, 0.92 mol L^{-1}, 0.69 mol L^{-1}, 0.46 mol L^{-1}, 0.23 mol L^{-1}). Known volumes of aqueous and organic solutions of known concentrations were added to Erlenmayer flasks and equilibrated in a temperature controlled shaker bath at 298.15 K for 2 h. This was found to be a sufficient

time for equilibration, as determined by preliminary testing procedures. Thereafter, the mixture was kept in a bath for another 6–8 h to reach full separation of phases.

The concentration of the acid in the aqueous phase was determined by titration with aqueous sodium hydroxide (relative uncertainty: 1 %).[19] Acid analysis was checked against a material balance. In most cases the deviation between the amount of acid analysed and the amount of acid known by preparing the solutions by weighing did not exceed 3 %. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

Results and discussion

Table 1 presents results of the experimental investigation. The concentrations of amines in solvents were between 0.23 mol L^{-1} and 1.72 mol L^{-1}. The gluconic acid concentration in the initial aqueous phase was 0.25 mol L^{-1} ($w = 4.7$ %).

The equilibrium data on the distribution of gluconic acid between water and Alamine 336 dissolved in hexane, cyclohexane, toluene, methyl isobutyl ketone, and propanol are presented in Table 2.

Figure 1 demonstrates the influence of the organic solvent on gluconic acid distribution between water and Alamine 336. It can be seen that the extraction power of Alamine 336 – diluent mixture

T a b l e 1 – *Experimental results of the extraction of gluconic acid with Alamine 336 / individual diluting solvents*

Diluent	$\dfrac{(c_e)^E}{\text{mol L}^{-1}}$	$\dfrac{(c_a)^R}{\text{mol L}^{-1}}$	$\dfrac{(c_a)^E}{\text{mol L}^{-1}}$	Z	D
hexane	1.72	0.35	1.30	0.75	3.65
	0.92	0.42	1.24	1.35	2.93
	0.69	0.44	1.23	1.78	2.79
	0.46	0.46	1.21	2.63	2.60
	0.23	0.53	1.15	5.02	2.15
cyclohexane	1.72	0.45	1.22	0.71	2.72
	0.92	0.49	1.19	1.29	2.41
	0.69	0.51	1.17	1.70	2.30
	0.46	0.57	1.12	2.44	1.97
	0.23	0.59	1.10	4.81	1.85
toluene	1.72	0.34	1.31	0.76	3.87
	0.92	0.44	1.23	1.34	2.79
	0.69	0.47	1.20	1.74	2.53
	0.46	0.51	1.17	2.55	2.30
	0.23	0.56	1.13	4.93	2.02
MIBK	1.72	0.32	1.33	0.77	4.15
	0.92	0.38	1.27	1.38	3.29
	0.69	0.42	1.24	1.80	2.93
	0.46	0.45	1.21	2.65	2.65
	0.23	0.47	1.20	5.23	2.53
propanol	1.72	0.32	1.32	0.77	4.07
	0.92	0.40	1.26	1.37	3.09
	0.69	0.47	1.20	1.74	2.53
	0.46	0.51	1.17	2.55	2.30
	0.23	0.52	1.16	5.05	2.20

T a b l e 2 – *Overall extraction constants*

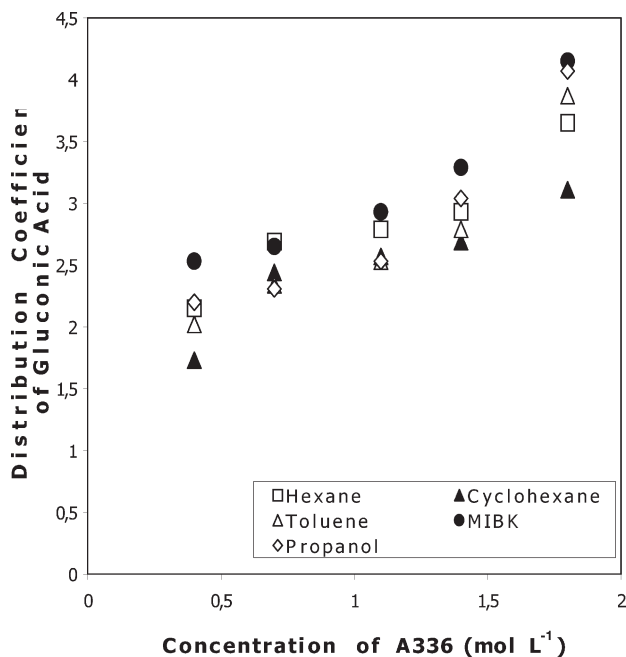| Diluent	$\dfrac{(C_e)^E}{\text{mol L}^{-1}}$	$\dfrac{K_{11}}{\text{L mol}^{-1}}$	$\dfrac{K_{23}}{\text{L}^4 \text{ mol}^{-4}}$	$\dfrac{K_{12}}{\text{L}^2 \text{ mol}^{-2}}$
hexane	1.72	2.12	1.23	–
	0.92	3.19	3.46	–
	0.69	1.92	5.86	–
	0.46	5.66	12.31	–
	0.23	9.38	40.79	–
cyclohexane	1.72	1.58	0.92	–
	0.92	2.62	2.85	–
	0.69	1.59	4.84	–
	0.46	4.28	9.31	–
	0.23	8.08	35.15	–
toluene	1.72	2.25	1.31	–
	0.92	3.03	3.29	–
	0.69	1.74	5.31	–
	0.46	5.01	10.90	–
	0.23	8.79	38.23	–
MIBK	1.72	2.41	1.40	–
	0.92	3.58	3.89	–
	0.69	2.02	6.16	–
	0.46	5.77	12.55	–
	0.23	11.00	47.86	–
propanol	1.72	2.36	–	2.45
	0.92	3.36	–	9..73
	0.69	1.74	–	16..19
	0.46	5.01	–	46.48
	0.23	9.59	–	344.1209

F i g . 1 – *Variation of distribution coefficients with concentration of Alamine 336 in different diluting solvents.*

changes with increasing the initial concentration of Alamine 336 in the organic phase.

According to Table 1 and Figure 1 for Alamine 336 extraction, the following orders were found for the respective.

MIBK > propanol > toluene > hexane > cyclohexane

This fact can be explained by the formation of two or three acid : amine complexes, which are effected by the diluents in different way. In this study, using Bizek's approach three acid : amine *complexes*, $(HO) \cdot (R_3N)$; $(HO) \cdot (R_3N)_2$ and $(HO)_2 \cdot (R_3N)_3$ have been assumed to exist in organic phase.[1]

Solvation of the complex by the diluent is a critical factor in the extraction of acid. The interactions between the *complex* and the diluent can be divided into the general solvation interactions and specific interactions of the diluent with the *complex*. Inert diluents, such as non–polar alkanes hexane and cyclohexane, provide very low solvation of the polar complexes. Thus they do not contribute significantly to the distribution of the acid into the solvent phase, and give low values of distribution coefficients. Aromatic diluent (toluene) gives higher distribution coefficient, which has been rationalized in terms of solvation due to the interaction of the aromatic π–electrons with the complex. MIBK is polar and can promote extraction by providing a good solvating media for the ion pair. However, polarity (or polarizability) alone does not completely account for the solvating ability. Alco-

hol diluent (propanol) gives unusually high equilibrium constants, higher than would be expected from the polarity arguments alone.

In Figure 2, the effect of Alamine 336 concentration on loading is shown. The loading curve is a plot of *Z* vs. amine concentration. Overloading (loading greater than unity) indicates that complexes with more than one acid per amine have been formed. Overloading can be observed with all of the solvents, especially at high Alamine 336 concentrations (Figure 2).
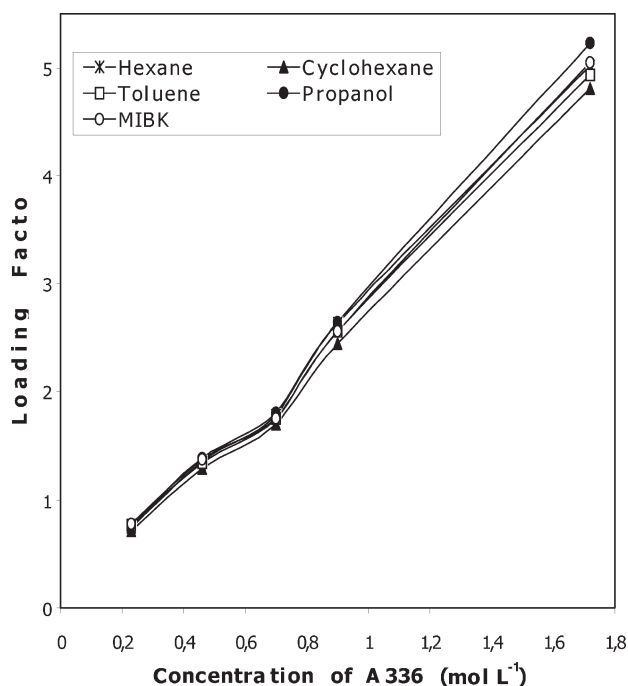

F i g . 2 – *Variation of loading factors with concentration of Alamine 336 in different diluting solvents.*

For systems with only one amine per *complex*, there is no effect of total amine concentration on the loading. If there is more than one amine per *complex*, the loading increases with the increasing amine concentration. Systems that exhibit aggregation, i.e., formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading.

In this work, the loading increases with all the solvents, indicating that complexes include more than one amine molecule.

The values of the overall extraction constants, K_{11}, K_{12}, K_{23}, are calculated using equation (5) and presented in Table 3. In the case of proton–donating diluent (propanol) the extraction process can be described by the reactions:

$$(HA)^R + (R_3N)^E \rightleftarrows ((HA) \cdot (R_3N))^E \qquad K_{11} \qquad (9)$$

$$(HA)^R + 2(R_3N)^E \rightleftarrows ((HA) \cdot (R_3N)_2)^E \qquad K_{12} \qquad (10)$$

The resulting acid : amine complexes are supposed to be stabilized due to hydrogen bonding with the diluent. Only the values of K_{11} and K_{12} for propanol presented in Table 3.

In the case of non–proton donating diluents (hexane, cyclohexane, toluene, MIBK) the process can be described by the reactions:

$$2(HA)^R + 3(R_3N)^E \rightleftharpoons ((HA)_2 \cdot (R_3N)_3)^E \quad K_{23} \quad (11)$$

Only the values of K_{11} and K_{23} for non–proton donating diluents presented in Table 3. Reaction (11) can be understood as a result of three consecutive reactions – (9), (10) and;

$$(HA \cdot (R_3N)_3)^E + ((HA) \cdot (R_3N)_2)^E \rightleftharpoons$$
$$\rightleftharpoons ((HA)_2 \cdot (R_3N)_5)^E \qquad K_A \qquad (12)$$
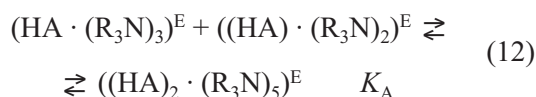
The aggregation of highly polar primary acid: amine complexes according to reaction (12) is supposed to proceed almost completely. As the $((HA) \times (R_3N)_2)^E$ *complex* is the minor component in the studied range of concentrations, its presence is not indicated. The extraction constant K_{23} is, in fact the product $K_{11} \times K_{12} \times K_A$.

Conclusion

This work examined the effect of diluents on the distribution of gluconic acid between water and Alamine 336. The diluents used were hexane, cyclohexane, toluene, methyl isobutyl ketone (MIBK), and propanol. The extraction of gluconic acid with 5 various solutions of amines increases the amine concentration with increasing amine. Among the diluents used in this study the largest distribution coefficients were obtained with MIBK.

Symbols and abbreviations

A336– Alamine 336

a_a – Molal activity coefficient of acid
a_e – Molal activity coefficient of amine
a_{ij} – Molal activity coefficient of *complex*
$(c_a)^R$ – Concentration of acid in the aqueous phase, mol L^{-1}
$(c_a)^E$ – Concentration of acid in the organic phase, mol L^{-1}
$(c_e)^E$ – Concentration of amine in the organic phase, mol L^{-1}
D – Distribution coefficient

HA   – Gluconic acid
K_A – Aggregation constant
K_{ij} – Overall thermodynamic extraction constants
$(b_a)^R$ – Molality of acid in the aqueous phase, mol kg^{-1}
$(b_a)^E$ – Molality of acid in the organic phase, mol kg^{-1}
$(b_e)^R$ – Molality of amine in the aqueous phase, mol kg^{-1}
$(b_{eo})^E$– Total molality of amine in organic phase, mol kg^{-1}
MIBK – Methyl isobutyl ketone
p – Number of acid molecules
q – Number of amine molecules
R_3N – Tertiary amine
w – Mass fraction
Z – Loading factor
$(\ )^E$ – Organic phase
$(\ )^R$ – Aqueous phase

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