Asian Journal of Chemistry Vol. 14, Nos. 3–4 (2002), 1711–1718

Liquid-Liquid Equilibria of Gluconic Acid between Water and Trin-n-Octylamine in various Diluents

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Gluconic acid, $C_6H_{12}O_7$, is used for a large number of different industrial applications due to some exceptionally useful properties. However, data about gluconic acid and tri-n-octylamine/diluent system are not available in literature. The aim of this study is to investigate the extraction of gluconic acid from aqueous solutions by tri-n-octylamine dissolved in a variety of diluents a in wide range of amine concentrations (0.23–1.72 mol/L). Extractin equilibria of gluconic acid in the system solution of tri-n-octylamine in mixtures with 5 various solvents at temperature 298.15 K have been measured. Diluting solvents used in this study are hexane, cyclohexane, toluene, methyl isobutyl ketone (MIBK) and propanol. Using Bizek approach three acid : amine complexes, (Acid)·(Amine); Acid)·$(Amine)_2$ and $(Acid)_2$· $(Amine)_3$ have been assumed to exist in organic phase. As a result of batch extraction experiments distribution coefficients, loading factors and overall extraction constants were calculated.

Key Words: Extraction, Gluconic acid, Tri-n-octylamine.

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 in different metal ions and to plastify concrete and retard the setting process.

As shown by Kertes and King[1], the extractibility of most organic acids by current solvents is very low, and reactive extraction must be considered. High molecular amines seem to be promising extractants for this purpose.[2]

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.[2]

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.[3,4]

The resulting acid : amine complexes are supposed to be stabilised due to the hydrogen bonding with the diluent[5,6]. The structures of acid amine complexes in diluents were determined by Barrow and Yerger[7]. They proposed 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[8,9].

Several workers[10–17] have investigated the extraction of different carboxylic acids by amines dissolved in organic solvents. However, data about gluconic acid and tri-n-octylamine/diluent system has not been found in literature. In the 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 concentration (0.23–1.72 mol/L).

Batch extraction experiments were performed with tri-n-octylamine dissolved in the diluents of various types—methyl isobutyl ketone (MIBK), aromatic (toluene), different alkanes (hexane, cyclohexane) and alcohol (propanol). As a result of batch extraction experiments distribution coefficients were calculated. In addition to distribution coefficients, overall extraction constants and variation of loading factors were obtained. Furthermore, they were used to obtain 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

$$iHA+j{}^{*}R_3N = {}^{*}(H_3A)_i \cdot (R_3N)_j \qquad i = 1, p;\ j = 1, q \tag{1}$$

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 amine has been observed i is expected to be lesser than or equal to j for any value of p and q. Reactions (1) can be characterised by the overall thermodynamic extraction constants.

$${}^{*}K_{ij} = {}^{*}[(H_3A)_i \cdot (R_3N)_j] /[HA]^{i\,*} [R_3N]^j \tag{2}$$

where square brackets denote activities.

Equation (1) could be written in terms of dissociated species hydrogen ions—and acetate anions-as it is used in the literature[18] on amine extraction of acids. 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, eq. (2) take the form.

$${}^{*}K_{ij} = {}^{*}m_{ij} \cdot a_{ij}/{}^{*}(m_a a_a)^{i*}(m_a a_e)^j \tag{3}$$

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

As presented by Levien[19], the activity coefficients of nondissociated gluconic acid in water can be neglected in the first approximation. Moreover, supposing the ratio of the activity coefficients of organic phase species to be constant, it can be incorporated into the equilibrium constants. The conditioned overall extraction constants are given by the expression

$$K_{ij} = {}^*m_{ij} / m_a^{i\,*}m_e^j \qquad i = 1, p, j = 1, q \qquad (4)$$

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

$$^*m_a = \Sigma\,\Sigma\, iK_{ij}\, m_a^{i\,*} \qquad i = 1, p;\ j = 1, q \qquad (5)$$

where the molality of free amine is given by the equation

$$^*m_a + \Sigma\,\Sigma\, jK_{ij}m_a^{i*}m_e^j - m_e^0 = 0, \qquad i = 1, p;\ j = 1, q \qquad (6)$$

where m_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 nondissociated acid according to the dissociation equilibrium. As can be seen from the results by Vanura and Kuca[20] and Sato *et al.*[21], all possible (i, j) combinations for i = 1, p and j = 1, q need not 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 real value of this coefficient in the presence of amine and it complexes with the acid. The changes of acids with amine concentration can be caused by both the conditioned 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[1]. The expression for the loading, Z, can be derived from eqs. (5) and (6) in the form

$$Z = {}^*m_a / {}^*m_e^0 = \Sigma\, i\, K_{i1}m_a^i / (1 + \Sigma K_{i1}\, m_a^i), \qquad i = 1, p;\ j = 1, q \qquad (7)$$

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

$$D = {}^*m_a / m_a \qquad (8)$$

EXPERIMENTAL

Gluconic acid (Merck, > 99%), tri-n-octylamine (Merck, > 99%, d = 0.812 g/cm^3, M = 353.7), 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 concentration of acid 2.10 mol/L (= 4.8% w/w). 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, 0.92 mol/L, 0.69 mol/L, 0.46 mol/L, 0.23 mol/L). Known volumes of aqueous and organic solutions of known concentration were added to Erlenmayer flasks and equilibrated in a temperature controlled shaker bath at 298.15 K for 2 h, which preliminary tests demonstrated to be a sufficient time for equilibration. 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[22] (relative uncertainty: 1%). Acid analysis was checked against a material balance. In most cases the deviation between the amount of acid analyzed 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 and 1.72 mol/L. The gluconic acid concentration in the initial aqueous phase was 0.25 mol/L (= 4.7% w/w).

The equilibrium data on the distribution of gluconic acid between water and tri-n-octylamine dissolved in hexane, cyclohexane, toluene, methyl isobutyl ketone, and propanol are presented in Table-1.

TABLE-1
EXPERIMENTAL RESULTS OF THE EXTRACTION OF GLUCONIC ACID WITH TRI-N-OCTYLAMINE/INDIVIDUAL DILUTING SOLVENTS

Diluent	$C_{e\,org}$ (mol/ L)	C_a (mol/ L)	$C_{a\,org}$ (mol/ L)	Z	D
Hexane	1.27	0.40	1.26	0.74	3.12
	0.92	0.42	1.24	1.35	2.93
	0.69	0.51	1.17	1.71	2.30
	0.46	0.54	1.15	2.50	2.11
	0.23	0.59	1.10	4.81	1.86
Cyclohexane	1.72	0.45	1.21	0.71	2.70
	0.92	0.46	1.21	1.20	2.69
	0.69	0.47	1.20	1.75	2.56
	0.46	0.59	1.10	2.41	2.45
	0.23	0.62	1.08	4.72	1.73
Toluene	1.72	0.40	1.27	0.74	3.15
	0.92	0.40	1.26	1.37	3.12
	0.69	0.41	1.26	1.82	3.05
	0.46	0.45	1.23	2.67	2.75
	0.23	0.51	1.18	5.11	2.30
MIBK	1.72	0.35	1.30	0.76	3.71
	0.92	0.35	1.30	1.42	3.69
	0.69	0.40	1.26	1.82	3.09
	0.46	0.44	1.23	2.68	2.79
	0.23	0.51	1.17	5.11	2.30
Propanol	1.72	0.39	1.27	0.74	3.32
	0.92	0.40	1.27	1.31	3.16
	0.69	0.73	0.99	1.44	1.36
	0.46	0.87	0.87	1.91	1.01
	0..23	0.88	0.86	3.77	0.98

Fig. 1 demonstrates the influence of the organic solvent on gluconic acid distribution between water and tri-n-octylamine. It can be seen that the extraction power of tri-n-octylamine-diluent mixture changes with increasing initial concentration of tri-n-octylamine in the organic phase.

According to Table-1 and Fig. 1 for tri-n-octylamine extraction the following order was found for the respective diluents:

MIBK > propanol > toluene > cyclohexane > hexane

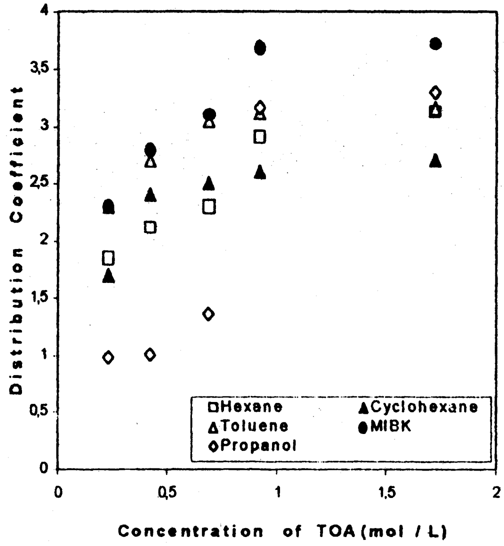

Fig. 1 Variation of distribution coefficients with concentration of tri-n-octylamine in different diluting solvents.

This fact can be explained by the formation of two or three acid : amine complexes, which are affected by the diluents in different ways. In this study, using Bizek approach three acid : amine complexes, (Acid)·(Amine); (Acid)·(Amine)$_2$ and (Acid)$_2$·(Amine)$_3$ have been assumed to exist in organic phase[2].

Solvation of the complex by the diluent is a critical factor in the extraction of acid. The interactions between the complex and diluent can be divided into general solvation and specific interactions of the diluent with the complex. Inert diluents—hexane, cyclohexane—give a very low distribution of the acid into the solvent phase. Alkanes being nonpolar provide very low solvation of the polar complexes. Aromatic diluent (toluene) gives higher distribution, which has been rationalized as solvation due to interaction of the aromatic π electrons with the complex. MIBK is polar and can promote extraction by providing a good solvating medium for the ion pair. However, polarity (or polarizability) alone does not completely account for solvating ability. Alcohol diluent (propanol) gives unusually high equilibrium constants, higher than would be expected from polarity arguments alone.

The effect of tri-n-octylamine concentration on loading is shown in Fig. 2. 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. With all of the solvents overloading can be observed, especially at low tri-n-octylamine concentrations.

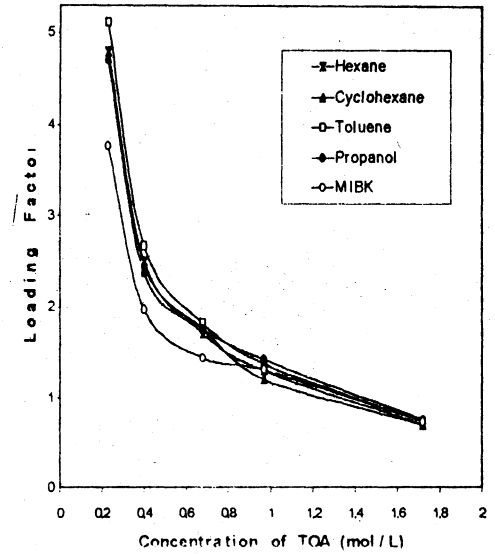

Fig. 2. Variation of loading factors with concentration of tri-n-octylamine (TOA) in different diluting solvents.

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, loading increases with increasing amine concentration. Systems that exhibit aggregation and formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading. MIBK (Fig. 2) exhibits abrupt increase at 1.0–1.2 mol/L amine concentration indicating that complexes include large numbers of acid and amine molecules.

In this work, with all of the solvents loading decreases, indicating that complexes include the diluent specifically.

The values of the overall extraction constants, K_{11}, K_{12}, K_{23} are calculated (using eq. (5)) and presented in Table-2. In the case of proton-donating diluent (propanol) the extraction process can be described by the reactions;

$$HA + {}^*R_3N = {}^*(HA)\cdot(R_3N) \qquad K_{11} \qquad (9)$$

$$HA + 2{}^*R_3N = {}^*(HA)\cdot(R_3N)_3 \qquad K_{12} \qquad (10)$$

The resulting acid : amine complexes are supposed to be stabilized due to hydrogen bonding with the diluent.

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

$$2HA + 3{}^*R_3N = {}^*(HA)_2\cdot(R_3N)_3 \qquad K_{23} \qquad (11)$$

Reactions (11) can be understood as a result of three consecutive reactions—(9), (10) and

$$*HA.(R_3N)_3 + *(HA).(R_3N)_2 = *(HA)_2{\cdot}(R_3N)_3 \qquad K_A \qquad (12)$$

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

TABLE-2
OVERALL EXTRACTION CONSTANTS

Diluent	$C_{e\,org}$ (mol/ L)	K_{11} (L / Lmol)	K_{23} (L^4/ mol^4)	K_{12} (L^2/ mol^2)
Hexane	1.72	1.81	1,05	—
	0.92	3.19	3,46	—
	0.69	1.59	4,84	—
	0.46	4.59	9,97	—
	0.23	8.08	35,15	—
Cyclohexane	1.72	1.80	1,05	—
	0.92	2.92	3,18	—
	0.69	1.77	5,39	—
	0.46	5.32	11,57	—
	0.23	7.54	32,79	—
Toluene	1.72	1.83	1,06	—
	0.92	3.39	3,69	—
	0.69	2.11	6,42	—
	0.46	5.97	12,99	—
	0.23	9.99	43,44	—
MIBK	1.72	2.15	1,25	—
	0.92	4.01	4,36	—
	0.69	2.13	6,49	—
	0.46	6.06	13,18	—
	0.23	10.03	43,62	—
Propanol	1.72	1.92	—	1.68
	0.92	3.25	—	8.62
	0.69	0.93	—	5.65
	0.46	2.19	—	11.90
	0.23	4.26	—	91.13

Symbols and Abbreviations

a_a = Molal activity coefficient of acid
a_e = Molal activity coefficient of amine
a_{ij} = Molal activity coefficient of complex

C_a = Molar concentration of acid in the aqueous phase, mol/L
$C_{e, org}$ = Molar concentration of acid in the organic phase, mol / L
$C_{a, org}$ = Molar concentration of amine in the organic phase, mol/ L
D = Distribution coefficient
HA = Gluconic acid; KA = Aggregation constant
Kij = Overall thermodynamic extraction constants
m_a = Molality of acid in the aqueous phase, mol/kg of solvent
$^*m_a$ = Molality of acid in the organic phase, mol/kg of solvent
m_e = Molality of amine in the aqueous phase, mol/kg of solvent
$^*m_e^0$ = Total molality of amine in organic phase, mol/kg of solvent
MIBK = Methyl isobutyl ketone
m_{ij} = Molality of amine in the aqueous phase
p = Number of acid molecules
q = Number of acid molecules
R_3N = Tertiary amine; Z = Loading factorj* = Organic phase
[ ] = Activities

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(*Received:* 5 April 2002; *Accepted:* 3 June 2002) AJC–2753