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Influence of the Nature of Solvent on Extraction of Acetic Acid with Alamine 336

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Studies have been made on the extraction of acetic acid by Alamine 336, a mixture of aliphatic tertiary amines, dissolved in various diluents. Diluents were chosen from different chemical classes—electron donating, electron accepting, polar and nonpolar—so as to examine the effects of diluent-complex interactions. These interactions were found to affect both the stoichiometry of reaction and the magnitudes of the corresponding equilibrium constants. As a result of batch extraction experiments distribution coefficients, loading factors and overall extraction constants were calculated. The results were interpreted by "acid-amine complex formation" approach, in which the stoichiometries of acid-amine complexes and corresponding equilibrium constants have been studied.

Key Words: Extraction, Acetic acid, Alamine 336

INTRODUCTION

Amine extraction has been found to be a prospective method of separation of carboxylic or hydroxycarboxylic acids from aqueous solutions. A number of papers have been published on this subject up to now. Nevertheless, many interesting problems have been left for future work, *e.g.*, influence of amine concentration in a wide range of concentrations, effect of diluent at high concentrations, and interpreting the effect of high amine concentrations and complex formation.

Long-chain, aliphatic tertiary amines with seven to nine carbon atoms in each alkyl group are very effective extractants for carboxylic acids and their derivatives. For physical reasons they must be applied in solutions with suitable organic diluents[1–3]. The diluents, however, may modify the extraction power of the amine for a particular acid.

The resulting acid : amine complexes are supposed to be stabilised due to the hydrogen bonding with the diluent[4, 5]. The structure of acid amine complexes in diluents were determined by Yerger and Barrow[6, 7]. They propsed 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.

Several scientists examined the extraction of acetic acid by amines dissolved in organic solvents[8–14]. Vieux[13] studied the extraction of acetic acid with triisooctylamine/xylene (0.10 mol/L). Kawano *et al.*[11] have found the extractability of acetic acid with Amberlite LA-2 (0.44–0.51 mol/L) and trioctylamine (0.05–0.20 mol/L) in various solvents. In these works usually the concentration range of amines was taken narrow. The work done on acetic acid extraction systems studied by previous workers is given in Table-1.

TABLE-1
A SUMMARY OF ACETIC ACID EXTRACTION SYSTEMS STUDIED BY PREVIOUS WORKERS

Extractant (conc, mol/L)	Diluent	Workers
Adogen 283 (0.429)	2-Heptanone	Ricker,[8] Ricker *et al.*[9]
Alamine 336 (0.02–0.10)	2-Ethyl-1-hexanol	Ricker,[8] Ricker *et al.*[9]
Alamine 336 (0.68)	Chloroform	Spala[10]
Tridecylamine (0.186–0.745)	Benzene	Chaikorski *et al.*[12]
Triisooctylamine (0.10)	Benzene	Vieux[12]
Triisoocylamine (0.10)	Xylene	Vieux[13]
Alamine 336 (0.1–0.58)	Chloroform-heptane	Tamada *et al.*[2, 3]
Tridecylamine (0.372–1.49)	Carbon tetrachloride	Chaikorski *et al.*[12]
Trilaurylamine (0.08–0.32)	*o*-Xylene	Högfelt and Fredlund[14]
Trilaurylamine (0.08–0.32)	Heptane	Högfelt and Fredlund[14]

In the present work the extraction of acetic acid from aqueous solutions by Alamine 336 in a variety of diluents was examined in a wide range of amine concentration (0.23–1.72 mol/L) and no data could be found about systems under consideration in literature.

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 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 acetic acid (HA) with amine (R_3N) can be described by the set of reactions (1), (2) and (3). In the case of proton-donating diluent the extraction process can be described by the reactions;

$$HA + {}^{*}R_3N = {}^{*}(HA)\cdot(R_3N) \qquad \beta_{11} \qquad (1)$$

$$HA + 2^{*}R_3N = {}^{*}(HA)\cdot(R_3N)_2 \qquad \beta_{12} \qquad (2)$$

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;

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

where HA represents the nondissociated part of the acid present in the aqueous phase and organic phase species are marked with (*). Reactions (1), (2) and (3) can be characterised by the overall thermodynamic extraction constants,

$${}^{*}\beta_{ij} = {}^{*}[(HA)_i\cdot(R_3N)_j]/[HA]^{i}\,{}^{*}[R_3N]^{j} \qquad i = 1, p;\quad j = 1, q \qquad (4)$$

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 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 (4) take the form:

$${}^{*}\beta_{ij} = {}^{*}m_{ij} \cdot a_{ij}/{}^{*}(m_a a_a)^{i}\,{}^{*}(m_e a_e)^{j}. \qquad (5)$$

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

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

$$\beta_{ij} = {}^{*}m_{ij}/m_a^{i}\,{}^{*}m_e^{j} \qquad i = 1, p;\quad j = 1, q \qquad (6)$$

Combining equation (6) with the balance equations of acid and amine in the organic phase, the mathematical model of equilibrium is obtained in the form:

$${}^{*}m_a = \Sigma\,\Sigma\, i\beta_{ij} m_a^{i}\,{}^{*}m_e^{j} \qquad i = 1, p;\quad j = 1, q \qquad (7)$$

where the molality of free amine is given by equation:

$${}^{*}m_e + \Sigma\,\Sigma\, j\beta_{ij} m_a^{i}\,{}^{*}m_e^{j} - m_e^{0} = 0 \qquad i = 1, p;\quad j = 1, q. \qquad (8)$$

Where m_e^0 is the total molality of amine in organic phase. Equation (8) has a unique solution for aqueous phase molalities of nondissociated acid. As can be seen from the results by Vanura and Kuca,[17] all possible (i, j) combinations for $i = 1, p$ and $j = 1, q$ need not be taken into account[17, 18]. 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 in the 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[19]. The expression for the loading, Z, can be derived from equations (7) and (8) in the form:

$$Z = {}^*m_a / {}^*m_e^0 = \Sigma\, i\beta_{i1} m_a^i / (1 + \Sigma\, \beta_{i1} m_a^i) \qquad i = 1, p; \quad j = 1, q. \tag{9}$$

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

$$D = {}^*m_a / m_a \tag{10}$$

EXPERIMENTAL

As extractant a commercial product was used. Alamine 336 is a mixture of straight-chain tertiary amines with seven to nine carbon atoms Per chain containing 2.75 mol/kg of active amines (392 g/mol). Acetic acid (Merck, > 90%), as well as other reagents used, were of analytical grade purity.

Acetic acid, a concentrated aqueous solution, was diluted to 2.10 mol/L (= 11.35% w/w). The initial organic phases were prepared by the dissolution 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). The measurements of equilibria were performed by shaking equal volumes of initial organic and aqueous phases in a thermostated bath for 2 h at 298.15 K. Thereafter the mixture was kept in a bath for another 2–6 h to reach full separation of phases. In each experiment the equilibrium acid concentrations were determined independently in both phases The concentration of the acid in the aqueous phase was determined by titration with aqueous sodium hydroxide (relative uncertainty: 1 per cent)[20]. 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 per cent. The solubilities of amine salts and diluents in the aqueous phase were negligible in the range of variables investigated.

RESULTS AND DISCUSSION

Table-2 presents results of the experimental investigation. The concentrations of amines in solvents were between 0.23 mol/L and 1.72 mol/L. The acetic acid concentration in the initial aqueous phase was 2.10 mol/L (= 11.35 per cent w/w).

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

TABLE-2
EXPERIMENTAL RESULTS OF THE EXTRACTION OF ACETIC ACID WITH ALAMINE 336/INDIVIDUAL DILUTING SOLVENTS

Diluent	$C_{e\,org}$ (mol/L)	C_a (mol/L)	$C_{a\,org}$ (mol/L)	Z	D
Hexane	1.72	0.89	0.85	0.51	1.04
	0.97	0.88	0.86	0.95	1.01
	0.69	0.79	0.96	1.15	0.82
	0.46	0.69	1.09	1.50	0.63
	0.23	0.46	1.36	2.03	0.34
cyclohexane	1.72	0.83	0.91	0.52	1.09
	0.97	0.93	0.82	0.89	0.88
	0.69	0.95	0.80	1.16	0.84
	0.46	1.08	0.69	1.51	0.64
	0.23	1.32	0.50	2.19	0.38
Toluene	1.72	0.55	1.13	0.66	2.03
	0.97	0.57	1.12	1.22	1.95
	0.69	0.65	1.05	1.53	1.61
	0.46	0.90	0.84	1.84	0.93
	0.23	1.10	0.68	2.95	0.61
MIBK	1.72	0.34	1.31	0.76	3.80
	0.97	0.38	1.27	1.39	3.31
	0.69	0.43	1.24	1.79	2.87
	0.46	0.48	1.19	2.59	2.44
	0.23	0.86	0.88	3.84	1.02
propanol	1.72	0.44	1.22	0.71	2.73
	0.97	0.53	1.15	1.25	2.17
	0.69	0.60	1.10	1.59	1.82
	0.46	0.68	1.03	2.25	1.52
	0.23	0.85	0.89	3.89	1.05

Fig. 1 demonstrates the influence of the organic solvent on acetic acid distribution between water and Alamine 336. It can be seen that the extraction power of Alamine 336-diluent mixture changes with increasing initial concentration of Alamine 336 in the organic phase.

According to Table-2 and Fig. 1 for Alamine 336 extraction the order was as follows:

MIBK > propanol > toluene > cyclohexane > hexane.

This fact can be explained by the formation of two or three acid : amine complexes, which are effected by the diluents in different ways. In this study, using Bizek approach[1] three acid : amine complexes, (Acid)·(Amine); (Acid)·$(Amine)_2$ and $(Acid)_2$·$(Amine)_3$ have been assumed to exist in organic phase.

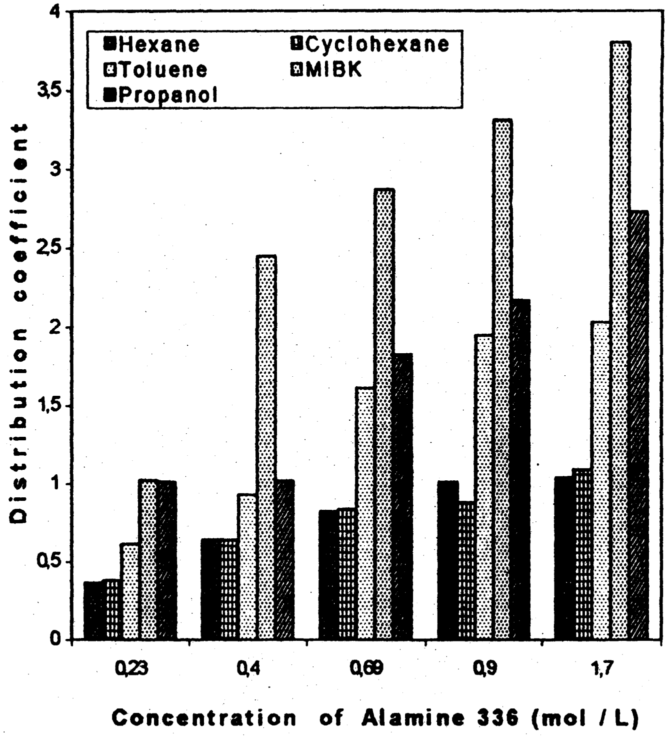

Fig. 1. Variation of distribution coefficients with concentration of Alamine 336 in different diluting solvents.

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 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.

In Fig. 2, the effect of Alamine 336 concentration on loading is shown. The loading curve is a plot of Z *vs.* amine concentration. Overloading (loading > 1), indicates that complexes with more than one acid per amine have been formed. With all of the solvents overloading can be observed, especially at high Alamine 336 concentrations (Fig. 2).

Systems that include the diluent specifically in the complex stoichiometry show decreased loading with increase in amine concentration. None of the

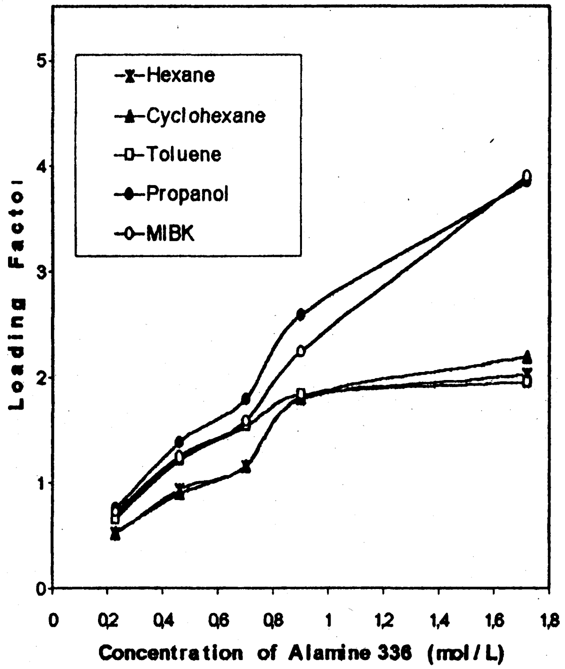

Fig. 2. Variation of loading factors with concentration of alamine 336 in different diluting solvents.

solvents at Alamine 336 extraction loading decreases, thereby indicating that complexes include the diluent specifically (Fig. 2). Systems that exhibit aggregation, formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading. All of the solvents exhibit abrupt increase at 0.6–1.0 mol/L amine concentration, thereby indicating that complexes include large number of acid and amine molecules (Fig. 2).

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 increase in amine concentration.

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

The values of the overall extraction constants, β_{11}, β_{12}, and β_{23}, are calculated (using eq. 5) and presented in Table-3. The large differences among β values for the acetic acid in different diluents indicate that solvation of the complex by the diluent is a critical factor in the extraction of the acid. In this study, using Bizek approach[1] three acid : amine complexes, (Acid)·(Amine); (Acid)·$(\text{Amine})_2$ and $(\text{Acid})_2$·$(\text{Amine})_3$ have been assumed to exist in organic phase. In the case of proton-donating diluent (propanol) (Acid)·(Amine) and $(\text{Acid})_2$·$(\text{Amine})_3$ have been assumed to exist. In the case of non-proton donating diluents (hexane, cyclohexane, toluene, MIBK), (Acid)·(Amine) and $(\text{Acid})_1$·$(\text{Amine})_2$ have been assumed to exist.

The values of the overall extraction constants at 298.15 K are summarized in Table-3.

TABLE-3
OVERALL EXTRACTION CONSTANTS

Diluent	$C_{e, org}$ (mol/L)	β_{11}	β_{23}	β_{12}
Hexane	1.72	0.60	0.35	–
	0.97	1.10	1.19	–
	0.69	0.56	1.73	–
	0.46	1.38	3.00	–
	0.23	1.49	6.49	–
Cyclohexane	1.72	0.63	0.37	–
	0.97	0.95	1.04	–
	0.69	0.58	1.76	–
	0.46	1.39	3.03	–
	0.23	1.65	7.20	–
Toluene	1.72	1.18	0.68	–
	0.97	2.12	2.30	–
	0.69	1.11	3.39	–
	0.46	2.02	4.40	–
	0.23	2.66	11.60	–
MIBK	1.72	2.21	1.28	–
	0.97	3.60	3.91	–
	0.69	1.98	6.04	–
	0.46	5.32	11.57	–
	0.23	4.44	19.33	–
Propanol	1.72	1.59	–	1.19
	0.97	2.36	–	5.25
	0.69	1.26	–	9.25
	0.46	3.31	–	23.01
	0.23	4.57	–	101.77

Abbreviations and Notations

a_a = Molal activity coefficient of acid
a_e = Molal activity coefficient of amine
a_{ij} = Molal activity coefficient of complex
β_{ij} = Overall thermodynamic extraction constants
C_a = Molar concentration of acid in the aqueous phase, mol/L
$C_{a, org}$ = Molar concentration of acid in the organic phase, mol/L
$C_{e, org}$ = Molar concentration of amine in the organic phase, mol/L

D = Distribution coefficient

HA = Acetic acid

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 amine molecules

R_3N = Tertiary amine

Z = Loading factor

* = Organic phase

[ ] = Activities

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