Liquid + liquid equilibria of the (water + tartaric acid + Alamine 336 + organic solvents) at 298.15 K

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Abstract

The extraction of tartaric acid with Alamine 336 which is a mixture of tertiary amines (C_8–C_{10}) dissolved in five single solvents (cyclohexane, hexane, toluene, methyl isobutyl ketone, butan-1-ol) and three binary solvent mixtures (MIBK + toluene (50%, v/v), MIBK + hexane (50%, v/v), hexane + toluene (50%, v/v)) were investigated. All measurements were carried out at 298.15 K. The extent to which the organic phase may be loaded with tartaric acid is expressed as a loading ratio, Z, extraction efficiency E and overall particular distribution coefficients D were calculated. Equilibrium complexation constants for (acid:amine) (1:1), (1:2) and (2:3) have been determined. The maximum removal of tartaric acid is mass 97.983% with methyl isobutyl ketone with a 1.736 mol dm^{-3} initial concentration of Alamine 336.
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Keywords: Reactive extraction; LLE; Tartaric acid; Alamine 336

1. Introduction

Tartaric acid is a white crystalline organic acid. It occurs naturally in many plants, particularly grapes and tamarind, and is one of the main acids found in wine. It is added to other foods to give a sour taste, and is used as an antioxidant. Salts of tartaric acid are known as tartrates. It is a dihydroxy derivative of dicarboxylic acid. Naturally occurring tartaric acid is chiral, meaning that it has molecules that are nonsuperimposable on their mirror-images. It is a useful raw material in organic chemistry for the synthesis of other chiral molecules.

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. 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 stabilized due to the hydrogen bonding with the diluent [5,6]. The structure 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 have investigated the extraction of different carboxylic acids by amines dissolved in organic solvent [10–20]. Besides İnci and Uslu have studied the extraction of citric and glycolic acids with trioctyl methyl ammonium chloride as a extractant and they have found low distribution coefficients [21,22].

The aim of this study was to explore the reactive extraction of tartaric acid from aqueous solutions using tertiary amine

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consisting of Alamine 336 dissolved in several solvents and solvent mixtures. The extraction of tartaric acid from aqueous solutions by a Alamine 336 extractant in a variety of diluents was examined in a wide range of amine concentration (0.422–$1.736 \, \mathrm{mol \, dm^{-3}}$). 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 (butan-1-ol). Distribution coefficients were calculated as a result of batch extraction experiments. In addition to distribution coefficients, overall extraction constants and variation of loading factors obtained.

2. Theoretical

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

$$i\mathrm{HA} + j^*\mathrm{R_3N} = {}^*(\mathrm{HA})_i \cdot (\mathrm{R_3N})_j, \quad i = 1, p, \quad j = 1, q \quad (1)$$
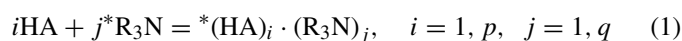
where HA represents the nondissociated part of the acid present in the aqueous phase and organic phase species are marked with (*). As no overloading of amine has been observed i is expected to be lesser than or equal to j for any p and q. Reaction (1) can be characterised by the overall thermodynamic extraction constants:

$$K_{ij} = \frac{{}^*[(\mathrm{HA})_i \cdot (\mathrm{R_3N})_j]}{[\mathrm{HA}]^i {}^*[\mathrm{R_3N}]^j} \quad (2)$$

where square brackets denote activities.

Eq. (1) could be written in terms of dissociated species – hydrogen ions and acid radical anions – as it is used in the literature 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 [2]. Replacing the activities by the products of molalities ($\mathrm{mol \, kg^{-1}}$ of solvent) and molal activity coefficients Eq. (2) take the form

$$K_{ij} = \frac{{}^*m_{ij} \cdot \gamma_{ij}}{(m_a \cdot \gamma_a)^i {}^*(m_e \cdot \gamma_e)^j} \quad (3)$$

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

As presented by Levien [23], the activity coefficients of nondissociated carboxylic 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 expressions

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

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

$$^*m_a = \sum \sum i K_{ij} m_a^i {}^*m_e^j, \quad i = 1, p, \quad j = 1, q \quad (5)$$

where the molality of free amine is given by equation

$$^*m_e + \sum \sum j K_{ij} m_a^i {}^*m_e^j - {}^*m_e^o = 0, \quad i = 1, p, \quad j = 1, q \quad (6)$$

where m_e^o is the total molality of amine in organic phase. As can be seen from the results by Vanura and Kuca [11] and Sato et al. [12] 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 real value of this coefficient in the presence of amine and its complexes with the acid. The change of distribution coefficients 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

$$Z = \frac{{}^*m_a}{{}^*m_e^o} = \frac{\sum i K_{i1} m_a^i}{1 + \sum K_{i1} m_a^i}, \quad i = 1, p \quad (7)$$

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

$$D = \frac{C_{\mathrm{org \, tar}}}{C_{\mathrm{aq \, tar}}} \quad (8)$$

Extraction efficiency is defined as follows:

$$E = \left(1 - \left(\frac{C_{\mathrm{aq \, tar}}}{C_{\mathrm{I \, tar}}}\right)\right) \times 100 \quad (9)$$

where $C_{\mathrm{I \, tar}}$ is the initial concentration of tartaric acid in the aqueous phase, $C_{\mathrm{org \, tar}}$ and $C_{\mathrm{aq \, tar}}$ are the concentration of tartaric acid in the organic and aqueous phase after reactive extraction, respectively.

3. Experimental

Alamine 336, a commercial product ((Henkel Corp., USA) >99%,), was used—a mixture of straight-chain tertiary amines with eight to ten carbon atoms per chain containing $2.75 \, \mathrm{mol \, kg^{-1}}$ of active amines ($M = 363.3 \, \mathrm{g \, mol^{-1}}$). Other used chemicals in this study, L (+) tartaric acid (Merck >99%), hexane (Merck >99%), cyclohexane (Merck >99%), toluene (Merck >99%), MIBK (Merck >99%), and butan-1-ol (Merck >99%) were used without further purification.

The known amounts of tartaric acid was dissolved in water to prepare the solutions with initial concentrations of acid $0.347 \, \mathrm{mol \, dm^{-3}}$ because in the practical case of acid recovery from fermentation broths. The initial organic phases were prepared by the dissolution amine (Alamine 336) in the diluents to produce solutions with approximately constant concentrations (1.736, 1.449, 1.049, 0.736, $0.422 \, \mathrm{mol \, dm^{-3}}$). Known volumes of aqueous and organic solutions of known concentration were added to Erlenmayer flasks and equilibrated in a shaker bath at $298.15 \, \mathrm{K}$ 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 (relative uncertainty: 1%). Acid analysis was checked against a material balance [3,4]. The volume of phases changing after the extraction is neglected so that the changing of the phase volume is very small. 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.

4. Results and discussion

4.1. Experimental results

Table 1 presents results of the equilibrium data on the distribution of tartaric acid between water and Alamine 336 dissolved in hexane, cyclohexane, toluene, methyl isobutyl ketone, and butan-1-ol. The concentrations of amines in solvents were between 0.422 and 1.736 mol dm^{-3}. The tartaric acid concentration in the initial aqueous phase was 0.347 mol dm^{-3}.

Fig. 1 demonstrates the influence of the organic solvent on tartaric 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.
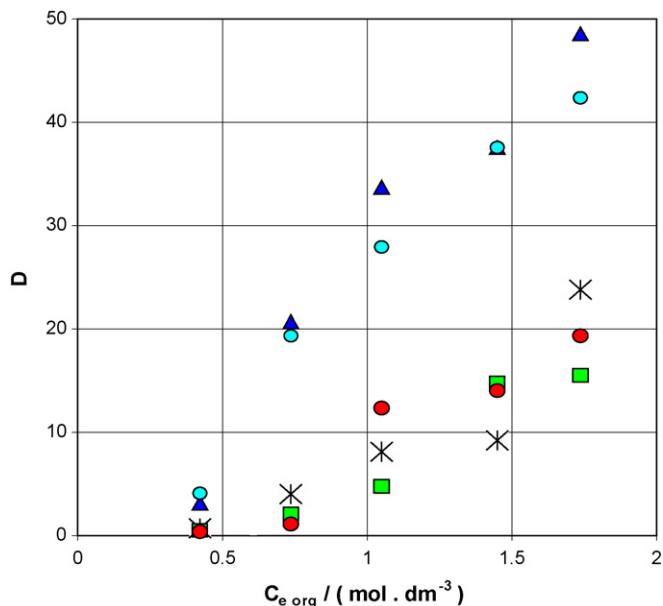

Fig. 1. Plot of distribution coefficients D against concentration of Alamine 336 in different individual diluting solvents: ●, cyclohexane; ●, butan-1-ol; ✳, toluene; ▲, methyl isobutyl ketone; ■, hexane.

According to Table 1 and Fig. 1 for Alamine 336 extraction the following obviously orders were found for the respective:

MIBK > butan-1-ol > toluene > cyclohexane > hexane

This fact can be explained by the formation of two or three acid:amine complexes, which are effected by the dilu-

Table 1
Results for extractions with individual diluting solvents

Diluent	$C_{e\,org}$ (mol dm^{-3})	$C_{aq\,tar}$ (mol dm^{-3})	$C_{org\,tar}$ (mol dm^{-3})	Z	D	E
Hexane	1.736	0.021	0.326	0.188	15.524	93.948
	1.449	0.022	0.325	0.224	14.773	93.659
	1.049	0.060	0.286	0.273	4.767	82.421
	0.736	0.113	0.234	0.318	2.071	67.435
	0.422	0.231	0.116	0.275	0.502	33.429
Cyclohexane	1.736	0.017	0.329	0.189	19.352	94.813
	1.449	0.023	0.323	0.223	14.043	93.084
	1.049	0.026	0.321	0.306	12.346	92.507
	0.736	0.164	0.182	0.247	1.109	52.449
	0.422	0.251	0.095	0.225	0.378	27.377
Toluene	1.736	0.014	0.333	0.192	23.786	95.965
	1.449	0.034	0.313	0.216	9.206	90.202
	1.049	0.038	0.308	0.294	8.105	88.761
	0.736	0.069	0.277	0.376	4.014	79.827
	0.422	0.204	0.143	0.339	0.701	41.210
MIBK	1.736	0.007	0.340	0.196	48.571	97.983
	1.449	0.009	0.338	0.233	37.555	97.406
	1.049	0.010	0.337	0.321	33.700	97.118
	0.736	0.016	0.331	0.449	20.687	95.389
	0.422	0.084	0.263	0.623	3.131	75.792
Butan-1-ol	1.736	0.008	0.339	0.195	42.375	97.694
	1.449	0.009	0.338	0.233	37.556	97.406
	1.049	0.012	0.335	0.319	27.917	96.542
	0.736	0.017	0.329	0.447	19.353	94.813
	0.422	0.068	0.278	0.659	4.088	80.115

ents in different way. 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) give 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 media for the ion pair. However, polarity (or polarizability) alone does not completely account for solvating ability. Alcohol diluent (butanol) give 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 versus amine concentration. 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 increase with increasing amine concentration. Systems that exhibit aggregation, formation of complexes with large numbers of acid and amine molecules, exhibit increase in loading. MIBK exhibit increase at 1.0–1.5 mol dm^{-3} amine concentration indicating that complexes include large numbers of acid and amine molecules.

In Fig. 3, the concentration of Alamine 336 is varied from 0.422 to 1.736 mol dm^{-3}. The initial concentration of tartaric acid is about 5% (w/w), which is based on the concentration of tartaric acid produced from fermentation. As can be seen from Fig. 3, the increase of amine concentration brings about gradual increase of extraction efficiency. Near 1.736 mol dm^{-3}, most of the tartaric acid is extracted.

Fig. 3. Plot of extraction efficiency E against concentration of Alamine 336 in different individual diluting solvents: ●, cyclohexane; ●, butan-1-ol; ✳, toluene; ▲, methyl isobutyl ketone; ■, hexane.

The equilibrium data about distribution of tartaric acid between water and Alamine 336 dissolved in toluene + MIBK, hexane + MIBK and toluene + hexane mixtures presented in Table 2. It can be seen that the effect of diluting solvents mixtures on extraction power of Alamine 336 in Fig. 4. It has been found that the extraction power of Alamine 336 is most effective with MIBK + toluene mixture. It has been found that the maximum removal of tartaric acid is 98.753% with MIBK + toluene at 1.702 mol dm^{-3} initial concentration of
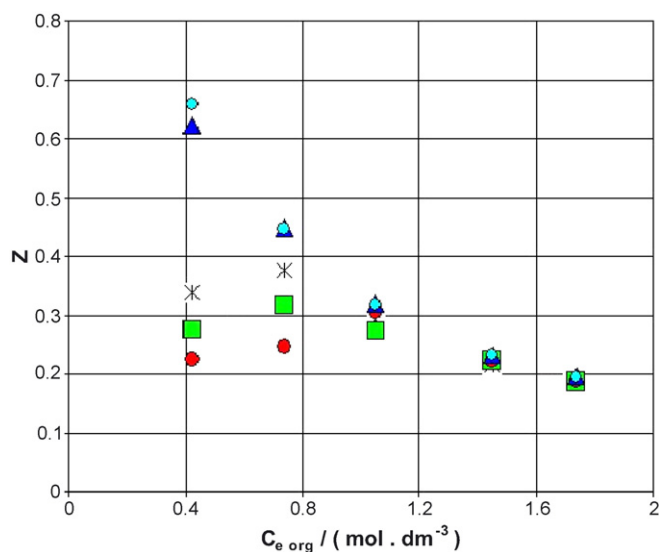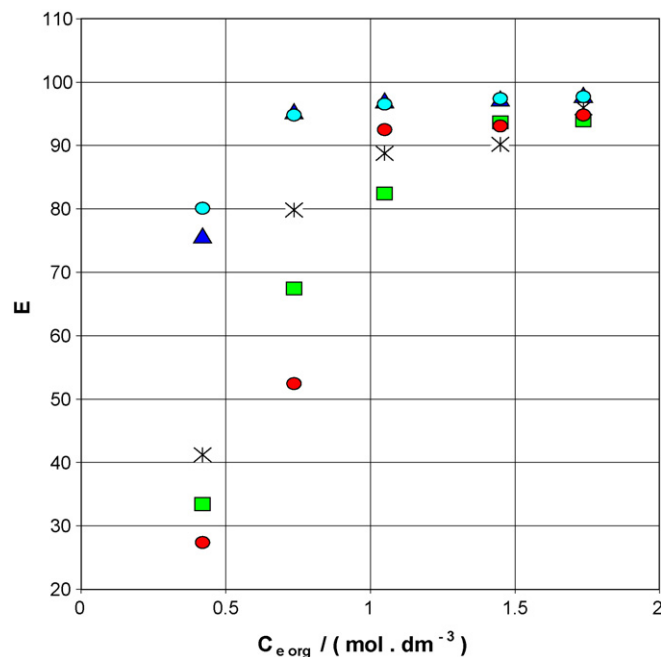

Fig. 2. Plot of loading factors Z against concentration of Alamine 336 in different individual diluting solvents: ●, cyclohexane; ●, butan-1-ol; ✳, toluene; ▲, methyl isobutyl ketone; ■, hexane.
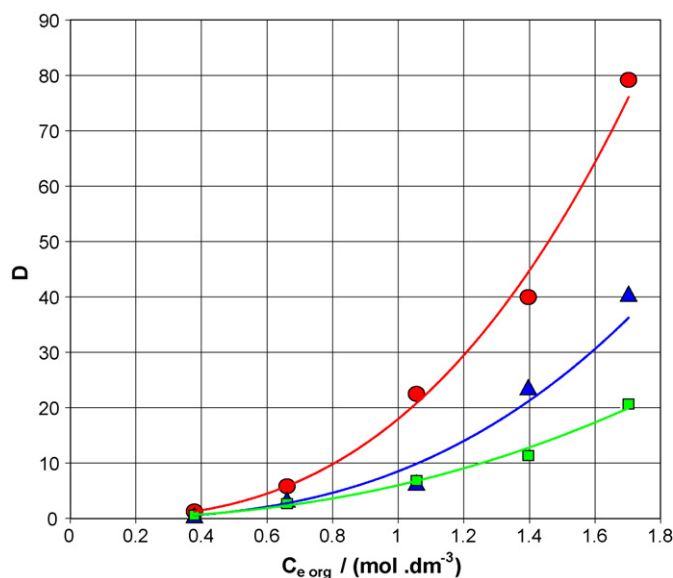

Fig. 4. Plot of distribution coefficients D against concentration of Alamine 336 in different binary diluting solvents: ●, toluene + methyl isobutyl ketone; ▲, methyl isobutyl ketone + hexane; ■, hexane + toluene.

Table 2
Results for extractions with diluting (50–50%, v/v) solvent mixtures

Diluent	$C_{e\,org}$ (mol dm^{-3})	$C_{aq\,tar}$ (mol dm^{-3})	$C_{org\,tar}$ (mol dm^{-3})	Z	D	E
MIBK + hexane	1.702	0.008	0.339	0.199	42.375	97.694
	1.396	0.014	0.333	0.238	23.785	95.965
	1.055	0.046	0.301	0.285	6.543	86.743
	0.661	0.079	0.268	0.405	3.392	77.233
	0.378	0.216	0.131	0.346	0.606	37.752
Toluene + MIBK	1.702	0.004	0.343	0.201	85.750	98.847
	1.396	0.008	0.338	0.242	42.250	97.406
	1.055	0.015	0.332	0.314	22.133	95.677
	0.661	0.051	0.296	0.447	5.803	85.302
	0.378	0.152	0.195	0.515	1.282	56.195
Hexane + toluene	1.702	0.016	0.331	0.194	20.687	95.389
	1.396	0.028	0.319	0.228	11.392	91.930
	1.055	0.044	0.303	0.287	6.886	87.319
	0.661	0.093	0.254	0.384	2.731	73.198
	0.378	0.214	0.133	0.351	0.621	38.328

Alamine 336. The acid concentration of water at equilibrium $C_{aq\,tar}$ decreases from 0.152 to 0.004 mol dm^{-3} with increasing amount of Alamine 336 from 0.378 to 1.702 mol dm^{-3} for MIBK + toluene. Distribution coefficient increases from 1.282 to 79.190 with decreasing in the amount of Alamine 336. In Fig. 5, the effect of solvents mixtures on loading of Alamine 336 is presented.

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 3. Furthermore Uslu calculated overall extraction constants for propionic acid + amine + toluene ternary system by graphical method [24].

In the case of proton-donating diluent (butan-1-ol) the extraction process can be described by the reactions

$$HA + {}^*R_3N = {}^*(HA) \cdot (R_3N) \quad K_{11} \tag{10}$$

$$HA + 2{}^*R_3N = {}^*(HA) \cdot (R_3N)_2 \quad K_{12} \tag{11}$$
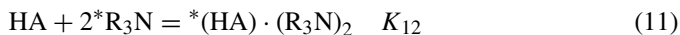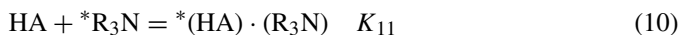
The resulting acid:amine complexes are supposed to be stabilized due to hydrogen bonding with the diluent.

Table 3
Results of overall extraction constants

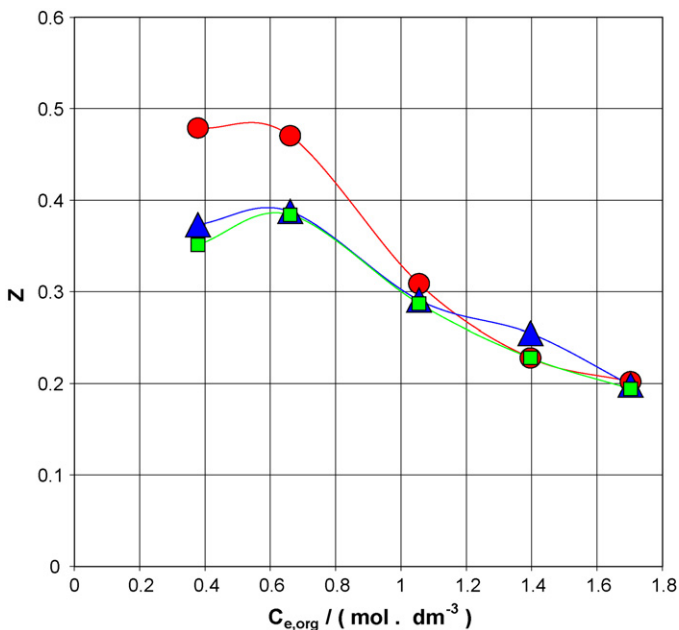| Diluent	$C_{e\,org}$ (mol dm^{-3})	K_{11} (mol dm^{-3})	K_{23} (dm^{12} mol^{-4})	K_{12} (dm^6 mol^{-2})
Hexane	1.736	8.742	131.257	–
	1.449	10.582	244.698	–
	1.049	4.615	71.774	–
	0.736	2.783	44.873	–
	0.422	1.281	36.352	–
Cyclohexane	1.736	11.133	221.641	–
	1.449	9.369	182.594	–
	1.049	11.672	393.747	–
	0.736	1.764	27.063	–
	0.422	0.933	22.403	–
Toluene	1.736	13.918	331.784	–
	1.449	6.573	98.495	–
	1.049	8.094	214.433	–
	0.736	5.494	150.988	–
	0.422	2.191	104.162	–
MIBK	1.736	27.496	1220.061	–
	1.449	23.344	1092.760	–
	1.049	31.031	2665.199	–
	0.736	26.599	2732.920	–
	0.422	6.333	307.425	–
Butan-1-ol	1.736	25.766	–	15.833
	1.449	24.168	–	16.387
	1.049	26.477	–	24.657
	0.736	23.590	–	29.184
	0.422	8.230	–	16.584

Fig. 5. Plot of loading factors Z against concentration of Alamine 336 in different binary diluting solvents: ●, toluene + methyl isobutyl ketone; ▲, methyl isobutyl ketone + hexane; ■, hexane + toluene.

In the case of nonproton donating diluents (hexane, cyclohexane, toluene, MIBK) the process can be described the reaction

$$2HA + {}^*R_3N = {}^*(HA)_2 \cdot (R_3N)_3 \quad K_{23} \quad (12)$$

Reaction (13) can be understood as a result of three consecutive reactions—(10) and (11) and

$${}^*HA \cdot (R_3N) + {}^*(HA) \cdot (R_3N)_2 = {}^*(HA)_2 \cdot (R_3N)_3 \quad K_A \quad (13)$$
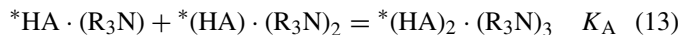
The aggregation of highly polar primary acid:amine complexes according to reaction (12) is supposed to proceed almost completely. As the ${}^*(HA) \cdot (R_3N)_2$ complex is minor in the studied range concentrations, its presence is not indicated. The extraction constant K_{23} is, in fact the product K_{11}, K_{12}, K_A.

4.2. LSER model results

The properties of an acid/amine system of hydrogen bond formation can be estimated through theoretically based models of the mass action law including the physical interaction terms, or by using the concept of multiscale association, as well as by applying a generalized solvatochromic approach with linear solvation energy relationship (LSER) [14]. A modified version of LSER for predicting the extraction equilibria of an amine/diluent/acid system is given by Bizek et al. [25].

How to calculate distribution coefficients of solvents in amine with LSER model equation was described in my previous work [24]. Briefly, following equation can be used to describe the effect of diluents on the values of distribution coefficients (D):

$$\ln D = \ln D^0 + s(\pi^* + d\delta) + b\beta + a\alpha \quad (14)$$

The values of the distributions coefficients can be correlated with the solvatochromic parameters of the solvents from Table 4 [26] according to Eq. (14). The resulting fitting curves are included in Fig. 6 and that the calculated values shows a good correlation to the experimental data. The estimated values of parameters of the model are presented in Table 5. It has been concluded that by using this model, distribution coefficients of tartaric acid between water and amine + solvent system can be described.

The root mean square deviations (rmsd) are calculated from the difference between the experimental data and the predictions of the LSER model according to the following equation:

$$\text{rmsd} = \sqrt{\frac{1}{N} \sum_{i=1}^{n} (D_{i,\text{exp}} - D_{i,\text{calc}})} \quad (15)$$

Table 4
Solvatochromic parameters: hydrogen bond donor acidities, π^* and δ and hydrogen bond acceptor basicities, α and β for pure diluents [26]

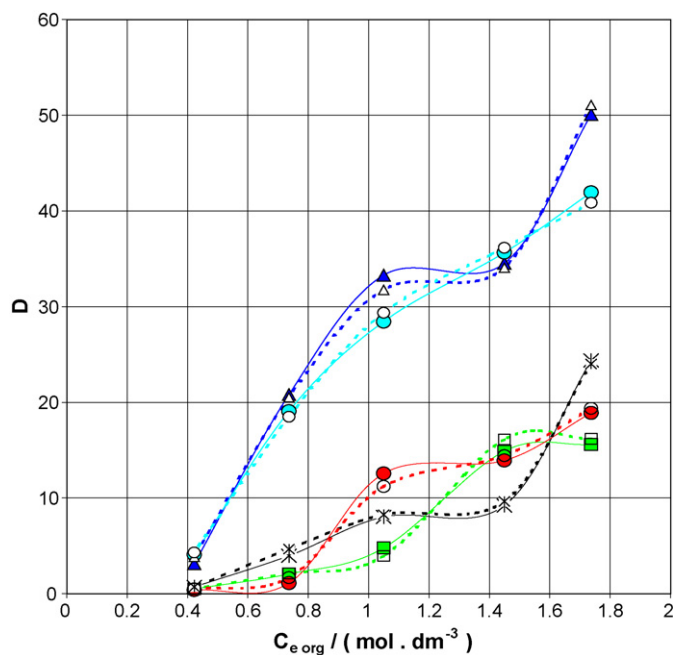| Solvents	π^*	β	α	δ
Toluene	0.54	0.11	0	1
MIBK	0.63	0.48	0	0
Cyclohexane	0	0	0	1
Hexane	−0.08	0	0	0
Butan-1-ol	0.47	0.88	0.79	0

Fig. 6. Plot of distribution coefficients D against concentration of Alamine 336 $C_{e\,\text{org}}$ to compare the experimental data with calculated values using the LSER model equation: ▲, MIBK; -△-, MIBK model; ●, butan-1-ol; -○-, butan-1-ol model; ✕, toluene; -✱-, toluene model; ●, cyclohexane; -○-, cyclohexane model; ■, hexane; -□-, hexane model.

Table 5
The values of LSER model parameters (D^0, s, d, b, a) coefficient of linear regression, R^2; standard error, S.E.

LSER model parameters	
$\ln D^0$	2.1236
S	−0.5604
d	0.9131
a	3.0831
b	−1.7457
R^2	0.85
S.E.	0.71

where $D_{i,\text{exp}}$ is the experimental distribution coefficient and $D_{i,\text{calc}}$ is the calculated distribution coefficient. N is the number of experimental data. The rmsd value of LSER model is found to be 0.0912.

The rmsd value shows all predicted distribution coefficients agree well with each other, and also the agreements between predictions and measurements is acceptable considering experimental uncertainty.

5. Conclusion

The aim of this study is to determine the extractability of tartaric acid by Alamine 336 dissolved in several diluents. Some physical and chemical equilibria for tartaric acid extraction by Alamine 336 in five diluents and three binary diluents have been determined. The extraction equilibrium was interpreted as a result of consecutive formation of two acid–amine species with stoichiometries of 1:1, 1:2, 2:3. Overall thermodynamic extraction constants K_{11}, K_{12} and K_{23} have been determined.

The results of the liquid–liquid equilibrium measurements were correlated by a linear solvation energy relationship-LSER model which takes into account physical interactions from the regression coefficients, information on the solvent–solute interaction is obtained and solvation models are proposed.

List of symbols

a_a	molal activity coefficient of acid
a_e	molal activity coefficient of amine
a_{ij}	molal activity coefficient of complex
$C_{aq\,tar}$	molar concentration of acid in the aqueous phase $(mol\,dm^{-3})$
$C_{e\,org}$	molar concentration of amine in the organic phase $(mol\,dm^{-3})$
$C_{org\,tar}$	molar concentration of acid in the organic phase $(mol\,dm^{-3})$
D	distribution coefficient
HA	tartaric acid
K_{ij}	overall thermodynamic extraction constants
K_A	aggregation constant
m_a	molality of acid in the aqueous phase, $mol\,kg^{-1}$ of solvent
m_e	molality of amine in the aqueous phase, $mol\,kg^{-1}$ of solvent
m_{ij}	molality of amine in the aqueous phase
$*m_a$	molality of acid in the organic phase, $mol\,kg^{-1}$ of solvent
$*m_e^o$	total molality of amine in organic phase, $mol\,kg^{-1}$ of solvent
MIBK	methyl isobutyl ketone
p	number of acid molecules
q	number of acid molecules
R_3N	tertiary amine
Z	loading factor
$*$	organic phase
[ ]	activities

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