Extraction Equilibria of Succinic Acid from Aqueous Solutions by Amberlite LA-2 in Various Diluents

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The aim of this study is to investigate the extraction of succinic acid from aqueous solutions by different organic solutions containing Amberlite LA-2, a secondary amine mixture. Extraction equilibria of succinic acid in the solution of Amberlite LA-2 in seven individual diluents at a temperature of 298.15 K have been measured. Using Bizek's approach, two acid−amine complexes, $(HO)\cdot(R_2N)$ and $(HO)\cdot(R_2N)_2$, are assumed to exist in the organic phase in the case of proton-donating diluents, while the complexes $(HO)\cdot(R_2N)$ and $(HO)_2\cdot(R_2N)_3$ are suggested in the case of nonproton-donating diluents. Important data for the design of separation units have been obtained as a result of batch experiments. These data are distribution coefficients (D), loading factors (Z), extraction efficiencies (E), and overall extraction constants (K_{11}, K_{12}, and K_{23}).

Introduction

Succinic acid, a dicarboxylic acid having the molecular formula $C_4H_6O_4$, is of interest through its use as the raw material of polysuccinate, which is a biodegradable polymer, the importance of which has increased. Succinic acid is also used to produce numerous esters, salts, and other derivatives for use in the plastics, coatings, agricultural chemicals, food, flavor, and perfume industries.[1] Succinic acid has been produced by chemical processes using petroleum as a starting material. However, there has recently been much interest in the production of succinic acid from renewable resources by microbial fermentation because of the considerable increase in the cost of petroleum and ever-increasing environmental concerns.

Since Robert Knock, the Nobel Prize winner, proved that succinic acid has a positive influence on human metabolism and there is no risk of its accumulation in the human body, it has been used in food industries. Succinic acid is produced in many organisms as an intermediate of the tricarboxylic acid (TCA) cycle and also as one of the fermentation end products of anaerobic metabolism. It is synthesized in almost all microbial, plant, and animal cells.[2] Many different microorganisms have been screened and studied for succinic acid production from various carbon sources. Among them, *Anaerobiospirillum succiniciproducens*[3,4] and *Actinobacillus succinogenes*[5,6] have been most intensively studied because of their ability to produce a relatively large amount of succinic acid. More recently, a new succinic acid producing bacterium *Mannheimia succiniciproducens* (MBEL55E) was isolated from bovine rumen.[7] Also, there has been much effort in developing recombinant *Escherichia coli* strains which are capable of enhanced succinic acid production under aerobic and anaerobic conditions.[2,8,9]

It is well-known that the ideal way to produce carboxylic acids, and also other compounds having sufficient acidic properties, are fermentation processes that have been proven to be environmentally friendly and use renewable resources. One of the most common problems of fermentation in the production of these carboxylic acids is their low concentration.[10]

Traditional diluents such as alcohols, ethers, esters, and inert diluents (hexane, *n*-heptane), and so forth, give low distribution coefficients of carboxylic acids and thus are unsuccessful for recovery of acid from dilute streams.[11−16] The probable reason for this is the high affinity of the acids for water. Thus, physical extraction with conventional diluents is not an efficient method for recovery of carboxylic acids.[11] To increase selectivity and yield of the acids, a combination of diluent with an extractant, which can chemically complex the acid, was tried. The improved results laid down the establishment of the technology of reactive extraction for recovery of carboxylic acids. Organophosphorous compounds and secondary, tertiary, and quaternary amines are widely employed to extract carboxylic acids.[11,12]

Amine compounds are useful and valuable extractants for the separation of versatile carboxylic acids which became the subject of recent investigations.[13−16] They are of importance because of their high efficiency and selectivity. Amine compounds can provide much higher equilibrium distribution coefficients (D) for the extraction of carboxylic acids than diluents.[13,14]

There are a lot of articles about the separation of carboxylic acids. Wasewar and others have investigated the removal of a lot of carboxylic acids by different reactive extractions.[15−21] Hong and Hong have investigated the reactive extraction of succinic acid with different tertiary amines.[22,23] However, there are not sufficient data in relation to succinic acid and the Amberlite LA-2/diluent system. In the present work the extraction of succinic acid from aqueous solutions by Amberlite LA-2 in different diluents was examined over a wide range of amine concentration [(0.19 to 0.93) $\text{mol}\cdot\text{L}^{-1}$].

Extraction experiments were carried out with Amberlite LA-2 dissolved in diluents of various types: ketones (MIBK, 2-octanone), alkanes (iso-octane, cyclohexane, hexane), alcohols (1-octanol), and an aromatic hydrocarbon (toluene). Distribution coefficients were calculated from the results of batch extraction experiments. In addition to distribution coefficients, extraction efficiencies and loading factors have been obtained. Furthermore, they were used to obtain conclusions about the stoichiometry of complex formation.

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10.1021/je9004917 CCC: $40.75

Theoretical Section

The extraction of succinic acid (H_2A) with an amine (R_2N) can be described by the set of reactions:

$$i(H_2A)^R + j(R_2N)^E \rightleftarrows ((H_2A)_i \cdot (R_2N)_j)^E \quad i = 1, p; j = 1, q \tag{1}$$

where H_2A represents the undissociated part of the acid present in the raffinate or aqueous phase (R) and extract (organic) phase species are marked with a superscript E. As no overloading of the amine has been observed *i* is expected to be less than or equal to *j* for any *p* and *q*. The reaction stated by eq 1 can be characterized by the overall thermodynamic extraction constants:

$$(K_{ij})^E = [(H_2A)_i \cdot (R_2N)_i]^E/([H_2A]^i)^R([R_2N]^j)^E \tag{2}$$

where square brackets denote activities.

Equation 1 can be written in terms of dissociated species, hydrogen ions and succinate anions, as 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 the equilibrium constants.[24] Replacing the activities by the products of molalities ($mol \cdot kg^{-1}$ of diluent) and molar activity coefficients, eq 2 takes the form:

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

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

As presented by Levien, the activity coefficients of undissociated succinic acid in water can be neglected as a first approximation.[24,25] Moreover, supposing the ratio of the activity coefficients of organic phase species are constant allows them to be incorporated into the equilibrium constants. The conditional overall extraction constants are given by expressions:

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

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

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

where the molality of free amine is given by the equation:

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

where b_e^0 is the total molality of amine in the organic phase. Equation 6 has a unique solution between zero and the aqueous phase molalities of the undissociated acid, according to the dissociation equilibrium. As can be seen from the results by Vanura and Kuca and Sato et al., all possible (*i*,*j*) combinations for $i = 1,p$ and $j = 1,q$ need not to be taken into account.[24,25] It is possible to study the extraction of acid by pure diluents 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 the organic phase. The expression for the loading, *Z*, can be derived from eqs 5 and 6 in the form:

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

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

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

Experimental Section

Amberlite LA-2, a commercial product (Henkel Co.) was used: a mixture of straight-chain secondary amines ($M = 374\ g \cdot mol^{-1}$). Succinic acid (Merck, > 99 %), hexane (Merck, > 99 %), cyclohexane (Merck, > 99 %), toluene (Carlo Erba, > 99 %), iso-octane (Merck, > 99 %), MIBK (Merck, > 99 %), 2-octanone (Merck, > 99 %), and 1-octanol (Merck, > 99 %) were used without further purification.

The appropriate amounts of succinic acid were dissolved in water to prepare solutions with an initial concentrations of acid of 0.469 $mol \cdot L^{-1}$ ($w = 5.25$ %). The initial organic phases were prepared by the dissolution of amine in the diluents to produce solutions with approximately constant concentrations (0.93 $mol \cdot L^{-1}$, 0.74 $mol \cdot L^{-1}$, 0.56 $mol \cdot L^{-1}$, 0.37 $mol \cdot L^{-1}$, and 0.19 $mol \cdot L^{-1}$). Aqueous and organic solutions (3 mL) of known concentrations were added to Erlenmeyer 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 to 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 %).[24] The 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 the variables investigated.

Results and Discussion

Table 1 presents the results of the experimental investigation. The concentrations of amines in the diluents were between 0.19 $mol \cdot L^{-1}$ and 0.93 $mol \cdot L^{-1}$. The succinic acid concentration in the initial aqueous phase was 0.469 $mol \cdot L^{-1}$ ($w = 5.25$ %).

The equilibrium complexation constants on the distribution of succinic acid between water and Amberlite LA-2 dissolved in hexane, cyclohexane, toluene, methyl isobutyl ketone, iso-octane, 2-octanone, and 1-octanol are presented in Table 2. The improvement obtained with reactive extraction can be seen by comparing Table 1 with physical extraction values (Table 3).

Figure 1 demonstrates the influence of the organic diluent on succinic acid distribution between water and Amberlite LA-2. It can be seen that the extraction power of Amberlite LA-2 diluent mixture changes by increasing the initial concentration of Amberlite LA-2 in the organic phase. As shown in Figure 1 and Table 1, the effect of the diluents on the extraction of succinic acid were found as 1-octanol > 2-octanone > MIBK > toluene > iso-octane > 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 ways. In this study, using Bizek's approach, three acid−amine complexes, $(HO) \cdot (R_2N)$, $(HO) \cdot (R_2N)_2$, and $(HO)_2 \cdot (R_2N)_3$, have been assumed to exist in the organic phase.[24−27]

Solvation of the complex by the diluent is a critical factor in the extraction of the acid. The interactions between the complex

Table 1. Experimental Results of the Extraction of Succinic Acid with Amberlite LA-2/Individual Diluents at 25 °C

diluent	$(C_e)^E$ mol·L^{-1}	$(C_a)^R$ mol·L^{-1}	$(C_a)^E$ mol·L^{-1}	*D*	*Z*	*E* (%)
cyclohexane	0.19	0.318	0.151	0.474	0.816	32.18
	0.37	0.183	0.286	1.569	0.774	61.08
	0.56	0.103	0.366	3.560	0.666	78.07
	0.74	0.061	0.408	6.636	0.551	86.91
	0.93	0.043	0.426	10.021	0.461	90.93
iso-octane	0.19	0.266	0.203	0.766	1.100	43.39
	0.37	0.112	0.357	3.172	0.964	76.03
	0.56	0.058	0.411	7.089	0.747	87.64
	0.74	0.045	0.424	9.394	0.573	90.38
	0.93	0.031	0.438	13.912	0.473	93.29
MIBK	0.19	0.171	0.298	1.742	1.610	57.87
	0.37	0.046	0.423	9.200	1.143	84.89
	0.56	0.020	0.449	22.019	0.816	94.75
	0.74	0.014	0.455	31.521	0.614	97.83
	0.93	0.010	0.459	45.094	0.496	98.92
1-octanol	0.19	0.198	0.271	1.374	1.467	55.41
	0.37	0.071	0.398	5.617	1.076	85.99
	0.56	0.025	0.444	18.041	0.808	93.48
	0.74	0.010	0.459	45.094	0.620	96.74
	0.93	0.005	0.464	91.244	0.502	98.19
2-octanone	0.19	0.209	0.260	1.243	1.405	37.61
	0.37	0.066	0.403	6.137	1.090	74.55
	0.56	0.031	0.438	14.328	0.797	87.64
	0.74	0.015	0.454	29.711	0.613	91.47
	0.93	0.008	0.461	54.324	0.498	94.39
toluene	0.19	0.293	0.176	0.603	0.953	29.45
	0.37	0.119	0.350	2.929	0.945	65.21
	0.56	0.058	0.411	7.089	0.747	75.66
	0.74	0.040	0.429	10.727	0.580	84.98
	0.93	0.026	0.443	16.809	0.479	91.84
hexane	0.19	0.331	0.138	0.417	0.747	32.18
	0.37	0.163	0.306	1.875	0.827	61.08
	0.56	0.114	0.355	3.108	0.645	78.07
	0.74	0.070	0.399	5.657	0.539	86.91
	0.93	0.038	0.431	11.251	0.466	90.93

and the diluent can be divided into general solvation interactions and specific interactions of the diluent with the complex. Inert diluents, such as the nonpolar alkanes hexane, iso-octane, and cyclohexane, provide very low solvation of the polar complex.

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 increasing amine concentration. Systems that exhibit aggregation, that is, formation of complexes with large numbers of acid and amine molecules, exhibit an abrupt increase in loading. In this work, loading factors of all diluents decrease with increasing amine concentration, indicating that complexes include more than one amine per complex.[22] Thus, they do not contribute significantly to the distribution of the acid into the diluent phase and give low values of distribution coefficients. Aromatic diluents (toluene) gives a higher distribution coefficient than nonpolar diluents. This behavior has been rationalized in terms of solvation due to the interaction of the aromatic π-electrons with the complex. MIBK and 2-octanone are polar and can promote extraction by providing a good medium for the ion pair. However, polarity (or polarizability) alone does not completely account for the solvating ability. The capability for hydrogen bonding is important in the case of using an alcohol diluent as a result of this effect,[21] and 1-octanol has shown high distribution coefficients in this study.

In Figure 2, the effect of Amberlite LA-2 concentration on loading is shown. The loading curve is a plot of *Z* versus amine concentration. Overloading (loading greater than unity) indicates that complexes have more than one acid per amine.

Table 2. Values of Changing the Overall Extraction Constants for Different Diluents

diluent	$(C_e)^E$ mol·L^{-1}	K_{11} L·mol^{-1}	K_{23} L^4·mol^{-4}	K_{12} L^2·mol^{-2}
cyclohexane	0.19	2.50	217	
	0.37	4.24	169	
	0.56	6.36	197	
	0.74	8.97	266	
	0.93	10.8	292	
iso-octane	0.19	4.03	420	
	0.37	8.57	557	
	0.56	12.7	696	
	0.74	12.7	513	
	0.93	15.0	549	
MIBK	0.19	9.17	1484	
	0.37	24.9	3950	
	0.56	39.3	6154	
	0.74	42.6	5393	
	0.93	48.5	5509	
1-octanol	0.19	7.23	1013	38.1
	0.37	15.2	1564	41
	0.56	32.2	4170	57.5
	0.74	60.9	10937	82.4
	0.93	98.1	22311	105
2-octanone	0.37	6.54	866	
	0.37	16.6	1843	
	0.56	25.6	2666	
	0.74	40.2	4801	
	0.93	58.4	7966	
toluene	0.19	3.17	300	
	0.37	7.92	484	
	0.56	12.7	696	
	0.74	14.5	661	
	0.93	18.1	793	
hexane	0.19	2.20	183	
	0.37	5.07	226	
	0.56	5.55	155	
	0.74	7.65	198	
	0.93	12.1	365	

Table 3. Distribution of Succinic Acid between Diluents and Water at 25 °C

diluent	$(C_a)^R$ mol·L^{-1}	$(C_a)^E$ mol·L^{-1}	*D*	*E* (%)
cyclohexane	0.463	0.006	0.014	1.354
iso-octane	0.448	0.021	0.048	4.562
MIBK	0.393	0.076	0.192	16.10
1-octanol	0.390	0.079	0.203	16.89
2-octanone	0.435	0.034	0.077	7.160
toluene	0.455	0.014	0.030	2.959
hexane	0.044	0.425	0.010	0.952

In the case of the nonproton donating diluents (hexane, cyclohexane, iso-octane, toluene, 2-octanone, MIBK) the process can be described by the reaction:

$$2(\mathrm{HA})^{R} + 3(\mathrm{R_2N})^{E} \rightleftarrows ((\mathrm{HA})_2 \cdot (\mathrm{R_2N})_3)^{E} \quad K_{23} \qquad (9)$$

Only the values of K_{11} and K_{12} for 1-octanol have been presented in Table 2. Reaction 9 can be understood as a result of three consecutive reactions: 10, 11, and 12;

$$(\mathrm{HA})^{R} + (\mathrm{R_2N})^{E} \rightleftarrows ((\mathrm{HA})_2 \cdot (\mathrm{R_2N}))^{E} \quad K_{11} \qquad (10)$$

$$(\mathrm{HA})^{R} + 2(\mathrm{R_2N})^{E} \rightleftarrows ((\mathrm{HA}) \cdot (\mathrm{R_2N})_2)^{E} \quad K_{12} \qquad (11)$$

$$(\mathrm{HA} \cdot (\mathrm{R_2N})_3)^{E} + ((\mathrm{HA}) \cdot (\mathrm{R_2N})_2)^{E} \rightleftarrows ((\mathrm{HA})_2 \cdot (\mathrm{R_2N})_5)^{E} \quad K_{A} \qquad (12)$$

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 the proton-donating diluent (1-octanol), the extraction process can be described by the reactions 10 and 11.

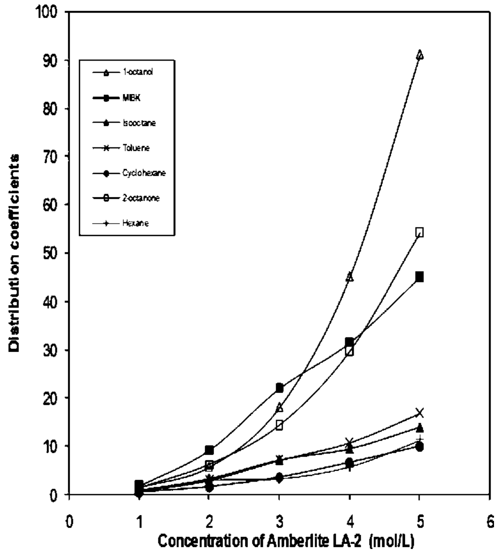

Figure 1. Variation of distribution coefficients with the concentration of Amberlite LA-2 in different individual diluents at 25 °C: Δ, 1-octanol; ■, MIBK; ▲, iso-octane; ×, toluene; ●, cyclohexane; □, 2-octanone; +, hexane.

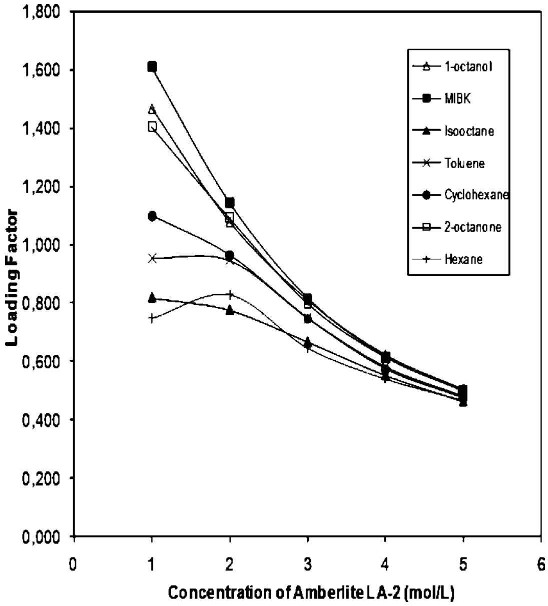

Figure 2. Variation of loading factors with concentration of Amberlite LA-2 in different diluents at 25 °C: Δ, 1-octanol; ■, MIBK; ▲, iso-octane; ×, toluene; ●, cyclohexane; □, 2-octanone; +, hexane.

The resulting acid−amine complexes are supposed to be stabilized because of hydrogen bonding with the diluent.

The aggregation of highly polar primary acid−amine complexes according to reaction 12 are supposed to proceed almost completely. As the $((HA)\cdot(R_2N)_2)^E$ complex is the minor component in the studied range of concentrations, its presence is not indicated.

The distribution data of succinic acid between the water and the diluents used in this study (1-octanol, 2-octanone, cyclohexane, iso-octane, hexane, cyclohexane, MIBK) are presented in Table 3 and shown in Figure 3.

Conclusions

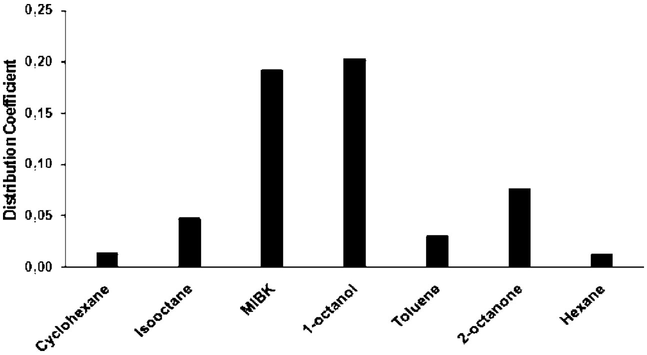

Figure 3. Distribution coefficients of succinic acid between water and diluents used in this study.

This work examined the effect of diluents on the distribution of succinic acid between water and Amberlite LA-2. The diluents used were hexane, cyclohexane, iso-octane, toluene, MIBK, 1-octanol, and 2-octanone. The extraction of succinic acid increases with increasing amine concentration for all of the diluents. Among the diluents used in this study, the largest distribution coefficients were obtained with 1-octanol, 2-octanone, and MIBK. In the experiments, the concentration of succinic acid in the aqueous phase varied between 0.271 $mol\cdot L^{-1}$ and 0.464 $mol\cdot L^{-1}$ for 1-octanol. The best distribution ratio of succinic acid is obtained with 1-octanol as 91.2.

The maximum extraction efficiencies for diluents used at the maximum Amberlite LA-2 (0.93 $mol\cdot L^{-1}$) concentration are determined as 1-octanol > 2-octanone > MIBK > toluene > iso-octane > hexane > cyclohexane.

Appendix

Symbols and Abbreviations

a_a	molal activity coefficient of acid
a_e	molal activity coefficient of amine
a_{ij}	molal activity coefficient of complex
$(c_a)^R$	concentration of acid in the aqueous phase, $mol\cdot L^{-1}$
$(c_a)^E$	concentration of acid in the organic phase, $mol\cdot L^{-1}$
$(c_e)^E$	concentration of amine in the organic phase, $mol\cdot L^{-1}$
D	distribution coefficient
HA	succinic acid
K_A	aggregation constant
K_{ij}	overall thermodynamic extraction constant
$(b_a)^R$	molality of acid in the aqueous phase, $mol\cdot kg^{-1}$
$(b_a)^E$	molality of acid in the organic phase, $mol\cdot kg^{-1}$
$(b_e)^R$	molality of amine in the aqueous phase, $mol\cdot kg^{-1}$
$(b_{eo})^E$	total molality of amine in the organic phase, $mol\cdot kg^{-1}$
MIBK	methyl isobutyl ketone
p	number of acid molecules
q	number of amine molecules
R_2N	secondary amine
w	mass fraction
Z	loading factor
$()^E$	organic phase
$()^R$	aqueous phase

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Received for review June 10, 2009. Accepted September 3, 2009.

JE9004917