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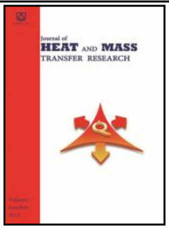

Separation of methacrylicacid from aqueous phase using quaternary amine

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ABSTRACT

The feasibility of extractive reaction of methacrylic acid from aqueous solution using a quaternary amine, Tri–OctylMethyl Ammonium Chloride (TOMAC) as an extractant, was studied. The diluents chosen in the present study belong to different chemical classes, including n–butyl acetate, carbon tetrachloride, isoamyl alcohol, methyl isobutyl ketone, and toluene. The effect of initial acid concentration in the aqueous phase, and initial extractant concentration in the organic phase was studied. The performances of physical and reactive extraction of individual diluents were reported in terms of overall distribution coefficient, overall loading ratios, and stoichiometric loading ratios. The maximum extractability was observed in case of methyl isobutyl ketone, while the minimum with carbon tetrachloride. The remarkable feature of Linear Solvation Energy Relationship (LSER) modelling is that it takes into account physical interactions. To check the accuracy of the experimental observations, they were correlated with the LSER modelling parameters, and a fairly good agreement was observed between them.

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1. Introduction

Reactive extraction is an integrated reaction and separation process wherein the product is extracted by a second liquid phase which is immiscible with the other liquid phase. It links chemical sources and sinks to improve the rate of reaction, selectivity, and yield. Consequently, it is being preferred to recover carboxylic acids from dilute aqueous solutions, may it be from fermentation broth, or industrial effluents. In case of reactive extraction, the organic phase contains an extractant (or reactant) which yields higher distribution coefficients for carboxylic acid (or solute) compared to the traditional (physical) liquid–liquid extraction.

Methacrylic acid (IUPAC 2–methylpropenoic acid), is a corrosive liquid with an acrid unpleasant odor. It is directly used as a co-monomer in various polymers and is also used to make a variety of small volume methacrylates. Its methyl ester is a key intermediate chemical with a global demand in excess of 4.5 billion pounds per year. Methacrylic acid (MAA) is manufactured by hydrolysis of methacryl–amide stream under the pressure of up to 790 kPa (100 psig) at 100–150°C. The reactor effluent is separated into 2 phases. The upper organic layer is distilled to provide high purity MAA. However, other methods are also being explored by many investigators because this method emits 5.5 kg CO2 per each kg MAA produced and produces 1.5 tons of solid waste pereach ton of MAA [1].

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Recently, Rajagopalan et al. have studied production of MAA via heterogeneous selective gas-phase oxidation of propene by CO2. They concluded that the lattice oxygen from the polyoxometalates (POM) catalysts (Keggin type (POM) Ni3[PW12O40]2 and Ni3[PMo12O40]2) acted as anoxidizing agent [2]. Residues from production and cleaning operations as well as waste material from spills, if containing MAA, cannot be biologically treated as the MAA is toxic to the bacteria in the system. Hence, there is a need to search for a suitable effluent–treatment method before their discharge into navigable waters and the concentration of MAA should not exceed 1000 mg/l in the stream to be disposed. In the present study, the reactive extraction of MAA is studied. The extractant used is a quaternary amine, commercially known as Aliquat 336, here after mentioned as A336. It is used with five diluents belonging to different categories including an alcohol (isoamyl alcohol), an aromatic hydrocarbon (Toluene), a strong polar diluent (MIBK), an ester (Butyl acetate), and a non–polar solvent (Carbon tetra chloride).

In the open literature, lot of successful researches have been found using A336. It was first used by Yang et al [3]. They studied the effect of aqueous pH on the extraction of lactic, acetic, propionic, and butyric acids using A336 in kerosene and 2–octanol. It is reported that a polar diluent (here, 2–octanol) increases the extracting power of non–polar amines. They carry out Spectroscopic studies and conclude that the amine binds the non-dissociated part of the acid in the organic phase through reversible complexation. Recently, Pehlivanoglu et al. have performed the extraction studies of oxoethanoic acid (OCHCO2H) using A336 in ten different diluents, which included isoamyl alcohol, octan–1–ol, nonan–1–ol, decan–1–ol, methyl ethyl ketone (MEK), diisobutyl ketone (DIBK), hexan–2–one, toluene, kerosene, and n–hexane. The initial acid concentration in the aqueous phase was 8%, (by weight) and the temperature was maintained at 295 K. The experimental results of the four alcohols were fitted to the LSER model parameters and they agreed well with each other [4]. Wasewar et al. performed extraction study on itaconic acid by A336 using solvents such as ethyl acetate, kerosene, toluene, and hexane. They anticipated 1:1 acid‒amine solvates in the extract phase. In their study, they reported highest values of the distribution coefficient (KD) and the degree of extraction (E) was found to be 2.65 and 72.66%, respectively, with A336 + ethyl acetate system [5]. As a particularly important aspect, the diluent has a remarkable effect on the reaction stoichiometry. The study of Keshav et al. on recovery of propionic acid using A336 in diluents of different classes elucidates that the extent of solvation of acid/amine complexes depends on the diluent, and decreases as, 1–octanol> 1–decanol> petroleum ether > n–heptane [6]. The aim of the present study is to determine the extractability of MAA from water using a quaternary amine, A336 dissolved in the diluents of various types–alcohols (isoamyl alcohol), ketone (MIBK), ester (butyl acetate), aromatics (toluene), and a liquid with no hydrogen–bond forming capability (carbon tetrachloride).

2. Materials and Methods

Equal volumes of the aqueous and organic solution (20 ml of each phase) were contacted in 100 ml conical flasks. Theaqueous phase was prepared by dissolving methacrylic acid in de–ionized water produced by Millipore Milli-Q Water System. The initial concentration of acid was kept within 0.05 and 0.6 mol/l. The organic phase was prepared by dissolving A336 (10–30%) (by volume) in individual diluents. Due to the high viscosity ofAliquat 336 (A336), its concentration in organic phase was not increased further as it could lead to third phase formation. The A336 is a mixture of C8–C10 chains with C8 predominating. It is a transparent reddish brown liquid with the molecular mass of 0.404 kg/mol and density of 0.88 kg/dm3. It was obtained from Himedia and it had 90% purity; methacrylic acid was procured from Himedia having 99% purity, and sodium hydroxide with 97% purity was obtained from Merck. The sources and initial purity of the diluents are tabulated along with their properties (Table 1). All the chemicals were used without further treatment. A temperature controlled water bath shaker (REMI, India) was used for the extraction experiments. Four hours duration was found to be sufficient to attain equilibrium. The shaking speed was maintained at 120 strokes per minute and the temperature was maintained at (303 ± 1) K. After attaining equilibrium, both the phases were allowed to settle for 2 hours at the same temperature for complete phase disengagement. Then, the aqueous phase was analyzed to determine the concentration of acid by titration using freshly prepared NaOH solution and phenolphthalein as an indicator. For the standardization of the NaOH, oxalic acid (Qualigens Fine Chemicals, 99.5%

purity) was used. The acid concentration in the organic phase was calculated by mass balance.

3. Results and Discussion

The dissociation of methacrylic acid depends on its pKa value which is 4.65 [7]. At pH below the pKa, the acid exists in un–dissociated form and above the pKa value, the dissociated form is predominant. Generally, most of the extractants do perform well at pH below the pKa. However, the specific characteristic of A336 makes it a suitable extractant for a wide pH range. As the model solutions are of relatively small acid concentration, it can be safely assumed that only acid–extractant complex and un–dissociated acid exist in the organic and aqueous phases respectively.

The distribution coefficient (K_D) of acid is given by the following:

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \tag{1}$$

Where [HA] is acid concentration, and subscripts “aq” and “org” represent aqueous and organic phases. The extraction of methacrylic acid (HA) by chemical interaction using A336 (B) can be represented as follows:

$$HA_{aq} + B_{org} \leftrightarrow [B : HA]_{org} \tag{2}$$

Where $[B: HA]_{org}$ represents acid–A336 complexes. The physical and chemical equilibria of extraction of MAA using A336 in individual diluents are reported in Table 2. The overall distribution coefficients K_D, (obtained by experiment and predicted by LSER model), acid concentration in organic phase (at equilibrium) $[HA]_{org}$, and overall loading ratio Z_t, (ratio of total extracted acid in organic phase to initial extractant concentration) are reported. The loading ratio, Z_t, is a measure of the extent to which the organic phase can be loaded with acrylic acid. It can be defined as the total concentration of acid (all forms) in the organic phase, divided by the total concentration of amine (all forms) in the organic phase. The loading ratio depends on the extractability of the acid (strength of the acid–base interaction) and its aqueous concentration. The stoichiometry of the overall reaction is determined by the loading ratio in the organic phase as follows:

$$Z_t = \frac{[HA]_{org}}{[B]_{o;org}} \tag{3}$$

Table 1 indicates the diversities in properties of the diluents used in this study. The molecular weight has two opposite effects on distribution coefficients. For the solvents with similar properties, distribution coefficients generally decrease with increasing molecular weight making low molecular weight solvents more preferable over those having high molecular weights. However, an opposite effect is observed in distribution coefficients when the miscibility of water and solvent is considered. The miscibility of solvents and water increases with decreasing molecular weight, so larger amounts of low molecular weight solvents need to be used for extraction procedures. An optimization is therefore made between these solvents and the intermediate molecular weight solvents are generally preferred. Butyl acetate, isoamyl alcohol, and MIBK have higher dipole moment than toluene, and CCl_4. The greater the dipole moment, the greater is the solvating power of solvent. This confirms that the extraction probably occurs via solvation of the acid–amine complex based on dipole–dipole interaction. The effect of high diluent polarity reflects a high equilibrium distribution coefficient for the acid-amine complex which is extracted into the organic phase.

Hildebrand solubility parameter (square root of the cohesive energy density) has also been reported as a measure of solvation of the acid/amine complex by the diluent [9]. The sequence, alcohol < aromatic < ester < ketone, corresponds to increasing acid distribution and increasing solubility parameters. The effects of initial A336 concentration (in organic phase) on distribution coefficients of individual diluents (for 0.05, 0.2, and 0.6 mol/l of initial acid concentration) are shown in Figures 1–3.

In almost all the diluents, except isoamyl alcohol, physical extraction shows poor performance in comparison with reactive extraction. The maximum extractability is obtained in case of maximum A336 content in organic phase (comprising of A336 and MIBK). The loading ratio is plotted against, $[HA]_{aq}^{initial}$ in Figures 4–6 for all the three A336 concentrations. In almost all the cases, MIBK exhibits maximum loading ratio at all the $[HA]_{aq}^{initial}$, which further increases with increasing A336 concentrations. All the diluents show loading ratio less than unity at low $[HA]_{aq}^{initial}$ (< 0.4 mol/l). CCl4, an inert diluent, gives very low loadings of the amine because, being non–polar, it provides very little solvation of the polar complexes. There is little observable effect of A336 concentration on loading, as the inert diluent and A336 have similar solvating abilities.

Several investigators have correlated their experimental findings with solvatochromic parameters of diluents (used by them) for different acid/extractant systems. An overview of the earlier study done using LSER modelling is presented in Table 3. In the highly cited paper of Kamlet and co–workers, they show that solubility properties, SP, of organic non–electrolytes are well correlated by equations that include linear combinations of an exoergic dipolar term, and one or several exoergic hydrogen–bonding terms [10] as follows:

$$SP = SP_0 + s\,(\pi^* + d\delta) + b\beta + a\alpha \qquad (4)$$

where π*, d, and δ are the solvatochromic parameters that measure solute+solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. The SP_0 represents the solubility property for an ideal–inert diluent. The solvatochromic parameter α scale of solvent HBA (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond. The β scale of HBA (hydrogen–bond acceptor) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, respectively. The coefficients p, s, d, a, and b include the properties of solute and are estimated by the regression analysis of the experimental data. The values of solvatochromic parameters π*, δ, α, and β of the diluents used in this investigation are reported in Table 2.

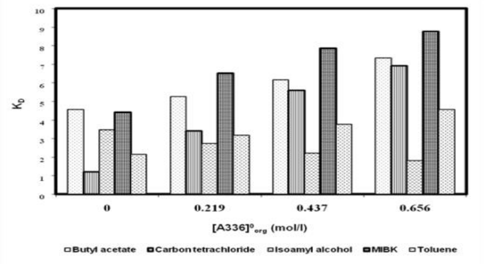

Fig.1 The effect of extractant concentration on distribution coefficients; $[HA]^{initial}_{aq}$ = 0.05 mol/l

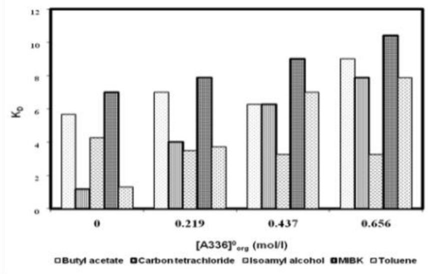

Fig. 2 The effect of extractant concentration on distribution coefficients; $[HA]^{initial}_{aq}$ =0.2mol/l

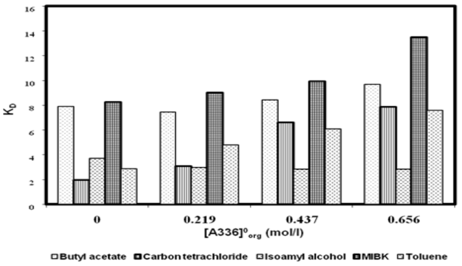

Fig. 3 The effect of extractant concentration on distribution coefficients; $[HA]^{initial}_{aq}$ = 0.6 mol/l

Table 1.Theproperties of diluents [8]

Diluent	Molar Mass (g/mol)	Solubility in water (wt %)	Dipole Moment (Debye unit)	Source	Initial Purity (%)
Butyl acetate	116.2	0.68	1.84	Merck	98.0
Carbon tetrachloride	153.8	0.077	0.00	Loba Chemie	98.0
Isoamyl alcohol	88.2	2.97	1.82	Molychem	99.0
Methyl isobutyl ketone	100.2	1.7	2.70	Merck	99.0
Toluene	92.1	0.0515	0.31	Loba Chemie	99.5

Table 2.The solvatochromic parameters of the diluents [10]

Diluent	π^*	δ	β	α
Butyl acetate	0.46	0.0	0.45	0.00
Carbon tetrachloride	0.21	0.5	0.10	0.00
Isoamyl alcohol	0.40	0.0	0.84	0.84
MIBK	0.51	0.0	0.12	0.00
Toluene	0.49	1.0	0.11	0.00

Table 3.Theoverview of the acid/extractant/diluent systems used for LSER modelling

Acid	Initial acid concentration	Extractant	Diluent	Ref. No.
Succinic acid	0.6 mol/l	Tridodecyl amine	1–octanol, 2–octanone	11
Picric acid	14 gm/l	Trioctyl amine	Isoamyl alcohol, octan-1-ol, decan-1-ol	12
Propionic acid	0.05 – 0.4 mol/l	Aliquat 336	2–octanol	13
Propionic acid	0.05 – 0.4 mol/l	Aliquat 336	MIBK	14
Levulinic acid	1.17 mol/l	Tripropyl amine	Toluene	15
Citric acid	0.42 mol/l	Aliquat 336	2–octanol, 2–propanol	16
Propionic acid	1.17 mol/l	Alamine 336	Toluene	17

The results predicted by the model are compared with the experimental findings of physical and reactive extraction (Table 4). It can be seen that there is a good description of the distribution of methacrylic acid (between aqueous and organic phase) using LSER model.

Thus, the LSER model successfully predicts the equilibrium behaviour of methacrylic acid extraction using A336 in various diluents. Among all the diluents used in the current study, the maximum resemblance (between the experimental observations and model predictions) is obtained in case of the isoamyl alcohol. The model parameter equations, along with the coefficient of linear regression R2 and standard error, are presented in Table 5.

Table 4.Theresults of thereactive extraction of methacrylic acid; $[HA]_{aq}^{initial}$ = 0.05 mol/l.

Solvent	Initial Conc. of amine (mol/l)	Acid Conc. in organic phase (mol/l)	K_D^{exp}	K_D^{model}	Z_t
A336 + n–Butyl acetate	0.000	0.041	4.56	4.37	–
	0.219	0.042	5.25	5.32	0.192
	0.437	0.043	6.14	6.38	0.098
	0.656	0.044	7.33	7.53	0.067
A336 + Carbon tetrachloride	0.000	0.020	1.20	1.66	–
	0.219	0.039	3.39	3.05	0.177
	0.437	0.042	5.58	4.16	0.097
	0.656	0.044	6.90	5.62	0.067
A336 + Isoamyl alcohol	0.000	0.039	3.47	3.47	–
	0.219	0.036	2.72	2.72	0.167
	0.437	0.034	2.19	2.19	0.078
	0.656	0.032	1.79	1.79	0.048
A336 + MIBK	0.000	0.040	4.42	4.58	–
	0.219	0.043	6.50	6.43	0.198
	0.437	0.044	7.86	7.61	0.101
	0.656	0.045	8.75	8.55	0.068
A336 + Toluene	0.000	0.034	2.15	1.82	–
	0.219	0.038	3.17	3.33	0.174
	0.437	0.039	3.76	4.36	0.090
	0.656	0.041	4.56	5.05	0.062

Table 5.TheLSER Model equations for the physical and reactive extraction of methacrylic acid; $[\mathrm{HA}]_{\mathrm{aq}}^{\mathrm{initial}}$ = 0.05 mol/l.

A336 concentration (mol/l)	Model equations	R^2	Standard Error
0.000	$\ln K_D = -0.535 + 1.902(\pi^* - 0.883\delta) + 0.144\beta - 0.205\alpha$	0.89	0.40
0.219	$\ln K_D = 1.161 + 1.453(\pi^* - 0.630\delta) - 0.351\beta + 0.531\alpha$	0.98	0.13
0.437	$\ln K_D = 1.493 + 1.138(\pi^* - 0.539\delta) - 0.363\beta - 1.023\alpha$	0.88	0.36
0.656	$\ln K_D = 1.900 + 0.555(\pi^* - 0.519\delta) - 0.302\beta - 1.529\alpha$	0.96	0.25

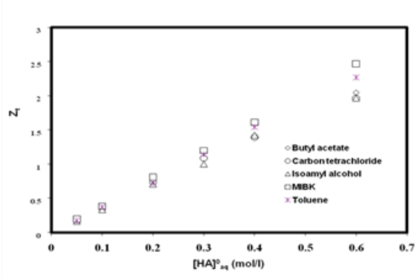

Fig.4 The plot of loading ratio vs. initial acid concentration; $[\mathrm{A336}]^0_{\mathrm{org}} = 0.22$ mol/l

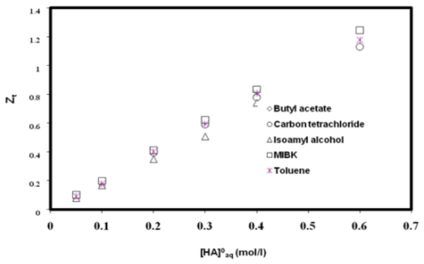

Fig.5 The plot of loading ratio vs. initial acid concentration; $[\mathrm{A336}]^0_{\mathrm{org}} = 0.44$ mol/l

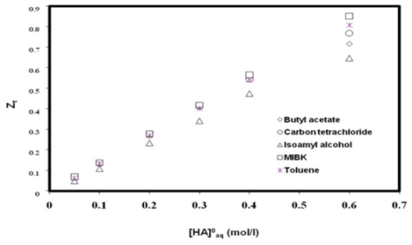

Fig. 6 Plot of loading ratio vs. initial acid concentration; $[\mathrm{A336}]^0_{\mathrm{org}} = 0.66$ mol/l

4. Conclusion

The reactive extraction allows effective removal of methacrylic acid from the aqueous phase. The effectiveness of this technique depends on the concentration of acid in the initial aqueous phase, type and concentration of extractant, and the type of diluent used.

The loading ratios for most of the extractions are found to be less than one, though high loadings are obtained for high initial acid concentration in aqueous phase. The studies carried out with model solutions of acid (at ambient temperature, about 303 K) and the correlation obtained with solvatochromic parameters of the diluents according to the Linear Solvation Energy Relationship (LSER) can be used to estimate the extractability of methacrylic acid for a wide range of diluents or their mixtures.

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