4.2 Extraction of citric acid using Aliquat 336 in natural diluents

Acid concentration was varied from 0.1 to 0.8 mol/l for Aliquat 336 concentration of 0.22, 0.44 and 0.66 mol/l in different diluents. Figure (2) shows the effect of acid concentration on the extractability by Aliquat 336 in sunflower oil. Similar plot have been obtained for other natural diluents. For extraction of citric acid using Aliquat 336 in different diluents, K_D was found to decrease with increase in acid concentration; however the decrease was marginal for lower concentrations of acid 0.1-0.4 mol/l whereas for higher acid concentration (0.6 and 0.8 mol/l) the decrease was great. Thus reactive extraction is more successful in separation of acid from dilute solutions. Initially as the acid shall be produced in the bioreactor, its concentration shall be low and hence the success of using reactive extraction technology for acid separation is justified.

Among the various diluents used, better solvation of Aliquat 336-acid complexes were found in the case of soya-bean oil with E% as high as 51.81%. The trend of extractability of the acid using Aliquat 336 in various diluent is as: soya-bean oil ($E\%_{Bo=0.22}$ = 31.41-11.39%; $E\%_{Bo=0.44}$ = 42.18-18.33%; $E\%_{Bo=0.66}$=51.81-25.83%) >sunflower oil($E\%_{Bo=0.22}$ = 27.97-12.58%; $E\%_{Bo=0.44}$ =43.61-18.85%; $E\%_{Bo=0..66}$=49.75-25.65)>sesame oil ($E\%_{Bo=0.22}$ = 21.02-5.77; $E\%_{Bo=0.44}$ = 35.73-11.22%; $E\%_{Bo=0.66}$=45.53-14.49)>rice bran oil ($E\%_{Bo=0.22}$ = 17.73-10.12%; $E\%_{Bo=0.44}$ = 34.83-18.76%; $E\%_{Bo=0.66}$=45.51-23.74). Thus it could be suggested that Soya–bean and sunflower oil are better solvents for reactive extraction of citric using Aliquat 336.

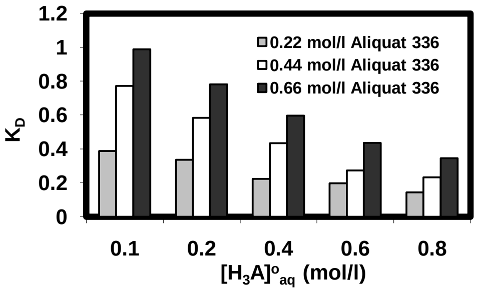
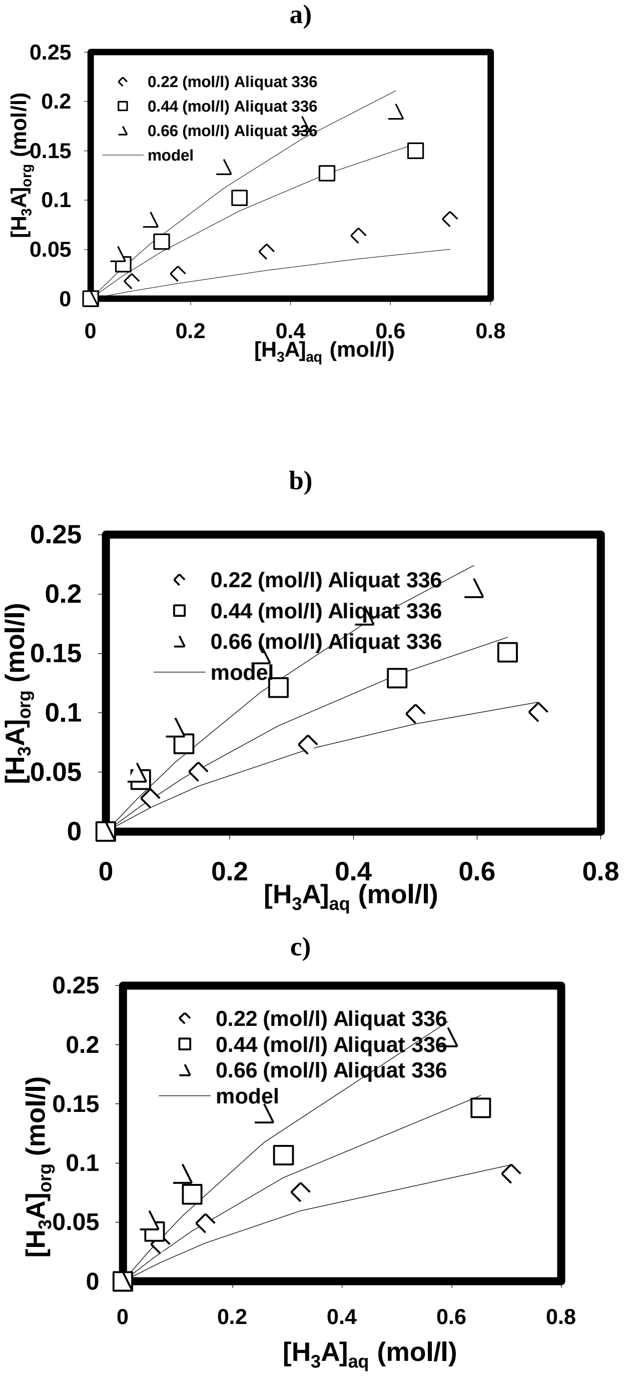


Figure 2: Effect of acid and Aliquat 336 concentration on the reactive extraction of citric acid using Aliquat 336 in sunflower oil

Figure (3) shows the equilibrium curves showing the effect of Aliquat 336 concentration on the extractability of acid. Aliquat 336 was employed in four different diluents; rice bran oil, sunflower oil, soya–bean oil, sesame oil, respectively. It could be easily seen that in all the diluents employed, higher is the percentage of Aliquat 336, higher in the extraction obtained at all the acid concentration studied (0.1–0.8 mol/l). This suggests that it shall be better to use higher percentage of Aliquat 336. The average increase in K_D values when Aliquat 336 concentration was increased from 0.22 to 0.44 mol/l was 63%, 47%, 47%, 61% for when rice bran oil, sunflower oil, soya-bean oil, sesame oil was used as diluents, respectively. However, since extraction of citric acid is mostly to be done from bioreactor, where the problem of toxicity is of major concern, it is preferable to use extractant is low concentrations. Further, Aliquat 336 is highly viscous (μ = 1500 Pa.s at 30 °C) so in any case its volume percentage above 30 % could create problems of three phase formation in inert diluents. So in the present study only volume percentages of 10 to 30% were employed. In some cases where the three phase formation was encountered, the two phases were separated by centrifugation at 10,000 rpm for 10 minutes.



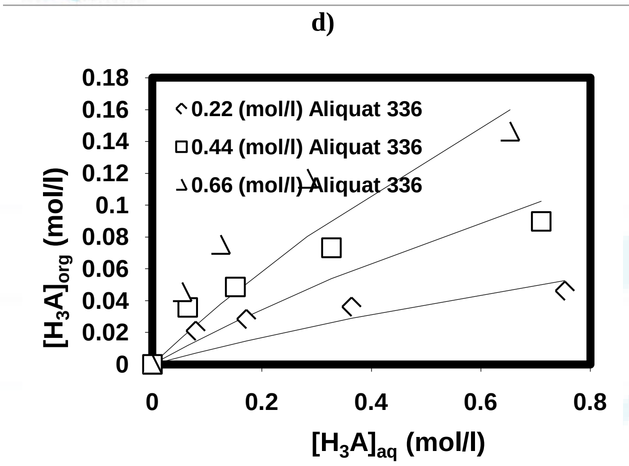


Figure 3: Equilibrium curves for reactive extraction of citric acid (0.1-0.8 mol/l) using Aliquat 336 (10-30%) a) rice bran oil, b) sunflower oil, c) soyabeen oil and d) sesame oil, respectively

Experiments involving 30% Aliquat 336 concentration and lower acid concentrations provided the highest degree of extractions. This extraction could have raised the pH of the solution. So even if excess amount of Aliquat 336 is present it would have gone without recovering anything and hence additions cost would have to be faced for recycling this Aliquat 336 back to the broth. So it is optimum to use 30 % Aliquat 336. This is also justified in view of the problem of toxicity it could raise. Further it has been mentioned that distribution coefficient of acid using various concentration of amine goes through a maxima [12, 13]. The reason for this being that Aliquat 336 in alone is a relatively poor solvation media for the complexes.

Citric acid is a tri-carboxylic acid and has the tendency to interact with 1-3 extractant molecules. In some cases however a single extractant molecule can complex with more than one acid molecule or form aggregates and hence could result in higher loading ratio values. If z>0.5, it is expected that extractant exhibits higher acid-amine complexations such as 1:2 or 1:3, whereas if it is low only 1:1 complexations dominates. Solid lines in Figure (4) show the model values of the data. It can be seen that in the extraction of citric acid using Aliquat 336 in rice bran oil and sunflower oil there has been a good fit of experimental data by the model values.

Figure (5) represents the loading curves for extraction of citric acid using Aliquat 336 in various diluents respectively. In most of the cases loading was lower than 0.5, hence suggesting that the association is 1:1.

4.3 Equilibrium complexation constant using law of mass action modeling

Equilibrium complexation constant (K_E) determine the complexation ability of a particular extractant. Since solvation is the major criterion that decides the amount of acid extracted with the particular extractant, K_E shall be the deciding parameter for choosing a particular diluent with the extractant. There are three types of K_E values:

i) Overall complexation constant for reactive extraction using Aliquat 336 in natural diluents

Plot of Eq. (4) i.e. the plot of log K_D versus amine concentration could predict the number of molecules of Aliquat 336 associated with one molecule of solute and equilibrium complexation constant value. A good fit of Eq. (4) gives a good fit of the experimental data, still the values of stoichiometric complexation constant (m) has been found to be negative, suggesting that more than one Aliquat 336 complexes with the acid molecule. K_E values were found to be 1.41, 2.36, 3.29 and 1.84, 3.78, 3.44 and 3.12, 3.97, 3.86 and 10.88, 9.45, 0.97 for Aliquat 336 in rice bran oil, sunflower oil, soya-bean oil, sesame oil for 10%, 20%, 30%, respectively.

ii) From loading ratio considering 1:1 complexation for reactive extraction using Aliquat 336 in natural diluents

Kertes et al., [3] predicted that the plot of z/(1–z) against acid concentration in the aqueous phase could predict the equilibrium complexation constant value for (1:1) complexation provided loading ratio value (z) is less than 0.5. In the studies on natural diluents, z values were less than 0.5 and hence on 1:1 complexation are dominating. K_E(1:1) values for reactive extraction of citric acid using Aliquat 336 in rice bran oil, sunflower oil, soya-bean oil, sesame oil were found to be 0.796, 1.4, 1.147, 0.416 and 0.854, 0.910, 0.852, 0.427 and 0.77, 0.86, 0.842, 0.489 l/mol for 10%, 20% and 30% extractant in diluent respectively. Solid lines in Figure 3 were drawn by using these model values.

4.4 Differential Evolution Modeling

Global optimization is necessary in field of engineering. For problems, such as non-differentiable, non-linear, multi-dimensional or have many local minima, which are difficult to solved mathematically optimization technique can be really useful. Differential Evolution (DE) is a population based optimization technique that tries to improve solutions of a given objective function with respect to given measure of quality. It is based on Genetic Evolution methodology in which Global optimum is determined.

Population of points within the range of the function to be maximized or minimized is used to search for the optimum. Assume P_n= size of population and D = Dimension of population. Target vector is selected from one out of these P_n vectors. Two other vectors from the same population are selected at random and their difference is evaluated, this difference is vectorial in nature. Weight factor ‘W’ which is specified initially is then multiplied to this difference and result is added to a third vector which is again randomly selected. The result is called noisy random vector. Then Crossover is done between target vector and noisy random vector and the result is called trial vector. Both trial vector and noisy random vector is evaluated for objective function and the winner is replaced by the other one in the population. This process is carried on till a sufficient convergence criterion is obtained [14–18].

Steps performed while exercising Differential evolution is explained below with the help of Figure (19) [18]

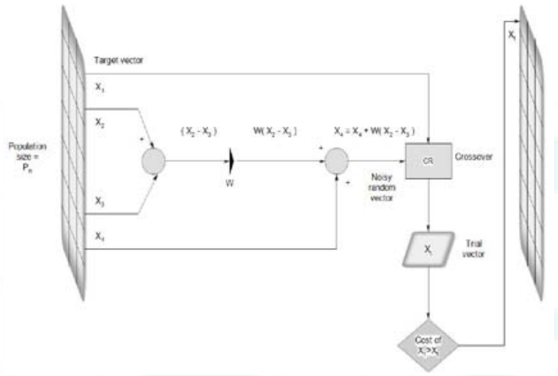


Figure 7: Steps performed while exercising Differential evolution

Table 1 shows the value of model parameters (a, b and K_E) along with the model K_D values. The experimental K_D and model K_D shows slight deviation (less than 5%) in all cases. Thus differential evolution modeling approach could successfully evaluate the model values.

5. Conclusion

Experimental and modeling approach was followed to find the equilibrium and kinetic data for reactive extraction of citric acid using Aliquat 336 in various diluents. Chemical extraction using Aliquat 336 was studied for acid concentration in the range of 0.1-0.8 mol/l in natural diluents (sunflower oil, soya-bean oil, rice bran oil and sesame oil, respectively). K_D was found to decrease with increase in acid concentration. Better solvation of Aliquat 336-acid complexes were found in the case of soya-bean oil with E% as high as 51.81%. In all the diluents employed, higher is the percentage of Aliquat 336, higher is the extraction obtained at all the acid concentrations studied. In most of the cases loading was lower than 0.5, hence suggesting that the association is 1:1. Equilibrium complexation constant was obtained using mass action law equilibria modeling. K_E values were found to be 1.41, 2.36, 3.29 and 1.84, 3.78, 3.44 and 3.12, 3.97, 3.86 and 10.88, 9.45, 0.97 for Aliquat 336 in rice bran oil, sunflower oil, soya-bean oil, sesame oil for 10%, 20%, 30%, respectively. 1:1 equilibrium complexation constant was also evaluated using theory and K_E values were reported. Algorithm for differential evolution modeling was generated and the approach was used to model the K_E and stoichiometric association constant values. Though the use of natural diluents makes the process of reactive extraction environment-friendly; however, there is a scope to explore this field at different isothermal conditions with binary extractants and/or diluents to estimate the parameters which can intensify the process.

Table 1: Differential evolution model parameters and comparison of model K_D obtained with the experimental K_D

$[H_3A]_o$	$[B]_o$	*Diluent*	*Model Parameters*				K_D^{exp}
			a	b	K_E	K_D	
0.1	0.22	rice bran oil	0.99	1.1	1.10	0.20	0.22
0.2			0.94	1.0	0.78	0.13	0.14
0.4			0.99	1.1	0.83	0.13	0.14
0.6			0.55	1.2	0.82	0.11	0.12
0.8			0.39	1.2	0.97	0.11	0.11
0.1	0.44		0.97	1.5	1.31	0.50	0.53
0.2			0.89	1.5	1.08	0.40	0.41
0.4			0.90	1.6	1.31	0.33	0.34
0.6			0.94	1.6	1.36	0.24	0.27
0.8			0.34	1.4	0.80	0.19	0.23
0.1	0.66		0.98	1.2	0.80	0.84	0.84
0.2			1.00	1.9	1.16	0.64	0.67
0.4			-	1.6	0.96	0.50	0.5
0.6			1.00	1.5	0.82	0.38	0.42
0.8			0.94	1.4	0.68	0.30	0.31
0.1	0.22	sunflower oil	0.99	1.2	2.12	0.40	0.39
0.2			1.00	1.2	2.20	0.34	0.34
0.4			0.94	1.1	1.49	0.22	0.22
0.6			0.73	1.1	1.72	0.20	0.2
0.8			0.86	1.2	1.59	0.13	0.14
0.1	0.44		1.00	1.6	1.97	0.76	0.77
0.2			0.99	1.5	1.65	0.52	0.58
0.4			0.95	1.6	1.80	0.40	0.43
0.6			0.59	1.5	1.03	0.26	0.27
0.8			0.73	1.2	0.80	0.23	0.23
0.1	0.66		1.00	2.4	1.64	0.97	0.99
0.2			0.98	2.3	1.53	0.76	0.78
0.4			0.62	2.4	1.23	0.52	0.6
0.6			1.00	1.8	1.12	0.42	0.44
0.8			0.72	1.5	0.77	0.31	0.35
0.1	0.22	soya-bean oil	1.00	1.2	2.46	0.44	0.46
0.4			0.87	1.2	1.78	0.23	0.23
0.8			0.74	1.2	1.06	0.10	0.13
0.1	0.44		0.99	1.6	1.89	0.69	0.73
0.2			0.93	1.6	1.64	0.56	0.58
0.4			0.92	1.3	1.08	0.33	0.36
0.8			0.76	1.2	0.75	0.22	0.22
0.1	0.66		1.00	2.5	1.77	1.06	1.08
0.2			1.00	2.1	1.50	0.80	0.84
0.4			0.91	1.9	1.10	0.48	0.55
0.8			-	1.5	0.80	0.33	0.35
0.1	0.22	sesame oil	0.97	1.2	1.40	0.25	0.27
0.2			1.00	1.2	1.83	0.15	0.17
0.4			0.93	1.1	0.60	0.09	0.1
0.8			0.72	1.1	0.35	0.05	0.06
0.1	0.44		0.94	1.6	1.39	0.52	0.56
0.2			0.95	1.6	1.06	0.31	0.32
0.4			0.88	1.6	0.77	0.20	0.22
0.8			0.75	1.2	0.37	0.12	0.13
0.1	0.66		0.98	2.4	1.43	0.83	0.84
0.2			0.91	2.2	1.07	0.57	0.6
0.4			1.00	1.6	0.77	0.39	0.42
0.8			0.94	1.4	0.34	0.16	0.17

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