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Extraction Equilibrium of Monocarboxylic Acids in Aqueous Solution by Using Tributyl Phosphate in Dodecane

Bhupesh C. Roy, M. J. Alam and M. Goto

Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto City 860-9555, Japan

Abstract: Liquid-liquid extraction based on reversible chemical complexation is an efficient separation technique that is highly effective and selective for separating polar organic acids (monocarboxylic acids) from their aqueous medium. Extraction equilibria of aqueous solutions of monocarboxylic acids such as acetic acid, propionic acid and butyric acid with Tri-n-butyl phosphate (TBP) in dodecane were measured at the temperature $(20 \pm 1)^\circ\text{C}$ under various concentrations of acids, extractant (TBP) and also with the variation of organic/aqueous phase ratio. An expression for the extraction equilibrium was derived by which the extraction equilibrium constant (K_e) as well as the number of apparent reacting molecules of extractant (n) were evaluated. From the experimental data it was observed that the estimated values of extraction equilibrium constant (K_e) and the apparent number of extractant molecules reacting with one molecule of each acid dependent on the organic phase composition as well as on the concentration of aqueous phase, due to which each acid gave different extraction isotherms.

Key words: Extractant, diluent, monocarboxylic acids, extraction equilibrium constant, distribution coefficient

INTRODUCTION

Many separation processes in chemical industries utilize a reactive extraction system. A reactive extraction process, which exploits reversible chemical complexation in the extractant phase, provides an effective separation, especially relatively dilute solutions, such as the aqueous solution of carboxylic acids in a fermentation broth^[1]. The pharmaceutical, food and biotechnology industries abound with examples where there is a need to remove organic acids from aqueous effluents.

Solvent extraction have received attention for the recovery of carboxylic acids from dilute aqueous solutions, especially with hydrophobic tertiary amines dissolved in various inert and active diluents^[2,3]. The solutions of long-chain tertiary amine, such as Trioctylamine (TOA) and organophosphorous compound, such as Tri-n-butyl Phosphate (TBP) in diluents, such as alkane, alcohol, ketone and chloroform are very effective extractants for the extraction of carboxylic acids^[4-6]. The specific chemical interactions among the amines and acids molecules to form acid-amine complexes in the extractant phase allow more acid to be extracted from the aqueous phase^[7]. The formation of acid-amine complexes depend on the nature of diluents, which affect the basicity of the amine and stability of the ion-pair association in the extractant phase and these diluents may be hydrogen bond with the oxygen accessible on the carboxylic acid.

Several factors have an important influence on the extraction characteristics, such as the nature of the acid extracted, the concentration of the aqueous phase, the compositions of the acid and the extractant and the type of diluent used. The effect of the concentration of tributyl phosphate in hexane on the extraction constant for butyric acid was investigated^[8]. The extraction constant for several monocarboxylic acids with trioctylphosphine oxide in hexane was determined and it was concluded that the number of carboxylic groups and the extraction equilibrium were controlled by the hydrophobicity of the acids, not by the P^{K_a} value^[6].

The extractants are dissolved in different types of diluents, which influence the distribution of acids between the coexisting phases in equilibrium. Owing to separation of organic acids, it is very important to understand the effect of different parameters on the overall distribution coefficient of each organic acid. For the evaluation of distribution coefficient, it is necessary to know the values of extraction constant as well as the number of reacting molecules of extractants. Extraction constant and the number of reacting molecules of extractant are computed by applying Law of Mass Action that is the ratio between concentrations of reactant molecules and concentrations of the product species, according to the general equation of interaction between the extractant and the extracted substances.

In this study, monocarboxylic acids (acetic acid, propionic acid and butyric acid) was extracted from its aqueous phase of various concentrations by using Tri-n-butyl Phosphate (TBP) as solvent with dodecane (diluent) at various phase ratios of organic to aqueous phase as well as different concentrations of TBP in order to study their influence on the equilibrium extraction constant.

MATERIALS AND METHODS

All the chemicals used in this study were of laboratory reagent grade and the experiment was conducted in April to June, 2005. Monocarboxylic acids such as acetic acid (99.7%), propionic acid (99%) and butyric acid (90%) were provided by wako chemical Ltd, Japan, used without any other treatment to prepare the aqueous phase, (V) of each with distilled water of various pH values and concentrations. The concentrations were comprised between 0.025 and 0.25 mol L⁻¹. Dodecane (99%) was used as diluent and Tri-n-butyl Phosphate (TBP) was used as extractant without further any treatment. The organic phase, (\bar{V}) was prepared with TBP in dodecane of 4 different concentrations as 0.368, 1.104, 1.84 and 2.94 mol L⁻¹.

All experiments were carried out at the constant temperature of (20±1)°C. About 40 mL of organic phase of known concentration and the same volume of aqueous phase of known pH were taken in a 150 mL separating funnel and shaken for about 30 min by an electric shaker and then was left to equilibrate for 1 h to separate the two phases. The reproducibility of the equilibrium time was ensured by repeating the same experiments by using different shaking time as well as settled time of the two phases.

After separation of two phases, pH of aqueous phase and volumes of the two phases were measured. The pH measurement was conducted by compact pH -meter, B-212. The pH meter was standardized against standard solutions at pH 4 and 7.

Aqueous phases of each monocarboxylic acids were prepared in four different concentrations. For conducting each run, three different phase ratios between organic phase and aqueous phase (\bar{V}/V) such as 1:1, 3:1 and 5:1 and four different concentrations of TBP in dodecane such as 0.368, 1.104, 1.84 and 2.94 mol L⁻¹ were used.

The equilibrium concentration of monocarboxylic acid in the aqueous phase, [HA] was determined by High-Performance Liquid Chromatography (HPLC) using a column Inertsil ODS-3V, 5 M (150×4.6 mm), 0.02 M K₃(PO₄) buffer of pH 3.0 as mobile phase and a spectra of UV-vis detector at 210 nm wavelength. Monocarboxylic acid concentration in organic phase at equilibrium, $\overline{[HA]}$ was calculated by the following mass balance equation:

$$V_{init} C_{init} - VC = \overline{VC} \tag{1}$$

Where, the volume and the concentration of the phases are represented by V and C, respectively. Subscript init. refers to the initial condition, without any subscript refers aqueous phase and an overbar for organic phase.

After knowing the equilibrium concentrations of monocarboxylic acid in both aqueous and organic phases, the equilibrium distribution coefficient, K_D was calculated by using the following equation:

$$K_D = \frac{\overline{[HA]}}{[HA]} \tag{2}$$

Where, $\overline{[HA]}$ and [HA] are equilibrium concentrations of studied acids in organic (extractant) phase and aqueous phase, respectively.

RESULTS AND DISCUSSION

The equilibrium concentrations of reactive liquid-liquid extraction of monocarboxylic acids from its aqueous solutions by using organic extractant n-tributyl phosphate (TBP) with diluent (dodecane) were investigated. The equilibrium isotherms of each acid were determined for four different aqueous solution concentrations of organic acids, four concentrations of TBP dissolved in dodecane and three volume ratios (1, 3 and 5) of organic phase to aqueous phase, \bar{V} . The experimental equilibrium concentrations of acids [HA] of liquid-liquid equilibrium for acetic acid, propionic acid and butyric acid are shown in Table 1-3, respectively.

Extraction equilibrium isotherms of acetic acid at different concentrations of TBP in dodecane is represented by Fig. 1 that revealed that the overall distribution coefficient (the ratio of the equilibrium concentration of extracted acid in organic phase to that in the aqueous phase) increased with increase in

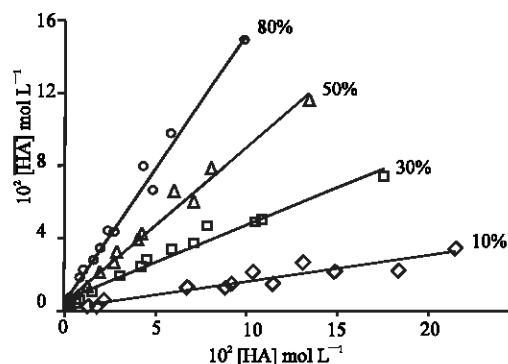


Fig. 1: Extraction equilibrium isotherms of acetic acid for different volume ratios of TBP in dodecane

Table 1: Equilibrium concentration, [HA] of liquid-liquid equilibrium for acetic acid using TBP in dodecane at 20±1 °C

\bar{V}/V	[TBP]	V_{TBP}/V	[HA] _{mit} = 0.025, pH = 2.92			[HA] _{mit} = 0.125, pH = 2.78		
			10 ² [HA]	10 ¹ [HA]	K _D	10 ² [HA]	10 ¹ [HA]	K _D
1/1	0.368	0.1	2.1	0.56	0.267	10.4	2.19	0.210
	1.104	0.3	1.5	1.07	0.713	7.91	4.66	0.59
	1.84	0.5	1.17	1.40	1.197	6.0	6.57	1.095
	2.94	0.8	0.85	1.78	2.094	4.39	7.94	1.81
3/1	0.368	0.1	1.76	0.276	0.157	8.85	1.25	0.141
	1.104	0.3	0.855	0.585	0.684	4.53	2.73	0.60
	1.84	0.5	0.551	0.675	1.22	2.80	3.25	1.16
	2.95	0.8	0.372	0.715	1.92	1.93	3.45	1.795/1
	0.368	0.1	1.29	0.272	0.21	6.70	1.26	0.186
	1.104	0.3	0.62	0.399	0.643	3.11	1.93	0.62
	1.84	0.5	0.367	0.442	1.21	1.87	2.14	1.14
	2.95	0.8	0.21	0.458	2.18	1.06	2.23	2.10
\bar{V}/V	[TBP]	V_{TBP}/V	[HA] _{mit} = 0.16, pH = 2.57			[HA] _{mit} = 0.25, pH = 2.45		
			10 ² [HA]	10 ¹ [HA]	K _D	10 ² [HA]	10 ¹ [HA]	K _D
1/1	0.368	0.1	13.10	2.68	0.205	21.53	3.40	0.158
	1.104	0.3	10.88	4.98	0.458	17.56	7.39	0.421
	1.84	0.5	8.05	7.81	0.97	13.40	11.58	0.864
	2.94	0.8	5.90	9.72	1.65	9.95	14.84	1.491
3/1	0.368	0.1	11.48	1.46	0.217	18.32	2.25	0.123
	1.104	0.3	5.93	3.37	0.568	10.53	4.92	0.467
	1.84	0.5	4.02	3.96	0.985	7.14	6.01	0.842
	2.95	0.8	2.71	4.30	1.59	4.90	6.61	1.349
5/1	0.368	0.1	9.15	1.45	0.158	14.87	2.19	0.147
	1.104	0.3	4.23	2.38	0.563	7.14	3.68	0.515
	1.84	0.5	2.65	2.65	1.00	4.20	4.18	0.995
	2.95	0.8	1.60	2.78	1.74	2.40	4.39	1.830

All concentrations [] are in mol L⁻¹

Table 2: Equilibrium concentration, [HA] of liquid-liquid equilibrium for propionic acid using TBP in dodecane at 20±1 °C

\bar{V}/V	[TBP]	V_{TBP}/V	[HA] _{mit} = 0.081, pH = 2.92			[HA] _{mit} = 0.125, pH = 2.82		
			10 ² [HA]	10 ¹ [HA]	K _D	10 ² [HA]	10 ¹ [HA]	K _D
1/1	0.368	0.1	4.43	4.13	0.932	6.94	5.82	0.838
	1.104	0.3	2.93	5.63	1.921	4.97	7.79	1.567
	1.84	0.5	1.65	6.90	4.182	2.64	10.20	3.863
	2.94	0.8	0.795	7.12	8.956	1.28	10.6	8.281
3/1	0.368	0.1	2.07	2.16	1.043	3.53	3.08	0.872
	1.104	0.3	0.912	2.53	2.774	1.64	3.67	2.237
	1.84	0.5	0.503	2.62	5.209	0.78	3.90	5.00
	2.95	0.8	0.246	2.63	10.69	0.42	3.90	9.285
5/1	0.368	0.1	1.40	1.43	1.021	2.12	2.13	1.005
	1.104	0.3	0.463	1.58	3.412	0.83	2.32	2.795
	1.84	0.5	0.288	1.59	5.521	0.46	2.37	5.152
	2.95	0.8	0.150	1.57	10.46	0.25	2.35	9.40
\bar{V}/V	[TBP]	V_{TBP}/V	[HA] _{mit} = 0.162, pH = 2.75			[HA] _{mit} = 0.241, pH = 2.72		
			10 ² [HA]	10 ¹ [HA]	K _D	10 ² [HA]	10 ¹ [HA]	K _D
1/1	0.368	0.1	9.59	7.01	0.731	14.99	10.10	0.673
	1.104	0.3	7.12	9.47	1.33	12.30	12.72	1.034
	1.84	0.5	3.88	12.7	3.273	6.55	18.51	2.826
	2.94	0.8	1.72	13.8	8.023	2.71	20.52	7.572
3/1	0.368	0.1	4.74	3.95	0.833	7.07	6.01	0.850
	1.104	0.3	2.38	4.70	1.974	4.52	6.82	1.509
	1.84	0.5	1.08	5.04	4.666	1.81	7.57	4.182
	2.95	0.8	0.584	5.05	8.647	0.94	7.61	8.096
5/1	0.368	0.1	2.76	2.77	1.003	4.20	4.18	0.995
	1.104	0.3	2.73	2.78	1.018	2.73	4.42	1.619
	1.84	0.5	0.65	3.07	4.723	1.12	4.62	4.125
	2.95	0.8	0.33	3.03	9.182	0.54	4.60	8.518

concentration of extractant, TBP. Isotherms of all studied acids at a constant concentration of TBP in dodecane (1.84 mol L⁻¹ or 1:1 vol %) is indicated by Fig. 2. From

Fig. 2, it was observed that the distribution coefficients were different to different acids in such an order as: butyric acid>propionic acid>acetic acid. This result

Table 3: Equilibrium concentration, [HA] of liquid-liquid equilibrium for butyric acid using TBP in dodecane at 20±1°C

\bar{V}/V	[TBP]	V_{TBP}/V	[HA] _{init} = 0.081, pH = 3.031			[HA] _{init} = 0.119, pH = 2.91		
			10^2 [HA]	10^1 [HA]	K_D	10^2 [HA]	10^1 [HA]	K_D
1/1	0.368	0.1	2.40	5.54	2.308	3.73	7.95	2.131
	1.104	0.3	0.932	7.16	7.68	1.42	10.25	7.218
	1.84	0.5	0.53	7.00	13.20	0.80	10.62	13.27
	2.94	0.8	0.34	7.16	21.06	0.49	10.52	21.47
3/1	0.368	0.1	0.813	2.38	2.927	1.305	3.47	2.659
	1.104	0.3	0.29	2.50	8.620	0.468	3.672	7.846
	1.84	0.5	0.176	2.52	14.32	0.259	3.74	14.44
	2.95	0.8	0.112	2.50	22.32	0.187	3.61	19.30
5/1	0.368	0.1	0.485	1.47	3.031	0.813	2.17	2.67
	1.104	0.3	0.155	1.54	9.935	0.275	2.25	8.181
	1.84	0.5	0.099	1.54	15.55	0.175	2.26	12.91
	2.95	0.8	0.063	1.49	23.65	0.101	2.18	21.58
			[HA] _{init} = 0.162, pH = 2.75			[HA] _{init} = 0.0241, pH = 2.72		
\bar{V}/V	[TBP]	V_{TBP}/V	10^2 [HA]	10^1 [HA]	K_D	10^2 [HA]	10^1 [HA]	K_D
1/1	0.368	0.1	5.18	10.98	2.12	9.02	13.56	1.503
	1.104	0.3	1.975	14.01	7.093	2.97	19.64	6.612
	1.84	0.5	1.101	14.14	12.84	1.75	20.21	11.55
	2.94	0.8	0.773	14.48	18.73	1.12	20.22	18.05
3/1	0.368	0.1	1.85	4.74	2.562	3.21	6.45	2.01
	1.104	0.3	0.693	5.06	7.301	1.10	7.161	6.51
	1.84	0.5	0.375	5.13	13.68	0.596	7.25	12.16
	2.95	0.8	0.272	4.96	18.23	0.421	7.165	17.02
5/1	0.368	0.1	1.13	2.98	2.637	1.868	4.12	2.205
	1.104	0.3	0.354	3.07	8.672	0.587	4.33	7.376
	1.84	0.5	0.225	3.08	13.69	0.365	4.34	11.89
	2.95	0.8	0.143	2.98	20.84	0.235	4.18	17.79

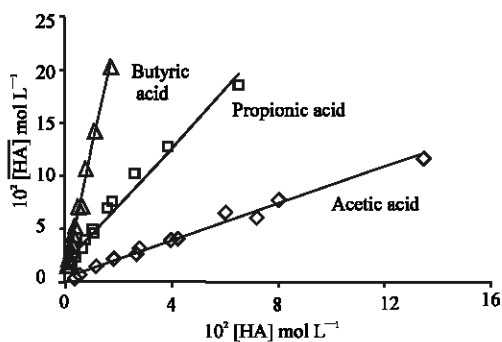


Fig. 2: Extraction equilibrium isotherms of studied acids with TBP in dodecane at the volume ratio 1:1

indicated the best possibility to use this solvent for the separation of specific organic acids from its dilute aqueous phase.

The experiment for the equilibrium extraction isotherms of studied monocarboxylic acids of various concentrations at various volume phase ratios of organic to aqueous phase was conducted with TBP in order to study the effect of initial acid concentration, [HA]_{init}, the concentration of extractant in dodecane [TBP] as well as of volume phase ratio \bar{V}/V on the equilibrium concentrations, K_D . This effect was shown in Fig. 3a and b for the initial concentration of propionic acid in aqueous phase 0.241 and 0.125 mol L⁻¹, respectively. The data revealed that the equilibrium concentrations varied with

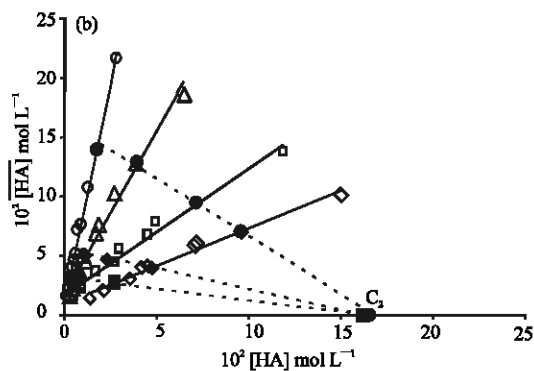
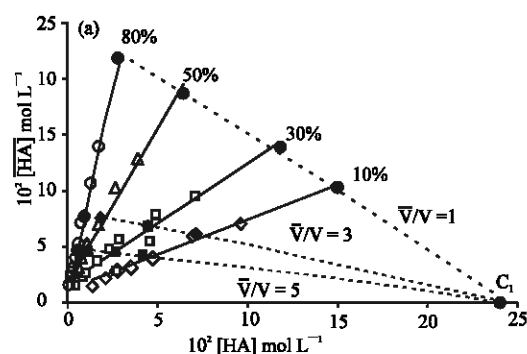


Fig. 3: Extraction equilibrium isotherms of propionic acid versus the initial acid concentration (a) $C_1 = 0.241$ and (b) $C_2 = 0.125$ mol L⁻¹ with the volume phase ratio of organic to aqueous ($\bar{V}/V = 1, 3, 5$)

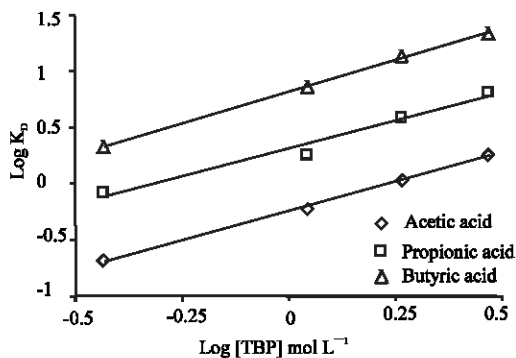


Fig. 4: Estimation of extraction equilibrium constant (K_e) and apparent number of reacting molecules (n) at the acid concentration of 0.125 mol L^{-1}

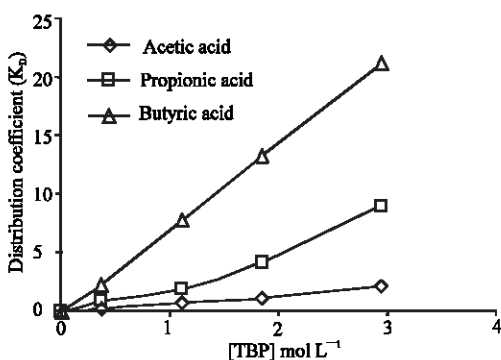


Fig. 5: Effect of concentration of TBP on distribution coefficient of these studied acids

the variation of acid concentrations as well as with the volume phase ratio of organic to aqueous (\bar{V}/V).

The values of equilibrium extraction constant (K_e) and the number of apparent reacting extractant molecules (n) were estimated from the intercept and from the slope, respectively, shown in Fig. 4, obtained by plotting $\log K_D$ versus $\log [TBP]$. It was observed that the equilibrium isotherms for all the acids are straight lines and almost parallel to each other having the slope of 0.992-1.19, but different intercept from -0.24-0.81. This indicates a little influence of diluent on the equilibrium extraction constant.

The influence of diluent can be also shown in Fig. 5, indicated the experimental results as a plot of distribution coefficient versus the concentration of extractant for the initial acid concentration of 0.125 mol L^{-1} of all studied acids. There was observed in butyric acid a greater positive influence of dodecane (diluent) concentration on the solubility of the reaction product in the organic phase.

CONCLUSIONS

The influence of diluent and the phase ratio of organic phase to aqueous phase on the extraction equilibrium constant of monocarboxylic acid were investigated by using n-Tributyl phosphate (TBP) as solvent with dodecane. The equilibrium extraction constant (K_e) and the number of apparent reacting molecules were estimated by the Law of Mass Action assuming chemical interaction between extractant and the solute. From the experimental results, it was concluded that the values of equilibrium extraction constant dependent on the initial aqueous concentration of extracted acids as well as on the phase ratio. This method gave the greater efficiency to extract butyric acid than the other two acids. The distribution coefficient of all acids increased with increase in concentration of TBP while dodecane acts as an active solvent that causes a change of solubility of the reaction product in the organic phase and, consequently influences the overall distribution coefficient.

This influence of diluent (dodecane) on the equilibrium extraction is very important and must be taken quantitatively into account for the treatment of these types of data and the equilibrium extraction constant is necessary to predict the liquid-liquid equilibrium to achieve specific objects.

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