



## Modelling of Yield and Distribution Coefficient in a Liquid-Liquid Extraction: Effect of the Concentration of Ligand

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(Received: 6 August 2011;

Accepted: 7 May 2012)

AJC-11424

This work is a contribution to the development of model equations to simulate the yield and the distribution coefficient in a liquid-liquid extraction of formic acid from an aqueous solution. Three cases were studied: (i) the acid is the only constituent in the initial solution, (ii) a mixture of formic acid and benzoic acid, (iii) a mixture of formic acid and ammonia. In each case, the values of the distribution coefficient and the yield of extraction calculated by our models were compared with experimental values. It should be noted that at fixed pH the highest yield of extraction is obtained when the solution contains only a single acid, the yield decreases if the solution contains a mixture of acids and/or bases. We also studied the influence of pH of the solution on the yield and on the distribution coefficient of the extraction over a wide range of pH values from 1.5-11.0.

**Key Words:** Liquid extraction, Yield, Distribution coefficient, Solvent, Solute, Modeling.

### INTRODUCTION

Liquid-liquid extraction is a method of separation of one or more components from a mixture. It is based on the distribution of the solute between two liquids practically immiscible. The yield and the distribution coefficient are the most critical factors in liquid-liquid extraction and consequently it is very difficult to predict these two parameters because they are influenced by other parameters such as solutes concentration, nature of solvent, pH of the solution, temperature, hydrophobicity of extracted substances<sup>1</sup>.

The present work is a contribution to the development of theoretical models for the estimation of the yield and the distribution coefficient of extraction for a system containing one or multi-constituents. The proposed models are based on the interface reaction mechanism<sup>2</sup>. The developed models show that the most influential factor on the extraction is the pH of the solution<sup>1,3,4</sup>.

Our theoretical models is validate experimentally in laboratory using the parameters of the extraction of formic acid from its aqueous solution. The following three cases were studied: (i) extraction of formic acid from an aqueous solution containing only formic acid; (ii) extraction of formic acid from a solution containing a mixture of formic and benzoic acid; (iii) extraction of formic acid from a solution containing a mixture of formic acid and ammonia.

In each case, the yield and the distribution coefficient, calculated at different pH were determined and compared with experimental values.

**Theoretical concepts and definitions:** The common case of the equilibrium established between two immiscible liquids containing the same solute A, is when one of the solvents is water and the other is an organic liquid, this transfer can be represented by the following equilibrium<sup>5</sup>:



The distribution coefficient D and the yield of extraction R of the solute A in a liquid-liquid extraction are given by the following equations<sup>6-8</sup>,

$$D = \frac{[A]_{org}^T}{[A]_{aq}^T} \quad (2)$$

$$R = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \quad (3)$$

where  $[A]_{org}^T$  and  $[A]_{aq}^T$  are, respectively the total concentration of A in the aqueous and the organic phases,  $V_{aq}$  and  $V_{org}$  are the volumes of the aqueous and the organic phases, respectively.

## Equations modeling

**Case of extraction of weak acids:** The distribution coefficient of an acid  $[H_nA]$  in equilibrium between a solvent and aqueous solution is given by:

$$D = \frac{[H_nA]_{org}^T}{[H_nA]_{aq}^T} \quad (4)$$

where  $[H_nA]_{org}^T$  and  $[H_nA]_{aq}^T$  are, respectively the total concentration of the acid  $H_nA$  in the organic phase and the aqueous phase.

If we consider that dissociation of the  $H_nA$  acid can only occur in aqueous solution and polymerization occur only in organic phase, then the total concentration of the acid in the organic phase  $[H_nA]_{org}^T$  and aqueous phase  $[H_nA]_{aq}^T$  is given by the following equation,

$$\begin{aligned} [H_nA]_{org}^T &= [H_nA]_{org} + [(H_nA)_n]_{org} \\ &= K[H_nA]_{aq} + K_p[H_nA]_{aq}^n \end{aligned} \quad (5)$$

$$[H_nA]_{aq}^T = [H_nA]_{aq} + [A^{n-}] = [H_nA]_{aq} \left( 1 + \frac{K_a}{[H_3O^+]^n} \right) \quad (6)$$

where  $K$  is the partition coefficient,  $K_p$  is the constant of polymerization,  $K_a$  is the dissociation constant of the acid  $H_nA$ ,  $[H_3O^+]$  is the concentration of hydronium ion and  $n$  is their number.

Reporting eqns. 5 and 6 in 4 we obtain the modulated distribution coefficient  $D_{mod}$ ,

$$D_{mod} = \frac{K + K_p[H_nA]_{aq}^T}{1 + \frac{K_a}{[H_3O^+]^n}} \quad (7)$$

The yield of extraction of the acid  $H_nA$  is obtained when  $D$  is replaced by  $D_{mod}$  in eqn. 3.

**Extraction of weak bases:** By analogy to acids the expression of estimated distribution coefficient and the yield of the extraction of a weak base  $B$  is given by,

$$D_{mod} = \frac{K + K_p[B]_{aq}^T}{1 + \frac{K_b}{[HO^-]^n}} \quad (8)$$

where  $K$  is the partition coefficient,  $K_p$  is the constant of polymerization,  $K_b$  is the dissociation constant of the weak base  $B$ ,  $[HO^-]$  is the concentration of hydroxyl ion and  $n$  is their number.

If the dissociation constants of the conjugate acid of the base  $B$  is introduced in eqn. 8 we obtain,

$$D_{mod} = \frac{K + K_p[B]_{aq}^T}{1 + \frac{[H_3O^+]}{K_a}} \quad (9)$$

The yield of extraction of the weak base  $B$  is obtained when  $D$  is replaced by  $D_{mod}$  in eqn. 3.

## EXPERIMENTAL

Formic acid (99 %) was purchased from Riedel-de-Haën (Germany), butan-1-ol (99 %) was purchased from Biochem

Chemopharma Co (Canada), benzoic acid (99.5%) was purchased from Biochem Chemopharma Co. (Canada) and ammonia (98.47 %) was purchased from Fisher Scientific Co. (UK).

UV-Visible spectrophotometer (Spectrophotometer: SpectroScan 80D/80DV Biotech Engineering Management Co. Ltd.), mechanical shaker (Edmund Buhler GmbH, 420 stroke by min), pH meter (HI255 pH/mV/°C).

## RESULTS AND DISCUSSION

**General procedure:** 20 mL of aqueous analyte solution was shaken at room temperature with a similar amount of the extractive organic solvent in glass flasks of 100 mL using a mechanical shaker, after phase separation, the concentration of the analyte in the aqueous layer is determined by UV-visible spectrophotometer and in the organic layer is deduced by mass balance. The distribution coefficient and the yield of extraction are then calculated. The pH of the solution is then varied from 1.5-11.0 by adding 2 N aqueous HCl or NaOH solutions using a pH meter with temperature compensation. The distribution coefficient and the yield of extraction are then calculated at different pH.

Studied solutions: (i) 20 mL of 0.1 N aqueous formic acid solution. (ii) A mixture containing 10 mL of 0.1 N aqueous formic acid solution and 10 mL of 0.025 N aqueous benzoic acid solution. (iii) A mixture containing 10 mL of 0.1 N aqueous formic acid solution and 10 mL of 0.1 N aqueous ammonia solution.

### Determination of partition and dimerization constants:

Fig. 1 shows the isotherms of organic and aqueous concentrations of formic acid in three different solvents *i.e.*, pentanol, butanol and cyclohexanol. The results showed that butanol gives the highest physical distribution as represented on Fig. 1.

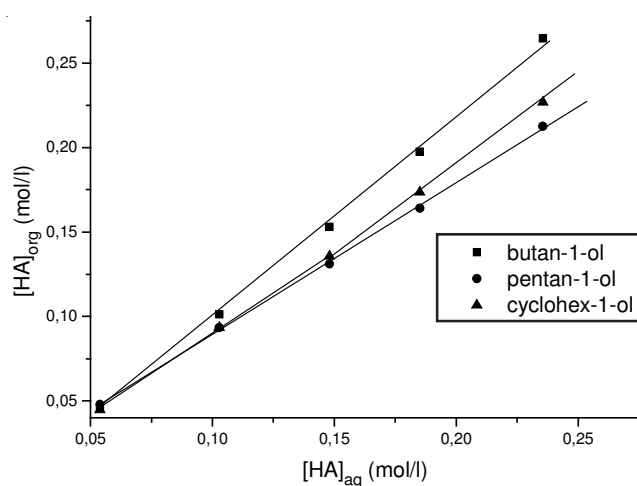


Fig. 1. Isothermal concentrations of aqueous and organic phases of formic acid in various alcohols

The values of partition coefficient and dimerization constant of formic acid are concluded from the graph on Fig. 1. The results are summarized in Table-1.

The partition coefficients of benzoic acid and aqueous ammonia in the butanol determined by the same techniques are, respectively:  $K_{(C_6H_5COOH)} = 29.26$  and  $K_{(NH_4OH)} = 0.65$ .

TABLE-1  
K AND  $K_p$  VALUES OF FORMIC ACID IN:  
PENTANOL, BUTANOL AND CYCLOHEXANOL

Solvent	Pentan-1-ol	Butan-1-ol	Cyclohexanol
K	0.896	0,902	0.351
$K_p$	–	–	0.833

**Extraction without pH correction:** Table-2 showed the values of the distribution coefficient and the yield of the extraction of formic acid at initial concentration equal to 0.1 mol/L, at fixed pH, the studied cases are (i) a single acid (0.1 N HCOOH); (ii) a mixture of two weak acids (HCOOH 0.1 N and  $C_6H_5COOH$  0.025 N) and (iii) a mixture of a weak acid and a weak base (HCOOH 0.1 N +  $NH_4OH$  0.1 N). The highest yield 46.57 % is obtained in the first case (*i.e.*, extraction of a single acid at pH = 2.29) then the yield decrease to 37.30 in the case of a mixture of two acids at pH 2.47. For the third case, at pH = 5, neither the acid nor the base can be extracted quantitatively. In this case formic acid is extracted in a very poor yield (2.85 %). We recommend carrying out the calculations in four decimals, with the final value of coefficient distribution and yield of the extraction rounded to two decimals.

#### Effect of the pH on the extraction

**Case of a weak acid (formic acid):** The results obtained for the extraction of formic acid from an aqueous solution at a concentration of 0.1 M are summarized in Table-3. Values of experimental  $D_{exp}$  and modulated  $D_{mod}$  distribution coefficient in one hand and experimental  $R_{exp}$  and modulated yield  $R_{mod}$  in the other hand are in good agreement.

The highest yield of the extraction of formic acid is 46.15 % at pH less than  $pK_a$  value (*i.e.*, 3.75), beyond this value; the acid can not be extracted.

Figs. 2 and 3 represent the variations of the yield of the extraction and the logarithm of the distribution coefficient as function of pH values.

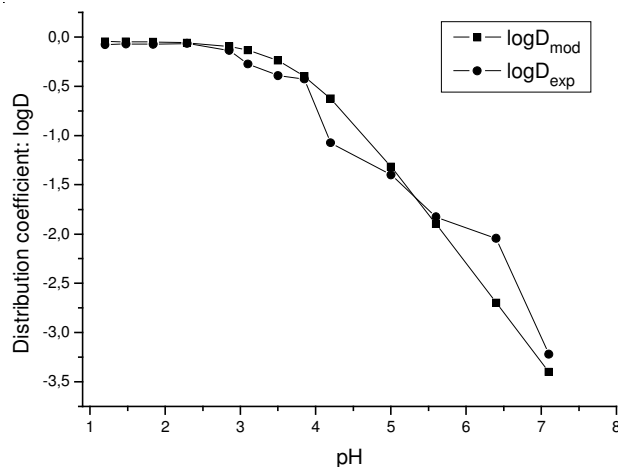


Fig. 2.  $\log(D)$  as a function of pH for extraction of formic acid ( $C_i = 0.1$  mol/L)

Figs. 4 and 5 shows the correlation between experimental and modulated coefficient distribution and yields of extraction from eqns. 7 and 3 for formic acid. Value for  $r^2$  of 0.937 was found for eqn. 3 and  $r^2$  of 0.968 for eqn. 7.

**Case of a mixture of two weak acids (formic acid and benzoic acid):** The results in Tables 4 and 5 show that benzoic acid can be quantitatively isolated from formic acid with a yield of extraction of 19 % in the range of pH between the  $pK_a$  of the two acids: 3.75 and 4.2, respectively in this range the formic acid completely dissociated in its ionic form. Formic

TABLE-2  
VALUES OF DISTRIBUTION COEFFICIENT AND THE YIELD FOR THE EXTRACTION OF FORMIC ACID  
ALONE AND IN MIXTURE WITHOUT pH CORRECTION (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ,  $T = 20^\circ C$ )

Initial solution	Entity extracted	$C_i$ (mol/L)	$pH_{exp}$	$[HA]_{org}^T$ (mol/L)	$[HA]_{aq}^T$ (mol/L)	$D_{mod}$	$D_{exp}$	$R_{mod}$ (%)	$R_{exp}$ (%)
HCOOH	HCOOH	0.100	2.29	0.0538	0.0462	0.87	0.86	46.57	46.15
HCOOH and $C_6H_5COOH$	HCOOH	0.100	2.47	0.0534	0.0466	0.87	0.87	37.30	37.28
	$C_6H_5COOH$	0.025	–	0.0004	0.0246	65.90	61.50	19.70	19.68
HCOOH and $NH_4OH$	HCOOH	0.100	5.01	0.0067	0.0933	0.06	0.07	2.85	3.36
	$NH_4OH$	0.100	–	0.0002	0.0998	0.00	0.00	0.05	0.08

TABLE-3  
EXPERIMENTAL AND MODEL VALUES OF R AND D FOR FORMIC ACID  
EXTRACTION AS A FUNCTION OF pH (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ;  $T = 20^\circ C$ )

pH	$[HA]_{org}^T$	$[HA]_{aq}^T$	$D_{mod}$	$D_{exp}$	Error	$R_{mod}$	$R_{exp}$	Error
1.20	0.0544	0.0456	0.90	0.84	0.06	47.35	45.57	1.78
1.48	0.0541	0.0459	0.90	0.85	0.05	47.29	45.87	1.42
1.84	0.0543	0.0457	0.90	0.84	0.06	47.12	45.73	1.39
2.29	0.0538	0.0462	0.87	0.86	0.01	46.57	46.15	0.42
2.85	0.0578	0.0422	0.80	0.73	0.07	44.47	42.17	2.30
3.10	0.0654	0.0346	0.74	0.53	0.21	42.42	34.65	7.77
3.50	0.0712	0.0288	0.58	0.40	0.18	36.60	28.78	7.82
3.85	0.0728	0.0272	0.40	0.37	0.03	28.54	27.25	1.29
4.20	0.0922	0.0078	0.24	0.08	0.16	19.12	7.77	11.35
5.00	0.0962	0.0038	0.05	0.04	0.01	4.59	3.83	0.76
5.60	0.0985	0.0015	0.01	0	0.01	1.25	1.47	0.22
6.40	0.0991	0.0009	0	0	0	0.20	0.89	0.69
7.10	0.0999	0.0001	0	0	0	0.04	0.06	0.02
8.00	0.1000	0	0	0	0	0	0	0
9.45	0.1000	0	0	0	0	0	0	0

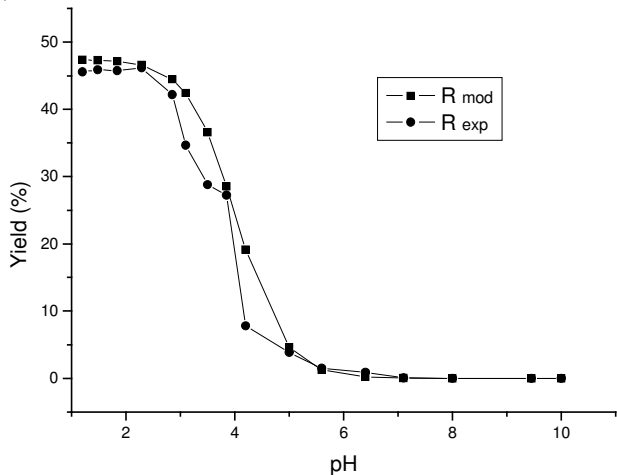


Fig. 3. R as a function of pH for extraction of formic acid ( $C_i = 0.1 \text{ mol/L}$ )

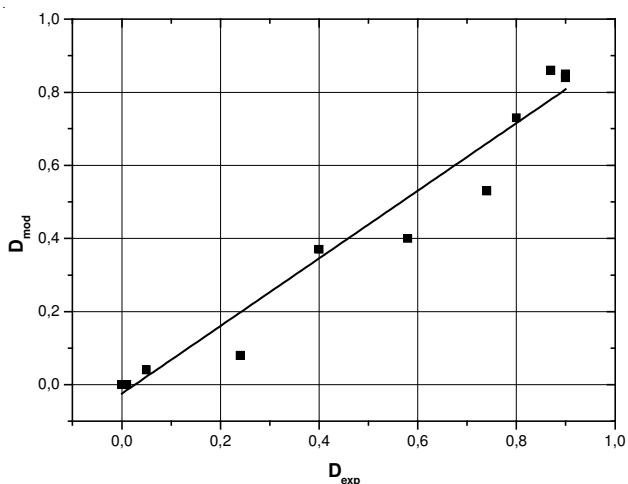


Fig. 4. Correlation between experimental and calculated distribution coefficient from eqn. 8 for formic acid

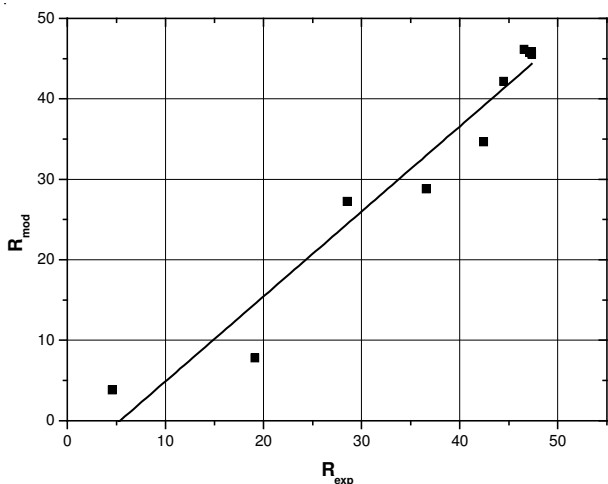


Fig. 5. Correlation between experimental and calculated yields of extraction from eqn. 3 for formic acid

acid can be extracted by decreasing further the pH to 1.5 with a yield of 37.5 %.

Figs. 6 and 7 represent the variations of the yield of the extraction and the logarithm of the distribution coefficient as function of pH values.

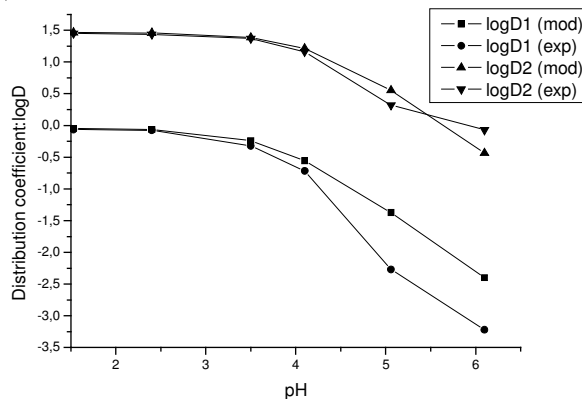


Fig. 6.  $\log(D)$  as a function of pH for the extraction of formic acid (1) in mixture with benzoic acid (2)

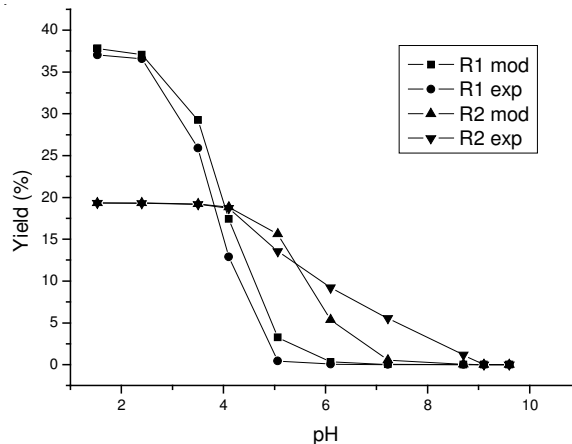


Fig. 7. R as a function of pH for the extraction of formic acid (1) in mixture with benzoic acid (2)

**Case of a mixture of weak acid and weak base (formic acid and ammonia):** Tables 6 and 7 show that formic acid can be isolated quantitatively from the ammonia base with an extraction yield of 22.5 % in the area where the pH is lower than 3, in contrast, the base can be isolated beyond pH 9 with a yield of 17 %. Between these two values, none of the above entities can be extracted quantitatively.

Figs. 8 and 9 represent the variations of the yield of the extraction and the logarithm of the distribution coefficient as function of pH values.

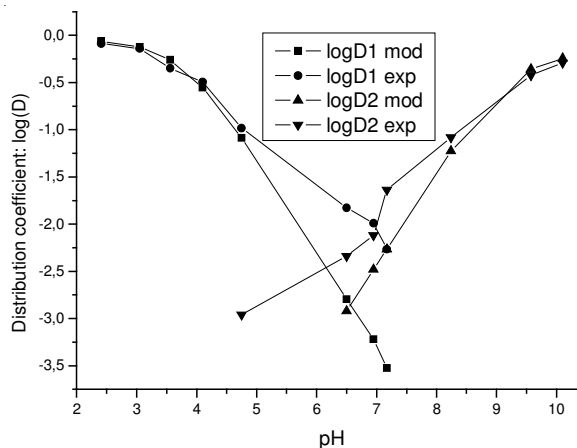


Fig. 8.  $\log(D)$  as a function of pH for the extraction of formic acid (1) in mixture with ammonia (2)

TABLE-4  
EXPERIMENTAL AND MODELS VALUES OF R AND D AS A FUNCTION OF pH FOR THE EXTRACTION OF FORMIC ACID (1)  
CONTENT IN COMBINATION WITH BENZOIC ACID (2) (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ;  $T = 20\text{ }^\circ\text{C}$ )

pH	Component 1 : HCOOH							
	$[HA_1]_{org}^T$	$[HA_1]_{aq}^T$	$D_{1mod}$	$D_{1exp}$	Error	$R_{1mod}$	$R_{1exp}$	Error
1.53	0.0537	0.0463	0.90	0.86	0.04	37.82	37.04	0.78
2.4	0.0543	0.0457	0.86	0.84	0.02	37.06	36.58	0.48
3.5	0.0677	0.0324	0.58	0.48	0.10	29.28	25.88	3.40
4.1	0.0839	0.0161	0.28	0.19	0.09	17.44	12.90	4.54
5.06	0.0995	0.0005	0.04	0	0.04	3.25	0.43	2.82
6.1	0.0999	6E-05	0.004	0	0.004	0.32	0.05	0.27
7.22	0.1	0	0	0	0	0.02	0	0.02
8.7	0.1	0	0	0	0	0	0	0
9.1	0.1	0	0	0	0	0	0	0
9.6	0.1	0	0	0	0	0	0	0

TABLE-5  
EXPERIMENTAL AND MODELS VALUES OF R AND D AS A FUNCTION OF pH FOR THE EXTRACTION OF BENZOIC (2) ACID  
CONTENT IN COMBINATION WITH FORMIC ACID (1) (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ;  $T = 20\text{ }^\circ\text{C}$ )

pH	Component 2 : $C_6H_5COOH$							
	$[HA_2]_{org}^T$	$[HA_2]_{aq}^T$	$D_{2mod}$	$D_{2exp}$	Error	$R_{2mod}$	$R_{2exp}$	Error
1.53	0.0008	0.0242	29.20	28.42	0.78	19.34	19.32	0.02
2.4	0.0009	0.0241	28.80	27.17	1.63	19.33	19.29	0.04
3.5	0.0010	0.0240	24.38	23.57	0.81	19.21	19.18	0.03
4.1	0.0016	0.0234	16.30	14.49	1.81	18.84	18.71	0.13
5.06	0.0081	0.0169	3.55	2.10	1.45	15.61	13.55	2.06
6.1	0.0135	0.0115	0.36	0.85	0.49	5.35	9.21	3.86
7.22	0.0181	0.0069	0.03	0.38	0.35	0.54	5.52	4.98
8.7	0.0236	0.0014	0.001	0.06	0.06	0.02	1.16	1.14
9.1	0.025	0	0.0004	0	0	0.008	0	0.008
9.6	0.025	0	0.0001	0	0	0.002	0	0.002

TABLE-6  
EXPERIMENTAL AND MODEL VALUES OF R AND D AS A FUNCTION OF pH FOR THE EXTRACTION OF FORMIC ACID (1)  
CONTENT IN COMBINATION WITH AMMONIA (2) (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ;  $T = 20\text{ }^\circ\text{C}$ )

pH	Component 1 : HCOOH							
	$[HA_1]_{org}^T$	$[HA_1]_{aq}^T$	$D_{1mod}$	$D_{1exp}$	Error	$R_{1mod}$	$R_{1exp}$	Error
2.41	0.0550	0.045	0.86	0.82	0.04	23.16	22.49	0.67
3.05	0.058	0.042	0.75	0.72	0.03	21.46	21.00	0.46
3.56	0.0690	0.031	0.55	0.45	0.01	17.70	15.49	2.21
4.1	0.0757	0.0243	0.28	0.32	0.04	10.90	12.13	1.23
4.75	0.0906	0.0094	0.08	0.14	0.06	3.80	4.70	0.91
6.5	0.0985	0.0015	0	0.01	0.01	0.08	0.73	0.65
6.95	0.099	0.0010	0	0.001	0.001	0.03	0.50	0.47
7.17	0.0995	0.0005	0	0.005	0.005	0.01	0.27	0.26
8.24	0.1	0	0	0	0	0	0	0
9.57	0.1	0	0	0	0	0	0	0
10.1	0.1	0	0	0	0	0	0	0

TABLE-7  
EXPERIMENTAL AND MODEL VALUES OF R AND D AS A FUNCTION OF pH FOR THE EXTRACTION OF AMMONIA (2)  
CONTENT IN COMBINATION WITH FORMIC ACID (1) (SOLVENT: BUTAN-1-OL;  $V_{aq}/V_{org} = 1:1$ ;  $T = 20\text{ }^\circ\text{C}$ )

pH	Component 2 : $NH_4OH$							
	$[B_2]_{org}^T$	$[B_2]_{aq}^T$	$D_{2mod}$	$D_{2exp}$	Error	$R_{2mod}$	$R_{2exp}$	Error
2.41	0.1	0	0	0	0	0	0	0
3.05	0.1	0	0	0	0	0	0	0
3.56	0.1	0	0	0	0	0	0	0
4.1	0.1	0	0	0	0	0	0	0
4.75	0.0999	0.0001	0	0.0011	0.0011	0	0.05	0.05
6.5	0.0995	0.0005	0.0012	0.0046	0.0034	0.06	0.23	0.17
6.95	0.0993	0.0008	0.0033	0.0076	0.0043	0.16	0.38	0.22
7.17	0.0977	0.0023	0.0054	0.0231	0.0177	0.27	1.13	0.86
8.24	0.0924	0.0077	0.06	0.08	0.02	2.79	3.82	1.03
9.57	0.0726	0.0274	0.44	0.38	0.06	15.26	13.70	1.56
10.1	0.0661	0.0339	0.57	0.51	0.06	18.14	16.90	1.24

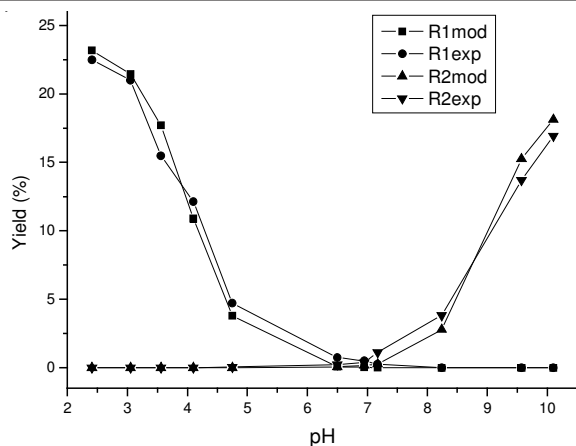


Fig. 9. R as a function of pH for the extraction of formic acid (1) in mixture with ammonia (2)

### Conclusion

The experimental validation of the equations used to estimate the yield and distribution coefficient in a liquid-liquid extraction developed in this study, applied to the recovery of formic acid from its aqueous solution at different pH of the solution, shows that the yield and the distribution coefficient

predicted by our models are in good agreement with those obtained from experimental procedures. Indeed, it was noticed that on one hand and if any prior adjustment of pH is made to the initial solution, formic acid can be extracted with good efficiency up to 46.6 %, when alone in solution. The yield decrease to 37.4 % if it is mixed with benzoic acid and fall to 2 % in the presence of ammonia, it can never be extracted in the latest case. On the other hand, by varying the pH of initial solution on a wide range of pH (1.5-11.0), it was possible to extract separately formic acid from benzoic acid and ammonia, with yield equal to 37.8 and 23.2 %, respectively.

### REFERENCES

1. Y. Wang, L.Y. Wang, J. Li and Z. Dai, *J. Chem. Eng. Data*, **6**, 831 (2001).
2. F.H. Mahfud, F.P. Van, R.H. Geel and H.J. Heeres, *Sep. Sci. Technol.*, **43**, 3056 (2008).
3. R. Salhi, K. Bouhidel and A. Rigorous, *Asian J. Chem.*, **17**, 245 (2005).
4. G. Kyuchoukov, D. Yankov, M. Marinova, J. Molinier and J. Albet, *Ind. Eng. Chem. Res.*, **44**, 5733 (2005).
5. A.S. Kertes and C.J. King, *Biotechnol. Bioeng.*, **28**, 269 (1986).
6. S. Chang-Hoon, *J. Hazard. Mater.*, **162**, 1278 (2009).
7. K. Amit, C. Shri and L. Kailas, *J. Chem. Eng.*, **152**, 95 (2009).
8. M. Fan, W. Qun and Y. Dai, *J. Chem. Eng. Data*, **47**, 941 (2002).