Partition Coefficients of Tartaric and Malic Acids between Dilute Aqueous Solutions and Amine Extractants Dissolved in Various Diluents

Guy H. Malmary, Jean F. Mourgues,[†] Jos Bakti,[‡] Thierry S. Conte,[†] Djilali Achour,[§] Freddy J. Smagghe, and Jacques R. Molinier*

Laboratoire de Chimie des Procédés, Groupe Génie Chimique, Ecole Nationale Supérieure de Chimie, 118 route de Narbonne, 31077 Toulouse Cedex, France

Distilleries and grape sugar producing cooperatives throw back into the environment loaded aqueous effluents which contain essentially tartaric and malic acids. The elimination of tartaric and malic acids is a way of reducing that pollution. The possibility of using the liquid–liquid extraction process for the recovery of these acids was explored. In this work the two organic solvents employed are tris(6-methylheptyl)amine and an equimolar mixture of trioctylamine + tridecylamine which are dissolved in various diluents such as 1-hexanol, chloroform, a mixture of heptane (50 vol %) + 1-hexanol (50 vol %), and 2,6-dimethyl-4-heptanone. The distribution coefficients of each separate acid have been determined in the range of amine–diluent concentration comprised between 0.1 and 0.8 mol of amine per liter of solution. With the tris(6-methylheptyl)amine extractant, the values of partition coefficients of separated tartaric acid and malic acid were found to be in the ranges of 2.5–165.1 and 1.7–73.9, respectively, for each acid. With the equimolar mixture of trioctylamine + tridecylamine extractant, the distribution coefficients of tartaric and malic acids were found to be in the ranges of 2.7–117.2 and 1.4–84.4, respectively.

Introduction

The liquid–liquid extraction process can be considered as an alternative to the precipitation techniques for the recovery of tartaric and malic acids from wine distillery wastewater. These acids are used in the food processing, chemical, and pharmaceutical industries (*1*). Extractions with conventional solvents such as alcohols and ketones (*2, 3*) are not efficient when applied to dilute carboxylic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients. The strong amine interaction with the acid allows for formation of acid–amine complexes and thus provides for high distribution coefficients. When using amine extractants, a proton transfer occurs during the extraction and the acid prevails in the organic phase as an amine–acid ion pair complex. Several aliphatic amines have been used successfully to extract carboxylic acids (*4–6*). The long-chain tertiary amines have received the most attention principally owing to their very low miscibility in the aqueous phase. In this work, two aliphatic amine extractants such as tris(6-methylheptyl)amine and an equimolar mixture of trioctylamine + tridecylamine dissolved in various diluents were studied for their abilities to extract tartaric and malic acids. Four diluents such as 1-hexanol, chloroform, a mixture of heptane (50 vol %) + 1-hexanol (50 vol %), and 2,6-dimethyl-4-heptanone were investigated for their abilities to increase the extracting power of the amine extractants.

The type of diluent and its concentration in the mixture extractant–diluent have an important effect on the distribution coefficients because the diluent affects the basicity of the amine and the stability of the ion pair complex formed and consequently its extracting power (*7*).

Experimental Section

Chemicals for the extraction experiments, tartaric acid, malic acid, diluents, and tris(6-methylheptyl)amine with a purity of 99% were obtained from Aldrich Chemical Co. The solubility in water of tris(6-methylheptyl)amine is less than 20 mg/L. The equimolar mixture of trioctylamine + tridecylamine is a straight-chain tertiary amine produced by Henkel Corp. (Alamine 336) and by Hoechst (Hostarex A 327); its solubility in water is less than 10 mg/L. The analysis by high-performance liquid chromatography (HPLC) confirmed the purity of the products.

Procedures. Some separate solutions of individual tartaric acid and malic acid were prepared at a concentration of exactly 1 mass %. A 25-g of a separate solution of individual acid was mixed with 50 g of solvent (amine + diluent) by shaking in glass-stoppered separatory funnels thermostated at 25 °C for 3 h. After settling over a period of 1 h, the phases were analyzed. As was shown by analysis, the acid concentrations in the organic phase and the aqueous phase in the contacting device do not change beyond 2 h of mixing. Consequently, a contact between the phases equal to 3 h can be considered as sufficient for equilibration. Extraction experiments were carried out with a mass phase ratio equal to 2. The aqueous-phase acid concentration was analyzed by titrating with standard sodium hydroxide solutions (0.1 or 1.0 M), and phenolphthalein was used as indicator. The acid concentration in the organic phase was determined by first stripping the organic phase with an known excess amount of NaOH solution (0.1 M). The alkaline solution containing the organic salt was back-titrated with HCl solution (0.05 M). A material balance was also used to determine the resulting organic-phase acid concentration. The material balance closes to around 1 mass %. The partition coefficient (*m*) defined as the ratio of acid concentration (mass %) in the organic phase to acid concentration (mass %) in the aqueous phase was calculated. The error induced from titrating and weighing was less than 1%. The acid concentration in each phase was confirmed by using high-performance liquid chromatography (HPLC). In the case of the determination of the acid concentration in the organic phase by HPLC a first stripping of the acid from the organic phase with H_2SO_4 solution (0.5 M) was necessary. The HPLC system consisted essentially of a pump (SpectraPhysics Model SP 8800), an integrator

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[†] Institut National de Recherche Agronomique, 11 104 Narbonne, France.

[‡] Chemical Engineering Department, Diponegoro University, Semarang, Indonesia.

[§] University of Chlef, Algeria.

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Table I. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Trioctylamine + Tridecylamine Dissolved in 1-Hexanol at 25 °C

concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.05	59.9	39.9	0.30	104.3	59.4
0.07	69.9	52.7	0.32	100.0	57.6
0.09	80.0	60.1	0.35	95.0	53.7
0.13	96.7	74.8	0.37	89.5	51.4
0.17	103.2	81.8	0.40	83.9	50.1
0.20	110.7	84.4	0.45	77.2	46.3
0.22	114.8	67.3	0.50	73.3	43.5
0.24	117.2	68.4	0.55	77.1	43.2
0.28	109.8	62.6	0.65	62.5	42.8

Table II. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Trioctylamine + Tridecylamine Dissolved in Chloroform at 25 °C

concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.05	6.3	4.4	0.34	16.6	11.9
0.08	8.5	7.1	0.40	14.9	10.9
0.12	93.1	9.3	0.49	13.1	9.6
0.16	17.6	12.3	0.59	11.1	8.0
0.20	20.5	15.1	0.65	10.6	6.6
0.24	19.1	14.2	0.67	10.1	7.1

Table III. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Trioctylamine + Tridecylamine Dissolved in Heptane (50 vol %) + 1-Hexanol (50 vol %) at 25 °C

concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixtue ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.15	23.4	6.8	0.47	57.4	20.1
0.20	32.9	10.7	0.50	54.0	19.7
0.25	38.7	14.4	0.55	52.6	18.9
0.30	44.7	16.1	0.60	51.9	18.7
0.35	49.2	18.3	0.62	51.7	18.3
0.40	53.6	20.0	0.70	31.1	18.1
0.42	55.0	20.4	0.75	31.1	18.2
0.45	57.1	21.1			

Table IV. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Trioctylamine + Tridecylamine Dissolved in 2,6-Dimethyl-4-heptanone at 25 °C

concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.10	2.7	1.4	0.45	8.4	6.1
0.20	3.8	2.1	0.50	8.1	5.7
0.30	4.8	3.3	0.60	7.7	5.6
0.35	7.6	5.0	0.70	7.8	5.6
0.40	9.8	6.8	0.80	7.7	5.6

(Chromjet SP 4400), an UV spectrophotometer (Spectra 100 UV–vis detector), and an analysis column Aminex HPX-87 H which worked at 40 °C. The eluent was 0.005 M H_2SO_4 at a flow rate of 0.4 mL/min.

The peak height on the chromatogram was used to compare with known standards to determine the acid concentration in the sample. The percentage standard deviation of the partition coefficient values mentioned in Tables I-VIII was estimated to be 1% for all of the experiments.

Table V. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Tris(6-methylheptyl)amine Dissolved in 1-Hexanol at 25 °C

concn of amine in the mixtue ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixtue ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.10	42.1	16.3	0.45	165.1	73.9
0.15	49.9	21.1	0.47	159.8	70.5
0.20	60.5	24.3	0.50	154.2	64.2
0.25	72.9	32.5	0.55	140.0	61.7
0.30	89.6	36.7	0.60	139.3	56.2
0.35	108.4	52.1	0.65	136.5	57.3
0.40	140.3	61.3	0.70	132.1	55.9
0.42	152.2	67.1	0.75	132.0	56.1

Table VI. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Tris(6-methylheptyl)amine Dissolved in Chloroform at 25 °C

concn of amine in the mixture ($\mathrm{mol{\cdot}^{L-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.03	9.2	2.5	0.37	78.3	28.3
0.12	22.5	4.8	0.40	73.8	25.2
0.15	29.1	7.7	0.42	67.6	20.2
0.17	37.2	9.2	0.50	57.4	16.6
0.20	46.1	13.10	0.55	52.1	13.1
0.30	89.3	30.1	0.60	47.4	13.4
0.33	95.9	35.3			

Table VII. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Tris(6-methylheptyl)amine Dissolved in Heptane (50 vol %) + 1-Hexanol (50 vol %) at 25 °C

concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.10	24.7	9.5	0.50	72.3	31.1
0.20	28.7	11.3	0.55	69.7	29.4
0.30	39.8	14.4	0.65	68.2	29.1
0.35	50.0	17.4	0.75	68.7	28.7
0.40	64.8	25.2	0.80	68.4	28.5
0.45	82.4	40.5			

Table VIII. Partition Coefficients *m* of Tartaric and Malic Acids between Aqueous Solution and Tris(6-methylheptyl)amine Dissolved in 2,6-Dimethyl-4-heptanone at 25 °C

concn of amine in the mixture ($\mathrm{mol{\cdot}^{l-1}}$)	*m*(tartaric acid)	*m*(malic acid)	concn of amine in the mixture ($\mathrm{mol \cdot L^{-1}}$)	*m*(tartaric acid)	*m*(malic acid)
0.10	2.5	1.7	0.50	10.3	8.3
0.20	3.5	2.5	0.55	10.1	8.3
0.25	5.5	3.5	0.60	10.0	8.2
0.30	6.6	4.3	0.65	9.9	8.2
0.35	9.0	7.4	0.70	9.9	8.2
0.40	11.7	9.7	0.80	9.8	8.1

Results and Discussion

The effects of the nature of the diluent and amine concentration on partition coefficients for tartaric and malic acids were shown in Tables I-VIII. A polar diluent will increase the extracting power of tertiary amines by providing additional solvating power that allows higher levels of polar acid–amine complexes to stay in the organic phases (*3*). The differences between the values of partition coefficients depend on effects of the polarity of the diluents used with regard to the formation of the complex acid–tertiary amines.

Tertiary amines such as tris(6-methylheptyl)amine and an equimolar mixture of trioctylamine + tridecylamine extract only the undissociated acid by forming an acid–base complex (*4*). Extractions of organic acids depend on the pH of the initial aqueous solutions and consequently the pK_a for tartaric and malic acids which are about 2.9 and 3.4, respectively. Tertiary amines will be good for use in organic acids which can work at a pH value of initial aqueous phase as low as 3 (*3*). In this study, the pH of the initial aqueous solution containing 1 mass % tartaric acid is 2.3 and the pH of the aqueous solution at a concentration of 1 mass % of malic acid is 2.1. Under acidic conditions the undissociated tartaric and malic acid concentrations in the separate aqueous phases increase, and consequently these acids are extracted by the tertiary amines. After extraction experiments, the pH of the final aqueous solutions varies between 2.9 and 3.1. Taking into consideration that values of partition coefficients presented in Tables I-VIII are relatively high, the extraction of tartaric and malic acids with these tertiary amine extractants represents an attractive method for recovering these acids from dilute aqueous solutions. Furthermore, some technical problems concerning the contamination of the water by extractants involves a choice of solvent that is less miscible in the aqueous phase such as tertiary amines. The separation processes based on the dissociation–extraction can be successfully adapted to recover carboxylic acids from aqueous mixtures by tertiary amine extractants.

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