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Note

An application of the ligand exchange method to the separation of some aliphatic carboxylic acids

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The ligand exchange method is generally used in the chromatographic separations of compounds of the same series but with different coordinating powers¹. This technique has been applied mainly in the analysis of amines and other nitrogen-containing ligands, but in few other cases. In order to investigate the exchange ability and selectivity of the conjugated bases of aliphatic carboxylic acids, we have examined a mixture containing glycolic, oxalic, malonic and succinic acids. The choice was made taking into account that there must be an appreciable difference among the formation constants of the complexes that the carboxylate ligands form with the metal ion fixed on the exchanger. This condition is realized for the above acids by using a chelating exchanger column treated with $\text{Ni}(\text{NH}_3)_6^{2+}$.

EXPERIMENTAL

Materials and apparatus

All chemicals were analytical-grade products. A cation exchanger of the polystyrene-iminodiacetic acid type (Chelex 100, 100-200 mesh) was used (Bio-Rad Labs., Richmond, Calif., U.S.A.). Spectral measurements were performed on a Beckman DK-2A spectrophotometer with quartz cells (1.00-cm path length) and pH measurements were made on a Radiometer pHM-22r instrument equipped with external glass and saturated calomel electrodes.

Operating conditions

A 10-g amount of the exchanger was washed with several portions of 2 M sodium chloride solution until free from iron(III), then with deionized water. A 1:1 ammonia solution of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ complex prepared according to the literature² was added: the dark green suspension was stirred for about 20 h, adding the nickel(II) complex continuously until no colour variation could be detected. Then the exchanger was placed in a chromatographic column (25 cm high and 0.8 cm I.D.), which was loaded until the packed resin was 15 cm high. The system was stabilized by washing it successively with ammonia solutions of 10^{-3} and 10^{-5} M concentration until the eluate was free from nickel(II), checking by the usual method with dimethylglyoxime.

Glycolic, oxalic, malonic and succinic acids were determined by the methods reported in the literature³; it was necessary to perform the quantitative analysis after

the colour development by an indirect colorimetric method in which the sample solution was compared with standard solutions. The initial concentration of the acids was $10^{-2} M$ in deionized water and 1 ml of each solution was employed. Standard comparison samples contained $0.01 \cdot 10^{-5}$ – $0.5 \cdot 10^{-5}$ mole of the acid under examination. The flow-rate was 0.5 ml/min. Elution curves were obtained from the absorbance of the acid in 1 ml of successive 2-ml fractions of eluate. The same amount of each acid solution was examined separately in preliminary tests.

RESULTS AND DISCUSSION

Preliminary tests showed that the acids were not retained on the exchanger that had not been treated with the nickel(II)-ammonia complex. In order to establish the most suitable ammonia concentration for performing the separation, we checked various solutions from 1 to $10^{-5} M$, owing to the selectivity of the eluting solution, which varies with its concentration⁴.

We found that the best separation of the mixture of the four acids was achieved using $10^{-5} M$ ammonia solution as eluent, which we have also used for the column pre-treatment. Prolonged washing with water does not displace the acids retained on the nickel(II)-ammonia column.

A typical elution curve is shown in Fig. 1.

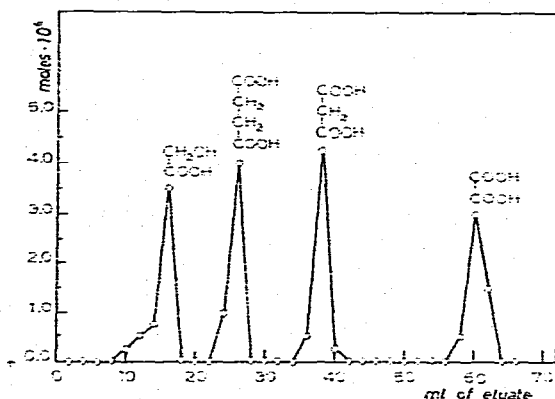


Fig. 1. Elution curve of a mixture of the four aliphatic carboxylic acids from Chelex 100 ($\text{Ni}(\text{NH}_3)_n^{2+}$), 100–200 mesh. Eluent, $10^{-5} M$ ammonia solution.

The successful separation of the mixture of the four carboxylic acids by ligand exchange may be interpreted on the basis of their different formation constants with nickel(II) at a complexation ratio of 1:1 (Table I). Even if one takes into account that the central metal ion is bound to the donor groups of the exchanger and hence the actual formation constants can be affected, it is reasonable to consider that the four complexes undergo such an effect to the same extent. The $\log \beta_1$ values follow the order expected on the basis of the chelation ring stabilization. Considering the acidity constants of the four acids (see Table I, $\text{p}K_{a_1}$ and $\text{p}K_{a_2}$), chelation probably does not occur with glycolic acid owing to the low coordination ability of the hydroxyl group,

TABLE I

pK_a VALUES OF THE ACIDS AND FORMATION CONSTANTS OF NICKEL(II) COMPLEXES

Acid	pK_{a_1} *	pK_{a_2} *	Log β_1 of the nickel(II) complex
Oxalic	1.24	4.14	5.2**
Malonic	2.71	5.36	4.1**
Succinic	4.19	5.46	2.4**
Glycolic	3.71	—	1.7***

* From ref. 5.

** Potentiometric values at 25° reported by Sillen and Martell⁶.

*** From ref. 7.

which is further decreased by deprotonation of the carboxylic group. Consequently, glycolic acid is the least retained of the four acids on the exchanger. In particular, this effect has permitted the separation of glycolic and succinic acids, which is not readily achieved by conventional ion-exchange chromatography⁸.

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