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Note

Selective adsorption of non-ionic surfactants using an anion-exchange resin in the cobaltithiocyanate form

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Alkylene oxide-type non-ionic surfactants are widely used as emulsifiers, wetting agents and detergents. However, there have been few studies on the adsorption of these surfactants by means of ion-exchange resins. As non-ionic surfactants have no charge, coulombic forces are not available to collect them. Amberlite XAD resin has often been used for the collection of these surfactants[1,2]. The selectivity of the resin is poor for non-ionic surfactants, and pre-treatment is necessary to prevent the interference. Carunchio *et al.*[3] reported that non-ionic surfactants were adsorbed on iminodiacetic acid resin treated with $[Co(NH_3)_5OH_2]^{3+}$ or $[Co(NH_3)_6]^{3+}$. However, the method was applied only to the adsorption of ethoxylated alkylphenols, and these non-ionic surfactants were not adsorbed and recovered quantitatively.

In the study described here, the cobaltithiocyanate form of a resin was used to adsorb alkylene oxide-type non-ionic surfactants. Cobalt thiocyanate has been used as a complexing agent for non-ionic surfactants and anion-exchange resins adsorb the cobalt thiocyanate complex strongly with the development of a blue colour on account of the formation of a tetragonal complex of cobalt thiocyanate. The proposed resin quantitatively adsorbs alkylene oxide-type non-ionic surfactants and they are recovered quantitatively by elution with an appropriate organic solvent.

EXPERIMENTAL

Reagents

The anion-exchange resin Diaion SA10AS (Cl^- form, 50–100 mesh) (Mitsubishi Chemical Industry) was used.

Ammonium thiocyanate, cobalt nitrate, methanol, ethanol and isopropanol were of analytical-reagent grade. Polyethylene glycol (average molecular weight 4000, abbreviated to PEG 4000) was obtained from Wako (Osaka, Japan) and polypropylene glycol (average molecular weight 400, abbreviated to PPG 400) from Asahi Denka Kogyo (Tokyo, Japan). Other non-ionic surfactants were synthesized in our laboratories.

Preparation of resin in the cobaltithiocyanate

The anion-exchange resin in the Cl^- form was poured into a glass column (I.D. 15 mm) by the slurry method and its amount was adjusted so as to give a column height of 20 cm. To prepare the cobaltithiocyanate form of the anion-exchange resin, 100 ml of 3 *M* ammonium thiocyanate and 0.1 *M* cobalt nitrate solution were passed successively through the column. It was then washed with 500 ml of deionized water until the eluate became colourless. The flow-rate during the column preparation was *ca.* 2 ml/min.

Adsorption of non-ionic surfactants on the resin

To determine the amount of surfactants adsorbed by the resin in the cobaltithiocyanate form, 100 ml of aqueous surfactant solutions, each containing 30–50 mg of non-ionic surfactants, were passed through the column at a flow-rate of 0.5–1.0 ml/min. The column was then washed out with 300 ml of deionized water. The adsorbed surfactants were eluted with 50 ml of an appropriate organic solvent. After evaporating the solvent from the eluate, the residue was weighed to quantitate the non-ionic surfactants.

RESULTS AND DISCUSSION

Table I shows that the amount of non-ionic surfactant adsorbed on the resin is not related to the number of ethylene oxide (EO) or propylene oxide (PO) units alkyl chain length or type of non-ionic surfactant. The non-ionic surfactant seems to be adsorbed on the cobaltithiocyanate form of the resin by coordinate bonds between the cobalt atom on the resin surface and ether oxygen in the EO or PO chain.

To elute the adsorbed non-ionic surfactant, the eluents listed in Table II were passed through the column. The sample was ethoxylated lauryl alcohol (12 EO units per molecule). After evaporating the solvent to dryness, the surfactant in each eluate was determined gravimetrically. Although the recovery is not quantitative when elution is performed with methanol–water (1:1), the use of methanol, ethanol or isopropanol as the eluent gave satisfactory results. These results mean that the cleavage of the

TABLE I

ADSORPTION OF VARIOUS KINDS OF NON-IONIC SURFACTANTS ON ANION-EXCHANGE RESIN IN THE COBALTITHIOCYANATE FORM

Eluent: 50 ml of ethanol.

*Sample**	*Amount added (mg)*	*Amount adsorbed (mg)*
Lauryl alcohol (3 EO)	45.5	42.9
Lauryl alcohol (12 EO)	43.8	43.5
Nonylphenol (50 EO)	39.3	38.5
PEG 4000	36.8	35.2
Stearic acid (99 EO)	40.2	40.0
Tween 20 (sorbitan ester EO)	41.1	39.9
EO/PO copolymer (MW = 4800)	35.2	33.9
Lauryl alcohol (10 PO/3 EO)	38.2	37.8
PPG 400	30.5	29.5

* EO = ethylene oxide units; PO = propylene oxide units.

TABLE II

RECOVERY OF LAURYL ALCOHOL (12 EO) FROM ANION-EXCHANGE RESIN IN THE COBALTITHIOCYANATE FORM

Eluent	*Amount added (mg)*	*Amount found (mg)*
Methanol–water (1:1)	45.0	23.5
Methanol	43.2	41.8
Ethanol	47.6	47.1
Isopropanol	41.0	40.7

coordinate bond occurs between the cobalt atom and the non-ionic surfactant by solvation of the organic solvent.

The reproducibility of the recovery of non-ionic surfactants from the resin was tested with ethoxylated lauryl alcohol (12 EO units per molecule) as the sample. Sample elution was repeated five times and the average recovery was 98.0% with a relative standard deviation of 2.3%.

The influence of ionic surfactants and inorganic salts on the adsorption and recovery of non-ionic surfactants was investigated. The ionic surfactants used were sodium alkylbenzenesulphonate and dodecyltrimethylammonium chloride, and the inorganic salts were sodium chloride and sodium sulphate. Solutions containing only anionic or cationic surfactants and mixtures of non-ionic and ionic surfactants were passed through the column. It was found that the resin in the cobaltithiocyanate form adsorbs anionic and cationic surfactants slightly. The adsorption of anionic surfactants is attributed to the partial adsorption of the cobalt thiocyanate complex on the anion-exchange resin, and of cationic surfactants to coulombic forces. However, the ionic surfactants were not removed by the eluent. Inorganic salts were also adsorbed on the ion-exchange resin. The adsorption and recovery of non-ionic surfactants were not influenced by ionic surfactants (equal amount) and inorganic salts (100-fold excess). This means that the separation of non-ionic surfactants in a mixture of surfactants and inorganic salts is easily performed without any pre-treatments.

Table III shows the results of the enrichment of non-ionic surfactants. Volumes of 1000 ml of dilute aqueous solutions (15 and 100 ppm) of PEG 4000 and ethoxylated lauryl alcohol (12 EO units per molecule) were tested. The adsorbed surfactant and PEG 4000 were eluted with 50 ml of ethanol and were determined gravimetrically. The surfactant and PEG 4000 was concentrated on the resin and recovered quantita-

TABLE III

ENRICHMENT OF ETHOXYLATED LAURYL ALCOHOL AND POLYETHYLENE GLYCOL

Sample	*15 ppm*		*100 ppm*	
	Calculated (mg)	*Found (mg)*	*Calculated (mg)*	*Found (mg)*
Lauryl alcohol (12 EO)	14.8	13.9	98.7	97.6
PEG 4000	15.2	14.4	102.5	100.9

tively. This means that the resin enriches dilute solutions of non-ionic surfactants and polyethylene glycols.

In conclusion, this anion-exchange resin in the cobaltithiocyanate form is effective for separating or enriching alkylene oxide-type non-ionic surfactants.

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