

# Sorption Behaviour of Dodecylsulphate and Other Anionic Surfactants on Anion-exchange Resins

G. J. Moody, J. O. Rutherford and J. D. R. Thomas

Chemistry Department, University of Wales Institute of Science and Technology, Cardiff, CF1 3NU

Concentration isotherms have been determined for sodium dodecylsulphate from aqueous solution on the chloride form of Amberlyst A27, Cellex-T, Amberlyst IRA68, Zerolit FF(IP), Dowex 1-X8, Amberlite IRA401, Amberlite IRA904, Zerolit MPH, Amberlite IRA47S and Amberlyst IRA93 and on bromide and tetrafluorobromate forms of Amberlyst A27. Isotherms have also been determined on Amberlyst A27 (chloride) for increased ionic strength in the presence of sodium chloride adjuster at 20 and 50 times the resin capacity and for various organic - aqueous media, including 50% and 75% ethanol - water, dimethylformamide - water and tetrahydrofuran - water.

Amberlyst A27 (chloride) was selected for concentration isotherm studies of dodecyl- and tetradecylsulphate from water and 75% ethanol - water, decyl-, tetradecyl- and pentadecylbenzenesulphonate from water and 75% ethanol - water, and *sec*-dodecylsulphate, dodecane- and dodecenesulphonate, dodecanoate, 4-toluenesulphonate, tripolyphosphate and sulphate from water.

Column experiments designed to desorb and separate various anions with Amberlyst A27 are described and separations of anion pairs such as dodecanoate and dodecylsulphate, and tripolyphosphate and decylbenzenesulphonate, are discussed.

**Keywords:** *Anion exchange; anionic surfactants; alkylsulphates; alkylbenzenesulphonates; carboxylates*

Alkylsulphates, alkanesulphonates, alkenesulphonates, alkylbenzenesulphonates and alkyl-carboxylates with appropriate alkyl chains are widely used as anionic surfactants. They are frequently encountered as complex mixtures or in effluents as components of samples that can include inorganic salts, other surfactant types and miscellaneous materials. The analysis of such samples involves chromatography, ion exchange and other methods. Application of ion exchange has generally meant separation into different ionic types,<sup>1-6</sup> but recent studies concern the effects of various counter ions and non-aqueous eluents on the separation of anionic surfactants.<sup>7</sup>

This paper extends the previous studies on the ion-exchange behaviour of anionic surfactants, and includes the sorption behaviour of dodecylsulphate on a range of anion-exchange resins and of various representative anionic surfactants on Amberlyst A27 from aqueous and mixed aqueous - organic media.

## Experimental

### Materials

Chemicals were generally the best available analytical-reagent grade; for example, sodium dodecylsulphate had a rated purity of 99.9%. Alkylsulphates of chain length  $>C_{12}$  were obtained from Cambrian Chemicals Ltd. Alkylbenzenesulphonates and sodium tripolyphosphate dodecahydrate were gifts from Unilever Research, Port Sunlight.

### *Ion-exchange resins*

These were obtained from BDH Chemicals, except for Cellex-T (Bio-Rad) and Amberlyst IRA68 (Lancaster Synthesis). The anion exchangers were standard-grade chloride-form resins except for Cellex-T (bromide), Amberlyst IRA93 (hydroxide), Zerolit 625 (hydrogen) and Amberlite XAD12 sorption resin.

The ion-exchange resins were purified by successively passing 0.1 M aqueous sodium chloride (500 cm<sup>3</sup>) and absolute ethanol (500 cm<sup>3</sup>) at 5 cm<sup>3</sup> min<sup>-1</sup> up a resin column (12.5 cm

long and 1 cm diameter) by a counter flow technique. This was repeated and the resin washed with de-ionised water (500 cm<sup>3</sup>). The wet resin was dried by vacuum filtration for 5 h and its dry mass determined by drying a known amount to constant mass at 60 °C. The actual samples used for water regain measurements were not used for studies of ion-exchange behaviour. The various exchangers were converted into the appropriate ionic forms and characterised by their exchange capacities and water regain values (Table I).

TABLE I  
CHARACTERISATION OF ION-EXCHANGE RESINS

Resin	Type	Ionic form	Exchange capacity/ mequiv g <sup>-1</sup> dry resin	Water regain/ g H <sub>2</sub> O g <sup>-1</sup> dry resin
Amberlyst A27 .. ..	Macroporous	Cl <sup>-</sup>	2.40	0.85
		Br <sup>-</sup>	2.30	0.93
		BF <sub>4</sub> <sup>-</sup>	2.60	0.93
Cellex-T .. ..	Cellulose matrix	Br <sup>-</sup>	0.54	1.67
Amberlyst IRA68 .. ..	Acrylic matrix	Cl <sup>-</sup>	2.60	1.34
Zerolit FF(IP) .. ..	Microporous	Cl <sup>-</sup>	3.85	2.19
Dowex 1-X8 .. ..	Microporous	Cl <sup>-</sup>	3.16	0.73
Amberlite IRA401 .. ..	Macroporous	Cl <sup>-</sup>	3.29	1.74
Amberlite IRA904 .. ..	Macroporous	Cl <sup>-</sup>	2.07	1.14
Zerolit MPH .. ..	Weak base	Cl <sup>-</sup>	3.33	1.29
Amberlite IRA47S .. ..		Cl <sup>-</sup>	2.60	1.14
Amberlyst IRA93 .. ..		Cl <sup>-</sup>	3.19	1.30
Zerolit 625 .. ..	Macroporous cation exchanger	H <sup>+</sup>	2.70	0.83
Amberlite XAD2 .. ..	Sorption resin, washed free of chloride	—	—	—

The anion-exchange capacity of the resins were determined by Wilson's method<sup>8</sup> whereby a weighed sample of resin (~1 g) was treated in a column (1 cm internal diameter) with aqueous 4% sodium sulphate (1 dm<sup>3</sup> for chloride and bromide-form resins and 2 dm<sup>3</sup> for tetrafluoroborate-form resins) to elute counter ions. Chloride and bromide were determined by potentiometric titration with 0.1 M silver nitrate solution using an Orion 94-17 A chloride ion-selective and silver - silver bromide indicator electrodes, respectively. Tetrafluoroborate was monitored by the decrease in sulphate eluent concentration by potentiometric titration in 20% ethanol with 0.1 M barium chloride solution using a PVC matrix membrane barium ion-selective indicator electrode.<sup>9</sup>

Water regain values were determined by placing a weighed sample of dry resin (~0.5 g) in a grade 2 sintered-glass filter-stick and immersing in de-ionised water for 1 h. The gain in mass was assessed after removing the interstitial water by centrifuging (for 20 min), the removal of water being aided by incorporating 0.5% *m/m* Antarox CO-630 (an anionic surfactant) in order to decrease surface tension and thus decrease the entrapment of interstitial water.<sup>10</sup>

### Batch Procedure for Concentration Isotherms

Two main ion-exchange systems were examined for the construction of concentration isotherms, namely  $0.1 \pm 0.001$  g of resin in 50 cm<sup>3</sup> of surfactant solution in the  $5 \times 10^{-2}$  to  $2 \times 10^{-3}$  M concentration range, and  $0.02 \pm 0.0001$  g resin in 50 cm<sup>3</sup> surfactant of  $10^{-3}$  to  $2 \times 10^{-4}$  M concentration. In each instance the resin - surfactant system was agitated at  $25 \pm 0.5$  °C in a closed 100-cm<sup>3</sup> flask for 3 h (separate experiments established that equilibration was reached in 2 h) and the external solution analysed for residual surfactant and eluted counter ions. The performance of the analyses with a knowledge of resin exchange capacities permitted the resin concentrations of the surfactant and counter ions at equilibrium to be deduced.

### Analytical procedures

Solution anionic surfactant concentrations were normally monitored potentiometrically with a PVC matrix membrane anionic surfactant ion-selective electrode<sup>11-13</sup> spanning the linear range of  $10^{-3}$ – $10^{-6}$  M surfactant. Typically, 10 cm<sup>3</sup> of, say, dodecylsulphate solution

would be titrated with cationic surfactant (cetyldimethylbenzylammonium chloride) in 0.1-cm<sup>3</sup> aliquots to a total of 1 cm<sup>3</sup> and the end-point found using Orion 90-00-90 Gran plot paper.<sup>14</sup>

For resins in the tetrafluoroborate form the anionic surfactant concentration in solution was determined by Epton's titration.<sup>15</sup>

Because of the restricted range of surfactant ion-selective electrodes towards 4-toluene-sulphonate, this species was determined spectrophotometrically at 273 nm on sample aliquots (10 parts by volume) treated with 0.1 M sodium chloride (1 part by volume) in order to mask any effect by eluted chloride.

Dodecanoate was determined spectrophotometrically, in the 10<sup>-3</sup>-10<sup>-6</sup> M range, by comparing with standards the colour produced on treating 5 cm<sup>3</sup> of sample with 10<sup>-3</sup> M hydrochloric acid (0.1 cm<sup>3</sup>) in the presence of bromocresol green (0.1 cm<sup>3</sup>).

Tripolyphosphate was also determined spectrophotometrically as the phosphorus - molybdenum complex following conversion to orthophosphate by acid hydrolysis.<sup>16</sup>

Sulphate, chloride, bromide and tetrafluoroborate were determined as described above for determinations of anion-exchange capacity.

### Procedure for Column Experiments

Ion-exchange resin columns (0.7 cm i.d.) were prepared from aqueous slurries (2 cm<sup>3</sup> containing 0.7 g of resin for short columns and 20 cm<sup>3</sup> containing 7.0 g of resin for long columns) of Amberlyst A-27 of appropriate anionic form (chloride or citrate). These were pre-treated by back-washing with 100-cm<sup>3</sup> aliquots of de-ionised water, a 1 M aqueous solution of the sodium salt of the anion form of the resin, 75% ethanol - water and de-ionised water, respectively.

Column effluent fractions were generally monitored by potentiometric titration with a PVC matrix membrane anionic surfactant ion-selective electrode<sup>11-13</sup> as used in the above batch experiments. A barium ion-selective electrode<sup>9</sup> was used for sulphate, and carboxylate and tripolyphosphate were determined by the spectrophotometric procedures described above.

Anion surfactant [0.1 cm<sup>3</sup> (0.5 cm<sup>3</sup> in some instances) of 0.1 M aqueous sodium dodecylsulphate solution or 5 cm<sup>3</sup> of 10<sup>-3</sup> M aqueous solutions of other surfactants] was introduced on to the top of the column followed by elution (0.5 cm<sup>3</sup> min<sup>-1</sup>) with de-ionised water (50 cm<sup>3</sup>), during which there was no leaching of surfactant. Columns loaded with surfactant anions were eluted with the various sodium chloride solutions under study and fractions (10 or 25 cm<sup>3</sup>) collected with a fraction collector.

## Results

### Concentration Isotherm Studies

#### *Concentration isotherms of dodecylsulphate for various resins*

The preference of surfactant ions over counter ions is conveniently summarised by concentration isotherms which consist of plots [see Fig. 1(a)] of the ionic fraction of surfactant,  $x_{\text{surf}}$ , in solution against the ionic fraction of the surfactant,  $\bar{x}_{\text{surf}}$ , in the resin phase. The selectivity coefficient,  $K_{\text{B}}^{\text{surf}}$ , at any point may be conveniently calculated from the ratios of the areas C and D, and in the example of Fig. 1(a) represents a preference by the resin for surfactant over the counter ion, B.

Fig. 1 displays the concentration isotherms of dodecylsulphate for different anion-exchange resins and two ratios of initial solution surfactant concentration that embrace the critical micelle concentration ( $8 \times 10^{-3}$  M) of dodecylsulphate, namely,  $5 \times 10^{-2}$ - $2 \times 10^{-3}$  M dodecylsulphate with 0.1 g of resin and  $10^{-3}$ - $2 \times 10^{-4}$  M dodecylsulphate with 0.02 g of resin [Figs. 1(b) and 1(j)]. The isotherm for Amberlyst A27 (chloride) is repeated on several of the diagrams in order to facilitate the comparison of the various effects, namely, different resins [Figs. 1(c) to 1(f)], increased ionic strength [Fig. 1(g)], different ionic forms of Amberlyst A27 [Figs. 1(h) and 1(j)] and mixed organic - aqueous solvents [Figs. 1(i) to 1(l)].

Fig. 2 displays the concentration isotherms for Amberlyst A27 of various surfactants and anions encountered in surfactant formulations.

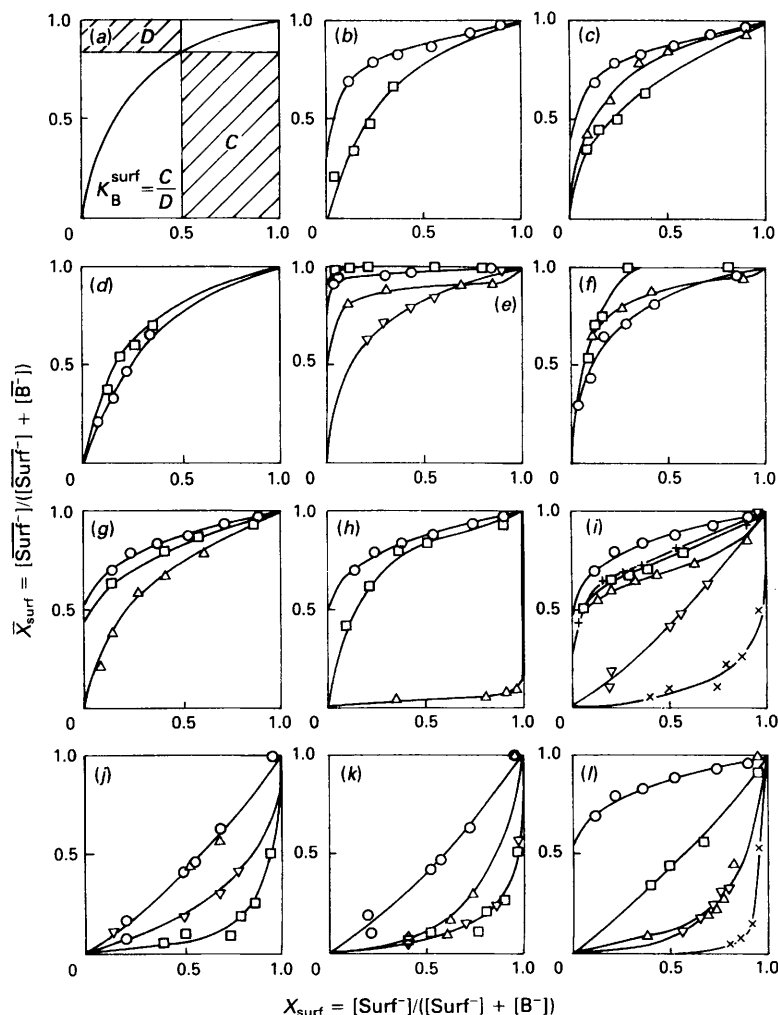


Fig. 1. Concentration isotherms of dodecylsulphate for different anion-exchange resins and under various solution conditions; 0.1-g amounts of resin were studied for surfactant concentrations in the  $0.1\text{--}10^{-3}\text{ M}$  range and 0.02-g amounts for surfactant concentrations of  $10^{-3}\text{--}2 \times 10^{-4}\text{ M}$  each in aqueous solution unless specified otherwise. (a) Typical isotherm. (b) Amberlyst A27 (chloride):  $\circ$ , 0.1 g of resin;  $\square$ , 0.02 g of resin. (c) 0.1 g of resin for Amberlyst A27 (chloride) ( $\circ$ ), Cellex T (bromide) ( $\square$ ) and Amberlyst A27 (bromide) ( $\Delta$ ). (d) 0.02 g of chloride-form resin for Amberlyst A27 ( $\circ$ ) and Amberlyst IRA68 ( $\square$ ). (e) 0.1 g of chloride-form resin for Zerolit FF(IP) ( $\circ$ ), Dowex 1-X8 ( $\square$ ), Amberlite IRA401 ( $\Delta$ ) and Amberlite IRA904 ( $\nabla$ ). (f) 0.1 g of chloride-form resin for Zerolit MPH ( $\circ$ ), Amberlite IRA47S ( $\square$ ) and Amberlite IRA93 ( $\Delta$ ). (g) 0.1 g of Amberlyst A27 (chloride) for demonstrating effect of increased ionic strength;  $\circ$ , surfactant/counter ions only;  $\square$ ,  $I = 20 \times$  resin capacity; and  $\Delta$ ,  $I = 50 \times$  resin capacity. (h) 0.1 g of Amberlyst A27 in different ionic forms:  $\circ$ , chloride;  $\square$ , bromide; and  $\Delta$ , tetrafluoroborate. (i) 0.1 g of Amberlyst A27 (chloride) in mixed organic - aqueous solvents:  $\circ$ , water;  $\square$ , 10% ethanol,  $\Delta$ , 20% ethanol;  $\nabla$ , 50% ethanol; and  $\times$ , 75% ethanol + 10% methanol. (j) Amberlyst A27 (chloride) in ethanol - water:  $\circ$  and  $\square$ , 0.1 g in 50% and 75% ethanol, respectively;  $\Delta$  and  $\nabla$ , 0.02 g in 50% and 75% ethanol, respectively. (k) 0.1 g of Amberlyst A27: chloride form in 50% ( $\circ$ ) and 75% ( $\square$ ) ethanol; bromide form in 50% ( $\Delta$ ) and 75% ( $\nabla$ ) ethanol. (l) 0.1 g of Amberlyst A27 (chloride) in mixed organic - aqueous solvents:  $\circ$ , water;  $\square$ , 50% dimethylformamide;  $\Delta$ , 75% dimethylformamide;  $\nabla$ , 50% tetrahydrofuran; and  $\times$ , 75% tetrahydrofuran.

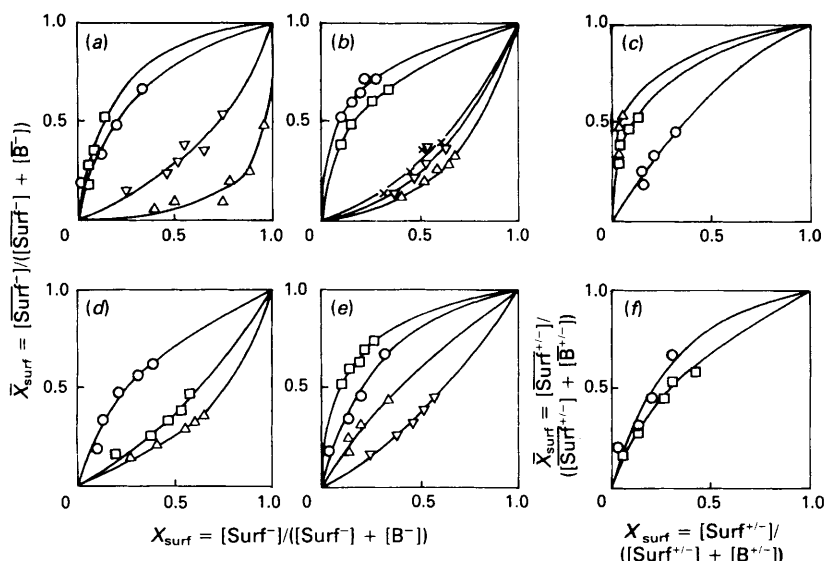


Fig. 2. Concentration isotherms of anionic surfactants and other anions with Amberlyst A27 (chloride) (0.02 g) [(a)–(e)] and a comparison of the concentration isotherm of dodecylsulphate for Amberlyst A27 (chloride) and of cetyltrimethylammonium for Zerolit 625 (0.02 g) [(f)]. (a)  $\circ$ , Dodecylsulphate;  $\triangle$ , dodecylsulphate in 75% ethanol; and  $\nabla$  tetradecylsulphate in 75% ethanol. (b)  $\circ$ , Decylbenzenesulphonate;  $\square$ , tetradecylbenzenesulphonate; and  $\triangle$ ,  $\nabla$  and  $\times$ , decylbenzenesulphonate, tetradecylbenzenesulphonate and pentadecylbenzenesulphonate, respectively, in 75% ethanol. (c)  $\circ$ , *sec*-Dodecylsulphate;  $\square$ , dodecenesulphonate; and  $\triangle$ , dodecanesulphonate. (d)  $\circ$ , 4-Toluenesulphonate;  $\square$ , triphenylphosphate; and  $\triangle$ , sulphate. (e)  $\circ$ , Dodecylsulphate;  $\square$ , decylbenzenesulphonate;  $\triangle$ , *sec*-dodecylsulphate; and  $\nabla$ , dodecanoate. (f)  $\circ$ , Dodecylsulphate; and  $\square$ , cetyltrimethylammonium with Zerolit 625 (hydrogen).

## Column Ion Exchange

### Studies with sodium dodecylsulphate on Amberlyst A27 (chloride form)

Dodecylsulphate was not eluted from chloride-form Amberlyst A27 even on treatment with 250 bed volumes (500 cm<sup>3</sup>) of 0.2 M aqueous sodium chloride. The anion was, however, released by 2 M aqueous sodium chloride, but although 42% appeared in the first 10-cm<sup>3</sup> fraction there was then considerable tailing and only 79% had been leached by fraction 10 and trace amounts were still present in subsequent fractions. Such elution was contrary to the prediction of concentration isotherms and may be attributed to effects of resin shrinkage arising from the osmotic effects of the concentrated sodium chloride solution and superposed on normal ion exchange.

Elution patterns for the short column obtained with sodium chloride in 50% and 75% ethanol-water are shown in Fig. 3. In each instance leaching was incomplete because of tailing. The long column of the chloride-form ion exchanger, prepared from 20 cm<sup>3</sup> of slurry containing 7 g of resin, when charged with 0.5 cm<sup>3</sup> of 0.1 M aqueous sodium dodecylsulphate gave similar elution tailing behaviour with 0.2 M sodium chloride in 50% ethanol-water and with 0.02 M sodium chloride in 75% ethanol-water. There was no leaching of the anion from the long column on eluting with 0.02 M sodium chloride in 50% ethanol-water.

Exponential gradient elution data using the long column were obtained by gravity feeding (0.5 cm<sup>3</sup> min<sup>-1</sup>) from a first reservoir container (50-cm<sup>3</sup> capacity and containing a magnetic stirrer) and a second reservoir containing the appropriate addition eluent. The elution patterns obtained are summarised in Fig. 4.

Checks on recovery of dodecylsulphate (50  $\mu$ mol) by elution with 0.2 M sodium chloride in 75% ethanol-water (0.5 cm<sup>3</sup> min<sup>-1</sup>) indicated recoveries of 87.5% [standard deviation

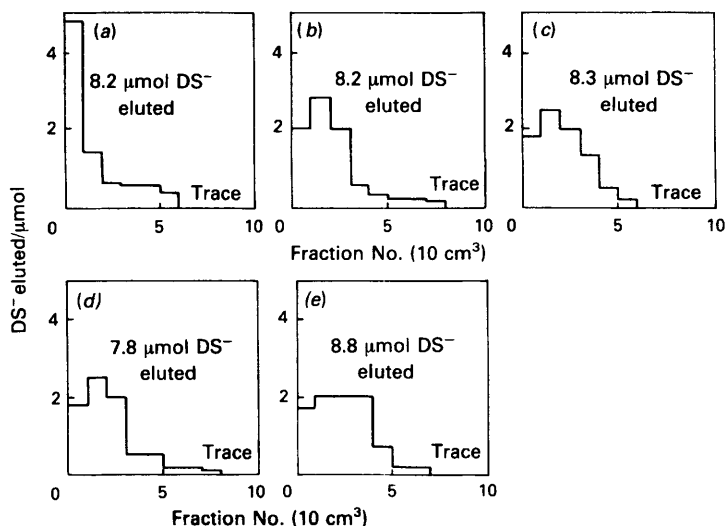


Fig. 3. Elution patterns of dodecylsulphate ( $\text{DS}^-$ ) (column load =  $10\text{ }\mu\text{mol}$ ) from Amberlyst A27 (chloride) (7 g of resin in 0.7 cm i.d. column) on elution with sodium chloride in ethanol - water mixtures. Eluents: (a) 0.2 M NaCl in 75% ethanol - water; (b) 0.02 M NaCl in 75% ethanol - water; (c) 0.002 M NaCl in 75% ethanol - water; (d) 0.02 M NaCl in 50% ethanol - water; and (e) 0.002 M NaCl in 50% ethanol - water.

(s.d.) = 2.40 for  $n = 5$ ] and 99.3% (s.d. = 1.78 for  $n = 5$ ) for the long ( $500\text{ cm}^3$  of eluate) and short ( $100\text{ cm}^3$  of eluate) columns, respectively.

No elution of dodecylsulphate occurred within  $250\text{ cm}^3$  when using either 0.2 or 0.02 M sodium acetate in 75% ethanol - water as eluent, but subsequent elution with  $100\text{-cm}^3$  bed volumes of 0.2 M sodium chloride in 75% ethanol - water gave quantitative recovery for the short column of Amberlyst A27 (chloride). Similar elution with 0.2 M sodium citrate in 75% ethanol - water ( $100\text{ cm}^3$ ) gave 71% recovery of dodecylsulphate and a similar recovery was obtained for the resin in the citrate form.

#### *Behaviour of a range of anionic surfactants on Amberlyst A27 (chloride form)*

Selected anionic surfactants were similarly assessed regarding their behaviour on Amberlyst A27 (chloride) in the presence of 0.2 M aqueous sodium chloride and 0.2 M sodium chloride in 75% ethanol - water as eluents. Because of the low solubility of certain materials, columns were loaded to  $5\text{ }\mu\text{mol}$  with  $5\text{ cm}^3$  of  $10^{-3}\text{ M}$  solutions of the sodium salts. Elution recoveries were assessed on  $100\text{ cm}^3$  of eluate.

Of the anionic surfactant materials studied, the carboxylate (dodecanoate) was eluted quantitatively with 0.2 M aqueous sodium chloride whereas all of the others remained on the ion-exchange column. These, namely dodecylsulphate, pentadecylsulphate, hexadecylsulphate, *sec*-dodecylsulphate, decylbenzenesulphonate, toluenesulphonate, dodecanesulphonate and dodecenesulphonate, were each quantitatively eluted by  $100\text{ cm}^3$  of 0.2 M sodium chloride in 75% ethanol - water.

#### *Column separation of anionic surfactants*

The above and other data indicate possible ion-exchange column separations and Table II illustrates some quantitative and reproducible separations obtained.

Attempts to resolve alkylsulphates from sulphonates were unsuccessful. For example, a short column of the Amberlyst A27 resin loaded with  $2.5\text{ }\mu\text{mol}$  each of dodecylsulphate and decylbenzenesulphonate on gradient elution with 0.02 M aqueous sodium chloride in the first reservoir and addition eluent consisting of 0.2 M sodium chloride in 75% ethanol - water



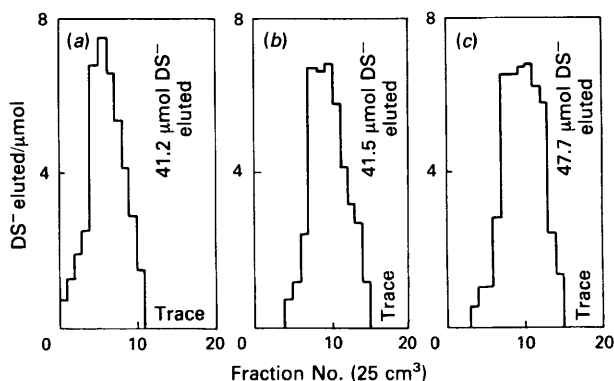


Fig. 4. Exponential gradient elution patterns of dodecylsulphate ( $\text{DS}^-$ ) (column load =  $50 \mu\text{mol}$ ) from an Amberlyst A27 (chloride) ( $7.0 \text{ g}$  of resin in  $0.7 \text{ cm i.d.}$  column) on gradient elution with various sodium chloride solutions in ethanol - water. Initial first reservoir and addition eluent composition, respectively: (a)  $0.02 \text{ M NaCl}$  in  $75\%$  ethanol - water and  $0.2 \text{ M NaCl}$  in  $75\%$  ethanol - water; (b)  $0.2 \text{ M aqueous NaCl}$  and  $0.2 \text{ M NaCl}$  in  $75\%$  ethanol - water; and (c)  $0.02 \text{ M aqueous NaCl}$  and  $0.2 \text{ M NaCl}$  in  $75\%$  ethanol - water.

yielded both anions quantitatively as a characteristic single peak with a head and long tail and spread over  $8 \times 5 \text{ cm}^3$  fractions.

A mixture containing sodium dodecanoate ( $5 \mu\text{mol}$ ), sodium tripolyphosphate ( $1 \mu\text{mol}$ ), sodium sulphate ( $2.5 \mu\text{mol}$ ) and sodium dodecylsulphate ( $5 \mu\text{mol}$ ), on being loaded on to a short column of Amberlyst A27 (chloride) and subsequent elution with  $0.2 \text{ M}$  aqueous sodium chloride ( $100 \text{ cm}^3$ ), quantitatively released the first three components, the dodecylsulphate being quantitatively released on subsequent elution with  $0.2 \text{ M}$  sodium chloride in  $75\%$  ethanol - water.

TABLE II

SEPARATIONS OF ANION PAIRS ON AMBERLYST A27 (CHLORIDE) BY ELUTION WITH  
 $0.2 \text{ M}$  AQUEOUS SODIUM CHLORIDE AND  $0.2 \text{ M}$  SODIUM CHLORIDE IN  
 $75\%$  ETHANOL - WATER

$0.7 \text{ g}$  of Amberlyst A27 in a  $0.7 \text{ cm i.d.}$  column. The numbers in parentheses indicate the amounts of each component in the mixture loaded on the column before commencing elution. Recoveries were quantitative in each instance.

Mixture No.	Eluted by $0.2 \text{ M}$ aqueous $\text{NaCl}$ ( $100 \text{ cm}^3$ )	Eluted by $0.2 \text{ M}$ $\text{NaCl}$ in $75\%$ ethanol - water ( $100 \text{ cm}^3$ )
1	Dodecanoate ( $5 \mu\text{mol}$ )	Dodecylsulphate ( $5 \mu\text{mol}$ )
2	Tripolyphosphate ( $1 \mu\text{mol}$ )	Dodecylsulphate ( $5 \mu\text{mol}$ )
3	Tripolyphosphate ( $1 \mu\text{mol}$ )	Pentadecylsulphate ( $5 \mu\text{mol}$ )
4	Tripolyphosphate ( $1 \mu\text{mol}$ )	Decylbenzenesulphonate ( $5 \mu\text{mol}$ )
5	Sulphate ( $2.5 \mu\text{mol}$ )	Dodecylsulphate ( $5 \mu\text{mol}$ )
6	Sulphate ( $2.5 \mu\text{mol}$ )	Pentadecylsulphate ( $5 \mu\text{mol}$ )
7	Sulphate ( $2.5 \mu\text{mol}$ )	Decylbenzenesulphonate ( $5 \mu\text{mol}$ )

## Discussion

### Batch Experiments and Concentration Isotherms

Concentration isotherms lying well above the diagonal are indicative of high relative affinity by the resin for the surfactant ion. Hence, for devising any separation scheme for surfactants by ion-exchange resins at least some of the concentration isotherms should lie near to the diagonal and be widely separated from other isotherms.

*Studies with sodium dodecylsulphate*

The similarities between the isotherms for different initial solution surfactant concentrations and which embrace the critical micelle concentration (CMC) of dodecylsulphate [Figs. 1(b) and 1(j)] indicate that any micelle formation, associated with the CMC, does not affect the general form of the isotherms, suggesting that there is a dynamic condition between the free dodecylsulphate anions and those in micelles.

Figs. 1(c) and 1(d) show that the isotherms for Amberlyst A27 (polystyrene matrix), Cellex T (cellulose matrix) and Amberlite IRA68 (polyacrylic matrix) depict high relative affinity for dodecylsulphate by resins with very different matrix structures, with Cellex T showing a lesser relative affinity than the other exchangers. These studies on resins with different matrices are associated with the possibility of the matrix itself interacting with the surfactant. A mass balance assessment of the external solution ionic strength by each of the resins before and after equilibration (Table III) shows that whereas the extent of physical sorption (loss of ionic strength from solution) by Amberlyst A27 was less than for the sorption resin, Amberlyst XAD2 (polystyrene matrix with no ion-exchange sites), physical sorption by Amberlite IRA68 was greater and by Cellex-T was much greater.

TABLE III

MASS BALANCES OF SOLUTION IONIC STRENGTHS BEFORE AND AFTER  
EQUILIBRATION WITH VARIOUS RESINS

0.1 g of resin and 50 cm<sup>3</sup> of sodium dodecylsulphate solution.

Solution ionic strength before equilibration/mm	Solution ionic strength after equilibration/mm			
	Amberlyst A27 (chloride)	Cellex-T (bromide)	Amberlite IRA68 (chloride)	Amberlyst XAD2
1.0	0.95 (5)*	0.77 (23)*	0.83 (17)*	(13)*
0.8	0.74 (8)	0.51 (37)	0.72 (10)	(9)
0.6	0.59 (2)	0.39 (35)	0.54 (10)	(8)
0.4	0.39 (2)	0.29 (28)	0.37 (8)	(2)

\* Percentage physical sorption in parentheses.

The microporous resins Zerolit FF(IP) (a conventional Type I strong base anion exchanger) and Dowex I-X8 (a Type II strong base anion exchanger), surprisingly show an even greater relative affinity towards dodecylsulphate than do the macroporous resins Amberlyst A27, Amberlite IRA401 and Amberlite IRA904 [Fig. 1(e)]. For the three macroporous resins, the greatest relative affinity is shown by the highly porous, low cross-linked Type I strong anion exchanger Amberlite IRA401, designed for holding high relative molecular mass anions. The weak base exchangers Zerolit MPH, Amberlite IRA47S and Amberlyst IRA93 also have high relative affinity towards dodecylsulphate [Fig. 1(f)], that is, similar to the strong base Amberlite IRA401 and IRA904 [Fig. 1(e)] and Amberlyst A27 [Fig. 1(b)] resins.

Increasing the ionic strength of the solution with sodium chloride effectively reduces the affinity of Amberlyst A27 for dodecylsulphate [Fig. 1(g)]. This approach, but with 5 M sodium chloride, has been used in the salting-out elution chromatographic separations of naphtholsulphonic acids.<sup>17,18</sup>

Of the resins studied, Amberlyst A27 exhibits typical behaviour; this resin was therefore chosen for studying the effect of varying the counter ion. It also has utility in partially non-aqueous media. The bromide-form resin still exhibits a strong relative affinity for dodecylsulphate, but this is completely lost when the resin is in the tetrafluoroborate form [Fig. 1(h)] and the isotherm depicts very little affinity by the resin for dodecylsulphate.

The use of partially non-aqueous media in the ion exchange of surfactants introduces the possibility of combined ion exchange and solvent extraction (CSISE). In all instances studied, the use of mixed organic - aqueous solvents reduces the relative affinity of Amberlyst A27 for dodecylsulphate [Figs. 1(i)-(l)] and tetrahydrofuran is most effective [Fig. 1(l)]. Nevertheless, the isotherm for 50% ethanol - water lies near the medium to the diagonal, and tetrahydrofuran is less obnoxious than dimethylformamide.



*Studies of other surfactants and related anions*

Amberlyst A27 was considered suitable for characterising the isotherms of other anionic surfactants and related anions. There is little difference in the relative affinity of dodecylsulphate and tetradecylsulphate for the resin in water, but some distinction is apparent in 75% ethanol-water [Fig. 2(a)]. Such an effect is not characteristic of the similar solvent system for arylsulphonates, namely decyl-, tetradecyl- and pentadecylbenzenesulphonate [Fig. 2(b)].

The aqueous isotherm for *sec*-dodecylsulphate falls near the diagonal, but those of dodecane- and dodecenesulphonate resemble the aqueous isotherms of dodecylsulphate and decylbenzenesulphonate [Fig. 2(c)]. It is interesting that the aqueous isotherm of the cationic surfactant cetyldibenzylammonium on Zerolit 625 (hydrogen) is similar to that of dodecylsulphate on Amberlyst A27 [Fig. 2(f)].

The isotherms depicted in Fig. 2 suggest possibilities for using Amberlyst A27 to separate anionic surfactants and other significant ions such as sulphate and tripolyphosphate. Some examples of widely different isotherms that can lead to separations are depicted in Figs. 2(d) and 2(e). Thus, it may be possible to separate dodecanoate from dodecylsulphate, dodecylsulphate from tripolyphosphate, etc. Such possibilities have been examined briefly in the column studies of this work and the results, summarised in Table II, are discussed below.

**Column Experiments**

Quantitative ion-exchange separation of different ionic types of surfactants was first reported by Voogt,<sup>2-4</sup> who separated cationic, anionic and non-ionic surfactants from each other. This is relatively straightforward but, as demonstrated by the above data, separation within ionic types is more difficult. Previous methods have involved uptake by ion-exchange resins followed by multi-stage treatment with reagents, such as aqueous ethanol and hexane, 5% potassium hydroxide solution and 2 M hydrochloric acid for recovering carboxylates, alkylsulphates and alkylbenzenesulphonates.<sup>5</sup> Here it has been shown that dodecanoate may be separated from alkylsulphates and sulphonates simply by eluting the ion-exchange column with 0.2 M aqueous sodium chloride and subsequently with 0.2 M sodium chloride in 75% ethanol-water in order to recover the alkylsulphates and arylsulphonates. Tripolyphosphate and sulphate may also be separated from alkylsulphates and arylsulphonates (Table II).

Further separation within the anionic surfactants by ion exchange will require more refined techniques that will benefit from the data in Figs. 1-4. Such techniques can include resort to chromatographic grade ion exchangers and use of pressure during the elution stages. A further possible approach is that of salting-out elution chromatography<sup>19</sup> on ion-exchange columns, which, although not involving ion exchange *per se*, can be a very useful complementary technique which has previously proved successful for resolving naphtholsulphonate isomers.<sup>17-21</sup> In this respect it should be noted that the ion-exchange behaviours reported in this work for toluenesulphonate and decylbenzenesulphonate are similar despite the longer alkyl chain in decylbenzenesulphonate.

**Conclusion**

Concentration isotherms obtained by batch ion-exchange experiments provide helpful data for selecting resins and conditions for designing conditions appropriate for column sorption and desorption by ion exchange. However, further improvements in resolving mixtures of anionic surfactants by ion exchange require more refinement, although it has been shown here that carboxylate, represented by dodecanoate, can readily be separated from alkylsulphates and sulphonates.

The authors thank the Science Research Council for a studentship (to J.O.R.) under the Cooperative Awards in Science and Engineering Scheme in conjunction with Unilever Research, Port Sunlight Laboratory. The valuable guidance and advice of Dr. B. J. Birch and the keen interest of Dr. T. H. Shuttleworth and Mr. R. Wellwood (all of Unilever Research) are also gratefully acknowledged.

## References

1. Gin, R. T., and Church, F. L., *Anal. Chem.*, 1959, **31**, 551.
2. Voogt, P., *Rec. Trav. Chim. Pays-Bas*, 1958, **77**, 889.
3. Voogt, P., *Rec. Trav. Chim. Pays-Bas*, 1959, **78**, 899.
4. Voogt, P., *Vortraege Originalfassung Int. Kongr. Grenzflaechenaktive Stoffe*, **3**, Cologne, 1960, **3**, 78.
5. Rosen, M. J., *J. Am. Oil Chem. Soc.*, 1960, **38**, 218.
6. Hempel, H., and Kirschnek, H., *Fette, Seifen, Anstrichm.*, 1959, **61**, 369.
7. Midler, Q., Vallmalle, G., and Karleskind, F., *Proc. 13th World Congr., Int. Soc. Study Fats*, 1976, Sect. G.17.
8. Wilson, A. L., *J. Appl. Chem.*, 1959, **9**, 466.
9. Jaber, A. M. Y., Moody, G. J., and Thomas, J. D. R., *Analyst*, 1976, **101**, 179.
10. Parish, J. R., *J. Appl. Chem.*, 1965, **15**, 281.
11. Birch, B. J., and Clarke, D. E., *Anal. Chim. Acta*, 1972, **61**, 59.
12. Birch, B. J., and Clarke, D. E., *Anal. Chim. Acta*, 1973, **67**, 581.
13. Birch, B. J., and Clarke, D. E., *Anal. Chim. Acta*, 1974, **69**, 473.
14. *Orion Research Newsl.*, 1969, **1**, 5.
15. Epton, S. R., *Trans. Faraday Soc.*, 1948, **44**, 226.
16. Murphy, J., and Riley, J. P., *Anal. Chim. Acta*, 1962, **27**, 31.
17. Funasaka, W., Kojima, T., and Fujimara, K., *Bunseki Kagaku*, 1961, **10**, 374.
18. Funasaka, W., Kojima, T., Fujimara, K., and Minami, T., *Bunseki Kagaku*, 1963, **12**, 446.
19. Rieman, W., and Walton, H. F., "Ion Exchange in Analytical Chemistry," Pergamon Press, Oxford, 1970, Chapter 9.
20. Funasaka, W., Kojima, T., Fujimara, K., and Koshida, S., *Bunseki Kagaku*, 1963, **12**, 1170.

Received October 2nd, 1980

Accepted January 29th, 1981