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Experimental Foam Fractionation Selectivity Coefficients for the Alkali (Group IA) Metals

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Abstract

An experimental investigation is presented of the continuous-flow foam fractionation of each of the colligends Li^+, K^+, Rb^+, and Cs^+ versus Na^+, the counterion of the dodecylsulfate anion over the aqueous solution concentration range of 1.0×10^{-4} to 6.0×10^{-4} *M*. Initial experiments with K^+ confirm the achievement of a single-equilibrium-stage separation. Surfactant selectivity coefficients, defined in terms of a colligend-surfactant counterion exchange model at the interfaces of the rising gas bubbles, are established. They represent the ratio of colligend to sodium in the interfacial "stream" to that in the residual steam and are Li^+, 0.92; K^+, 1.10; Rb^+, 1.51; Cs^+, 1.65. The selectivity sequence is compared to the sequence of absolute partial molal entropies of the cations in aqueous solution.

INTRODUCTION

Foam fractionation processes have been used rather extensively to concentrate and to remove selectively nonsurface-active ions from dilute (10^{-6}-10^{-3} *M*) aqueous solutions. In the case of cations, an anionic surfactant interacts preferentially with the cation of interest, termed the colligend, in competition with cations of like charge (including the surfactant's counterion). The surfactant-colligend ion pairs or soluble complexes (no particles are formed) are concentrated in the foam which

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is formed by the passage of gas bubbles through the bulk solution. Foam fractionations have been included in recent reviews of foam separation processes (*1, 2*), updating earlier reviews (*3–6*).

The most convenient mode of operation, which provides readily-interpretable and reproducible separation data, is a continuous-flow, steady-state, single-equilibrium-stage unit. A useful way to describe a foam fractionation is in terms of a dimensionless selectivity coefficient which is defined on the basis of the hypothesis made concerning the colligend–surfactant interaction which occurs. For monovalent, anionic colligends, a model based on an exchange reaction between the surfactant counterion and the colligend at the interfaces of the rising gas bubbles has been validated in comparison with other possible interaction models (*7*).

The objectives of this investigation are (a) to determine if the experimental, continuous-flow foam fractionation unit in fact produces a single-equilibrium-stage separation for an anionic surfactant and a cationic colligend and if consistent selectivity coefficients can be established on the basis of the interface ion-exchange model; and (b) to determine experimentally accurate and reproducible values of the selectivity coefficient for K^+, Rb^+, Cs^+, and Li^+, each versus Na^+, the counterion of the surfactant, dodecylsulfate (DS^-), anion. No data have been reported in the literature for the entire series of alkali (Group IA) metals. Foam fractionation studies have been limited to Na^+ versus Ca^{2+} or K^+ (*8, 9*) and the development of a predictive theory, based on the Gouy-Chapman model of the diffuse double layer and the hydrated radii of the cations, which could be applied to the alkali metals (*10*). Extensive studies have been reported on foam separation processes to remove Cs^+ from low-level, radioactive wastes (*11–19*), including selectivities versus Ca^{2+}, Sr^{2+}, and Ce^{3+}, but no comparisons have been made with the other alkali metals.

THE SELECTIVITY COEFFICIENT

A schematic diagram of a continuous-flow, single-equilibrium-stage foam fractionation unit is presented in Fig. 1. The feed stream from the mix tank contains concentrations e_i of the dodecylsulfate (DS^-) anion; n_i of DS^-'s counterion, Na^+; c_i of the colligend cation, either K^+, Rb^+, Cs^+, or Li^+; and z_i of the anion of the colligend salt, Cl^-, with all concentrations in mole/liter. The flow rate of the feed stream is L, liter/min, the flow rate of the gas stream is A, cm^3/min, and the average bubble diameter is D_b, cm. The steady-state foam stream (collapsed, as liquid)

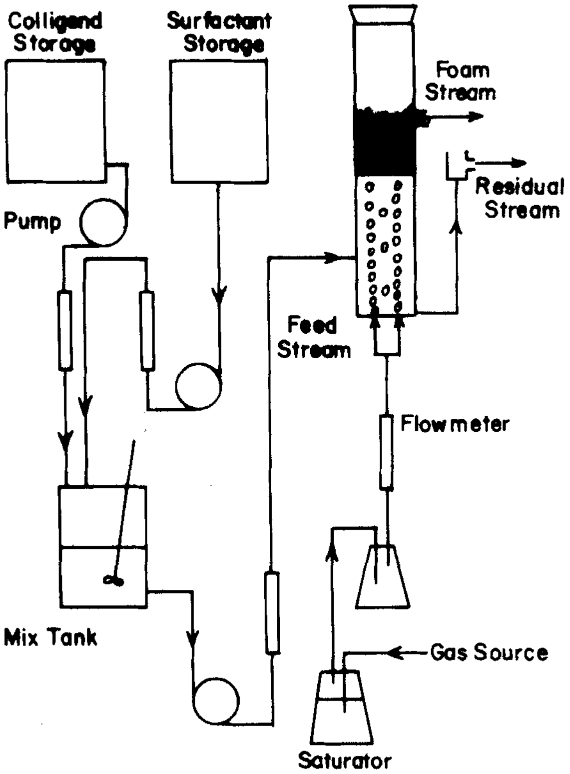

FIG. 1. Schematic diagram of continuous-flow, single-equilibrium-stage, foam fractionation unit.

contains the concentrations e_f, n_f, c_f, and z_f of the four ionic species, respectively, and similarly for the residual or bulk steam, the steady-state concentrations are e_r, n_r, c_r, and z_r, respectively. As the gas bubbles rise through the bulk solution, the surfactant rapidly diffuses to the gas–solution interfaces, and for a single-equilibrium stage, the surface excess of surfactant adsorbed in the interfacial fraction of the foam liquid (or interfacial "stream"), Γ_e, is in equilibrium with e_r.

Based on several key assumptions (*7*) which have been verified experimentally (*20*), the following mass balance equations may be written for the column:

$$\Gamma_e = \frac{D_b L}{6A}(e_i - e_r) \tag{1}$$

$$\Gamma_n = \frac{D_b L}{6A}(n_i - n_r) \tag{2}$$

$$\Gamma_c = \frac{D_b L}{6A}(c_i - c_r) \tag{3}$$

in which Γ_e, Γ_n, and Γ_c are the surface excesses of surfactant, sodium, and colligend, respectively, in mole/cm^2. Experiments have shown (*19*) that chloride is neither positively nor negatively adsorbed at the gas–solution interface, and therefore Γ_z, the surface excess of chloride, is zero.

Of the various possible models for colligend–surfactant interaction, the most valid for the monovalent colligends is that based on colligend-surfactant counterion exchange at the interfaces of the rising gas bubbles (*7*). The model hypothesizes that the surfactant anions rapidly diffuse to and are adsorbed at the gas–solution interfaces and behave as mobile cation exchangers according to the following "reaction,"

$$(\mathrm{Na{-}DS})_s + (\mathrm{K^+})_r \rightleftarrows (\mathrm{K{-}DS})_s + (\mathrm{Na^+})_r$$

where the subscripts *s* and *r* indicate the interfacial or surface "stream" and residual stream (bulk solution), respectively. For a single-equilibrium-stage foam fractionation, and from Eqs. (2) and (3), the surface exchange reaction equilibrium constant, which is also a surfactant selectivity coefficient, may be written (neglecting activity coefficient contributions)

$$K_{se} = \left(\frac{\Gamma_c}{c_r}\right)\bigg/\left(\frac{\Gamma_n}{n_r}\right) = \left(\frac{c_i - c_r}{c_r}\right)\bigg/\left(\frac{n_i - n_r}{n_r}\right) \tag{4}$$

All of the terms on the right-hand side of Eq. (4) can be found from single-equilibrium-stage fractionation data, and the separation can be described in terms of K_{se}. The selectivity coefficient, K_{se}, represents the ratio of colligend to sodium in the interfacial "stream" to that in the residual stream, or alternatively, the ratio of the distribution coefficients of colligend and sodium.

EXPERIMENTAL

A schematic diagram of the experimental unit is shown in Fig. 1. Surfactant and colligend feed solutions were prepared by dissolving the reagent in the appropriate amount of doubled distilled water with a conductivity of 6 μmho/cm at 25°C. The concentration of surfactant in the stream entering the foam fractionation column was held constant at approximately 4.5×10^{-4} *M* (well below the critical micelle concentration), and the concentration of the colligend salts ranged from 1.0×10^{-4} to 6.0×10^{-4} *M*. Both the surfactant feed solution and each colligend salt feed solution were pumped to the mixing tank through calibrated flowmeters by peristaltic pumps. The liquid volume in the mixing tank, agitated by a magnetic stirrer, was maintained at 2.1 L, corresponding to a 50-min holding time. The feed to the column was pumped from the mixing tank at 0.043 L/min. The feed entered the column through a glass port at a height 10 cm above the base of the column.

The inside diameter of the cylindrical glass column was 9.7 cm, with an overall height of 89.5 cm. In most experiments the liquid solution height was maintained at 33.5 cm above the base of the column, and the foam height was maintained at 16.0 cm above the foam–liquid solution interface, with the foam being continuously removed from the column at this point. In a few experiments the liquid solution height was varied from 16.0 to 47.0 cm. The residual steam was continuously removed through an exit port located 0.5 cm above the base of the column. Residual stream flow rates averaged 0.034 L/min for all runs, corresponding to 79% of the feed flow rate. The column operating temperature was held at 24°C.

Nitrogen, saturated with water, was introduced to the column through sintered glass diffusers, 3.0 cm in diameter and of 10–15 μm porosity, at a constant flow rate of 220 cm^3/min. The bubble diameter was measured by photographing the bubbles and a wire of known diameter in the column, using a Nikon F2 Photomic camera (lens *f* 1.4, 50 mm), with Kodak Plus-X film in conjunction with a Sunpak 511 strobe flash unit. From the pictures obtained, the diameter of the bubbles was determined to be $D_b = \Sigma n_j D_{bj} / \Sigma n_j = 0.070$ cm, with a standard deviation of 0.020 cm.

The system reached steady-state in a shorter time if the column was originally filled with a surfactant–colligend salt solution of concentration corresponding rather closely to the expected residual stream concentration. Each experimental run was carried out for a minimum of 4 h. Steady-state was assured by the constancy of the analysis of consecutive samples.

Reagents and Analysis

The surfactant was sodium dodecylsulfate, Technical Grade, Matheson, Coleman, and Bell. The colligend salt reagents and modes of analysis were as follows: Lithium chloride, Fisher Certified, analyzed with a Varian AA-575 Atomic Absorption Spectrophotometer with an air–acetylene flame. All lithium standards and samples were matched with 2000 mg/L potassium to prevent ionization of lithium in the flame. Sodium chloride, Fisher Certified, analyzed with an air–acetylene flame and matched with 2000 mg/L cesium. Potassium chloride, Reagent Grade, J. T. Baker, analyzed with an air–acetylene flame and matched with 2000 mg/L cesium. Rubidium chloride, Purified Grade, Fisher, analyzed with an air–acetylene flame and matched with 2000 mg/L potassium. Cesium chloride, Fisher Certified, analyzed with an air–acetylene flame and matched with 2000 mg/L potassium.

The accuracy of all the analyses was in the 4–5% range at the concentration levels employed in the foam fractionations.

RESULTS AND DISCUSSION

An initial series of experiments was carried out with potassium as the colligend to test the validity of the assumption of a single-equilibrium-stage operation, with results presented in Table 1. In these experiments, and all others detailed below, the operational variables L, A, and D_b appearing in Eqs. (1)–(3) were 0.043 L/min, 220 cm^3/min, and 0.070 cm, respectively. The liquid solution height was varied from 16.0 to 47.0 cm, without an observable trend in the values of the surfactant selectivity coefficient, K_{se} (calculated from the experimentally determined con-

TABLE 1

Effect of Liquid Solution Height on the Foam Fractionation of Potassium Versus Sodium

$e_i = n_i = 4.5 \times 10^{-4} M$

$c_i = 4.1 \times 10^{-4} M$

Liquid solution height above column base (cm)	K_{se}
16.0	1.15
28.0	1.09
33.5	1.21
47.0	1.07

centrations and Eq. 4). This indicates that a single-equilibrium-stage separation was achieved at the lowest height with rather little modification produced as the height was elevated. (The sensitivity of K_{se} to small concentration changes, in turn producing variations in K_{se}, will be discussed below.) Evidently the surfactant diffused rapidly to the interfaces of the rising gas bubbles, resulting in equilibrium adsorption, and the surface exchange reaction between Na^+ and K^+ had reached equilibrium by the time the bubbles rose to the lowest solution height of 16.0 cm. All additional experiments were conducted at a liquid solution height of 33.5 cm, and the same foam height of 16.0 cm, with reasonable assurance of the attainment of a single equilibrium stage.

A second series of experiments was carried out for a sequence of colligends: potassium, rubidium, cesium, and then lithium, each exchanging with the surfactant counterion sodium. The feed stream concentration of sodium dodecylsulfate (and thus of sodium) was about 4.5×10^{-4} *M* and the concentrations of potassium, rubidium, cesium, or lithium in the feed stream ranged from 1.7×10^{-4} to 5.6×10^{-4}, 2.0×10^{-4} to 6.1×10^{-4}, 1.3×10^{-4} to 3.3×10^{-4}, or 1.0×10^{-4} to 2.0×10^{-4} *M*, respectively. The pH values of the feed streams were set by those of the double distilled water solutions and were in the 6.0–6.5 range.

Experimental data for potassium, rubidium, and cesium are presented in Figs. 2, 3, and 4 with $(c_i - c_r)/(n_i - n_r)$ plotted against c_r/n_r. The best, least squares, straight lines are drawn through the data and (0,0), the slopes of which are K_{se} according to Eq. (4). An additional method of computing K_{se} is by plotting $(c_i - c_r)/c_r$ vs $(n_i - n_r/n_r$: the slopes of the best, least squares, straight lines drawn through the data and (0,0) are also K_{se} according to Eq. (4). The purpose of the second analysis is to give a balanced weighting to all of the data for each colligend: points with large values of $(c_i - c_r)/(n_i - n_r)$ and of c_r/n_r have small values of $(c_i - c_r)/c_r$ and $(n_i - n_r)/n_r$, and vice versa.

Results of the analysis of the data are summarized in Table 2, including a very limited number of data points for lithium. The least squares correlation coefficient, *r*, is defined by

$$r = 1 - \left[\frac{\sum (g_{\text{experimental}} - g_{\text{calculated}})^2}{\sum (g_{\text{experimental}} - g_{\text{mean}})^2}\right]^{1/2} \tag{5}$$

in which *g* stands for $(c_i - c_r)/(n_i - n_r)$ or $(c_i - c_r)/c_r$ and the calculated values are computed from Eq. (4) with K_{se} the appropriate value in Table 2. The correlation coefficients indicate a reasonable fit for Eq. (4). The last column in Table 2 presents the "best" value of K_{se} for each colligend, the average of the values determined by the two methods of analysis.

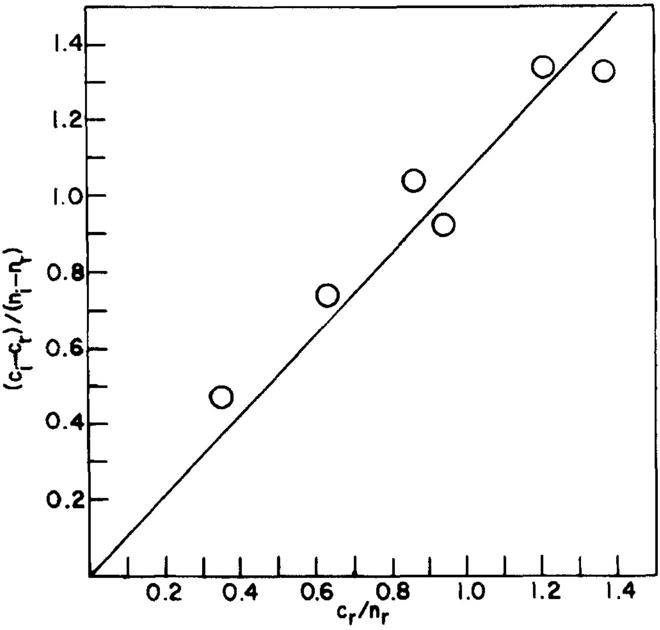

FIG. 2. Relationship between $(c_i - c_r)/(n_i - n_r)$ and c_r/n_r for potassium versus sodium.

TABLE 2
Summary of Experimental Results for Alkali Metal Colligends Versus Sodium

		K_{se}, based on				
Colligend	Number of experimental points	$(c_i - c_r)/(n_i - n_r)$ vs c_r/n_r	r	$(c_i - c_r)/c_r$ vs $(n_i - n_r)/n_r$	r	Best K_{se}
Potassium	6	1.06	0.95	1.15	0.87	1.10
Rubidium	6	1.53	0.98	1.49	0.76	1.51
Cesium	5	1.65	0.99	1.64	0.97	1.65
Lithium	2	0.93	0.99+	0.92	0.99+	0.92

A further indication of the validity of the model of Eq. (4) and of the goodness of fit of the linear correlations in Figs. 2–4 is the extreme sensitivity of the surfactant selectivity coefficient, K_{se}, to the measured values of the residual stream concentrations of colligend (c_r) and of the surfactant counterion, sodium (n_r). For example, from Fig. 3 for rubidium and the data point at $(c_i - c_r)/(n_i - n_r) = 0.94$, $c_r/n_r = 0.64$, let us assume

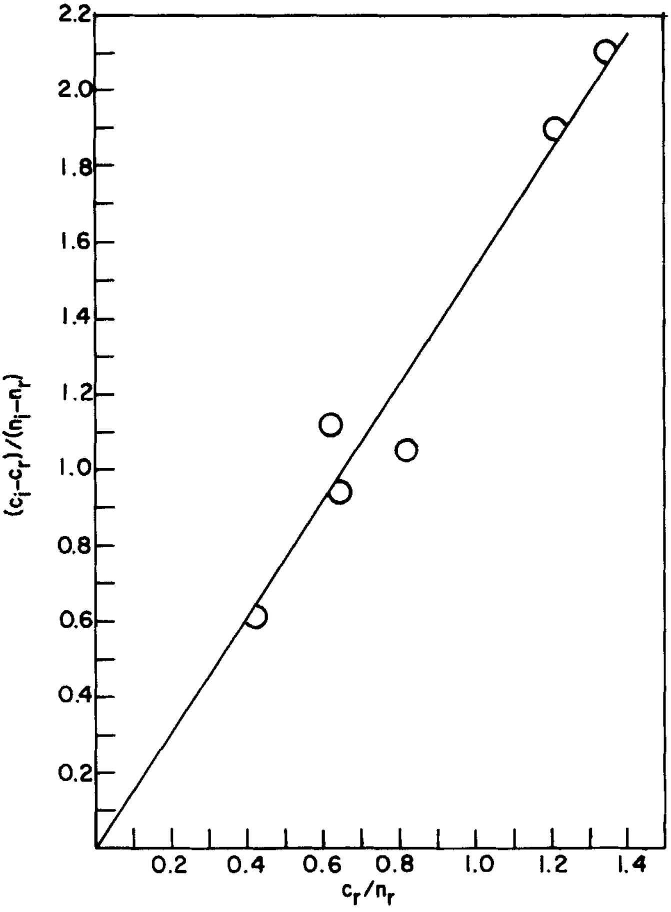

FIG. 3. Relationship between $(c_i - c_r)/(n_i - n_r)$ and c_r/n_r for rubidium versus sodium.

that the measured value of c_r was 2% high and the measured value of n_r was 2% low. That would change the value of K_{se} for that point from 1.47 to 2.01, for a 47% variation.

Efforts have been made to predict the selectivity of cationic surfactants for a series of anions and of anionic surfactants for a series of cations (*1*). The extent of interaction with an anionic surfactant should be determined by the cation's charge, structure (if polyatomic), and degree of hydration. The absolute partial molal entropy of the cation in aqueous solution, $\bar{S}^{\circ}_{298}$abs, has been suggested as a possible selectivity criterion (*21*). For monovalent, monatomic cations, the surfactant selectivity

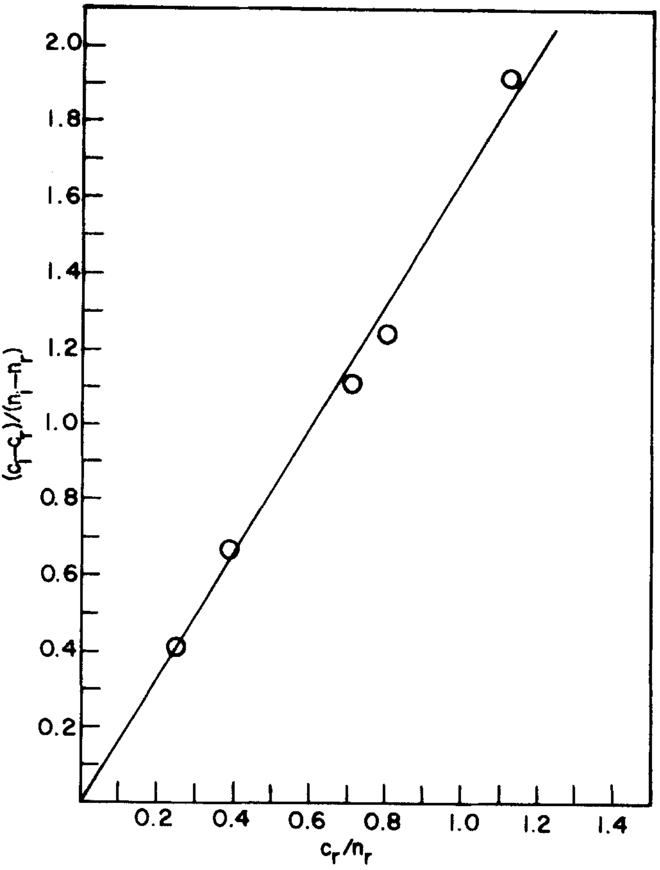

FIG. 4. Relationship between $(c_i - c_r)/(n_i - n_r)$ and c_r/n_r for cesium versus sodium.

should increase as the degree of cation hydration decreases, and therefore as $\bar{S}^o_{298}$abs increases. Table 3 presents the alkali metal cations sequenced by increasing selectivity, the corresponding "best" values of K_{se}, and $\bar{S}^o_{298}$abs for the cations. Values of $\bar{S}^o_{298}$abs were taken from the National Bureau of Standards (*22*) and from Gurney (*23*). The correlation is not unreasonable, although it may be argued that other parameters indicating the degree of hydration would be equally appropriate.

CONCLUSIONS

A continuous-flow foam fractionation unit is shown to provide a single-equilibrium-stage separation of an ionic surfactant and a colligend

TABLE 3
Selectivity Coefficients and Absolute Partial Molal Entropies in Aqueous Solution of Alkali Metal Cations

Colligend	K_{se}	$\bar{S}^{\circ}_{298}$abs (e.u.)
Lithium	0.92	−2.1
Sodium	(1.00)	8.9
Potassium	1.10	19.0
Rubidium	1.51	24.2
Cesium	1.65	26.3

in competition with the surfactant's counterion, sodium, with aqueous solution concentrations of the order 10^{-4} *M*. Based upon an interaction model hypothesizing colligend–surfactant counterion exchange at the gas–solution interfaces of the rising gas bubbles, surfactant selectivity coefficients for each of the colligends lithium, potassium, rubidium, and cesium versus sodium are determined to be 0.92, 1.10, 1.51, and 1.65, respectively. The correlation coefficients, generally of the order 0.95+, indicate a reasonable fit for the model and for the linear selectivity coefficient correlations, particularly considering the sensitivity of the selectivity coefficient to variations in the measured residual stream concentrations of the alkali metals. The selectivity coefficients can be correlated with the absolute partial molal entropy of the alkali metal cations in aqueous solution, $\bar{S}^{\circ}_{298}$abs, which increases as the degree of cation hydration decreases, for a series of monatomic cations of like charge. For these experiments, the foam stream, collapsed as liquid, is about 21% of the feed stream.

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