

CHAPTER V

REMOVAL OF TRACE Cd²⁺ USING CONTINUOUS MULTISTAGE ION FOAM FRACTIONATION PART III—EFFECT OF SALT ADDITION

5.1 Abstract

In this study, a multistage foam fractionation column with 5 bubble-cap trays was used to remove cadmium (Cd) at a low concentration (10 ppm) with sodium dodecyl sulfate (SDS) used to generate foam. The effects of anions (NO₃⁻, Cl⁻, and SO₄²⁻) and cations (Na⁺, K⁺, Mg²⁺, and Ca²⁺) were investigated by addition of sodium salts and nitrate salts, respectively. The addition of each studied salt was found to increase the residual factor of Cd (Cd concentration in effluent/Cd concentration in feed) due to the effect of the competitive adsorption of added counterions with Cd²⁺ at the air–water interface of foam at a relatively high concentration of salt whereas the added anions had a little effect. The effect of added cations and anions on the reduction of Cd removal are in the following order: Ca²⁺>Mg²⁺>>K⁺>Na⁺ and SO₄²⁻≈Cl⁻>NO₃⁻, respectively. The SDS recovery was found to increase significantly with increasing added salt concentration because the repulsion force between the head groups of SDS is greatly reduced by the co-adsorption of the counterions from added salt, leading to increasing SDS adsorption at the air–water interface of foam. The added salts of divalent cations were found to affect both Cd and SDS separation performance more than those of monovalent cations.

Keywords: ion foam fractionation, heavy metal, cadmium removal, sodium dodecyl sulfate

5.2 Introduction

Ion foam fractionation is an adsorptive bubble separation process in which a surface active agent and its counterions adsorb preferentially at the air–water interface or bubble surface of the foam, leading to the sequential separation of both surface active agent and counterions from the bulk liquid at the foam exit of the process [1]. The removal effectiveness of dissolved substances involves the differences in their distribution or partitioning between the air–water interface and the bulk aqueous phase. Our previous study reveals that ionic surfactant adsorption associated with co-adsorbed counterions at the air–water interface of the foam plays an important role in foaming properties and amounts of surfactant and counterion transferred per unit area of foam (adsorption density), thus affecting the separation performance of ion foam fractionation [2,3].

A mole balance of any material transferred out to the collapsed foam solution, foamate, at the foam exit of single stage foam fractionation can be expressed by that the molar flow rate of adsorbed materials in foamate ($C_f V_f$) is equal to the summation of the mass transfer by the bulk liquid and adsorptive transports [4]:

$$C_f V_f = C_e V_f + A\Gamma \quad (5.1)$$

where V_f is the volumetric flow rate of foamate which is equal to that of lamella liquid of the generated foam, C_e is the component concentration in the effluent, C_f is the component concentration in the foamate. By assuming that the component concentration in the lamella liquid (bulk liquid) is equal to that in the effluent, the $C_e V_f$ is the product of the component concentration and the liquid volume in the foam lamella, known as bulk liquid transport. The bulk liquid transport represents unadsorbed molecules in upward stream of lamella liquid. The $A\Gamma$ is the product of the flow rate of the interfacial area (A , cm^2/min) and the adsorption density or surface excess concentration (Γ , mol/cm^2), known as adsorptive transport. The adsorptive transport is responsible for the reduction in the residual factor of a

component (concentration in effluent/concentration in feed) whereas the bulk liquid transport does not reduce the residual factor if the concentration of the component in the lamellae liquid is not significantly larger than that in the effluent (i.e. single stage foam fractionation) but it does in multistage foam fractionation due to the fact that material enrichment between stages results in increasing concentration of the component in liquid pool of the upper tray. Our previous study reveals that sodium dodecylsulfate (SDS) can be removed by both adsorptive and bulk liquid transports because a significant amount of SDS was found in both foam interface and lamella liquid whereas cadmium ion was mainly removed by adsorptive transport because of most Cd ions co-adsorb with the SDS onto the foam interface [2,3].

The molar flow rate of adsorbed component in foamate can be enhanced by increasing adsorptive transport. With unchanged flow rate of the interfacial area (A), it can be enhanced with increasing adsorption density of the adsorbed component (Γ). The concentration of the transferred component in foamate (C_f) can be decreased by increasing bulk liquid flow rate, resulting in the reduction of the enrichment of component. However, the bulk liquid transport increases the molar flow rate of non-surface active component and an unadsorbed fraction of the surface active component in foamate. As a consequence, the separation efficiency of component in terms of percentage recovery can be enhanced by both increases in adsorptive and bulk liquid transports but that in terms of separation factor (concentration in foamate/concentration in effluent) and enrichment ratio (concentration in foamate/concentration in feed) can be enhanced only by adsorptive transport.

It has been reported that added counterions have profound effects on the adsorption behavior of ionic surfactants at the air–water interface [5,6]. The amount of surfactant adsorbed on the air–water interface per unit area, called adsorption density [5], the ability to form foam [7], and liquid film drainage [8] are strongly dependent on the type and concentration of counterions. However, the adsorption mechanism of ionic surfactant under the presence of various types and concentrations of added electrolytes is still under debate [9]. Pandey et al. [10] found that, for a dodecyl sulfate system, the type of surfactant counterion influenced the surface activity of the surfactant solution and the order of decreasing surface tension was $\text{Li}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Mg}^{2+}$, while the surfactant adsorption density exhibited the reverse

relationship. Para et al. [9] investigated the influence of added KBr and KCl on hexatrimethylammonium bromide (CTABr) and hexatrimethylammonium chloride (CTACl) adsorptions and they found that the surfactant counterions (i.e. Br⁻ and Cl⁻) in the adsorption layer could be replaced by added anions present in excess in the solution.

From our previous study, the separation efficiency of multistage foam fractionation for the recovery of cetylpyridinium chloride (CPC), a cationic surfactant, from water was found to be much higher than a single-stage system, especially in terms of the enrichment ratio and the percent recovery of the surfactant [11]. The application of continuous multistage foam fractionation with bubble-cap trays was extended for the removal of cadmium at low Cd concentrations from water and the effects of feed SDS/Cd molar ratio, air flow rate, foam height, feed flow rate, and feed Cd concentration on Cd removal were investigated [2,3]. The effects of NaCl and Na₂SO₄ addition on ion flotation of cadmium were investigated [12,13] but the role of the added salts on removal efficiency were not elucidated systematically. The purpose of this present work was to further investigate the effect of type of added salts (NaNO₃, KNO₃, NaCl, Na₂SO₄, Mg(NO₃)₂, Ca(NO₃)₂) on the removal efficiency of cadmium from water at low Cd concentrations by continuous multistage ion foam fractionation and the correlation between counterion adsorption on the air-water interface and the effectiveness of Cd removal was discussed.

5.3 Experimental

5.3.1 Materials

Sodium dodecyl sulfate (SDS) with 97 % purity; and cadmium nitrate (Cd(NO₃)₂·4H₂O), sodium nitrate (NaNO₃), and potassium nitrate (KNO₃) with a purity of > 99 %, were obtained from CARLO ERBA REAGENTI (Italy). Sodium sulphate anhydrous (Na₂SO₄), magnesium nitrate (Mg(NO₃)₂·6H₂O), calcium nitrate (Ca(NO₃)₂·4H₂O) and sodium chloride (NaCl) were obtained from Ajax Finechem (UNILAB) with a purity of > 99 %. All chemicals were used as received without further purification. Deionized water was used in all experiments.

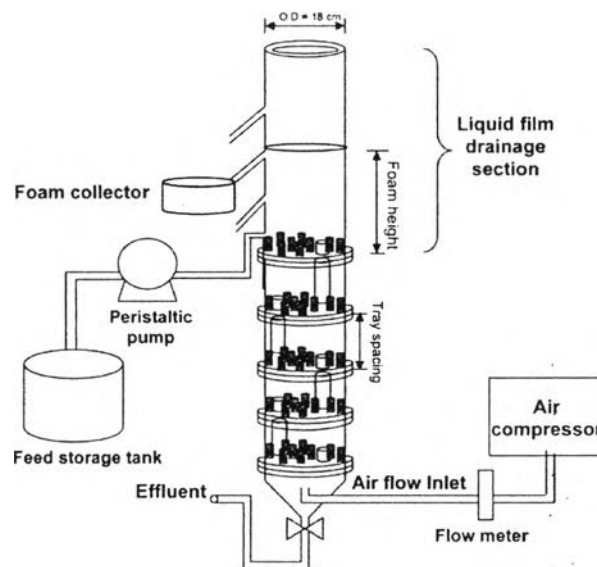


Figure 5.1 Schematic of a multistage foam fractionation unit.

5.3.2 Multistage Ion Foam Fractionation System

The experimental setup of the continuous multistage ion foam fractionation unit used in this study is shown in Figure 5.1. It is composed of three main parts: an air supply unit, a feed unit, and a multistage ion foam fractionation column. The multistage ion foam fractionation column was made of an acrylic cylinder with a 17.4 cm inside diameter and it was assembled to have different trays and up to 5 stages. Each tray had 22 stainless steel bubble caps with a cap diameter of 2 cm and the height of each tray was 15 cm. On the top tray, the column was connected with an acrylic pipe having the same inside diameter and different outlet pipes to obtain three foam heights of 30, 60, and 90 cm. In each tray, there was a downcomer having a 4 cm diameter to allow liquid overflow down to a lower tray. The liquid level was designed to be 3 cm by the weir height of the downcomer.

5.3.3 Methodology

The multistage ion foam fractionation system was operated in continuous mode in this study. A feed solution containing 10 mg/L Cd with a molar ratio

of SDS/Cd of 10/1 was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and SDS in deionized water. Each studied salt (i.e. NaNO_3) at different concentrations was added in the feed solution. The feed solution was fed into the top of the column at a flow rate of 60 mL/min using a peristaltic pump. Compressed air from an air compressor was introduced under the bottom tray and was regulated by a rotameter to have an air flow rate of 35 dm³/min. The experiments were carried out at room temperature (25–27 °C) due to insignificant influence of temperature on the Cd^{2+} removal [14]. The foam was collected at the top of the column from the liquid pool of the top tray by allowing it to flow out at different foam heights of 30, 60, and 90 cm. The collected foam was left to collapse by itself to obtain the foamate. After steady state conditions were achieved (around six hours), samples of the feed solution, the foamate, and the effluent were collected and then analyzed for SDS and Cd concentrations. The volumetric flow rates of both foamate and effluent were also measured. All samples were acidified with a concentrated nitric acid to a pH just below 2 for preservation before the determination of surfactant and Cd ion concentrations. The data obtained from at least three runs were averaged and used to assess the process performance of the multistage ion foam fractionation system. By performing mass balances of Cd and SDS, the average error was found to be less than 10 %. Various evaluating parameters were used to assess the process performance of the studied multistage ion foam fractionation system, including the enrichment ratios of SDS and Cd, SDS recovery, Cd removal, foamate volumetric ratio, the residual factors of SDS and Cd, and the separation factors of SDS and Cd [2,15], as expressed below:

$$\text{Enrichment ratio} = C_f/C_i, \quad (5.2)$$

$$\% \text{ SDS recovery or } \% \text{ Cd removal} = (C_i V_i - C_e V_e)(100)/(C_i V_i), \quad (5.3)$$

$$\text{Residual factor} = C_e/C_i, \quad (5.4)$$

$$\text{Foamate volumetric ratio} = V_f/V_i, \quad (5.5)$$

$$\text{Separation factor} = C_f/C_e, \quad (5.6)$$

where C_f and C_i are the SDS or Cd concentration in the foamate (collapsed foam solution) and in the influent (feed), respectively. C_e is the SDS or Cd ion concentration

in the effluent stream. V_i , V_f , and V_e are the volumetric flow rates of feed, foamate, and effluent, respectively.

5.3.4 Analytical Methods

The concentration of SDS was measured by using a total organic carbon analyzer (Shimadzu, TOC-VCSH). The concentration of Cd ions was determined by an atomic adsorption spectrophotometer (AAS, Varian, SpectrAA 300) at a recommended wave length of 228.8 nm. The procedure for determining Cd concentration was carried out with consideration of the interference from both SDS and added salts (i.e. NaNO_3), referring to the procedure reported in literature [16] and Parts I and II of this work [2,3]. A cadmium standard solution containing SDS at the same concentration as in the diluted sample was used for obtaining a calibration curve. The measurement range of cadmium with high accuracy is 0.02–3 mg/L, according to the AAS specification. Therefore, all sample solutions were diluted to approximately 1 mg/L Cd concentration before the determination.

5.3.5 Surface Tension Measurement

The surface tension was measured by using a drop shape analysis instrument (Kruss, DSA 10). The pendant drop technique was used to measure the surface tension of surfactant solutions containing different concentrations of SDS, $\text{Cd}(\text{NO}_3)_2$ and different added salts (i.e. NaNO_3). The sample chamber temperature was kept constant at room temperature (25–27°C) and the humidity in the sample chamber was kept saturated in order to minimize the evaporation effect during measurements.

5.4 Results and Discussion

5.4.1 Specie Distribution Diagrams

When a Cd salt is dissolved in water, various cadmium-containing species are possible, result from the reactions between Cd ions and common ligands present in the water. These species include nitrate, sulfate, and chloride, depending on the concentrations of the cadmium salt and the ligands and the thermodynamics of

the reactions. Figure 5.2 shows Cd specie distribution in the aqueous solutions containing 10 mg/L $\text{Cd}(\text{NO}_3)_2$ and different added sodium salts without SDS addition as a function of the concentration of anion dissociated from the sodium salts. The Cd specie distribution was obtained from thermodynamic equilibrium calculations [17]. The calculations were carried out using Minteq ver 2.6 [18] which can be used successfully as a potential alternative tool for the determination of Cd specie distribution beside ion chromatography [19,20]. The initial solution pH and initial Cd concentration were fixed at 7 and 10 mg/L, respectively. The stability constants for the reactions used in the calculations are shown in Table 5.1 [21]. The presence of some species such as $\text{Cd}(\text{SO}_4)_3^{4-}$ and CdCl_3^- are negligible due to their extremely low concentrations (in the order of 0.1% or less) in the systems under the studied conditions and so they were not shown in the figure.

Table 5.1 Chemical equilibrium reactions of cadmium complexes with different ligands and their stability constants [21]

Reaction	Log K
1. with Cl^-	
$\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+$	1.98
$\text{Cd}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CdCl}_2(\text{aq})$	2.6
2. with SO_4^{2-}	
$\text{Cd}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CdSO}_4(\text{aq})$	2.37
$\text{Cd}^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Cd}(\text{SO}_4)_2^{2-}$	3.5
3. with NO_3^-	
$\text{Cd}^{2+} + \text{NO}_3^- \rightleftharpoons \text{CdNO}_3^+$	0.5
$\text{Cd}^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{Cd}(\text{NO}_3)_2(\text{aq})$	0.2
4. with OH^-	
$\text{Cd}^{2+} + \text{OH}^- \rightleftharpoons \text{CdOH}^+$	-10.097
$\text{Cd}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_2(\text{aq})$	-20.294
$2\text{Cd}^{2+} + \text{OH}^- \rightleftharpoons \text{Cd}_2\text{OH}^{3+}$	-9.397

As shown in Figure 5.2a, the $\text{Cd}(\text{NO}_3)_2$ salt used to prepare the solution almost completely dissociates to give free Cd^{2+} and NO_3^- under a very low feed Cd concentration (lower than 10 mg/L) because of the low stability constant of $\text{Cd}(\text{NO}_3)_2$. An increase in nitrate concentration slightly reduces the free Cd^{2+} concentration whereas the free Cd^{2+} concentration is reduced significantly with increasing sulfate or chloride concentration due to the formation of CdSO_4 and $\text{Cd}(\text{SO}_4)_2^{2-}$; or CdCl^+ , respectively, as shown in Figures 2b and 2c.

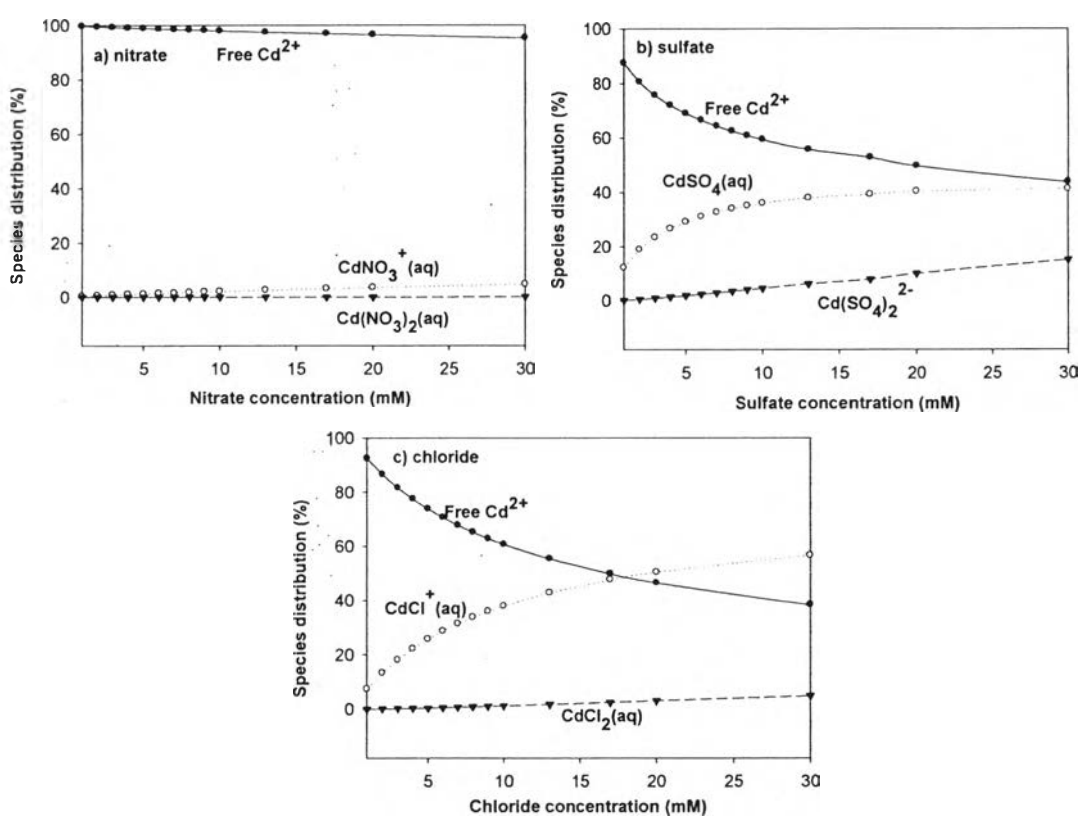


Figure 5.2 Specie distribution diagrams of Cd in aqueous solutions having different Cd salts as a function of (a) nitrate, (b) sulfate, and (c) chloride concentration at total Cd concentration = 10 mg/L (0.09 mM), initial solution pH = 7, and temperature = 25 °C.

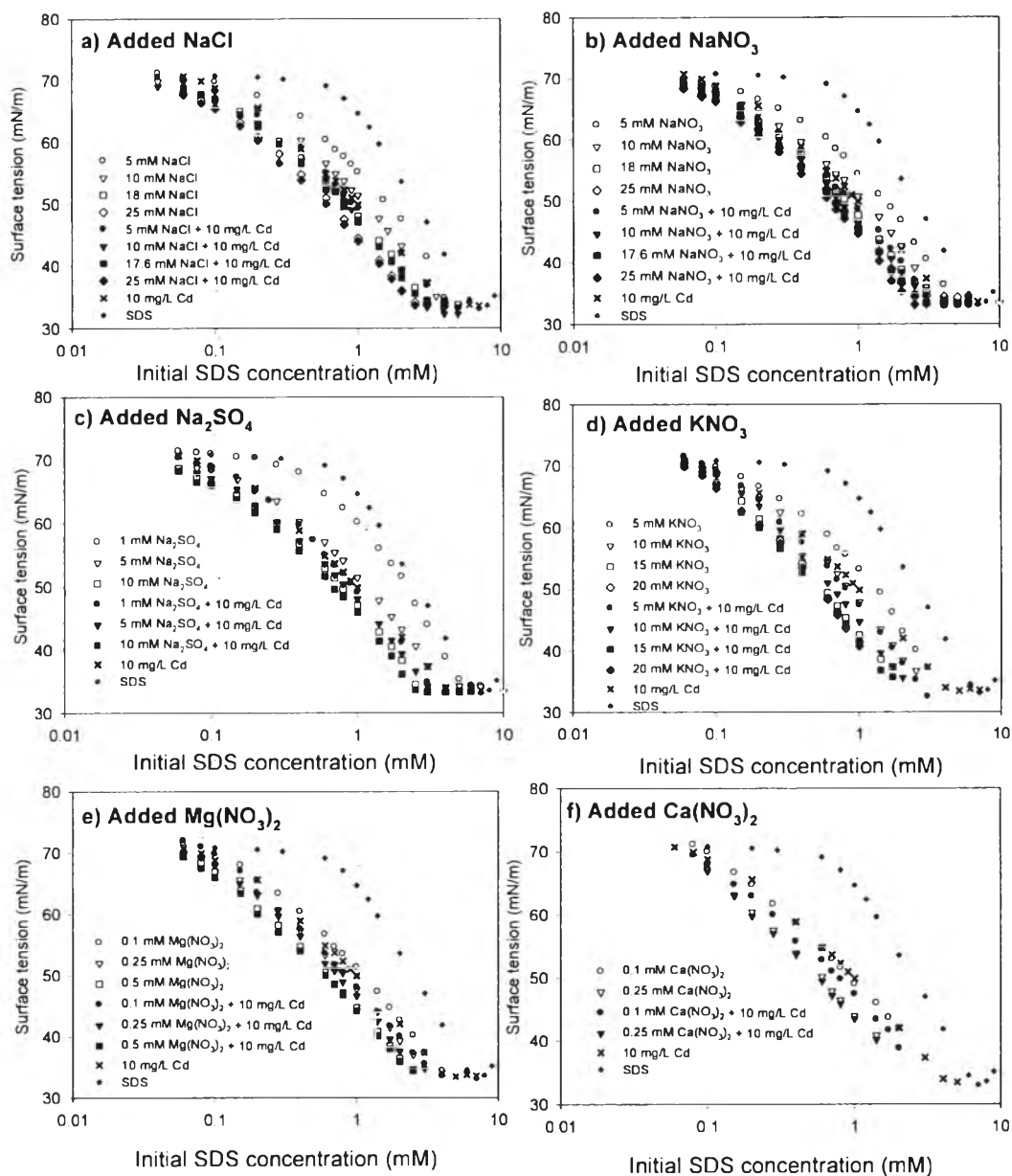


Figure 5.3 Surface tension isotherms of SDS at various concentrations of added NaCl (a), NaNO₃ (b), Na₂SO₄ (c), KNO₃ (d), Mg(NO₃)₂ (e), Ca(NO₃)₂ (f) in the presence and absence of 10 mg/L of Cd at 25–27 °C as compared with that of pure SDS system.

5.4.2 Surface Tension Isotherm Results

Surface tension, one of fundamental surface properties, is mainly governed by the adsorption of all species at the air–water interface [5]. Figure 5.3 shows the surface tension isotherms of SDS in the absence and the presence of various salts: NaCl, NaNO₃, Na₂SO₄, KNO₃, Mg(NO₃)₂, and Ca(NO₃)₂ with and without 10 mg/L of Cd²⁺. For all types of added salts, the surface tension isotherm of the SDS solution containing any given added salt shifted downward and its shape was changed significantly as compared with that of pure SDS system even at a low added salt concentration of 5mM for monovalent salts and 0.1 mM for divalent salts. The results suggest that the adsorption of anionic dodecylsulfate ion (DS⁻) is facilitated significantly by the salt addition because the electrical repulsive interaction between the headgroups in the adsorbed surfactant layer, considered as electrical double layer (EDL), is reduced with increasing counterion concentration [6,9]. The results also reveal that the shapes and slopes (below CMC) of the surface tension isotherm of ionic surfactant are governed by type of counterion which is in good agreement with the studies on specific ion effect on the interfacial properties of ionic surfactants [6,9].

For any given added salt at a low salt concentration, an addition of cadmium (10 mg/L) was also found to remarkably further decrease the surface tension. The results suggest that the surface tension isotherm of SDS was significantly affected by cadmium ions more than sodium ions because the divalent cadmium ions can coadsorb much more preferentially than the monovalent sodium ions [2,22].

For any given studied salt at a high added salt concentration, the shapes and slopes (below the CMC) of the surface tension isotherms look almost the same for both absence and presence of 10 mg/L Cd, as shown in Figure 5.3. The results suggest that not only Cd²⁺ ions adsorb preferentially at the air–water interface but Na⁺ ions, which is present in excess at high concentrations, also do and the adsorbed Cd ions in the Stern layer can be replaced by Na⁺ ions to some extent. This can be explained in that the counterion exchange reaction can be pushed toward dodecylsulfate co-adsorbed with added sodium counterion at sufficiently high initial sodium concentration (Chatelier's principle) even though the Cd has higher ability to penetrate adsorbed dodecylsulfate layer, as discussed later in section 5.3.3.2. An es-

estimated value of initial added counterion concentration in the SDS solution which an addition of 10 ppm Cd begins to provide the same shapes and slopes (below the CMC) of the surface tension isotherms of SDS as the system without Cd addition is arbitrarily defined as “the swamping counterion concentration”. The swamping counterion concentration can be used to indicate the ability of the added counterion to competitively adsorb with Cd ion at the air–water interface in the presence of SDS because the counterion having higher ability to penetrate the adsorbed surfactant layer requires a lower initial concentration to be adsorbed at the interface and affect the surface tension, as discussed later in section 5.3.3.2. The swamping counterion concentration of each added salt for the SDS system obtained from Figure 5.3 is summarized in Table 5.2.

Table 5.2 Dependence of swamping counterion concentration, effective hydrated diameter, and the calculated value of a partition coefficient ($k_{M^{n+}}$) for the partition of a counterion between the air–water interface and the bulk liquid

Added salts	Counterion	Hydrated diameters (pm) [23]	Swamping counterion concentration (mM)	$k_{M^{n+}}$ ($m \times 10^{-6}$)
NaCl	Na ⁺	450	18	-
Na ₂ SO ₄	Na ⁺	450	20	-
NaNO ₃	Na ⁺	450	25	2.2
KNO ₃	K ⁺	300	15	2.5
Mg(NO ₃) ₂	Mg ²⁺	800	0.5	12
Ca(NO ₃) ₂	Ca ²⁺	600	0.25	13
Cd(NO ₃) ₂	Cd ²⁺	500	-	13

In the present work, the added counterion concentration was used instead of the added salt concentration because the surfactant adsorption behavior depends strongly on counterions [6,9]. Figure 5.4 shows the negative logarithm of the concentration of surfactant in bulk phase required to produce a 20 mN/m reduction in the surface tension (pC_{20}) of SDS solution as a function of added counterion concen-

tration. All the values of pC_{20} were obtained from Figure 5.3. The efficiency of surfactant adsorption and surface tension reduction, related to the free energy change involved in the adsorption [23], can be indicated by the pC_{20} value. For any given studied counterion, the pC_{20} value was found to increase with increasing added counterion concentration due to the EDL compression, as discussed above. As compared with the $pC_{20} = 2.68$ for the pure SDS system, the presence of all studied counterions was found to increase the pC_{20} value. The higher the pC_{20} value, the higher the surfactant adsorption and the greater the surface tension reduction.

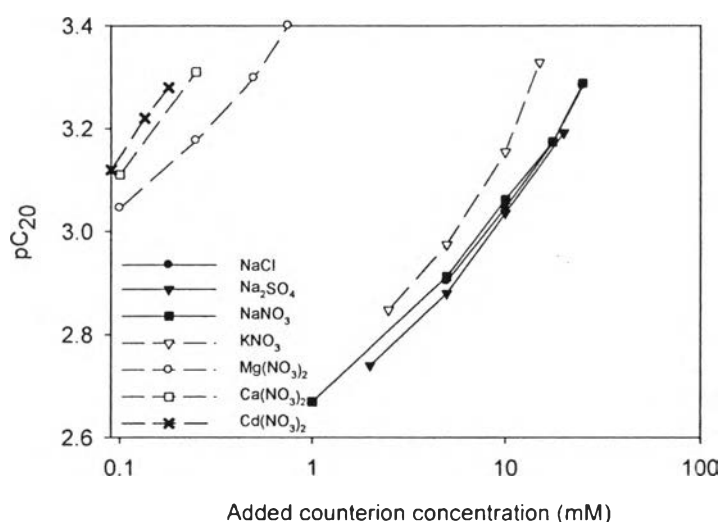


Figure 5.4 Effect of type and concentration of counterion on surface tension reduction (pC_{20}) of SDS solution at 25–27 °C ($pC_{20} = 2.68$ for the pure SDS system).

5.4.2.1 Type of Counterion

The effect of cation counterions on the surface tension isotherm of the SDS system was investigated by comparisons among different added nitrate salts, as the NO_3^- anion has a little effect on Cd complexation under the studied concentration range (see Figure 5.2) and it does not adsorb preferentially at the air–water interface without the aid of surfactant [24]. As shown in Figure 5.4, the effect of added cation counterions on the pC_{20} enhancement increases in the following order: $\text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} \approx \text{Cd}^{2+}$, which corresponds well to the decrease in the swamping counterion concentration in the following order: $\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} >$

Ca^{2+} . These results suggest that the studied divalent cation counterions are more effective in surface tension reduction and adsorb more preferentially at the air–water interface than the studied monovalent cation counterions. In comparisons of the studied cations with the same valences (i.e. Na^+ and K^+ or Mg^{2+} , Ca^{2+} and Cd^{2+}), the efficiencies of surfactant adsorption and surface tension reduction were found to increase with decreasing effective hydrated diameters [25], as shown in Table 5.2. These observations can be explained in terms of the ability of counterions to penetrate the adsorption layer (Stern layer) [6,9]. During the counterion adsorption process, the hydration shell of counterion must undergo dehydration (at least partially) or deformation upon adsorption (penetration) in the surfactant monolayer [26] because the counterions located in the Stern layer are not solvated but they appear as bare ions; otherwise, the penetration of hydrating ions into the outermost surface layer are prevented [5]. The higher surface activity of the system with divalent counterion is due, most likely, to a strongly attractive interaction between a divalent cation and two dodecylsulfate ions in the adsorbed layer, facilitating the dehydration, and hence, it favors the adsorption of surfactant molecules [10,27]. For a counterion with the same valency, the higher surface activity of the counterion with a smaller hydrated size might be due to the fact that it is easier to be dehydrated and can more easily penetrate the Stern layer. Therefore, they are more effective in neutralization of the surface charge of surfactant head-groups and thus in surface tension reduction at the same bulk concentrations of counterions. These results are in good agreement with the effect of NaClO_4 , KClO_4 , LiClO_4 , NH_4ClO_4 , and $\text{Mg}(\text{ClO}_4)_2$ addition on the degree of micelle dissociation of SDS (α) [27]. The smaller the hydrated cation derived from an electrolyte added, the lower the α value for SDS micelles.

The effect of cation counterion can also be interpreted in a different way by applying the surface tension model for metal ion selectivity [28] derived from Gibbs equation. According to the model, the surface tension of stoichiometric counterion-ionic surfactant solution is linearly proportional to the surfactant concentration under the region below the CMC and can be expressed as

$$\gamma_0 - \gamma = bC_A^- \quad (5.7)$$

where γ_0 and γ are the surface tension of pure water and surfactant solution, respectively. b is a linear constant determined from the slope of the plot and C_A^- is the concentration of ionic surfactant. The adsorption density of the counterion ($\Gamma_{M^{n+}}$) is proportional to the counterion concentration in the bulk solution ($C_{M^{n+}}$) under the presence of a stoichiometric amount of surfactant, and can be expressed as

$$\Gamma_{M^{n+}} = \frac{nb}{RT(n+1)} C_{M^{n+}} \quad (5.8)$$

where n is the valency of the counterion, R is the gas constant, and T is the absolute temperature. As a result, one can determine a partition coefficient ($k_{M^{n+}}$) for the partition of any counterion between the air–water interface and the bulk aqueous phase, which is defined as $\Gamma_{M^{n+}}/C_{M^{n+}}$, by using Equation 5.8. Figure 5.5 shows the surface tensions of SDS–Na, SDS–K, SDS–Mg, SDS–Ca, and SDS–Cd systems as a function of dodecylsulfate concentration at pH 7 where the added cation counterions (as nitrate salts) and dodecylsulfate are present in stoichiometric ratios. The surface tension plots were fitted well with $R^2 > 0.99$. The constant b (slope) for each studied SDS–cation counterion system, is also shown in Figure 5.5. The calculated value of $k_{M^{n+}}$ for each studied SDS–cation counterion system is shown in Table 5.2. The $k_{M^{n+}}$ value was found to vary substantially, depending on cation counterion in the following order: $\text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} \approx \text{Cd}^{2+}$ which follows the same trend as the pC_{20} enhancement and is in good agreement with the swamping counterion concentration. These results suggest that the $k_{M^{n+}}$ value is related to the ability of counterion to penetrate the Stern layer and the ability of the added counterion to competitively adsorb at air–water interface, as discussed above.

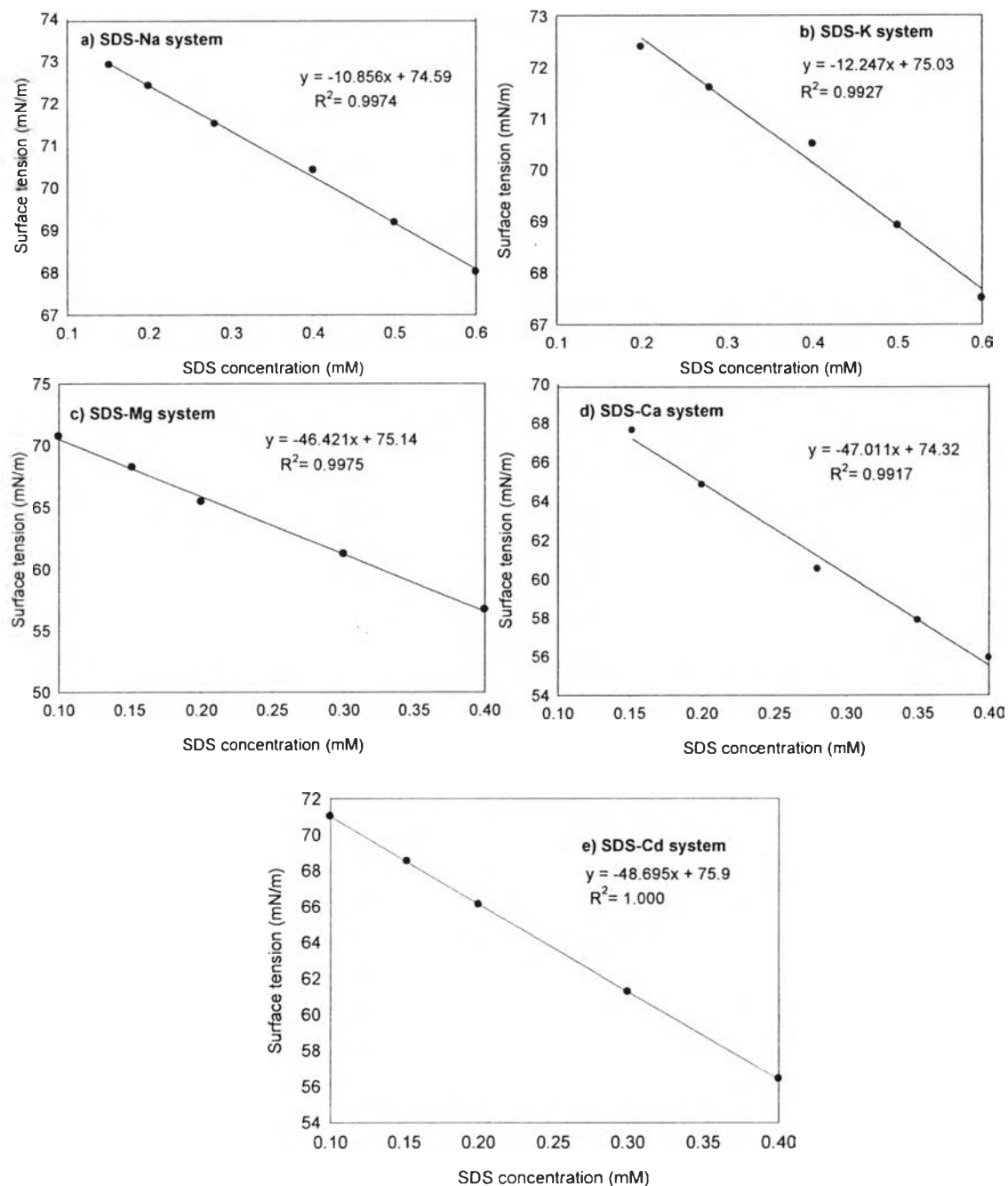


Figure 5.5 Surface tensions of (a) SDS–Na, (b) SDS–K, (c) SDS–Mg, (d) SDS–Ca, and (e) SDS–Cd systems as a function of dodecylsulfate concentration at pH 7. The added cation counterions and dodecylsulfate were present in stoichiometric ratios.

5.4.2.2 Type of Co-ions

As shown in Figure 5.4, in the absence of 10 mg/L Cd, the dependence of pC_{20} of the SDS system on added counterion concentration using various sodium salts: NaNO_3 , NaCl and Na_2SO_4 are almost identical. For any given pC_{20} , the concentration of co-ions (NO_3^- , SO_4^{2-} , and Cl^-) did not significantly differ. These results suggest that the type of studied co-ions (NO_3^- , SO_4^{2-} , and Cl^-) has little effect on the adsorbed dodecyl sulfate layer which it only co-adsorbs with the sodium counterion.

As mentioned before, in the presence of 10 mg/L Cd, the swamping counterion concentration were found to be different among the three added sodium salts (see Table 5.2), indicating a significant effect of the anion. As shown in Table 5.2, the swamping counterion concentration of NaNO_3 is higher, suggesting that the chloride anion should facilitate the co-adsorption of Na^+ counterion with dodecylsulfate (DS^-) onto the air–water interface greater than the nitrate anion (in the presence of cadmium) or the chloride anion might reduce the ability of cadmium counterion to penetrate the Stern layer. However, both chloride and nitrate co-ions equally facilitate the adsorption of dodecyl sulfate and sodium ions on the air–water interface in the absence of cadmium, as shown in Figure 5.4. The results indicate that the surface activity of cadmium counterion is altered significantly by the presence of co-ions. This can be explained by the fact that chloride ion can react with cadmium ion under the studied anion concentration range (1–25 mM) to form a less surface active cadmium-containing specie (CdCl^+), resulting in lowering active free Cd^{2+} concentration, as shown in Figure 5.2. There are two possible explanations why the CdCl^+ has a lower surface activity as compared with the free Cd^{2+} . Firstly, the CdCl^+ complex has a lower charge than the free Cd^{2+} and, secondly, the CdCl^+ complex cannot adsorb at the air–water interface directly but might undergo ligand dissociation before adsorption. This is because any counterion must have a smaller size than the dodecylsulfate head group [29] (the radius of sulfate head group is 2.5 Å [26] and the ionic radii of Cd^{2+} and Cl^- are 0.95 Å and 1.81, respectively [30]). These results are in good agreement with a work to investigate the effect of NaCl and NaNO_3 addition on counterion dissociation in cadmium dodecyl sulfate micelles [31]. The dissociation of cadmium ion from micelles was also found to increase with complexation

of cadmium ion by chloride whereas the addition of NaNO_3 causes less reduction in the fraction of bound cadmium counterion [31].

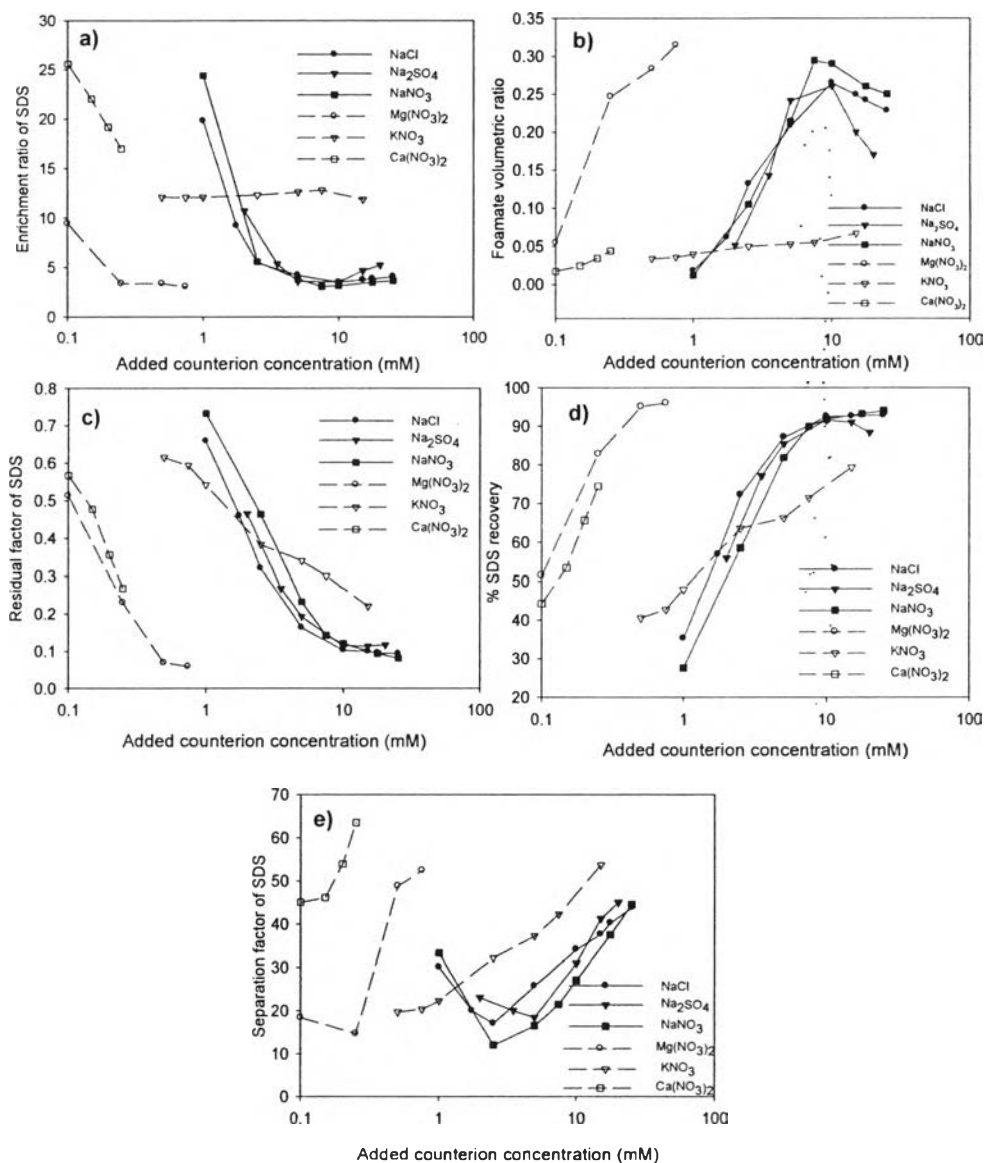
5.4.3 The Effect of Salt Addition on Separation Efficiency of Multistage Ion Foam Fractionation

The effect of salt addition on the Cd^{2+} separation efficiency of the studied multistage ion foam fractionation system was investigated under the base conditions [3] (an air flow rate of $35 \text{ dm}^3/\text{min}$, a feed flow rate of $60 \text{ mL}/\text{min}$, a foam height of 60 cm , number of trays of 5, and a feed molar ratio of SDS/Cd of 10/1). The effect of divalent counterion addition was also conducted at much lower added concentrations due to the low solubility limit of SDS in the presence of divalent cations [32,33].

5.4.3.1 *Separation Efficiency of SDS*

Figure 5.6a shows the effects of type and concentration of counterions on the enrichment ratio of SDS. For any studied salt except KNO_3 , the enrichment ratio of SDS decreased with increasing added counterion concentration. This is due to a dilution effect by the increasing liquid entrainment in foam lamellae, as evidenced experimentally by the increase in foamate volumetric ratio (see Figure 5.6b). The results can be explained by the fact that addition of salt increases the flow rate of the interfacial area (as observed visually) as a result from an increase in the SDS adsorption at the air/water interface of the produced foam. In the case of either KNO_3 or $\text{Ca}(\text{NO}_3)_2$ addition, the flow rate of the produced foam was found to increase whereas the foamate volumetric ratio increased slightly with increasing added counterion concentration. This is most likely because the flow rate of produced foam (the interfacial area) and the liquid film drainage both affect the foamate volumetric ratio. These results suggest that an addition of KNO_3 or $\text{Ca}(\text{NO}_3)_2$ provides higher liquid film drainage or thinner foam film as compared to the system with NaNO_3 or $\text{Mg}(\text{NO}_3)_2$ addition. The increase in foam film drainage (or foam film thinning) is attributed to the reduction in repulsive interaction between the two air–water interfaces facing each other in a foam film (disjoining pressure) with increasing salt addition (known as the double layer compression) [34,35]. As a result, potassium and calcium which are more effective in neutralization of the

surface charge of sulfate headgroups than sodium and magnesium, respectively, can decrease foam film thickness more effectively. For any given sodium salt, the foamate volumetric ratio decreased when the counterion concentration increased beyond 10 mM. These results are also attributed to the reduction in disjoining pressure at a very high counterion concentration.



Without salt addition: Enrichment ratio of SDS = 40.3, Foamate volumetric ratio = 0.006, Residual factor of SDS = 0.764, SDS recovery = 24.1%, and Separation factor of SDS = 52.7

Figure 5.6 Effect of counterion addition on (a) enrichment ratio, (b) foamate volumetric ratio, (c) residual factor, (d) recovery, and (e) separation factor of SDS at an air flow rate of 35 dm³/min, a feed flow rate of 60 mL/min, a foam height of 60 cm, the number of trays equal to 5, and a feed molar ratio of SDS/Cd of 10/1.

For the studied salts, the residual factor of SDS decreases dramatically while the SDS recovery increases substantially with increasing counterion concentration, as shown in Figures 6c and 6d, respectively. The results suggest that the adsorptive transport increases with increasing counterion concentration, leading to the enhancement of the flow rate of the interfacial area of foam (as observed visually). This is due to the fact that an added salt increases pC_{20} , facilitating surfactant adsorption [6,34] and surface tension reduction [23], and increasing foaming efficiency [7].

In the case of KNO_3 addition, with increasing added counterion concentration, the enrichment ratio of SDS increased slightly whereas the residual factors of SDS decreased substantially. These results suggest that the amount of SDS transferred with the produced foam increases with increasing added counterion concentration and a dilution effect caused by the increasing liquid entrainment in foam lamellae is insignificant.

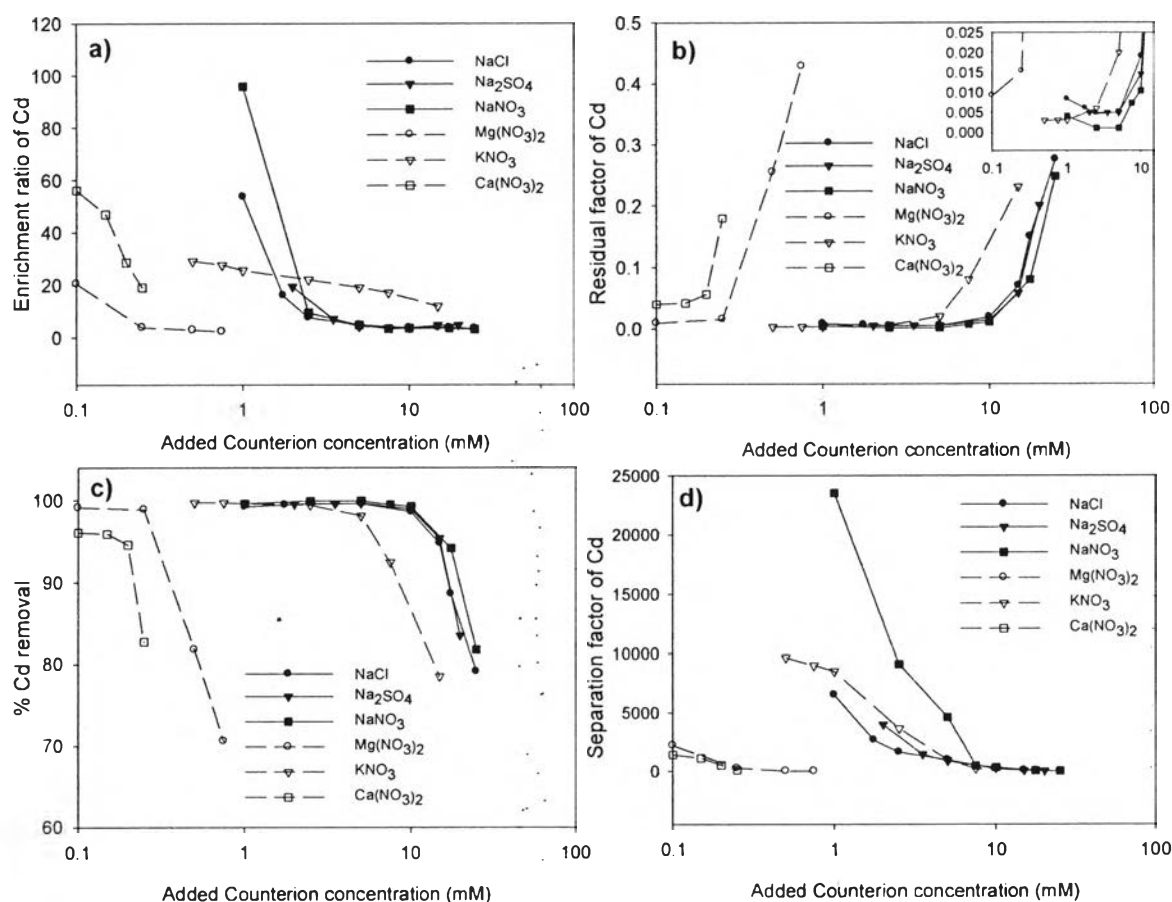
Interestingly, with $NaNO_3$ addition, the residual factor of SDS was slightly higher than that with $NaCl$ addition at a counterion concentration below 10 mM. However, beyond an added counterion concentration of 10 mM, the residual factors of SDS of the systems with $NaCl$ and $NaNO_3$ addition were not significantly different. The small difference in the residual factors of SDS is likely due to the differences in the hydration of the chloride and nitrate anions. Due to the fact that nitrate displays slightly salting-in effect on non-electrolytes in aqueous solution whereas chloride exhibits salting-out effect [36]. Hence, chloride anion can dehydrate the dodecylsulfate headgroup more effectively than nitrate, resulting in facilitating SDS adsorption and thus the addition of $NaCl$ exhibits the enhancement of SDS recovery. These results are in good agreement with previous work [37] in that the anion which is more strongly hydrated tends to dehydrate negatively charged phospholipid bilayer more effectively.

In comparisons among the systems with different monovalent counterions, the system with KNO_3 addition showed a higher enhancement in SDS recovery at a concentration below 2 mM but, beyond 2mM, the SDS recovery of the system with KNO_3 was lower than those with the other sodium salts. The results can be explained by the higher ability of potassium counterion to penetrate the Stern

layer as compared with the other sodium cations. However, beyond 2 mM of added counterion concentration, the foamate volumetric ratio of the system with the KNO_3 remained almost unchanged while those with the other sodium cations increased drastically with increasing counterion concentration. These results indicate that the separation efficiency of SDS by the presence in the lamella liquid (bulk liquid transport) is promoted significantly with the addition of sodium cations, resulting in a decreasing residual factor of SDS and increasing SDS recovery whereas the bulk liquid transport is not promoted with KNO_3 addition. In comparisons between the systems with $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ addition, the larger SDS recovery for the system with $\text{Mg}(\text{NO}_3)_2$ addition can also be explained by the same reasoning.

As shown in Figure 5.6, the concentration of any given divalent counterions required to obtain a certain level of residual factor of SDS or SDS recovery was much lower than those of any monovalent counterions. The results can be explained in that the flow rate of the interfacial area and the surfactant adsorption density of produced foam are promoted more effectively by divalent counterions, as compared with monovalent counterions. This is due to the higher ability of divalent counterions to penetrate the adsorbed dodecyl sulfate layer, facilitating more surfactant adsorption and surface tension reduction.

For all studied added salt except $\text{Ca}(\text{NO}_3)_2$ and KNO_3 , the separation factor of SDS tends to be reduced to a minimum at a certain added counterion concentration and then increases significantly with further increasing counterion concentration, as shown in Figure 5.6e. This can be explained by the combined effect between the enhancement in foamate volumetric ratio (reducing the SDS concentration in foamate and lowering the separation factor of SDS) and foaming efficiency (increasing the separation factor of SDS). For added $\text{Ca}(\text{NO}_3)_2$ or KNO_3 , the separation factor of SDS tends to increase with increasing counterion concentration, as shown in Figure 5.6e, because only the foaming efficiency but not foamate volumetric ratio is enhanced by the salt addition.



Without salt addition: Enrichment ratio of Cd = 165, Residual factor of Cd = 0.01, Cd removal = 99.0%, and Separation factor of Cd = 16000

Figure 5.7 Effect of counterion addition on (a) enrichment ratio, (b) residual factor, (c) recovery of Cd, and (d) separation factor of Cd at an air flow rate of 35 dm³/min, a feed flow rate of 60 mL/min, a foam height of 60 cm, the number of trays equal to 5, and a feed molar ratio of SDS/Cd of 10/1.

5.4.3.2 Separation Efficiency of Cd

Figure 5.7 shows the effect of salt addition on the enrichment ratio, residual factor, recovery, and separation factor of Cd. As shown in Figures 7a and 7b, for the studied salts, the enrichment ratio of Cd decreases whereas the residual factor of Cd tends to increase with increasing added counterion concentration. These results suggest that the amount of Cd transferred with foam tends to decrease with increasing added counterion concentration. As a result, the reduction in enrich-

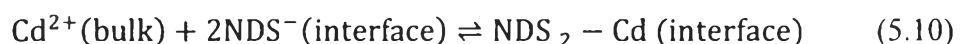
ment ratio of Cd is attributed to the decrease in Cd adsorption at foam interface and the dilution effect caused by the increasing liquid entrainment in foam lamellae which was evidenced experimentally by the increase in foamate volumetric ratio with increasing counterion concentration (Figure 5.6b).

For all studied sodium salts, at low concentrations, the residual factor of Cd decreases slightly with increasing counterion concentration, as shown in Figure 5.7b. The decreasing residual factor of Cd suggest that Cd^{2+} is partly replaced by the added sodium counterion adsorbing with dodecyl sulfate (DS^-) at the air–water interface. The explanation can be illustrated by using the ion binding model [38], as discussed below.

The adsorption of the dodecyl sulfate (DS^-) at bubble surface can be represented by the equilibrium reaction (Equation 5.9):



where N denotes the generated bubble surface or empty site available for surfactant adsorption and NDS^- denotes the adsorbed dodecyl sulfate at the bubble surface [38]. However, the bubble stabilized by adsorbed dodecylsulfate without the counterion from added salt and added Cd^{2+} has a very short life time. It was found by visual observation that a SDS solution having a low concentration of 0.9 mM could not exist even 1 cm of steady foam height but the SDS solution with 10 mg/L of Cd^{2+} could generate highly stable foams to pass through the foam exit of the column. With cadmium addition, Cd^{2+} in bulk solution can co-adsorb with the dodecylsulfate at bubble surface (NDS^-) given by Equation 5.10:



where $\text{NDS}_2\text{-Cd}$ denotes the DS^- co-adsorbed with Cd^{2+} at the bubble surface [38].

With a second salt, the added counterion can also co-adsorb with the adsorbed dodecylsulfate at bubble surface (Equation 5.11), resulting in an increase in an extra amount of dodecyl sulfate adsorption in which the rate of foam

generation is subsequently increased, as evidenced by the reduction in the residual factor of SDS (see Figure 5.6c).



Because different counterions will accumulate at the interface at different degrees due to the different specific counterion effect [39], the exchange of added counterions and cadmium ions can occur as shown in Equation 5.12.



The equilibrium constant of the counterion exchange reaction (K_{ex}) is given by Equation 5.13:

$$K_{ex} = \frac{(K_{Cd})^n}{(K_M)^2} \quad (5.13)$$

where K_{Cd} and K_M are the equilibrium constants corresponding to Equation 5.10 and 5.11, respectively. The equilibrium constant of the counterion exchange reaction (K_{ex}) suggests that an initial added counterion concentration required to replace a certain amount of cadmium at bubble surface or swamping counterion concentration is lower for the added counterion with higher K_M . For the addition of a monovalent salt, the forward reaction of the counterion exchange reaction (Equation 5.12) is favored because of greater attractive interaction between a divalent cation (cadmium) and two dodecylsulfate ions than that between the added monovalent cation and one dodecylsulfate ion in the adsorbed layer. Due to the counterion exchange reaction, an extra amount of dodecyl sulfate adsorption provided by salt addition ($NDS_n - M$) can co-adsorb with Cd, resulting in decreasing residual factor of Cd^{2+} . As compared to the system without salt addition, the results reveal that the addition of monovalent salt at a low concentration reduces the residual factor of Cd. This can be explained by the same explanation. However, in case of divalent $Ca(NO_3)_2$ and $Mg(NO_3)_2$, the residual factor of Cd remained almost unchanged with increasing counterion concentration at low levels and was higher as compared to the system without salt addition. These results suggest that both Cd^{2+} and the divalent Ca^{2+} or Mg^{2+} cannot replace

each other for adsorbing with the DS^- at the air–water interface. In other word, the values of K_{Cd} and K_M are in the same order of magnitude (Equation 5.13). This is because both Cd^{2+} and the divalent Ca^{2+} and Mg^{2+} have approximately the same ability to penetrate the Stern layer, as discussed in the previous section.

For all studied salts, at high counterion concentrations, the residual factor of Cd increased substantially with increasing counterion concentration. The results reveal that at high counterion concentrations, the competitive adsorption of counterion to replace the adsorbed Cd^{2+} becomes dominant. This is because the counterion exchange reaction (Equation 5.12) is driven backward by the increase in initial added counterion concentration. Moreover, the initial added counterion concentration required to maintain the residual factor of Cd to a certain degree (i.e. 0.1) is correlated well with the swamping counterion concentration and it is found to increase in the following order: $Ca^{2+} < Mg^{2+} \ll K^+ < Na^+$. Figure 5.7c shows the removal of Cd as a function of counterion concentration of different salts. The effectiveness for Cd separation efficiency in terms of Cd removal is in good agreement with the residual factor of Cd, as discussed above.

The effect of co-ions on the residual factor of Cd was further investigated by adding different sodium salts ($NaCl$, Na_2SO_4 and $NaNO_3$) at various co-ion concentrations, as shown in Figure 5.7b. The residual factor of Cd was found to be slightly lower for the system with $NaNO_3$ addition as compared with that with $NaCl$ addition. This result indicates that cadmium ion has less ability to competitively adsorb with sodium ion in the presence of $NaCl$ than that of $NaNO_3$ because Cl^- can react with free cadmium ion under the studied anion concentration range to form a less surface active cadmium-containing specie (i.e. $CdCl^+$), resulting in a lower amount of adsorbed Cd^{2+} at the air–water interface of foam for the system with $NaCl$ as compared with that with $NaNO_3$.

Because the concentration of cadmium nitrate complex is very low under the studied range of nitrate concentration, as revealed in Figure 5.2a, the decrease in Cd removal at a high $NaNO_3$ concentration is mainly due to the role of the sodium counterion and not due to formation of cadmium nitrate complex. The conglutination mechanism [12], by which the metal-dodecylsulfate complex is formed in the liquid at first and then adhere to the bubbles, cannot give a rational ex-

planation for this result because Na-dodecylsulfate complex does not theoretically exist in aqueous solution under the studied concentration. Hence, these results suggest the adsorption mechanism [12], in which dodecyl sulfate ions adsorb at the air–water interface first and then counterions (Cd^{2+} and Na^+) competitively co-adsorb with dodecyl sulfate.

As shown in Figure 5.7d, for all studied added salts, the separation factor of Cd decreases with increasing added counterion concentration because of increases in both liquid entrainment in foam and the complete adsorption of added counterion with Cd with increasing counterion concentration. In comparisons between monovalent and divalent cations, the effects of divalent cation (either Mg^{2+} or Ca^{2+}) on the separation factor of Cd were much higher than those of all monovalent cations, suggesting that the added divalent cations (Mg^{2+} and Ca^{2+}) have higher ability to competitively adsorb with Cd^{2+} . For all studied monovalent salts, although the effectiveness for Cd removal is enhanced at a low added counterion concentration, the separation factor of Cd decreases substantially with further increasing added counterion concentration because of the increasing liquid entrainment in foam at high added counterion concentrations. However, the addition of 1 mM NaNO_3 gave a much higher separation factor of Cd as compared to the system without salt addition. The results can be explained in that the addition of 1 mM NaNO_3 can provide a high flow rate of the interfacial area with a small foamate volumetric ratio (see Figure 5.6b). Hence, a small addition of monovalent counterion with low ability to competitively adsorb with the Cd ions and co-ion without ability to form a less surface active complex with Cd ions is recommended for maximizing Cd removal using continuous multistage ion foam fractionation.

5.5 Conclusions

The effectiveness for Cd removal was found to decrease with the addition of salts especially at high concentrations because the presence of added salts can reduce the ability of Cd to adsorb at the air–water interface of foam. The cation counterion derived from an added salt can compete with Cd ion to adsorb at the air–water interface at a certain concentration, depending on the ability of counterions to

penetrate the adsorption layer (Stern layer). The effect of added counterion concentrations on the reduction of Cd removal was found to be in the following order: $\text{Ca}^{2+} > \text{Mg}^{2+} \gg \text{K}^+ > \text{Na}^+$ whereas the added anions (co-ions) had a little effect. The SDS recovery was found to improve, depending on type of added salt because the repulsion force between the head groups of SDS is greatly reduced by adding counterions, leading to increasing SDS adsorption at the air–water interface of foam. A small amount of monovalent counterion with low ability of competitive adsorption with Cd^{2+} (i.e. 0.1 mM NaNO_3) can enhance the removal efficiency of Cd^{2+} by continuous multistage ion foam fractionation.

5.6 Acknowledgements

The financial support from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No, PHD/0059/2550) to Visarut Rujirawanich and an Advanced Research Scholar Grant (BRG5080028) to the corresponding author are acknowledged. The Research Unit of Applied Surfactants for Separation and Pollution Control under the Ratchadapisak Somphot Fund, Chulalongkorn University, is also acknowledged for providing financial support for this research.

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