Bicontinuous Microemulsions as Adsorbents for Liquid-Phase Separation/Purification

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Novel concepts of liquid-phase adsorption at the oil/water interface of a bicontinuous microemulsive phase are presented. These ideas are assessed using a tetradecane/didodecyldimethylammonium bromide/water bicontinuous microemulsion (BME) to adsorb chromate anions from aqueous solution. The adsorption isotherms are investigated as a function of solution ionic strength. Our results show that the BME is an effective adsorbent for removing CrO_4^{2-} from solutions with good selectivity over Br^- and high enrichment ratio, arising from the large internal surface area of the oil/water interface. An approximate model adsorption isotherm is derived from basic thermodynamic considerations. The proposed model is validated against our experimental data with satisfactory agreement for low chromium content in the BME. Implications of these concepts and results for adsorptive separation of generic contaminant from a liquid phase are discussed in comparison with conventional adsorption processes using solid adsorbents and also with micellar-enhanced ultrafiltration process. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2767–2773, 2006
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Introduction and Basic Concept

Bicontinuous microemulsions (BMEs) are constituted by two continuous network phases—typically, one being aqueous, the other organic—interpenetrating each other. The two phase networks display disordered structure with characteristic size of the phase domains of a few nanometers and are separated by a continuous monolayer of surfactant molecules located at the interphase throughout.[1-4] The presence of surfactant strongly depresses the surface tension between the two phases; thus, BMEs are thermodynamically stable, despite the very large interfacial area. On the microscopic scale these systems feature a random spongelike structure, as schematically sketched in Figure 1. However, at the macroscopic level they appear as a single homogeneous liquid phase. It is worthwhile noting here that BMEs may be thought of as microporous liquid media exhibiting very large internal surface area, the latter of which is also fully accessible to a solute diffusing through either phase network. These considerations have led us to envisage BMEs as potential adsorbent media for chemical operations where adsorption of solutes from a liquid phase is involved, such as certain separation or purification processes. Besides the large internal surface area (of the order of the reciprocal size of phase domain; that is, $\approx 10^3$ m^2 mL^{-1}), there are also other reasons that make BMEs potentially attractive as adsorbent phases; some are discussed below.

First, BMEs are liquid systems with acceptably low viscosity. Thus, it is not required that the exhausted adsorbent phase be regenerated in situ because the microemulsion phase can be pumped to a separate desorption/regeneration unit. That affords the opportunity to carry out the adsorption process in a continuous fashion, which is a challenge long pursued by adsorption technologists.[5] Another potential benefit enabled by BMEs as adsorbent media is the accomplishment of specific/selective adsorption, especially from an aqueous phase, by proper choice or design of the surfactant molecule utilized. In fact, surfactants

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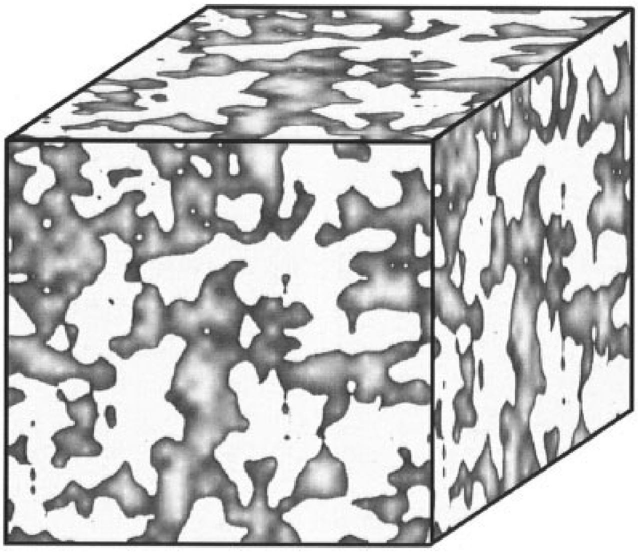

Figure 1. Spongelike microstructure of a disordered bicontinuous microemulsion.

exist or may be synthesized with a wide variety of polar (hydrophilic) headgroups. In principle, it is possible to select a surfactant with a functional headgroup able to specifically bind a determined solute molecule. A fascinating example, although not strictly related to BMEs, is represented by surfactant monolayers with thiol terminal groups that have successfully been used as adsorbents with high specific affinity for mercury.[6]

As a "proof of principle" probation of the concept of BMEs as adsorbent media we investigated in this work adsorptive removal of chromate anions from aqueous solutions by means of BMEs formed with didodecyldimethylammonium bromide (DDAB) as the surfactant. Removal of chromate anions from aqueous effluents holds substantial environmental relevance because hexavalent chromium is nonbiodegradable and highly toxic—even in amounts of only parts per million (ppm)—and because it is present in a variety of industrial wastewaters, such as those coming from the plating industry and the leather industry, for example.[7] DDAB has been selected as the microemulsive surfactant in this investigation for two reasons. First, it is a cationic surfactant that can bind the negatively charged chromate ions. Second, it is a double-tailed surfactant that forms BME in a relatively vast compositional area of the water/surfactant/organic (oil) phase diagram compared to other surfactants.[8,9]

It is useful, at this stage, to consider how such an adsorption process may be operated in practice. It should be pointed out that the microemulsion adsorbent cannot be brought into direct contact with the solution; otherwise, the surfactant progressively transfers to the solution and the microemulsion is destroyed. We envisage a process where BME and solution are kept separated by a semipermeable membrane. The membrane has to allow passage of the solute to be adsorbed from the solution to the BME. At the same time, the membrane has to prevent transfer of surfactant and oil molecules from the BME phase to the solution. In general, water flow through the membrane may arise as a consequence of osmotic pressure differences. The entity of the osmotic flow will depend on salt concentration in the solution and on the characteristics of the membrane. In the next section, besides describing the relevant experimental procedures, we address the necessary qualifications of the membrane with respect to the chromate/DDAB case study. In the subsequent section we propose a simplified single-parameter model isotherm—derived from basic thermodynamic considerations—applied to competitive anion adsorption (ion exchange) in the BME. In the Results and Discussion section we describe and discuss the experimental CrO_4^{2-}/Br^- (ion-exchange) adsorption isotherms for the BME as a function of solution ionic strength. Finally, we show how all the adsorption data points—for all values of solution ionic strength—are nicely fitted by the above-mentioned model adsorption isotherm. The CrO_4^{2-}/Br^- ion-exchange constant (that is, adsorption selectivity at equilibrium) is also calculated from the fit.

Experimental

Materials and preparation procedures

Oil/water bicontinuous microemulsions were prepared using tetradecane (TD, >99%, Sigma-Aldrich, Milan, Italy) as the oil phase and DDAB (>98%, Fluka, Milan, Italy) as the surfactant. Deionized (DI) water (~18 MΩ cm) was used for the experiments. The chosen composition was always 23.8 wt % DDAB, 52.5 wt % water, and 23.7 wt % tetradecane. This compositional point falls well within the BME region of the phase diagram for the TD/DDAB/water ternary system.[9] To obtain the BME, prescribed amounts of the three components were charged to a beaker and subsequently stirred (generally for 12 h) until a fully transparent liquid formed. No phase change was observed for the BME thus prepared as its temperature was varied within the interval 16–35°C.

Aqueous solutions with chromate anion concentrations between 52 and 520 ppm Cr were prepared by dissolving predetermined amounts of K_2CrO_4 (>99%, Carlo Erba Reagenti, Milan, Italy) in DI water. The measured pH of the resulting solutions was nearly 8.5 in all cases. Under this pH condition chromium is present in solution entirely as CrO_4^{2-} anion.[10]

The experiment

A two-compartment diffusion cell was used to conduct the adsorption experiments. The compartments, separated by a semipermeable membrane, were filled respectively with chosen amounts of BME and of K_2CrO_4 solution of known concentration. The membrane is required to allow exchange of Br^- anions from the BME with CrO_4^{2-} anions from the solution while preventing permeation of didodecyldimethyl ammonium and potassium cations as well as oil molecules (Figure 2). A dense (nonporous) anion-exchange membrane (model ADP, Solvay, Belgium) was well suited for this purpose. The membrane, made from a perfluorinated crosslinked polymer with quaternary ammonium exchange groups, has a thickness of 140 μm and an ion-exchange capacity of about 1.30 meq g^{-1}. Before use, all membranes were exchanged in KBr (99.5%, Carlo Erba) solution overnight and then soaked in DI water for 2–3 h. In a typical adsorption experiment the two compartments of the cell were allowed to reach equilibrium. Afterward, the chromium concentration in solution was determined and the corresponding chromium uptake in the BME (corrected for the amount sequestered by the membrane; see further below) was

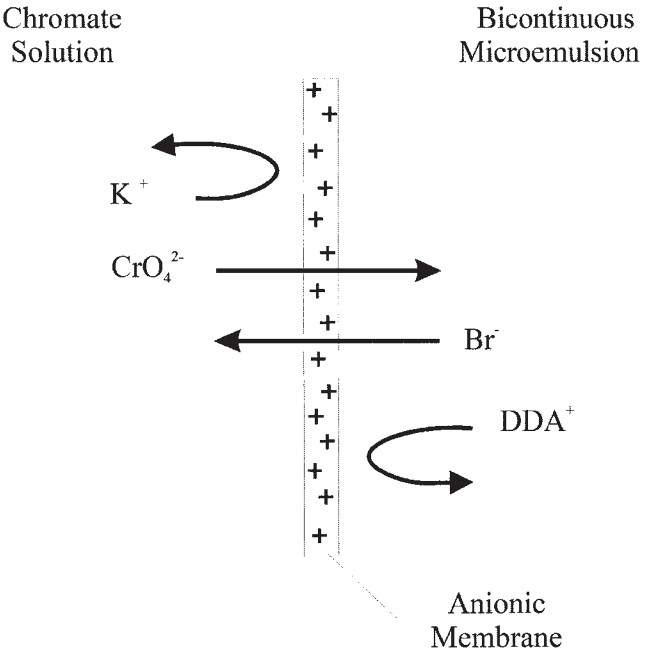

Figure 2. Basic ion-exchange experiment.

calculated. By varying the amounts of BME and of solution (at fixed initial K_2CrO_4 concentration) in the cell compartments, the chromium uptake in the BME as a function of concentration (that is, the adsorption isotherm) was obtained. By varying the initial K_2CrO_4 concentration in the solution, the adsorption isotherms at varying ionic strength were determined. All experiments were carried out at room temperature (~23°C).

Chromium determinations

Hexavalent chromium was determined by spectrophotometric analysis following a standard protocol (IRSA-CNR methods, book 100, Sep. 1, 1994). Briefly, a sample is first diluted, if necessary, to the 0.1–1.0 mg L^{-1} chromium concentration range, where linear correspondence subsists between absorbance and concentration. Then, 10 μL of 1:1 vol H_2SO_4–H_2O solution and 20 μL of a 0.63 wt % solution of 1,5-diphenylcarbazide in acetone are added to 1 mL of sample. The latter turns to violet as a result of formation of chromium (III) complexes with 1,5-diphenylcarbazone. After 10 min the sample is analyzed on a UV–Vis spectrophotometer (model 2100, Shimadzu, Kyoto, Japan) at 540-nm wavelength (maximum absorbance). The instrument was previously calibrated with three standards with 0.1, 0.5, and 1.0 mg L^{-1} chromium. To determine the amount of chromium sequestered by the membrane after an experiment, the latter was equilibrated with 50 mL of 1 M KCl solution. This volume is adequate to fully exchange CrO_4^{2-} in the membrane with Cl^- anions. The chromium amount released into the solution was determined according to the above protocol.

The Model Adsorption Isotherm

The adsorptive ion exchange between the BME phase (marked by overbar) and the bulk solution is described by the following stoichiometric equation:

$$CrO_4^{2-} + 2\overline{Br} = \overline{CrO_4^{2-}} + 2Br$$

The (electro)chemical potential of the CrO_4^{2-} (or Br^-) counterion in the BME and in the bulk solution is: $\bar{\mu} = \overline{\mu^0} + RT \ln \bar{a} + zFE$ and $\mu = \mu^0 + RT \ln a$, respectively. E is the electrostatic potential in the BME phase relative to the bulk solution (with the latter being conventionally zero). E always sets in when a generic ion-exchange material is placed into an aqueous solution and is sometimes referred to as the Donnan potential.[11] z is the electrostatic charge of the relevant ion (-2 for CrO_4^{2-} or -1 for Br^-). The ion-exchange free energy must be zero at equilibrium. That translates into the following equality:

$$\overline{a_{Cr}}/\overline{a_{Br}^2} = a_{Cr}/a_{Br}^2 \exp(-\Delta G°/RT) \tag{1}$$

where $\Delta G°$ is the standard ion-exchange free energy: $\Delta G° = \overline{\mu_{Cr}^0} - \mu_{Cr}^0 + 2(\mu_{Br}^0 - \overline{\mu_{Br}^0})$. If we assume ideal behavior of CrO_4^{2-} and Br^-counterions adsorbed at the oil/water interface in BME, the ion activity therein is equal to the fraction of neutralized charge, $\bar{x}$. Thus, Eq. 1 becomes

$$\overline{x_{Cr}}/(1 - \overline{x_{Cr}})^2 = K(a_{Cr}/a_{Br}^2) \tag{2}$$

where $K = \exp(-\Delta G°/RT)$ (ion-exchange equilibrium constant). The assumption of ideal behavior for mixtures of adsorbed counterions has been used in various models of mixed ions binding onto a charged micelle surface.[12-15] Equation 2 will be used in the next section to fit the experimental data points of CrO_4^{2-} adsorption in the BME.

Results and Discussion

Chromium uptake and selectivity

Figure 3 displays the adsorption isotherms of chromate anions in the BME from K_2CrO_4 solutions of different ionic strengths (initial K_2CrO_4 concentration 10^{-3}, 2.5×10^{-3}, 5×10^{-3}, 10^{-2} mol L^{-1}). Each data point shown is the average value from determinations on three separate samples individually prepared for the analysis. The standard deviation was typically <3%. Furthermore, determinations from independent equilibration experiments were also reproducible generally within 3%. All isotherms were obtained at room temperature. No significant change of pH was observed in the aqueous solution during an experiment, suggesting negligible transfer of hydroxyl ions across the membrane. It should be pointed out that equilibrium was always attained except for solutions with 10^{-3} mol L^{-1} K_2CrO_4. In this case CrO_4^{2-} concentration in solution first decreased normally with time during an equilibration experiment and then started increasing, although very little, thereby passing through a weak minimum.

At present we have no convincing explanation for this behavior. A tentative reason we may think of might be related to possible diffusion across the membrane of small amounts of DDA^+ cations from BME to solution, which would be accompanied by CrO_4^{2-} back-diffusion (from BME to solution). Whatever the reason is, it is worthwhile noting that data points of the isotherm at 10^{-3} mol L^{-1} K_2CrO_4 refer to the above-noted minima of the concentration vs. time curves; they do not

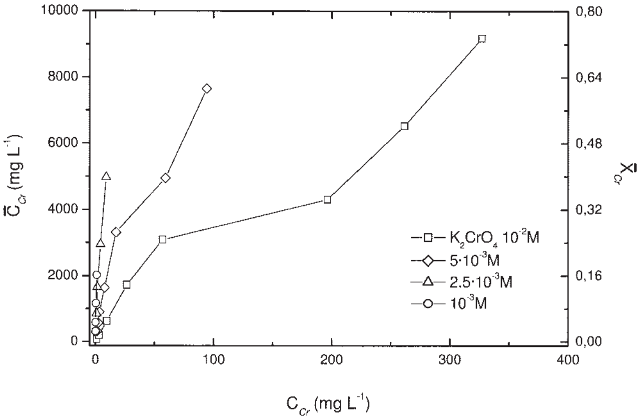

Figure 3. **Cr content in bicontinuous microemulsion vs. Cr content in the solution at equilibrium for various values of solution ionic strength.**

refer to equilibrium condition. Because ion-exchange involved unequally charged ions (Br^- and CrO_4^{2-}), ionic strength of solution decreases during an equilibration experiment, with the variation being typically about 30%. On the right side of the diagram, the ratio of CrO_4^{2-} to DDA^+ equivalents ($\overline{x}_{Cr}$) in the BME is also reported for each value of ionic strength as a function of CrO_4^{2-} concentration in the solution at equilibrium. This ratio measures the percentage of DDA^+ headgroups in the BME neutralized by adsorbed chromate anions.

The isotherms in the low Cr concentration range are shown in Figure 4. It can be immediately noted in Figures 3 and 4 that the chromium content on unit volume base in the BME ($\overline{c}_{Cr}$) is generally much larger than in the solution at equilibrium (c_{Cr}). This is especially true at low concentration. As a consequence, the TD/DDAB/water BME appears as a potentially effective medium to extract and concentrate chromium anion from aqueous solutions. The ability of the BME to remove chromium can be quantified by the enrichment ratio $R = \overline{c}_{Cr}/c_{Cr}$. R is plotted in Figure 5 as a function of c_{Cr} in the 0–15 mg L^{-1} concentration range at various ionic strengths of solution. The enrichment ratio is substantially enhanced with decreasing ionic strength. Significantly, it can attain to values as high as several thousands. The reason for the high chromium uptake is twofold: on the one hand, the adsorptive surface of BME—that is, the interfacial monolayer where the DDAB molecules are confined—is very large. On the other hand, the cationic TD/DDAB/water BME is chromium selective, that is, it has higher affinity for CrO_4^{2-} than for Br^- anions. The latter aspect is considered in detail and discussed further below.

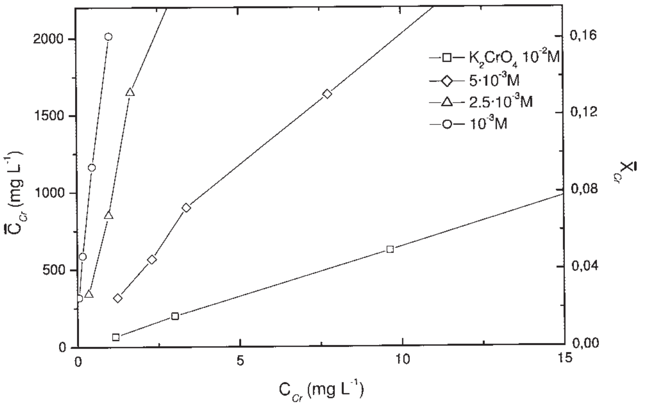

Figure 4. **Cr content in bicontinuous microemulsion vs. Cr content in the solution at equilibrium at the low Cr concentration limit for various values of solution ionic strength.**

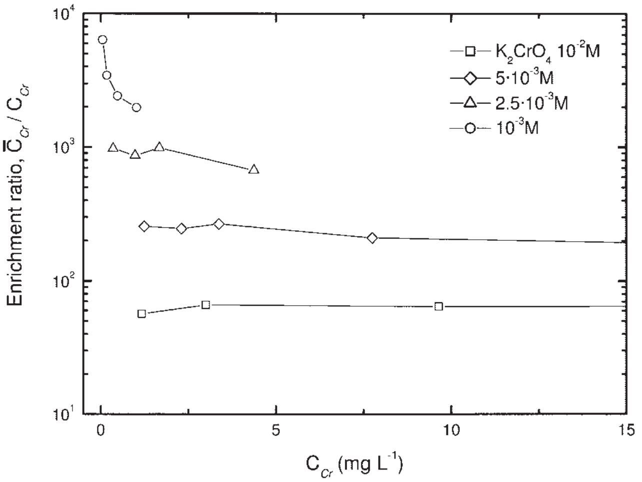

Figure 5. **Cr enrichment ratio in BME vs. Cr content in the solution at equilibrium for various values of solution ionic strength.**

Here we turn our attention to one feature displayed by the adsorption isotherms in Figure 3. In fact, it can be noted that, in particular, the isotherm with 10^{-2} M K_2CrO_4 exhibits a large plateau within the range of approximately 50–200 mg L^{-1} Cr in the solution at equilibrium. Beyond the plateau region the isotherm displays a further regular growth of chromium uptake in the BME up to at least 9000 mg L^{-1} with no apparent saturation. A similar shape, although with considerably less pronounced plateau, is noted for the isotherm with the 5×10^{-3} M K_2CrO_4 solution. Interestingly, both isotherms feature saturation with curvature inversion at about the same Cr uptake in the BME ($\sim$3500 mg L^{-1}). We should also emphasize here that, regardless of the solution ionic strength, the TD/DDAB/water system turns from transparent to highly opaque for chromium uptake exceeding 3000 mg L^{-1}. Moreover, its apparent viscosity increases dramatically. Same behavior was observed for the isotherms with the 2.5×10^{-3} and 10^{-3} M K_2CrO_4 solutions, although no apparent plateau is exhibited in the latter cases. Manifestly, as a certain critical Cr uptake is exceeded, the single bicontinuous microemulsive phase is progressively destroyed and new phases form.

It is not our intent here to identify the phases formed nor to investigate the details of phase transformation. Nonetheless, the above observations as a whole could suggest that CrO_4^{2-} can replace Br^- anions in the BME up to a saturation limit of nearly 3000 mg L^{-1} chromium. This limit corresponds to about 25% of the nominal ion-exchange capacity of the BME, which would be consistent with the plateaus observed in Figure 3. When it is attempted to exceed the above limit the BME structure is no longer stable for the TD/DDAB/water system. New phases form that are progressively able to take in the

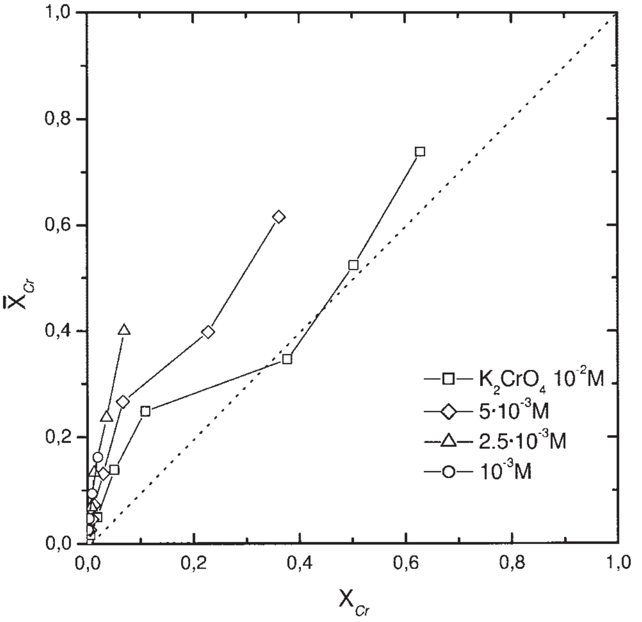

Figure 6. CrO_4^{2-}/Br^- ion-exchange isotherms for the BME/solution system at various K_2CrO_4 concentrations.

excess CrO_4^{2-} anions, which would account for the increase featured by the isotherms past the plateau with simultaneous clouding and thickening of the microemulsive phase. On the other hand, it has been well established that the structure of self-assembled systems of ionic amphiphiles can be sensitive to the type of counterion.[16,17]

Another feature of the isotherms to be noted in Figures 3 and 4 is that chromium uptake in the BME at a given Cr concentration of solution at equilibrium is a strong function of the solution ionic strength, with the uptake growing as the ionic strength is diminished, primarily because of the increasingly stronger BME affinity toward CrO_4^{2-} with respect to Br^- anions at lower solution ionic strength. This aspect is discussed in further detail below in connection with CrO_4^{2-}/Br^- ion-exchange selectivity. To have an immediate perception of the BME selectivity, the ion-exchange isotherms are plotted in Figure 6 in terms of CrO_4^{2-} counterions equivalent fraction in the BME ($\overline{x_{Cr}}$) and in the solution at equilibrium (x_{Cr}) for various values of solution ionic strength. It can be noted that the curves all generally lie above the bisector, which indicates stronger affinity of the BME for the CrO_4^{2-} anion with respect to Br^-, that is, ion-exchange selectivity. The latter is higher at lower ionic strength, as clearly noted in Figure 7. Again, it is worthwhile recalling that equilibrium was not fully attained for the data points referring to 10^{-3} M K_2CrO_4. Thus, the corresponding curve in Figure 7 is not truly representative of the *equilibrium* isotherm. A quantitative assessment of ion-exchange selectivity can be made in terms of the CrO_4^{2-}/Br^- separation factor,[11] defined as the quotient of the CrO_4^{2-}/Br^- equivalent fraction ratios in the BME and the solution at equilibrium: $\alpha = (\overline{x_{Cr}}/\overline{x_{Br}})[(x_{Cr}/x_{Br})^{-1}]$.

Figure 8 is a semilogarithmic plot of the separation factor as a function of chromium concentration in the solution at equilibrium for various values of ionic strength. The separation factor is rather independent of Cr concentration for solutions with 2.5×10^{-3}, 5×10^{-3}, and 10^{-2} M K_2CrO_4. Actually, a sharp increase of the separation factor is noted at high Cr concentration for the curves referring to 5×10^{-3} and 10^{-2} M K_2CrO_4. We deem this increase connected with phase transition of BME because the related data points correspond to high Cr loading (beyond the plateau region in Figure 3) where BME has degenerated into other phases. Different behavior is encountered for the curve referring to low solution ionic strength (10^{-3} M K_2CrO_4). Here we note a decrease of the separation factor vs. Cr concentration. This qualitatively different behavior with respect to higher ionic strength could be related to failure in reaching the equilibrium condition with the 10^{-3} M

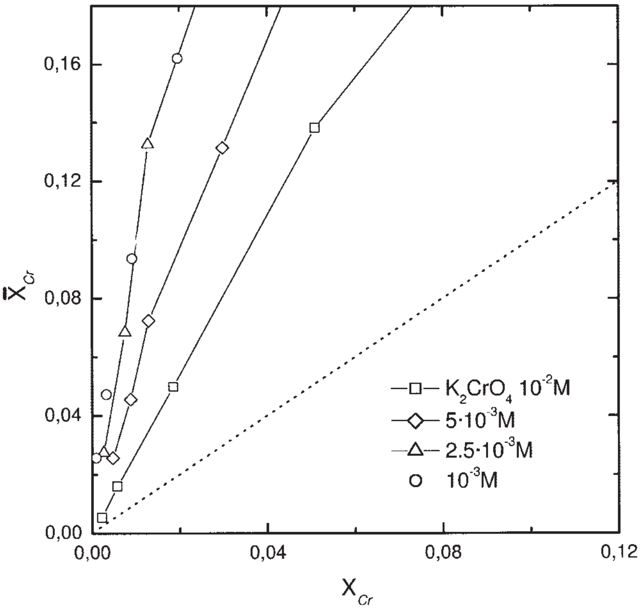

Figure 7. CrO_4^{2-}/Br^- ion-exchange isotherms for the BME/solution system at the low Cr concentration limit for various K_2CrO_4 concentrations.

Dotted line is the quadrant bisector.

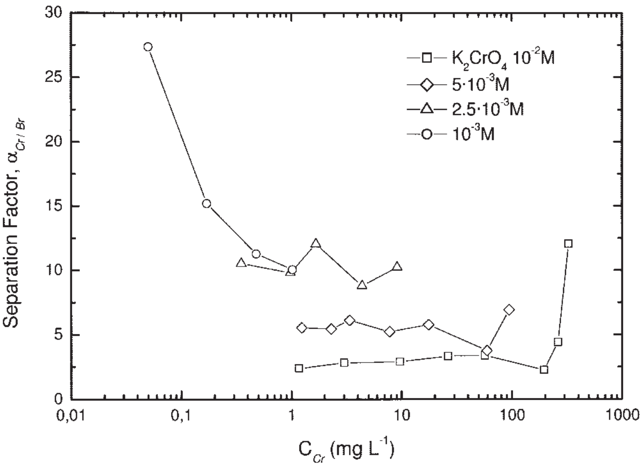

Figure 8. CrO_4^{2-}/Br^- separation factor vs. Cr concentration for various values of solution ionic strength.

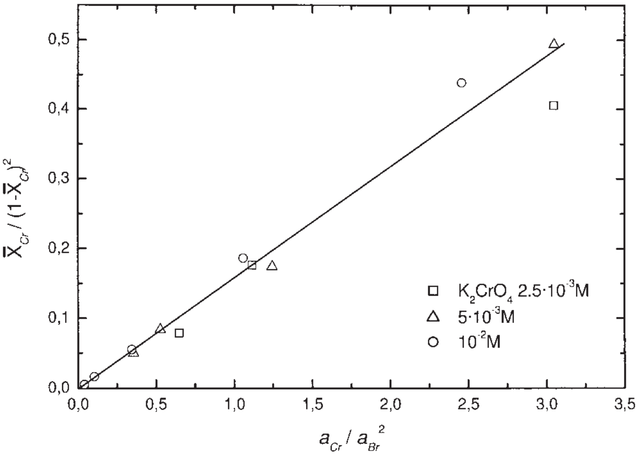

Figure 9. Experimental validation of the model adsorption isotherm (Eq. 2).

$[K_2CrO_4] = 2.5 \times 10^{-3}$, 5×10^{-3}, and 10^{-2} M.

K_2CrO_4 solution. In general, it is noted that the separation factor increases significantly as the ionic strength is diminished, reaching nearly 30 for the 10^{-3} M K_2CrO_4 solution. This can be rationalized—at least partly—on the basis of the so-called Donnan potential effect. In fact, similarly to solid ion exchangers, an electrostatic potential difference (the Donnan potential) sets up between the BME and the solution at equilibrium, pulling counterions from the solutions into the BME.[11] Obviously, counterions with higher valence or smaller size are more strongly attracted at the DDA^+ sites in the BME, which accounts for the higher affinity toward CrO_4^{2-} with respect to Br^- anions (ion-exchange selectivity). Moreover, the Donnan potential grows larger as the solution ionic strength is diminished,[11] a phenomenon that accounts for the higher CrO_4^{2-}/Br^- separation factor observed from Figure 8 at smaller K_2CrO_4 concentration in the solution.

Model validation

The model adsorption isotherm deduced in the previous section (Eq. 2) suggests a useful way of unifying all the experimental data points recorded at various ionic strengths into a single standardized plot. Accordingly, the left-hand side of Eq. 2 is plotted vs. the a_{Cr}/a_{Br}^2 ratio in Figure 9. Different symbols in the plot correspond to different initial K_2CrO_4 concentrations (that is, ionic strength) in solution. Data points referring to the 10^{-3} M K_2CrO_4 solution are not reported because equilibrium was not attained in that case. The basic Debye–Hückel theory is used to calculate the activity coefficients of chromate and bromide anions. At a chromium content < 3000 mg L^{-1} in the BME, experimental data points recorded at different solution ionic strengths are remarkably well aligned in Figure 9 on a single straight line passing through the origin, in good accordance with the proposed model isotherm. Above 3000 mg L^{-1} Cr the experimental data points (not shown) increasingly deviate from the model. In this regard it should be recalled here that Eq. 2 relies on the assumption of ideal behavior, particularly of CrO_4^{2-} ions in the BME phase. On the other hand, it was shown earlier that Cr content exceeding 3000 mg L^{-1} (well below the nominal BME capacity) causes disruption of the BME. In this concentration range the proposed model isotherm is obviously no longer valid. Thus it is not surprising that Eq. 2 fails to fit the experimental data points above 3000 mg L^{-1}. From the slope of the straight line in Figure 9 the value of about 0.16 is calculated for the equilibrium constant in Eq. 2.

BME-based separation process

Here we turn our attention to some possible technical implications of the above results. In particular, we attempt a qualitative comparative discussion of a process for removing CrO_4^{2-} ions based on the ideas presented earlier in the Introduction and using the BME as the adsorbent. First, it is worthwhile mentioning that observed enrichment ratios of the order of 10^4 accompanied by CrO_4^{2-}/Br^- separation factors reaching 30 at low chromium concentration make the TD/DDAB/water BME appear as an attractive adsorbent for CrO_4^{2-} removal, especially from dilute solutions. Furthermore, because the adsorbent is a liquid, the BME process makes continuous operation possible during both the adsorption step and the regeneration step (true moving bed adsorption), as opposed to processes that use traditional solid adsorbents. Removal of metal ions from aqueous streams by means of an organic solvent is a well-established operation in hydrometallurgical processes.[18] Micellar-enhanced ultrafiltration (MEUF) has also been proposed as a novel viable process to remove chromate anions from aqueous solutions.[19,20] It also seems useful to discuss the BME-based process in comparison to MEUF because they share a few common features. In fact, both processes use a surfactant with a proper polar headgroup forming self-assembled structures capable of adsorbing the relevant solute molecules. Moreover, MEUF also enables a continuous removal/regeneration operation.[21,22] However, the BME process has in principle at least three important advantages over MEUF. One is that no ultrafiltration step is required in the BME process, whereas the whole process solution has to be ultrafiltrated in MEUF. Another advantage is related to the loss of surfactant. In fact, the filtered solution from the MEUF process contains dissolved surfactant at the critical micellar concentration. On the other hand, loss of surfactant is prevented in the BME process by the semipermeable membrane dividing the solution from the BME phase. Finally, it is worthwhile noting that the BME phase generally contains very little water as compared to the micellar dispersion phase. This should afford a significant advantage, especially during adsorbent regeneration.

Final Remarks

The present work has explored the potential of BMEs as adsorbent materials for treating liquid streams. Because of the very large internal surface area of the oil/water interface, BMEs can adsorb a contaminant from a solution with high enrichment ratio. As a "proof of principle" test of these ideas we have investigated adsorption of CrO_4^{2-} into a TD/DDAB/water BME, showing that chromate anions are effectively removed from solutions with high enrichment ratio and good selectivity over Br^- anions. A simple model adsorption isotherm has been proposed. The model has proved adequate to fitting experimental data for chromium content in the BME up to 3000 mg L^{-1}.

Although our investigation has been confined to the CrO_4^{2-}–TD/DDAB/water system, implications of the presented concepts and results apparently outreach mere chromium removal. In fact, BMEs can be prepared with a variety of surfactants besides DDAB.[23-25] In turn, the surfactant headgroup can in principle be tailored so as to make it specific for adsorbing a given solute from solution. Another remarkable implication of BMEs as adsorption media is associated with their liquid nature. Because the adsorbent is a liquid, it can be circulated between the adsorption step and the regeneration step (moving bed adsorption), thereby allowing continuous operation. For instance, one may envisage carrying out adsorption in a hollow-fiber membrane contactor with the BME phase passing continuously through the fiber lumen. Apparently, these final considerations encourage further research work.

Of course, application of these concepts to process-scale separation/purification bears a number of potential challenges. For instance, with reference to a chromate removal process based on DDAB BME, it would be necessary to investigate CrO_4^{2-} selectivity over anions other than bromine, particularly sulfate anions. Another issue is related to phase changes occurring in the microemulsive phase as a function of counterion type and concentration. In general, shifting of cationic microemulsions from Type I (oil in water) to Type III (bicontinuous) and subsequently to Type II (water in oil) is observed as salinity of the aqueous phase is increased.[26] Now, given that the equivalent salinity is also related to the anion valence, it turns out that by substitution of a monovalent counterion (anion) with a multivalent one can produce phase changes in BMEs as well and, in particular, this has also been observed for the system investigated here and could pose restrictions to the actual ion-exchange capacity in a process for chromate removal. Similar issues may also arise during the regeneration step, where the relevant counterion is recovered from BME. A further issue could arise in connection with osmotic water flow through the semipermeable membrane. Although we found no evidence of significant osmotic flow in the experiments carried out in the present work, water exchange across the membrane between BME and solution could in general occur, also depending on the characteristics of the BME/solution system and the membrane.

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