

Extractive removal of Cr(VI) from aqueous acidic media by aliquat 336/xylene system: Optimization and modelling of equilibrium

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The extractive removal of Cr (VI) from aqueous sulfate and nitrate solutions by Aliquat 336/xylene system has been studied at 298.2 K and 101.3 kPa. The extraction efficiency of Cr (VI) by Aliquat 336 follow the order $\text{H}_2\text{SO}_4 > \text{HNO}_3$. The carrier yields a maximum Cr (VI) removal efficiency fixed at the concentration ratio (Aliquat 336/Cr (VI) ≤ 0.5) for 0.1 mol/dm³ aqueous acidity. Separation profile of Cr (VI) is dependent equally strongly on the types and concentrations of the carrier, acid and the transferred Cr (VI) species. Distribution data have been subjected to formulation of an optimization structure for an effective Cr (VI) separation based on a derivative variation method. The method calls for the use the first order derivatives of the optimized quantity. 0.2 mol/dm³ Aliquat 336 concentration is optimal for achieving 99 and 80% Cr (VI) removal from aqueous sulfate and nitrate media, respectively. Re-extraction results indicate that Cr (VI) is stripped successfully from the organic phase by NaOH, NaCl and Na₂SO₄ solutions, yielding 88, 54.5 and 13.8% stripping degrees, respectively. Modelling efforts based on the LSER (linear solvation energy relation) and mass-action law principles have shown considerable success. The LSER-based solvation model using nine physical descriptors of components yielded a mean error of 10% and satisfies established limiting behaviour of the physical event.

Keywords: Aliquat 336, Chromium(VI), Extraction, Modelling, LSER, Optimization

Chromium, Cr(VI), produces a toxic influence on the aquatic life, discharging the environment from various industrial plants such as chromic acid anhydride production, the chromium electroplating, cooling towers, corrosion inhibitor of stainless steels and leather tanning^{1,2}. The deleterious effect of Cr(VI) ions on biological systems is harmful endangering the quality of surface water, therefore, emphasis in recent years has been focused on Cr(VI) removing, recovery and reuse from contaminated wastewaters¹⁻⁵. However, the maximum contaminant level (MCL) and the World Health Organization level of Cr(VI) represent a guideline value of 4×10^{-4} mol/dm³ Cr(VI) in wastewater and many organizations have regulated this standard for water supplies^{1,3-5}. To prevent reducing the activity of microorganisms, the maximum permissible levels of Cr(VI) in drinking water and wastewater were set by EPA at 20 and 200 µg/L, respectively^{1,3,5}.

Two stable oxidation states of chromium Cr(III) and Cr(VI), basely presented in aerobic biological systems, possess contrasting characteristics in toxicity, solubility and mobility for aquatic environment^{4,6}. Because Cr(VI) ions are weakly bounded to inorganic surfaces or

biological membranes, the oxidized state of Cr(VI) is much more toxic, soluble and mobile at neutral pH values than the reduced oxidation state of Cr (III)^{4,6-8}. Therefore, the reduction of Cr(VI) into Cr(III) is usually practiced for Cr(VI) removal from contaminated waters⁴.

Recently, different techniques of treating contaminated wastewaters have been used for Cr (VI) removal from industrial effluents like reverse osmosis, ion-exchange, adsorption by numerous natural and synthetic adsorbents, liquid membranes in hollow-fiber modules, electrocoagulation, as well as chemical, photochemical and biological reduction to Cr(III) and subsequent precipitation of Cr(III) ions, induced by increasing the solution pH⁹⁻²³. However, the application of these physic-chemical methods has some limitations and disadvantages of high operation cost, recontamination, operational complexity and low efficiency⁹. Particularly frustrating aspects of the reduction method are the significant sludge production and the long term environmental consequences. Generally, the adsorption process is costly. Biotransformation of Cr(VI) to Cr(III) in several Cr(VI)-reducing microorganisms is a well-recognized low-cost detoxification process being

capable of protecting against high toxicity of Cr(VI) at doses that do not overwhelm reductive capacity^{4,24}. Typically, bioremediation of Cr(VI)-containing wastewater with bacteria, algae and fungi is difficult to achieve and expensive to maintain in a large scale process. A relatively new technique is photocatalytic reduction using various metal oxides such as TiO₂, organic acids and Fe(III)-carboxylate complex reductants that can display fairly strong photoreduction activity converting Cr(VI) to Cr(III)²⁵⁻²⁷. However, the intrinsic limitation of photocatalysis is the low efficiency caused by light scattering effects in the presence of high amounts of suspended matter.

Nevertheless, solvent extraction is the most effective conventional method capable of reducing significantly the Cr(VI) discharge levels. Within the limited number of potential extractants, tributyl phosphate, tri-*n*-octylphosphine oxide, tetrabutylammonium iodide, secondary and tertiary amines, quaternary ammonium compounds, alkylphosphoric acids and phosphine oxides, oxime derivatives and neutral crown ethers have some significant advantages over other solvents such as coordination ability and stability of the complex strength²⁸⁻³⁹.

Most of experimental efforts published to date are typically limited to recovering Cr(VI) effluents at lower concentrations less than 0.01 mol/dm³. It is, therefore, of interest to extend the previous works to accommodate the additional data on the extraction of high concentrated Cr(VI) aqueous contents over than 0.01 mol/dm³ by the commercial solvent Aliquat 336 (NR₄X) dissolved in the inert xylene diluent. However, the study mainly deals with optimizing the extraction conditions in terms of a derivative variation method through analyzing the non-linear variation profile of the optimized quantity and its derivatives³⁵.

The primary objectives of this work were: (a) to obtain optimum extraction conditions based on an extended matrix of equilibrium data for Cr(VI) removal from aqueous acidic sulfate and nitrate media by Aliquat 336/xylene solvent system. However, the optimization technique calls for the use, the derivative variation method proposed by Senol³⁵ to identify the optimum extraction field; (b) to demonstrate the ability of the equilibrium models derived from the LSER (linear solvation energy relation) and mass-action law principles to accurately represent the physical properties of extraction. To attain these

objectives the following case studies were carried out sequentially: (i) It has been analyzed the influence of the acid, carrier and Cr(VI) concentrations on the extraction degree of Cr(VI) at isothermal conditions (298.2 K) and atmospheric pressure, using the initial Cr(VI) content in the aqueous solution larger than 0.01 mol/dm³. (ii) Optimum extraction conditions have been defined both experimentally and analytically by analyzing the deviation profile of the first order derivatives of the observed and modeled performance due to the derivative variation method³⁵. (iii) The equilibrium data have been correlated satisfactorily through the LSER-based solvation model comprising the magnitude of nine physical descriptors.

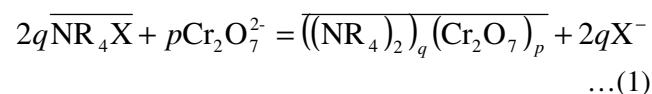
Theoretical background

Criteria of extraction efficiency

The results have been interpreted in terms of the distribution ratio, $D = \overline{C_{\text{Cr(VI)}}} / C_{\text{Cr(VI)}}$, i.e. the ratio of the overall extracted Cr(VI) in the organic phase $\overline{C_{\text{Cr(VI)}}}$ (mol/dm³) to total aqueous phase Cr(VI) concentration $C_{\text{Cr(VI)}}$ (mol/dm³) at the equilibrium, degree of extraction, $E = 100 D / (1 + D)$ (%), for the equal volumes of organic and aqueous phases, and overall loading factor (Z_t)^{34,35}. The overall loading factor is the ratio of total amount of Cr(VI) extracted $\overline{C_{\text{Cr(VI)}}}$ (mol/dm³) to the initial amount of the quaternary ammonium compound in the organic phase $C_{\text{NR}_4\text{X}}^0$ (mol/dm³), $Z_t = \overline{C_{\text{Cr(VI)}}} / C_{\text{NR}_4\text{X}}^0$.

Equilibrium mass-action law models

Starting from the chemical modeling concepts for the extraction of Cr(VI) by a tertiary amine^{34,35}, the overall extraction equilibrium of Aliquat 336/diluent/Cr(VI) system can be characterized by Eq. (1), where the quaternary ammonium compound is being regarded as an ion-exchanger.



where $\text{Cr}_2\text{O}_7^{2-}$, X^- , $\overline{\text{NR}_4\text{X}}$ and $\left(\overline{(\text{NR}_4)_2}\right)_q \left(\text{Cr}_2\text{O}_7\right)_p$ stand for the dichromate ion, inorganic acid anion, quaternary ammonium

compound (Aliquat 336) and carrier_q-Cr(VI)_p complex, respectively. Overbar is attributed to the species in the organic phase. The conditioned overall extraction constant of equilibrium β_{pq} in terms of Eq. (1) including the activity coefficients of species is defined in the molarity scale $(\text{mol/dm}^3)^{1-p-q}$ as follows:

$$\beta_{pq} = \frac{\overline{C_{((\text{NR}_4)_2)_q(\text{Cr}_2\text{O}_7)_p)} C_X^{2q}}}{C_{\text{Cr}_2\text{O}_7}^p \overline{C_{\text{NR}_4\text{X}}^{2q}}} \quad \dots (2)$$

where $C_{\text{Cr}_2\text{O}_7}$, C_X , $\overline{C_{\text{NR}_4\text{X}}}$ and $\overline{C_{((\text{NR}_4)_2)_q(\text{Cr}_2\text{O}_7)_p}}$ (mol/dm^3) designate the equilibrium concentrations of noncomplexed dichromate ion and free inorganic acid anion in the aqueous phase, free (noncomplexed) quaternary ammonium salt and $(\text{NR}_4)_q\text{-Cr(VI)}_p$ (q, p) complex, respectively. The total equilibrium content of complexed Cr(VI) is the sum of contributions of the individual complexes, $\overline{C_{\text{Cr(VI)}}} = p \overline{C_{((\text{NR}_4)_2)_q(\text{Cr}_2\text{O}_7)_p}}$ (mol/dm^3). Using Eqs. (1) and (2), the chemical model can be expressed in terms of Z_t quantity given by Eq. (3). In this approach, C_X is considered to be equal to the initial acid molarity.

$$Z_t = \frac{\overline{C_{\text{Cr(VI)}}}}{C_{\text{NR}_4\text{X}}^0} = \frac{\sum_{p=1}^k \sum_{q=1}^l p \beta_{pq} C_{\text{Cr(VI)}}^p \overline{C_{\text{NR}_4\text{X}}^{2q}}}{C_{\text{NR}_4\text{X}}^0 C_X^{2q}} \quad \dots (3)$$

In the prediction of equilibrium, different ion-pair $(\text{NR}_4)_q\text{-Cr(VI)}_p$ (q, p) aggregations of one carrier per multiple chromates have been selected for Cr(VI) regarding the maximum loading factor. Cr(VI) may exist in the aqueous phase in different ionic forms, such as chromate (HCrO_4^- and CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and polychromate ($\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$) ions with regard to the total amount of chromium and pH variables dictating which particular chromate species will predominate^{40,41}. Higher forms of chromate polymers are prevalent at high acidic media and Cr(VI) concentration larger than 0.1 mol/dm^3 ^{40,41}. This would call for the assumption that a more complex aggregation between Aliquat 336 and polychromate species would likely proceed.

In this study, the Li-Bowman approach⁴² for the Langmuir type sorption of ionic species onto a solid through ion-exchange mechanism has been adapted and applied to Aliquat 336-Cr(VI) system, where the quaternary ammonium salt and Cr(VI) are being regarded as adsorbent and adsorbate, respectively. Assuming that $z = Z_{t,\text{max}} = \overline{C_{\text{Cr(VI),max}}} / C_{\text{NR}_4\text{X}}^0$, the Li-Bowman model is modified to Eq. (4) including both loading factor Z_t and equilibrium extraction constant K_L variables.

$$Z_t = \frac{\overline{C_{\text{Cr(VI)}}}}{C_{\text{NR}_4\text{X}}^0} = \frac{z K_L C_{\text{Cr(VI)}}}{1 + K_L C_{\text{Cr(VI)}}} \quad \dots (4)$$

where $C_{\text{Cr(VI)}}$, $\overline{C_{\text{Cr(VI)}}}$ and $\overline{C_{\text{Cr(VI),max}}}$ (mol/dm^3) stand for the aqueous phase Cr(VI) concentration, the overall complexed Cr(VI) amount and the maximum possible extraction capacity of the carrier, respectively. The Langmuir extraction constant K_L (mol/dm^3)⁻¹ is attributed to the ion-exchange mechanism in terms of Eq. (1) considering a single carrier_q-Cr(VI)_p (q, p) aggregation of the type (1, 1).

Finally, a linear differential equation, including two substance-dependent adjustable coefficients a and b , has been performed to correlate the equilibrium data. Basically, the modeled quantity (log-basis) is made up of two balancing terms combined with the limiting properties. Applied specifically to extraction degree (E) correlation, the relation is written as,

$$E = E_{\text{max}} \left[1 - \exp\left(a \overline{V}_e + b C_{\text{acid}}^0\right) \right] \quad \dots (5)$$

where the E_{max} is the maximum possible limit of E for the system studied ($E_{\text{max}} = 100\%$), the \overline{V}_e (vol %) is the initial carrier concentration in the solvent mixture, the C_{acid}^0 (mol/dm^3) is the initial molarity of inorganic acid in the aqueous solution. The model presumes that the effect of the solute concentration is incorporated into the coefficients a and b .

Basic principles of LSER modeling

Marcus and co-workers have revealed that the distribution of nonelectrolyte solutes between water and an immiscible organic solvent can be well correlated by LSER⁴³⁻⁴⁵. The design of a perceptible

model structure depending on the LSER principles, argues combining the limiting property with the solubility and solvatochromic indicators of the solvent, the concentrations of the carrier ion and the physical properties of the distributed ion. As reported by Senol³⁵, the LSER based solvation model can be expressed in the general form by Eq. (6).

$$Pr = Pr_0 + F(Pr_{\text{solvent}} + Pr_{\text{ion}}) \quad \dots (6)$$

where the Pr (log-mean) designates the modeled property, the Pr_0 (log-mean) stands for the limiting value of the observed property, and the Pr_{solvent} represents the overall property of the solvent defined by the Hildebrand solubility parameter [δ_{H} (MPa^{0.5})] and solvatochromic parameters (π , β , α and δ)⁴³⁻⁴⁵. The solvatochromic parameter π is an index of polarity/polarizability and δ is a polarizability correction parameter reflecting differences in the component polarizability. The polarity/polarizability term ($\pi + \delta$) is a measure of the endoergic effects of dipole-dipole and dipole-induced dipole interactions. The hydrogen-bonding indices β and α characterize the hydrogen bond donation (HBD) and acceptance (HBA) properties of the solute and solvent, respectively. The β scale is the HBA (hydrogen-bond acceptor) ability of the solute to accept a proton in a solute-to-solvent hydrogen bond, and α is the HBD (hydrogen-bond donor) ability of the solute to donate a proton in a solvent-to-solute hydrogen bond. The Hildebrand solubility parameter δ_{H} (MPa^{0.5}) is a measure of the cohesive energy density (square of δ_{H}) in Eq. (6). The Pr_{ion} denotes the overall property characterizing the distributed ion ($\text{Cr}_2\text{O}_7^{2-}$), namely, the charge of the ion, z_c , the normalized reciprocal of the Pauling crystal ionic radius r (nm), $r' = 0.1/r$ (nm⁻¹), the normalized volume v (nm³) occupied by the ion, $v' = 10v = 40\pi r^3/3$ (nm³), the normalized molar refractivity, $R'_D = R_D/100$ (cm³/mol) with R_D (cm³/mol) being the molar refractivity of the ion⁴⁵⁻⁴⁷. The softness parameter is being regarded as characteristic of the enthalpy of interaction between ions of opposite charge⁴⁷. For large ionic species, the softness parameter of the ion should be omitted,

because it plays a significant role only for smaller ions with $r \leq 0.25$ nm⁴⁵. Normalized properties are used, which are approximately in the range from 0 to 1, so that the relative contributions of the various variables can be more readily compared. A concentration-dependent correction factor F is incorporated into the integrated-property term ($Pr_{\text{ion}} + Pr_{\text{solvent}}$) to account for the limiting concentration conditions. Following Senol³⁵, the generalized solvation model is given by Eq. (7). It covers two dependently varying parts, i.e. one part accounted for the limiting observed property, Pr_0 (log-mean), and an integration term with respect to the solubility and solvatochromic parameters (δ_{H}^* , π^* , β^* , α^* and δ^*) of the solvent mixture, and the overall physical properties characterizing the distributed ion (z_c , r' , v' , R'_D). The concentration-dependent correction factor $F = \left(1/C_{\text{Cr(VI)}}^0 + 1/C_{\text{NR}_4\text{X}}^0\right)$ describes the concentration effect of the carrier and the transferred ion, and on its account, an indefinable character of the function appears for two limiting conditions when either the initial Cr(VI) concentration $C_{\text{Cr(VI)}}^0$ (mol/dm³) is zero ($C_{\text{Cr(VI)}}^0 = 0$) or the initial carrier concentration $C_{\text{NR}_4\text{X}}^0$ (mol/dm³) is zero ($C_{\text{NR}_4\text{X}}^0 = 0$).

$$Pr = Pr_0 + \left(\frac{1}{C_{\text{Cr(VI)}}^0} + \frac{1}{C_{\text{NR}_4\text{X}}^0} \right) \left[(C_{\text{H}}\delta_{\text{H}}^* + C_{\pi}(\pi^* - 0.35\delta^*) + C_{\beta}\beta^* + C_{\alpha}\alpha^*) + \dots (7) \right. \\ \left. (C_z z_c + C_{r'} r' + C_v v' + C_R R'_D) \right]$$

where C_{H} , C_{π} , C_{β} , C_{α} , C_z , C_r , C_v and C_R are adjustable coefficients of Eq. (7). The solubility and solvatochromic parameters of the solvent mixture (δ_{H}^* , π^* , β^* , α^* and δ^*) are derived from the corresponding parameters ($\delta_{\text{H},i}$, π_i , β_i , α_i , δ_i) and volume fractions ($v_{f,i}$) of the individual components (Aliquat 336 and xylene) by applying a mean value estimation rule, i.e., $\delta_{\text{H}}^* = \frac{1}{1000} \sum_i v_{f,i} \delta_{\text{H},i}^2$, $\pi^* - 0.35\delta^* = \sum_i v_{f,i} (\pi_i - 0.35\delta_i)$, $\beta^* = \sum_i v_{f,i} \beta_i$, $\alpha^* = \sum_i v_{f,i} \alpha_i$.

For achieving a reasonable confidence of prediction, it is presumed that $\text{Cr}_2\text{O}_7^{2-}$ is the only counterion exchanged at acidic pH. In this study, the ability of the LSER-based solvation model, Eq. (7), to reproduce the observed performance has been tested through executing the following Pr and Pr_0 quantities given in a logarithmic scale.

$$\begin{aligned} Pr &= \ln(Z_t); Pr_0 = \ln(Z_{t,\max}) \\ Pr &= \ln(E); Pr_0 = \ln(E_{\max}) \\ Pr &= \ln(D); Pr_0 = \ln(D_{\min}) \end{aligned} \quad \dots (8)$$

where, $Z_{t,\max}$, E_{\max} and D_{\min} stand for the experimentally defined limiting values of the observed performance.

Experimental Section

The commercial extractant Aliquat 336 (Acros Organics, New Jersey, USA) is a viscous colorless liquid mixture of $\text{C}_8\text{--C}_{10}$ trialkylmethylammonium chlorides, mainly tricaprylmethylammonium chloride $\text{CH}_3\text{N}((\text{CH}_2)_7\text{CH}_3)_3\text{Cl}$, with a mean molecular weight of $M = 404.15 \text{ g/mol}$, a density of $d = 0.884 \text{ g/cm}^3$, a viscosity of $\mu = 1500 \text{ mPa s}$ and a boiling point of $T_b = 498.2 \text{ K}$. Xylene, a mixture of isomers with a 99% purity utilized as an inert and nontoxic diluent for Aliquat 336 system, was supplied by Merck. Chromium(VI) aqueous acidic solutions, acted as the simulated wastewater samples for analyzing the extraction efficiency of the carrier, were prepared from analytical grade $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck), H_2SO_4 (Merck) and HNO_3 (Merck), using deionized water (Milli-Q Millipore, $18 \text{ M}\Omega/\text{cm}$ conductivity). Reagent grade NaOH , NaCl and Na_2SO_4 from Merck were employed as strippants in the re-extraction experiments. All chemicals were used as received without further purification.

Extraction experiments were performed using an equilibrium glass cell of 75 cm^3 volume with a water jacket to maintain isothermal conditions. The extraction cell was equipped with a magnetic stirrer and the conjugate phases were equilibrated at $T = 298.2 \pm 0.2 \text{ K}$ and $P = 101.3 \pm 0.7 \text{ kPa}$. The equal volumes (10 cm^3) of initial aqueous and organic phases were agitated for 1 h and then left for 2 h to settle down into aqueous and solvent layers at a fixed

temperature and atmospheric pressure. The effective separation of the phases was ensured by centrifugation. The aqueous concentration of Cr(VI) was measured by 1,5-diphenylcarbazine colorimetric method⁴⁸ at 540 nm using Shimadzu UV-160 A visible UV-spectrophotometer. The Cr(VI) concentration in the organic phase was determined by mass balance. Concentration determinations were made with an uncertainty of $\pm 0.0003 \text{ mol/dm}^3$.

Tests covering the influence of the carrier (Aliquat 336), acid (H_2SO_4 or HNO_3) and Cr(VI) amounts on the extraction degree have been performed using the initial Aliquat 336 concentrations ($C_{\text{NR},X}^0$) in the inert xylene diluent restricted in the range $0.01\text{--}0.44 \text{ mol/dm}^3$ for two initial Cr(VI) concentrations ($C_{\text{Cr(VI)}}^0$) of 0.019 and 0.192 mol/dm^3 and six aqueous sulfuric acid molarities of 0.001 , 0.05 , 0.1 , 0.5 , 1 and 2 mol/dm^3 . In the extraction experiments by nitric acid, the initial aqueous acid molarities of HNO_3 were kept at 0.1 and 0.5 mol/dm^3 . Subsequently, the recovery of Cr(VI) from the loaded organic phase by NaOH , NaCl and Na_2SO_4 solutions used as stripping agents for Cr(VI) has been carried out. The recovery of Cr(VI) from the loaded organic phase containing 0.05 mol/dm^3 Aliquat 336/xylene solution enriched with 0.016 mol/dm^3 Cr(VI) has been carried out at different concentrations ($0.05\text{--}3 \text{ mol/dm}^3$) of NaOH , NaCl and Na_2SO_4 salts. The stripping solution was adjusted to the desired salt molarity and was mixed for 1 h with the equal volume of Aliquat 336/xylene/Cr(VI) solution. The recovery degree of Cr(VI) was measured spectrophotometrically. The equilibrium data for extraction of Cr(VI) by Aliquat 336/xylene are provided completely in Figs. 1-3.

Results and Discussion

Factors affecting the extraction equilibria of Cr(VI)

Figures 1–3 present detailed descriptive data for the extraction efficiency of Aliquat 336/xylene system obtained for two initial Cr(VI) contents ($C_{\text{Cr(VI)}}^0$) of 0.019 and 0.192 mol/dm^3 , six aqueous phase molarities of H_2SO_4 (0.001 , 0.05 , 0.1 , 0.5 , 1 and 2 mol/dm^3) and two molarities of HNO_3 (0.1 and 0.5 mol/dm^3). Inspection of Figs. 1–3 reveals that the extraction degree (E), distribution ratio (D) and the overall loading factor of the carrier (Z_t) are hardly

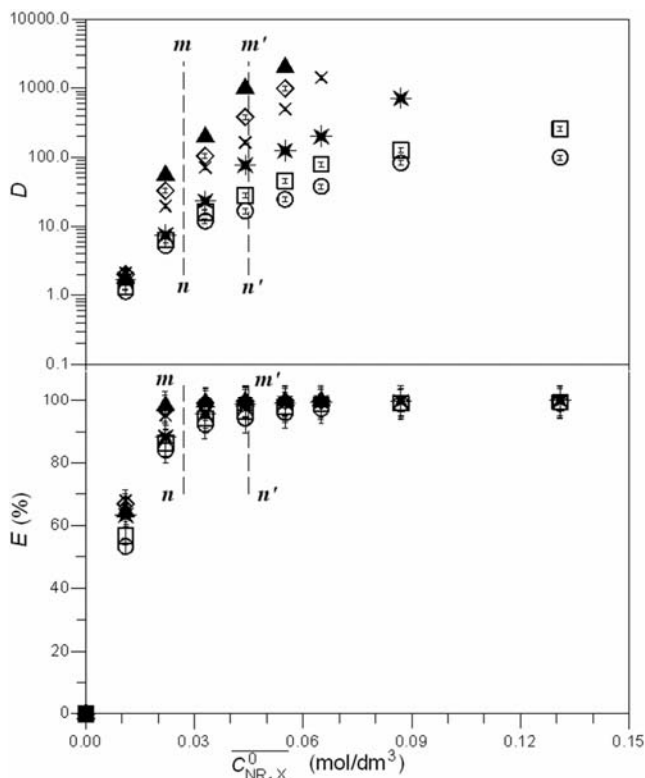


Fig. 1 — Variation of extraction degree (E) and distribution ratio (D) with Aliquat 336 concentration $\overline{C_{NR_4X}^0}$ for initial $C_{Cr(VI)}^0 = 0.019 \text{ mol/dm}^3$. Aqueous-phase sulfuric acid molarities ($C_{H_2SO_4}^0$) \blacktriangle 0.001, \diamond 0.05, \times 0.1, $*$ 0.5, \square 1, \circ 2 mol/dm^3 . The mm' - nn' section refers to the observed optimum extraction conditions.

dependent on the type of inorganic acid and the initial concentrations of Cr(VI) and Aliquat 336 (NR_4X). It is seen from Figs. 1 and 2 that the ranges of E and D extraction factors are varying against the Aliquat 336 concentration asymptotically towards the largest extraction degree of 99.8% (in H_2SO_4 media) for the initial contents of $C_{Cr(VI)}^0 = 0.019 \text{ mol/dm}^3$ and $\overline{C_{NR_4X}^0} = 0.055 \text{ mol/dm}^3$, whereas for the initial contents of $C_{Cr(VI)}^0 = 0.192 \text{ mol/dm}^3$ and $\overline{C_{NR_4X}^0} = 0.196 \text{ mol/dm}^3$ the corresponding optimum extraction degrees are 99% (in H_2SO_4 media) and 76.5% (in HNO_3 media), respectively. Since Aliquat 336 by itself is a relatively poor solvating medium for the polar complexes, the rate of increasing the slope of the E curve above 85-90% extraction limits is

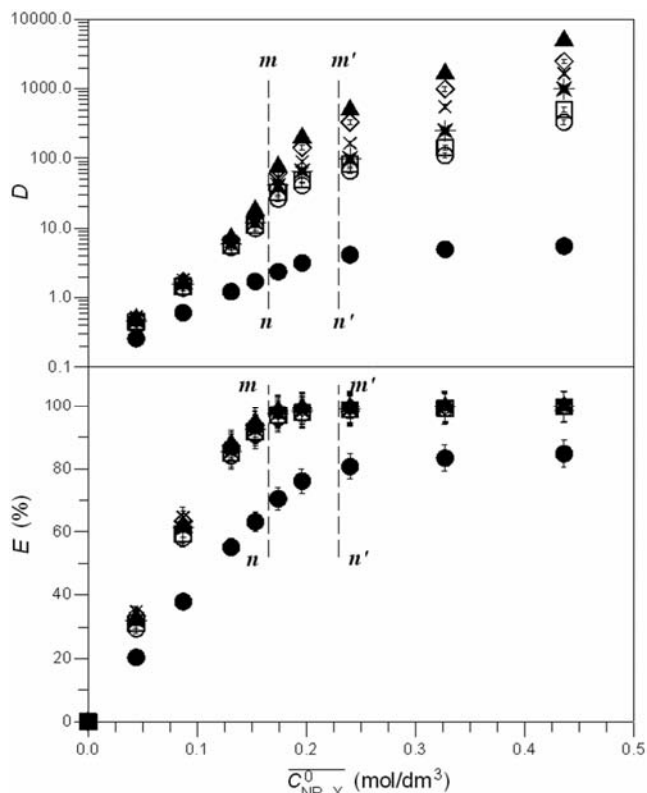


Fig. 2 — Variation of extraction degree (E) and distribution ratio (D) with Aliquat 336 concentration $\overline{C_{NR_4X}^0}$ for initial $C_{Cr(VI)}^0 = 0.192 \text{ mol/dm}^3$. Aqueous-phase acid molarities: sulfuric acid ($C_{H_2SO_4}^0$) \blacktriangle 0.001, \diamond 0.05, \times 0.1, $*$ 0.5, \square 1, \circ 2 mol/dm^3 , nitric acid ($C_{HNO_3}^0$) \bullet 0.5 mol/dm^3 . The mm' - nn' section refers to the observed optimum extraction conditions.

rather low by reason of an enhanced amount of the carrier probably reducing the solvation degree of the formed complexes. Regarding Figs. 1 and 2, one may conclude that the same remarks hold for the D factors of the Aliquat 336/xylene system yielding comparatively larger uptake capacities from acidic sulfate media ($D \approx 100$ and $D \approx 350$ for $C_{Cr(VI)}^0$ of 0.019 and 0.192 mol/dm^3 , respectively) than those from acidic nitrate media ($D \approx 4.5$ for $C_{Cr(VI)}^0 = 0.192 \text{ mol/dm}^3$).

It turns out from Figs. 1–3 that E , D and Z_t factors decrease continually with increasing the acid content in the aqueous phase, being indicative of a reasonably large competitive effect between the acid and Cr(VI) anions to interact with the carrier at high acidic media. As depicted in Figs. 1 and 2, the

magnitude of E and D factors is ranging against the aqueous acidity in the order, $\text{SO}_4^{2-} \succ \text{NO}_3^-$, along with a favourable trend of a continual decrease of extraction factors with increasing the aqueous acidity for the whole working range. It can be recognized depending on the repartition diagram of Cr(VI) species that different in the nature species of Cr(VI) are prevalent at a given pH ^{40,41}. Increasing acidity favours acidic species of chromate likely comprising a complex formation of lower solvation degree. The noticeably lower D values at a high acidity range may also be attributed to the formation of an intramolecular bonded ion between the inorganic acid (HA) and Cr(VI) species like CrSO_7^{2-} , being responsible for decreasing the extraction efficiency of Aliquat 336⁴¹. Additionally, besides extraction of

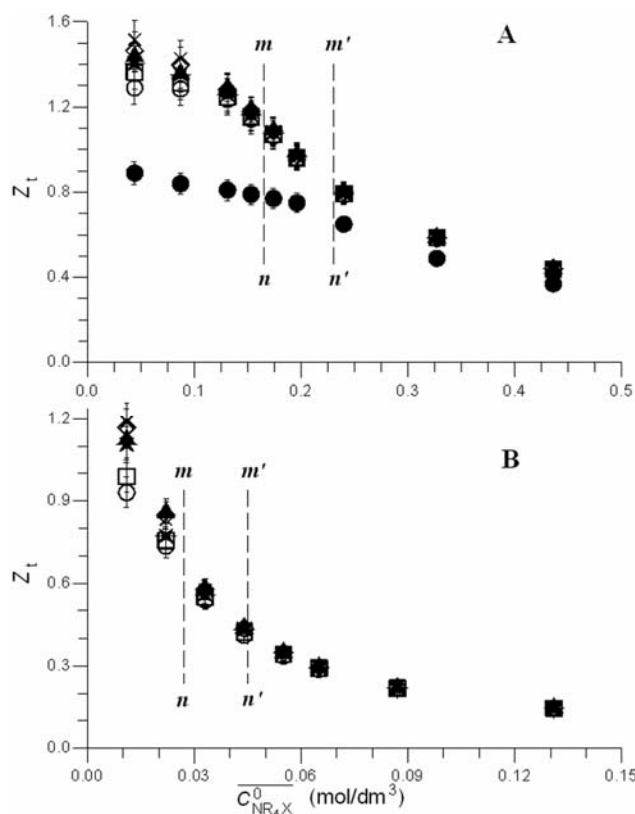


Fig. 3 — Variation of loading factor (Z_t) with Aliquat 336 concentration $\overline{C_{\text{NR}_4\text{X}}^0}$ for different aqueous-phase acid molarities: sulfuric acid ($C_{\text{H}_2\text{SO}_4}^0$) \blacktriangle 0.001, \diamond 0.05, \times 0.1, \star 0.5, \square 1, \circ 2 mol/dm³, nitric acid ($C_{\text{HNO}_3}^0$) \bullet 0.5 mol/dm³; (A) $C_{\text{Cr(VI)}}^0 = 0.192$ mol/dm³, (B) $C_{\text{Cr(VI)}}^0 = 0.019$ mol/dm³. The mm' – nn' section refers to optimum extraction conditions.

chromate ions, extraction of isopoly-acids may occur especially in the concentrated solutions of $\text{Cr}_2\text{O}_7^{2-}$ and H_2SO_4 ^{40,41}.

At a low acidity range, the Aliquat 336/xylene system favours the formation of overloaded polar $(\text{NR}_4)_q\text{-Cr(VI)}_p$ structures ($q \leq p$) corresponding to $Z_t \geq 1$. Inspection of Figs. 1–3 reveals that the variation of extraction factors Z_t and D with the aqueous acid molarity exhibits a maximum fixed at 0.1 mol/dm³ aqueous acidity relative to the ratio $\overline{C_{\text{NR}_4\text{X}}^0} / C_{\text{Cr(VI)}}^0 \leq 0.5$. In view of the results from Figs. 1–3, one may conclude that 0.2 mol/dm³ initial concentration of Aliquat 336 in the solvent mixture is optimal for 99% and 80% Cr(VI) uptake capacities from H_2SO_4 and HNO_3 media, respectively.

To estimate the strength of Aliquat 336–Cr(VI) complexation depending on the chromium concentration, runs were performed using various Cr(VI) solutions. It is seen from Fig. 4 that the Aliquat 336/xylene system yields the highest strength of the complex solvation at $C_{\text{acid}}^0 = 0.1$ mol/dm³ H_2SO_4 content, which pertains to the largest loading factor $Z_{t,\text{max}} = 1.6$ corresponding to the plateau in the

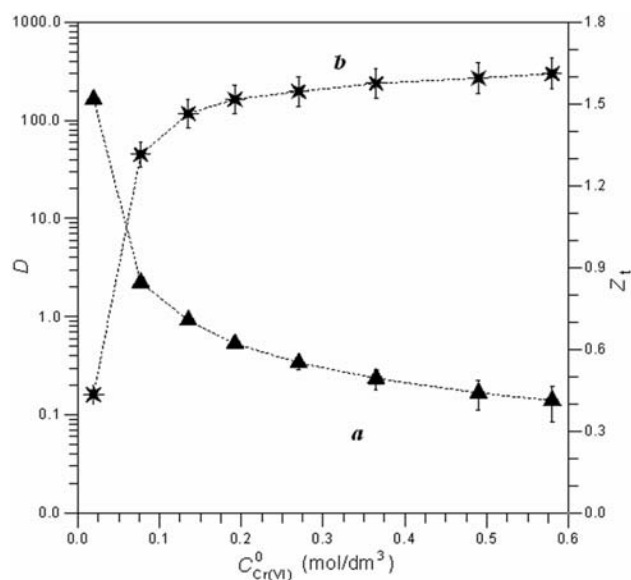
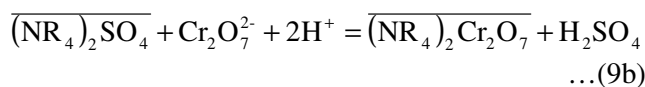
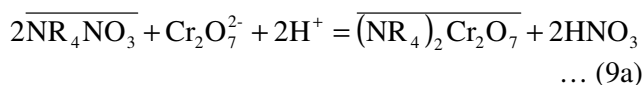


Fig. 4 — Variation of extractability variables, loading factor (Z_t) and distribution ratio (D) with aqueous-phase Cr(VI) concentration: \blacktriangle a -curve D , \star b -curve Z_t ; $C_{\text{H}_2\text{SO}_4}^0 = 0.1$ mol/dm³ and $\overline{C_{\text{NR}_4\text{X}}^0} = 0.044$ mol/dm³.

loading curve. From that figure, graphically defined D_{\min} value of the relevant system is 0.14. This deduction for the $Z_{t,\max}$ (or D_{\min}) is confirmed by the results from Figs. 2 and 3, manifesting the fact that at overly high Cr(VI) concentration levels in the bulk the hydrophobicity, polarity and ionizing strength of the formed polychromate ions are predominant factors for a chemical interaction between the carrier and Cr(VI). By analogy, a simultaneous co-extraction of dichromate (dimer) and chromate (monomer) species would likely proceed by ion-exchange mechanism. The physical extraction of Cr(VI) through dipole-dipole interaction with the diluent is negligible in the nature. The results from Figs. 1–4 suggest that different mechanisms control one or simultaneously at least two complex formations of the type (one mole carrier per one mole chromate) or (one mole carrier per multiple moles chromates). This may be ascribed to the relatively large size of Cr(VI) anionic species responsible for steric hindrances in interactions with the carrier and mass transfer resistance.

In a strong acidic solution, $\text{Cr}_2\text{O}_7^{2-}$ is the major ionic form of chromium^{40,41}, thereby referring to Z_t values from Fig. 3 it is presumed that, for both H_2SO_4 and HNO_3 media, a $\left(\left(\text{NR}_4\right)_2\right)_q - \left(\text{Cr}_2\text{O}_7\right)_p$ aggregation with a stoichiometric ratio of $q:p = 1:1$ would likely proceed according to the anion exchange mechanism given by Eq. (9a-b). Unexpectedly, the classical slope analysis technique does not provide a real picture for the Aliquat 336-Cr(VI) association and accordingly the method is not presented here. It is worthwhile to mention here that Das and co-workers⁴⁹⁻⁵¹ have reported a cationic type exchange mechanism for the reactive extraction of U(VI) from mineral acids by acidic and neutral ligands (D2EHP, PC88, Cyanex 272, TBP and its homologus), which in turn have favoured a solute-extractant aggregation reaction similar to Eq. (9).



Consequently, regarding the reported Cr(VI) removal efficiencies of tertiary and secondary amines from acidic media³³⁻³⁵, it is argued that the uptake

capacity of the amine-based commercial extractant decreases in the order: quaternary ammonium compound > tertiary amine > secondary amine. As well, the nature of inorganic acid can influence the extraction degree of Cr(VI) increasing in the order $\text{H}_2\text{SO}_4 \rangle \text{HCl} \rangle \text{HNO}_3$, i.e., the co-extraction effect of competitive acid anions on the removal efficiency of Cr(VI) is much more readily strong in the presence of nitrate and chloride ions. As opposed to the above findings, Das *et al.*⁴⁹ have found that the extraction of U(VI) by D2EHPA, PC88A and Cyanex 272 acidic ligands in different mineral acids followed the order $\text{HNO}_3 \rangle \text{HCl} \rangle \text{H}_2\text{SO}_4$. This may be ascribed to the competition between X^- ion of the Aliquat 336 carrier and A^- ion of the mineral acid that should affect the extraction equilibria in an unexpected way. This is perhaps not surprising, considering the large ionizing strength of HNO_3 which promotes more readily a cationic type exchange mechanism of U(VI)-acidic carrier aggregation as compared to other mineral acids⁴⁹. In contrast, the complexation between basic Aliquat 336 and Cr(VI) is necessarily realized by an anion exchange mechanism, which works more effectively in H_2SO_4 medium rather than HNO_3 medium, due to a less affinity of SO_4^{2-} to aggregate with Aliquat 336 molecules.

Evaluation of optimum extraction conditions

A survey of the literature has revealed that only few works have focused on assessing and generating an efficient method for optimizing analytically the extraction efficiency of a reactive liquid-liquid extraction system composed of associating components³⁵. However, the study deals with a new conceptual definition for optimum extraction as the locus of the proposed non-homogenous differential equations for extraction factors being used as the optimization criteria. The goal is to determine the most suitable extract composition $\overline{C_{\text{Cr(VI)}}}$ for Cr(VI) recovery against practically permissible optimum concentration range of the carrier $C_{\text{NR}_4\text{X}}^0$ at given initial concentrations $C_{\text{Cr(VI)}}^0$ and C_{acid}^0 . For this purpose, the optimum extraction conditions have been analyzed in terms of the derivative variation method applied to the extraction factors Z_t and E , as described in detail by Senol³⁵. The method is based on

an identification of both the first order derivatives of the quantity in question, and the differences between the values of neighboring derivatives throughout the working range. This method implies that, (a) the contribution of the derivatives to the optimized property is validated by the slope analysis, and (b) the identification of the optimum conditions is governed by the range of changes in the derivative value³⁵. The first approach involves the calculation of the derivatives of the quantity in question for all the data points included. In the second approach, the most significant optimum conditions are identified by analyzing the non-linear deviation profile of the derivative value. The largest changes in the derivative value of the optimized quantity (or the equivalent slope of related curve) should separate the location of the optimum point.

Depending on the derivative variation method, the optimum conditions for the extraction of Cr(VI) by Aliquat 336 have been obtained experimentally through the slope analysis of the observed curves $E = f(\overline{C_{NR_4X}^0})$, $D = f(\overline{C_{NR_4X}^0})$ and $Z_t = f(\overline{C_{NR_4X}^0})$ given in Figs. 1–3. The regions relative to the asymptotically linear sections at the left side of the $mm'-nn'$ area for two initial Cr(VI) concentrations

reflect an extraction capacity of the carrier at a highly low degree. Conversely, the regions corresponding to the linear sections at the right side of the $mm'-nn'$ area are attributed to the extremely large loading regime (small loading factors) of Aliquat 336 presumably favouring an undesirable third phase formation due to an excess amount of the carrier. Therefore, the conditions relative to these linear regions are practically not appropriate for an effective extraction process. The intersection of the asymptotical linear lines at the intercepting points restricted in the $mm'-nn'$ section for each curve should provide the conditions of optimum extraction in terms of E , Z_t , D , $C_{Cr(VI)}^0$, C_{acid}^0 and $\overline{C_{NR_4X}^0}$ variables. However, the $mm'-nn'$ section reflects the optimized conditions where the slope (dy/dx) of the curves is changed considerably. Regarding the initial Cr(VI) content in the aqueous phase, an interpolation of the conditions attributed to the $mm'-nn'$ section results in the observed optimum ranges summarized in Table 1. As illustrated in Figs. 1-3, the conditions on the E , D and Z_t curves pertained to either the asymptotically linear sections at the left side of mn

Table 1 — Observed and modeled optimization ranges due to Z_t and E variables evaluated for different aqueous acidities of relevant systems

System	Observed optimization range			Modeled optimization range			
	$\overline{C_{NR_4X}^0}$ (mol/dm ³)	$Z_{t,obs}^a$	E_{obs}^a (%)	Eq. (10) x_{iv}^Z	Eq. (11) $Z_{t,mod}^b$	x_{iv}^E	E_{mod}^c (%)
Aliquat 336– $H_2SO_4^d$	0.027–0.045	0.42–0.61	86.4–99.4	$C_{Cr(VI)}^0 = 0.019 \text{ mol/dm}^3$			
				12.6–16.3	0.59–1.17	18.5–29.7	90.1–98.5
Aliquat 336– $H_2SO_4^d$	0.165–0.230	0.83–1.09	93.2–99.6	$C_{Cr(VI)}^0 = 0.192 \text{ mol/dm}^3$			
				21.3–31.4	0.95–1.32	10.5–15.3	84.5–96.5
Aliquat 336– HNO_3^e	0.165–0.230	0.67–0.77	66.2–80.5	1.17–2.05	0.34–0.55	1.91–3.40	66.2–85.3

^a Observed performance; the corresponding optimum D_{obs} ranges are: 6.4–165.7 for $C_{Cr(VI)}^0 = 0.019 \text{ mol/dm}^3$ and H_2SO_4 media, 13.7–284.7 for $C_{Cr(VI)}^0 = 0.192 \text{ mol/dm}^3$ and H_2SO_4 media, 1.96–4.13 for $C_{Cr(VI)}^0 = 0.192 \text{ mol/dm}^3$ and HNO_3 media.

^b Modeled performance; $Z_{t,max} = 1.60$, the independent variable $x_{iv}^Z = C_{Cr(VI)}^0 / (\overline{C_{NR_4X}^0} C_{acid}^0)$ in non-homogenous differential equation, Eq. (10).

^c Modeled performance; $E_{max} = 100\%$, the independent variable $x_{iv}^E = \overline{C_{NR_4X}^0} / (C_{Cr(VI)}^0 C_{acid}^0)$ in non-homogenous differential equation, Eq. (11).

^d The optimization range due to the acid molarities of 0.05 and 0.1 mol/dm³.

^e The optimization range due to the acid molarity of 0.5 mol/dm³.

corresponding to a low extraction capacity of the carrier or the linear sections at the right side of $m'n'$ corresponding to extremely small loading factors of the carrier are not appropriate for an effective extraction process. The intersection of the asymptotical drawing lines at the intercepting points restricted at the $mm'-nn'$ region should provide the conditions of optimum extraction in terms of E , Z_t , $C_{Cr(VI)}^0$ and $C_{NR_4X}^0$ variables. As illustrated in Figs. 1-3, the aqueous sulfate medium provides more effective Cr(VI) removal efficiencies of Aliquat 336 as compared to the nitrate medium.

To develop a new conceptual definition of optimum extraction conditions for the Cr(VI) recovery from industrial wastewaters by Aliquat 336/diluent system, it requires an interpretation of the $F_O = f(x_{iv})$ curve both experimentally and analytically, where F_O and x_{iv} examine the selected optimization factor and independent variable, respectively. Since Z_t is inversely proportional to $C_{NR_4X}^0$ and C_{acid}^0 , and E is varying inversely with $C_{Cr(VI)}^0$ and C_{acid}^0 , the analysis of optimum extraction conditions in terms of Z_t and E factors has been performed using the independent variables, x_{iv}^Z and x_{iv}^E , respectively. To reduce the complexity of the optimization problem, only the variation of the derivatives (slopes of the curve) relative to $Z_t = f(x_{iv}^Z)$ and $E = f(x_{iv}^E)$ functions will be processed.

$$Z_t = Z_{t,max} (1 - \exp(kx_{iv}^Z)) \quad \dots (10)$$

$$E = E_{max} (1 - \exp(Lx_{iv}^E)) \quad \dots (11)$$

where $Z_{t,max}$ and E_{max} designate the maximum values of extraction factors. The independent variables x_{iv}^Z and x_{iv}^E are defined as follows, $x_{iv}^Z = C_{Cr(VI)}^0 / (C_{NR_4X}^0 C_{acid}^0)$ and $x_{iv}^E = C_{NR_4X}^0 / (C_{Cr(VI)}^0 C_{acid}^0)$.

The reliability analysis of Eqs. (10) and (11) was performed in terms of the mean relative error ($\bar{e} = (100/N) \sum_{i=1}^N |(Y_{i,obs} - Y_{i,mod}) / Y_{i,obs}|$ (%)) and

root-mean-square deviation ($\sigma = \left[\sum_{i=1}^N (Y_{i,obs} - Y_{i,mod})^2 / N \right]^{0.5}$) of the model estimates by compiling the regressed coefficients k and l ."

Figures 5 and 6 present a quantitative assessment of prediction achieved for Eqs. (10) and (11), considering the limiting properties $Z_{t,max} = 1.60$ and $E_{max} = 100\%$, respectively. As shown in Figs 5 and 6, both Eqs. (10) and (11) yielded a fair distribution verifying the goodness-of-fit relative to aqueous acid molarities of 0.05, 0.1 and 1 mol/dm³ for H₂SO₄ medium and 0.5 mol/dm³ for HNO₃ medium, respectively.

The modeled optimum conditions due to Eqs. (10) and (11) have been identified by processing the optimization procedures of the derivative variation method, as described above. To confirm the validity of the obtained optimum conditions, the derivative variation tests of the considered variables have been also performed using multivariable linear programming and goal programming algorithms of QSB+ software⁵², as well as Linpack packet program⁵³. The optimization method calls for the use the derivatives $dE/d(x_{iv}^E)$ and $dZ_t/d(x_{iv}^Z)$ and an independent analysis of the non-linear deviation profile of the derivative value (or the slope of the relevant curve), as described above. It is seen from Figs. 5 and 6 that the modeled optimization range restricted at the $rr'-ss'$ section is optimal for estimating the most appropriate extraction factors. Table 1 presents a brief summary of the modeled optimization ranges due to the derivative variation method depending on Eqs. (10) and (11). Regarding Figs 5 and 6 one may conclude that the conditions ascribed to the left-side and right-side regions of the $rr'-ss'$ section are practically not convenient for an effective extraction process. Consequently, the part relative to the extremely derivative changes in the slope of the modeled curve will separate the location of the optimum point restricted at the $rr'-ss'$ section. Inspection of Figs. 1-6 and Table 1 reveals that the $Z_{t,opt}$ increases as the $C_{Cr(VI)}^0$ concentration becomes larger, and the $Z_{t,opt}$ and E_{opt} increase as the affinity of competitive acid anions to the carrier becomes less favourable, signifying an energetic preference of the Cr(VI) anions for a strongly dipole-dipole interaction with Aliquat 336 in sulfuric acid medium.

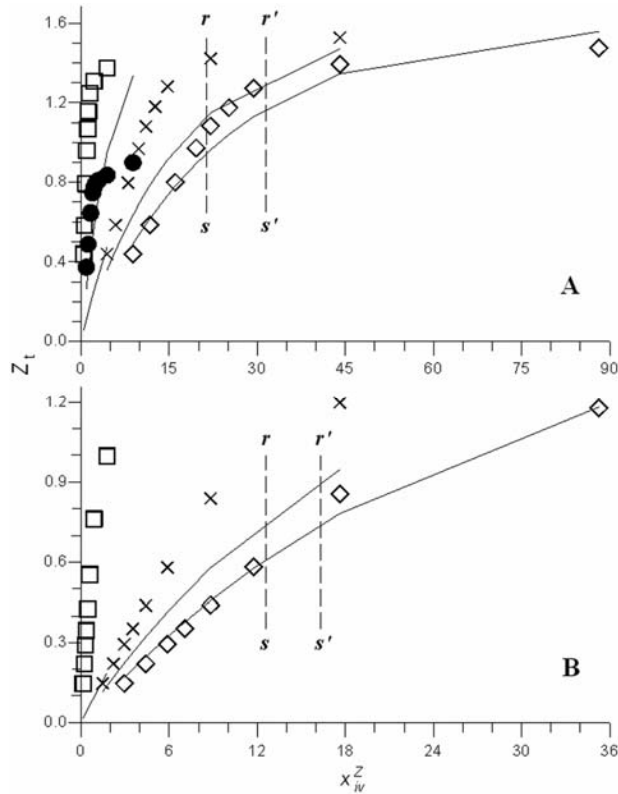


Fig. 5 — Plot of the loading factor (Z_t) vs $x_{iv}^Z = C_{Cr(VI)}^0 / (C_{NR_4X}^0 C_{acid}^0)$. Sulfuric acid concentration ($C_{H_2SO_4}^0$) \diamond 0.05, \times 0.1, \square 1 mol/dm³, nitric acid concentration ($C_{HNO_3}^0$) \bullet 0.5 mol/dm³. (A) $C_{Cr(VI)}^0 = 0.192$ mol/dm³, (B) $C_{Cr(VI)}^0 = 0.019$ mol/dm³. Solid line modeled through Eq. (10), root-mean-square deviation of estimates $\sigma(Z_t) = 0.29$. The rr' – ss' section refers to optimum extraction conditions.

For both the optimization cases, as marked in Table 1, the E_{opt} factors are ranging about 85-99% and 65-80% for H₂SO₄ and HNO₃ media, respectively. For achieving a reasonable Cr(VI) removal efficiency by Aliquat 336/xylene system, required $Z_{t,opt}$ factors are ranging about 0.83-1.09 for H₂SO₄ medium and 0.67–0.77 for HNO₃ medium, when an optimal carrier content restricted in the range of $C_{NR_4X}^0 \approx 0.165 - 0.230$ mol/dm³ is employed for the treatment of 0.192 mol/dm³ aqueous Cr(VI) amount. On the contrary, the $Z_{t,opt}$ factors for $C_{Cr(VI)}^0 = 0.019$ mol/dm³ are almost invariably

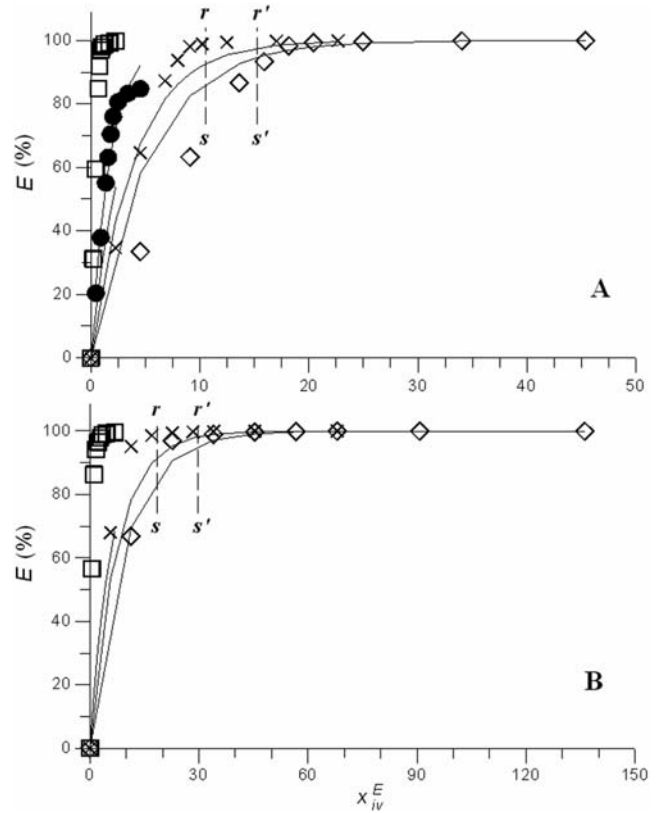


Fig. 6 — Plot of extraction degree (E) vs $x_{iv}^E = C_{Cr(VI)}^0 / (C_{NR_4X}^0 C_{acid}^0)$. Sulfuric acid concentration ($C_{H_2SO_4}^0$) \diamond 0.05, \times 0.1, \square 1 mol/dm³, nitric acid concentration ($C_{HNO_3}^0$) \bullet 0.5 mol/dm³. (A) $C_{Cr(VI)}^0 = 0.192$ mol/dm³, (B) $C_{Cr(VI)}^0 = 0.019$ mol/dm³. Solid line modeled through Eq. (11), root-mean-square deviation of estimates $\sigma(E) = 16.7$. The rr' – ss' section refers to optimum extraction conditions.

small restricted at 0.42–0.61 for the Cr(VI) removal from H₂SO₄ media. However, the results presented in Table 1 show that the aqueous sulfate medium permits markedly larger extraction degrees of Cr(VI), as compared to those achieved for the nitrate medium. The preference of the Cr(VI) ions for water over the reactive carrier in the nitrate media could be described by the small size of the water molecule permits it to approach closer and hence makes its dipole more effective in inducing dipoles in the large ions.

Statistical analysis of equilibrium models

The reliability analysis of the equilibrium models, i.e. the chemodel Eq. (3), the Langmuir model Eq. (4),

the log-basis linear differential relation Eq. (5) and LSER-based model Eq. (7), has been performed statistically against the observed performance in terms of the mean relative error \bar{e} (%), and root-mean-square deviation σ . Table 2 presents the equilibrium extraction constants β_{pq} of Eq. (3) and K_L of Eq. (4) being regressed through the multivariable Linpack algorithm⁵³ for one and two appropriate complex combinations regarding the maximum loading factor $z = Z_{t,\max}$ from Fig. 4. As shown in Table 2, the best fits display the approach comprising the formation of only one associated $(NR_4)_q\text{-Cr(VI)}_p$ (q, p) structure of different stoichiometry depending on the acid molarity used, i.e., (1, 2), (1, 3), (1, 4) and (2, 3) associations for Eq. (3), and (1, 1) association for Eq. (4).

Inspection of the simulated statistical deviation results from Table 2 indicates that the Langmuir model (Eq. (4)) reproduces the extraction data for the Aliquat 336 – Cr(VI) association slightly more accurately as compared to the chemodel (Eq. (3)), yielding the overall mean deviations $\sigma(Z_t)$ of 0.34 and 0.64, respectively for all of the systems studied. The reliability analysis of mass-action law models, Eqs (3) and (4), calls for the assumption that the (Aliquat 336)_q – (Cr(VI))_p complexation of the type $q : p = 1 : 1$ should be favourably prevalent due to the

Langmuir approach. The equilibrium data presented in Figs. 1 and 2 have also been correlated due to a linear differential relation, which explicit form especially applied to E is given by Eq. (5). Estimates have been performed using the regressed substance-dependent coefficients a and b for the relevant systems defined as follows: (a) for $C_{\text{Cr(VI)}}^0 = 0.019$ mol/dm³ and H₂SO₄ media, $a = -1.8540$ and $b = 0.7023$ ($\bar{e} = 11.3\%$); (b) for $C_{\text{Cr(VI)}}^0 = 0.192$ mol/dm³ and H₂SO₄ media, $a = -0.4140$ and $b = 0.3849$ ($\bar{e} = 9.8\%$); (c) for $C_{\text{Cr(VI)}}^0 = 0.192$ mol/dm³ and HNO₃ media, $a = -0.1037$ and $b = -0.3950$ ($\bar{e} = 2.3\%$). Regarding the statistical deviation results, Eq. (5) proved to be reasonably accurate reproducing the observed performance with a mean error of $\bar{e}(E) = 7.8\%$ for all the considered systems. Consequently, the evaluated mass-action law models, Eqs. (3)–(5), appear to be perceptible model structures adequate for modeling a reactive extraction system.

The distribution data of Cr(VI) from Figs. 1–3 have been processed to analyze the reliability of the LSER-based solvation model, Eq. (7). The adjustable coefficients C_i of Eq. (7) have been regressed by the

Table 2 — Equilibrium extraction constants β_{pq} and K_L of Eqs. (3) and (4) and root-mean-square deviation $\sigma(Z_t)^a$ of model estimates for Aliquat 336–Cr(VI) aggregation relative to H₂SO₄ media

C_{acid}^0 ^b (mol/dm ³)	$C_{\text{Cr(VI)}}^0 = 0.019$ mol/dm ³		$C_{\text{Cr(VI)}}^0 = 0.192$ mol/dm ³	
	$K_L, \sigma(Z_t)$ (mol/dm ³) ⁻¹	$\beta_{pq}, (q, p)^c, \sigma(Z_t)$ (mol/dm ³) ^{1-p-q}	$K_L, \sigma(Z_t)$ (mol/dm ³) ⁻¹	$\beta_{pq}, (q, p)^c, \sigma(Z_t)$ (mol/dm ³) ^{1-p-q}
0.05	494.2, (0.33)	0.1779×10 ⁴ , (1, 2), 0.43 0.1247×10 ⁶ , (1, 3), 0.44 0.1261×10 ⁸ , (1, 4), 0.44 0.1520×10 ⁹ , (2, 3), 0.44	114.9, (0.48)	0.1061×10 ² , (1, 2), 0.86 0.2637×10 ² , (1, 3), 0.92 0.1182×10 ³ , (1, 4), 0.94 0.2059×10 ⁶ , (2, 3), 0.86
0.1	568.1, (0.27)	0.4050×10 ⁴ , (1, 2), 0.42 0.2865×10 ⁶ , (1, 3), 0.43 0.2985×10 ⁸ , (1, 4), 0.44 0.4009×10 ⁹ , (2, 3), 0.43	159.4, (0.38)	0.2549×10 ² , (1, 2), 0.86 0.5956×10 ² , (1, 3), 0.92 0.2678×10 ³ , (1, 4), 0.94 0.8725×10 ⁶ , (2, 3), 0.71
1	247.0, (0.17)	0.1572×10 ⁵ , (1, 2), 0.37 0.8832×10 ⁶ , (1, 3), 0.40 0.6929×10 ⁸ , (1, 4), 0.41 0.5192×10 ⁹ , (2, 3), 0.37	63.4, (0.44)	0.1569×10 ³ , (1, 2), 0.84 0.4244×10 ³ , (1, 3), 0.88 0.1885×10 ⁴ , (1, 4), 0.91 0.6966×10 ⁶ , (2, 3), 0.78

^a $\sigma = \left[\sum_{i=1}^N (Z_{t,\text{obs}} - Z_{t,\text{mod}})^2 / N \right]^{0.5}$. ^b Initial aqueous sulfuric acid concentration. ^c Stoichiometric ratio Aliquat 336_q–Cr(VI)_p (q, p) in the complex formation.

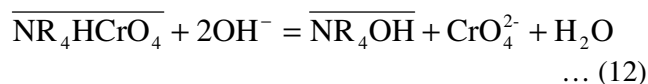
Linpack algorithm⁵³, using the solubility and solvatochromic parameters of the solvents and the physical properties of the transferred ion listed in Table 3. The resulting C_i coefficients of Eq. (7) corresponding to Z_t , E and D extraction factors, as well as a comparison with the observed performance in terms of the mean relative error (\bar{e}) and root-mean-square deviation (σ). The limiting values of $Z_{t,\max} = 1.60$, $D_{\min} = 0.14$ and $E_{\max} = 100\%$ have been processed in model development. Inspection of the statistical deviation reveals that the integrated property-basis solvation model, Eq. (7), matches relatively well with the observed performance over the entire composition range, yielding the overall mean deviations of $\bar{e}(Z_t) = 11.3\%$ ($\sigma(Z_t) = 0.09$), $\bar{e}(E) = 8.2\%$ ($\sigma(E) = 7.97$), $\bar{e}(D) = 28.4\%$ ($\sigma(D) = 26.16$) considering all of the systems studied. The solvation model, Eq. (7), coincides with the observed performance for the Aliquat 336 – nitric acid system slightly more reliably, yielding $\bar{e} = 8.3\%$ ($\sigma = 2.67$) as compared to $\bar{e} = 19.8\%$ ($\sigma = 15.78$) for the Aliquat 336 – sulfuric acid one. Overall, Eq. (7) yields a fair distribution verifying the goodness-of-fit with a mean error of $\bar{e} = 10.1\%$. The detailed deviation statistics demonstrate a rigorous validation of the considered LSER model structure on an integrated property-basis involving solvatochromic parameters evaluated due to Marcus and co-workers⁴³⁻⁴⁵.

Recovery of Cr(VI) from the loaded organic phase

The recovery of Cr(VI) from the loaded organic phase, containing 0.05 mol/dm^3 Aliquat 336/xylene solution enriched with 0.016 mol/dm^3 Cr(VI), has

been carried out at different concentrations ($0.05\text{--}3 \text{ mol/dm}^3$) of NaOH, NaCl and Na_2SO_4 salts used as stripping agents for Cr(VI). Preliminarily, it has been found that Milli-Q water is completely ineffective in the stripping process at 298 K. The re-extraction results cleared that the alkaline solutions were capable of stripping Cr(VI). Expectedly, OH^- ions have a stripping efficiency as high as 88% due to their strong affinity to Aliquat 336, while Cl^- and SO_4^{2-} ions produce moderate stripping efficiencies of 54.5% and 13.8% for a 0.75 mol/dm^3 salt concentration, respectively. At low ($0.05\text{--}0.5 \text{ M}$) and high ($1\text{--}3 \text{ M}$) strippant molarities, the lowered recovery degrees of 65% for NaOH, 35% for NaCl and 8% for Na_2SO_4 have been obtained. Sodium hydroxide stripped the most effectively, but at higher NaOH concentrations over than 2 mol/dm^3 , however, the solubility of Aliquat 336 increased, i.e. the loss of extractant increased. The beneficial NaOH concentration was found to be about 0.7 mol/dm^3 .

In strong alkaline solution, CrO_4^{2-} is the major ionic form of chromium^{40,41}, thereby alkaline solution will reduce the concentration of HCrO_4^- according to the following,



It turns out from the extraction–stripping efficiency results that the present extraction method based on Aliquat 336/xylene provides a relatively large Cr(VI) uptake capacity of 99% in sulfuric acid media, a high stripping of 88% and reusability.

Table 3 — Hildebrand solubility parameter (δ_H), and solvatochromic parameters (π , β , α , δ) of solvents and the normalized physical properties of the $\text{Cr}_2\text{O}_7^{2-}$ ion (z_c , r' , v' , R_D')

Component	$\pi^{a,b}$	$\beta^{a,b}$	$\alpha^{a,b}$	$\delta_H^{c,d}$ (MPa ^{0.5})	$\delta^{a,b}$	z_c^e	$r' = 0.1/r^f$ (nm ⁻¹)	$v' = 10v^g$ (nm ³)	$R_D' = R_D/100^h$ (cm ³ /mol)
$\text{Cr}_2\text{O}_7^{2-}$ ion						-2	0.467	0.411	0.607
Xylene ⁱ	0.50	0.12	0.0	18.00	1.0				
Aliquat 336 ^j	0.16	0.62	0.0	19.28 ^k	0.0				

^a Due to Kamlet *et al.*⁴³; ^b Due to Marcus⁴⁴; ^c Due to Barton⁵⁴; ^d Due to Riddick *et al.*⁵⁵; ^e z_c denotes the charge of anion; ^f r examines the Pauling crystal ionic radius (coordination number 6); ^g v stands for the volume occupied by the ion, $10v = 40\pi r^3/3$; ^h R_D designates the molar refractivity for the mean sodium D line at infinite dilution in water, R_D' was calculated due to the approach of Soffer *et al.*^{45,46}; ⁱ Mean for mixture of isomers; ^j Parameters of tri-*n*-butyl amine; ^k Calculated for $\text{C}_{25}\text{H}_{54}\text{NCl}$ structure.

Conclusion

A detailed study on Cr(VI) removal from aqueous acidic sulfate and nitrate media by Aliquat 336/xylene solvent system has been carried out at 298.2 K and 101.3 kPa. The existing models Eqs. (3)-(5), (7), (10) and (11) match well with the observed performance and the regressed coefficients support the conditions of favourable extraction. The present work leads to the following conclusions.

- The uptake capacity of Aliquat 336/xylene towards Cr(VI) is very much dependent on the concentrations of components and the nature of inorganic acid. The extraction efficiency of Cr(VI) by Aliquat 336/xylene followed the order $\text{H}_2\text{SO}_4 > \text{HNO}_3$. Experimental findings revealed that 0.2 mol/dm³ initial concentration of Aliquat 336 was optimal for 99% and 80% Cr(VI) removal efficiencies from H_2SO_4 and HNO_3 media, respectively. Cr(VI) was stripped successfully from the organic phase by sodium hydroxide, yielding 88% stripping degree.
- Optimum extraction conditions have been successfully quantified through the derivative variation method applied to the complex reactive extraction system with a non-linear character. Accordingly, an optimum carrier amount of $\overline{C_{\text{NR}_4\text{X}}^0} \approx 0.165 - 0.230$ mol/dm³ allows for achieving optimal loading factors of $Z_{\text{t,opt}} \approx 0.83 - 1.09$ and $Z_{\text{t,opt}} \approx 0.67 - 0.77$ for Cr(VI) removal from sulfate and nitrate media, respectively. Optimization results demonstrate an underlying physical significance for the optimized functional variables and show an excellent potential for generalized predictions on a derivative-basis.
- The LSER-based solvation model was able to simulate the experimental data satisfactorily with a mean error of 10%. All the extraction data show good compliance with a model structure involving nine physical descriptors.

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