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Determination of Size of the Chromate Ion—A Solvent Extraction Study

V. M. RAO* and A. KUNTAM RAJU

Department of Physical and Nuclear Chemistry and Chemical Oceanography
School of Chemistry, Andhra University, Visakhapatnam, 530 003, India

The extraction of Cr(VI) into benzene solutions of Aliquot-336 has been studied from chloride, bromide and nitrate systems and the extracted species has been determined. An attempt is made to determine the size of the anion of chromium(VI) (*i.e.* $HCrO_4^-$) from the distribution data. Experimentally determined values of the size of the ion are comparable with those obtained by theoretical calculation.

INTRODUCTION

Several workers[1–4] have studied the extraction of Cr(VI) by alkylammonium salts and related system from various acid solutions. Most of these studies are on the speciation and determination of chromium. The present work was undertaken with the aim of determining the size of the chromium species from the distribution coefficient measurements, making use of the values of free energy of distribution of Cr(VI) between the aqueous solutions and benzene solutions of quaternary ammonium salt, tricapryl methyl ammonium chloride (Aliquot-336).

EXPERIMENTAL

Aliquot-336 supplied as a gift by M/s General Mills, Kankaki, Illinois was used without further purification. A 5% (v/v) stock solution of Aliquot-336 in benzene was prepared. It was standardised gravimetrically as AgCl[5]. Other solutions of Aliquot-336 were prepared by making suitable dilutions of the stock solution with benzene. Tricapryl methyl ammonium bromide solution was prepared by equilibrating a 1.0×10^{-1} M solution of Aliquot-336 in benzene with successive portions of 4 M aqueous solution of NaBr. Similarly Tricaprylmethyl ammonium nitrate was prepared by equilibrating Aliquot-336 in benzene with 4 M sodium nitrate. Thiophene free benzene was employed as a solvent for preparation of these solutions. All other chemicals used were of AnalaR grade or they were purified by standard methods. ^{51}Cr in the form of sodium chromate in isotonic saline solution (15 m Ci/mg specific activity) was obtained from Board of Radiation and Isotope Technology, Department of Atomic Energy, Bombay. In all these studies the initial concentration of the tracer in the aqueous phase was maintained always less than 5×10^{-5} M.

A single channel analyser SC-600 (ECIL) coupled with 3 inch well type, scintillation detector (Nuclear Chicago) was used for γ-activity measurements. Toshniwal digital pH meter of the type C-46 provided with a combination electrode was used for pH measurements.

Procedure

15 ml of the aqueous phase containing appropriate concentrations of the supporting electrolyte (NaCl, NaBr or $NaNO_3$) and added tracer, adjusted the desired pH (3.0) were equilibrated with an equal volume of the solution of 2.15×10^{-2} M quaternary ammonium salt in benzene for *ca.* 5 minutes. Unless stated otherwise the equilibration was done at room temperature which varied from 24° to 27°C. Most of the measurements reported were done at 24° ± 1°C. After equilibration, the two phases were separated after allowing the mixture to stand for 10 minutes. Equal volumes of each phase were used to measure the activity and the distribution coefficient (K_d) was calculated using the equation:

$$K_d = \frac{\text{counts per minute in the organic phase}}{\text{counts per minute in the aqueous phase}}$$

The extractions were repeated for establishing reproducibility.

The aqueous phase pH adjustment was made with the respective mineral acid and the supporting electrolyte (*e.g.*, for chloride system pH adjustment was made with HCl and NaCl).

RESULTS AND DISCUSSION

The quaternary ammonium salts behave like liquid anion exchangers. The distribution of any salt (CY) either in the presence or absence of supporting electrolyte (CX), between the aqueous phase and the organic phase containing the quaternary ammonium salt (R^+X^-) can be represented by the following equilibrium:

$$R^+X^-_{(org)} + Y^-_{(aq)} \rightleftharpoons R^+Y^-_{(org)} + X^-_{(aq)} \tag{1}$$

The equilibrium constant of reaction (1) in the case of distribution of tracer amount of Y^- (in the form of salt CY) in the presence of macro amounts of supporting electrolyte (CX) can be written as[6]

$$K = \frac{[R^+Y^-]_{org}}{[R^+X^-]_{org}} \cdot T_{org} \cdot T_{aq} \tag{2}$$

where T_{aq} and T_{org} are the ratios of the mean activity coefficients of the components of the aqueous phase and that of the organic phase respectively

Calling 'Q', the concentration quotient $[R^+Y^-]_{org}/[R^+X^-]_{org}$, the equation (2) can be written as

$$K = Q \cdot T_{aq} \cdot T_{org} \tag{3}$$

The standard free energy change ΔF° of the reaction (2) can therefore be obtained using the thermodynamic relation,

$$\Delta F^\circ = -2.303RT \log K \tag{4}$$

The values of Q are obtained from the distribution measurements of radio tracer Y^- between the two phases. Making measurements over wide range of concentrations of the supporting electrolyte, the effects of T_{aq} and T_{org} can be evaluated.

The concentration quotients log Q versus log (NaX) are plotted for the systems, ($Cl^- - H\overset{*}{Cr}O_4^-$), ($Br^- - H\overset{*}{Cr}O_4^-$) and ($NO_3^- - H\overset{*}{Cr}O_4^-$).

The star indicates the tracer isotope and RX is the initial concentration of quaternary ammonium salt (RX) in the organic phase. The supporting electrolyte in aqueous phase was a sodium salt (NaX) with the same anion as that of the quaternary ammonium salt. The dependence of Q on the concentration of the supporting electrolyte is not the same for all the three systems studied.

In each of these systems the nature of the extracted species was determined (at Cr(VI) concentration 10^{-3} M) at aqueous phase pH, (3.0) by distribution ratio method[7]. The log-log plots of K_d vs. RX obtained by this method gave a unit slope (Fig. 1) with the three systems, indicating the nature of extracted species as ($R_4N^+HCrO_4^-$). In aqueous systems under the experimental conditions Cr(VI) exists predominantly as monomeric oxy-anion[8] *i.e.* $HCrO_4^-$. Therefore the extraction of Cr(VI) as protonated oxy-anion can be envisaged. This is in conformity with the observation that other elements which form oxy-anions in their highest oxidation states are extracted as protonated oxy-anions (*e.g.*, W(VI)[9], Mo(VI)[9], Re(VIII)[10] and Te(VI)[11]).

The change in free energy ΔF for the exchange equilibrium (1) is related to the dielectric constants of the two phases (ϵ_{aq} and ϵ_{org}), the radii of the exchanging anion (r_x and r_y), and the radius of the quaternary ammonium cation (r_c) by the following equation,

$$\Delta F = \frac{Ne^2}{2}\left[\frac{1}{\epsilon_{org}}\left\{\left(\frac{1}{r_y}-\frac{1}{r_x}\right)+2\left(\frac{1}{d_1}-\frac{1}{d_3}\right)\right\}+\frac{1}{\epsilon_{aq}}\left(\frac{1}{r_y}+\frac{1}{r_x}\right)\right] \tag{5}$$

where N is the Avagadro's number, e is the electronic charge, d_1 is the distance of closest approach of the quaternary ammonium cation and the anion (*i.e.* $r_c + r_x$) and d_3 is the distance of closest approach of the quaternary ammonium cation and the other anion extracted into the organic phase (*i.e.* $r_c + r_y$). This relation is derived by Scibona *et al.*[6] by considering the electrostatic model of the distribution of simple ions between two phases with alkyl-ammonium salts as extractants.

Using, the above equation the radius of the exchanging metallic anion, r_y, (*i.e.* chromate ion in the present study) can be determined, if ΔF, r_x,

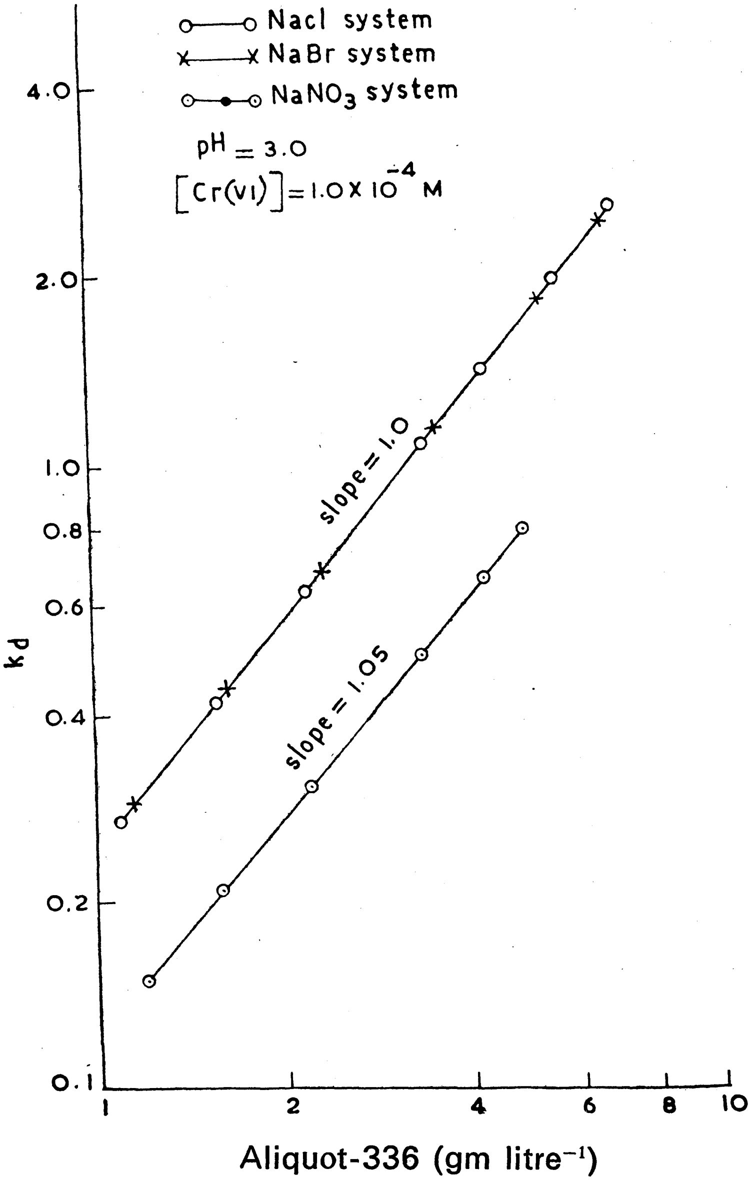

Fig. 1. Composition of the Extracted Species.

ϵ_{org}, ϵ_{aq} and r_c are known. Substituting the values of these parameters, equation (5) can be represented in the quadratic equation form (in terms of r_y) whose solution gives the value of r_y. For the $Cl^-–H\overset{*}{C}rO_4^-$, $Br^-–H\overset{*}{C}rO_4^-$ and $NO_3^-–H\overset{*}{C}rO_4^-$ systems the free energy change (ΔF) of exchange equilibrium (1) was determined by distribution measurements and the results are tabulated (Table 1). The ionic radii of the anions (Cl^-, Br^-, NO_3^-) and the other parameters shown in Table 2 have been used with equation (5) for calculation of r_y. The values of r_y thus obtained are presented in Table 3.

TABLE 1

VALUES OF EQUILIBRIUM CONSTANTS AND STANDARD FREE ENERGY CHANGE OF THE EXCHANGE REACTION (1)

System	$RX_{(org)}$ (M)	K*	$-\Delta F$†	
			K cal/mole	(Joules/mole) × 10^{-3}
Cl^-–$H\overset{*}{C}rO_4^-$	2.15×10^{-2} M	2.3×10^1	1.857	7.77
Br^-–$H\overset{*}{C}rO_4^-$	2.15×10^{-2} M	2.3×10^1	1.857	7.77
NO_3^-–$H\overset{*}{C}rO_4^-$	2.15×10^{-2} M	$1.2 - 10^1$	1.471	6.16

*Equilibrium constant defined by equation (3) is obtained by extrapolation of curve Q vs (NaX) to zero ionic strength.

†From equation (4), temperature = 25°C.

TABLE 2

THE VALUES OF IONIC RADII AND OTHER PARAMETERS USED IN THE EQUATION (5)

	Ionic radii				Dielectric constant	
	Cl^-	Br^-	NO_3^-	r_c*	ϵ_{aq}	ϵ_{org}†
Values	1.81	1.95	2.01	5.71	78.54	2.471
References	(12)	(12)	(12)	(13)	(14)	(6)

* $r_c = 0.72\,\bar{V}_{-}^{\circ\,1/3}$

where $\bar{V}_{-}^{\circ\,1/3}$ = molar volume of Aliquot–336

$$= \frac{\text{Molecular weight}}{\text{Density}}$$

The density of Aliquot–336 = 0.884 gm/cm³.

†Since the organic phase during equilibration is saturated with water, the dielectric constant of water saturated benzene at 25°C is used for calculation. The effect of solubilities of benzene on the dielectric constants of the aqueous phase is negligible and so the dielectric constant of water (ϵ_{aq}) at 25°C is used for calculation.

TABLE 3

COMPARISON OF THE EXPERIMENTAL AND THEORETICAL VALUES OF THE SIZE OF THE CHROMATE ION ($H\overset{*}{Cr}O_4$) OBTAINED FROM DIFFERENT SYSTEMS

System	Radius of $HCrO_4^-$ (r_y)* (Å)
Cl^-–$H\overset{*}{Cr}O_4^-$	1.94
Br^-–$H\overset{*}{Cr}O_4^-$	2.09
NO_3^-–$H\overset{*}{Cr}O_4^-$	2.16
$HCrO_4^-$	2.32†

*Value—Experimental, †Value—Theoretical

Theoretical Calculation of r_y

The expression for ionic volumes $\bar{V}^{\circ}_{-}$ of oxy-anions derived by Laidler[15] can be represented as

$$\bar{V}^{\circ}_{-} = 58.8 + 0.89\,(0.25\ nrL)^3 - 26\,|Z_-| \qquad (6)$$

where n = number of charge bearing ligands

Z_- = charge of the anion

$rL = r_{12} + 1.40\ \text{Å} = 1.86\ \text{Å} + 1.40\ \text{Å} = 3.26\ \text{Å}$

(Here r_{12} is the metal-oxygen distance as calculated by Pauling[16] using covalent radii and the latter being taken as the radius of O^{2-} ion. The value[17] of r_{12} is 1.86 Å.)

Assuming the ions are spherical in shape, one would expect the ionic radii to be directly proportional to the cube roots of the ionic volumes. Therefore the ionic radius of chromate ion ($HCrO_4^-$) is taken as $\bar{V}^{\circ\,1/3}_{-}$

It can be seen from Table 3 that the experimentally determined values of the size of the chromate ion ($HCrO_4^-$) seems to be reasonable as the values are in agreement with the value determined by theoretical calculations with an error of $\leqslant 16\%$.

It is well known that the size of any ion is dependent on the physical properties of the medium (such as the density, dielectric constant of the medium), temperature and also on the solvation of the ion in the medium in which it exists. For example the presence of even a fraction of a percent of water significantly increases the bulk dielectric constant of the benzene phase which alters the exchange equilibrium (Eq. 1). The differences in the size of the chromate ion determined with different exchange systems (Table 3) may be attributed to the differences in physical properties of the two phases and also to the differences in the extent of of solvation of the ion in the two phases.

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