

ON THE EXTRACTION
OF PICRIC ACID, ALKALI METAL PICRATES
AND TRACES OF CAESIUM
FROM WATER INTO NITROBENZENE

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Extraction of picric acid and of alkali metals picrates into nitrobenzene is studied. The term of limiting distribution ratio is introduced, describing the distribution of microamounts of cation M^+ between the aqueous and organic phases in the presence of macroamounts of N^+A^- salt and under the assumption of total dissociation in both phases. The corresponding extraction constants are given and practical applications to extraction of microamounts of ^{137}Cs are discussed.

Our previous papers dealt with the extraction of alkali metal cations, in the form of salts of dipicrylamine¹ and picryl-2,4-dinitronaphthylamine² into nitrobenzene. Both compounds proved very effective for the extraction of caesium, rubidium and potassium from aqueous solutions of $\text{pH} > 8$. In our search for reagents convenient for the extraction of caesium we tried to find a compound permitting the extraction of this element from a neutral or mildly acid medium. This requirement has been found fulfilled in the extraction of ^{137}Cs from the medium of picric acid or alkali metal picrates.

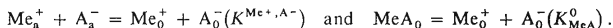
The extraction of picric acid and picrates is of interest also from the theoretical point of view. The problem has not as yet been studied systematically and the search for anions suitable for the extraction of alkali metals into nitrobenzene has lacked a rational basis. We believe that comparison of the above-mentioned compounds and picric acid makes it possible to draw some theoretical deductions since the corresponding anions contain about the same number of nitro groups per benzene ring. Provided that the affinity of a compound to nitrobenzene is given mainly by specific interactions of $-\text{NO}_2$ groups of the two molecules there should be no significant differences among the three anions (*i.e.* the anions of dipicrylamine, picryl-2,4-dinitronaphthylamine and picric acid) in their extraction into nitrobenzene. A different idea has been advanced by Diamond³; this author assumes that the extraction

of ion pairs into nitrobenzene proceeds by the mechanism of "coordination-unsolvated" salts, the extraction constant being given exclusively by the hydration of a given ion in the aqueous solution, *i.e.*, essentially, by the volume of this ion. Bulky ions, which are hydrated less, enter the organic phase more readily³.

The extraction of picric acid into nitrobenzene has already been studied by Gorbačev and Mindovič⁴.

THEORETICAL

The extraction of a compound Me^+A^- into a polar solvent is essentially governed by two equilibria:



The corresponding mathematical relations for the extraction of salts of dipicrylamine and alkali α -hexylates into nitrobenzene were described elsewhere^{1,2}.

A prerequisite for further considerations is to know the distribution of the microquantity of Cs^+ ions between the aqueous and the organic phases of a system containing Me^+A^- as the only salt. For the sake of simplicity we shall start from the assumption that this salt and the salt Cs^+A^- are fully dissociated in either phase. In this case the equilibrium is given by the two extraction constants

$$K^{\text{Me}^+, \text{A}^-} = \frac{[\text{Me}^+]_o [\text{A}^-]_o}{[\text{Me}^+]_a [\text{A}^-]_a} \quad \text{and} \quad K^{\text{Cs}^+, \text{A}^-} = \frac{[\text{Cs}^+]_o [\text{A}^-]_o}{[\text{Cs}^+]_a [\text{A}^-]_a}. \quad (1)$$

The concentrations $[\text{A}^-]_o$ and $[\text{A}^-]_a$ are given by the distribution of the macrocomponent MeA and the distribution ratio $D_{\text{Cs}} = [\text{Cs}^+]_o/[\text{Cs}^+]_a$ can be expressed, because $[\text{A}^-]_o/[\text{A}^-]_a = (K^{\text{Me}^+, \text{A}^-})^{1/2}$, as follows:

$$D_{\text{Cs}} = K^{\text{Cs}^+, \text{A}^-} / \sqrt{K^{\text{Me}^+, \text{A}^-}} = K_{\text{Me}}^{\text{Cs}} \sqrt{K^{\text{Me}^+, \text{A}^-}}, \quad (2)$$

where $K_{\text{Me}}^{\text{Cs}} = [\text{Cs}^+]_o [\text{Me}^+]_a ([\text{Cs}^+]_a [\text{Me}^+]_o)^{-1}$. Then, neglecting the exact values of the activity coefficients, the distribution coefficient of the microquantity of Cs^+ ions in the considered system is independent of $[\text{Me}^+\text{A}^-]$, and is also unaffected by the possibly present associated forms of MeA or HA in the organic phase, unless their content is considerable. However, if CsA were associated in the organic phase, the value of D_{Cs} would increase with the concentration of Me^+A^- , as a result of the reaction $\text{Cs}_a^+ + \text{A}_a^- = \text{CsA}_o$. If equation (2) is to be more exact, the ratio of the activity coefficients, $\gamma_{\pm}^2(\text{Cs}^+\text{A}^-)_a \cdot \gamma_{\pm}(\text{Me}^+\text{A}^-)_a / \gamma_{\pm}^2(\text{Cs}^+\text{A}^-)_o \cdot \gamma_{\pm}(\text{Me}^+\text{A}^-)_o$, will figure on its right-hand side. For a number of compounds it was found that in the extraction into nitrobenzene $\gamma_{\pm}(\text{Me}^+\text{A}^-)_o \approx \gamma_{\pm}(\text{Me}^+\text{A}^-)_a$ (for example in the ex-

traction of Cs^+I_3^- , Na^+I_3^- , H^+I_3^- up to a ionic strength 0.1 in the aqueous phase, see⁵), so that the considered activity ratio can generally be assumed to be close to 1.

The value of D_{Cs} , defined above, will hereafter be called the limiting distribution ratio of Cs^+ ions in the presence of Me^+A^- in the given system, and designated as $D_{\text{Cs}}^0(\text{Me}^+, \text{A}^-)$. A similar definition is currently employed in the theory of ion exchange for the distribution of a trace of Cs^+ ions between the aqueous and the ion-exchanger phase in the Me^+ form. Equation (2) can be employed practically to determine the extraction constant of an unknown salt Me^+A^- . The exchange extraction constants $K_{\text{Me}}^{\text{Cs}}$ for the system water-nitrobenzene are known¹, and from the measured value of D_{Cs} it is possible to calculate directly the value of $K^{\text{Me}^+, \text{A}^-}$. This calculation is especially useful if the extraction constant of Me^+A^- is very low, so that the usual method (determination of the equilibrium concentration of A^- in the aqueous phase^{1,2}) is not applicable. From equation (2) it further follows that the distribution ratio D_{Cs}^0 may be rather high even if the salt Cs^+A^- , in a macroquantity, does not pass readily into the nitrobenzene phase. This conclusion will be demonstrated on the extraction of a microquantity of Cs into nitrobenzene in the presence of picric acid.

It is evident that the value of D_{Cs} will change (if $K^{\text{Cs}^+, \text{A}^-} > K^{\text{Me}^+, \text{A}^-}$ decreases) from D_{Cs}^0 to D'_{Cs} (given by the distribution of a macroquantity of Cs^+A^- , $D'_{\text{Cs}} = \sqrt{(K^{\text{Cs}^+, \text{A}^-})}$, Eq. (1)) with the increasing concentration of caesium in the system. The equation describing the dependence of D_{Cs} on the concentration of Cs can be derived as follows: in an equilibrium state definition (1) and the condition of electroneutrality in the organic phase ($[\text{Cs}^+]_o + [\text{Me}^+]_o = [\text{A}^-]_o$) are fulfilled; disregarding again the effect of the activity coefficients and the formation of associated molecules in the organic phase, the concentration $[\text{A}^-]_o$ can be expressed by

$$[\text{A}^-]_o^2 = K^{\text{Me}^+, \text{A}^-} [\text{Me}^+]_a [\text{A}^-]_a + K^{\text{Cs}^+, \text{A}^-} [\text{Cs}^+]_a [\text{A}^-]_a. \quad (3)$$

After extracting the root, division by $[\text{A}^-]_a$ and combination with the definition of $K^{\text{Cs}^+, \text{A}^-}$ we obtain.

$$D_{\text{Cs}} = K^{\text{Cs}^+, \text{A}^-} \left(\frac{[\text{A}^-]_a}{K^{\text{Me}^+, \text{A}^-} [\text{Me}^+]_a + K^{\text{Cs}^+, \text{A}^-} [\text{Cs}^+]_a} \right)^{1/2}. \quad (4)$$

Equation (4) can be rewritten into a simpler form if the compounds Me^+A^- and Cs^+A^- enter the organic phase to a very low extent only. The concentrations $[\text{Me}^+]_a$ and $[\text{A}^-]_a$ can then be expressed by the original concentrations of these ions in the aqueous solution ($C_{\text{Me}}, C_{\text{A}}$). If we introduce $D_{\text{Cs}} = C_{\text{Cs}}(D_{\text{Cs}} + 1)$ and if the organic and the aqueous phases have the same volume, it applies

$$D_{\text{Cs}}^3 K^{\text{Me}^+, \text{A}^-} \cdot C_{\text{A}} + D_{\text{Cs}}^2 (K^{\text{Cs}^+, \text{A}^-} \cdot C_{\text{Cs}} + K^{\text{Me}^+, \text{A}^-} \cdot C_{\text{A}}) - D_{\text{Cs}} (K^{\text{Cs}^+, \text{A}^-})^2 C_{\text{A}} - K^{\text{Cs}^+, \text{A}^-} \cdot C_{\text{A}} = 0. \quad (5)$$

Distribution of picric acid itself between water and nitrobenzene can be described by the ordinary equations applicable to the extraction of normal ionic aggregates. For picric acid is strong if present in an aqueous solution, but in an organic solution its acidity is considerably lower. It is evident that

$$D_{HA} = \frac{[A^-]_o + [HA]_o}{[A^-]_a} = \sqrt{K^{H^+, A^-}} + \frac{K^{H^+, A^-}}{K_{HA}^o} [H^+]_a \quad (6)$$

If $D_{HA} \geq 1$ the first term on the right hand side of equation (6) is negligible compared to the second one for the extraction of picric acid, whose anions enter the nitrobenzene phase very sparingly. In the exact form of equation (6) the concentration of protons on its right-hand side is replaced by their activity $[H^+]_a \gamma(H^+)_a$, which equals $[H^+]_a$ at low concentrations only.

EXPERIMENTAL

All reagents were of reagent grade purity and were used without further purification. The radioisotope ^{137}Cs was used whose radiochemical purity was determined earlier¹.

Sodium and caesium picrates were prepared by mixing stoichiometric amounts of picric acid with sodium or caesium hydroxide and by subsequent recrystallization from distilled water. An analogous preparative route could not be employed in preparing lithium picrate, owing to its great solubility in water. Aqueous solutions of lithium picrate were prepared directly by neutralization of the respective hydroxide with picric acid.

Extractions were performed in glass test tubes, volume of the phases being 2 ml ($v_a/v_o = 1$). Extraction equilibrium was attained in less than 15 minutes as determined by independent experiments. In all cases the extraction time was 30 min, temperature $24^\circ \pm 1^\circ\text{C}$.

Radioactivity measurement was described in another paper¹. Distribution of picric acid between water and nitrobenzene was established by measuring the equilibrium concentration of picric acid in the aqueous phase using photocolormetry (double-beam apparatus FEK-M, blue filter). Extinction curves of sodium picrate were identical with those of picric acid, were independent of ionic strength (up to 0.1M- NaNO_3) and obeyed Lambert-Beer's law for extinctions < 0.2 .

RESULTS AND DISCUSSION

Extraction of Picric Acid

The distribution ratio of picric acid as a function of its equilibrium concentration in the aqueous phase is given in Fig. 1a,b. Its linear course at low concentrations of picric acid (Fig. 1a) well accords with equation (6), because in this region the equilibrium concentration of picric acid in the aqueous phase is practically equal to $[H^+]_a \approx [H^+]_a \gamma(H^+)_a$.

According to Eq. (6) the slope of this line ($\alpha = 950$) gives the ratio of the extraction constant of the dissociated picric acid (K^{H^+, A^-}) to its dissociation constant in nitro-

benzene saturated with water. The correctness of this idea can be verified as follows: since the extraction constant of caesium picrate is known ($\log K^{Cs^+, A^-} = -1.92$, see further) and the exchange extraction constant K_H^{Cs} was determined^{6,7} as $\log K_H^{Cs} = 3.0$ for the system water nitrobenzene, the value of K^{H^+, A^-} can be calculated ($\log K^{H^+, A^-} = \log K^{Cs^+, A^-} - \log K_H^{Cs} = 4.92$). Employing the slope of the line in Fig. 1, the dissociation constant of picric acid in water-saturated nitrobenzene is determined as $pK_{HA}^0 = 7.90$. This value is in a fairly good agreement with that reported for dry nitrobenzene, $pK_{HA}^0 = 7.46$, determined spectrophotometrically⁸ (consider the wide range of the estimated values of the dissociation constant of picric acid in water, $pK_{HA}^0 = 0.29$ to 0.96 , see^{9,10}). The value of D_{HA} for $[HA]_0 = 0$ equals $\sqrt{(K^{H^+, A^-})} = 3.46 \cdot 10^{-3}$, so that the line in Fig. 1a practically passes through the origin of coordinates. At high concentrations of HA the value of D_{HA} is lower. This decrease is probably caused by association of picric acid in the aqueous phase.

To corroborate the proposed mechanism of the extraction we compared some reported data^{11,12} on the extraction of picric acid into other solvents than nitrobenzene. Plotting of D_{HA} vs. $[H^+]_a$ yields straight lines of the following slopes (and intercepts on the axis of ordinates): benzene, toluene 142 (0.6), diethyl ether 100 (0), chloroform 36 (0.5), bromoform 16 (0.6). Hence it seems that in all cases the distribution between water and the organic solvent is given by the reaction $H_a^+ + A_a^- \rightleftharpoons HA_0$. The presence of associated molecules $(HA)_n$ in an organic solvent can never be assumed (this fact was already stated by Boyles and Chetwyn in the extraction

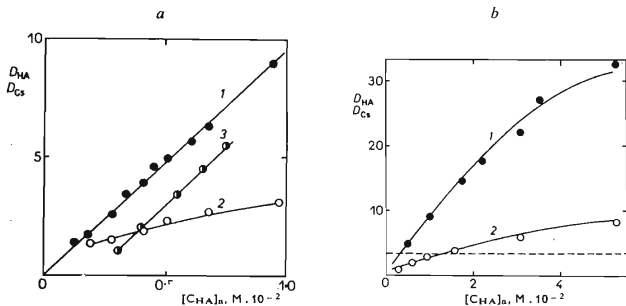


FIG. 1 *ab*

Extraction of Picric Acid and a Microquantity of Caesium into Nitrobenzene

$[CHA]_a$ designates the equilibrium concentration of picric acid in the aqueous phase; D_{HA} and D_{Cs} the distribution ratios of picric acid and a microquantity of caesium, respectively. 1 Distribution of picric acid, 2 distribution of a microquantity of caesium in the presence of picric acid, 3 distribution of picric acid (taken from ref.⁴); the dashed curve represents the theoretical course of the limiting distribution ratio of caesium.

of picric acid into chlorobenzene¹³). From the slopes of the lines expressing the dependence of D_{HA} on $[\text{H}^+]_{\text{a}}$ it is possible to derive the extracting powers of the individual solvents for the molecular form of picric acid; it applies that $\log K^{\text{H}^+ \cdot \text{A}^-} - \log K_{\text{HA}}^0 = \log D - \log K_{\text{HA}}^{\text{a}}$, where D is the distribution ratio of the nondissociated acid¹⁴. If we assume that the dissociation constant K_{HA}^{a} is not appreciably affected by the presence of an organic solvent in the aqueous phase (the considered solvents are practically insoluble in water), the affinity of picric acid to the organic phase increases in the order: bromoform < chloroform < diethyl ether < benzene, toluene < < nitrobenzene. This order is not consistent with that deduced from Hildebrand's theory of regular solutions¹⁵, and it is probable that with certain solvents, especially nitrobenzene, some specific effects are operative. The literature gives some data on the association of picric acid with aromatic hydrocarbons¹⁶ and indicates that its association with nitrobenzene is possible as well⁸.

Fig. 1 also gives the reported data⁴ on the extraction of picric acid into nitrobenzene. It seems that these data are not sufficiently exact, to say nothing of their evidently wrong interpretation (criticized by Kulikov¹⁷). From our mechanism of the extraction it follows that the value of D_{HA} increases linearly with $[\text{H}^+]_{\text{a}}$, which would not be the case with the data reported in the cited paper⁴ for $[\text{H}^+]_{\text{a}} \rightarrow 0$.

Extraction of Alkali Metal Picrates

We have determined the distribution ratio of caesium picrate (labelled with ¹³⁷Cs) between water and nitrobenzene in relation to the starting concentration of this compound in the aqueous solution. The distribution ratio proved constant in the range of the starting concentrations from $4 \cdot 10^{-5}$ to $7 \cdot 10^{-3}$ M, the average value being $D_{\text{Cs}} = 1.1 \cdot 10^{-1}$; from this value it is possible to derive the extraction constant

TABLE I
Limiting Distribution Ratios, D_{Cs}^0 , in the Presence of Some Alkali Picrates

Picrate	D_{Cs}^0 experimental	D_{Cs}^0 calculated ^a
Li	7.9 ^b	11
Na	3.5 ^c	4.9
K	0.51 ^b	0.55
Rb	0.23 ^b	0.24

^a Calculated from exchange extraction constants, reported in ref.², according to equation (2);
^b read off from the plot $D_{\text{Cs}} = f([\text{Me}^+]_{\text{a}})$, the value of $[\text{A}^-]_{\text{a}}$ was 10^{-2} M (with rubidium picrate 10^{-3} M); ^c the value for $2 \cdot 10^{-2}$ M-NaA.

$K^{\text{Cs}^+, \text{A}^-} = 1.2 \cdot 10^{-2}$. The extraction constants for caesium 2,6-dinitrophenolate and caesium 2,4-dinitrophenolate were determined analogously ($K = 7.6 \cdot 10^{-5}$ and $1.0 \cdot 10^{-4}$, respectively).

The foregoing results show that the extraction of caesium picrate alone into nitrobenzene is negligible, much smaller than the extraction of analogous compounds having dipicrylamine or picryl-2,4-dinitronaphthylamine anions². Nevertheless, the extraction of microquantities of caesium is appreciable in the presence of picric acid (Fig. 1a,b) or other alkali picrates (Table I). We believe that this fact can be explained by the concept of limiting distribution ratios (see the theoretical part). Table I gives some experimentally available values of D_{Cs} and values calculated from equation (2), employing the known exchange extraction constants $K_{\text{Me}}^{\text{Cs}}$ for the system water-nitrobenzene.

It can be seen that in the extraction from a medium of rubidium and potassium picrates the agreement of the calculated and the experimental values is very good, whereas with sodium and lithium picrates the measured distribution ratios are lower than the calculated ones. This fact cannot be ascribed to the presence of heavier alkali metals as impurities in the employed preparations of sodium and lithium picrates, nor it can be attributed to a higher concentration of caesium in the preparation of the "carrier-free" ^{137}Cs (this was ascertained by independent experiments). Although our results do not allow of a clear-cut explanation of this discrepancy, they still may accord with the observation that the exchange extraction constants

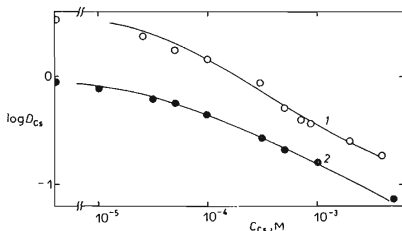


FIG. 2

Distribution Ratio of Caesium in Relation to Its Original Concentration in the Aqueous Phase

C_{Cs} denotes the original concentration of caesium ions in the aqueous phase, D_{Cs} the distribution ratio of caesium. 1 Extraction from an $8.4 \cdot 10^{-3}\text{M}$ aqueous solution of NaA, 2 from a 4.38M aqueous solution of HA. The courses of the solid curves were calculated from Eq. (5), employing the exp. values of D_{Cs}^0 . The concentration of the dissociated acid, $[\text{H}^+ \text{A}^-]$ in the aqueous phase, needed for the calculation, was determined from equation (6).

K_{Me}^{Cs} in the water-nitrobenzene system are independent of the kind of the present anion¹. This fact has been confirmed with substances readily entering the organic phase, and caesium picrate is the first studied compound whose extraction constant is lower than 1. The values of the exchange extraction constants K_{Li}^{Cs} and K_{Na}^{Cs} can be affected by several factors: the concentrations of $Li^+ A^-$ and $Na^+ A^-$ in the organic phase are very low (c. $1 \cdot 1 \cdot 10^{-4} M$ and $3 \cdot 5 \cdot 10^{-4} M$, respectively, in the extraction of these salts from 0.1M aqueous solutions), other particles may interfere (e.g. the solvated cations $C_6H_5NO_2 \cdot H^+$, see⁸) and the concentration of the reagent in the aqueous phase is so high that the properties of this phase may possibly be somewhat modified by it. In the extraction of ^{137}Cs from aqueous picric acid the theoretical value of D_{Cs}^0 is 3.46. From Fig. 1a,b it is seen that this value is exceeded at high concentrations of HA in the organic phase; it should be borne in mind, however, that high concentrations of the acid (1M) can substantially distort the character of nitrobenzene as solvent.

For analytical purposes it is important that microquantities of caesium can be extracted from mildly acid solutions of picric acid or neutral solutions of sodium (lithium) picrate. If the acidity of the aqueous phase is increased the reagent passes into the organic phase according to equation (6) and caesium is extracted back into the aqueous phase.

The dependence of D_{Cs} on the total content of caesium in the aqueous phase offers an easy analytical method for the determination of this element. Typical calibration curves are shown in Fig. 2, together with the theoretical curves calculated from equation (5). The very good agreement of theory with experiment also vindicates our considerations on the limiting distribution ratios.

To conclude it can be said that the extraction constant of caesium picrate is about six orders of magnitude lower than that of the dipicrylamine salt. This indicates that the affinity of an anion to nitrobenzene is not governed by the interaction of the NO_2 groups with the molecules of the solvent. What is more likely to be correct is Diamond's idea of the effect of volume of the anion on its capacity to enter the polar organic phase.

Although the extraction constant of caesium picrate is lower than 1, microquantities of caesium are extracted efficiently. We interpret this phenomenon by a hypothesis of limiting distribution ratios.

Picric acid itself passes into nitrobenzene mainly in the undissociated monomeric form.

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