# INDIVIDUAL EXTRACTION CONSTANTS OF UNIVALENT IONS IN THE SYSTEM WATER-NITROBENZENE

J.RAIS

Institute of Nuclear Research, Czechoslovak Academy of Sciences, Prague-Řež

Received April 4th, 1970

On the assumption that tetraphenylarsonium and tetraphenylborate ions enter the organic phase with the same readiness, the individual extraction constants of 22 univalent ions in the system water-nitrobenzene have been determined. Comparison with some other non-thermodynamic assumptions has also been made. The ion  $Cs^+$  is less solvated by nitrobenzene than it is hydrated by water. Pleskov's postulate of equal solvation of the Rb<sup>+</sup> ion in various solvents is criticized; a different reference ion is proposed.

In the extraction of ionic salts of the type 1 : 1 into organic polar solvents the salts considerably dissociate in the organic phase. If a sufficiently polar solvent, such as nitromethane and nitrobenzene, is employed the ionic association is not significant and the extraction equilibrium is essentially given by the distribution of the ionic forms between the two phases.

The thermodynamic extraction constants  $K^{C_{3}+,A^{-}} = [C_{3}^{+}]_{0} [A^{-}]_{0} ([C_{3}^{+}]_{a} [A^{-}]_{a}]^{-1}$  are a measure of the transfer of the electrolyte  $C_{3}^{+}A^{-}$  from the aqueous phase into the organic one. Friedman and Haugen<sup>1</sup> proposed an extraction method to determine the free enthalpies,  $\Delta^{o}G^{tr}$ , of the transfer of alkali reineckates and perrhenates from water into nitromethane. Compared to the conventional methods for determining the values of  $\Delta^{0}G^{tr}$  (solubility measurements, determination of electromotoric forces) Friedman and Haugen's method offers some advantages. The correction for the ionic association can usually be neglected or calculated (this association may be considerable in the case of saturated solutions in organic solvents). The formation of crystalline solvates with one of the solvents, irreversibility of the electrodes in organic solvents and corrosion of amalgam electrodes<sup>1,2</sup> need not be considered either. On the other hand, the extraction method is applicable to polar organic solvents that are little soluble in water and to calculate the values of  $\Delta^{0}G^{tr}$  for the distribution between the pure solvents supplementary data are needed.

The present paper gives a set of data describing the transfer of some univalent ions from nitrobenzene-saturated water into water-saturated nitrobenzene. The results are presented in the form of extraction constants and individual extraction constants,  $K^i$ , correlated with the free enthalpies of transfer by the simple equation

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 $\Delta^0 G^{\text{tr}} = -RT \ln K^i$ . The values of the extraction constants are taken from our earlier papers<sup>3-5</sup> and from other publications<sup>6,7</sup>; the necessary supplementary data have been determined in this work.

To estimate the individual extraction constants  $K^i$  we adopted an assumption of equal extractibilities of the tetraphenylarsonium and tetraphenylborate ions. Both these ions are sufficiently and practically equally bulky and their "covers" of phenyl group are identical. On the basis of these facts it is justifiable to assume that their specific interactions with the molecules of the solvent will be very limited and virtually equal<sup>7.9</sup>.

The results presented in this paper can be employed practically to estimate the extractibilities of a number of electrolytes into nitrobenzene. A more general discussion of the results will be the subject of our next communication.

#### EXPERIMENTAL

### Chemicals

The radionuclides employed were <sup>137</sup>Cs (a Soviet preparation) and <sup>131</sup>I (Institute of Nuclear Research, Řež). The stock solution of Na<sup>131</sup>I (carrier-free) contained Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 .  $10^{-4}$ <sub>M</sub>) to prevent oxidation of the iodide. The radiochemical purity of these radionuclides was verified *y*-spectrometrically and by measuring the half-life of <sup>131</sup>I.

Nitrobenzene, a.r., was not further purified. Tetraalkylammonium hydroxides, a.r., were employed in the form of 10% aqueous solutions. The purity of tetraphenylarsonium chloride (Laborchemie Apolda) was ascertained spectrophotometrically<sup>10</sup>; no appreciable impurities were detected.

### Preparation of Reagents

Picrates and tetraalkylammonium 2,6-dinitrophenolates were prepared by mixing stoichiometric amounts of aqueous picric acid and aqueous 2,6-dinitrophenol with aqueous solutions of the corresponding hydroxides. The yellow precipitates were washed with water and dried at room temperature. Tetraethylammonium dipicrylaminate was obtained analogously from aqueous sodium dipicrylaminate.

Tetraphenylarsonium iodide was obtained by dissolving tetraphenylarsonium chloride in hot water ( $\approx 60^{\circ}$ C) and precipitation with aqueous NaI at the same temperature. It was also prepared in the form of a stock solution in nitrobenzene by extraction from a mixture of tetraphenylarsonium chloride and NaI in water. The organic phase was washed with water. The yield of the extraction and the concentration of the product in the organic phase were determined by measuring the activity of <sup>131</sup>I.

### Determination of the Distribution Ratios

In all cases the system was composed of three constituents only: the studied compound, water and the organic solvent. The volume ratio of the phases was 1 : 1. The distribution ratios were determined radiometrically (CsI, CsClO<sub>4</sub>, Ph<sub>4</sub>AsI and tetraalkylammonium iodides) by measuring the ratio of activities of dry residues of aliquot portions of the two phases in equilibrium

#### Individual Extraction Constants

or colorimetrically by determining the equilibrium concentration of the coloured anions in the aqueous phase (dipicrylaminate<sup>3</sup>, picrate and 2,6-dinitrophenolate<sup>5</sup>). The distribution of tetraphenylarsonium chloride between the aqueous and the organic phases was determined by measuring the electric conductivity of the aqueous phase in equilibrium with the organic one, employing a calibration curve. All experiments refer to  $25 \pm 1^{\circ}$ C. By other experiments it was found that the differences caused by this temperature range were smaller than the experimental error (0:1 logarithmic unit for the calculated extraction constants, unless otherwise stated).

All the reported values refer to molar concentrations.

# **RESULTS AND DISCUSSION**

# Extraction Constants

The thermodynamic extraction constants  $K^{Me^+,A^-}$  are correlated with the free enthalpy of transfer of the individual ions into the organic phase by the equation

$$-\log K^{\mathrm{Me}_{+},\mathrm{A}_{-}} = -\log \frac{(a_{\mathrm{Me}_{+}})_{0}(a_{\mathrm{A}_{-}})_{0}}{(a_{\mathrm{Me}_{+}})_{a}(a_{\mathrm{A}_{-}})_{a}} = \frac{\Delta^{0}G_{\mathrm{Me}_{+}}^{\prime\prime}}{2\cdot 3RT} + \frac{\Delta^{0}G_{\mathrm{A}_{-}}^{\prime\prime}}{2\cdot 3RT}, \qquad (1)$$

where  $(a_{Me^+})_0$  and  $(a_{Me^+})_a$  are the activities of ions in the organic and the aqueous phases respectively and  $\Delta^0 G_{Me+}^{tr}$  is the free enthalpy of transfer of the Me<sup>+</sup> ion from nitrobenzene-saturated water into water-saturated nitrobenzene. The quantities  $-\Delta^0 G_{Me^+}^{tr}/2.3RT$  will hereafter be designated as log  $K^{Me^+}$ , where  $K^{Me^+}$  is the individual thermodynamic extraction constant of the ion Me<sup>+</sup>. Evidently it applies that  $\log K^{Me^+,A^-} = \log K^{Me^+} + \log K^{A^-}$ . The following two conclusions can be deduced from this additivity: 1. The so-called exchange extraction constants, e.g.  $K_{Me}^{Cs}$  =  $= (a_{Cs^+})_0 (a_{Me^+})_a [(a_{Cs^+})_a (a_{Me^+})_0]^{-1}$ , must generally be independent of the kind of anion present in the system water-polar organic solvent (log  $K^{Cs+} - \log K^{Me+} =$ = const.). This fact has already been discussed by  $us^3$  and has been confirmed by results of many papers. 2. The experimentally determined values of  $K^{Me^+,A^-}$  can formal-Iv be divided into ion contributions by the assignment of one absolute value (e.g.  $\log K^{Cs+} = 0$ ; in further text, however, this value will be assigned in a more rational way). Employing this value the constants  $K^{i}$  of other ions can be obtained by calculation. On the other hand, from the values of  $K^{i}$  it is possible to calculate the extraction constant of the salt Me<sup>+</sup>A<sup>-</sup> even if its distribution between water and nitrobenzene has not been studied (provided the distributions of the ions Me<sup>+</sup> and A<sup>-</sup> in the form of other salts are known).

In the system water-nitrobenzene the extraction constants have been determined for dipicrylaminates<sup>3</sup>, picryl-2,4-dinitronaphthylaminates<sup>4</sup>, alkali metal tetraphenylborates<sup>7,11</sup>, for caesium picrate and caesium 2,4 and 2,6-dinitrophenolates<sup>5</sup> and for the compounds  $CsI_3$  and  $CsI_5^6$ . However, no detailed quantitative data on the extraction of bulky organic ions and univalent inorganic anions into nitrobenzene have been reported. The present paper deals with the determination of the extraction constants of these ions in the form of some of their typical salts.

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Fig. 1 gives the distribution ratios of tetramethylammonium picrate, tetraethylammonium picrate, tetrabutylammonium 2,6-dinitrophenolate, tetraphenylarsonium iodide and tetraphenylarsonium chloride plotted against their original concentrations in the organic phase. The selection of these salts was governed by the possibility of accurate determinations of the distribution ratios (with the employed method of determining the distribution ratios of coloured anions it is desirable that these ratios be  $\geq 1$ ; thus tetramethylammonium 2,6-dinitrophenolate is too little extracted by nitrobenzene, whereas the distribution ratios of tetrabutylammonium and tetraphenylarsonium picrates are too high). The distributions of CsI and CsClO<sub>4</sub> between water and nitrobenzene are shown in Fig. 2.

With the exception of CsI the distribution ratios of the salts are roughly constant, independent of their concentrations. Consequently, the extraction constants  $K^{Me+,A^-}$  can be calculated directly from the distribution ratios using the equation  $K^{Me+,A^-} = D_{Me^+}^2 = D_{A^-}^2$  (if association  $Me_0^+ + A_0^- \rightleftharpoons MeA_0$  occurred in the organic phase the distribution ratios would necessarily increase with the increasing concentrations of the salts). The calculated extraction constants are listed in Table I. For the calculation of extraction constant of CsI we have taken as a basis the value  $D_{Cs} = 10^{-3}$ ; this is an average calculated from our measurements and agrees well with that reported by Tribalat and Grall<sup>6</sup>.

It is of interest that in these experiments the distribution ratios proved virtually independent of the total quantity of the salt. An analogous phenomenon had already

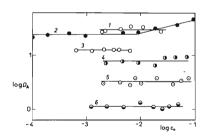


Fig. 1

Distribution of Some Electrolytes with an Organic Ion between Water and Nitrobenzene

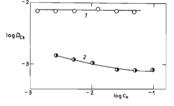
 $D_{\rm A}$  distribution ratio of the anion,  $c_0$  initial concentration of the electrolyte in the organic phase, volume ratio of the phases 1 : 1, agitated for 20 min, 1 tetraphenylarsoniun; iodide, 2 tetrabutylammonium 2,6-dinitrophenolate, 3 tetraethylammo ium dipicrylaminate (the axis of abscissae gives the value  $-2 + \log c_0$ , the axis of ordinates the value  $-2.8 + \log D_{\rm A}$ ), 4 tetraethylammonium picrate, 5 tetraphenylarsonium chloride, 6 tetramethylammonium picrate. been observed<sup>6</sup> and ascribed to the probable intercompensation of the activity coefficients in the two phases. The extraction constants of some caesium polyiodides were independent of ionic strength up to  $I = 10^{-1}$ . Also Haugen and Friedman's paper<sup>1</sup> shows concentration independence of the distribution ratio of CsClO<sub>4</sub> in the system water-nitromethane within the concentration range studied (up to 8 .  $10^{-3}$  M-CsClO<sub>4</sub> in the equilibrium aqueous phase). On the basis of this fact the average values of the measured extraction constants have been set equal to the thermodynamic extraction constants in equation (*I*). In other experiments (alkali dipicrylaminates) the extraction constants decreased with the increasing ionic strength of the aqueous phase<sup>3</sup>; in these cases the thermodynamic constants were obtained by extrapolating the extraction constants to zero ionic strength.

The distribution of tetraethylammonium dipicrylaminate between water and nitrobenzene was studied by us previously<sup>3</sup>. However, subsequent experiments have revealed that the correctness of the extraction constant reported therein is rather doubtful. The distribution of tetraethylammonium dipicrylaminate vs. its initial

FIG. 2

Distribution of Some Inorganic Caesium Salts between Water and Nitrobenzene

 $D_{Cs}$  Distribution ratio of <sup>137</sup>Cs,  $c_a$  initial concentration of the electrolyte in the aqueous phase, volume ratio of the phases 1:1, agitated for 20 min, 1 caesium perchlorate, 2 caesium iodide.



# TABLE I

Extraction Constants of Some Electrolytes in the Water-Nitrobenzene System

Electrolyte	log K	
Tetramethylammonium picrate	0.12	
Tetraethylammonium picrate	1.80	
Tetrabutylammonium 2,6-dinitrophenolate	2.80	
Tetraphenylarsonium chloride	1.04	
Tetraphenylarsonium iodide	2.96	
Tetraethylammonium dipicrylaminate	7.80	
Caesium perchlorate	4.24	
Caesium iodide	- 6.0	

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concentration in the organic phase is given in Fig. 2 (curve 3). The distribution ratio of the dipicrylaminate anion,  $D_{A^-}$ , equals 7950  $\pm$  300 for a range of the initial concentrations of tetraethylammonium dipicrylaminate in the organic phase 6.5.  $.10^{-2}$  to 6.5.  $10^{-1}$  mol  $1^{-1}$ . The resulting extraction constant (log K = 7.80) is in a fairly good agreement with the rule of additivity of logarithms of the individual extraction constants (see Table 1). The logarithm of the exchange extraction constant for the ions ( $C_2H_3$ )<sub>4</sub>N<sup>+</sup> and Cs<sup>+</sup> calculated from the distributions of the corresponding picrates (this paper and ref.<sup>5</sup>) equals 3.72; if calculated from the distributions of dipicrylaminates (this paper and ref.<sup>3</sup>) its value is 3.60.

# The Individual Extraction Constants

In order to estimate the individual extraction constants it is necessary to introduce some nonthermodynamic assumption on the basis of which it would be possible to attribute an individual constant  $K^i$  to at least one of the ions. The selection of helpful assumptions is facilitated by two recent review articles<sup>9,12</sup>. According to Popovych<sup>9</sup> the most rewarding methods are based on the use of the so-called "reference" electrolyte, such as triisoamyl-n-butylammonium tetraphenylborate and tetraphenylarsonium tetraphenylborate (the "Ph<sub>4</sub>AsBPh<sub>4</sub> assumption"). At present there seems to be no reason why any of these assumptions should be preferred; however, the "Ph<sub>4</sub>AsBPh<sub>4</sub> assumption" has been employed for a number of systems water–polar organic solvent<sup>8,13,14</sup>.

The extraction constant of  $Ph_4AsBPh_4$  is difficult to determine directly in view of the high value of its distribution ratio. The indirect method implies the use of the extraction constants of the salts  $Cs^+BPh_4^-$ ,  $Ph_4As^+1^-$  and  $Cs^+1^-$ . In the case of cassium tetraphenylborate we employed in the subsequent calculations the value log  $K^{Cs^+,BPh4^-} = 3.60$ , determined from the data reported previously<sup>7</sup>. The recently published value 5.11 (ref.<sup>11</sup>) does not seem to be correct. Employing the value 3.60 and the data determined in this work we have calculated the extraction constant of  $Ph_4AsBPh_4$  as log K = 12.6. Under the "Ph\_4AsBPh\_4 assumption" the individual extraction constants of the ions  $Ph_4As^+$  and  $BPh_4^-$  are log  $K^1 = 6.3$ .

The derived individual extraction constants of some univalent ions are listed in Table II. In their calculation we employed the data reported in the present paper and data taken from other communications<sup>3-7</sup>. The individual extraction constants of alkali metal cations have been calculated from the known exchange extraction constants  $K_{Me}^{Cs}$  in the system water-nitrobenzene. The values of these constants and their independence of the presence of anions was discussed previously to some extent<sup>3</sup>. Since then two papers reporting the values of  $K_{Me}^{Cs}$  have appeared (for tetraphenylborates<sup>11</sup> and alkali metal dipicrylaminates<sup>15</sup>). The reported values are in very good agreement with ours and other authors'. On the basis of a set of the literature values of  $K_{Me}^{Cs}$  it is possible to assess their most probable values (with root-mean-square deviations ( $\sum^2/n$ )<sup>1/2</sup>, where *n* is the number of data of different authors):  $\log K_{Li}^{Cs} = 4.04$ ( $\pm 0.06$ ; 8) and  $\log K_{Rb}^{Cs} = 0.70$  ( $\pm 0.09$ ; 8). The value of  $\log K_{L}^{Cs}$  determined by us previously<sup>16,17</sup> to be 3.00. The expected change of the exchange extraction constants  $K_{Me}^{Cs}$  and  $K_{He}^{Cs}$  with ionic strength is negligible in the range l = 0 to 0.1; the above-given values can therefore be regarded as thermodynamic ones.

We consider it worthwhile to confront the "Ph<sub>4</sub>AsBPh<sub>4</sub> assumption" with others. Parker and coworkers<sup>12</sup> proposed an "iodine-triiodide assumption", postulating the same free enthalpy of transfer for the two particles. This assumption is obviously farther from reality than the "Ph4AsBPh4 assumption". The specific interactions of  $I_2$  and the electrostatic interaction of  $I_3^-$  with the organic solvent are disregarded, but apart from these facts the sizes of the two particles are, at best (disregarding the negative charge of  $I_{1}^{-}$ ), in the ratio 2 : 3. For these reasons we have preferred the hypothetical "iodine - diiodide assumption" (the extraction constant of "Cs<sup>+</sup>I<sub>2</sub>" can be estimated by interpolation employing the values for  $Cs^+I^-$ ,  $Cs^+I^-_3$  and  $Cs^+I^-_5$ ). Combination with the distribution ratio of iodine in the system water-nitrobenzene  $(\log D_{1} = 2.3, \text{ref.}^{6})$  yields the value of  $\log K^{C_{s}} \approx -3.2$ , which relatively is not very different from the value reported by ourselves, viz. -2.70. Strehlow has proposed a method of determining the individual constants based on a modification of Born's equation<sup>2</sup>. This method will be discussed in detail in our next communication. Here it should only be mentioned that agreement of theory with experiment for  $K_{Rh}^{Cs}$ ,  $K_{K}^{Cs}$ and  $K_{Na}^{Cs}$  can be obtained with parameters  $\delta_{H_{2}O} = 0.75$  Å and  $\delta_{nitrobenzene} = 0.92$  Å; the individual extraction constant of the caesium ion then results as  $\log K^{Cs+}$ = -3.8

#### TABLE II

Cation	log K <sup>i</sup>	Anion	log K <sup>i</sup>
Li <sup>+</sup>	- 6·7ª	CI <sup>-</sup>	- 5.2
Na <sup>+</sup>	$-6.0^{a}$	Ι-	-3.3
H+	$-5.7^{a}$	CIO <sub>4</sub>	-1.4
$NH_4^+$	$-4.7^{a}$	2,6-Dinitrophenolate	$-1.4^{b}$
K <sup>+</sup>	-4·1ª	2,4-Dinitrophenolate	$-1.3^{b}$
Rb <sup>+</sup>	$-3.4^{a}$	Picrate	$0.8^{b}$
Cs <sup>+</sup>	-2.7	13	4·1°
Tetramethylammonium	0.6	Tetraphenylborate	6.3 <sup>d</sup>
Tetraethylammonium	1.0	15	6.8°
Tetrabutylammonium	4.2	Dipicrylaminate	6.9 <sup>e</sup>
Tetraphenylarsonium	6.3	Picryl-2,4-dinitronaphthyl aminate	7.7 <sup>5</sup>

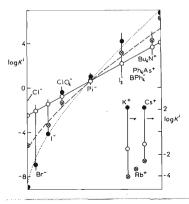
Individual Extraction Constants for the System Water-Nitrobenzene at 25°C on the basis of "Ph<sub>4</sub>AsBPh<sub>4</sub> Assumption" (see the text)

<sup>*a*</sup> Average values from 3 to 10 independent determinations of  $K_{Me}^{Cs}$  (see the text);<sup>*b,e,d,e,f*</sup> values calculated from data taken from papers<sup>3-7</sup>.

# Comparison with Other Systems Water-Polar Organic Solvent

To compare the affinities of some univalent ions to several organic solvents we have employed Parker's data<sup>13</sup> (obtained by solubility measurements without corrections for the ionic association and on the basis of the "Ph<sub>4</sub>AsBPh<sub>4</sub> assumption"). These data were recalculated into a scale chosen by ourselves according to the equation log  $K^i = -\log \gamma_{0,i}$ , where  $\gamma_{0,i}$  is a quantity currently referred to in the literature as the medium effect<sup>2.13</sup>. Fig. 3 gives the data for three typical systems water-organic polar solvent (the points on the axis of abscissae were so selected that the values of log  $K^i$  for the water-methanol system would lie on a straight line).

Fig. 3 reveals that bulky organic ions are invariably preferred by the organic phase to the halogen anions, which are more hydrated than solvated<sup>8</sup>. What is noteworthy is the constancy of the individual extraction constant of the picrate ion. For the four systems investigated by Parker the values of log  $K^1$  lie within the range from 0.5 to 1.0. Popovych reported a value of log  $K^i = 1.05$  for the picrate ion in the system water-methanol and values from -0.10 to +0.26 for the transfer from water into aqueous ethanol<sup>9</sup>. The value of log  $K^i$  for the ion  $K^+$  ranges in the latter case in a much wider interval, from -2.74 to -0.08. From this point of view the choice of the picrate ion as the reference one appears to be more appropriate than the assumption of constancy of  $K^i$  for Rb<sup>+</sup> (ref.<sup>18</sup>); as can be seen from the right lower part of Fig. 3 it is just with the alkali cations that the values of  $K^i$  strongly vary from solvent to solvent. In the case of a picrate ion interacting with the solvent two effects are probably operative: hydration of the strongly hydrophilic group O<sup>-</sup> (like with the



# FIG. 3

Comparison of the Individual Extraction Constants for Some Systems Water-Organic Polar Solvent

 $\odot$  Water-methanol<sup>13</sup>,  $\otimes$  nitrobenzene-saturated water-water-saturated nitrobenzene (our data),  $\bullet$  water-dimethylformamide<sup>13</sup>. The points on the axis of abscissae were so chosen that the data for the water-methanol system lied on a straight line. The vertical lines give approximate ranges of values for other systems in paper<sup>13</sup>. anions Cl<sup>-</sup> and Br<sup>-</sup>) and hydrophobicity, due to the bulky organic residue. The two effects may compensate for each other because the hydration of Cl<sup>-</sup> and Br<sup>-</sup> increases with the number of hydrogen bonds of the solvent<sup>8</sup>, whereas the transfer of bulky organic ions into the organic phase seems to exhibit a decreasing trend (Fig. 3).

From Fig. 3 and other results it is clear that solvents differ mainly in their power of solvating the univalent inorganic cations. In this aspect it is useful to employ the conception of "donor numbers", introduced by Gutmann<sup>19</sup>. The "donor number" of a solvent is defined as the negatively taken enthalpy of the reaction  $SbCl_5 + S = SbCl_5.S$ , where S designates the solvent. This quantity is a sufficiently general characteristic of the ability of a solvent to solvate cations and molecules acceptors of electronic pairs. According to Gutmann this power increases in the order nitromethane < nitrobenzene < acetonitrile < water < dimethylfornamide < dimethylfornamide < dimethylfornamide < dimethylfornamide solvent is according to the stated order nitrobenzene is a much worse solvent of alkali cations than water, as is also apparent from our data.

It should be pointed out, however, that the values of  $K^i$  may be rather different, considering the transfer of a cation from water to water-saturated nitrobenzene and from water to dry nitrobenzene (the effect of nitrobenzene in water can be neglected; this assumption has been justified by measuring the solubilities of alkali dipicrylaminates in pure water and in water saturated with nitrobenzene at 25°C). This fact must be expected to play a significant role in the transfer of strongly hydrated cations such as Li<sup>+</sup> and Na<sup>+</sup> (present as hydrates even in water-saturated nitrobenzen<sup>3</sup>). Such cations will enter a water-saturated solvent more readily than the pure solvent.

A good demonstration of this fact is comparison of  $\Delta^0 G^{\text{tr}}$  values for the water  $\rightarrow$  nitromethane transfer (A) and for the transfer from nitromethane-saturated

### TABLE III

System	Water-nitromethane <sup>a</sup>	Nitrobenzene-saturat- ed water-water- saturated nitrobenzene	Nitromethane-saturat- ed water-water- saturated nitromethane <sup>a</sup>
$\Delta^0 G^{tr}_{Cs+} - \Delta^0 G^{tr}_{Rb+}$	- 1.02	0.95	0.72
$\Delta^0 G^{\mathrm{tr}}_{\mathrm{Cs}} + - \Delta^0 G^{\mathrm{tr}}_{\mathrm{K}} +$	2.13	1.88	1.37
$\Delta^0 G^{\rm tr}_{\rm Cs +} - \Delta^0 G^{\rm tr}_{\rm Na +}$	- 6.18	4.52	3.12
$\Delta^0 G^{\rm tr}_{\rm Cs^+} \sim \Delta^0 G^{\rm tr}_{\rm Li^+}$	- 11.86	- 5.51	- 3.52

Relative Free Enthalpies of Transfers of Alkali Metal Cations from Water to Nitromethane and Nitrobenzene at 25°C [kcal mol<sup>-1</sup>]

<sup>a</sup> Data taken from ref.<sup>1</sup>.

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water to water-saturated nitromethane (C), ref.<sup>1</sup>. These data, along with our own (B), are compiled in Table III. The difference in separation properties between the systems A and C is highest with the pair  $Cs^+-Li^+$ , whereas the relative free enthapies change very little for the pair  $Cs^+-Rb^+$ . The content of water in the organic solvent also increases from A to C. Hence it can be deduced that the solubility of water in an organic solvent will be the decisive factor for the separation properties of analogous extraction systems (extraction into nitrobenzene and nitrated aliphatic hydrocarbons). Further work on this subject is in progress<sup>20</sup>.

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Translated by J. Salák.