

# Gibbs Energies of Transfer of Alkali Metal Cations between Mutually Saturated Water–Solvent Systems Determined from Extraction Experiments with Radiotracer $^{137}\text{Cs}$

Jiří Rais,<sup>\*,†</sup> Tatsuhiro Okada,<sup>‡</sup> and J. Alexová<sup>†</sup>

Nuclear Research Institute plc Řež, 25068 Řež, Czech Republic, and National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Central 5, Tsukuba, Ibaraki 305-8565, Japan

Received: January 17, 2006; In Final Form: February 22, 2006

Thermodynamic standard Gibbs energies of transfer of alkali metal cations related to  $\text{Cs}^+$  cation  $[\Delta_r G^\circ(\text{Cs}^+) - \Delta_r G^\circ(\text{M}^+)]$  between several mutually saturated solvents of the type water–solvent were calculated from determined extraction exchange constants  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$ . The used liquid–liquid extraction method with radioactive tracing by  $^{137}\text{Cs}$  permits attaining higher precision of the values as compared to the methods used up to now. The data for *o*-nitrophenyloctyl ether, 1,2-dichloroethane, and 1-octanol were compared with literature sources and recommended absolute values of  $\Delta_r G^\circ(\text{M}^+)$  are reported. For dissociating solvents, the dependences of  $[\Delta_r G^\circ(\text{Cs}^+) - \Delta_r G^\circ(\text{M}^+)]$  on Gibbs energy of hydration of an ion,  $\Delta G_{\text{hydr}}^\circ$  are straight lines either for four cations  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ , and  $\text{Na}^+$  (nitrosolvents) or for three cations  $\text{Cs}^+$ ,  $\text{Rb}^+$ , and  $\text{K}^+$  (1,2-dichloroethane and 1-octanol). The hydration of  $\text{Na}^+$  and still more of  $\text{Li}^+$  in the water-saturated organic phase is apparent from the results. This manifests for high-water-content equilibrium 1-octanol even in a reversal of the values [i.e.,  $\Delta_r G^\circ(\text{Li}^+)$  being more negative than  $\Delta_r G^\circ(\text{Na}^+)$ ], although for  $\text{Cs}^+$ ,  $\text{Rb}^+$ , and  $\text{K}^+$ , the general trend is conserved. Water-saturated 1-octanol is thus slightly less basic than water, but the overall selectivity is very low. For one studied nondissociating solvent, dioctyl sebacate, the trend of the dependences of  $\log K_{\text{exch}}^{\circ,*}(\text{CsB}/\text{M}^+)$  on  $\Delta G_{\text{hydr}}^\circ$  is similar to that of  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for polar solvents, but different for different anions B, thus reflecting ion association in the organic phase.

## Introduction

Transfer of ions from water into immiscible organic solvents is a key process, taking place in different areas such as extraction processes,<sup>1</sup> electrochemical phenomena at interface between two immiscible electrolyte solutions (ITIES), and electroanalysis,<sup>2</sup> development and theory of ion selective electrodes,<sup>3</sup> and a plethora of biochemical and biomimetic studies.<sup>4</sup>

There are nowadays various approaches and theories of how to understand and evaluate the individual values of Gibbs energies of transfer of an ion *i*,  $\Delta_r G^\circ(i)$  from one solvent (usually water) into another (polar organic solvent).

To start with the matter, the choice of the correct data used in the models is in no case a trivial matter. In the following, we give a short survey of the used data sets and of some of the models.

Perhaps the best known is a database of  $\Delta_r G^\circ(i)$  of some 45 ions and their transfers from water into 47 solvents and a consequent multiple regression analysis of the data, providing the most important empirical parameters responsible for the transfer published by Marcus (**Md**).<sup>5</sup> Reported overall uncertainty of about 470 data items is ca. 6 kJ/mol.<sup>6</sup> The database **Md** became quite popular, and the data from it are often used in various proposed models. Thus, Fawcett used **Md** in his nonprimitive mean-spherical approximation model of  $\Delta_r G^\circ(i)$ .<sup>7</sup> Other models are those of Moyer et al. (also **Md** based), the first one using the electrostatic approach based on a modified Born equation,<sup>8</sup> and in another one, Hildebrand solubility parameters are assigned to ions as a decisive parameter.<sup>6</sup> One

recent approach by Abraham and Zhao uses ion solvation descriptors as hydrogen bond acidities and basicities.<sup>9</sup> The authors make use of our own older data (of the first author) and **Md**-based data.<sup>9,10</sup> No particular distinction was made in the two papers where a particular set was used for a particular ion/solvent (**Azd** database).

Somewhat overlooked is a large data set of thermodynamic data  $[\Delta_r G^\circ(i), \Delta_r H^\circ(i), \Delta_r S^\circ(i)]$  for alkali metal cations and  $\text{Ti}^+$  and  $\text{Ag}^+$  and 21 solvents and for  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  and 18 solvents published by Gritzner of some 176 data (reference solvent was acetonitrile, but recalculation of data into water-referred is simple), **Gd**.<sup>11</sup> We argued in our previous article that the data set **Gd** might form a more reliable particular basis of data than **Md** because the overall uncertainty of data can be lower than 0.7 kJ/mol.<sup>12</sup> This is comprehensible when taking into account that the **Md** set is based on various older, sometimes contradicting data, as reported by different authors, and the data had to be judiciously evaluated and averaged. On the other hand, the **Gd** set is based on the results done in one laboratory by one technique, and thus apt to be more precise, although for a somewhat smaller amount of data.

Whereas both **Md** and **Gd** provide the  $\Delta_r G^\circ(i)$  of transfers from one pure solvent into another pure solvent, during past decades, the two methods of determination considerably grew up, which provide the  $\Delta_r G^\circ(i)$  values for real transfer between two mutually saturated phases. These values were denoted previously<sup>13</sup> as  $\Delta_r G^\circ(i, a_{(o)} \rightarrow o_{(a)})$  for the transfers from water into an immiscible solvent *o*, where  $a_{(o)}$  and  $o_{(o)}$  denote the aqueous phase saturated with organic solvent and vice versa, respectively. For simplicity, these values are denoted here as  $\Delta_r G^\circ,* (i)$ . These values are relatively simply measured, but on the provision that the role of the mutual solubility might

\* Corresponding author. E-mail: jrai@nri.cz.

<sup>†</sup> Nuclear Research Institute plc Řež.

<sup>‡</sup> National Institute of Advanced Industrial Science and Technology.

complicate the theoretical treatment and, of course, also that no  $\Delta_f G^{\circ,*}(i)$  for miscible solvent cannot be measured, thus limiting the repertory of available systems.

The first method is extraction, which we used from time to time in our earlier publications.<sup>14</sup> In it, cesium salt of some hydrophobic anion  $\text{Cs}^+\text{B}^-$  is dissolved in the organic phase, and after addition of the aqueous phase of  $\text{M}^+\text{X}^-$  ( $\text{X}^-$  being hydrophilic anion like  $\text{NO}_3^-$ ) having the desired composition, the phases are shaken until equilibrium is reached. The extraction exchange constant of the type  $K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+) = [\text{Cs}^+]_o[\text{M}^+]_a/[\text{Cs}^+]_a[\text{M}^+]_o$  is then calculated for a polar organic solvent and a thermodynamic constant of ion exchange,  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+) = K^{\circ,*}(\text{Cs}^+)/K^{\circ,*}(\text{M}^+)$ , where  $K^{\circ,*}(i)$  is a thermodynamic individual extraction constant of the ion  $i$ , can be deduced. The extraction method permits also the determination of another constant if an organic solvent is essentially nondissociating. In the latter case,  $K_{\text{exch}}^*(\text{CsB}/\text{M}^+)$ , which is equal to  $K_{\text{exch}}^*(\text{CsB}/\text{M}^+) = [\text{CsB}]_o[\text{M}^+]_a/[\text{MB}]_o[\text{Cs}^+]_a$ , applies (see Appendix).

The value of  $K_{\text{exch}}^*(\text{CsB}/\text{M}^+)$  cannot be measured by electrochemical methods, which are the second widespread method of the determination of  $\Delta_f G^{\circ,*}(i)$  nowadays. For this purpose, both phases must be conducting. The  $\Delta_f G^{\circ,*}(i)$  value for the case of conducting phases is calculated from the standard distribution potential of the ion under consideration, read usually from cyclic voltammetry curves,  $\Delta^w_o \varphi^{\circ,*}(i)$ . The relation connecting the thermodynamic individual extraction constants, standard Gibbs energies of transfers, and standard distribution potentials reads as (for 25 °C, kJ/mol and volts, respectively):<sup>13</sup>

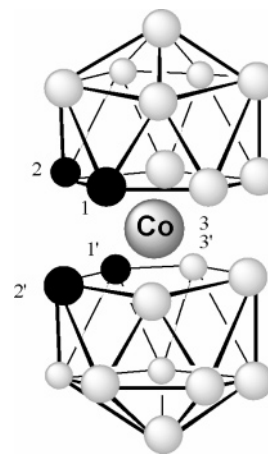
$$\Delta_f G^{\circ,*} = -5.711 \log K^{\circ,*}(i) = -96.52z_i \Delta^w_o \varphi^{\circ,*}(i) \quad (1)$$

Thus, the two experimental methods, i.e., extraction and electrochemical, although totally different in subject and experimental setup, ought to lead to the same values of  $\Delta_f G^{\circ,*}$ .

In this work, we attempt to broaden the repertory of organic solvents for which the values of  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for the series of alkali metal cations, proton, and ammonium cation will be determined. Comparison with the tabulated electrochemical data will show that extraction methods can be more precise. Also, the methods of extrapolation of the measured  $K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  toward zero ionic strength of either aqueous or organic phase are used in the extraction method, thus the resulting  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  are not derived only from one measurement. Although in modern electrochemical methods for studying ITIES very small concentrations of supporting electrolytes are used (e.g.,  $10^{-4}$  M in water and  $10^{-3}$  M in organic solvent,<sup>15</sup> or  $5 \cdot 10^{-3}$  M in water and organic phases<sup>16</sup>), extrapolations of data obtained for a larger span of ionic strengths to zero ionic strength are as a rule not done. This might even be dangerous because, as shown in this paper, at just low concentration of electrolyte in the aqueous phase, some irregularities occurred. Moreover, in interpreting the electrochemical data in terms of standard distribution potentials, the ratio of diffusion coefficients in both phases is involved, but the exact values of them are often not exactly known.

The second aim of this paper is to check whether for the values  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  and for the studied systems, the earlier criterion of linearity of the values  $K_{\text{exch}}^{\circ}(\text{Cs}^+/\text{M}^+)$  on the standard Gibbs hydration energy<sup>12</sup> applies.

We studied as organic solvents 1-nitropropane, *o*-nitrophenyloctyl ether, 1,2-dichloroethane, 1-octanol, and dioctyl sebacate. Whereas the first two are dissociating solvents, the second two



**Figure 1.** Structure of the cobalt bis(dicarbollide) anion; one minus charge, which is spread over the anion, is not shown.

are of moderate dielectric constant, and the last one is a completely nondissociating solvent.

We suppose complete dissociation of ions in all solvents but dioctyl sebacate. This is based on preliminary measurements of the conductivities of cesium salts of dicarbollide anions in the solvents, the fact that the used anions are both very bulky with a small tendency of association, and also because we used small concentrations of them in the organic phase.

The data collected here consist of our earlier data referred to the temperature  $25 \pm 1$  °C, and new data we measured exclusively in a thermostated box with  $25 \pm 0.1$  °C.

## Experimental Section

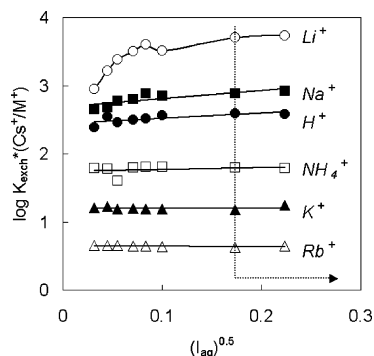
All chemicals, including solvents, were of a.r. purity and were not additionally purified before use. Cobalt bis(dicarbollide) anion in its cesium form  $\text{Cs}^+[(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2\text{-3-Co}]^-$ ,  $\text{Cs}^+\text{B}^-$ , of purity >99%, was purchased from Katchem Ltd., Praha, Czech Republic. Hexabromo derivative  $\text{Cs}^+[(1,2\text{-C}_2\text{B}_9\text{H}_8\text{Br}_3)_2\text{-3-Co}]^-$ ,  $\text{Cs}^+\text{BBr}_6^-$ , was of the same origin.

Organic solutions of cobalt bis(dicarbollide) cesium salts  $\text{Cs}^+\text{B}^-$  were generally 0.005 mol/L, but in some solvents,  $\text{Cs}^+\text{B}^-$  was not soluble enough and  $\text{Cs}^+\text{BBr}_6^-$  had to be used at a lower concentration. As aqueous solutions, the respective alkali metal nitrates, chlorides, and sulfates were used.

The extraction experiments were done upon spiking the aqueous electrolyte solution containing  $\text{M}^+$  ion with  $^{137}\text{Cs}$  of standard radiochemical purity; organic solvent solution of  $\text{Cs}^+\text{B}^-$  was added, and test tubes were shaken for 1 h (equilibrium distribution was reached in all cases). The volumes of each phase were 1 mL, and aliquots were withdrawn with Eppendorf micropipets. The temperature of shaking was  $25 \pm 1$  °C for older data and  $25 \pm 0.1$  °C for newer experiments done in a thermobox.

## Results

**Choice of Organic Electrolyte with Highly Hydrophobic Anion.** For the present study, we have chosen cobalt bis(dicarbollide) anion in its cesium form  $\text{Cs}^+[(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2\text{-3-Co}]^-$ ,  $\text{Cs}^+\text{B}^-$  (Figure 1). This anion is highly hydrophobic, and because of the absence of any interacting groups on its surface, the association with proton or metal cations is minimal, even in the media of a low dielectric constant. The acid  $\text{H}^+\text{B}^-$  is nearly fully dissociated, even in organic media of dielectric constant  $\epsilon = 10\text{--}15$ , and consequently, the anion persists as ionic species in the organic phase, even if contacted with



**Figure 2.** Logarithmic values of extraction exchange constants  $\log K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  for the system water–1-nitropropane. Initial concentration of  $\text{Cs}^+\text{B}^-$  in the organic phase was  $1 \cdot 10^{-3}$  mol/L,  $t = 25 \pm 0.1$  °C. Dashed lines denote the origin of the concentrations used mostly in this paper.

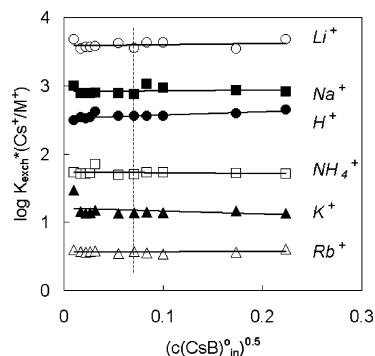
concentrated mineral acids in the aqueous phase.<sup>17</sup> The dicarbolide anions were largely used in the radiochemical technology for the separation of  $^{137}\text{Cs}$ ; the mechanism of the extraction of this cation is just given by a sufficiently high value of  $K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  values for a suitable combination of a water–organic solvent system.<sup>17</sup>

**Nitrosolvents.** *1-Nitropropane as a Model System.* We have chosen this system as a model one in order to show the ways for obtaining the thermodynamic values of extraction exchange constants and for the evaluation of the probable uncertainties of the resulting constants obtained by thorough analysis of all necessary factors. Apparently, the system water–1-nitropropane was never before studied, but it had been shown as a promising system in extractions of radioactive cesium with calixcrowns.<sup>18</sup> Reported dielectric constant of 1-nitropropane is  $\epsilon = 23.73$  (25 °C), Abraham's hydrogen bond basicity is  $\beta = 0.31$ .<sup>19</sup> Solubility of water in the solvent at 20 °C is 0.333 mol/L.<sup>20</sup>

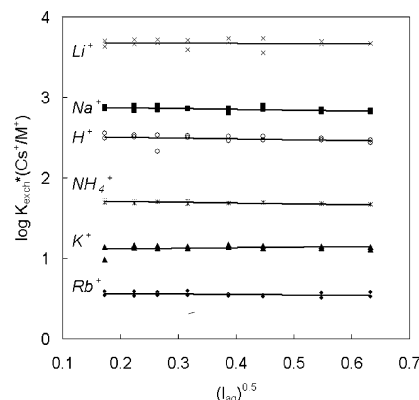
Because, in an absolute majority of cases, the values  $\log K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  could be expressed as straight lines when plotted vs the square root of the aqueous ionic strength  $(I)^{0.5}$ , we first determined for which range of aqueous concentrations this applies. The results are depicted in Figure 2. It is seen that, for all alkali cations, with the exception of  $\text{Li}^+$ , the straight lines are obtained already from the lowest concentration of  $\text{M}^+\text{NO}_3^-$  in the aqueous phase. The dashed line denoted the start of the concentration range used mostly in this paper also for other solvents, which is thus justified. The observed irregularity for  $K_{\text{exch}}^*(\text{Cs}^+/\text{Li}^+)$  at concentrations of aqueous  $\text{Li}^+\text{NO}_3^- < 10^{-2}$  mol/L is with all probability to be ascribed to some small amount of protonizable impurity in the organic phase. Such an effect would occur just for the least competing cation and its least concentration in the aqueous phase.

Cross check of the suitable concentration ranges is that of the influence of the  $\text{Cs}^+\text{B}^-$  salt in the organic phase on  $\log K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  values. The result is depicted in Figure 3. Rather unexpectedly there is practically no influence of the  $\text{Cs}^+\text{B}^-$  concentration.

The last final check consisted in using cesium salt of brominated dicarbolide  $\text{Cs}^+\text{BBr}_6^-$  instead of  $\text{Cs}^+\text{B}^-$ . In the case of full dissociation in the organic phase, the constants  $K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  ought to be independent of the type of the hydrophobic anion. This is really the case, and both series for each individual anion are practically identical and could be plotted together in Figure 4. The statistics of such common data (standard deviations of the intercept were calculated using Excel Data Analysis macro) is given in Table 1. The average standard deviation of the thermodynamic values of exchange constants



**Figure 3.** Logarithmic values of extraction exchange constants  $\log K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  for the system water–1-nitropropane. Initial concentration of  $\text{M}^+\text{NO}_3^-$  in the aqueous phase was 0.1 mol/L,  $t = 25 \pm 0.1$  °C. Dashed line denotes the concentration of  $\text{Cs}^+\text{B}^-$  used mostly in this paper.



**Figure 4.** Logarithmic values of extraction exchange constants  $\log K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  for the system water–1-nitropropane. Aqueous phase was corresponding  $\text{M}^+\text{NO}_3^-$  salt. Initial concentration of  $\text{Cs}^+\text{B}^-$  or  $\text{Cs}^+\text{Br}_6^-$  in the organic phase was  $5 \cdot 10^{-3}$  mol/L,  $t = 25 \pm 0.1$  °C. The results for two anions are merged into single lines.

expressed in kJ/mol is only  $\pm 0.13$ , thus lower than that of assembly of electrochemical methods as discussed below. However, it must be kept in mind that this particular system behaves almost ideally; the obtained straight lines in Figure 4 are very regular and  $K_{\text{exch}}^*(\text{Cs}^+/\text{M}^+)$  are practically independent of the ionic strength of the aqueous phase.

*o-Nitrophenyloctyl Ether, NPOE.* This is a very important solvent used both in electrochemistry (ITIES, ion selective electrodes (ISE)) and extraction chemistry. Its practical advantages are very low solubility in water and supposedly lower toxicity in comparison with highly toxic nitrobenzene. Its low vapor pressure allows construction of time stable ISEs. Its dielectric constant is  $\epsilon = 24.2$  at 25 °C,<sup>21</sup> hence it is still a highly dissociating solvent. Reported solubility of water in the solvent at 25 °C is 0.046 mol/L.<sup>21</sup> In two studies, it has been shown that PVC contained in the membrane phase has no practical effect on the relative magnitude of  $\Delta_i G^{\circ,*}(i)$ .<sup>22,23</sup>

$\Delta_i G^{\circ,*}(i)$  values derived from measured  $\Delta_a^{\circ}\varphi^{\circ,*}(i)$  for  $i$  = alkali metal cations, ammonium, and proton were published in several electrochemical studies, the references to which are given in Table 2. In calculating the averages in the Table, the data with membranes were not used, and if the same value is reported by the original author and in the database of Girault, both values were used for the average (double weight for successively tabulated value by another author). The averages are compared with our own values referred to the average value of  $\Delta_i G^{\circ,*}(\text{Cs}^+)$  from the electrochemical measurements, namely  $\Delta_i G^{\circ,*}(\text{Cs}^+) = 22.9$  kJ/mol.



**TABLE 1: Extraction Exchange Constants  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for Transfers into 1-Nitropropane, 1-Octanol, and DOS with CsB and CsBBR<sub>6</sub> at  $25 \pm 0.1$  °C<sup>a</sup>**

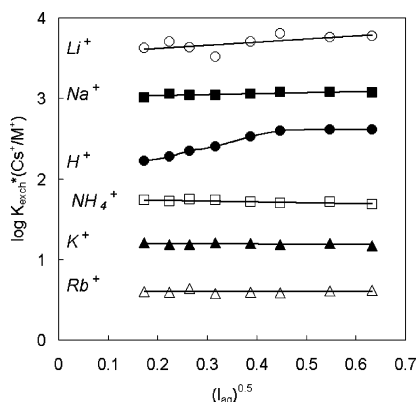
system	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	H <sup>+</sup>
1-nitropropane <sup>b</sup>	3.69 ± 0.03	2.89 ± 0.02	1.11 ± 0.03	0.57 ± 0.02	1.73 ± 0.01	2.52 ± 0.03
1-octanol	−0.02 ± 0.03	0.20 ± 0.02	0.15 ± 0.03	0.14 ± 0.02	−0.40 ± 0.03	−1.46 ± 0.09
DOS, CsB <sup>c,d</sup>	2.25 ± 0.18	1.91 ± 0.11	0.66 ± 0.15	0.21	0.98 ± 0.01	1.61 ± 0.02
DOS, CsBBR <sub>6</sub> <sup>e</sup>	1.95 ± 0.05	1.56 ± 0.01	0.82 ± 0.02	0.56 ± 0.04	0.95 ± 0.06	1.02 ± 0.01

<sup>a</sup> Standard deviations are those of intercepts of the plots of  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  vs  $(I_{\text{aq}})^{0.5}$  if not stated otherwise. <sup>b</sup> From series with Cs<sup>+</sup>B<sup>−</sup> and Cs<sup>+</sup>BBR<sub>6</sub><sup>−</sup> put together. <sup>c</sup> At  $25 \pm 1$  °C, average for three different aqueous media (MCl, MNO<sub>3</sub>, and M<sub>2</sub>SO<sub>4</sub>) and standard deviation of that average. <sup>d</sup> Log  $K_{\text{exch}}^{\circ,*}(\text{CsB}/\text{M}^+)$  values. <sup>e</sup> Log  $K_{\text{exch}}^{\circ,*}(\text{CsBBR}_6/\text{M}^+)$  values.

**TABLE 2:  $\Delta_r G^{\circ,*}(i)$  Data for Transfer of Alkali Metal Cations, Ammonium, and Proton from Water into *o*-Nitrophenyloctyl Ether at 25 °C, kJ/mol**

ion	this paper <sup>a</sup>	Ulmeanu et al. <sup>b</sup>	other electrochemical data	electrochemical average	PVC electrode with NPOE plasticizer <sup>i</sup>	calculated values <sup>k</sup>
Li <sup>+</sup>	43.5; ±0.23	47.1	47.08 <sup>c</sup> , 46.5 <sup>g</sup>	46.9; ±0.34	42.3; 47 <sup>j</sup>	
Na <sup>+</sup>	40; ±0.17	38.5	36.3 <sup>d</sup> , 36.3 <sup>h</sup>	37.0; ±1.27	40.0	42
K <sup>+</sup>	29.7; ±0.06	31.4	32.8 <sup>e</sup> , 32.8 <sup>h</sup>	32.3; ±0.81	28.6	27
Rb <sup>+</sup>	26.3; n/a			n/a	26.3	24
Cs <sup>+</sup>	22.9; n/a		23 <sup>f</sup> , 21 <sup>h</sup> , 23 <sup>h</sup> , 24.4 <sup>h</sup>	22.9; ±1.40	22.9	23
NH <sub>4</sub> <sup>+</sup>	32.7; ±0.23	32.1		32.1; n/a	32.6	
H <sup>+</sup>	34.4; ±1.40	44.2		44.2; n/a		

<sup>a</sup> Average values from measurements from Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, and NO<sub>3</sub><sup>−</sup> media at  $25 \pm 1$  °C, referred to the value  $\Delta_r G^{\circ,*}(\text{Cs}^+) = 22.9$  kJ/mol, the second entry in this column gives standard deviation of respective value  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for the above three media expressed in kJ/mol. <sup>b</sup> Ref 16. <sup>c</sup> Ref 22. <sup>d</sup> Ref 24. <sup>e</sup> Ref 22. <sup>f</sup> Ref 21. <sup>g</sup> Ref 22. <sup>h</sup> Ref 25. <sup>i</sup> Ref 26; selectivity calculated from selectivity electrochemical coefficient  $\log K^{\text{Pot}}_{\text{Na,M}}$  after conversion to  $K(\text{Cs}^+/\text{M}^+)$  and referred to  $\Delta_r G^{\circ,*}(\text{Cs}^+) = 22.9$  kJ/mol, the values were read off from Figure 1 of the reference. <sup>j</sup> Ref 22. <sup>k</sup> Ref. 27 calculation performed according to supplement information to that article by previously derived algorithm of calculation in which both Born terms and Hildebrand solubility parameters were used (Baes C. F., Jr.; Moyer B. A. *J. Phys. Chem. B*, **1997**, *101*, 6566).



**Figure 5.** Logarithmic values of extraction exchange constants  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for the system water–*o*-nitrophenyloctyl ether. Aqueous phase was corresponding  $\text{M}^+\text{NO}_3^-$  salt. Initial concentration of  $\text{Cs}^+\text{B}^-$  in the organic phase was  $5 \cdot 10^{-3}$  mol/L,  $t = 25 \pm 1$  °C.

The standard deviations of the measurements were evaluated from the mean value of three determined  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for respective alkali metal nitrates (Figure 5), chlorides, and sulfates, respectively.

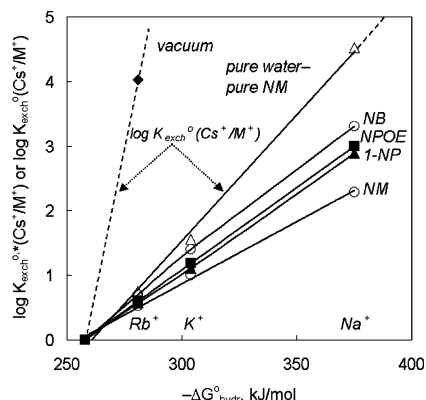
Inspections of Table 2 show limited agreement of extraction and mean electrochemical constants, with the exception of the proton for which the difference attains 10 kJ/mol. The overall precision of extraction results attains some  $\pm 0.2$  kJ/mol (with exception of H<sup>+</sup>), whereas mean values from electrochemical measurements do not exceed a precision of  $\pm 1$  kJ/mol. The obtained extraction results are corroborated by almost complete agreement with electrochemical values obtained with PVC membrane.<sup>26</sup> Calculated values in a paper<sup>27</sup> reasonably agree with the extraction data.

**Evaluation of Data for Nitrosolvents.** With two new nitrosolvents, 1-nitropropane, 1-NP, and NPOE, and older data for nitrobenzene<sup>13</sup> and transfer data for pure system water–nitromethane, NM, and mutually saturated water–nitromethane,<sup>28</sup> the repertory of these solvents enables comparisons in this

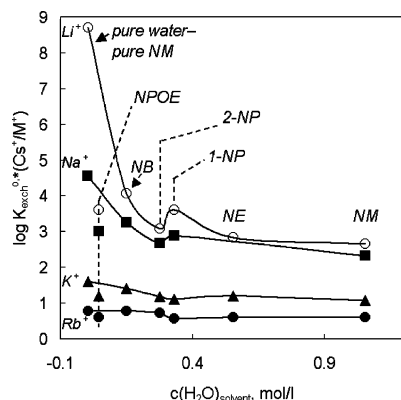
family. Also used are our own former data on selectivities obtained with dipicrylamine anion for nitroethane, NE, and 2-nitropropane, 2-NP.<sup>29</sup> Literature donor numbers, DN, for these solvents are limited to nitrobenzene (DN = 4.4 or  $8.1 \pm 0.7$  kcal/mol) and nitromethane (DN = 2.7 kcal/mol).<sup>30</sup> Reported solubility of water in solvents at 25 °C is for 2-NP, 0.277 mol/L, for NE, 0.555 mol/L, and for NM, 1.055 mol/L.<sup>31</sup> For the solubility of water in nitrobenzene, we used a previous value (0.15 M at 20 °C).<sup>29</sup> The dielectric constants at 25 °C of the solvents are as follows: NM, 36.562; NE, 28.29; 1-NP, 23.73; 2-NP, 25.654; NB, 34.809.<sup>19</sup> Abraham's hydrogen bond basicity indexes  $\beta$ , which correlate rather well with DNs, can be used as a provisional measure of the solvent solvation ability. The respective literature values are NB, 0.28; 2-NP, 0.33; 1-NP, 0.31; NE, 0.33; NM, 0.31.<sup>19</sup>

At first, we plotted the thermodynamic extraction exchange constants  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  against standard Gibbs energies of hydration,  $\Delta G_{\text{hydr}}^{\circ}$  of respective ions.<sup>32</sup> The results plotted in Figure 6 show that, in all cases, a good linearity is observed.<sup>33</sup> The straight line for the transfer into vacuum (obtained from the respective differences of  $\Delta G_{\text{hydr}}^{\circ}$  values recalculated into  $K_{\text{exch}}^{\circ}(\text{Cs}^+/\text{M}^+)$ ) give the maximum selectivity that could be obtained if the accepting phase has no solvating power. The straight-line dependences corroborate results of our previous paper<sup>12</sup> in which the causal origin in the behavior of particular solvate clusters copying the overall solvation energy was discussed. The character of dependences in Figure 6 allows still another point of view. The selectivity in a particular water–solvent system is proportionally decreased by some constant  $\gamma$ ,  $\alpha_{\text{real}} = \gamma \cdot \alpha_{\text{vacuum}}$ , as compared to the water–vacuum system. The highest value of  $\gamma$  for pure NM and pure water amounts only to  $\gamma = 22.6\%$  of expected maximum selectivity.

Particularly, it must be noted that, for a system of pure NM and water, the linearity extends even for the  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{Li}^+)$  constant, thus the system closely resembles that of no solvating power at all. In all other cases, there is a relative decrease of  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{Li}^+)$  as compared with given straight lines. This



**Figure 6.** Logarithmic values of thermodynamic extraction exchange constants  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  or  $K_{\text{exch}}^{\circ}(\text{Cs}^+/\text{M}^+)$  for water–nitrosolvent systems plotted against the standard Gibbs energies of hydration  $\Delta G_{\text{hydr}}^{\circ}$  of individual alkali metal cations. See text.

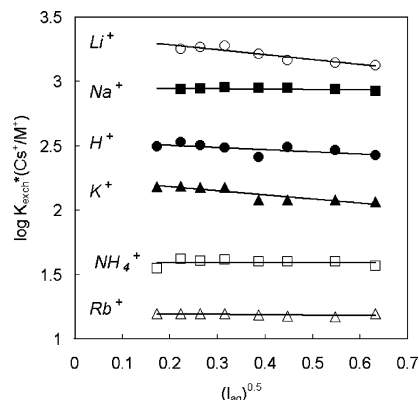


**Figure 7.** Dependence of  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for the family of nitrosolvents on the equilibrium solubility of water in the solvent.

enhanced relative affinity of  $\text{Li}^+$  toward the organic phase thus suggests that the dissolved water in organic phase might be the main responsible effect for the family of nitrosolvents.

This effect is better seen from Figure 7, in which the selectivity constants were plotted against the water content of the organic solvent. We used our former data from the paper,<sup>29</sup> in which the alkali metal dipicrylaminates were used and NPOE and 1-NP were not studied. In contrast to previous work, the dependences become more involved. NPOE is clearly out of the trend; this can be explained by the presence of strong donor  $-\text{O}-$  group in it. If the contributions from  $\text{NO}_2$  and  $-\text{O}-$  are additive, then a strong donor group must lead to the decrease of the selectivity of the molecule of solvent with otherwise lower donicity than water.<sup>12,13</sup> The reversal of the behavior of 1-NP and 2-NP is now not clear, and more conclusive results with dicarbollide anion are perhaps needed for 2-NP.

It might be argued that the proposed correlation is not well-founded because different solvents with differing solvation power might be concerned. However, on the basis of the present knowledge, we believe that the overall tendency in Figure 7 is significant. No other meaningful correlation with two other parameters, namely dielectric constant  $\epsilon$  or hydrogen bond basicity parameter  $\beta$  can be found. The  $\beta$  values of concerned solvents differ very slightly, corroborating that idea that, in these systems, the  $\text{NO}_2$  group solvation ability is nearly the same, disregarding the rest of the molecule. For the sake of completeness, it must be said that the influence of solvent dissolved at equilibrium water might also play a role. This effect seems to not be studied from the times of the now already classical paper<sup>28</sup> of Haugen and Friedman.



**Figure 8.** Logarithmic values of extraction exchange constants  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for the system water–1,2-dichloroethane. Aqueous phase was corresponding  $\text{M}^+\text{NO}_3^-$  salt. Initial concentration of  $\text{Cs}^+\text{BBR}_6^-$  in the organic phase was  $2.24 \cdot 10^{-3}$  mol/L,  $t = 25 \pm 1$  °C.

Nonzero effects were found for nitromethane dissolved in water. However, these were much smaller than the reverse effects of water dissolved in nitromethane. Because the solubility of all other solvents in water must be still lower, we can neglect the effect in the first approximation.

In summary, Figure 7 shows that already a small amount of water in the solvent leads to the resolution gain in the organic phase, the biggest one being observed for the  $\text{Li}^+$  ion, which is the most hydrated. The data might be rather well expressed also in the form of straight lines if  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  are plotted against  $\log c(\text{H}_2\text{O})_{\text{solvent}}$  (not shown, the correlation parameters  $R^2$  are 0.964 and 0.974 for  $\text{Cs}^+/\text{Li}^+$  and  $\text{Cs}^+/\text{Na}^+$  exchange, respectively).

**1,2-Dichloroethane, DCIE.** Besides nitrobenzene and NPOE, DCIE belongs to the often-studied systems by voltammetry at ITIES. One extraction study was done with the solvent, aimed at practical separations of  $^{137}\text{Cs}$  from acidic solutions by cobalt bis(dicarbollides).<sup>34</sup> More hydrophobic anion  $\text{BBR}_6^-$  instead of  $\text{B}^-$  had to be used, and the practical selectivities had been shown to be very similar to the nitrobenzene solvent.

The solvent is of low basicity ( $\text{DN} = 0$  by definition,<sup>30</sup>  $\beta = 0.11^{19}$ ), its dielectric constant is around  $\epsilon = 10.3$  ( $10.125^{19}$ ,  $10.36^{21}$  at 25 °C), hence the solvent is at the border between dissociating and not dissociating solvents, but  $\text{Cs}^+\text{BBR}_6^-$  is at the used experimental low concentration apparently fully dissociated there.<sup>35</sup> The equilibrium solubility of water in DCIE is 0.11 mol/L at 25 °C,<sup>21</sup> very similar to nitrobenzene.

In this study, we examined the extraction with nitrate salts and temperature  $25 \pm 1$  °C. The results are shown in Figure 8 and Table 1. Because  $\text{Cs}^+\text{B}^-$  was only sparingly soluble in the solvent, we used  $\text{Cs}^+\text{BBR}_6^-$  at concentration  $2.24 \cdot 10^{-3}$  mol/L. Obtained data are collected together with the literature electrochemical values in Table 3. Some other literature data do not at all conform to the range of values in Table 3 and were consequently not used.<sup>36</sup> When calculating the average, a double weight was given to results that appeared three times, as an original paper, Girault's database, and the review article of the same author (Samec), or the following article (Shao).

Again, limited agreement is seen between extraction and electrochemical results, with higher precision of the former. It is interesting to see that electrochemical results see no discrimination between transfers of  $\text{Li}^+$  and  $\text{Na}^+$  cations into DCIE, whereas the discrimination between  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  is larger than that for extraction data. But the extraction data for all alkali cations fall into the range of uncertainties of electrochemical data, hence these trends appear as artifacts.

**TABLE 3:  $\Delta_r G^{\circ,*}(i)$  Data for Transfer of Alkali Metal Cations, Ammonium, and Proton from Water into 1,2-dichloroethane at 25 °C, kJ/mol**

ion	this paper <sup>a</sup>	Ulmeanu et al. <sup>b</sup>	Sabela Samec <sup>c</sup>	Yoshida Shao <sup>f</sup>	other electrochemical data <sup>k</sup>	electrochemical average
Li <sup>+</sup>	54.1; $\pm 0.16$	58.8	57 <sup>e</sup>	63 <sup>e</sup> , 55.6 <sup>f</sup>	48.4 <sup>g</sup>	56; $\pm 4.4$
Na <sup>+</sup>	51.7; $\pm 0.06$	59.3	57 <sup>e</sup>	63.9 <sup>e</sup> , 55.9 <sup>f</sup>	63.9 <sup>h</sup> , 48.7 <sup>g</sup> , 47.7 <sup>i</sup>	56.6; $\pm 5.7$
K <sup>+</sup>	47.7; $\pm 0.15$	51.5	50 <sup>e</sup>	58.5 <sup>e</sup> , 51.9 <sup>f</sup>	49 <sup>d</sup> , 47.7 <sup>g</sup>	50.9; $\pm 3.9$
Rb <sup>+</sup>	41.8; $\pm 0.04$		42 <sup>d</sup>	51.8 <sup>e</sup> , 45.8 <sup>f</sup>	38.6 <sup>g</sup> , 41.4 <sup>i</sup> , 50 <sup>j</sup>	44.7; $\pm 4.5$
Cs <sup>+</sup>	34.9; n/a		35 <sup>d</sup>	37.2 <sup>f</sup>	30.1 <sup>g</sup> , 37.3 <sup>g</sup> , 34.7 <sup>i</sup> , 37.3 <sup>f</sup>	34.9; $\pm 2.6$
NH <sub>4</sub> <sup>+</sup>	44; $\pm 0.15$	51				51
H <sup>+</sup>	49.4; $\pm 0.18$	56.4	53 <sup>c</sup>	53 <sup>e</sup>		53.7; $\pm 1.5$

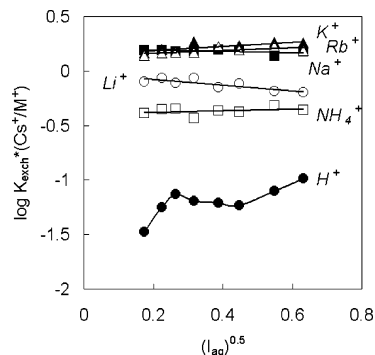
<sup>a</sup> Average values from measurements from NO<sub>3</sub><sup>−</sup> media at 25  $\pm$  1 °C, referred to the value  $\Delta_r G^{\circ,*}(\text{Cs}^+) = 34.9$  kJ/mol. The second entry in this column gives standard deviation of respective value  $K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  as intercept standard deviation expressed in kJ/mol. <sup>b</sup> Ref 16. <sup>c</sup> Ref. 37. <sup>d</sup> Ref. 38. <sup>e</sup> Ref. 39. <sup>f</sup> Ref. 40. <sup>g</sup> Ref. 41. <sup>h</sup> Ref. 42. <sup>i</sup> Ref. 43. <sup>j</sup> Ref. 44. <sup>k</sup> Ref 25.

The values of  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for DCIE are plotted against respective  $\Delta_r G_{\text{hydr}}^{\circ}$  in Figure 10. It is seen that, again, a straight line will pass through the data for Cs<sup>+</sup>, Rb<sup>+</sup>, and K<sup>+</sup>, and relative decrease is observed for Li<sup>+</sup>, but here also for Na<sup>+</sup>. In this respect, the solvent does not behave as nitrosolvents. With all probability, the effect is again connected with the presence of water in the solvent and relative increase of affinity of Li<sup>+</sup> and Na<sup>+</sup> ions toward the water-rich organic phase. The larger effect of dissolved water can be explained by much higher overall energies of transfer of alkali metal cations from water into DCIE than into nitrosolvents ( $\Delta_r G^{\circ,*}$  of Na<sup>+</sup> ion is 34.3 for nitrobenzene,<sup>13</sup> 40 for NPOE, but 51.7 for DCIE, in kJ/mol).

The slope of the straight line connecting points for Cs<sup>+</sup>, Rb<sup>+</sup>, and K<sup>+</sup> in Figure 10 is nearly a perfect straight line with slope 0.048, which is still higher than that for the system of pure water—pure nitromethane.<sup>45</sup> This is to be expected due to the still lower basicity and solvating power of DCIE in comparison with nitrosolvents.

**1-Octanol.** This is an important solvent, both for its biomimetic properties,<sup>46</sup> as well as because the solvent is widely used in organic chemistry and pharmacology, with the partition coefficients  $\log P_{\text{oct}}$  being one of the key descriptors in QSAR studies.<sup>10</sup> Its dielectric constant is moderate,  $\epsilon = 9.8629$  at 25 °C.<sup>19</sup> Its basicity is not exactly known; we have used in our previous paper the mean values for MeOH, EtOH, PrOH, and BuOH the following values of DN: 19.6, 19.9, 22.1, and 20.7, respectively.<sup>12</sup> From these, the extrapolation for 1-octanol cannot be done, but with all probability the DN of 1-octanol must be very close to the value for water. The Abraham's hydrogen bond basicity descriptor is 0.48.<sup>19</sup> The solubility of water in it is high, 2.6256 mol/L at 25 °C.<sup>47</sup> It is argued that, in 1-octanol saturated with water, for every 100 molecules of 1-octanol, 38 water molecules are present, thus rendering the solvent rather hydrophilic.<sup>48</sup> In recent studies of water-saturated 1-octanol performed by various diffraction methods, the existence of "water pockets" on a scale smaller than mesoscopic was detected and described as "molecular confinement".<sup>46</sup> What happens with these pockets in the presence of small ions was not studied, but certainly they would be disrupted, since otherwise there would be no selectivity of transfers at all.

Assignment of individual transfer  $\Delta_r G^{\circ,*}$ 's for simple ions was performed by several authors but without a conclusive result. Scholz used for the estimate of  $\Delta_r G^{\circ,*}$ 's of halide anions an extrapolation method, in which a function of the number of C atoms is needed.<sup>49</sup> However, the literature data are available only for MeOH, EtOH, PrOH, and BuOH, hence the extrapolation is too long and strongly dependent on the particular function chosen for the extrapolation. In another publication,<sup>48</sup> the similarity between the transfers of anions from water to DCIE

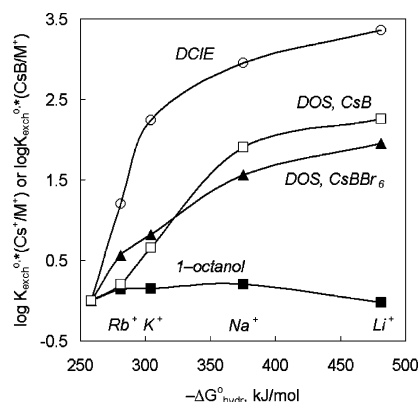


**Figure 9.** Logarithmic values of extraction exchange constants  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for the system water–1-octanol. Aqueous phase was corresponding  $\text{M}^+\text{NO}_3^-$  salt. Initial concentration of  $\text{Cs}^+\text{B}^-$  in the organic phase was  $3 \cdot 10^{-3}$  mol/L,  $t = 25 \pm 1$  °C.

and 1-octanol was used as a criterion. The numerical values of the two methods are in good accord, namely  $\Delta_r G^{\circ,*}$ 's (water–1-octanol) = 33.6 kJ/mol for Br<sup>−</sup> by the first method and 36 kJ/mol by the second. But Abraham gives this anionic value as  $\Delta_r G^{\circ,*}$ 's (water–1-octanol) = 21.6 kJ/mol, again obtained partly by extrapolation and partly based on the fact that the transfers of NaCl and KCl are numerically very close for the water–PrOH “dry” system and 1-octanol “wet” systems.<sup>10</sup>

For alkali metal cations and 1-octanol, Abraham gives the values of  $\Delta_r G^{\circ,*}$ 's (cation/ $\Delta_r G^{\circ,*}$  in kJ/mol) as Li<sup>+</sup>/14.3, Na<sup>+</sup>/17.4, K<sup>+</sup>/18.1. The range of these values, 3.8 kJ/mol is, however, larger than what could be deduced from the paper of Ohde et al.<sup>15</sup> These authors had measured the formal (TPHAs TPhB assumption referred) potentials corresponding to the standard distribution potentials of ions, assuming no ionic association in the organic phase. Under that provision, the values of  $\Delta_r G^{\circ,*}$ 's (water–1-octanol) would be (cation/ $\Delta_r G^{\circ,*}$ ' in kJ/mol): Li<sup>+</sup>/8.7, Na<sup>+</sup>/6.7, K<sup>+</sup>/7.7, Rb<sup>+</sup>/0, Cs<sup>+</sup>/0. Thus the span of Li<sup>+</sup> to K<sup>+</sup> value is only 1 kJ/mol and also absolute values are lower than the former results.

The values measured in this study are plotted in Figure 9 and constants are given in Table 1. It is seen that the differences between Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> are really very small, but we believe they were correctly measured. Thus, from our measurements under the provisional assumption that, for Cs<sup>+</sup> ion  $\Delta_r G^{\circ,*}$ 's (water–1-octanol) = 0, the following scale originates: (cation/ $\Delta_r G^{\circ,*}$  in kJ/mol): Li<sup>+</sup>/−0.14, Na<sup>+</sup>/1.16, K<sup>+</sup>/0.87, Rb<sup>+</sup>/0.79, Cs<sup>+</sup>/0. The values in our standard view are shown in Figure 10. The values in fact form a curve with a minimum affinity for 1-octanol displayed by Na<sup>+</sup> and K<sup>+</sup> cations. The curve can be considered as ascending for K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, which are supposed to be essentially not hydrated in 1-octanol. This again might be expressed as a straight line of very low slope,<sup>50</sup> 1-octanol being thus very similar to water, as



**Figure 10.** Thermodynamic extraction exchange constants  $\log K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+)$  for 1,2-dichloroethane and 1-octanol and  $\log K_{\text{exch}}^{\circ,*}(\text{CsB}/\text{M}^+)$  for dioctyl sebacate with CsB or CsBBr<sub>6</sub> at 25 °C.

can be expected from its basicity and solvating power, but still a little less basic than water. The second part of the curve reflects excessive hydration in the water-rich organic phase and facilitated transfer of Li<sup>+</sup>, which has in this case even higher affinity for the organic phase than all other alkali metal cations.

**Dioctyl Sebacate, DOS.** This is another solvent largely used in ISEs aimed at measurements of cation concentrations, e.g.,<sup>51</sup> its selectivity in the absence of any cation complex-forming agent was measured for alkali metal cations.<sup>26</sup> The selectivity span is much lower than that for NPOE, and reported values read from Figure 1 of ref 26 are about  $\log K^{\text{pot}}_{\text{Na,M}} = 0.4$  for Cs<sup>+</sup> and as low as ca.  $-0.05$  for Li<sup>+</sup>. Solvent, in its mixture with *n*-dodecane, was also successfully used for the extraction of radioactive <sup>137</sup>Cs with dicarbollide anion.<sup>18</sup> It is essentially a nonpolar solvent with  $\epsilon = 4.01$  at 25 °C.<sup>52</sup> Zero conductivity of Cs<sup>+</sup>B<sup>−</sup> determined in our work is in accord with low  $\epsilon$  of the solvent. Basicity of DOS and water solubility in DOS were not found.

Because of nonconductivity of the organic phase, no electrochemical measurements can be done and the  $K_{\text{exch}}^{\circ,*}(\text{CsB}/\text{M}^+)$  and  $K_{\text{exch}}^{\circ,*}(\text{CsB}/\text{M}^+)$  can be obtained only by the extraction method. This is, to our knowledge, a new area of research.

We tested the extraction of Cs<sup>+</sup> both with CsB and CsBBr<sub>6</sub>. Typical plots of  $\log K_{\text{exch}}^{\circ,*}(\text{CsB}/\text{M}^+)$  on ionic strength of the aqueous phase were obtained as in Figure 9, and from them, the magnitudes of  $K_{\text{exch}}^{\circ,*}(\text{CsB}/\text{M}^+)$  were extrapolated (Table 1). However, in contrast to 1-nitropropane, now the resulting selectivities are dependent on the kind of the anion in the system (Figure 10). This may be supposed because nondissociated ion pairs are possibly extracted and the properties of them will differ from the properties of bare ions.

The character of the lines and their intersection can be explained from the sizes of the ion pairs and their solvations. Both ion pairs with BBr<sub>6</sub> (NaBBr<sub>6</sub> and CsBBr<sub>6</sub>) are more voluminous than their counterparts with the nonsubstituted B anion. We suppose further that the solvation shell around Na and Cs in the ion pair is proportionally attenuated, but of the same structure, in the ion pair compared with bare cation. Now for the situation of CsX exchanging with LiX or NaX, which are supposedly hydrated in organic phase, the relative change of properties upon hydration will be more pronounced for LiB than for LiBBr<sub>6</sub> due to the smaller size of the former ion pair. Thus, the LiBBr<sub>6</sub> will be more strongly expelled from the aqueous phase than LiB, which is the actual case. The situation is analogical but reverse for the case of nonhydrated ion pairs, like in the exchange of CsX for KX or RbX. Thus, in this picture, the intersection of the lines in Figure 10 is connected

with the shift of the solvation state with reference to the state in which both hydration and solvation play their roles. Further experiments are needed in order to prove this effect.

## Conclusions

A newly used extraction method for the determination of the selectivity of the mutually saturated water-immiscible solvent systems permits us to arrive at precise values of these constants.

One of the aim of the present paper was to ascertain our previous findings<sup>12</sup> about the linearities of  $\Delta_r G^{\circ,*}(\text{M}^+)$  values on respective  $\Delta_r G_{\text{hydr}}^{\circ}(\text{M}^+)$ 's. This empirical rule works well for either four cations Cs<sup>+</sup>, Rb<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> (nitrosolvents), or for three cations Cs<sup>+</sup>, Rb<sup>+</sup>, and K<sup>+</sup> (1,2-dichloroethane, and 1-octanol), and can be used as a normalizing function for newly determined  $\Delta_r G^{\circ,*}(\text{M}^+)$  values.<sup>13</sup> The anomalies for Li<sup>+</sup> and, to lesser extent for Na<sup>+</sup> can be accounted for by excessive hydration of these ions in the water-rich organic phases. However, more quantitative treatment of the latter effect could be done only after more reliable absolute  $\Delta_r G^{\circ,*}(\text{M}^+)$ 's are obtained.

As supposed in our previous paper,<sup>12</sup> the slopes of the straight lines plotted in Figures 6 and 10 are positive. This is because all the studied solvents are less basic than water. The only dubious case of 1-octanol, for which a donor number DN is not exactly known,<sup>12</sup> may be connected to the fact that water-saturated 1-octanol is very slightly less basic than water.

We plan in our forthcoming studies to broaden the repertoire of the solvents to more basic and water-immiscible solvents and also to the study of the selectivity of alkaline earth cations.

## Appendix

In the treatment of experimental data, we used a relation that was previously derived from mass balances of ions before and after extraction.<sup>14</sup> More rigorous derivation for the case of complete dissociation is given here. Full dissociation in the aqueous phase is supposed for all cases.

Two extraction constants for Cs<sup>+</sup> and M<sup>+</sup> ions are defined as follows, equating activities with concentrations:

$$K_{\text{Cs}} = [\text{Cs}^+]_o [\text{B}^-]_o / [\text{Cs}^+]_a [\text{B}^-]_a \text{ and } K_{\text{M}} = \frac{[\text{M}^+]_o [\text{B}^-]_o}{[\text{M}^+]_a [\text{B}^-]_a} \quad (1\text{A})$$

from which:

$$K_{\text{exch}}^{\circ,*}(\text{Cs}^+/\text{M}^+) = K_{\text{Cs}}/K_{\text{M}} = \frac{[\text{Cs}^+]_o [\text{M}^+]_a}{[\text{Cs}^+]_a [\text{M}^+]_o} \quad (2\text{A})$$

Electroneutrality in the organic phase is conserved:

$$[\text{Cs}^+]_o + [\text{M}^+]_o = [\text{B}^-]_o \quad (3\text{A})$$

Expressing from the extraction constants, the relation can be written:

$$[\text{B}^-]_o = K_{\text{Cs}}[\text{Cs}^+]_a [\text{B}^-]_a + K_{\text{M}}[\text{M}^+]_a [\text{B}^-]_a \quad (4\text{A})$$

or

$$D_{\text{B}} = [\text{B}^-]_o / [\text{B}^-]_a = \frac{1}{\sqrt{(K_{\text{Cs}}[\text{Cs}^+]_a + K_{\text{M}}[\text{M}^+]_a)(D_{\text{B}} + 1)/c_{\text{B}}^{\circ}}} \quad (5\text{A})$$

which for  $D_{\text{B}} \gg 1$  yields:



$$D_B = (K_{Cs}[Cs^+]_a + K_M[M^+]_a)/c_B^o \quad (6A)$$

where  $c_B^o$  denotes the initial concentration of  $Cs^+B^-$  in the organic phase.

Further, we use the notation  $c_{Cs}^o (= c_B^o)$  and  $c_M^o$ , which is total concentration of the salt  $M^+NO_3^-$  added initially into the aqueous phase.

Now, after using  $[Cs^+]_a = c_{Cs}^o/(D_{Cs} + 1)$ ,  $[M^+]_a = c_M^o/(D_M + 1)$ , which are valid for equal volumes of aqueous and organic phase and  $K_{exch}^*(Cs^+/M^+)$  (extraction exchange constant)  $= D_{Cs}/D_M$  we obtain:

$$c_{Cs}^o[D_{Cs} + K_{exch}(Cs^+/M^+)]/D_{Cs} = c_{Cs}^o[D_{Cs} + K_{exch}(Cs^+/M^+)]/(D_{Cs} + 1) + c_M^o \quad (7A)$$

and after rearrangements we get:

$$K_{exch}^*(Cs^+/M^+) = \frac{c_M^o D_{Cs}(D_{Cs} + 1)}{c_{Cs}^o} - D_{Cs} = D_{Cs} \left[ \frac{c_M^o(D_{Cs} + 1)}{c_{Cs}^o} - 1 \right] \quad (8A)$$

which is the same formula as that was used before.<sup>13,53</sup>

For the case of complete association in the organic phase, we have extraction constants in the form:

$$K_{CsB} = [CsB]_o/[Cs^+]_a[B^-]_a \quad \text{and} \quad K_{MB} = [MB]_o/[M^+]_a[B^-]_a \quad (9A)$$

from which:

$$K_{exch}^*(CsB/M^+) = K_{CsB}/K_{MB} = \frac{[M^+]_a[CsB]_o/[MB]_o[Cs^+]_a}{[M^+]_a[CsB]_o/[MB]_o[Cs^+]_a} \quad (10A)$$

The derivation is analogical as in the previous case, using instead of  $c_{Cs}^o$  a term  $c_{CsB}^o$ . The derivation in this case does not develop from electroneutrality in the organic phase, but rather from mass balance there. Calculation of  $K_{exch}^*(CsB/M^+)$  from experimental data is done by the eq 8A, provided that  $D_B \gg 1$  and using  $c_{CsB}^o$  instead of  $c_{Cs}^o$ . Care should be taken to have in all cases the first term in brackets on right-hand side of eq 8A much higher than 1 to guarantee the precision of calculated values.

**Acknowledgment.** Present research was supported by Czech Grant Agency, no. 104/05/2667 and we appreciate this support.

**Note Added in Proof.** New results for  $K_{exch}^*(Cs^+/M^+)$  for 2-nitropropane system with  $B^-$  anion and accordingly modified Figure 7 are given as Supporting Information.

**Supporting Information Available:** Results for  $K_{exch}^*(Cs^+/M^+)$  for 2-nitropropane system with  $B^-$  anion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Rais, J.; Selucký, P.; Kyrš, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1376.
- (2) Samec, Z. *Pure Appl. Chem.* **2004**, *76*, 2147.
- (3) Bakker, E.; Bühlman, P.; Pretsch, E. *Talanta* **2004**, *63*, 2004.
- (4) Schamberger, J.; Clarke, R. J. *Biophys. J.* **2002**, *82*, 2002.
- (5) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997; *Electrochim. Acta* **1998**, *44*, 91.
- (6) Baes, C. F., Jr.; Moyer, B. A. *J. Phys. Chem. B* **1997**, *101*, 6566.
- (7) Fawcett, W. R. *Mol. Phys.* **1998**, *95*, 507.

- (8) Moyer, B. A.; Sun, Y. In *Ion Exchange and Solvent Extraction*; Marinsky, J. A., Marcus, Y., Eds.; Marcel Dekker: New York, 1997; Vol. 13.
- (9) Abraham, M. H.; Zhao, Y. H. *J. Org. Chem.* **2004**, *69*, 4677. Interestingly, this same author (M.H.A.) some 25 years ago developed a model based on a modified two-layer Born model (*J. Chem. Soc., Faraday Trans. 1*, **1978**, *74*, 1604, 2858), from which a newer model of ref 8 evolved.
- (10) Zhao, Y. H.; Abraham, M. H. *J. Org. Chem.* **2005**, *70*, 2633.
- (11) Gritzner, G. *Electrochim. Acta* **1998**, *44*, 73.
- (12) Rais, J.; Okada, T. *J. Phys. Chem. A* **2000**, *104*, 7314.
- (13) Rais, J. In *Ion Exchange and Solvent Extraction*; Marcus, Y., SenGupta, A. K., Eds.; Marcel Dekker: New York, 2004; Vol. 17.
- (14) Rais, J.; Selucký, P.; Kyrš, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1376. Rais, J.; Selucký, P.; Kyrš, M.; Kadlecová, L. *J. Radioanal. Nucl. Chem.* **1993**, *27*, 1347.
- (15) Ohde, H.; Uehara, A.; Yoshida, Y.; Maeda, K.; Kihara, S. *J. Electroanal. Chem.* **2001**, *496*, 110.
- (16) Ulmeanu, S. M.; Jensen, H.; Samec, Z.; Bouchard, G.; Carrupt, P. A.; Girault, H. H. *J. Electroanal. Chem.* **2002**, *530*, 10.
- (17) Rais, J.; Grüner, B. In *Ion Exchange and Solvent Extraction*; Marcus, Y., SenGupta, A. K., Eds.; Marcel Dekker: New York, 2004; Vol. 17.
- (18) Rais, J.; Šístková, N.; Alexová, J. unpublished results.
- (19) Winget, P.; Dolney, D. M.; Giesen, D. J.; Cramer, C. H.; Truhlar, D. G. *Minnesota Solvent Descriptor Database*. <http://comp.chem.umn.edu/solvation/mnsddb.pdf> (last accessed Dec 2005).
- (20) IUPAC–NIST Solubility Database NIST Standard Reference Database 106, online ed. [http://srdata.nist.gov/solubility/sol\\_detail.asp?sys\\_ID=77\\_136](http://srdata.nist.gov/solubility/sol_detail.asp?sys_ID=77_136) (last accessed Dec 2005).
- (21) Samec, Z.; Langmaier, J.; Trojáněk, A. *J. Electroanal. Chem.* **1996**, *409*, 1.
- (22) Langmaier, J.; Stejskalová, K.; Samec, Z. *J. Electroanal. Chem.* **2001**, *496*, 143.
- (23) Rais, J.; Mason, C. V.; Abney, K. D. *Sep. Sci. Technology*, **1997**, *32*, 951.
- (24) Chrisstoffels, L. A. J.; de Jong, F.; Reinhoudt, D. N. *Chem.–Eur. J.* **2000**, *6*, 1376.
- (25) Girault, H. H. *Electrochemical Online Database*. <http://serveur-isic.epfl.ch/labo/girault/cgi/DB/InterrDB.pl> (last accessed December 2005).
- (26) Sakaki, T.; Harada, T.; Kawahara, Y.; Shinkai, S. *J. Inclusion Phenom.* **1994**, *17*, 377.
- (27) Levitskaia, T. G.; Macdonald, D. M.; Lamb, J. D.; Moyer, B. A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1481.
- (28) Haugen, G. R.; Friedman, H. L. *J. Phys. Chem.* **1968**, *72*, 4549.
- (29) Selucký, P.; Rais, J.; Krtíl, J. *International Solvent Extraction Conference*; The Hague, 1971; paper 79, p 14.
- (30) Abboud, J. L. M.; Notario, R. *Pure Appl. Chem.* **1999**, *71*, 645.
- (31) IUPAC–NIST Solubility Database NIST Standard Reference Database 106, online edition. [http://srdata.nist.gov/solubility/sol\\_detail.asp?sys\\_ID=77\\_146](http://srdata.nist.gov/solubility/sol_detail.asp?sys_ID=77_146), [http://srdata.nist.gov/solubility/sol\\_detail.asp?sys\\_ID=77\\_1](http://srdata.nist.gov/solubility/sol_detail.asp?sys_ID=77_1), respectively (last accessed Dec 2005).
- (32) Marcus, Y. *Ion Solvation*; John Wiley: Chichester, 1985.
- (33) The parameters of the straight lines in Figure 6 are as follows (slope, intercept,  $R^2$ ): vacuum, 0.1751, −45.18, 1; pure NM, 0.0395, −10.30, 0.9993; NB, 0.0281, −7.21, 0.9989; NPOE, 0.0256, −6.60, 1; 1-NP, 0.0247, −6.38, 0.9999; NM, 0.0193, −4.92, 0.9971.
- (34) Selucký, P.; Rais, J.; Kyrš, M.; Kadlecová, L. *J. Radioanal. Nucl. Chem.* **1991**, *148*, 227.
- (35) The following values (concentration of reagent in water-saturated 1,2-DCIE in mol/L; equivalent conductivity  $\Lambda$  of  $Cs^+B^-$  in  $\Omega^{-1}cm^2val^{-1}$ ; equivalent conductivity  $\Lambda$  of  $Cs^+BBr^-$  in  $\Omega^{-1}cm^2val^{-1}$  at  $25 \pm 1$  °C) were obtained: 0.0006; 115; 225, 0.0008; 104; 225, 0.001; 97; 202, 0.002; 67, 172. About twice higher conductivity of the brominated than of nonhalogenated derivative is spectacular. When the specific conductivity of the solution was plotted against the concentration, in both cases, straight lines were obtained and we suppose that  $Cs^+BBr^-$  is under the experimental conditions fully dissociated in water-saturated 1,2-DCIE.
- (36) Abraham and Zhao in their two recent papers give the values for  $\Delta G^{\circ,*}$  from water to DCIE as (ion/ $\Delta G^{\circ,*}$  in kJ/mol):  $Li^+/27$ ,  $Na^+/25$ ,  $K^+/26$ ,  $Rb^+/25$ , and  $Cs^+/24$ . Marcus gives for transfer of  $H^+$  2 kJ/mol in ref 5, which is largely an outlier value (based according to the references in ref 5 on two older papers: Kihara, S.; Suzuki, M.; Maeda, K.; Ogura, K.; Umetani, S.; Matsui, M.; Yoshida, Z. *Anal. Chem.* **1986**, *58*, 2954 and Kihara, S.; Suzuki, M.; Maeda, K.; Ogura, K.; Matsui, M. *J. Electroanal. Chem.* **1986**, *210*, 147). The values for alkali metal cations of Marcus read in ref 5 as  $Na^+/56$ ,  $K^+/52$ ,  $Rb^+/46$ ,  $Cs^+/37$ . However, in another monograph of the author (Marcus, Y. *Ion Solvation In Liquid–Liquid Interfaces, Theory and Methods*; Volkov, A. G., Deamer, D. W., Eds.; CRC Press: New York, 1996), the values are as follows:  $H^+/56$ ,  $Li^+/56$ ,  $Na^+/52$ ,  $K^+/46$ ,  $Rb^+/37$ . This seems to be a typographical error for alkali metal cations in the latter publication. The former values well agree with the original paper denoted as f in Table 3.



- (37) Sabela, A.; Mareček V.; Samec, Z.; Fuoco, R. *Electrochim. Acta* **1992**, *37*, 231.
- (38) Samec, Z.; Mareček, V.; Colombini, M. P. *J. Electroanal. Chem.* **1988**, *257*, 147.
- (39) Yoshida, Y.; Kihara, S. *Bunseki Kagaku* **2002**, *51*, 1103.
- (40) Zhan, D.; Xiao, Y.; Yuan, Y.; He, Y.; Wua, B.; Shao, Y. *J. Electroanal. Chem.* **2003**, *553*, 43.
- (41) Shao, Y.; Stewart, A. A.; Girault, H. H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2593.
- (42) Yoshida, Y.; Matsui, M.; Shirai, O.; Maeda, K.; Kihara, S. *Anal. Chim. Acta* **1998**, *373*, 213.
- (43) Abraham, M. H.; Danil de Namor, A. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 955–962.
- (44) Kontturi, A. K.; Kontturi, K.; Manzanarez, J. A.; Mafe, S.; Murtomäi, L. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 1131.
- (45) The parameters of the straight line are (slope, intercept,  $R^2$ ): 0.048, –12.566, 0.9984. See note 33 for comparison.
- (46) Sassi, P.; Paolantoni, M.; Cataliotti, R. S.; Palombo, F.; Morresi, A. *J. Phys. Chem. B* **2004**, *108*, 19557.
- (47) Margolis, S. A.; Levenson, M. *Fresenius' J. Anal. Chem.* **2000**, *367*, 1.
- (48) Bouchard, G.; Galland, A.; Carrupt, P.-A.; Gulaboski, R.; Mirčeski, V.; Scholz, F.; Girault, H. H. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3748.
- (49) Scholz, F.; Gulaboski, R. *ChemPhysChem.* **2005**, *6*, 16; Gulaboski, R.; Mirčeski, V.; Scholz, F. *Electrochem. Commun.* **2002**, *4*, 277.
- (50) The parameters of the straight line are (slope, intercept,  $R^2$ ): 0.0007, –0.0556, 0.9982. See notes 33 and 45 for comparison.
- (51) Bedlechowicz, I.; Maj-Zurawska, M.; Sokalski, T.; Hulanicki, A. *J. Electroanal. Chem.* **2002**, *537*, 111.
- (52) *Handbook of Chemistry and Physics*, 84th ed.; Lide, D. R. Ed.; CRC Press: New York, 2003.
- (53) There is a typographical error in ref 13 on page 346, line 9 from the top. The equation containing on both sides  $D_{Cs}$  has on the left-hand side instead of  $D_{Cs}$  correctly  $[Cs^+]_{or}$ .