

EXTRACTION OF ALKALI METAL AND AMMONIUM DIPCRYLAMINATES INTO NITROBENZENE IN THE PRESENCE OF SOME ACYCLIC POLYETHERS

Emanuel MAKRLÍK^{a,*}, Jaroslava HÁLOVÁ^b and Petr VAŇURA^c

^a *Motorlet, 158 01 Prague 5*

^b *Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 250 68 Řež*

^c *Department of Analytical Chemistry,
Prague Institute of Chemical Technology, 166 28, Prague 6*

Received January 17, 1991

Accepted April 28, 1991

The effect of the presence of six different acyclic polyethers (2-glym, 3-glym, 4-glym, PEG 200, PEG 300 and PEG 400), denoted by L, on the distribution of alkali metal dipicrylamines and ammonium dipicrylaminate (MA) between the aqueous and nitrobenzene phases has been studied. The two-phase system can be quantitatively described by the following five chemical equilibria: $M_a^+ + A_a^- + L_o \rightleftharpoons ML_a^+ + A_a^-$, $M_a^+ + A_a^- \rightleftharpoons M_o^+ + A_o^-$, $MLA_o \rightleftharpoons ML_o^+ + A_o^-$, $MA_o \rightleftharpoons M_o^+ + A_o^-$, $L_a \rightleftharpoons L_o$, for which the respective equilibrium constants $K_{ex}(ML^+, A^-)$, $K_{ex}(M^+, A^-)$, $K_d^0(MLA)$, $K_d^0(MA)$ and K_D were determined. The values of $K_{ex}(ML^+, A^-)$ increase with the increasing crystallographic radius of the M^+ ion and with the number of oxyethylene units in the molecule of the ligand, L, in the series 2-glym < 3-glym < 4-glym < PEG 200 < PEG 300 < PEG 400. In addition, it has been demonstrated that the stability of the ML_o^+ species in the nitrobenzene phase has a maximum value for $M^+ = Na^+$ for all the studied ligands. The presence of the polyethers is detrimental to the separation of Cs^+ from the other cations, but improves the separation of Na^+ from Li^+ . The extraction selectivities for the K^+/NH_4^+ , K^+/Li^+ and NH_4^+/Li^+ pairs was not significantly affected by the presence of the ligands, except for 2-glym.

An earlier paper¹ described the rather large synergic effect of polyethylene glycols on the extraction of alkaline earth cations into nitrobenzene in the presence of a number of hydrophobic anions. A model was proposed for the Sr^{2+} extraction to quantitatively explain the maximum on the dependence of the logarithm of the Sr^{2+} distribution ratio on the logarithm of the initial concentration of polyethylene glycol with a mean molecular weight of 400 in the aqueous phase².

This paper describes a study of the distribution of alkali metal and ammonium dipicrylamines in the presence of some acyclic polyethers in the two-phase water–nitrobenzene system and represents a continuation of the study of the extraction

* Present address: 341 42 Kolinec 250.

of pure alkali metal dipicrylamines in the water–nitrobenzene system³; simultaneously, it is a contribution to the study of the interactions of cations with neutral ligands in a nonaqueous solvent.

EXPERIMENTAL

Chemicals

Nitrobenzene (analytical grade, Lachema, Brno, Czechoslovakia) was used without further purification. The studied dipicrylamines were prepared by dissolving dipicrylamine (Koch–Light, Great Britain) in an aqueous solution of the given alkali metal hydroxide or NH_3 , with subsequent crystallization³. The polyethylene glycols PEG 200, PEG 300 and PEG 400 (where the numbers denote the mean molecular weights) and di-, tri-, and tetraethylene glycol dimethyl ethers (denoted here as 2-glym, 3-glym and 4-glym, respectively)* were also supplied by Koch–Light. All the other reagents (with the exception of the radionuclides) were the products of Lachema, Brno. The radionuclides ^{137}Cs , ^{86}Rb and ^{133}Ba , supplied by the Nuclear Research Institute (Swierk, Poland), were of standard radiochemical purity.

Procedures and Apparatus

Dipicrylamines were extracted in glass test tubes using a ratio of the aqueous to the nitrobenzene phase (V_a/V_o) of 1 : 9. The alkali metal hydroxide concentration employed ($3 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$) in the initial aqueous phase (for the NH_4^+ cation, the initial aqueous phase contained $3 \cdot 10^{-3} \text{ mol l}^{-1} \text{ NH}_3$ and $2.8 \cdot 10^{-3} \text{ mol l}^{-1} \text{ NH}_4\text{NO}_3$) hindered the formation of dipicrylamine and simultaneously ensured approximately constant ionic strength of the aqueous phase. The initial dipicrylamine concentration in the organic phase, c_A , varied from $1 \cdot 10^{-3}$ to $3 \cdot 10^{-2} \text{ mol l}^{-1}$ and the analogous quantity value for the acyclic polyether ligands in the aqueous phase, c_L , varied from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-2} \text{ mol l}^{-1}$.

The time required for establishment of equilibrium under these experimental conditions and at a temperature of $25 \pm 2^\circ\text{C}$ was not greater than 15 min; nonetheless, the solutions were shaken for 1 h in test tubes closed by polyethylene stoppers using a laboratory shaker ZK III (Chirana, Czechoslovakia).

The equilibrium concentrations of the dipicrylamine anion $[\text{A}^-]_a$ in the aqueous phase were determined spectrophotometrically (VSU-VIS, Carl Zeiss, Jena, Germany) using a 1 cm quartz cuvette and a calibration graph for the concentration range $0 - 5 \cdot 10^{-5} \text{ mol l}^{-1}$, measured at a wavelength of 425 nm; the distribution ratios of this anion, D_A , were then calculated using the relationship $D_A = c_A/[\text{A}^-]_a - V_a/V_o$, where the symbols V_a and V_o correspond to the volumes of the aqueous and organic phases, respectively. The concentrations $[\text{M}^+]_a$ were obtained from the equation $[\text{M}^+]_a = [\text{A}^-]_a + [\text{OH}^-]_a$ (and for solutions containing the ammonium ion $[\text{NH}_4^+]_a = [\text{A}^-]_a + [\text{OH}^-]_a + [\text{NO}_3^-]_a$), similarly as in ref.³.

The equilibrium distribution of the ligand, L, required for the evaluation of the distribution constant $K_D = [\text{L}]_o/[\text{L}]_a$ between the nitrobenzene and aqueous phases, was determined from the calibration curve for the dependence of the distribution ratio of microamounts of ^{133}Ba

* According to IUPAC nomenclature, the compound with the trivial name tetraethylene glycol dimethyl ether is correctly named 2,5,8,11,14-pentaoxapentadecane.

on the initial concentration c_L in the water–nitrobenzene– H^+ $[(B_9C_2H_{11})_2Co]^-$ –L–Ba system, similarly as in ref.¹.

The γ -activities of the aqueous and nitrobenzene samples were measured using an NaI(Tl) detector in combination with the NK 350/A gamma analyzer (Gamma, Budapest, Hungary).

RESULTS AND DISCUSSION

Interpretation of the experimental data indicated that the extraction equilibria in the test systems can best be described by assuming the presence of the following species: M_a^+ , A_a^- , M_o^+ , A_o^- , MA_o and MLA_o , where a and o refer to the aqueous and organic phases, respectively, and M^+ , A^- and L correspond to the univalent cation, dipicrylaminate anion and polyether ligand, respectively.

The concentrations $[MA]_a$, $[MLA]_a$ and $[ML^+]_a$ could be neglected as a consequence of the low values of the association constants of the alkali metal dipicrylamines⁴ and the stability constants of the complexes of the alkali metal cations with linear polyethers in water^{5,6}. The presence of electroneutral nondissociated dipicrylamine (HA) was suppressed by maintaining the pH of the aqueous phase above 10 in all the experiments.

Figure 1 depicts the equilibrium distribution of ammonium dipicrylaminate in the presence of polyethylene glycol PEG 200. The extraction curves for all the other cations and ligands have an analogous shape and are thus not presented. The distribution ratios D_A increase in all the systems with increasing content of acyclic ligand under otherwise constant conditions and also with decreasing initial concentration of the given dipicrylaminate MA ($M^+ = Li^+, Na^+, NH_4^+, K^+$) in the organic phase at a constant initial ligand concentration c_L in the aqueous phase.

The following equilibria (A)–(E) and the corresponding equilibrium constants (1)–(5) were employed for quantitative description of the system.

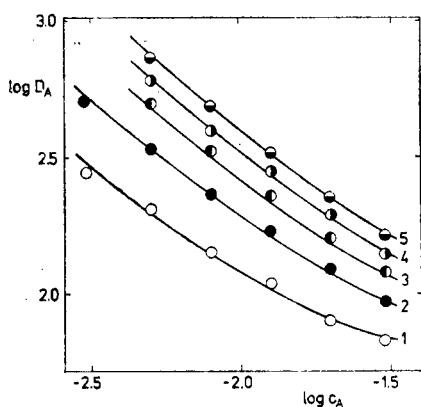
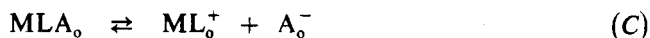
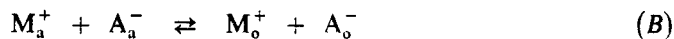
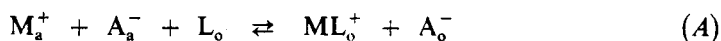


FIG. 1

Extraction of ammonium dipicrylaminate into nitrobenzene in the presence of PEG 200. $V_a/V_o = 9$; $c_{NH_3} = 3 \cdot 10^{-3} \text{ mol l}^{-1}$ and $c_{NH_4NO_3} = 2.8 \cdot 10^{-3} \text{ mol l}^{-1}$ in the initial aqueous phase; c_L in mol l^{-1} : 1 0; 2 $5 \cdot 10^{-3}$; 3 $1 \cdot 10^{-2}$; 4 $1.5 \cdot 10^{-2}$; 5 $2 \cdot 10^{-2}$. The curves were calculated: 1 by the method given in ref.³; 2–5 from Eqs (11) and (13)–(19) using the constants given in Tables I and II



$$K_{ex}(ML^+, A^-) = [ML^+]_o [A^-]_o / [M^+]_a [A^-]_a [L]_o \quad (1)$$

$$K_{ex}(M^+, A^-) = [M^+]_o [A^-]_o / [M^+]_a [A^-]_a \quad (2)$$

$$K_d^0(MLA) = [ML^+]_o [A^-]_o / [MLA]_o \quad (3)$$

$$K_d^0(MA) = [M^+]_o [A^-]_o / [MA]_o \quad (4)$$

$$K_D = [L]_o / [L]_a \quad (5)$$

Reactions (B) and (D) are important in the extraction of alkali metal dipicrylamines in the absence of the ligand and the corresponding equilibrium constants $K_{ex}(M^+, A^-)$ and $K_d^0(MA)$ have already been determined for some ionic strengths in the aqueous phase³. In this study, the values of $K_{ex}(M^+, A^-)$ and $K_d^0(MA)$ and the K_D values for the individual ligands (Table I) were determined as described in refs^{1,3}.

The formation of ML_2^+ cations (and, in general, of all other species ML_n^+ , $n > 2$) was neglected as inclusion of these species decreased the agreement between the

TABLE I

Equilibrium extraction constants $K_{ex}(M^+, A^-)$ and $K_{ex}(ML^+, A^-)$, dissociation constants $K_d^0(MA)$ and distribution constants K_D

| M ⁺ | log $K_{ex}(M^+, A^-)$ ^a | p $K_d^0(MA)$ ^a | log $K_{ex}(ML^+, A^-)$ ^b | | | | | |
|------------------------------|-------------------------------------|----------------------------|--------------------------------------|----------|----------|------------------------|------------------------|------------------------|
| | | | 2-glym | 3-glym | 4-glym | PEG 200 | PEG 300 | PEG 400 |
| Li ⁺ | 0.16 | 1.43 | 3.50(17) ^c | 4.01(33) | 4.47(29) | 5.52(26) | 6.29(18) | 6.75(16) |
| Na ⁺ | 1.00 | 1.32 | 4.42(24) | 5.06(22) | 6.12(18) | 6.98(30) | 7.83(25) | 8.37(20) |
| NH ₄ ⁺ | 2.41 | 1.43 | 5.36(15) | 6.07(13) | 6.67(11) | 7.47(21) | 8.50(16) | 9.08(14) |
| K ⁺ | 2.97 | 1.29 | 5.77(12) | 6.55(11) | 7.33(8) | 8.06(16) | 9.08(12) | 9.76(7) |
| Rb ⁺ | 3.72 | 1.30 | 6.45(10) | 7.14(9) | 7.40(9) | 8.70(8) | 9.30(10) | 9.85(8) |
| Cs ⁺ | 4.41 | 1.31 | 6.80(8) | 7.26(8) | 7.47(8) | 9.27(8) | 9.45(8) | 9.90(8) |
| K_D ^d | — | — | 0.25 | 0.30 | 0.45 | 1.6 · 10 ⁻³ | 1.5 · 10 ⁻³ | 1.3 · 10 ⁻³ |

^a Determined as described in ref.³; ^b calculated by the nonlinear regression using Eqs (11) and (13)–(19) for Li⁺, Na⁺, NH₄⁺, K⁺, or Eq. (22) for Rb⁺, Cs⁺; ^c the number of experimental points in parentheses; ^d determined as described in ref.¹.

theory and experimental results. The presence of a single type of complex species, ML^+ , was also demonstrated for the other solvents^{5,6} studied elsewhere.

The distribution ratio of dipicrylaminat in the presence of the ligand L (at $pH > 10$) is then given by the equation

$$D_A = ([A^-]_o + [MLA]_o + [MA]_o)/[A^-]_a \quad (6)$$

Simultaneously, for neutrality of the electric charges in the organic phase,

$$[ML^+]_o + [M^+]_o = [A^-]_o \quad (7)$$

It follows from Eq. (7) and definitions (1) and (2) that

$$[A^-]_o/[A^-]_a = \{[M^+]_a [K_{ex}(ML^+, A^-) [L]_o + K_{ex}(M^+, A^-)]/[A^-]_a\}^{1/2} \quad (8)$$

and, from definitions (1) and (3) that

$$[MLA]_o/[A^-]_a = K_{ex}(ML^+, A^-) [M^+]_a [L]_o/K_d^0(MLA), \quad (9)$$

while, analogously from Eqs (2) and (4),

$$[MA]_o/[A^-]_a = K_{ex}(M^+, A^-) [M^+]_a/K_d^0(MA). \quad (10)$$

Combination of Eqs (6), (8), (9) and (10) yields an expression for D_A :

$$D_A = \{[M^+]_a [K_{ex}(ML^+, A^-) [L]_o + K_{ex}(M^+, A^-)]/[A^-]_a\}^{1/2} + K_{ex}(ML^+, A^-) [M^+]_a [L]_o/K_d^0(MLA) + K_{ex}(M^+, A^-) [M^+]_a/K_d^0(MA). \quad (11)$$

The mass balance of the ligand L can be expressed by the relationship

$$m = V_o([L]_o + [ML^+]_o + [MLA]_o) + V_a[L]_a, \quad (12)$$

where $m = V_a c_L$.

The equilibrium concentration $[L]_o$ can be obtained from Eqs (1)–(12) by simple algebra:

$$[L]_o = (CF + GH)/(DG - CE), \quad (13)$$

where C, D, E, F, G and H are defined by the following equations:

$$C = r(V_o + V_o r[A^-]_a^2 + V_a/K_D), \quad (14)$$

$$D = mr + V_o D_A + V_o K_{ex}(ML^+, A^-) [M^+]_a + V_o r[A^-]_a D_A + V_a D_A/K_D - V_o s - V_o r s[A^-]_a - V_a s/K_D, \quad (15)$$

$$E = K_{\text{ex}}(\text{ML}^+, \text{A}^-) [\text{M}^+]_{\text{a}} + 2rD_{\text{A}}[\text{A}^-]_{\text{a}} - 2rs[\text{A}^-]_{\text{a}}, \quad (16)$$

$$F = K_{\text{ex}}(\text{M}^+, \text{A}^-) [\text{M}^+]_{\text{a}} + 2sD_{\text{A}}[\text{A}^-]_{\text{a}} - s^2[\text{A}^-]_{\text{a}} - D_{\text{A}}^2[\text{A}^-]_{\text{a}}, \quad (17)$$

$$G = r^2[\text{A}^-]_{\text{a}}, \quad (18)$$

$$H = m(D_{\text{A}} - s), \quad (19)$$

where $r = K_{\text{ex}}(\text{ML}^+, \text{A}^-) [\text{M}^+]_{\text{a}}/K_{\text{d}}^0(\text{MLA})$ and $s = K_{\text{ex}}(\text{M}^+, \text{A}^-) [\text{M}^+]_{\text{a}}/K_{\text{d}}^0(\text{MA})$.

Substituting expression (13) for $[\text{L}]_{\text{o}}$ and employing Eqs (11) and (15–19) yields the final expression for the evaluation of the constants $K_{\text{ex}}(\text{ML}^+, \text{A}^-)$ and $K_{\text{d}}^0(\text{MLA})$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{NH}_4^+, \text{K}^+$) by the method of nonlinear regression using a program on the EC 1040 computer (Tables I and II).

The above method could not be used for the determination of the constants $K_{\text{ex}}(\text{ML}^+, \text{A}^-)$ and $K_{\text{d}}^0(\text{MLA})$ for Cs^+ and Rb^+ because the very low concentrations of $[\text{A}^-]_{\text{a}}$ could not be determined spectrophotometrically. Consequently, traces of ^{137}Cs (or ^{86}Rb) were added to the systems together with a macroamount of NaA, used to determine $K_{\text{ex}}(\text{NaL}^+, \text{A}^-)$ and $K_{\text{d}}^0(\text{NaLA})$, and the distribution ratios

$$D_{\text{Cs}} = ([\text{Cs}^+]_{\text{o}} + [\text{CsA}]_{\text{o}} + [\text{CsL}^+]_{\text{o}} + [\text{CsLA}]_{\text{o}})/[\text{Cs}^+]_{\text{a}} \quad (20)$$

were measured in this modified system.

Relationship (20) can be rewritten using definitions (1)–(4) for $\text{M}^+ = \text{Cs}^+$:

$$[\text{A}^-]_{\text{o}} \{ D_{\text{Cs}}/[\text{A}^-]_{\text{a}} - K_{\text{ex}}(\text{Cs}^+, \text{A}^-)/[\text{A}^-]_{\text{o}} - K_{\text{ex}}(\text{Cs}^+, \text{A}^-)/K_{\text{d}}^0(\text{CsA}) \} / \\ / [\text{L}]_{\text{o}} = K_{\text{ex}}(\text{CsL}^+, \text{A}^-) + K_{\text{ex}}(\text{CsL}^+, \text{A}^-) [\text{A}^-]_{\text{o}}/K_{\text{d}}^0(\text{CsLA}). \quad (21)$$

TABLE II
Dissociation constants $K_{\text{d}}^0(\text{MLA})$

| M ⁺ | log $K_{\text{d}}^0(\text{MLA})^a$ | | | | | |
|------------------------------|------------------------------------|---------|---------|---------|---------|---------|
| | 2-glym | 3-glym | 4-glym | PEG 200 | PEG 300 | PEG 400 |
| Li ⁺ | 0.5(17) ^b | 1.2(33) | 1.3(29) | 0.5(26) | 0.6(18) | 1.5(16) |
| Na ⁺ | 0.7(24) | 1.1(22) | 1.6(18) | 0.7(30) | 1.4(25) | 1.6(20) |
| NH ₄ ⁺ | 0.6(15) | 1.4(13) | 1.6(11) | 0.6(21) | 1.4(16) | 1.6(14) |
| K ⁺ | 1.2(12) | 1.3(11) | 1.7(8) | 1.3(16) | 1.4(12) | 1.5(7) |

^a Calculated by the nonlinear regression using Eqs (11) and (13)–(19); ^b the number of experimental points in parentheses.

Assuming that microamounts of cesium have no effect on the equilibrium distribution in the original system containing a macroamount of NaA, the concentrations $[A^-]_o$ and $[L]_o$ in Eq. (21) can be evaluated using Eqs (8) and (13)–(19). If the left-hand side of Eq. (21) is denoted as y and $[A^-]_o$ as x , then Eq. (21) becomes an analytical expression for a straight line with an intercept on the y -axis equal to $K_{ex}(CsL^+, A^-)$ and with the slope $K_{ex}(CsL^+, A^-)/K_d^o(CsLA)$. However, considering that $[A^-]_o < c_A$ at $c_A = 1 \cdot 10^{-3} - 3 \cdot 10^{-2} \text{ mol l}^{-1}$ (where the upper limit is given by the solubility) and also assuming that the values of $K_d^o(CsLA)$ do not differ substantially from the values of $K_d^o(MLA)$ given in Table II, the term $K_{ex}(CsL^+, A^-) \cdot [A^-]_o/K_d^o(CsLA)$ on the right-hand side of Eq. (21) is roughly 2–4 orders of magnitude smaller than the required value of $K_{ex}(CsL^+, A^-)$. It thus follows that it is experimentally not possible to determine $K_d^o(CsLA)$ on the basis of Eq. (21). The determination of this value using a different experimental technique was not attempted here.

The values of the constants $K_{ex}(CsL^+, A^-)$ were therefore calculated using the expression

$$K_{ex}(CsL^+, A^-) = [A^-]_o \{ D_{Cs}[A^-]_a - K_{ex}(Cs^+, A^-)/[A^-]_o - K_{ex}(Cs^+, A^-)/K_d^o(CsA) \} / [L]_o \quad (22)$$

that can be obtained from Eq. (21) by neglecting the term $K_{ex}(CsL^+, A^-) \cdot [A^-]_o/K_d^o(CsLA)$, which is fully justified. The constants $K_{ex}(RbL^+, A^-)$ were determined by a completely analogous procedure – see Table I.

It can be seen from Table I that the values of $K_{ex}(ML^+, A^-)$ for nitrobenzene saturated with water increase from Li^+ to Cs^+ for all the ligands, while a maximum in these constants was observed in dichloromethane for $M^+ = Rb^+$ and for some linear polyoxyethylene compounds (ref.⁷). The values of $K_{ex}(ML^+, A^-)$ increase for an arbitrary cation in the series 2-glym < 3-glym < 4-glym < PEG 200 < PEG 300 < PEG 400.

The increase in the dissociation constants $K_d^o(MLA)$ with an increase in the number of oxyethylene units in both the glym and PEG groups for all the cations in the series Li^+ , Na^+ , NH_4^+ , K^+ by roughly 2–3 orders of magnitude compared with $K_d^o(MA)$ (see Tables I and II) is most probably a result of the screening of the positive charge of the alkali metal cation by the ligand and also of the decrease in the tendency to stronger interaction between the positive charge of the bulky ML_o^+ cation and the opposite charge of the dipicrylaminate anion when compared with the interaction between the M_o^+ and A_o^- species.

Because of the relatively high values of $K_d^o(MLA)$, the dissociation of the MLA_o species is practically complete in the organic phase so that the concentration $[MLA]_o$ is negligible in comparison with $[ML^+]_o$ and $[A^-]_o$. Consequently, equilibrium (C) can be neglected and the above model is simplified and characterized by equi-

libria (A), (B), (D) and (E) alone. On the basis of this simplified model, the constants $K_{\text{ex}}(\text{ML}^+, \text{A}^-)$ (Table III) were calculated by the method of nonlinear regression using the following relationships (23)–(26).

$$D_A = \{[\text{M}^+]_a [K_{\text{ex}}(\text{ML}^+, \text{A}^-) [\text{L}]_o + K_{\text{ex}}(\text{M}^+, \text{A}^-)] / [\text{A}^-]_a\}^{1/2} + K_{\text{ex}}(\text{M}^+, \text{A}^-) [\text{M}^+]_a / K_d^0(\text{MA}), \quad (23)$$

where

$$[\text{L}]_o = (V_a c_L - V_o R) / (V_o + V_a K_D^{-1}), \quad (24)$$

$$R = S - K_{\text{ex}}(\text{M}^+, \text{A}^-) [\text{M}^+]_a [\text{A}^-]_a / S \quad (25)$$

and

$$S = D_A [\text{A}^-]_a - K_{\text{ex}}(\text{M}^+, \text{A}^-) [\text{M}^+]_a [\text{A}^-]_a / K_d^0(\text{MA}) \quad (26)$$

The values of $\log K_{\text{ex}}(\text{ML}^+, \text{A}^-)$ in Table III calculated by this method are only 0.02 to 0.10 units lower than the corresponding values in Table I. In addition, the differences between the theoretical values of $\log D_A$ calculated assuming partial association of ML_o^+ and A_o^- to form MLA_o and the $\log D_A$ values calculated assuming complete dissociation are negligible, indicating that the undissociated species MLA_o plays a negligible role in the organic phase. The numerical values of the constants $K_d^0(\text{MLA})$ are thus only informative as their estimation is accompanied by a much larger error than the determination of $K_{\text{ex}}(\text{ML}^+, \text{A}^-)$.

To compare the selectivity of the extraction separation of the individual pairs of univalent ions $\text{M}_1^+/\text{M}_2^+$, it is useful to define the extraction exchange constants $K_{\text{M}_2\text{L}}^{\text{M}_1\text{L}} = K_{\text{ex}}(\text{M}_1\text{L}^+, \text{A}^-) / K_{\text{ex}}(\text{M}_2\text{L}^+, \text{A}^-)$, corresponding to the hypothetical reaction

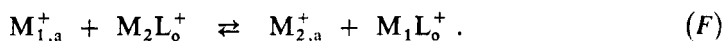


TABLE III
Extraction constants $K_{\text{ex}}(\text{ML}^+, \text{A}^-)$

| M^+ | $\log K_{\text{ex}}(\text{ML}^+, \text{A}^-)^a$ | | | | | |
|-----------------|---|----------|----------|----------|----------|----------|
| | 2-glym | 3-glym | 4-glym | PEG 200 | PEG 300 | PEG 400 |
| Li^+ | 3.46(17) ^b | 3.98(33) | 4.42(29) | 5.49(26) | 6.20(18) | 6.65(16) |
| Na^+ | 4.36(24) | 4.98(22) | 6.03(18) | 6.93(30) | 7.74(25) | 8.31(20) |
| NH_4^+ | 5.32(15) | 6.01(13) | 6.62(11) | 7.45(21) | 8.45(16) | 9.04(14) |
| K^+ | 5.73(12) | 6.52(11) | 7.31(8) | 8.03(16) | 9.05(12) | 9.75(7) |

^a Calculated by the method of nonlinear regression using Eqs (23)–(26); ^b the number of experimental points in parentheses.

The values of $K_{M_2L}^{M_1L}$ express the separation selectivity for the M_1^+/M_2^+ pair for the limiting case when the univalent cations are present in the nitrobenzene phase as the ML_o^+ species alone. Obviously, real extraction systems with sufficiently high c_L values approach this ideal more closely with increasing values of the stability constants of the ML_o^+ species in the organic phase, denoted here as $\beta_o(ML^+)$ (Table IV), for which $\beta_o(ML^+) = K_{ex}(ML^+, A^-)/K_{ex}(M^+, A^-)$. The constants $K_{M_2L}^{M_1L}$ can then be compared with the constants $K_{M_2}^{M_1} = K_{ex}(M_1^+, A^-)/K_{ex}(M_2^+, A^-)$ characterizing the extraction selectivity of the M_1^+/M_2^+ pair in the absence of the ligand, if the formation of the ion associate MA_o is neglected.

It follows from the values given in Table V and Fig. 2 that the separation selectivity of arbitrary pairs Cs^+/M^+ ($M^+ = Li^+, Na^+, NH_4^+, K^+, Rb^+$) in the presence of ligands is always lower than the extraction selectivity for the same pair in the absence of the polyoxyethylene ligand. The extraction selectivities for the K^+/NH_4^+ , K^+/Li^+ and NH_4^+/Li^+ pairs in the presence of the studied ligands (except for 2-glym) are practically identical with the values obtained in the absence of the ligand (because $\beta_o(LiL^+) \approx \beta_o(NH_4L^+) \approx \beta_o(KL^+) -$ cf. Table IV or Figs 3 and 4), while the separation selectivity for the Na^+/Li^+ pair increases in the presence of the ligand with increasing ligand molecular weight in both the glym and the PEG groups.

The dependence of $\log \beta_o(ML^+)$ on the crystallographic radius of the cation exhibits a maximum for all the ligands always for $M^+ = Na^+$ (Table IV, Figs 3 and 4). It follows from the literature data in Table IV that these maxima are apparently typical for the formation of the complexes of alkali metal cations with both acyclic and cyclic polyethers in organic solvents (however, in methanol, the maximum value of $\beta_o(ML^+)$ was found for $M^+ = K^+$ for the ligands in Table IV).

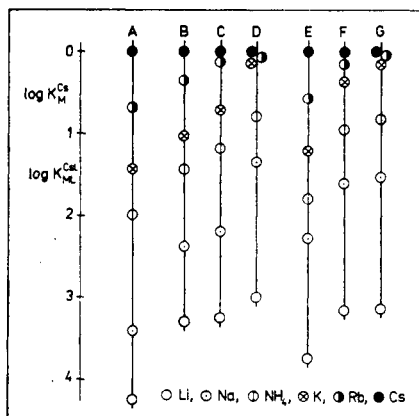


FIG. 2
Selectivities of the extraction separation of Cs^+ from alkali metal and ammonium cations in the presence of acyclic polyethers. A in the absence of the ligand; B 2-glym; C 3-glym; D 4-glym; E PEG 200; F PEG 300; G PEG 400

TABLE IV
Stability constants $\log \beta_0(\text{ML}^+)$ of the complexes of alkali metal cations, H^+ , NH_4^+ and Tl^+ with some polyethers in organic solvents

| Ligand | Nitrobenzene saturated with water | | | | | | | Methanol | | | | |
|---------------------------------|-----------------------------------|---------------|---------------|-----------------|--------------|---------------|----------------------------|---------------|--------------|---------------|---------------|---------------|
| | H^+ | Li^+ | Na^+ | NH_4^+ | K^+ | Rb^+ | Cs^+ | Ligand | | | | |
| | | | | | | | | Na^+ | K^+ | Rb^+ | Cs^+ | Tl^+ |
| 2-glym | — | 3.34 | 3.42 | 2.95 | 2.80 | 2.73 | 2.39 | 1.18 | 1.58 | 1.52 | — | — |
| 3-glym | — | 3.85 | 4.06 | 3.66 | 3.58 | 3.42 | 2.85 | 1.32 | 1.98 | 1.91 | — | — |
| 4-glym | — | 4.31 | 5.12 | 4.26 | 4.36 | 3.68 | 3.06 | 1.57 | 2.47 | 2.36 | — | — |
| PEG 200 | — | 5.36 | 5.98 | 5.06 | 5.09 | 4.98 | 4.86 | 1.87 | 2.70 | — | — | — |
| PEG 300 | — | 6.13 | 6.83 | 6.09 | 6.11 | 5.58 | 5.04 | 1.28 | 1.72 | — | 1.45 | 1.57 |
| PEG 400 | 5.69 ^c | 6.59 | 7.37 | 6.67 | 6.79 | 6.13 | 5.49 | 1.47 | 2.20 | — | 1.85 | 1.90 |
| Dibenzo-18-crown-6 ^d | — | 4.45 | 7.17 | — | 6.89 | 5.78 | { 4.79 4.5 ^e | 1.60 | 2.55 | — | 2.17 | 2.30 |
| | | | | | | | 7-glym ^b | 1.67 | 2.87 | — | 2.41 | 2.55 |

^a $\text{R} = \text{C}_6\text{H}_5$, from ref.⁵; ^b ref. 6; ^c ref. 2; ^d $\log \beta_0(\text{ML}^+)$ calculated using the data published in refs.^{8,9}; ^e ref. 10.

The stability of the ML_0^+ species, which increases with the increasing number of oxyethylene units in the ligand molecule, is clearly connected with the increasing number of the bonding oxygen atoms in the given ligand. However, at the same time it should be noted that the increase in the $\beta_0(ML^+)$ values with the increasing number of $-CH_2CH_2O-$ units in the ligand molecule cannot be a priori extrapolated to a number higher than that given in this study, as the chemical analysis of tetra-

TABLE V
Exchange extraction constants $\log K_{ML}^{CsL}$

| Ligand | $\log K_{LiL}^{CsL}$ | $\log K_{NaL}^{CsL}$ | $\log K_{NH_4L}^{CsL}$ | $\log K_{KL}^{CsL}$ | $\log K_{RbL}^{CsL}$ |
|----------------|----------------------|----------------------|------------------------|---------------------|----------------------|
| — ^a | 4.25 | 3.41 | 2.00 | 1.44 | 0.69 |
| 2-glym | 3.30 | 2.38 | 1.44 | 1.03 | 0.35 |
| 3-glym | 3.25 | 2.20 | 1.19 | 0.71 | 0.12 |
| 4-glym | 3.00 | 1.35 | 0.80 | 0.14 | 0.07 |
| PEG 200 | 3.75 | 2.29 | 1.80 | 1.21 | 0.57 |
| PEG 300 | 3.16 | 1.62 | 0.95 | 0.37 | 0.15 |
| PEG 400 | 3.15 | 1.53 | 0.82 | 0.14 | 0.05 |

• The values of $\log K_M^{Cs}$.

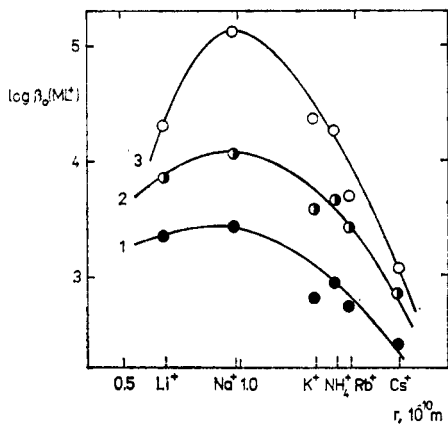


FIG. 3

Dependence of $\log \beta_0(ML^+)$ on the crystallographic radius of the cation. L: 1 2-glym; 2 3-glym; 3 4-glym

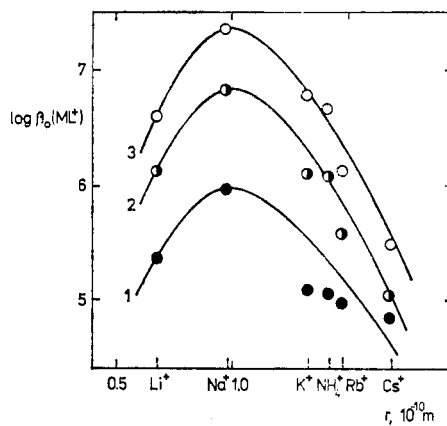


FIG. 4

Dependence of $\log \beta_0(ML^+)$ on the crystallographic radius of the cation. L: 1 PEG 200; 2 PEG 300; 3 PEG 400

phenyl borate salts and the NMR spectra revealed that for the PEG 1 540 ligand, 8.5 oxyethylene units correspond at most to one Na^+ cation¹¹. On the other hand, the extraction of KCNS into dichloromethane increases up to 140 oxyethylene units in the ligand molecule, as found by Yanagida et al.¹².

The almost identical stability of the ML_o^+ complex in the nitrobenzene phase for the Li^+ , NH_4^+ and K^+ cations (except for Li^+ and 2-glym; see Figs 3 and 4 – the maximum difference in the $\log \beta_o(\text{ML}^+)$ values for these three cations does not exceed 0.3) and the relatively low stability of the HL_o^+ species ($\text{L} = \text{PEG 400}$)² compared with that of the LiL_o^+ and NaL_o^+ complexes with the same ligand are rather surprising.

The fact that the stability of the ML_o^+ species with $\text{L} = 4\text{-glym}$ is far less than when $\text{L} = \text{PEG 200}$ (both ligands have approximately the same number of oxyethylene units) can be explained on the basis of the higher basicity of the oxygen atoms bonded to the terminal hydroxyl groups of PEG 200 compared with that of the oxygen in the methoxy groups $-\text{OCH}_3$ of 4-glym and also by the greater steric hindrance of the bulky $-\text{OCH}_3$ groups in comparison with the hydroxyl groups.

It follows from comparison of the $\beta_o(\text{ML}^+)$ values (see Table IV) that the selectivity of the complexation of alkali metal cations with acyclic polyethers in nitrobenzene saturated with water for the Na^+/Li^+ , Na^+/Rb^+ (except for 4-glym) and Na^+/Cs^+ pairs are lower than for dibenzo-18-crown-6. This difference is probably a result of the higher flexibility of the linear polyethers compared with the relatively rigid conformation of dibenzo-18-crown-6. On the other hand, the decrease in the cavity dimensions in the eighteen membered crown ligand as a result of substitution by two benzene rings reduces the favourability of this ligand for complexing the K^+ cation in comparison with the more flexible unsubstituted molecule so that the stability of KL_o^+ is even lower than that of NaL_o^+ (where $\text{L} = \text{dibenzo-18-crown-6}$). Consequently, the complexation selectivity for the Na^+/K^+ pair using dibenzo-18-crown-6 is much lower than that for the acyclic oxyethylene ligands studied here. An analogous effect of benzene substitution in a crown ligand on the selectivity for the Na^+/K^+ pair was found by Hofmanová in acetonitrile medium¹³.

As the formation of the ML^+ complex is assumed to be accompanied by competition for the given cation between the solvent molecules and the ligand bonding sites, the higher basicity of methanol compared with nitrobenzene is the main reason why the stability constants $\beta_o(\text{ML}^+)$ are several orders of magnitude higher in nitrobenzene saturated with water than in methanol.

SYMBOLS

| | |
|--------------|---|
| M^+ | univalent cation (Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+) |
| A^- | dipicrylaminate anion |
| L | polyoxyethylene ligand |
| V_a | volume of the aqueous phase |

| | |
|--|---|
| V_0 | volume of the nitrobenzene phase |
| c_A | initial analytical concentration of the dipicrylaminato anion in the nitrobenzene phase |
| c_L | initial analytical concentration of the polyoxyethylene ligand in the aqueous phase |
| D_A | distribution ratio of the dipicrylaminato anion between the nitrobenzene and aqueous phases |
| D_{Cs} | distribution ratio of Cs^+ between the nitrobenzene and aqueous phases |
| $K_{ex}(M^+, A^-)$ | extraction constant for the dipicrylaminato of a univalent cation, Eq. (2) |
| $K_{ex}(ML^+, A^-)$ | extraction constant for the dipicrylaminato of a univalent cation in the presence of the polyoxyethylene ligand, Eq. (1) |
| $K_d^0(MA)$ | dissociation constant for the MA ion pair in nitrobenzene saturated with water, Eq. (4) |
| $K_d^0(MLA)$ | dissociation constant of the MLA ion pair in nitrobenzene saturated with water, Eq. (3) |
| K_D | distribution constant of the polyoxyethylene ligand in the water-nitrobenzene system, Eq. (5) |
| $\beta_0(ML^+)$ | stability constant of the complex ML^+ cation in the organic solvent |
| $K_{M_2^+L}^{M_1^+} = K_{ex}(M_1^+L^+, A^-)/K_{ex}(M_2^+L^+, A^-)$ | exchange extraction constant characterizing the selectivity of the extraction separation of the M_1^+ and M_2^+ cations in the presence of the polyoxyethylene ligand in the water-nitrobenzene system |
| $K_{M_2^+}^{M_1^+} = K_{ex}(M_1^+, A^-)/K_{ex}(M_2^+, A^-)$ | exchange extraction constant characterizing the selectivity of the extraction separation of the M_1^+ and M_2^+ cations in the water-nitrobenzene system |
| C, D, E, F, G, H, R, S | — notation for algebraic expressions (14)–(19), (25) and (26) in which the symbols m, r and s are defined as follows: $m = V_a c_L$, $r = K_{ex}(ML^+, A^-) \cdot [M^+]_a / K_d^0(MLA)$, $s = K_{ex}(M^+, A^-) [M^+]_a / K_d^0(MA)$ |

REFERENCES

1. Rais J., Šebestová E., Selucký P., Kyrš M.: *J. Inorg. Nucl. Chem.* **38**, 1742 (1976).
2. Vaňura P., Rais J., Selucký P., Kyrš M.: *Collect. Czech. Chem. Commun.* **44**, 167 (1979).
3. Rais J., Kyrš M., Pivoňková M.: *J. Inorg. Nucl. Chem.* **30**, 611 (1968).
4. Rais J., Benešová-Pactlová M., Selucký P., Kyrš M.: *J. Inorg. Nucl. Chem.* **35**, 633 (1973).
5. Favretto L.: *Ann. Chim. (Rome)* **66**, 621 (1976).
6. Chaput O., Jeminet G., Juillard J.: *Can. J. Chem.* **53**, 2240 (1975).
7. Jaber A. M. Y., Moody G. J., Thomas J. D. R.: *J. Inorg. Nucl. Chem.* **39**, 1689 (1977).
8. Danesi P. R., Meider-Goričon H., Chiarizia R., Capuano V., Scibona G.: *J. Inorg. Nucl. Chem.* **37**, 1479 (1975).
9. Rais J.: *Collect. Czech. Chem. Commun.* **36**, 253 (1971).
10. Rais J., Kyrš M., Kadlecová L.: *Proceedings International Solvent Extraction Conference, Lyon, Sept. 1974*. Vol. II, p. 1705.
11. Delduce P. G., Jaber A. M. Y., Moody G. J., Thomas J. D. R.: *J. Inorg. Nucl. Chem.* **40**, 187 (1978).
12. Yanagida S. Y., Takahashi K., Okahara M.: *Bull. Chem. Soc. Jpn.* **50**, 1386 (1977).
13. Hofmanová-Matějková A.: *Thesis*. J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague 1976.

Translation revised by M. Štulíková.