stems from the C–heteroatom distances. In order to appreciate the effect of the presence of a positively charged carbon atom, we listed in Table VIII the C–heteroatom bond lengths of oxo-, thio-, and selenocarbenium ions together with typical single- and double-bond lengths of carbon with each heteroatom. Obviously, we see very significant bond shortening in all three types of carbenium ions. These bond shortenings can be converted into bond–order changes, at least on an approximate level, by means of interpolation on bond length vs. bond order plots, taken as straight lines for simplicity. The results of this procedure are also listed in Table VIII. It is to be noted, however, that because of the small negative slopes in the bond length vs. bond order plots a small variation in bond length gives rise to a large change in bond order, so that the error on the estimated bond orders in Table VIII may be quite important. The following example illustrates this point. In the case of bis(methylthio)benzylcarbenium ion, we determined $C_1^+–S_1$ and $C_1^+–S_2$ distances of 1.68 (1) and 1.67 (1) Å, respectively (Table VII). On the other hand, crystal structures of 1,2-dithiolylium ions have also been determined,[39,40] and the reported C–S bond length in bis(3,5-dimethyl-1,2-dithiolylium) tetrachloroferrate(II)[40] is 1.69 (2) Å, which is nearly identical with the values we found. Yet, the π bond orders are quite different, ~0.50 in our case and 0.67 in 1,2-dithiolylium ion.[39] This difference most certainly arises from the C=S bond length used to assess π bond orders, 1.61 Å in the case of 1,2-dithiolylium ion and 1.54 Å in ours.

Regardless the precise numerical values, inspection of Table VIII leads to the conclusion that the positive charge of the species we examined is efficiently delocalized and nearly to the same extent by both methylthio and methylseleno substituents.

A priori it may seem difficult to admit extensive overlap between the large 4p orbitals of selenium and the 2p orbital of the adjacent positive carbon atom. However, a plausible mechanism for making this overlap operational might be the valence-shell contraction of selenium under the influence of the strong ligand field due to the neighboring positive charge. Such phenomena have often been invoked in the past for the description of bonding in molecules containing third- and fourth-row elements.

Finally, the results we report here have bearing on the question of charge delocalization in species like 1,3-dithiol-2-ylium and 1,3-diselenol-2-ylium ions, which have been the subject of some controversy in recent years. It was indeed suggested[6b,41] for both ions that the whole positive charge resides on the C2 carbon atom with essentially no delocalization into the rest of the systems, the latters having therefore no aromatic character. Our results point to the opposite in accordance with the conclusion arrived at from ^{13}C chemical shift measurements.[42]

Acknowledgment. FNRS (Fonds National de la Recherche Scientifique, Belgium) is gratefully acknowledged for financial support.

Supplementary Material Available: Tables of amplitudes of thermal vibrations, fractional atomic coordinates, equivalent isotropic thermal parameters, and observed and calculated structure factors for **1**, $R = C_6H_5CH_2$, $Y^- = SbCl_6^-$, and its thio analogue (14 pages). Ordering information is given on any current masthead page.

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Affinities of Crown Ethers, Glymes, and Polyamines for Alkali Picrates in Toluene. Application of Polymer-Supported Linear Polyethers

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Received November 21, 1983

Abstract: A scale of relative ligand affinities of crown ethers, linear polyethers (glymes), polyamines, and other cation-binding ligands for lithium and sodium picrate in toluene at 25 °C was obtained. The experimental procedure utilizes solvent-swollen microporous polystyrene resins to which crown ethers or linear polyethers are anchored. The immobilized ligands, N*, are allowed to compete with a soluble ligand, L, for the ionic solute, A^-M^+, according to the reaction $A^-M^+N^* + L \rightleftarrows A^-M^+L + N^*$. The equilibrium constant, *K*, is calculated from the spectrophotometric determination of the soluble ligand–picrate salt complex A^-M^+L. For glymes the *K* values for lithium and sodium picrate rapidly increase up to glyme 5 (tetraethylene glycol dimethyl ether). For longer glymes the increase in *K* is chiefly due to a statistical factor as the number of binding sites increases. On a molar basis long-chain linear polyethers such as carbowax 6000 (134 oxygen atoms) have affinities comparable to those of crown ethers. Measurements of *K* for the same soluble ligand but with different resins afford a comparison of the affinities of immobilized ligands for picrate salts as a function of ligand structure and ligand content of the network. For example, the affinity of a benzo-18-crown-6 containing resin for sodium picrate in toluene exceeds that of a glyme-7 resin with the same ligand content by a factor 265. An increase in ligand content of the resin enhances the *K* for that resin. Measurements were also performed with a transparent, flexible, cross-linked polyacrylate film containing immobilized glyme chains. The implications of our results for phase transfer catalysis reactions are briefly discussed.

We recently demonstrated that crown ethers immobilized on cross-linked polystyrene resins can be used to determine formation constants of complexes between ionic solutes and ion binding ligands in solvents such as tetrahydrofuran or dioxane.[1,2] In the procedure the soluble ligand, L, and the immobilized crown, Cr*, are allowed to compete for the ionic solute according to the reaction

$$A^-M^+Cr^* + L \rightleftarrows A^-M^+L + Cr^* \qquad (1)$$

By using a picrate salt the release of A^-M^+L can be monitored

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spectrophotometrically as a function of the ligand concentration. The constant K thus obtained equals the ratio K_L/K_N, where K_L is the binding constant of A^-M^+ to L and K_N that of A^-M^+ to the resin-bound crown ether. By choosing a combination of crown resin, picrate salt, and solvent for which K_N is known (K_N values have been reported for sodium, potassium, and cesium picrate with five crown ether resins in dioxane and tetrahydrofuran, see ref 3), the formation constants, K_L, of several alkali picrate–crown ether complexes in dioxane were determined.[1,2]

In principle, L may be any kind of ligand capable of forming a complex with the ionic solute employed in reaction 1. However, if the added ligand has a much lower affinity for the solute than the immobilized crown ligand, the large quantity of L needed to release the resin-bound solute may modify the physical properties of the solvent. This is the case when in dioxane or toluene ligands like polyglycol dimethyl ethers (glymes), polyamines (e.g., pentamethyldiethylenetriamin), or dimethyl sulfoxide must compete with a crown-containing resin. Since these ligands are of great interest in many systems where salts of alkali and alkaline earth metals are the active components, we synthesized four oligooxyethylene or glyme-containing networks. With these polymer-supported polyethers the complexing properties of acyclic ligands can be effectively studied by the competition method.

This paper reports the measurements of K values (eq 1) for polyamines, glymes, a few glycols (including that of a long-chain polyethylene glycol, carbowax 6000), and some frequently used cation-binding ligands as complexers of lithium or sodium picrate in toluene as solvent. Since picrate salts are practically insoluble in toluene, no K_N values and, therefore, no K_L values can be obtained in this sovent. However, K values provide us with a relative scale of ligand affinities for these ionic solutes in a hydrocarbon solvent frequently used in phase transfer catalysis reactions. Moreover, K values for different resins obtained with the same soluble ligand provide a comparison of the effectiveness of these resins in binding ionic solutes.

Experimental Section

Materials. Triethylene glycol monomethyl ether (Chemical Samples Co.) and polyethylene glycol monomethyl ether of molecular weight 350 (Union Carbide) were used in the synthesis of four oligooxyethylene (glyme)-containing polystyrene resins. Both compounds were carefully fractionated under vacuum after a 48 h of treatment with activity 4A molecular sieves. The first glycol is pure $CH_3O(CH_2CH_2O)_3H$, while the middle fraction of the second compound yielded on integration of its ^1H NMR spectrum an average composition of $CH_3O(CH_2CH_2O)_6H$ (mol wt 300). A lower boiling fraction gave a compound with composition close to $CH_3O(CH_2CH_2O)_5H$. It was used as a ligand in one of the measurements (see Table II, the ligand glycol 6 monomethyl ether).

Dicyclohexano-18-crown-6, 4′-methylbenzo-18-crown-6, and dimethyldibenzo-18-crown-6 were purified samples obtained commercially or previously synthesized and used in our laboratory.[2] Penta-, hepta-, and nonaethylene glycol dimethyl ether (glyme 6, 8, and 10, respectively, the number following the glyme referring to the number of oxygen atoms in the ligand) were acquired from Parish Chemical Co. and purified by vacuum distillation, the middle fraction being used in the competition experiments. Di-, tri-, tetra-, hexa-, and octaethylene glycol dimethyl ether (glymes 3, 4, 5, 7, and 9, respectively) were commercial or laboratory-synthesized products previously used in experiments with carbanion salts.[4] The pure compounds had been distilled under vacuum from the blue potassium metal–glyme solutions and stored in sealed ampules. Purified samples of tetramethylethylenediamine (TMEDA), pentamethyldiethylenetriamine (PMDTA), hexamethyltriethylenetetramine (HMTTA), and the cyclic ligand tetramethyltetraazacyclotetradecane (TMTCT) were kindly supplied to us by Dr. Michel Fontanille of the University of Paris Nord. Polyethylene glycol 6000 (carbowax 6000, Union Carbide) was used without purification. Dimethyl sulfoxide (Me_2SO) was vacuum distilled, hexamethylphosphoramide (HMPA) was distilled from a carbanion solution, and triethanolamine (Fluka) was used without purification. Toluene was distilled from CaH_2, and dioxane and tetrahydrofuran from $LiAlH_4$.

Glyme-Containing Network Polymers. The synthesis of the four polymer-supported polyethers followed procedures similar to those described in the literature.[5-9] In a typical preparation, 0.24 g of NaH was dissolved in 6 mL of polyethylene glycol monomethyl ether (mol wt 300, the chief component being hexaethylene glycol monomethyl ether). After the mixture was stirred for 2 h at 50 °C, 1.9 g of 2% cross-linked chloromethylated polystyrene (Fluka, 0.7 mmol of Cl/g of resin, 200–400 mesh) was added and the mixture heated under nitrogen for 48 h at 90 °C. After the mixture was cooled the resin was recovered by filtration, washed repeatedly with small amounts of a mixture of THF, dioxane, and water (2:2:1 by volume), and finally extracted with THF in a Soxhlet for 48 h. Drying in vacuum at 80 °C for 2 days yielded 2.19 g of the glyme-containing resin.

Table I. Composition of Glyme-Containing Polystyrene Resins from Elemental Analysis[a]

network	% C	% H	% O	theor	found	% conversion
RG4-I						
found	88.24	7.82	3.94	7.6	7.1	93
calcd	89.01	7.39	4.19			
RG4-II						
found	77.74	7.99	15.02	44.0	42.0	95
calcd	77.1	8.26	14.82			
RG7-I						
found	86.19	7.57	5.76	7.6	6.2	82
calcd	86.34	7.90	5.64			
RG7-II						
found	73.27	8.09	18.35	44.0	35.2	80
calcd	73.26	8.12	18.49			

[a] The set of calculated percentages of C, H, and O is obtained by computing the percent ring substitution (indicated by the column "found") for which the set most closely matches the experimental values.

The composition of the four resins was determined by elemental analysis. No residual chlorine was found. Assuming $CH_3O(CH_2CH_2O)_3CH_2$– and $CH_3O(CH_2CH_2O)_6CH_2$– to be the two glyme structures anchored to the benzene rings, the percent ring substitution was computed by matching the experimental C, H, O analysis percentages with those calculated for different ring substitutions. This also yields the percent conversion. The data for the four resins are collected in Table I.

Glyme 5 Complex with Sodium Picrate. A toluene solution of tetraethylene glycol dimethyl ether and sodium picrate (molar ratio 4) was slowly concentrated until a few crystals were formed. On cooling, plate-like crystals were recovered by filtration, washed with hexane, and dried under vacuum. The ^1H NMR of the sharp melting product (64–65 °C) yielded an equimolar ratio of sodium picrate and glyme 5 and was identical with that of a mixture of the two components.

Measurement of Equilibrium Constants. The equilibrium constants of the competition reaction $Pi^-M^+, RG^* + L \rightleftarrows Pi^-M^+L + RG^*$ (RG^* being the glyme-containing resin) were determined for a series of cation-binding ligands, L, with lithium or sodium picrate in toluene at 25 °C. The salts can only be solubilized by using a small amount of the ligand (the lower the ligand affinity for the salt the more ligand is required to dissolve the salt). After the desired picrate concentration was obtained (about 5×10^{-5} M in the form of the complex Pi^-M^+L), a sufficient amount of a resin RG (5–15 mg) was added to bind approximately 60–90% of the picrate salt. After measuring the residual Pi^-M^+L in the solution by means of a Beckman Acta VI spectrophotometer, more ligand was added to the solution to release picrate salt from the glyme-containing resin. Each time, upon reaching equilibrium (≈30 min), the concentration of the Pi^-M^+L complex was measured. Details of the apparatus and the determination of extinction coefficients have recently been published.[2]

Results

Experimental analysis (Table I) of the resins RG4-I and RG4-II yielded ring substitutions of 7.1% and 42%, respectively. They contain the $CH_3O(CH_2CH_2O)_3CH_2$ ligand anchored to the polystyrene benzene rings. The conversion of the chloromethylated

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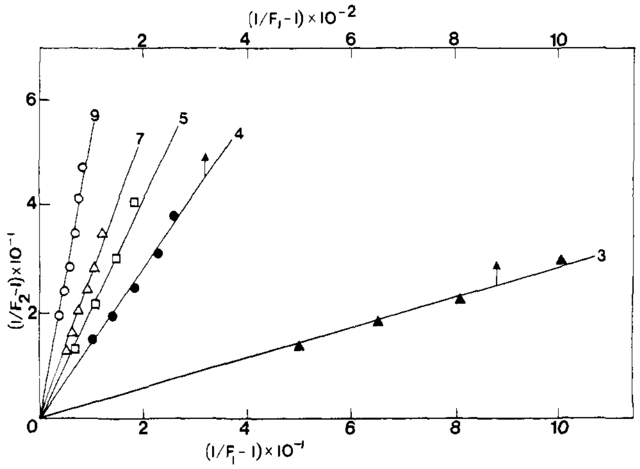

Figure 1. Plots of $(1/F_2) - 1$ vs. $(1/F_1) - 1$ for the binding of glymes to lithium picrate in toluene with use of the immobilized polyether RG7-I, T = 25 °C. Ligands: glymes 3 (▲), 4 (●), 5 (□), 7 (△), and 9 (○).

polystyrene is better than 90%. An 80% conversion was found for the RG7-I and RG7-II resins which possess ligands with an average composition of $CH_3O(CH_2CH_2O)_6CH_2$ (some chains probably contain six or eight oxygen atoms). The respective ring substitutions are 6.2% and 35.2%. The yields of these polyether resins compare favorably with those reported by other investigators[5] and with those found for crown ether containing networks derived from the chloromethylated resins. For the latter networks an independent determination of the ligand content could be obtained by saturating the resin with picrate salt in solvents such as dioxane or tetrahydrofuran.[3] This is more difficult for the acyclic polyether resins since binding constants of salts to glyme ligands are much lower.

The equilibrium constant of the competition reaction

$$\text{Pi}^-\text{M}^+,\ \text{RG}^* + \text{L} \rightleftarrows \text{Pi}^-\text{M}^+\text{L} + \text{RG}^* \qquad (2)$$

was measured in toluene at 25 °C for a series of lithium- and sodium-binding ligands. In most instances equilibrium was attained in approximately 30–40 min after each addition of a new quantity of ligand L. For reasons not clearly understood, the lithium picrate–polyamine systems took nearly 4 h.

The data can be plotted in a form similar to that derived for crown ether containing networks,[2] i.e.,

$$(1/F_2) - 1 = K[(1/F_1) - 1] \qquad (3)$$

In this expression, F_2 is the fraction of resin-bound glyme ligands complexed to Pi^-M^+ ion pairs, i.e., $F_2 = [\text{Pi}^-\text{M}^+, \text{RG}/\text{RG}_0]$, and F_1 denotes the fraction of ligand L bound to picrate salts, i.e., $F_1 = [\text{Pi}^-\text{M}^+\text{L}/\text{L}_0]$. The number of equivalents of resin-bound picrate (Pi^-M^+, RG) is obtained as the difference of the total amount of picrate added ($\text{Pi}^-\text{M}^+{}_0$) and that in the form of $\text{Pi}^-\text{M}^+\text{L}$. Since the latter concentration can be measured and the total concentrations of soluble (L_0) and bound ligand (RG_0) are known, F_1 and F_2 can be easily calculated. Equation 3 assumes a 1:1 complex, $\text{Pi}^-\text{M}^+\text{L}$, and not more than one bound ion pair per resin-bound glyme ligand. The latter assumption is realistic since F_2 in almost all systems is less than 0.1.

Two sets of plots of $(1/F_2) - 1$ vs. $(1/F_1) - 1$ for a series of polyethylene glycol dimethyl ethers with RG7-I as the competing resins are depicted in Figures 1 and 2 for lithium and sodium picrate, respectively. All plots show good linear behavior, implying that in the ligand concentration range of our experiments the glymes only form 1:1 complexes with lithium and sodium picrate ion pairs. Of course, the presence of free ions in the toluene solution can be neglected. Linearity also implies that the resin-bound ion pairs do not interact with one another. This is not surprising since, with $F_2 < 0.1$, the average distance between bound ion pairs is rather large, and restricted mobility limits the probability of interaction. The same was previously observed with crown ether networks, where linearity of binding plots was maintained close to the point of saturation even for resins with 40% ring substitution.[2,3] Linear plots were also found with the other three RG resins.

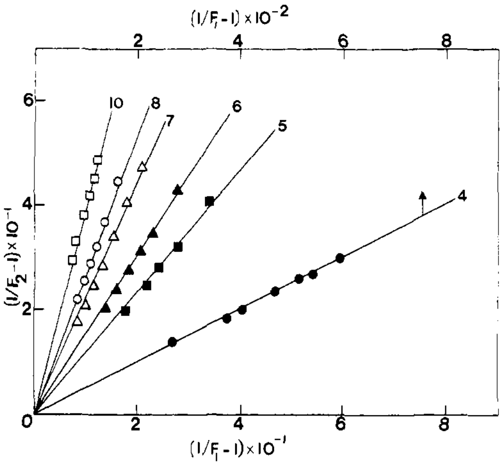

Figure 2. Plots of $(1/F_2) - 1$ vs. $(1/F_1) - 1$ for the binding of glymes to sodium picrate in toluene with use of the immobilized polyether RG7-I, T = 25 °C. Ligands: glymes 4 (●), 5 (■) 6 (▲), 7 (△), 8 (○), and 10 (□).

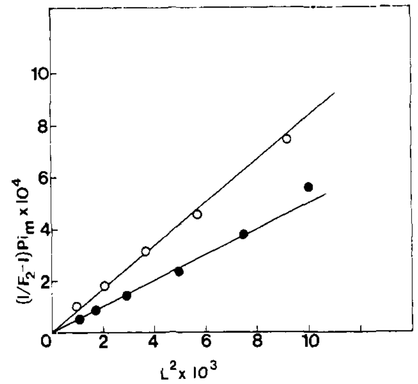

Figure 3. Plots of $[(1/F_2) - 1]\text{Pi}_\text{m}$ vs. L^2 for the binding of glyme 3 to sodium picrate in toluene with use of the immobilized polyethers RG7-I (○) and RG7-II (●), T = 25 °C.

Two exceptions from linear behavior must be noted. Plots for glyme 3 and sodium picrate exhibit a strong upward curvature, similar to that observed earlier in the complexation of methylbenzo-15-crown-5 and potassium picrate in the presence of a crown resin.[2] It indicates the formation of complexes of the type $\text{Pi}^-\text{M}^+\text{L}_2$.[2] If this is the only complex formed, then eq 3 must be replaced by

$$[(1/F_2) - 1]\text{Pi}_\text{m} = K'L^2 \qquad (4)$$

where the measured picrate concentration, Pi_m, is that of the complex $\text{Pi}^-\text{M}^+\text{L}_2$, and $L = \text{L}_0 - 2[\text{Pi}^-\text{M}^+\text{L}_2]$. The constant K' is the competition equilibrium constant leading to the formation of $\text{Pi}^-\text{M}^+\text{L}_2$ and cannot be compared to the K values for 1:1 complexes. Plots for glyme 3–sodium picrate with RG7-I and RG7-II shown in Figure 3 indicate that the complexes are indeed predominantly of the 2:1 type.

Deviation from linearity was also observed for polyamine complexes with lithium picrate in toluene. The first few points for all four polyamines (Table I) lie above the line connecting the origin with the last three or four points of the plot (a total of 7 points were usually obtained). Apparently, too much picrate is released at low polyamine concentration. Slow attainment of equilibrium in these systems may have affected the results to some extent. Also, studies with carbanion lithium salts and hexamethyltriethylenetetramine (HMTTA) in cyclohexane and toluene have shown the existence of complexes of two lithium ion pairs per ligand molecule, a structure stabilized by ion pair–ion pair interaction.[10] Such complexes are more likely to form at low

Table II. Equilibrium Constants, *K*, of the Reaction $Pi^-M^+\cdots RG7 + Ligand \rightleftarrows RG7 + Pi^-M^+\cdots Ligand$ for Lithium and Sodium Picrate in Toluene at 25 °C

	lithium		sodium	
ligand[a]	K	K_{rel}[c]	K	K_{rel}[c]
18-crown-6[b]			331	290
dicyclohexano-18-crown-6[b]			325	285
methylbenzo-18-crown-6[b]			176	154
dimethyldibenzo-18-crown-6			32.5	28.5
carbowax 6000 (134 oxygen atoms)[b]			197	173
glyme 22			13.0	11.4
glyme 10			4.0	3.5
glyme 9	4.89	2.36	4.0	3.5
glyme 8			2.74	2.40
glyme 7	2.52	1.22	2.18	1.51
glyme 6			1.51	1.32
glycol 6 (monomethyl ether)	5.57	2.69	4.14	3.63
glyme 5	2.07	1.00	1.14	1.00
glyme 4	0.14	0.068	0.050	0.044
glycol 4 (monomethyl ether)	0.12	0.058		
glyme 3	0.028	0.0145	(0.083 M^{-1})[d]	
TMEDA	0.027	0.013		
PMDTA	0.25	0.12		
HMTTA	3.0	1.45		
TMTCT	2.2	1.06		
Me_2SO	0.056	0.027		
HMPA	≃0.5	0.24		
TEA	0.50	0.24		

[a] The number specifying the glyme denotes the number of oxygen atoms in the polyethylene glycol dimethyl ether. Carbowax 134 = Carbowax 6000, a polyethylene glycol of molecular weight 6000. Glyme 22 = methoxy polyethylene glycol methacrylate (molecular weight of the methoxy polyethylene glycol is 1000). TMEDA = tetramethylethylenediamine; PMDTA = pentamethyldiethylenetriamine; HMTTA = hexamethyltriethylenetetramine; TMTCT = tetramethyltetraazacyclotetradecane; Me_2SO=dimethyl sulfoxide; HMPA = hexamethylphosphoramide; TEA = triethanolamine. [b] The *K* values of these compounds were computed from those determined with the R18C6 network, see text. [c] $K_{rel} = K(\text{ligand})/K(\text{glyme 5})$. [d] This is the *K* value for formation of a 2:1 complex (eq 4). The value for RG7-II (Figure 3) equals $K = 0.050\ M^{-1}$. These *K* values should not be compared with those of the other ligands which all form 1:1 complexes.

ligand concentration, with the result that more picrate is released from the resin than would be expected on the basis of the formation of 1:1 complexes. The latter are more stable at higher ligand concentration due to a redistribution of the ion pairs over the added ligand. A bathochromic shift of about 5 nm in the lithium picrate absorption peak is observed as more polyamine is added. This may be indicative of changes in the structure of the ion pair–ligand complex. In spite of the deviation from linearity, the *K* values derived from plots passing through the high ligand concentration points still can serve as a reliable measure of polyamine affinities toward lithium picrate.

K values computed from the respective plots have been collected in Table II and III. Their standard deviation in most instances is less than 5%. The polyamine values have an uncertaintly of about 15%. The data in Table II were all obtained by means of the RG7-I resin except those for 18-crown-6, dicyclohexano-18-crown-6, methylbenzo-18-crown-6, and carbowax 6000. These four ligands are much more powerful cation binders than the resin-bound glyme 7 in RG7-I. Therefore, the benzo-18-crown-6 containing network R18C6 [2] was employed for these compounds.

Table III. Comparison of the Binding of Sodium Picrate to Different Glyme- and Crown-Containing Networks in Toluene, *T* = 25 °C[a]

network	ligand	K	$K_N(A)/K_N(B)$
RG4-II(A)	glyme 4	0.27	1.93
RG4-I (B)		0.52	
RG7-II (A)	glyme 5	0.53	2.15
RG7-I (B)		1.14	
RG7-I (A)	glyme 4	0.050	10.4
RG4-I (B)		0.52	
R18C6 (A)	glyme 9	0.015	267
RG7-I (B)		4.0	
R18C6 (A)	DMB18C6	0.124	262
RG7-I (B)		32.5	
FMG9[b] (A)	glyme 22	1.3	10
RG7-I (B)		13	
FMG9[b] (A)	glyme 5	0.12	9.5
RG7-I (B)		1.14	

[a] Ring substitution by glyme chains is 6–7% for R-I networks and 35–40% for R-II networks. [b] FMG9 is a transparent film composed of a copolymer with a 4:1 molar ratio of methylmethacrylate and methoxy polyethylene glycol methacrylate (see text).[53]

Generally, the best results are obtained when the affinities of immobilized and soluble ligands do not differ too much. If the soluble ligand is much weaker it must be added in larger amounts to release the picrate from the resin. This could modify the physical properties of the medium, for example, its dielectric constant, and change the *K* value. Too strong a ligand would require more resin to bind sufficient picrate salt. This constitutes a cost-limiting factor, at least for crown-containing networks.

To use *K* values of crown ethers and acyclic polyethers as a scale of ligand affinities it is necessary to measure the *K* of at least one ligand with both networks R18C6 and RG7-I. This was done with dimethyldibenzo-18-crown-6, which in toluene yielded *K* values for sodium picrate of 0.124 with R18C6 [2] and 32.5 with RG7-I (Table II). The ratio of these two values equals 262. This factor was used to multiply the R18C6-based *K* values of carbowax 6000 and the three crown compounds listed above in order to obtain a scale of ligand affinities with *K* values based on the RG7-I network. We also defined a constant $K_{rel} = K(\text{ligand})/K(\text{glyme 5})$, taking glyme 5 as a standard for comparing the affinities of the various ligands with respect to lithium and sodium picrate (Table II). While the *K* value of a ligand is dependent on the network used in the measurements, K_{rel} should be independent of this variable. The choice of glyme 5 as a "standard" is rather arbitrary, but it may be noted that in the glyme series the *K* values for both lithium and sodium picrate rapidly increase up to a glyme with five oxygen atoms. We will return to this point later in the discussion.

Table III gives *K* values as a function of the resin structure. The data are arranged such that *K* values measured with two different resins but the same soluble ligand can be compared. It can easily be shown [2] that the constant *K* of reaction 2 equals

$$K = K_L/K_N \tag{5}$$

where K_L is the formation constant of the complex Pi^-M^+L ($Pi^-M^+ + L \rightarrow Pi^-M^+L$) and K_N the binding constant of Pi^-M^+ to the resin. K_N values for alkali picrates were recently measured for five crown ether containing networks in dioxane, tetrahydrofuran, and other ethereal solvents.[3] Coupled with the determination of *K* values for a series of soluble crown compounds it permitted us to obtain the formation constants, K_L, of alkali picrate–crown complexes in solvents where a direct measurement of K_L is difficult.[2] The insolubility of picrate salts in toluene prevents the determination of K_N values in this solvent. However, the ratio of two *K* values, *K*(A) and *K*(B), obtained with the same soluble ligand but with two different resins A and B, is equal to the ratio $K_N(B)/K_N(A)$ (see eq 5, K_L being the same for the two systems).

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Hence, a knowledge of these ratios makes it possible to quantitatively evaluate differences in the binding of ionic solutes to immobilized ligands as a function of the ligand content, ligand structure, and other network variables. The ratio $K_N(A)/K_N(B)$ also provides a test of the reliability of the competition method as a tool for determining ligand affinities, since its value should be independent of the type of ligand used in obtaining the K values. It is gratifying to find that entirely different ligands (glyme 9 and dimethyldibenzo-18-crown-6) yielded within experimental error the same ratio $K_N(R18C6)/K_N(RG7\text{-}I)$, namely 267 and 262, respectively (Table III). The same may be noted for the two resins FMG9 and RG7-I, where the use of ligands glyme 22 and glyme 5 yielded ratios $K_N(FMG9)/K_N(RG7\text{-}I)$ equal to 10 and 9.5, respectively. The resin FMG9, a transparent, flexible film used in a few experiments (Table III), was made by copolymerizing a 4:1 molar mixture of methylmethacrylate and methoxy polyethylene glycol methacrylate (Polysciences) in the presence of 5% ethylene dimethacrylate (molecular weight of the polyethylene glycol is 400, i.e., about nine oxygen atoms in the glyme chain).

Discussion

Interactions of macroheterocyclic and acyclic ligands with cations have been studied extensively in polar solvents such as methanol,[11-15] acetonitrile,[16] methyl ethyl ketone,[17] acetone,[18] propylene carbonate,[19] and water[20,21] by means of potentiometry, calorimetry, conductance, nuclear magnetic resonance, spectroscopy, and other techniques.[22-24] In these media interaction with the cation generally involves the free ion. Ion pairing occurs in less polar media like tetrahydrofuran, and optical spectroscopy, conductance, electron spin resonance, and nuclear magnetic resonance have provided a wealth of information on the structure and properties of ligand–ion pair complexes.[4,25-28] Most metal salts are difficult to dissolve in apolar solvents (e.g., chloroform or toluene). In these cases extraction methods have often been employed to determine ligand affinities with ionic solutes.[29-33] From the extraction equilibrium constant and the partition coefficient of the salt in the absence of ligand the formation constant of the complex in the organic phase can be computed,[32] but the reliability of this approach has been questioned.[34] Also, the organic phase is water saturated, and the presence of water can alter complex formation constants.[35] Ligand affinities have also been obtained from solubilization of salts into an apolar solvent by adding the ligand,[35-37] but the often made assumption that the concentration of free salt in the presence of ligand equals the solubility of the salt in its absence is difficult to verify. Moreover, the ligand–salt complex can end up in the solid state. For example, potassium *p*-nitrobenzoate treated with a chloroform solution of 15-crown-5 first solubilizes, but most of the crown complex rapidly precipitates.[38]

Our competition method using immobilized ligands circumvents some of the problems encountered in other methods. It is especially effective in apolar solvents like toluene, dioxane, or chloroform where conductance or potentiometric methods are not useful. Also, in these media formation constants for glyme or crown complexes with ionic solutes are often very high and difficult to measure directly. Toluene was chosen because of its frequent use as the organic phase in crown ether or glyme catalyzed phase transfer reactions. In such reactions the complexation characteristics of the ligands have often been discussed in terms of their binding constants derived from measurements in polar solvents like methanol. In our procedure no water interferes with the ligand complexation to the ionic solute. Ion pair–ion pair interactions which often occur in apolar solvents, especially with lithium salts, have been minimized by using a sensitive chromophore which makes it possible to work at low salt concentrations. Spectral overlap between the two ion pair–ligand complexes is avoided because one of them ($Pi^-M^+N^*$) is resin bound.

Ligand Affinities. The glyme affinity for lithium or sodium sharply increases with chain length until the polyether reaches five oxygen atoms. Beyond glyme 5 the effect on K or K_{rel} chiefly results from a statistical factor as more binding sites are available. This suggests that in a glyme–picrate ion pair complex in toluene both Li^+ and Na^+ can accommodate a maximum of five oxygen atoms.

For glyme 6 and longer glymes, an approximate K_{rel} can be computed by arguing that a chain with n ethylene oxide units can form a cation complex in $n - 4$ ways if the cation coordinates with five adjacent oxygen sites.[25] This gives $K_{rel} = 5$, 18, and 130 for glymes 9 and 22 and carbowax 6000, respectively. The actual values for sodium picrate are 3.5, 11, and 173, respectively. No close agreement is expected. For example, participation of nonadjacent ethylene oxide units in the complex may occur in longer polyethers. Also, in carbowax 6000 the bound ion pair may be in an environment that more resembles a glyme solvent than toluene. The higher polarity would enhance the stability of the bound ionic complex. At high salt-to-ligand ratios more than one ion pair can complex to a glyme 22 or a carbowax 6000 as previously shown for the binding of fluorenyl salts to glyme 22.[4] Recent work with NaSCN solubilized in solid polymers with glyme side chains yielded complexes with an oxygen-to-sodium ratio of 3.0.[40]

On a molar basis a linear polyether such as carbowax 6000 approaches the complexing power of 18-crown-6 (Table II). However, problems may be encountered in solubilization experiments when too many ion pairs are forced on these long glyme chains, especially in low-polarity solvents. For example, in toluene

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a polyether with 17 oxygen atoms was reported to solubilize $KMnO_4$ nearly as effectively as dibenzo-18-crown-6, but polyethers with 45 or 112 oxygen atoms did not dissolve the salt although they were effective in methylene chloride.[36] It is probable that the longer polyethers precipitate due to interactions between their bound ion pairs. Harris et al.[37] have argued in favor of the use of linear polyethers in phase transfer catalysis instead of the more expensive crown compounds. On a molar basis extractions with PEG 6800 in H_2O/CH_2Cl_2 were found to be as effective as 18-crown-6. The long polyethers selectively extract K^+ over Na^+, and the authors attribute this to steric preference for polyether coils that better sequester K^+ than Na^+.[37] However, it seems to us that the preference for K^+ results from the higher dehydration energy for Na^+.

Gokel and his co-workers,[14] as well as other researchers,[41] have reported binding constants of Na^+ to glymes 5, 6, 7, 8, 23, and 180 in CH_3OH of 29.5, 33, 39.8, 46.7, 355, and 5000 M^{-1}, respectively. A linear relationship exists between the logarithm of the binding constants and that of the molecular weights of the polyethers.[14] Interpolation yields a binding constant of 4000 M^{-1} for a glyme with 134 oxygen atoms, an increase of a factor 136 compared to glyme 5. The higher K_{rel} of 173 for our carbowax 6000 (134 oxygen atoms) most likely results from the presence of the anion as argued earlier.

It is instructive to compare our glyme data with those obtained in other systems. Formation constants of glyme-separated ion pairs of lithium fluorenyl from their respective tight ion pairs in dioxane are 3.1 for glyme 3, 130 for glyme 4, and 240 M^{-1} for glyme 5. For sodium fluorenyl in THF the values are 1.2, 9.0, 170, 450, 800, 4800, and 25 000 M^{-1} for glymes 3, 4, 5, 6, 7, 9, and 22, respectively.[4,25] In these solvents an effective solvation shell for Li^+ is apparently obtained with four oxygen atoms (glyme 4), contrary to our results in toluene with lithium picrate. In chlorobenzene the formation constants of glyme complexes of lithium picrate were found to be 2.74×10^4 for glyme 4 and 2.90×10^4 M^{-1} for glyme 5.[39] However, in this system the lithium salt is first solubilized in chlorobenzene with 0.5% THF. Therefore, the formation constants actually describe the interaction of glyme with a THF-solvated ion pair. This drastically affects their values since at least part of the bound THF molecules must be removed to accommodate the glyme. Moreover, it is not unlikely that the glyme complex with lithium picrate still contains a THF molecule. In that case, the fifth oxygen atom in glyme 5 is not needed for complexation. The same may be the case with lithium fluorenyl in dioxane.

Glyme complexes of the two picrate salts in toluene are essentially glyme-complexed tight ion pairs. The absorption maximum of a loose picrate ion pair is close to λ_{max} 380 nm.[30] The maxima of our glyme complexes with lithium picrate fall between 340 and 345 nm. It means that the glyme binding to the salt is most likely affected by the two nitro substituents ortho to the O^- anion. Therefore, relative glyme affinities with *p*-nitro- or dinitrophenolates[28] could turn out to be quite different.

The relative ligand affinities of linear polyethers in toluene roughly parallel those found in methanol. Differences between crown ethers are more significant. For example, binding constants of Na^+ to 18-crown-6 and glyme 6 differ by a factor 670 in methanol,[14] but only by a factor 200 in toluene (Table II). The 18-crown-6 is more effective when the cation can penetrate the crown cavity to better utilize its binding sites. Both the absolute values of ligand affinities, as well as their relative order, are strongly solvent dependent and, for ion pairs, also depend on the nature of the anion. A case in point is the complexation of sodium ions with 18-crown-6 vs. 15-crown-5. It is frequently stated that the binding constant in a series of crown ethers with increased cavity size reaches a maximum for Na^+ with 18-crown-6 because of the preference of this cation to bind six oxygen atoms.[14] However, for the ratio of the binding constants of 18-crown-6 and 15-crown-5 with Na^+ the following values have been reported: 80 in propylene carbonate,[19] 8[12] or 12[14] in methanol, 1.4 in water,[21] 0.67 in acetonitrile,[42] 0.48 in dioxane,[92] 0.28 in benzene (ratio of extraction equilibrium constants in H_2O/benzene[43]),), and 0.4 in $CHCl_3$ (ratio of transport rates through a $CHCl_3$ membrane[44]). For benzo-18-crown-6 and benzo-15-crown-5 the ratios are 31 in acetone,[18] 2.2 in acetonitrile,[16] 1.05 in dioxane,[2] and 0.62 in $CHCl_3$ (ratio of extraction equilibrium constants[31]). The tendency of acetonitrile to form complexes with 18-crown-6 may contribute to the preference of Na^+ for 15-crown-5 in this solvent. For ion pairs (dioxane, benzene, and chloroform) 15-crown-5 appears to be the choice over 18-crown-6, although in extractions and transport the selectivity also depends on factors other than the ligand-binding constants. The need for 18-crown-6 to fold around the sodium ion for effective complexation requires stretching of the interionic ion pair distance. This requires more energy in a tight ion pair, and one binding site remains occupied by the anion. The above examples demonstrate the difficulty in formulating rules to relate sizes of cations and crown cavities.

Under the conditions of our experiments, glyme 3 and sodium picrate form a 2:1 complex, although 1:1 complexes may exist at lower glyme concentrations. While glyme 4 and sodium picrate form a 1:1 complex (Figure 2) the free sodium ion or sodium ion pairs that easily form loose ion pairs (e.g., fluorenyl salts) are known to bind two glyme 4 ligands.[25] Also, crystalline 2:1 glyme 4 complexes exist, among others, with $NaBPh_4$[45] and sodium biphenyl.[46] Glyme 5 yields a sharp melting 1:1 complex with sodium picrate (Experimental Section). Crystalline 1:1 complexes have also been found with glymes 5, 6, and 7.[45]

The monomethyl ethers of the glycols appear to be slightly better complexers of alkali ions than the corresponding glymes (Table II). This was also found for the sodium ion in methanol.[14] The terminal methyl group undoubtedly causes some steric interference in the binding. With ion pairs a terminal *hydroxyl* group may assist by interacting with the anion.[47] However, its presence in crown ethers has also had a negative effect in cases where it can hydrogen bond with crown binding sites.[33]

Acyclic polyamides with two (TMEDA), three (PMDTA), and four nitrogen atoms (HMTTA), and especially with cyclic tetramine TMTCT, are effective catalysts for organolithium-metallation and polymerization reactions in hydrocarbons.[48-50] The affinity of TMEDA for lithium picrate is comparable with that of glyme 3, PMDTA with that of glyme 4, and the tetramine HMTTA with that of glyme 5 (Table II). Surprisingly, the cyclic TMTCT has a lower affinity than HMTTA. Effective binding to TMTCT probably requires some penetration of lithium into the cavity of this ligand, and this may be hindered by the strong $O^-\cdots Li^+$ interaction and the two ortho nitro groups on the picrate anion. Some stretching of the $O^-\cdots Li^+$ bond is suggested by the absorption maxima of the complexes (335–340 nm for the complex with TMEDA, 342 nm for PMDTA, 348 nm for HMTTA, and 350 nm for TMTCT). HMTTA and TMTCT easily form loose 1:1 ion pair complexes with 9-propylfluorenyllithium in toluene, while TMEDA only forms a tight 1:1 ion pair complex.[10] The bulky methyl groups on the polyamine ligands can cause steric interference between the complexed cation and its counteranion, and this is likely to make K_{rel} anion dependent.

K_{rel} values for dimethyl sulfoxide (Me_2SO), hexamethylphosphoramide (HMPA), and triethanolamine (TEA) with lith-

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ium picrate are 0.027, 0.24, and 0.24 (Table II; the plot for HMPA was slightly curved). For the same ligands, Gilkerson reported binding constants (in M^{-1}) in methyl ethyl ketone for free Li^+ ions of 12 (Me_2SO), 1500 (HMPA), and 6000 (TEA).[51] In THF the values are 140 (Me_2SO), 17000 (HMPA), and 50000 (TEA), while glyme 5 is 1900.[28,51,52] In acetonitrile, Me_2SO and HMPA yield values of 49 and 2100 M^{-1}, respectively. Not unexpectedly, the polar ligands Me_2SO and HMPA are more selective with free ions than with ion pairs. Effective binding with TEA requires penetration into the cavity of this tetradentate ligand.[28] This is more difficult when the cation is tightly associated with a picrate anion. Note that binding of glyme 5 to Li^+ in THF is nine times less effective than that for HMPA, while in toluene with lithium picrate glyme 5 is four times *stronger* than that for HMPA. This again suggests that tight ion pairs are less susceptible to changes in the polarity of the ligand.

Affinities of Immobilized Ligands. A comparison of the affinities of glyme- and crown-containing resins for sodium picrate in toluene can be made since the ratio of the binding constants, K_N, to two resins equals the inverse of the ratio of their K values with the same soluble ligand. Table III demonstrates that the higher capacity networks RG4-II and RG7-II (35–40% ring substitution) are about twice as effective in binding sodium picrate as they are in binding their corresponding low capacity analogues RG4-I and RG7-I (6–7% ring substitution). A similar observation was reported for resins with bound benzo-15-crown-5 and benzo-18-crown-6 ligands.[3] The higher concentration of immobilized glyme ligands in RG7-II or RG4-II provides a more polar environment for the ionic solute, which may contribute to the stability of the bound ion pair. Some interaction between the bound cation and an adjacent ligand may also occur. This is especially so when more than one ligand can complex with the cation as found in the binding of K^+ and Cs^+ to certain crown resins.[3]

The K value for glyme 5 with RG7 is larger than unity. Two reasons for this may be advanced. The oxygen atom bound to the bulky $PhCH_2$ moiety probably does not contribute to the cation solvation shell, leaving RG4 and RG7 with only three and six active binding sites per glyme chain. Moreover, the flexibility of the immobilized glyme is probably less than that of a free ligand. For crown-containing networks the affinity of the immobilized crown for sodium picrate exceeds that of the corresponding free crown ether. For example, the K for benzo-18-crown-6/R18C6/sodium picrate is 0.77 in dioxane and 0.67 in toluene, and the values for potassium picrate are 0.9 and 0.6, respectively.[2] With immobilized crown ligands endgroup effects do not exist and rotational restrictions are not likely to differ much from those of the free ligand.

Note that in toluene the immobilized glyme 4 in RG4 has a higher affinity for sodium picrate than has the soluble glyme 4 ($K = 0.52$, see Table III), although the former ligand probably has only three effective oxygen-binding sites. Even in low-capacity resins a number of sites are present with two ligands in close proximity, and the possibility exists that sodium ions in RG4 may complex simultaneously with two ligands. If so, it would make the RG4 resin a more effective binder. It would also explain why the ratio of K_N values for RG7-I and RG4-I is only 10 (Table III), while that of K values for the soluble glymes 7 and 4 is 34 (Table II).

The polyacrylate film FMG9 with immobilized glyme 9 ligands is about ten times more effective in binding sodium picrate in toluene than is RG7-I. This is to a large degree due to the longer glyme chain and a higher ligand density in FMG9. Also, the polyacrylate resin may provide a better microenvironment for the bound ionic solutes than do the polystyrene-type resins. The transparent films offer distinct advantages over the microporous polystyrene-based immobilized ligands, since they can simply be hung in the solution. Also, the optical spectra of the film-bound picrate ion pairs can be obtained. The absorption maximum of the picrate salt in the dry film was found to be close to that of a loose picrate ion pair. Some of the properties and uses of these materials have recently been published.[53]

Application to Phase Transfer Catalysis. The binding affinity of crown ethers and linear polyethers to cations is an important parameter in evaluating their usefulness as phase transfer catalysts. However, other factors must also be considered. The reactivity of a complex A^-M^+ in the organic phase can be modified when aggregates are formed. The tendency to aggregate varies significantly with the structure of the ligand and that of the ion pair complex, e.g., whether tight or loose ion pair–ligand complexes are formed.[54] The reactivity also depends on the ability of the ligand to stretch the interionic ion pair distance. A problem of a different nature may be encountered with long-chain polyethers. Their solubility and that of their ion pair complexes is strongly solvent dependent. For example, long-chain polyethers (mol wt 2000) are poorly soluble in aliphatic hydrocarbons. In partitioning PEG-6800 between water and organic solvents, CH_2Cl_2 favors the PEG while only 0.1% is transferred to benzene.[37] In this context recent conclusions on the effect of long-chain polyethers on the phase transfer reaction between aqueous NaCN and a mixture of chlorooctane and decane may be questioned.[14] Comparable activities of crown ethers and linear polyethers at the same *molar* concentration led to the conclusion that each polyether, *regardless of length*, transfers only a single cation. This was rationalized by arguing that the concerted movement of cation, anion, and ligand across a phase boundary would be more difficult if such a process occurred at more than one point along the polyether chain.[14] However, extraction data across a water/chloroform boundary demonstrate that poly(crown ether)s in the organic phase can contain many cations.[31] We suspect that most of the polyether (PEG-3400) may not have transferred to the aliphatic 1-chlorooctane/decane phase. What was transferred may have contained more than one bound ion pair per chain, and this could have resulted in precipitation. This was pointed out earlier as a possible explanation for the inability of long-chain polyethers to solubilize $KMnO_4$ in toluene.[36] The use of a PEG-20000 in the phase transfer catalytic displacement on 1-bromooctane was also reported to be ineffective in comparison to shorter glymes.[55] Even if no precipitation occurs, highly charged polymers tend to coil up in apolar media. Recent experiments with fully metallated poly(2-vinyl-fluorene) have shown that this poly(ion pair) in THF is tightly coiled and exhibits a low reactivity compared to that of the partially metallated polymer.[56] More polar solvents can alleviate such problems, and in the reaction of benzyl bromide with solid potassium acetate in acetonitrile, PEG-3400 and PEG-6800 were quite effective phase transfer catalysts.[37] The examples given here indicate the need for better data on the state of the reactive species in phase transfer reactions and the extent to which the catalyst solubilizes the ionic solutes.

Acknowledgment. The authors gratefully acknowledge the financial support of this research by the National Science Foundation, Grant CHE 8205881.

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