Table I. Fractional Atomic Coordinates of the Non-Hydrogen Atoms of 1a with Standard Deviations in Parentheses[a]

	x	y	z	B_{eq}
S (1)	0.4127 (2)	0.5606 (1)	0.4075 (2)	4.4 (1)
S (2)	0.7137 (2)	0.5423 (1)	0.4502 (2)	5.1 (1)
F (1)	0.8165 (6)	0.4892 (4)	0.7074 (5)	6.0 (2)
F (2)	0.9427 (9)	0.3443 (6)	0.8689 (5)	7.7 (3)
F (3)	1.1288 (8)	0.1989 (5)	0.8566 (6)	7.2 (3)
F (4)	1.1825 (7)	0.1937 (5)	0.6764 (7)	7.7 (2)
F (5)	1.0537 (8)	0.3362 (6)	0.5118 (6)	8.3 (3)
O (1)	0.3660 (7)	0.5867 (5)	0.4904 (6)	6.4 (3)
O (2)	0.4176 (7)	0.6401 (4)	0.3365 (6)	5.7 (2)
N (1)	0.5870 (6)	0.5030 (4)	0.4790 (5)	4.4 (2)
N (2)	0.8727 (7)	0.4905 (6)	0.5145 (6)	5.2 (2)
C (1)	0.2930 (7)	0.4603 (5)	0.3200 (6)	3.8 (2)
C (2)	0.1969 (8)	0.4091 (5)	0.3533 (6)	4.5 (3)
C (3)	0.1036 (9)	0.3310 (5)	0.2855 (7)	4.9 (3)
C (4)	0.1050 (8)	0.3028 (5)	0.1844 (6)	4.4 (3)
C (5)	0.2008 (9)	0.3561 (6)	0.1541 (6)	5.0 (3)
C (6)	0.2936 (9)	0.4355 (6)	0.2203 (7)	4.8 (3)
C (7)	−0.0007 (11)	0.2172 (7)	0.1104 (8)	5.9 (4)
C (8)	0.9248 (7)	0.4156 (5)	0.6004 (6)	4.1 (2)
C (9)	0.8996 (8)	0.4146 (6)	0.6946 (6)	4.6 (2)
C (10)	0.9679 (9)	0.3431 (7)	0.7794 (7)	5.2 (3)
C (11)	1.0642 (9)	0.2678 (6)	0.7736 (7)	5.2 (3)
C (12)	1.0908 (8)	0.2657 (6)	0.6813 (8)	5.1 (3)
C (13)	1.0221 (8)	0.3381 (6)	0.5970 (7)	5.3 (3)

[a] The given isotropic temperature parameters (B_{eq}) are one-third of the trace of the orthogonalized anisotropic B_{ij} tensor.

position for the S–S arrangement on a twofold axis. The structure was refined by least-squares methods first with isotropic and then with anisotropic temperature parameters. After some steps of refinement, only the two atoms H(1) and H(4) positioned next to the molecular center of mass could be clearly recognized in a difference Fourier synthesis. The remaining H positions were calculated to be in accord with expectation. Only the H atoms found in the difference Fourier synthesis and H(2) of the phenyl residue could be refined in the normal way with isotropic temperature parameters. The refinement of the remaining H atoms was carried out under constraints with fixed bond distances (1 Å) and temperature parameters (10 $Å^2$) and by taking the hydrogens of the methyl as a rigid group. The refinement was done in two strongly overlapping blocks. It converged to $R_w = 0.072$ ($R_w = \sum_w{}^{0.5}|F_c| - |F_c|/\sum_w{}^{0.5}|F_0|$). The following weighting scheme was applied: $w = k/[\sigma^2|F_0| + 0.001|F_0|^2)$. The final positional and isotropic temperature parameters of the nonhydrogen atoms are given in Table I.

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Registry No. **1a**, 82235-85-6; **1b**, 86410-95-9; **1c**, 52999-40-3; **2**, 513-35-9; **5a**, 86410-96-0; **5b**, 86410-97-1; **5c**, 86410-98-2; **7**, 86410-99-3.

Supplementary Material Available: Anisotropic temperature parameters, the positional and isotropic temperature parameters of the hydrogen atoms, tables of bond distances, bond angles, and torsion angles (partially) in comparison with values of compound **1d**, and a description of the crystal packing together with a stereoscopic representation (4 pages). Ordering information is given on any current masthead page. The lists of observed and calculated structure factors are available from A. Gieren.

Binding Profiles for Oligoethylene Glycols and Oligoethylene Glycol Monomethyl Ethers and an Assessment of Their Abilities To Catalyze Phase-Transfer Reactions

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The equilibrium binding or stability constants (K_s) between Na^+ and oligoethylene glycols [$HO(CH_2CH_2O)_nH$], monomethyl ethers [$HO(CH_2CH_2O)_nCH_3$], and dimethyl ethers [$CH_3O(CH_2CH_2O)_nCH_3$] have been determined in anhydrous methanol solution. The ranges of compounds involved are as follows: diols, n = 3–312; monoethers, n = 6–15; diethers, n = 3–21. Although the slopes vary some from species to species, the plot of log K_s vs. log molecular weight is an essentially straight line. There is no peak in binding observed when a particular number of oxygens might be present to provide, for example, an octahedron of donor groups or a quasi-crown coil. The molecular weight is not crucial to the binding since equal weights of different glycols afford the same net sodium binding. This similarity does not extend to reactivity in the liquid–liquid phase-transfer catalytic system in which it appears that one molecule of polyethylene glycol derivative effects one reaction at a time. Thus equal weights of shorter chains are much more effective than longer chain lengths of similar species.

Ever since Pedersen's discovery of crown ethers and their cation-binding properties,[1] there has been considerable general interest in the corresponding oligoethylene glycols as less expensive analogues. In the same year the crowns were reported, Smid and his co-workers reported the first results of their efforts to assess cation binding by the related open-chained materials.[2–4] Cram and his co-workers have compared the efficacy of open-chained equivalents of their crown host systems in binding a variety of cationic guests.[5]

The interest in these molecules has increased considerably in recent years. Efforts have been made to quantify

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0022-3263/83/1948-2837$01.50/0

Table I. Sodium Cation Binding by 1-4 in Methanol Solution at 25 °C

no. of O's[a]	structural type	R^1	R^2	mol wt[b]	log K_s[c]	ref
5	1	H	H	(200)	1.64	18
5	3	CH_3	CH_3	(222	1.28	14
5	4	15-crown-5		220	3.25	
5	3	CH_3	CH_3	266	1.47	14
6	3	CH_3	CH_3	266	1.52	14
6	4	18-crown-6		264	4.35	
7	1	H	H	(300)	2.02	18
7	3	CH_3	CH_3	310	1.60	14
7	3	CH_3	CH_3	(300)	1.55	18
7	4	21-crown-7		308	2.54	
8	2	H	CH_3	(350)	1.82	
8	3	CH_3	CH_3	354	1.67	14
8	4	24-crown-8		352	2.35	
9-10	1	H	H	(400)	2.00, 2.26	18
13	2	H	CH_3	(550)	2.11	
14	1	H	H	(600)	2.29, 2.59	18
14	3	CH_3	CH_3	(600)	2.09	18
17	2	H	CH_3	(750)	2.32	
23	1	H	H	(1000)	2.54, 2.88	18
23	3	CH_3	CH_3	(1000)	2.55	18
35	1	H	H	(1500)	3.09	18
46	1	H	H	(2000)	3.28	18
77	1	H	H	(3400)	3.23	
182	1	H	H	(8000)	3.70	
318	1	H	H	(14001)	4.08	

[a] Total number of oxygen atoms in the system. [b] Parentheses indicate average molecular weights of mixtures. [c] Errors in K_s are ±0.01 log units for compounds having molecular weights in the 0-1000 range. For higher molecular weight compounds, the error is ±0.03 log units.

the binding of several oligoethylene or polyethylene glycols (PEGs) with various cations in numerous solvents. These have included alkali metal cations with affinities assessed by NMR methods,[6-8] conductometric methods,[9,10] solution calorimetry,[11] and the picrate extraction technique.[12,13] Actual equilibrium binding constants have been obtained for a limited number of oligoethylene glycols in several separate studies.[11,14-18] In only a few of these efforts[13,18,19] was the relevance of the cation binding to phase-transfer catalysis[20-22] considered. Recently, Stott and co-workers compared decaglyme and Carbowax 20M with a variety of crown ethers and other phase-transfer catalysts.[19] Although comparative rate data were presented therein, no binding study accompanied the work, making comparison with our own work difficult.

The study reported here was an attempt to correlate the cation binding characteristics of oligoethylene and polyethylene glycols to their efficacy as phase-transfer catalysts. It was also hoped that some information would be obtained on the mechanism by which these compounds function in such reactions.

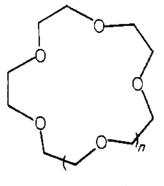
Results and Discussion

Binding Constants. The binding constants reported here were measured in anhydrous MeOH solution at 25.0 ± 0.1 °C. A constant temperature was maintained by using a bath of circulating di-*n*-butyl phthalate, and the entire apparatus was kept in a dry box flushed with dry N_2. Sodium concentration was measured with a sodium ion selective electrode (Corning 476210), and voltage changes were recorded with an Orion Model 701A Ionalyzer. Binding constants were calculated by using the technique developed by Frensdorff for the crown ethers.[23]

The data presented in Table I represent four groups of compounds. These are the oligo- or polyethylene glycols (1), the oligoethylene glycol monomethyl ethers (PEG MME, 2), the oligoethylene glycol dimethyl ethers (glymes 3), and the crown ethers (4). These compounds are illustrated below.

$R^1OCH_2(CH_2OCH_2)_nCH_2OR^2$

1, $R^1 = R^2 = H$; n = 3-312
2, $R^1 = H$; $R^2 = CH_3$;
n = 6-15
3, $R^1 = R^2 = CH_3$; n = 3-21



4, n = 1-4

Approximately half of the data tabulated derive from our own measurements, the remainder being literature

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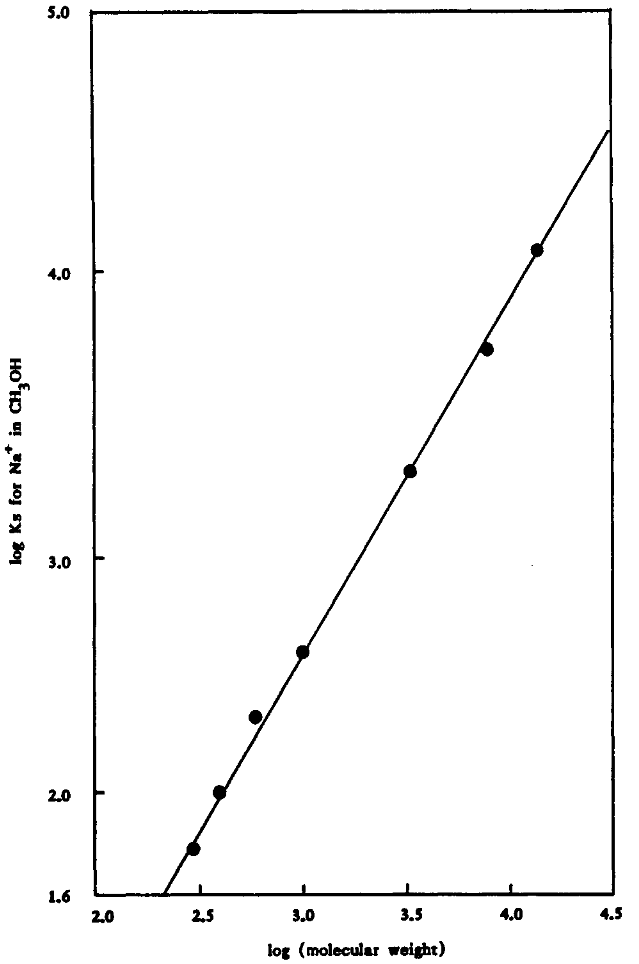

Figure 1. Sodium cation binding for polyethylene glycols (PEGs, 1) as a function of molecular weight.

values. All values, from whatever source, were determined in methanol solution and are more or less comparable. The lower molecular weight diols whose binding constants were previously reported[18] have K_s values which are systematically higher than our own values, but the differences are not large, and the variation does not appreciably affect either the trends or conclusions.

An important goal of the present work was to determine if cation binding exhibited some maximum which corresponded to, for example, an integral number of coils about the cation. A sodium cation which is normally solvated by six oxygen donor groups[24] might show a maximum at six or twelve ethyleneoxy units or some other readily comprehensible number. Precisely this possibility has recently been invoked by Harris et al.[13] to account for the K^+/Na^+ selectivity they observed in picrate extraction experiments. Their analysis applied to K^+ rather than Na^+ and was conducted in a two-phase water/CH_2Cl_2 system rather than in methanol. Nevertheless, we feel it is unlikely that the K^+ selectivity they observed is due to "...a steric preference for coils of a size more compatible with potassium rather than sodium".[13] Although not widely recognized,[25] virtually all simple crown ethers favor potassium over sodium cation, and this is probably a manifestation of the same phenomenon.

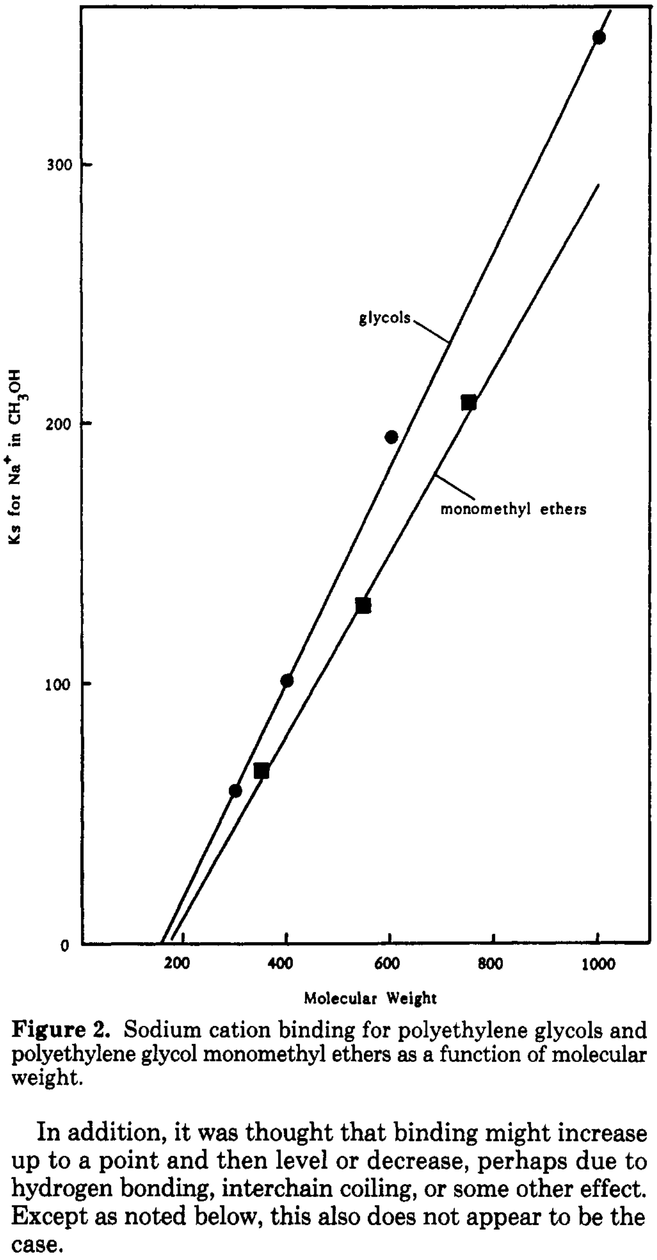

Figure 2. Sodium cation binding for polyethylene glycols and polyethylene glycol monomethyl ethers as a function of molecular weight.

In addition, it was thought that binding might increase up to a point and then level or decrease, perhaps due to hydrogen bonding, interchain coiling, or some other effect. Except as noted below, this also does not appear to be the case.

As reported by others, the binding constants for the diols increase less rapidly at lower values of *n* than at higher molecular weights (see Table I). The binding constant curve (stability constant K_s vs. molecular weight) assumes a constant slope, at least in a molecular weight range of ca. 500–14 000, the limit of our study (log K_s vs. log molecular weight is plotted in Figure 1). At the higher molecular weights, the measurements are less accurate because of the apparent formation of polymeric complexes, but the trends are clear enough.

In order to see if having the binding sites present in several shorter molecules or one long one was more useful, we compared the binding of **1** ($n = 13$) with **1** ($n = 317$). In both cases, an equal weight of diol produced an identical millivolt reading (see Experimental Section), indicating the same overall level of binding. This is especially interesting in light of the results with polyethylene glycol [$M_r = 3400$ (PEG 3400)] and an equal weight of PEG 400 as phase-transfer catalysts (see below).

Substitution of a methyl group for a hydrogen terminus converts **1** into **2**. These monomethyl ethers were commercially available in a smaller molecular weight range than were the diols. The binding for the $M_r = 350–750$ range (see Figure 2) parallels the binding profile observed

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Table II. Liquid–Liquid Phase-Transfer Synthesis of 1-Cyanooctane according to Eq 1 Using Various Catalysts

catalyst[a]	amt, g (mol %)	molar increase	halflife,[b] h	rate,[b] s^{-1}	rel rate	rel rate increase	rate increase/ mol
none[c]	0 (0)	0	0	0	0	0	0
Aliquat 336	0.404 (1.5)		0.5	3.85×10^{-4}	269		
18-crown-6	0.264 (1.5)		176 ± 12	1.09×10^{-6}	0.8		
PEG-400	0.400 (1.5)		135 ± 10	1.34×10^{-6}	1.00		
PEG-3400	3.400 (1.5)		92 ± 5	2.09×10^{-6}	1.5		
PEG-MME-750	0.750 (1.5)		500 ± 20	3.85×10^{-7}	0.3		
18-crown-6	3.400 (19.3)	12.9	5.0 ± 0.2	3.85×10^{-5}	27	33.8	2.62
PEG-400	3.400 (12.75)	8.5	7.2 ± 0.5	2.67×10^{-5}	18.7	18.7	2.20
PEG-3400	3.400 (1.5)	0	92 ± 5	2.09×10^{-6}	1.5		
PEG-MME-750	3.400 (6.8)	4.5	53 ± 6	3.63×10^{-6}	2.5	8.33	1.85

[a] See the Experimental Section for reaction conditions. [b] Average of three or more independent runs. [c] No reaction detected for more than 500 h. [d] Data from column 8 divided by data from column 4.

in the M_r 400–1000 range for the diols. The slope for the former (**2**) is slightly smaller than that for the latter in the comparable molecular weight range. The monomethyl ethers are clearly poorer sodium ion binders in methanol, but the difference in binding strength is not sufficient to merit extensive comment.

The glymes, **3** (Figure 2), showed a similar slope and similar absolute binding constants (see Table II) to those noted for the 200–1000 molecular weight range of diols examined above. The slope for the glymes is slightly greater than the slopes of either the diols or the monoethers, but since all of these data were obtained from literature sources and are not precisely calibrated to our own, it seems unlikely that these differences are of importance, especially in view of the limited range of molecular weights.

The slopes observed for these groups of compounds suggest two things. First, once a minimum is reached (apparently $n = 10$–12), binding continues to increase in proportion to chain length without any unusual structural requirements for cation complexation becoming apparent. Second, the near identity of slopes and binding profiles for **1**–**3** suggests that all of these species are binding cations in the same way, irrespective of the end group. The situation may be very different for basic reactions as noted below.

Binding constants for such macrocycles as 15-crown-5 and 18-crown-6 with sodium cation have been reported by a number of research groups.[25] Recently, the sodium binding constant of 21-crown-7 has been reported,[26] but to our knowledge, the stability constant for 24-crown-8 and this cation has not hitherto been measured. We include these values both because they should be available and because there is a discrepancy between the 21-crown-7 value obtained by Izatt and co-workers[26] and our own value. Furthermore, it is interesting to compare these binding constants with those exhibited by polyethylene glycol compounds. The log K_s values we have obtained for the four crowns **4** ($n = 1$–4) are as follows: 3.25, 4.35, 2.54, and 2.35. These compare with values obtained calorimetrically by Izatt et al.[26] of, respectively, 3.48, 4.36, and 1.73. No value was reported for 24-crown-8. The peak in this group, which appears at six oxygens, is not surprising in light of the six-oxygen preference of sodium cation.[24]

In summary, then, the binding of sodium ion by polyethylene glycols, and likely the corresponding mono- and dimethyl ethers as well, follows an essentially linear relationship as the chain length increases. This contrasts with an unequivocal peak in the sodium cation binding by the crowns, with 18-crown-6 at the maximum. Although binding by the PEGs increases less rapidly at first, they eventually attain a predictable slope near unity. No inflection points have been observed which suggest a special, most favorable chain length as has been observed for arenediazonium cation binding.[27,30] Substitution of an equal weight of a lower molecular weight diol affords the same level of cation binding as does the corresponding amount of longer chain material. The selection of a phase-transfer catalyst could therefore, in principle at least, be made as much on the basis of what compound is available as on theoretical considerations. The principle seems to be that more binding sites will give greater binding, irrespective of how many of those binding sites are present in the same molecule. This finding appears to contradict that of Stott, Bradshaw, and Parish,[19] who found that although decaglyme was more effective than Carbowax 20M in an unspecified reaction, it was better by less than a factor of 2 and that the reaction rate in either case was within 50% of hexadecyltributylphosphonium bromide.[28] Likewise, Harris and co-workers[13] found that "PEG-6800 is a more effective phase transfer agent than PEG-1000, even when the two are compared on an equal-mass basis". The difference to which they refer is 9.1×10^{-3} vs. 6.6×10^{-3} M^{-1} s^{-1} and is for a solid–liquid phase-transfer process. The meaning of their observations is difficult to assess relative to our own (see below).

Application to Phase-Transfer Catalysis. The implication from our measurements and from those of others recorded in Table I appears to be that any polyethylene glycol will be a decent cation binder just as long as it is present in high enough concentration. One might think that the binding ability of the crown ethers would not be approached at any length of PEG but that the catalyzed reaction might work well anyway. Indeed, the latter has previously been demonstrated.[19] In order to try to correlate the observed binding constants with actual chemical reactions, we duplicated the reaction shown in eq 1 which

$$C_8H_{17}Cl + NaCN \xrightarrow[\text{water and decane}]{\text{catalyst}} C_8H_{17}CN + NaCl \quad (1)$$

was reported originally by Starks.[29] A mixture of 1-

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(26) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475.

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(28) Decaglyme and Carbowax 20M are compared in Table II of ref 19. It is not clear to the present authors precisely what reaction is represented by the data in this table, but we presume that it is a liquid–liquid phase-transfer reaction between KSCN and 4-nitrobenzyl bromide as noted in the title to Table I and the caption beneath Figure 2. The standard for this reaction (i.e., $k_{rel} = 1.00$) is apparently hexadecyltributylphosphonium bromide although it is identified in the table (presumably due to a typographical error) as "hexadecyl*tetra*butylphosphonium bromide".

(29) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.

chlorooctane and *n*-decane was heated (reflux, 105 °C) with aqueous sodium cyanide solution in the presence of a potentially catalytic species (1.5 mol%). As the reaction progressed, aliquots of the organic phase were withdrawn and analyzed by gas–liquid chromatography. *n*-Decane served as both a diluent and an internal standard in the reaction. The reaction progress was assessed by the disappearance of chlorooctane (gas chromatography) in relation to inert *n*-decane. The rate constants shown in Table II were all obtained in this way (see Experimental Section for details).

Before presenting our results in detail, it is useful to briefly review the applications to which PEGs and their derivatives have been put in phase-transfer or phase-transfer-like processes. We have already noted their application in arenediazonium cation reactions.[27,30] In addition, PEGs have been used as catalysts in potassium permanganate[31] and potassium dichromate oxidations,[32,33] photocyanation of anisole,[34] carboxylate and other substitutions,[35,36] methylation of glycols,[37] ether and sulfide synthesis,[38] ester aminolysis,[39] base-catalyzed condensation reactions,[40] elimination reactions,[41] and, curiously, both enhancement of ester reduction[42] and retardation of ketone reduction with borohydride.[43] Recently, Santaniello, Manzocchi, and their co-workers have advocated the use of PEG 400 as a solvent and catalyst for a variety of phase-transfer reactions.[32,33,42]

For the most part, the examples presented above constitute surveys of a particular application with several substrates. Comparisons of the polyethylene glycols or derivatives with either phase-transfer-active quaternary ammonium salts or crown ethers have been rare. In several cases cited above, comparisons have been made with crowns,[13,33] quaternary ammonium salts,[40] or both.[19,31,43] With the exception of the two cases each in ref 13 and 19, only a general indication of relative reaction has been obtained. In all of the examples thus far reported, crowns, quats, and PEGs appear to more similar than different.

The results of our survey of the cyanide displacement reaction are shown in Table II. Our approach was to use the well-studied reaction of Starks[29] between sodium cyanide and 1-chlorooctane (eq 1). Our experiments differed from those performed by Starks only in the catalysts surveyed and that the reactions were conducted on one-tenth the scale previously reported.

First, we determined the reaction rates in the presence of either Aliquat 336 [$(C_8\text{–}C_{10})_3NMe^+Cl^-$] or 18-crown-6. By use of the rate observed with PEG-400 (see below) as a standard (relative rate = 1.00), it was found that the relative rates for the quaternary salt and crown were 269 and 0.8, respectively. In the absence of any catalyst, no reaction was observed even after 500 h.

When either of the polyethylene glycols, PEGs 400 or 3400, catalyze the reaction shown in eq 1, the rate difference is small. The rate difference for the PEGs is only about 50% compared to the difference between crowns and quats of more than two orders of magnitude. The monomethyl ether of PEG-750 is less effective still, inducing the reaction to occur with a relative rate of 0.3.

It is not the absolute values of these rates which are of interest but the fact that when approximately the same number of similar cation binders are present in solution, similar catalysis results. It appears from these results that one molecule of crown or one molecule of PEG-3400 transports a single ion at a time. If not, then one might expect, for example, PEG-3400 to bind more than one cation at a time and be superior to PEG-400 as a catalyst.

In order to test the notion that more molecules of binder and not more binding sites per se enhance catalysis, we conducted another series of experiments according to eq 1 using equal weights of 18-crown-6 and the PEGs. The results are shown on the last four lines of Table II. Notice that an increase in the number of catalyst molecules enhances the reaction rate significantly, even though an equal number of binding sites are now present in each case. Note also that the rate is enhanced approximately 2–3 times on a molar basis for all of the ligands except PEG-3400 which constitutes the standard in this case.

The conclusion, then, is that crowns and the PEGs, when used at similar concentrations, have similar activities. Aliquat is a more effective catalyst than either crowns or PEGs. A mechanistic comparison may not be appropriate because as an ammonium salt, it is exchanging cations rather than solvating one and is operating in a fashion different from the others. Note that had we used potassium rather than sodium cation, the rates might have been generally higher. This is because the affinity of polyethers for potassium is usually equal to or higher than it is for sodium.[25]

These data suggest that each polyether, irrespective of length, involves itself in the transfer of a single cation. This is not an unreasonable proposition, since phase transfer, involves movement of the cation, anion, and cation-solvating ligand in concert across or at least away from the phase boundary.[44] It would be substantially more difficult for this process to occur at two points along a chain simultaneously.

It seems to us that the one ion, one ligand concept is likely to be especially applicable in reactions which involve the deprotonation of PEG-MMEs when the latter are used as catalysts.[40,41] In these cases, Ugelstadt and co-workers[45] showed some years ago that "self-solvating bases" were formed from the PEG-MMEs on deprotonation and that such systems bear a striking resemblance to crown ethers in their chemical reactions.[46]

Limitations of the Study. The work presented here has dealt exclusively with the sodium cation because it seems likely to us that it is this cation which would be chosen for most reactions involving PEGs. If the more expensive crown ethers are shunned as catalysts, presumably the more expensive and higher molecular weight potassium cation likewise will be eschewed.

It should be noted that the data reported in this study and the conclusions drawn from them are likewise limited. The binding constants apply only to methanol solution,

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although extrapolations are clearly possible to other solvents.[47] Furthermore, the kinetic data apply only to the liquid–liquid system examined by Starks.[29] It has been shown that similarities exist for solid–liquid and liquid–liquid systems when a quaternary salt is used as the catalyst,[48] but it is not clear that our own work bears extension in accord with these observations.

Summary

It is shown that homogeneous sodium cation binding (K_s in methanol) is linearly proportional to the number of binding sites available in the PEG cation binder. It is further apparent that these substances can catalyze liquid–liquid phase-transfer reactions as well as aliphatic crown ethers can. From the kinetics and other comparisons, it seems that each oligoethylene glycol chain complexes and transports one cation in the phase-transfer process. Thus, increasing the number of PEG molecules without increasing the number of donor atoms increases the rate of the phase-transfer catalytic process.

Experimental Section

Binding Constants. The poly(ethylene glycols) and poly(ethylene glycol) methyl ethers of average molecular weight 300–14 000 were obtained from the Aldrich Chemical Co. The binding constants for these ligands with sodium ion (chloride counterion) were determined in absolute methanol solution at 25.0 ± 0.1 °C. The measurements were made with an Orion Model 701A Ionalyzer millivolt meter by using a Corning 476210 sodium ion electrode and an Ag/AgCl reference electrode. The apparatus was contained in a dry box, and the solution temperature was maintained by using di-*n*-butyl phthalate as a heat-transfer solvent.

Experiments consisted of measuring the emf of the cell for the solutions of sodium ions with and without the ligand. The typical concentration of sodium (NaCl) was approximately 2 mM, and that of the ligands was 3–5 mM. Binding constants were calculated by the method of Frensdorff.[23]

Since the binding constants varied linearly with the average molecular weight of the poly(ethylene glycol), a series of measurements were done in which complexation of sodium was studied with solutions containing a constant weight (0.5 g in 50 mL) of all the poly(ethylene glycols) in the molecular weight range 300–14 000. The emf readings showed that the extent of sodium ion complexation in all these solutions was nearly the same, with a slight peak at the poly(ethylene glycol) with an average molecular weight of 1000.

Kinetics of Phase-Transfer Processes. The reactions were conducted as described by Starks[29] except that one-tenth the scale was employed. A 100-mL round-bottomed flask was charged with *n*-octyl chloride (0.067 mol, 10 g), *n*-decane (2.5 mL), H_2O (2.5 mL), and the particular catalyst (1.5 mol %, 0.001 mol). This mixture was heated to ~50 °C and stirred magnetically at maximum speed. Sodium cyanide (0.204 mol, 10 g) was then added, and this mixture was quickly heated to the reflux temperature (~105 °C). Aliquots were removed from the reaction flask at various time intervals beginning with $t = 0$. The aliquots were diluted with an equal volume of H_2O. The samples were analyzed by injecting 1 μL of the organic layer into a Varian Associates Model 920 analytical gas chromatograph equipped with a thermal conductivity detector and a 5 ft × 0.25 in. 1.5% OV-101 on a 100–120-mesh NAW Chromosorb G column at a flow rate of ca. 60 mL/min of He with a column temperature of 70 °C. Chromatogram peak heights were then measured and compared relative to internal standard *n*-decane. The percent unreacted octyl chloride was calculated utilizing eq 2 and 3.

$$\frac{(\text{octyl chloride})_{t=0}(n\text{-decane})_{t=t}}{(n\text{-decane})_{t=0}} = (\text{octyl chloride})_{\text{initial}} \qquad (2)$$

$$\frac{(\text{octyl chloride})_{t=t_{\text{obsd}}}}{(\text{octyl chloride})_{\text{initial}}} \times 100 = \%\ \text{unreacted octyl chloride} \qquad (3)$$

Rate constants were obtained by averaging the percent halide remaining at each time interval, determining its natural logarithm, and then determining the slope (by least-squares analysis) of ln % vs. time. The pseudo-first-order rate constants are given in reciprocal seconds and are the average of at least three runs in each case.

Chemicals and Reagents. All solvents were of the highest grade commercially available and were used without further purification. Polyethylene glycols, monomethyl ethers, and crowns were purchased from the Aldrich Chemical Co. 21-Crown-7 and 24-crown-8 were prepared by a modification of our previously reported procedure,[49] and all crowns were distilled prior to use.

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Registry No. 1, 25322-68-3; **2**, 9004-74-4; **3**, 24991-55-7; 4 (n = 1), 33100-27-5; 4 (n = 2), 17455-13-9; 4 (n = 3), 33089-36-0; 4 (n = 4), 33089-37-1; sodium cation, 17341-25-2; 1-chlorooctane, 111-85-3.

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Formal Synthesis of Pentaprismane

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A new synthetic route to pentaprismane (1) has been developed. The key intermediate, *endo*-carbomethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one (**5a**), was prepared in six steps from 4,4-dimethoxycyclohexa-2,5-dien-1-one (**10b**) in an overall yield of 23%. Photochemical closure of the Diels–Alder adduct **8b**, obtained from cyclobutadiene and **10b**, gave 10,10-dimethoxypentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-7-one (**7b**). Methylenation of **7b** followed by hydroboration and oxidation afforded 9-hydroxy-10-oxahexacyclo[6.4.0.0^{2,7}.0^{3,6}.0^{4,12}.0^{5,9}]dodecan-11-one (**18a**), which was esterified to give **5a**.

The recent synthesis of pentaprismane (1)[1,2] follows more than a decade of research by numerous chemists employing diverse strategies to obtain this elusive hydrocarbon.[3] The attraction lies not only in the aesthetic

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