Effects of Salt Concentration and Anion on the Rate of Carrier-Facilitated Transport of Metal Cations through Bulk Liquid Membranes Containing Crown Ethers[1]

J. D. Lamb,* J. J. Christensen,* S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt*

Contribution from the Departments of Chemical Engineering and Chemistry and Contribution No. 154 from the Thermochemical Institute, Brigham Young University, Provo, Utah 84602. *Received January 26, 1979*

Abstract: A study is reported of the variation of cation transport rate through a bulk chloroform liquid membrane containing a neutral macrocyclic carrier with cation concentration in the source salt solution phase and with anion type. The transport rate was found to vary as the square of the cation activity in regions of low cation activity for the four salts studied (KCl, KI, KSCN, and KNO_3) using dibenzo-18-crown-6 (DB18C6) as membrane carrier. However, at high source phase cation activity, transport for some of the salts is less than that expected from this relationship. A mechanism is described to explain these results. The rates of transport of Li^+, Na^+, K^+, and Ba^{2+} salts by DB18C6 or 4-*tert*-butylbenzo-15-crown-5 were found to be strongly dependent on the anion present. The transport rates of K^+ salts with DB18C6 ranged over eight orders of magnitude according to anion. Anions with smaller Gibbs free energies of hydration allowed faster cation transport.

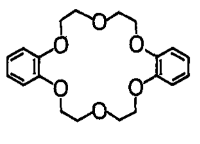
Introduction

Synthetic macrocyclic ligands such as crown ethers form unusually stable complexes with alkali and alkaline-earth cations and often demonstrate a high degree of cation selectivity.[2,3] In these respects they resemble the naturally occurring antibiotic macrocycles which have been shown to alter the permeability of biological membranes to certain cations.[4-6] Consequently, synthetic macrocycles have been studied as model carriers for transport of cations across cell membranes.[4-6] In addition, these ligands have potential in making separations among cations when introduced into liquid membrane systems.[7,8] For this latter reason, we have undertaken a systematic investigation of the factors which influence the rates of transport of cations across liquid membranes using macrocyclic ligand carriers.

A liquid membrane is a liquid phase which separates two other liquid phases with which it is immiscible. For example, in the liquid-membrane system depicted in Figure 1, cations are transported from one water phase (the source phase) to the other water phase (the receiving phase) through the "membrane." Movement of charged species through a hydrophobic membrane is accomplished by the presence of a macrocyclic ligand which acts as a cation carrier. Since macrocyclic ligands are neutral, the cation carries its co-anion with it across the membrane to maintain electrical neutrality in the system.[9,10]

The rate of cation transport through membranes by macrocyclic ligands has been shown to be influenced by the nature of the anion which accompanies the cation–macrocycle complex.[9,10] We reported in an earlier communication[11] the first systematic study of this effect. The present report gives details of these experiments as well as detailed analysis of the results. Experiments were also performed to determine the effect of source phase salt concentration on cation transport rates. Monovalent cation transport rates are shown to vary as the square of source phase cation activity, rather than concentration. The effects both of anion and of salt concentration are shown to conform to a transport mechanism described by Reusch and Cussler.[12]

The two macrocycles chosen as membrane carriers, dibenzo-18-crown-6 (DB18C6) and *tert*-butylbenzo-15-crown-5 (BB15C5), have ring structures whose cation complexation characteristics are well understood and have limited water solubility to prevent loss of carrier to the water phases. DB18C6 has been used as a membrane carrier by other workers[10,12,13] and is known to be effective in transport of Na^+, K^+, Rb^+, Cs^+, Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Hg^{2+}.[12]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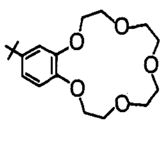
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Experimental Section

Materials. Reagent grade BB15C5 and DB18C6 (Parish Chemical Co., Provo, Utah) were used without further purification. Chloroform (Fisher reagent) was used as membrane solvent. The following reagent grade chemicals were obtained from the indicated sources: KI (MCB); KBr, KCl, $KC_2H_3O_2$, KOH, KSCN, $KBrO_3$, $Ba(NO_3)_2$ (Baker); KF, KNO_3 (B and A); K_3PO_4, K_2HPO_4, NaI, $BaCl_2$, K_2SO_4 (Fisher); NaCl (Allied); NaBr, KIO_4 (Mallinckrodt); LiCl, LiBr, LiI, $BaBr_2 \cdot 2H_2O$, BaI_2, KBF_4, KPF_6 (Alfa); potassium benzoate (Pfaltz and Bauer); $KClO_4$ (Research Chemicals); $NaClO_4 \cdot H_2O$ (G. F. Smith); $K_2Cr_2O_7$ (Merck); $LiClO_4$ (K and K). Potassium picrate was crystallized from a water mixture of picric acid (Baker) and KOH (Mallinckrodt).

Procedure. Liquid-membrane experiments were conducted using several sets of apparatus identical with that shown schematically in Figure 2. A chloroform solution (350 mL) containing 7.0×10^{-4} M crown ether was located at the bottom of a 120 × 65 mm glass crystallizing dish. Suspended 12 mm above the bottom of the dish (below the chloroform surface) was a glass cylinder open at both ends which separated inner and outer areas. Atop the outer ring of chloroform was placed 168 mL of distilled, deionized water (surface area = 76.8 cm^2). Atop the chloroform inside the cylinder was carefully placed 42 mL of salt solution (surface area = 36.3 cm^2). Where possible, 1 M solutions were prepared. The three phases were agitated by a stirring bar located at the bottom of the dish. Hurst synchronous motors (200 rpm) provided constant reproducible stirring. A second dish was placed inverted atop the first and the two sealed together with Parafilm to minimize evaporation. Samples of 2 mL were extracted from the outer receiving phase by syringe at 2-h intervals for 30 h starting 5 min after stirring began. The vessels were maintained at 25 ± 1 °C in a specially thermostated room. Samples were analyzed for cation content using a Perkin-Elmer Model 603 atomic absorption spectrophotometer.

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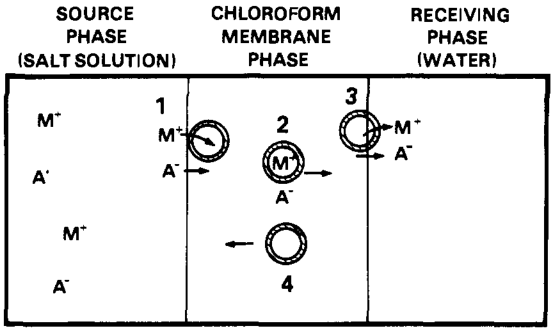

Figure 1. Salt transport across a liquid membrane: (1) cation, M^+, in source phase moves into the membrane phase (accompanied by anion, A^-) and is complexed by the macrocyclic ligand (represented by circle); (2) complex-anion pair move across the membrane; (3) cation and anion are released to receiving phase; (4) ligand returns to repeat the cycle.

Table I. Variation of K^+ Transport Rate with Salt Concentration and Activity in Source Phase

salt	C_{CS}, mol/L	$(a_{CS})^a$	j_c, mol/h × 10^7
KCl	0.10	0.078	0.15
	0.20	0.15	0.68
	0.30	0.21	1.0
	0.50	0.33	1.9
	0.75	0.48	3.4
	1.00	0.62	6.1
	2.50	1.54	30
KI	0.010	0.0090*	0.46
	0.10	0.079	34
	0.50	0.35	370
	1.00	0.68	620
KSCN	0.010	0.0090*	0.33
	0.030	*0.025**	2.7
	0.10	0.077	25
	0.30	0.21	150
	1.00	0.63	530
	2.50	1.59	917
	5.00	3.42	1183
KNO_3	0.010	0.0090*	0.12
	0.033	0.028*	1.2
	0.066	0.053*	4.6
	0.10	0.074	7.3
	0.33	0.20	67
	0.50	0.28	110
	0.66	0.34	180
	1.00	0.46	240
	2.00	0.70	380
	2.50	0.79	448
	3.00	0.86	522

[a] Activities calculated by converting C_{CS} to molal units[15] and multiplying by $\gamma_\pm$. Those marked with an asterisk were calculated using the extended Debye–Hückel equation,[16] $\log \gamma_\pm = (-0.5115I^{1/2})/(1 + 1.25I^{1/2})$ where I is the ionic strength; all others were calculated using $\gamma_\pm$ determined experimentally as tabulated by Robinson and Stokes.[16]

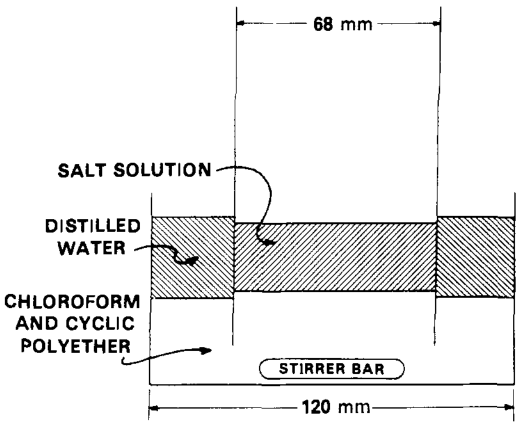

Figure 2. Liquid membrane cell using chloroform as membrane solvent.

Table II. Rate of Transport of Various Salts through a Chloroform Membrane Containing 7 × 10^{-4} M Crown Ether

salt		$(j_c)^a$ mol/h × 10^7	
type	C_{CS}, mol/L	DB18C6	BB15C5
$LiClO_4$	1.0	0.34	3.3
LiI	1.0	0.33	*b*
LiBr	1.0	*b*	*b*
LiCl	1.0	*b*	*b*
$NaClO_4$	1.0	58	98
NaI	1.0	15	*b*
NaBr	1.0	1.7	*b*
NaCl	1.0	0.31	*b*
KI	1.0	620	36
KSCN	1.0	530	13
potassium picrate	0.0020	510	1.9
KNO_3	1.0	240	1.9
$KClO_4$	0.10	120	2.0
potassium benzoate	1.0	110	
KBr	1.0	88	1.8
KPF_6	0.020	66	0.78
$KBrO_3$	0.40	8.5	
KCl	1.0	6.1	0.17
KIO_4	0.020	3.9	
KBF_4	0.020	3.1	*b*
KOH	1.0	2.1	
$K_2Cr_2O_7$	0.10	1.4	*b*
$KC_2H_3O_2$	1.0	1.2	
K_3PO_4	1.0	1.1	
KF	1.0	0.85	
K_2SO_4	0.48	*b*	
BaI_2	1.0	370	
$Ba(NO_3)_2$	0.20	*b*	*b*
$BaBr_2$	1.0	*b*	
$BaCl_2$	1.0	*b*	

[a] Each value is the average of two or more independent determinations. The experimental values deviate from the reported values by no more than ±10%. [b] Transport rate $<0.1 \times 10^{-7}$ mol/h.

Results

Transport rates, j_c, in mol/h for indicated source phase concentrations of salts of Li^+, Na^+, K^+, and Ba^{2+} by the two crown ether carriers studied are listed in Tables I and II. Two or three separate experimental units were employed in the determination of cation transport rate for each salt-macrocycle combination. In addition, a "blank" experiment was performed for each salt in which the membrane contained no carrier. No detectable movement of cation across the chloroform membrane was found in the blank unit. A plot of moles of cation transported into the receiving phase vs. time was made for each carrier-containing system. The data were fitted to a straight line, the slope of which gave values of j_c. Linear fits of the data were good, and agreement between different runs of the same system was within 10% in all cases. This linear increase in salt concentration in the receiving phase with time has been noted in similar experiments by other workers.[12,13]

Discussion

Variation of Transport Rate with Salt Concentration. The rate of cation transport across a liquid membrane has been shown to be a function of salt concentration in the source phase.[12] To determine quantitatively the effect of salt concentration on rate of transport, we varied the concentration in

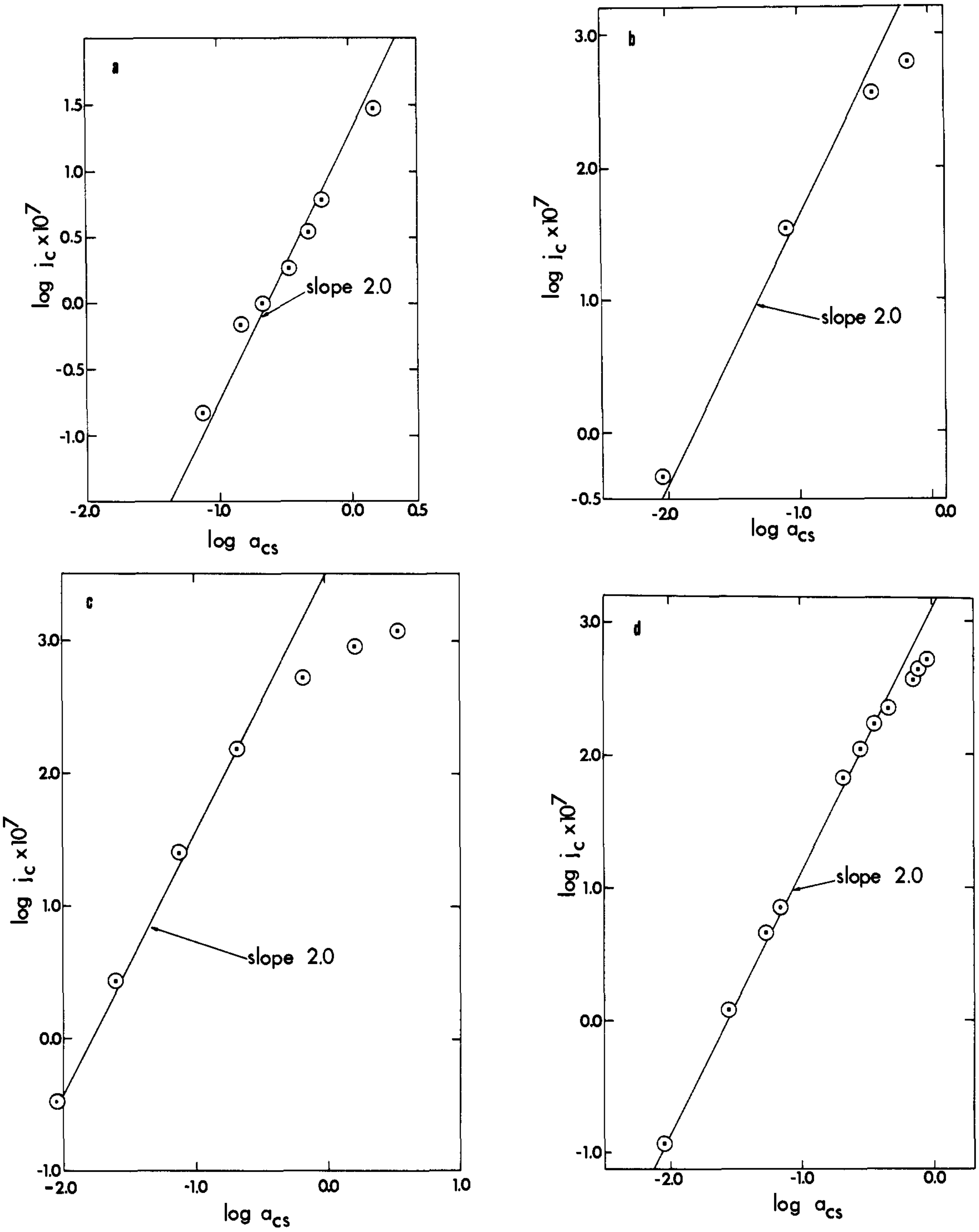

Figure 3. Variation of K^+ transport (as log j_c) with potassium ion activity in the source phase (as log a_{CS}) for (a) KCl; (b) KI; (c) KSCN; (d) KNO_3.

the source phase of four representative salts (KCl, KI, KSCN, and KNO_3). The results of this study are given in Table I.

In order to understand the results in Table I, we have used the following mechanism described by Reusch and Cussler:[12]

$$C_S^+ + A_S^- = (C^+A^-)_M \tag{i}$$

$$(C^+A^-)_M + L_M = (CL^+A^-)_M \tag{ii}$$

$(CL^+A^-)_M$ diffuses across the membrane (iii)

$$(CL^+A^-)_M = L_M + (C^+A^-)_M \tag{iv}$$

$$(C^+A^-)_M = C_R^+ + A_R^- \tag{v}$$

L_M diffuses back across the membrane. (vi)

In the above formulation, the following symbols are used: C^+, cation; A^-, anion; (C^+A^-), cation-anion pair; L, macrocyclic ligand; (CL^+A^-), cation complex associated with anion. The subscripts S, M, and R indicate species in the source, membrane, and receiving phases, respectively. Steps i and v are described by a partition coefficient, *k*, while step ii (the inverse of step iv) is described by the equilibrium constant *K*. In the development of this mechanism, steps i, ii, iv, and v are assumed to be rapid with respect to the others.

Following the reasoning of Ward,[14] Reusch and Cussler[12] derived the equation

$$j_c = \frac{D_{CLA}kKC_L}{l}\left(\frac{C_{CS}^2}{1 + kKC_{CS}^2}\right) \tag{1}$$

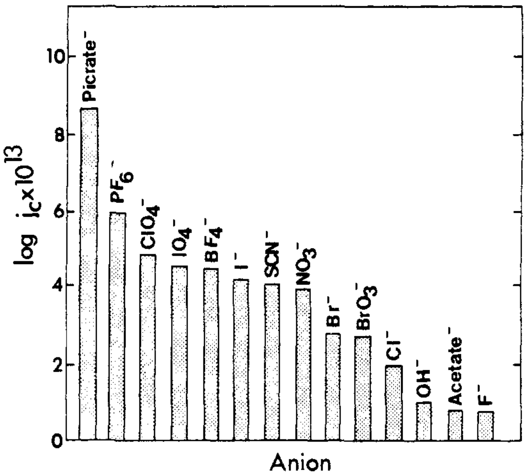

Figure 4. Variation of K^+ transport (as $\log j_c$) across a chloroform liquid membrane with anion (j_c for all salts adjusted to a source phase concentration of 0.0020 M for reasons given in text).

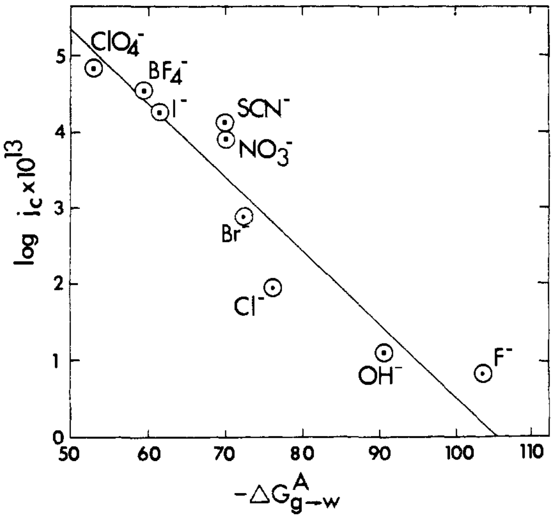

Figure 5. Plot of $\log j_c$ vs. $-\Delta G_{g\to w}{}^{A}$ for several anions.

to describe the cation flux, j_c, in terms of k, K, D_{CLA} (the diffusion coefficient of $(CL^+A^-)_M$), l (the length of the diffusion path), C_L (the total concentration of carrier), and C_{CS} (the concentration of cation in the source phase). The equation is valid for membrane transport such as that reported in this work where diffusion of $(C^+A^-)_M$ is negligible (as indicated by the results of "blank" experiments) and $C_{CS} \gg C_{CR}$. As shown by Reusch and Cussler,[12] if $kKC_{CS}{}^2 \ll 1$, the equation further reduces to

$$j_c = \frac{D_{CLA}kKC_L}{l} C_{CS}{}^2 \quad (2)$$

and j_c should be directly proportional to $C_{CS}{}^2$ if all other terms in eq 2 are constant. Indeed, these authors showed that relationship 2 holds for the transport of KCl through a chloroform membrane containing the carrier DB18C6 using various concentrations of KCl in the source phase.

In testing our concentration vs. transport rate data against eq 2, we found that the linear correspondence of j_c to $C_{CS}{}^2$ broke down at high C_{CS}. For this reason, activities, a_{CS}, were used as in the equations

$$j_c = \frac{D_{CLA}kKC_L}{l}\left(\frac{a_{CS}{}^2}{1 + kKa_{CS}{}^2}\right) \quad (3)$$

$$j_c = \frac{D_{CLA}kKC_L}{l} a_{CS}{}^2 \quad (4)$$

These activities, listed in Table I, were obtained by converting C_{CS} from molar to molal units[15] and by either referring to tables of empirically derived activity coefficients[16] or using the extended Debye-Hückel equation[16] as indicated in Table I (footnote *a*).

Equation 4 predicts that points on a plot of $\log j_c$ vs. $\log a_{CS}$ should lie on a line having a slope of 2. In Figures 3a-d are plotted the $\log j_c$ vs. $\log a_{CS}$ for the four potassium salts studied. In the case of KCl, whose transport rates are consistently lower than those of the other salts at corresponding concentrations, the points fall very close to a line having a slope of 2 as predicted by eq 4. Among the other three salts, the points at small a_{CS} also fall close to this line. However, negative deviation from the line is noted for KSCN, KI, and KNO_3 at high a_{CS}, and most significantly with KSCN. One possible explanation for this result is that at high concentrations of these salts the term $kKa_{CS}{}^2$ in eq 3 is not insignificant with respect to 1, an assumption used to give eq 4. This term, $kKa_{CS}{}^2$, should be greatest for KSCN, KI, and KNO_3, which transport considerably faster than KCl because of the relative values of k (see next section). Equation 3 correctly predicts that, as the term $kKa_{CS}{}^2$ becomes significant, $\log j_c$ should increase less rapidly with $\log a_{CS}$ than when $kKa_{CS}{}^2$ is negligible.

Variation of Transport Rate with Anion. The rates of transport of the cations Li^+, Na^+, K^+, and Ba^{2+} were determined using two carriers, DB18C6 and BB15C5, in the presence of several anions. These results, listed in Table II, indicate that the anion has a large effect on cation transport rate, as noted previously.[11]

Salts used in this study which were not soluble in water to 1.0 M were studied at lower concentrations (Table II). In order to compare the relative effectiveness of the various anions in promoting cation transport, transport rates for all anions were extrapolated to rates corresponding to a common salt concentration. The previous section indicates that extrapolation in the direction of lower concentration is valid if care is taken to avoid high-concentration regions where variation of transport rate with $a_{CS}{}^2$ is not linear. Therefore, the common concentration chosen for comparison was that of the least soluble salt, potassium picrate, at 0.0020 M. Values for the transport rates of potassium salts at 0.0020 M were calculated from measured rates at higher concentration (Tables I and II) using eq 4 and are listed in Table III in descending order of cation transport rate. These extrapolated transport rate values are useful in predicting the relative order of transport rates of anions. In using eq 4, activities were calculated as described in the previous section and these are also listed in Table III. Extrapolations to 0.0020 M involving KNO_3, KI, and KSCN transport with DB18C6 were made from measured transport rate values obtained at 0.1 rather than 1.0 M, inasmuch as these three salts behave according to eq 3 at higher concentrations as described in the above section. All other extrapolations were made from the values listed in Table II.

It is noteworthy that the order of anions listed in Table III is the same with both carriers, DB18C6 and BB15C5. The magnitude of this "anion effect" on K^+-DB18C6 transport is illustrated in Figure 4, which graphically compares the adjusted transport rates. From the figure it is apparent that the transport rate of K^+ varies over almost eight orders of magnitude according to the anion present. Examination of the data in Table II indicates that the same order of transport rates according to anion noted for salts of K^+ is observed among salts of Li^+, Na^+, and Ba^{2+} as well.

The variation of j_c with anion may be rationalized using eq 4. This equation predicts that j_c is a function of k, where k is related to the Gibbs free energy of partitioning between water and membrane, ΔG_p, according to the equation

$$\Delta G_p = -RT \ln k \quad (5)$$

Table III. K^+ Transport Rates Adjusted to a Common Source Phase Concentration (0.0020 M) Listed in Descending Order with Anion and Gibbs Free Energy of Anion Hydration

anion			$\log(j_c \times 10^{13})^c$	
type	$(-\Delta G_{g\to w}{}^A)^a$	$(a_{CS})^b(\times 10^3)$	K^+-DB18C6	K^+-BB15C5
picrate		1.90*	8.71	6.28
PF_6^-		17.4*	5.90	3.97
ClO_4^-	50.3	77.3*	4.86	3.08
IO_4^-		17.4*	4.67	
BF_4^-	59.8	17.4*	4.57	
I^-	61.4	78.6 (at $C_{CS} = 0.1$)	4.30	
		677 (at $C_{CS} = 1.0$)		2.45
SCN^-	69.9	77.7 (at $C_{CS} = 0.1$)	4.17	
		632 (at $C_{CS} = 1.0$)		2.07
NO_3^-	69.5	74.3 (at $C_{CS} = 0.1$)	3.92	
		456 (at $C_{CS} = 1.0$)		1.52
Br^-	72.5	646	2.88	1.19
BrO_3^-	76.3	239	2.73	
Cl^-	75.8	77.8 (at $C_{CS} = 0.1$)	1.95	
		622 (at $C_{CS} = 1.0$)		0.20
OH^-	90.6	777	1.10	
F^-	103.8	677	0.83	
$C_2H_3O_2^-$		827	0.80	
SO_4^{2-}	238.7		*d*	

[a] Data from Friedman and Krishnan[17] combined with those from Smith[18] in kcal/mol. [b] Activity of K^+ in the source solution used to produce the transport data in Table II (except KNO_3, KI, and KSCN with DB18C6, for which data in Table I at 0.1 M were used) from which extrapolations were made. These activities were obtained by converting M to m[15] and multiplying by $\gamma_\pm$, which was obtained using the extended Debye-Hückel equation as in Table I, footnote *a* (values marked by an asterisk) or from tables.[16] [c] Values at 0.0020 M source phase obtained from j_c at 0.0020 M = (j_c at measured C_{CS})(a at 0.002 M)^2/(a at experimental C_{CS})^2, where a at 0.0020 M is 0.0019. [d] No measured transport.

If all other terms in eq 4 are included in constant B, then combining eq 4 and 5 gives

$$J_c = Be^{-\Delta G_p/RT} \qquad (6)$$

The term ΔG_p can be divided into its component parts

$$\Delta G_p = \Delta G_p{}^C + \Delta G_p{}^A + \Delta G^{CA} \qquad (7)$$

where the first two terms represent the free energies of partitioning of the cation and anion, respectively, and ΔG^{CA} represents the free energy of interaction of the cation with the anion in the membrane phase. If $\Delta G_{g\to M}{}^A$ represents the free energy of transferring the anion from the gas phase to the membrane phase, and $\Delta G_{g\to w}{}^A$ that from the gas phase to water, then

$$\Delta G_p{}^A = \Delta G_{g\to M}{}^A - \Delta G_{g\to w}{}^A \qquad (8)$$

Therefore

$$\Delta G_p = \Delta G_p{}^C + \Delta G_{g\to M}{}^A - \Delta G_{g\to w}{}^A + \Delta G^{CA} \qquad (9)$$

Of the quantities in eq 9 Gibbs free energies of hydration, $\Delta G_{g\to w}{}^A$, are available[17,18] for most of the anions included in this study. These $\Delta G_{g\to w}{}^A$ values, listed in Table III, are seen to become more negative through the series of anions as transport rates decrease.

Equations 6 and 9 predict a simple correspondence between $\log j_c$ and $\Delta G_{g\to w}{}^A$ only if it is assumed that all other ΔG terms comprising ΔG_p in eq 9 are constant or compensate each other for all anions. While such an assumption is overly simplistic, Figure 5 demonstrates that the change in $\log j_c$ with increasing $\Delta G_{g\to w}{}^A$ is fairly regular. This regular trend may arise from the common factors (namely, anion size, charge, and polarizability) which influence the values of all the free-energy terms relating to the anion ($\Delta G_{g\to M}{}^A$, $\Delta G_{g\to w}{}^A$, ΔG^{CA}) in eq 9. Regardless of the reason for this regular behavior, the data in Figure 5 show that there is an empirical correlation between cation transport rate and anion hydration energy.

The magnitude of the effect of anion on the facilitated transport of cations across liquid membranes holds significant implications. Interpretation of results of cation-transport experiments where anions move through the membrane requires that the role of the anion(s) be understood. Comparisons of transport carrier effectiveness and system design ought to be made where a common anion has been employed. The anion effect may be exploited in that transport of cations across membranes can be turned on or off simply by altering the anion present in the source phase. This same anion effect has potential in separating or detecting anions themselves.

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References and Notes

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(15) Conversion of M to *m* for KSCN, $KClO_4$, KBr, $KBrO_3$, KOH, KF, and $KC_2H_3O_2$ solutions was made using the solution densities, which were determined by repeatedly delivering 250 μL of solution at 25 ± 1 °C onto an analytical balance using a calibrated Eppendorff pipet. For solutions of KCl, KI, and KNO_3, conversion of M to *m* was made from tables in Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolytic Solutions", 2nd ed.; Reinhold: New York, 1950; p 556.

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