

Selective Binding of Ions by Polyelectrolyte Gels. The Volume Change Criterion

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Contribution from the Oak Ridge National Laboratory,
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Abstract: The volume changes, ΔV , which accompany the selective binding of ions in ion-exchange reactions at 25° between aqueous electrolyte mixtures and polyelectrolyte gels were measured in an attempt to establish the range of applicability of the Katchalsky and the Rice-Harris theories. The ΔV for the exchange of singly charged ions in lightly cross-linked polystyrene type strong-acid or strong-base ion-exchanger gels were small and positive or negative depending on the nature of the ions. Large, positive volume changes were observed with multiply charged cations. In general, ΔV became more positive with increased gel cross linking and with the strength of binding as measured by the decrease in the standard free energy, ΔG° , in the ion-exchange reaction. Four types of ion-binding processes were distinguished: (a) field binding; (b) site binding *via* ion-pair formation; (c) structure-enforced binding; and (d) charge-transfer binding. Multiply charged cations (*i.e.*, Ca²⁺, Ba²⁺, La³⁺, Th⁴⁺) were selectively bound as ion pairs in all gels. Field binding could be inferred only for the selective uptake of singly charged cations in the lightly cross-linked gel.

Polyelectrolyte gels when placed in aqueous mixtures of simple electrolytes at room temperature are observed usually to undergo perceptible changes in their external volume. At the same time, a selective binding of some of the ions in solution occurs with a lowering of the free energy and with changes in the enthalpy, entropy, and heat capacity of the system. The volume of the system frequently appears to change only slightly suggesting that ΔV is small. This inference is consistent qualitatively with the results from fragmentary observations^{2,3} on the effect of pressure on the thermodynamic equilibrium constant, K_a , of an ion-exchange reaction at constant temperature and ionic composition

$$(d \ln K_a/dP)_{T,x} = -\Delta V^\circ/RT \quad (1)$$

where ΔV° is the algebraic difference between the apparent molal volumes of the products and reactants in their "standard states." Thus, a ΔV° of less than 0.2 ml mol⁻¹ may be inferred from the report² that hydrostatic pressures approaching 6670 bars had no effect on the potassium-hydrogen ion-exchange equilibrium with a highly cross-linked polystyrenesulfonic acid exchanger, assuming that a 5% change in the equilibrium constant could be detected. Measurements on the strontium-hydrogen ion-exchange equilibrium by the same investigators lead to the conclusion that as the pressure increases the affinity of the exchanger for Sr²⁺ increases; hence, according to eq 1, ΔV° for the reaction must be negative.

Strauss and Leung⁴ in their pioneering measurements on the volume changes accompanying ion binding by polyelectrolytes in aqueous solutions have obtained two results with a cross-linked polystyrenesulfonic acid gel indicating that ΔV° may be substantially larger than the values inferred from pressure coefficient determinations. Thus, a volume increase of 5.4 ml mol⁻¹ was

observed in the selective uptake of lithium ion by the tetramethylammonium salt form of a nominally 8% DVB cross-linked polystyrenesulfonate, and an increase of 13.0 ml mol⁻¹ was found in the selective binding of calcium ion by the gel.

Systematic additional measurements of the volume changes accompanying the selective binding of ions by polyelectrolyte gels appeared to be desirable because of their relevance to the theories of Katchalsky and Michaeli^{5,6} and of Rice and Harris⁷ which attempt to account for the equilibrium behavior of polyelectrolyte gels in terms of the interaction of the counterion with the fixed charge. The theory of Katchalsky, which is based on a cell model, should apply only to lightly cross-linked gels, although it has been extended to heavily cross-linked preparations by Miller, Bernstein, and Gregor.⁸ In this theory the interaction between all groups on one and the same chain in the gel network is calculated ignoring the interactions with neighboring chains. No chemical interactions between the counterions and fixed charges are assumed (*i.e.*, no ion-pair formation). Rather, the counterions are constrained by the electrostatic field (*i.e.*, "field binding"). The volume change for the replacement of one type of counterion by another therefore should be approximately the same magnitude (*i.e.*, ≤ 1 ml mol⁻¹) as that observed in the mixing of simple electrolytes.

The Rice-Harris theory, which is based on a lattice model, applies to moderately and heavily cross-linked polyelectrolyte gels. Ion pairs are assumed, and, in fact, these are the sole cause of the selective binding. Intrinsic dissociation constants (K_{AR} and K_{BR}) appear explicitly in the final expression for the selectivity coefficient. Volume changes of the same order of magnitude as for the formation of ion pairs in electrolyte solutions may be expected (*i.e.*, 3 to 15 ml mol⁻¹) depending on whether outer sphere (solvent-separated pairs) or inner sphere (contact ion pairs) complexes are

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(2) R. A. Horne, R. A. Courant, B. R. Myers, and J. H. B. George, *J. Phys. Chem.*, **68**, 2578 (1964).

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(7) S. A. Rice and F. E. Harris, *Z. Phys. Chem. (Frankfurt am Main)*, **8**, 207 (1956).

(8) I. F. Miller, F. Bernstein, and H. P. Gregor, *J. Chem. Phys.*, **43**, 1783 (1965).

formed. Recently, Hemmes⁹ has shown that the volume change, ΔV_F , for the creation of a "Fuoss ion pair" is given by

$$\Delta V_F = \frac{|Z_A Z_B| e_0^2 N}{aD} \left(\frac{d \ln D}{dp} \right)_T - RT\beta \quad (2)$$

where a is the distance of closest approach of the ions, D is the dielectric constant, e_0 is the electronic charge, and the other symbols have their usual meanings. The first term on the right-hand side of eq 2 is greater than the second; hence, the predicted volume change for ion-pair formation is positive. (A similar conclusion can be deduced for "Bjerrum ion pairs.") Further, eq 2 shows that ΔV_F increases as the distance of closest approach decreases. Hence, a criterion for site binding of ions by polyelectrolyte gels when ion association occurs is that ΔV will be positive and will increase as the strength of binding increases.

The origin of the volume change observed in site binding *via* ion-pair formation in polyelectrolyte gels deserves comment. As Hemmes has indicated, a large volume change cannot be attributed to the release of coordinated water molecules; this process should have only a small ΔV (*i.e.*, 1 to 5 ml mol⁻¹). However, a significant volume increase is expected to result from ion association because of the consequent destruction of the ordering of the solvent molecules.

Other types than purely electrostatic interactions between counterions and polyelectrolyte gels may be important in determining selective binding (*i.e.*, the formation of charge-transfer complexes or "structure-enforced binding"), and the sign and magnitude of the volume change for these are not easily predictable. Non-electrostatic effects on the hydrogen bonding of water must always be present and sometimes may be dominant. Standard enthalpy, ΔH° , and entropy change values, ΔS° , taken from previous researches¹⁰ may be useful in the interpretation of ΔV , as will be shown.

Experimental Section

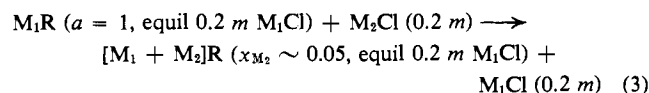
Apparatus and Procedure. Volume changes were measured with Carlsberg inverted "V" type, two-bulb instruments similar to those described by Linderström-Lang and Lanz.¹¹ An accurately predetermined quantity, usually 2–4 mequiv of air-dried, homoionic ion-exchange gel, was placed in one arm of the dilatometer and covered with 1 ml of an 0.2 *M* aqueous solution containing the same counterion as in the exchanger. Approximately 1 ml of 0.2 *M* solution containing a different cation (or anion) which was taken up preferentially by the gel was placed in the second arm. The amount of the latter was determined by weighing. All solutions were degassed to remove dissolved air which otherwise formed bubbles when the solutions were placed in the dilatometer, and the latter were brought to constant temperature. The upper portions of the arms of the dilatometer were filled with pure, water-saturated *n*-heptane, and a *ca.* 0.19-mm radius, constant bore capillary 40 cm long and graduated at 1.00-mm intervals was attached to the "V" through a 10/30 standard taper joint. Glycerol, phosphoric acid, and other recommended lubricants^{11,12} for the joint were unsatisfactory. However, a leak-free seal which held for several hours was obtained when a heptane-insoluble, fluorocarbon grease (KEL-F No. 90, 3M Co.) was used. After adjusting the level of

the heptane in the capillary, the dilatometer was immersed in a thermostat bath maintained at $25.00 \pm 0.001^\circ$ for short periods. Thermal equilibrium was reached usually within 20 min and the level of the meniscus in the capillary was read with a 50-mm range, 0.01-mm direct reading traveling microscope.

The contents of the dilatometer were mixed and the exchanger was stirred with the final solution by means of a small glass encased magnetic stirrer bar placed in one arm of the dilatometer. Volume changes were complete within 5–10 min after mixing, and final readings were taken after 30 min. The change in the heptane level in the capillary was determined to ± 0.2 mm. The limiting factor in estimating Δh was the constancy of the water bath temperature over a period of *ca.* 30 min. Calibrations with pure water at a known temperature gave 0.117 μ l per mm of capillary. No interaction of the water-saturated heptane with the aqueous solutions or with the polyelectrolyte gel in the dilatometer was observed. Blanks were measured by mixing water with water or by mixing identical solutions of dilute electrolyte to ensure that systematic errors were absent. Measurements also were made of the volume change¹³ in the neutralization of 0.1 *M* HCl with 0.1 *M* NaOH to check on the accuracy of the dilatometer.

A large excess of polyelectrolyte gel was used so that at least 95% of the preferred ion was removed from solution. The number of milliequivalents of exchange reaction, Δq , therefore, could be estimated with fair accuracy from the initial milliequivalents of preferred ion introduced into the dilatometer. When required, more accurate values for Δq were computed from the total milliequivalents of exchanger and the respective milliequivalents of the exchanging ions making use of the known ion-exchange reaction equilibrium constants and solving either quadratic, cubic, or quartic equations based on the mass law.

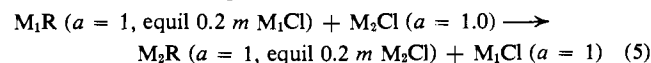
The normality of the aqueous solution in contact with the gel remained virtually constant at a value close to $N = 0.2$ throughout the reaction. Further, the amount of preferentially bound ion initially in the aqueous phase was so small that only 5–10% of the counterions in the gel were replaced. Hence, the volume change observed was the "volume of partial exchange," $\Delta \bar{V} = (\Delta V/\Delta x)$, where $x = \Delta q/q$ is the equivalent fraction of the preferred ion in the final gel and q is the total milliequivalents of exchange sites in the gel. The magnitude of $\Delta \bar{V}$ appeared to be independent of x , as expected if the apparent molar volumes of the two ionic forms present in the equilibrium gel were additive. Thus, for example, the reaction between singly charged cations may be written



The ΔV observed for eq 3 is then

$$\Delta V = [\phi_v^\circ(M_2R) - \phi_v^\circ(M_1R)] - [\phi_v(M_2Cl) - \phi_v(M_1Cl)] \quad (4)$$

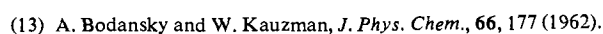
where $\phi_v^\circ(M_1R)$ and $\phi_v^\circ(M_2R)$ are the apparent molar volumes of the respective homoionic forms of the gel in their "standard states" defined for the gel in equilibrium with 0.2 *m* aqueous chloride solution containing the same cation as in the gel. The volume change, ΔV , is therefore seen to be equal to a "difference in differences" between apparent molar volumes. The correction for the difference for the electrolyte solutions to a standard state of infinite dilution is small; hence the observed ΔV approximates ΔV° , the volume change in the standard state binding reaction.



Materials. Strong-acid type cation-exchange gels (Dowex-50W) based on cross-linked sulfonated polystyrene were employed. Their cross-linkings in nominal per cent divinylbenzene (DVB) were 0.5, 8, and 24%; their exchange capacities were 5.46, 5.11, and 4.30 mequiv/g of dry hydrogen form, respectively. A strong-base anion-exchange gel (Dowex-1) of 0.5% nominal DVB cross-linking and 4.34 mequiv/g of dry chloride form capacity was employed for measurements of the anion selective binding reactions. Determinations of the weak-base capacity indicated less than 2% of the capacity was attributable to this source.

Results

The volume changes were observed to be additive



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(12) G. Johansen, *C. R. Trav. Lab. Carlsberg, Ser. Chim.*, **26**, 399 (1948).

within the limits of experimental error unless complications occurred. Thus, with the lightly cross-linked (*i.e.*, 0.5% DVB) cation-exchange gel, the measured ΔV for the exchange of tetramethylammonium with NH_4^+ ion in the exchanger was -0.94 ml/equiv. The sum of the ΔV 's for the reaction of Me_4N^+ with Na^+ ion (-1.23 ml/equiv), of Na^+ with Cs^+ ion (-0.66 ml/equiv), and of Cs^+ with NH_4^+ ion (0.92 ml/equiv) was -0.97 ml/equiv, which is considered to be in agreement with -0.94 ml/equiv. Additivity was not found in the reactions of thorium ion in 8% DVB cross-linked gel, where $\Delta V_{\text{H}^+ \rightarrow \text{Th}^{4+}}$ for the replacement of H^+ by Th^{4+} ion was 6.03 ml/equiv, but $\Delta V_{\text{Na}^+ \rightarrow \text{Th}^{4+}} = -2.07$ and $\Delta V_{\text{H}^+ \rightarrow \text{Na}^+} = 4.0$ ml/equiv, respectively. The decrease in volume in the replacement of sodium by thorium ion was probably caused by the hydrolysis of the latter. There was evidence for interaction in the reaction between Ag^+ and ammonium ion in the exchanger, presumably because of the formation of $\text{Ag}(\text{NH}_3)_2^+$ ion. The directly measured $\Delta V_{\text{NH}_4^+ \rightarrow \text{Ag}^+}$ was only 0.5 compared with 1.5 ml/equiv derived from additivity. With zinc ion the nature of the anion in the initial aqueous solution was important; with ZnCl_2 the volume change was but 0.8 compared with 1.9 ml/equiv for $\text{Zn}(\text{NO}_3)_2$ solution.

Values for the volume changes for the replacement of Me_4N^+ ion from the lightly cross-linked gel by Li^+ , Na^+ , and K^+ ions derived by additivity from the measurements in this research were in excellent agreement with the direct measurements of Strauss and Leung⁴ on a *ca.* 0.19 *m* solution of linear polystyrenesulfonate initially in the tetramethylammonium form. Thus, volume changes of 0.9 , and 0.9 , 1.3 , and 1.2 , and 1.4 and 1.5 ml/equiv, respectively, were observed for Li^+ , Na^+ , and K^+ ions. Satisfactory concordance with the ΔV observed by Strauss and Leung for the replacement of Me_4N^+ ion in a moderately cross-linked (8% DVB) polystyrenesulfonate gel by Li^+ ion also was observed (*i.e.*, 5.4 *vs.* 4.8 ml/equiv).

Because of the additivity of the observed volume changes, the ΔV values given in Tables I–III were made relative to the replacement of H^+ ion by cations and relative to the replacement of F^- ion by anions. Hy-

Table I. Volume, Standard Free Energy, Enthalpy, and Entropy Changes for the Replacement of H^+ Ion from a Lightly Cross-Linked Polystyrenesulfonate Gel

Cation	ΔV , ml mol ⁻¹	ΔG° , kcal mol ⁻¹	ΔH° , kcal mol ⁻¹	ΔS° , cal deg ⁻¹ mol ⁻¹
Li^+	0.1	-0.05	0.07	0.0
NH_4^+	0.2	-0.06	-0.28	-0.8
Na^+	0.4	-0.01	-0.26	-0.9
K^+	0.6	-0.13	-0.49	-1.2
Cs^+	1.1	-0.24	-0.62	-1.3
Ag^+	1.7	-0.23	-0.18	0.1
Me_4N^+	-0.8	-0.29	-0.82	-1.9
Et_4N^+	-2.5	-0.36	-0.76	-0.7
<i>n</i> - Pr_4N^+	-3.5	-0.40	+0.30	+2.2
<i>n</i> - Bu_4N^+	-2.0	-0.49	+1.95	+8.1
Me_3BzN^+	-1.2			
Mg^{2+}	2.6			
Ca^{2+}	4.2			
Ba^{2+}	6.2			
Zn^{2+}	3.8			
Cr^{3+}	1.8			
La^{3+}	12.3			
Th^{4+}	15.3			

Table II. Volume, Standard Free Energy, Enthalpy, and Entropy Changes for the Replacement of F^- Ion from a Lightly Cross-Linked Polyvinyl Trimethylbenzylammonium Anion Exchange Gel

Anion	ΔV , ml mol ⁻¹	ΔG° , kcal mol ⁻¹	ΔH° , kcal mol ⁻¹	ΔS° , cal deg ⁻¹ mol ⁻¹
F^-	0.00	0.0	0.0	0.0
Cl^-	0.68	-0.82	-1.61	-2.6
Br^-	0.73	-1.15	-2.79	-5.5
I^-	0.75	-1.94	-5.04	-10.4
<i>p</i> - EtBzSO_3^-	-0.58			

Table III. Volume, Standard Free Energy, Enthalpy, and Entropy Changes for the Replacement of H^+ Ion from Various Cross-Linked Polystyrenesulfonates^a

Cation	0.5% DVB	8% DVB	24% DVB
A. Singly Charged Cations			
Li^+	ΔV	0.1	0.8
	ΔG°	0.05	0.13
	ΔH°	0.07	0.26
	ΔS°	0.0	0.6
Na^+	ΔV	0.5	4.1
	ΔG°	-0.01	-0.23
	ΔH°	-0.26	-1.18
	ΔS°	-0.9	-3.0
NH_4^+	ΔV	0.2	5.1
	ΔG°	-0.06	
	ΔH°	-0.28	
	ΔS°	-0.8	
Cs^+	ΔV	1.2	4.8
	ΔG°	-0.24	-0.56
	ΔH°	-0.62	-1.95
	ΔS°	-1.3	-4.5
Ag^+	ΔV	1.8	3.1
	ΔG°	-0.23	-1.06
	ΔH°	-0.18	-1.07
	ΔS°	0.1	0.1
Me_4N^+	ΔV	-0.7	-4.0
	ΔG°	-0.29	0.04
	ΔH°	-0.82	-1.14
	ΔS°	-1.9	-3.8
B. Multiply Charged Cations			
Ca^{2+}	ΔV	4.2	9.8
	ΔG°		-1.16
	ΔH°		0.48
	ΔS°		5.8
Ba^{2+}	ΔV	6.2	15.4
	ΔG°		-2.04
	ΔH°		-0.86
	ΔS°		4.4
La^{3+}	ΔV	12.3	16.5
	ΔG°		-3.36
	ΔH°		0.60
	ΔS°		13.8
Th^{4+}	ΔV	15.3	24.0
	ΔG°		
	ΔH°		
	ΔS°		

^a ΔV in ml mol⁻¹; ΔG° and ΔH° in kcal mol⁻¹; ΔS° in eu mol⁻¹.

drogen ion is the least strongly bound ion, except for Li^+ , by polystyrenesulfonate in solution or in gels. Raman,¹⁴ ir,¹⁵ and nmr¹⁶ measurements are in agreement that polystyrenesulfonic acid is highly dissociated,

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(15) G. Zundel, "Hydration and Intermolecular Interaction—Infrared Investigations of Polyelectrolyte Membranes," Academic Press, New York, N. Y., 1969.

(16) L. Kotin and M. Nagasawa, *J. Amer. Chem. Soc.*, **83**, 1026 (1961).

hence the binding of H^+ may be assumed to be non-localized. Fluoride is the anion least strongly bound by polyvinyl trimethylbenzylammonium ion-exchange gels.

Discussion

Volume Changes in the Selective Binding of Ions in Lightly Cross-Linked Cation- and Anion-Exchange Gels. It will be noted in Table I that ΔV for the singly charged cations was small and was either positive or negative. Selective binding of the alkali-metal cations and NH_4^+ was accompanied by a volume increase and a negative ΔS° . Field binding of these ions may be inferred and the small decrease in the entropy may be attributed to the net increase in the ordering of the solvent molecules in the system.

The volume *decreases* which accompanied the selective binding of the *n*-alkylammonium cations were significant, as electrostatic ion-pair formation must be excluded. A substantial entropy increase and the absorption of heat also accompanied the uptake of the largest of these ions. The process may be described as "structure-enforced binding" because of the apparent importance of ion-solvent rather than ion-ion interactions. Since the researches of Frank and Wen^{17a} it has been recognized that large, organic cations interact in a special way with hydrogen-bonded solvents. Recent X-ray diffraction measurements¹⁸ with tetra-*n*-butylammonium fluoride solution have supplied convincing evidence that such ions promote short-range order in water. (1) The fraction of cavity sites occupied by water molecules in the expanded ice-I "structure" of liquid water decreases from 0.5 for pure water to zero for the solution. (2) The nearest neighbor network distances between water molecules are shortened. (3) The "root-mean-square" displacements associated with the network distances are significantly smaller than in pure water (*i.e.*, the interaction is sharper).

The foregoing changes in the short-range order in water caused by large, organic cations are reflected by the increased partial molar volume, \bar{V}_1 , of water in the solution, by an increase in its heat capacity, and by a decrease in its entropy. When, because of selective binding, R_4N^+ ions leave the aqueous phase, the cavities in the structure partially refill with water molecules and \bar{V}_1 decreases and approaches 18.068 ml mol⁻¹; hence, ΔV is negative and ΔS° is positive. Tetra-*n*-butylammonium ion appears (Table I) to be irregular in that the volume decrease it produces was smaller than with tetra-*n*-propylammonium ion. This behavior apparently arises because of interactions between the structural effects around the tetra-*n*-butylammonium ions in the gel solution of the ion exchanger.^{17b}

Perceptibly larger volume increases were observed (Table I) for the selective binding of multiply charged cations by the lightly cross-linked gel. In all cases site binding appears to occur; with Ba^{2+} , La^{3+} , and Th^{4+} ions, contact ion pairs may be formed.

The volume change criterion for the selective uptake of halide ions by a lightly cross-linked cationic gel based on polystyrene is not obeyed (Table II). The

magnitude of the volume increase suggests that only field binding is involved, yet other thermodynamic data, especially the changes in ΔH° , show that strong interactions are present, particularly with I^- ion. Other types of forces than purely electrostatic must be important, and, in view of the aromatic character of the polyelectrolyte gel, the possibility of binding *via* the formation of "charge-transfer" complexes must be considered. Earlier studies¹⁹ have shown that the concept of charge-transfer interactions of halide ions with ion-exchange gels and permselective membranes containing aromatic groups is consistent with their properties. Thus, I^- ion with the greatest charge-transfer (ct) interaction has a larger affinity than Cl^- ion which has the smallest ct interaction. Gels not containing aromatic groups, but otherwise similar in properties, bind I^- and Cl^- ion about equally strongly.

The ΔV for the selective binding of the *p*-ethylbenzenesulfonate ion was negative, suggesting that this species may induce short-range order in the aqueous phase. However, because of the polar sulfonate group in the anion, the volume decrease is appreciably smaller than was observed with the more hydrophobic trimethylbenzylammonium cation (*cf.* Table I).

Volume Changes in the Selective Binding of Ions in Moderately and Heavily Cross-Linked Polyelectrolyte Gels. Increasing the cross-linking of a polyelectrolyte gel increases the density of the structurally bound charged groups so that interactions with the counterions are enhanced. The hydration of the gel is also decreased (*i.e.*, reduced swelling). Thus, the amount of ion-solvent interaction is diminished while ion-ion interactions are increased; consequently an increase in ΔV should result as is suggested qualitatively by eq 2 (*i.e.*, because of a larger effective Z_B). This expectation appears to be confirmed by the entries in Table III, where it can be observed that the volume change increases with increased cross-linking and with the counterion charge, Z_A . Site binding occurs for nearly all ions, except H^+ and Li^+ , and, with the heavily cross-linked gel, it seems likely that contact ion pairs are formed by the multiply charged cations while the singly charged species give solvent-separated pairs (*i.e.*, "outer sphere" complexes). The selective binding of multiply charged ions is also accompanied by substantial entropy increases suggesting that ion dehydration must occur. However, as noted earlier the volume increase accompanying the release of water molecules is small relative to the increase consequent to the destruction of the ordering of the solvent when ion association occurs. It is not possible from the volume changes given in Table III to distinguish between solvent-separated and contact ion-pair formation. Results from studies on aqueous solutions indicate that ΔV for the conversion of outer-sphere to inner-sphere complexes is small and positive.⁹ The magnitude of some of the ΔV 's in the fifth column of Table III is so much greater than typical values from solutions that the assumption of the formation of at least some inner-sphere complexes must be allowed. For example, the volume change in the formation of $LaFe(CN)_6$ pairs in water²⁰ where only an outer-sphere complex is believed to exist is +8.0 ml/mol. The formation of

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(18) A. H. Narten and S. Lindenbaum, *J. Chem. Phys.*, **51**, 1108 (1969).

(19) W. Slough, *Trans. Faraday Soc.*, **55**, 1036 (1959).

(20) S. D. Hamann, P. J. Pearce, and W. Strauss, *J. Phys. Chem.*, **68**, 375 (1964).

solvent-separated pairs by MgSO_4 and MnSO_4 in water has been measured²¹ as 7.3 and 7.4 ml mol⁻¹, respectively.

Conclusions

Our researches on the volume changes which accompany the selective binding of ions by polyelectrolyte gels have led us to the following tentative conclusions.

(1) The binding of singly charged counterions by lightly cross-linked polystyrenesulfonate gels is non-localized (*i.e.*, no site binding) except possibly for Ag^+ ion. Alkaline earth, rare earth, and thorium ions appear to be site bound; solvent-separated ion pairs may be formed.

(2) With moderately and heavily cross-linked gels site binding of all cations except H^+ and Li^+ appears to occur. With singly charged cations the magnitude of ΔV is such that solvent-separated ion pairs are implied. Ba^{2+} , La^{3+} , and Th^{4+} ions, however, appear to form contact ion pairs. The release of water of coordination and changes in water structure are indicated by the positive entropy changes observed.

(3) The selective uptake of the larger tetraalkylammonium cations by lightly cross-linked polystyrenesulfonate gels appears to involve "structure-enforced"

(21) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962).

bonding.²² The ΔV values are negative and the selective uptake of large R_4N^+ ions is determined by the relatively large entropy increase in the reaction. The volume decrease and entropy increase can be explained by assuming that the "ice like" structure of the external water is destroyed when large, quaternary ammonium ions enter the gel.

(4) The selective binding of the heavier halide ions, especially I^- ion, appears to be a consequence of "charge-transfer complex formation" with the aromatic groups of the exchanger.

(5) The Katchalsky theory of ion-exchange selectivity in lightly cross-linked gels appears to be valid for the alkali-metal cations where field binding dominates. Multiply charged cations show significant site binding, however.

(6) The Rice-Harris theory of ion-exchange selectivity which is based on the assumption of extensive ion-pair formation appears to be supported by the ΔV measurements. Solvent-separated and contact ion pairs evidently occur.

Acknowledgment. This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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Thermodynamics of Molecular Association by Gas-Liquid Chromatography. VII. Hydrogen Bonding of Aliphatic Alcohols to Di-*n*-octyl Ether, Di-*n*-octyl Thioether, and Di-*n*-octylmethylamine

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Abstract: Equilibrium constants, enthalpies, and entropies of hydrogen bonding between six aliphatic alcohols and the electron donors of the title have been determined by gas-liquid chromatography in the range 30 to 60°. The equilibrium constants follow the general trend expected on the basis of alkyl group inductive and steric effects. The enthalpies are correlated within experimental error by the equation $|\Delta H_{i,j}| = Q_i^a Q_j^b$, where the Q 's represent parameters for acid i and base j , respectively. The ratios of the base parameter values for the amine, ether, and thioether are respectively 2.02:1.48:1.00, in good agreement with previously determined nmr ratios for haloform hydrogen bonding (2.01:1.49:1.00). The enthalpies are also analyzed in terms of Drago's double-scale equation for ΔH of adduct formation. Finally, all systems follow a common linear plot of ΔH vs. ΔS .

This paper represents a further contribution to the systematic study of molecular association in binary nonelectrolytic solutions by gas-liquid chromatography (glc)¹⁻⁵ and auxiliary techniques.⁶ In 1968 we proposed a quantitative glc method for obtaining thermo-

(1) Paper I: D. E. Martire and P. Riedl, *J. Phys. Chem.*, **72**, 3478 (1968).

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(3) Paper III: J. P. Sheridan, M. A. Capeless, and D. E. Martire, *J. Amer. Chem. Soc.*, **94**, 3298 (1972).

(4) Paper IV: J. P. Sheridan, D. E. Martire, and F. P. Banda, *J. Amer. Chem. Soc.*, **95**, 4788 (1973).

(5) Paper V: H.-L. Liao and D. E. Martire, *Anal. Chem.*, **45**, 2087 (1973).

(6) Paper VI: J. P. Sheridan, D. E. Martire, and S. E. O'Donnell, *J. Amer. Chem. Soc.*, submitted for publication.

dynamic parameters (K , ΔH , and ΔS) of 1:1 organic complex formation and applied it to study the hydrogen bonding of eight aliphatic alcohols to di-*n*-octyl ether and di-*n*-octyl ketone.¹ Recently, this method was used to investigate the association of various haloalkanes with di-*n*-octyl ether and di-*n*-octyl thioether² and with di-*n*-octylmethylamine and tri-*n*-hexylamine;⁴ *n*-octadecane was the "reference" liquid phase (chosen to have approximately the same molecular size, shape, and polarizability as the electron donor liquid phase^{1,2,4,5}). In conjunction with these association studies, alternative procedures have been developed⁷ for obtaining the required bulk (liquid/vapor) partition

(7) H.-L. Liao and D. E. Martire, *Anal. Chem.*, **44**, 498 (1972).