which would be expected to occur in the systems studied, the results of the three methods of attack are consistently negative. The results serve as additional magnetochemical evidence that the hydrogen bond occurs as simple electrostatic attraction.

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STORRS, CONNECTICUT

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The Partition of Electrolytes between Aqueous and Organic Phases. I. The Partition of the Alkali Reineckates and Perrhenates between Water and Nitromethane[1,2]

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An experimental approach to the thermodynanics of electrolytic solutions in organic solvents is provided by the study of the partition of electrolytes between aqueous and organic phases. An investigation of the distribution equilibria of the alkali reineckates [$MCr(NH_3)_2(SCN)_4$] and perrhenates ($MReO_4$) shows that these salts are strong electrolytes in the nitromethane phase as well as the aqueous phase in the concentration range investigated. For the reaction, $M^+(aq) + ReO_4^-(aq) = M^+(MeNO_2) + ReO_4^-(MeNO_2)$, with hyp. 1 molar std. states. ΔF^0_{298} is: Li, 6.23; Na. 5.83; K, 4.08; Rb, 3.43; Cs, 2.71; H, 5.32 kcal./mole. For the reaction, $ReO_4^-(aq) + Cr(NH_3)_2(SCN)_4^-(MeNO_2) = ReO_4^-(MeNO_2) + Cr(NH_3)_2(SCN)_4^-(aq)$, $\Delta F^0_{298} = 5.0$ kcal./mole. In simple cases both electrostatic and non-electrostatic contributions to the free energy of transfer of an ion from water to an organic phase tend to make this free energy more negative for larger ions. as observed.

The study of the partition of electrolytes between aqueous and organic phases provides a method of investigating the thermodynamic properties of the organic solutions. The direct results of such an investigation are limited to organic solvents in equilibrium with water, but it appears that partition experiments will be of value to supplement measurements on solutions in anhydrous solvents for the following reasons: First, the partition experiments are relatively easy and may be used to select the systems for which a complete investigation will yield the most information. Second, the partition experiments relate the state of the electrolyte in the organic solvent directly to its state in water, which is relatively well understood, rather than to its state in the solid electrolyte, possibly solvated, in equilibrium with the organic solvent. Finally, a recent theoretical development by McKay[3] leads to a method of calculating the free energy of transfer of an electrolyte from pure water to pure organic solvent from partition experiments combined with measurements of partial derivatives which are directly related to salting out constants. Thus the combined measurements can lead to knowledge of the thermodynamics of the anhydrous organic solutions relative to those of the pure aqueous solutions.

The experiments described here were undertaken to provide information about the effect of ion size upon the free energy of transfer of ions from an aqueous phase to an organic phase. Nitromethane was chosen as the organic medium in these experiments because it is incompletely miscible with water and has a dielectric constant high enough to avoid complications due to ion-pair formation at the concentrations employed here.

Experimental

Materials.—Redistilled water was used throughout. Nitromethane was distilled from phosphoric anhydride. The fraction boiling between 100.4 and 100.6° was taken. For the perrhenate studies, an acid impurity in the purified nitromethane was removed by washing with sodium bicarbonate solution. Commercial ammonium reineckate (C.P.) was recrystallized from water. The product was metathesized by CsCl, KCO_2CH_3 or $NaClO_4$ to produce the respective reineckate. This was recrystallized once from water for final purification in each case. The reineckate ion decomposes slowly (1% per day in 0.01 *M* solutions) at room temperature in the dark, and decomposes more rapidly at elevated temperatures or in diffuse sunlight. All recrystallizations were carried out from aqueous solution between 30 and 0°. The solutions were handled only in artificial light and were stored in an ice-box. C.P. potassium perrhenate was recrystallized twice from water and fused in a platinum crucible in air at 750° to constant weight. The stock perrhenate solution was made up from this known weight of $KReO_4$. $CsReO_4$ was prepared by the reaction in water of resublimed Re_2O_7 with recrystallized (from alcohol) Cs_2CO_3, and the product was recrystallized from water.

Partition of the reineckates was studied by equilibrating aqueous reineckate solutions with nitromethane at 25 ± 2°, and analyzing each phase by measuring the light absorption due to the reineckate ion near 5220 Å. (decadic molar extinction coefficient = 116). The extinction maximum was shifted slightly toward longer wave lengths in nitromethane, but the extinction coefficient at the peak remained unchanged. The results are presented in Fig. 1.

Partition of the perrhenates was studied by equilibrating accurately known amounts of $KReO_4$, an alkali metal chloride, water and nitromethane at 25.2°, and then analyzing each phase for rhenium by an application of the spectrophotometric Re(VI) thiocyanate method of Hurd and Babler.[4] A sample of each phase was evaporated to dryness with a drop of concd. HNO_3, taken up in 5–6 drops of concd. HNO_3, and evaporated again. The evaporation was carried out below 100° to avoid loss of Re_2O_7. The residue was dissolved in known volumes of KSCN and $SnCl_2$–HCl solutions and the resulting solution examined spectrophotometrically 15 min. after mixing. The molar decadic extinction coefficient depends upon the details of the procedure but is about 10^4, calculated on the basis of known ReO_4^- concentrations in standardizing experiments. Beer's law is obeyed up to optical densities of 1.5 (1 cm. light path) and the results seem reproducible to within ±2% in concentra-

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[1] Presented in part at the meeting of the American Chemical Society, Los Angeles, California, March, 1953.

[2] This work was supported by the U. S. Atomic Energy Commission.

[3] H. A. C. McKay, *Trans. Faraday Soc.*, **49**, 237 (1953).

[4] L. C. Hurd and B. J. Babler, *Anal. Chem.*, **8**, 112 (1936).

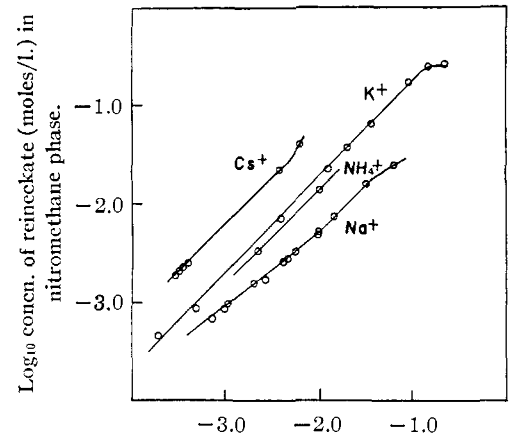

Fig. 1.—Partition of reineckates at 25°.

tion with only moderate care. Since the chlorides do not extract measurably, the initial stoichiometry, the measured equilibrium ReO_4^- concentration in each phase and the known volumes of the phases in equilibrium allow a calculation of the equilibrium concentration of each species in each phase and also a check of the internal consistency of the data. From experiments with KCl and $KReO_4$ the equilibrium constant for partition of $KReO_4$ was determined, and then from experiments with MCl and $KReO_4$ the constant for partition of $MReO_4$ was obtained.

The investigation of the low ionic strength region using $KReO_4$ without addition of KCl requires a greater completeness of phase separation in sampling than seems attainable by the simple pipetting techniques used. Small volumes of the aqueous phase taken with the sample of nitromethane phase give rise to anomalously large values of the partition coefficient, owing to the much larger concentration of perrhenate in the aqueous phase. These unreliable points have been omitted from Table I and Fig. 2. In order to confirm the interpretation of these anomalous results, the distribution of pure $CsReO_4$ was studied. The sampling error is smaller for this electrolyte because its partition coefficient is nearer to unity. As expected, then, the partition coefficient at the lowest accessible concentration of $CsReO_4$ lies on the curve extrapolated from higher concentrations.

The partition data for the perrhenates are presented in Table I. The calculations are relatively direct in the cases where there is only one cation in the system (all of the $KReO_4$ experiments, and the last six $CsReO_4$ experiments). The calculations in the other cases will be illustrated by outlining the calculation for the first $LiReO_4$ experiment: The analyses yield the concentrations in columns 1 and 2. Preliminary experiments showed that for the range of salt concentrations employed here, the aqueous phase increased in volume by 10% when it became saturated with nitromethane, while the total volume of the system remained unchanged within 1%. This allows the calculation of the final volumes of the phases from the initial volumes. In this case, the final volume of aqueous phase, 5.5 ml., combined with the amount of LiCl taken, 0.492 mmole, gives the values of $(Cl^-_{aq.})$ in column 3. The ionic strength of each phase may now be calculated and the value of P (defined below, recorded in column 3) of $KReO_4$ read from the curve in Fig. 2. Then the ratio $(K^+_{aq.})/(K^+_{org.})$ may be calculated as 153. Combined with the total amount of K^+, 152 $\times 10^{-3}$ mmole, and the final volumes of the phases ($V_{org.}$ = 14.5 ml.), this yields columns 5 and 6. The (Li^+) in each phase may be calculated from the charge balances as $(Li^+_{aq.}) = 0.0895\ M$ and $(Li_{org.}) = 1.56 \times 10^{-5}\ M$. When combined with columns 1 and 2 these yield column 7. A check is provided by the material balance $(ReO_4^-{}_{aq.})V_{aq.} + (ReO_4^-{}_{org.})V_{org.} = 1.49 \times 10^{-3}$ mmole. This agrees with the total amount of $KReO_4$ taken, 1.52×10^{-3} mmole, within 2%, as recorded in column 8.

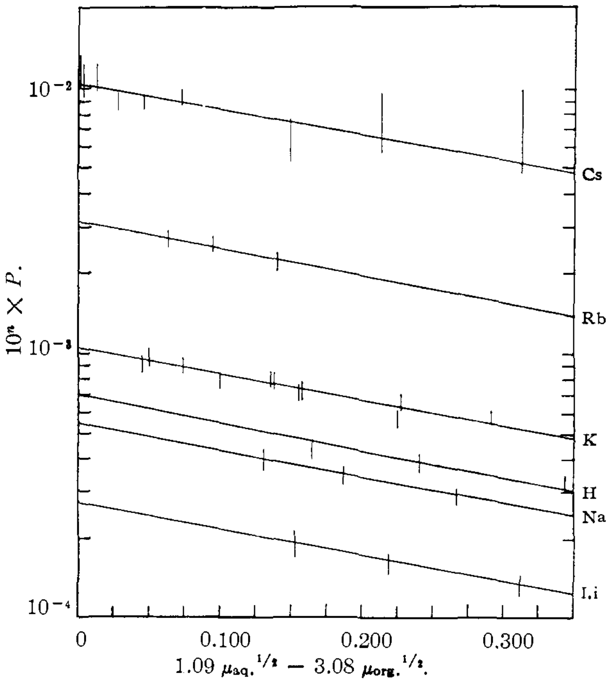

Fig. 2.—Partition ratio, P, as a function of concentration for the perrhenates at 25°. P is the concentration (moles/l.) equilibrium constant for transfer of electrolyte from the aqueous phase to the organic phase. $\mu_{org.}$ and $\mu_{aq.}$ are the respective ionic strengths (moles/l.). The best straight line of *theoretical* slope has been fitted to each set of points. The vertical length of the graph has been reduced by shifting the curves as follows, n values: $CsReO_4$, 0.0; $RbReO_4$, 1.0; $KReO_4$, 1.0; $HReO_4$, 1.7; $NaReO_4$, 2.0; $LiReO_4$, 2.0.

The material balances recorded in Table I indicate a systematic error in the perrhenate analyses of the order of a few per cent. An effort to find and remove the cause of this error was unsuccessful, but an analysis of the data and procedure suggests that this error produces an error in P of the same order as that arising from the 2% uncertainty in (ReO_4^-) indicated by the precision of the perrhenate analyses. In Fig. 2 each datum is represented by a line centered on the experimental value of P and having an upper end calculated on the assumption that the aqueous and organic ReO_4^- concentrations are, respectively, 2% lower and 2% higher than observed, and having a lower end calculated from the opposite set of assumptions.

Discussion

We define the partition ratio, $P = (M^+_{org.})(A^-_{org.})/(M^+_{aq.})(A^-_{aq.})$, for the partition of an electrolyte MA between aqueous and organic phases. Here the symbols in parentheses represent the equilibrium concentrations of the ions in the phases indicated.

The partition data for the reineckates (Fig. 1) show that for each of these except sodium reineckate the P is nearly independent of concentration over the range investigated. The aberration of the sodium reineckate curve at low concentrations is probably due to an acid impurity in the nitromethane. Measurements on the perrhenate system indicate that Na^+ and H^+ are about equally effective in promoting the extraction of anions from water to nitromethane.

The concentration independence of the P's shows that these reineckates, which are completely dissociated to metal ion and reineckate ion in water must also be completely dissociated in nitromethane in the concentration ranges investigated. If this were not true, but the electrolyte existed as ion pairs in nitromethane, one would expect a tenfold

TABLE I

DISTRIBUTION OF PERRHENATES BETWEEN WATER AND NITROMETHANE AT 25°
EQUILIBRIUM CONCENTRATIONS (MOLES/LITER) AND PARTITION RATIOS

$10^4[ReO_4^-{}_{aq}]$	$10^5[ReO_4^-{}_{org}]$	$10^3[Cl^-{}_{aq}]$	$10^4P_{KReO_4}$	$10^5[K^+{}_{org}]$	$10^4[K^+{}_{aq}]$	$10^4P_{MReO_4}$	Material balance ReO_4
				$KReO_4$			
2.13	8.10	54.0		8.10	542	5.68	4.6 low
1.88	9.65	86.9		9.65	870	5.70	4.0 low
2.11	8.70	55.5		8.70	556	6.45	3.3 low
2.19	6.50	27.1		6.50	273	7.07	5.9 low
2.18	6.60	27.6		6.60	278	7.19	5.9 low
1.94	3.88	9.79		3.88	99.9	7.77	5.9 low
2.08	4.48	12.1		4.48	123	7.85	6.6 low
2.23	6.25	21.6		6.25	218	8.04	4.6 low
2.85	4.28	6.91		4.28	72.0	8.93	4.6 low
2.39	2.55	2.76		2.55	30.0	9.07	7.9 low
2.91	3.23	3.46		3.23	37.5	9.56	5.9 low
				$LiReO_4$			
2.26	1.74	89.5	5.02	0.177	2.71	0.134	2.0 low
2.31	1.44	44.7	6.20	0.268	2.69	0.163	3.3 low
2.42	1.23	22.4	7.19	0.377	2.66	0.194	0.7 low
				$HReO_4$			
1.73	3.53	111	4.60	0.0619	2.74	0.637	4.0 low
1.85	2.86	55.3	5.90	0.104	2.73	0.773	5.3 low
2.04	2.28	27.6	6.97	0.169	2.72	0.858	4.6 low
				$RbReO_4$			
1.98	9.90	24.4	7.40	0.463	31.3	22.0	5.3 low
2.12	7.80	12.2	8.25	0.381	17.0	25.5	5.3 low
2.12	5.40	5.54	8.95	0.316	8.99	26.7	3.3 .ow
				$NaReO_4$			
2.02	2.05	66.6	5.54	0.149	2.72	0.290	7.2 low
2.12	1.69	33.3	6.65	0.226	2.70	0.351	6.6 low
2.22	1.40	16.7	7.58	0.322	2.68	0.408	6.6 low
				$CsReO_4$			
2.22	7.70	25.7	7.28	5.16	246	67.2	0.4 high
2.09	9.13	50.2	6.24	7.00	491	71.5	1.3 low
2.00	10.8	99.4	5.00	9.07	983	73.1	1.3 low
$10^4[ReO_4^-{}_{aq}]$	$10^5[ReO_4^-{}_{org}]$	$10^3[Cl^-{}_{aq}]$		$10^5[Cs^+{}_{org}]$	$10^4[Cs^+{}_{aq}]$	$10^4P_{CsReO_4}$	Material balance ReO_4
2.31	7.35	2.35		7.35	25.8	90.6	4.4 low
2.24	10.0	4.69		10.0	49.1	90.9	1.3 low
1.96	13.3	9.38		13.3	95.8	94.2	3.1 low
3.62	3.70	0.00		3.70	3.62	104	3.1 low
1.98	5.15	1.07		5.15	12.6	106	5.0 low
2.85	2.96	0.00		2.96	2.85	108	4.4 low

change in P for a tenfold change in aqueous reineckate concentration, contrary to what is observed.

The more accurate partition data for the perrhenates (Table I, Fig. 2) yield values of P which depend upon concentration, but in a way entirely consistent with the Debye–Hückel ion atmosphere theory. The dielectric constants for the calculation of the theoretical slopes were estimated from the values for pure water and pure nitromethane by assuming that the dielectric constant of a water–nitromethane mixture is a linear function of the volume fraction, by analogy with the behavior of water–methanol mixtures. The aqueous phase at equilibrium at 25°, 10.6 wt. % CH_3NO_2,[5] then has a dielectric constant of 74.6, the organic phase, 98.5 wt. % CH_3NO_2, has a dielectric constant of 37.4. Defining the thermodynamic equilibrium constant

$$K = P(\gamma_\pm \text{ org.})^2/(\gamma_\pm \text{ aq.})^2 \qquad (1)$$

and calculating $\gamma_\pm$ in each phase from the Debye–Hückel limiting law leads to the relation

$$\log_{10} P = \log_{10} K - 1.09\mu_{\text{aq.}}^{1/2} + 3.08\mu_{\text{org.}}^{1/2} \qquad (2)$$

Figure 2 demonstrates that the partition data are consistent with this equation. Therefore the equation of which K is the equilibrium constant

$$M^+(\text{aq.}) + ReO_4^-(\text{aq.}) = M^+(\text{org.}) + ReO_4^-(\text{org.})$$

accurately describes the net reaction in the transfer of electrolyte from aqueous to organic phase. That is, these perrhenates are all completely ionized in the nitromethane phase in the concentration range investigated.

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(5) R. M. Corelli, C. A., 46, 3370e (1952).

The standard free energies of transfer of the various electrolytes from the aqueous to the nitromethane phase, for hyp. 1 molar std. states, have been calculated from the partition data and are presented as functions of the cation crystal radius (Pauling) in Fig. 3. The parallelism of the curves for the reineckates and perrhenates confirms that ΔF^0 is composed of additive contributions from the ions, which is consistent with the earlier conclusion that the electrolyte is completely dissociated in each phase.

The vertical shift from the reineckate curve to the perrhenate curve of Fig. 3 shows that the standard free energy of transfer of the perrhenate ion from water to nitromethane is 5.0 kcal. more positive than that of the larger reineckate ion. For the cations, ΔF^0 also increases with decreasing ion radius. Although the linear dependence on crystal radius is surprising, the qualitative trend is consistent with the observation that electrolytes with large ions generally extract better than those with smaller ions of similar structure.[6]

This inverse dependence of ΔF^0 on ion radius is also consistent with the following theoretical considerations. The ionic contributions to ΔF^0 may be supposed to have the form[7]

$$\Delta F^0_{\text{ion}} = \{(z^2/2)[(1 - 1/D_w)/r_w - (1 - 1/D_o)/r_o]\} + \Delta F' \quad (3)$$

The term in braces accounts for the difference in work required to charge the ion in each of the solvents, z being the ionic charge, r_0 and r_w being the effective radii of the ion in each of the media, and D_o and D_w the dielectric constants. This is a direct adaptation of the modified[8,9] Born charging equation to this problem. The physical significance of $r_w - r_c$ and $r_o - r_c$ (r_c is crystal radius) namely the distance from the surface of the ion to the point at which the dielectric constant rises from a low value (near unity) to its macroscopic value, leads to the conclusion that in most cases $r_o \geq r_w$, and then the term in braces is positive, but becomes smaller with increasing ionic crystal radius.

Although the model from which (3) may be derived, that is, an ion in solution represented by a charged conducting sphere of radius r_c, in a concentric cavity of radius r_o or r_w, in a homogeneous dielectric of dielectric constant D_o or D_w, is a severe approximation to the electrostatic interaction of ion and solvent, its success in correlating the hydration energies of gaseous ions leads to the expectation of at least qualitatively correct predictions from (3) for the effect of ion size upon the electrostatic part of ΔF^0_{ion}. However, $\Delta F'$, the non-electrostatic part of the ion solvation energy, although quite negligible compared with the electrostatic part of the hydration energy of a gaseous monatomic ion, is relatively important compared to the electrostatic part of ΔF^0_{ion} which is estimated as only 2–3 kcal. for K^+ between water and nitromethane.

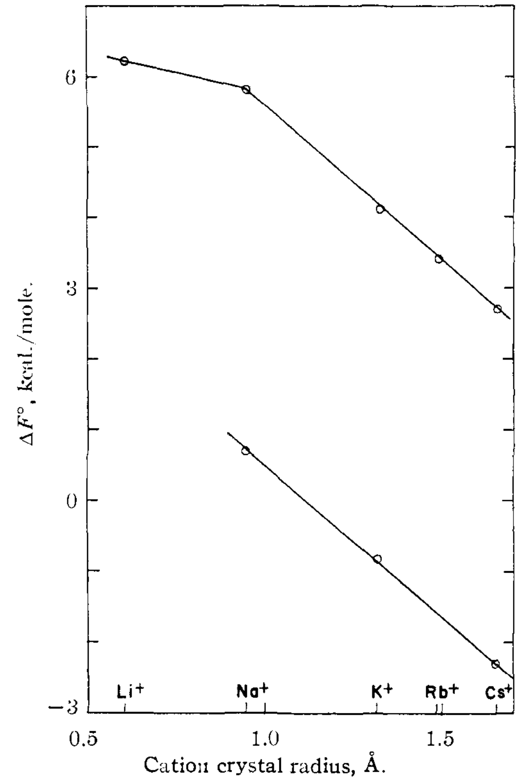

Fig. 3.—Standard free energy of transfer of perrhenates and reineckates from water to nitromethane at 25°, $M^+(H_2O) + A^-(H_2O) \rightarrow M^+(MeNO_2) + A^-(MeNO_2)$. ΔF^0: upper curve, perrhenates; lower curve, reineckates.

It may be possible to evaluate $\Delta F'$ from experiments with uncharged molecules similar in structure to the ions,[10,11] but lacking this detailed information it may be predicted that $\Delta F'$ will also become less positive or more negative with increasing ion size, for ions of similar structure. This is based upon regularities in the solubilities of non-electrolytes. For instance the free energies of transfer[7,11,12] (kcal./mole, 20°) from water to acetone at the same solute concentration are for Ne, −0.66; A, −1.26; Rn, −2.9; and $(C_2H_5)_4Si$, −7.77.

In this way we can explain the general increase of extractability of ions with increasing size. However, the smaller cations exhibit anomalous behavior in some systems. For instance, the order of increasing tendency of cations to transfer from pure water to pure methanol is $Rb^+ < Cs^+ < K^+ < Na^+ < Li^+$.[10,13] This anomalous radius dependence may arise from special features of the water structure[13] which are destroyed by the high concentration of organic component in the aqueous phase in the partition experiments. On the other hand, it may arise from specific interaction of the smaller ions with the methanol solvent structure.[13] Additional experiments should allow a decision here.

LOS ANGELES, CALIF.

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(6) For other examples, see H. M. Dawson, *J. Chem. Soc.*, **93**, 1308 (1908); S. Tribalat, *Anal. Chim. Acta*, **3**, 113 (1949); *ibid.*, **4**, 228 (1950); S. Tribalat and J. Beyden, *ibid.*, **6**, 96 (1952); J. T. Davies, *J. Phys. Chem.*, **54**, 185 (1950); F. M. Karpfen and J. E. B. Roules, *Trans. Faraday Soc.*, **49**, 823 (1953).

(7) *Cf.* A. Lannung, THIS JOURNAL, **52**, 68 (1930).

(8) A. Voet, *Trans. Faraday Soc.*, **32**, 1301 (1936).

(9) W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7** 109 (1939).

(10) J. N. Brönsted, A. Delbanco and K. Volqvartz, *Z. physik. Chem.*, **A162**, 128 (1932).

(11) N. Bjerrum and E. Jozefowicz, *ibid.*, **A159**, 194 (1952).

(12) Gmelin, "Handbuch der anorganischen Chemie," 8 ed., System No. 1, Verlag Chemie, Berlin, 1926, p. 216.

(13) W. M. Latimer and C. M. Slansky, THIS JOURNAL, **62**, 2019 (1940).