The results might also be rationalized in terms of the formation of a [RuO_4^--PI] intermediate. The latter might be more in accord with the large negative $\Delta S^\ddagger$ if an intermediate, which contains both tetrahedral P and Ru and a water or -OH bridge, is formed. But where the observed rate constant is a product of a rate and a preequilibrium constant, such speculation is probably unwarranted.

Registry No. $H_2PO_2^-$, 15460-68-1; RuO_4^-, 14333-21-2.

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Reduction of Vanadium(V) by L-Ascorbic Acid[1]

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The stoichiometry of the reduction of vanadium(V) by L-ascorbic acid (H_2A) has been experimentally determined to be $H_2A + 2V(V) \rightarrow A + 2V(IV) + 2H^+$. The kinetics of this reaction has been studied by stopped-flow procedures at 25° and ionic strength of 1 *M* ($LiClO_4$) in acid media (0.20-1.0 *M* $HClO_4$). Upon mixing acidic solutions of V(V) and L-ascorbic acid a transient appears, the uv-vis spectrum of which has a maximum at 425 nm. The observed pseudo-first-order rate constant, k_{obsd}, which was not acid dependent, is related to the concentration of the reagent in excess, V(V), according to the equation $k_{obsd} = kK[V(V)]/(1 + K[V(V)])$. This equation is the familiar one for rapid formation of a complex followed by its rate-limiting decomposition. The experimentally determined constants are the intermediate complex formation constant, $K = 488 \pm 28\ M^{-1}$, and the decomposition rate constant, $k = 12.1 \pm 0.2\ sec^{-1}$. On the basis of the measured value of k_{obsd} and the known value for the reaction $V(III) + V(V) \rightarrow 2V(IV)$, the two-electron reduction mechanism can be ruled out; an inner-sphere, one-electron reduction of vanadium(V) by L-ascorbic acid seems to be the most plausible mechanism.

Vanadium was discovered in the blood of certain marine invertebrates (*Ascidia*) in 1911,[2] yet neither the mechanism of vanadium extraction from the sea water nor the metabolic role of the element has been established. More recently,[3] it has been shown that vanadium is present in ascidians chiefly as V(III) within specific blood cells called vanadocytes. Unlike the animal's blood plasma (pH ≃7) or sea water (pH ≃8), these cells are about 1 *M* in sulfuric acid. In the course of our investigations into the mechanism of vanadium incorporation by ascidians,[4] specifically regarding the reduction of oceanic V(V) to V(III) by the animal, we have conducted studies of the kinetics of the reduction of V(V) by L-ascorbic acid in acidic media.

The reduction of V(V) by a variety of two-electron reductants has been the object of numerous studies. In a qualitative survey of the reduction of V(V) by a multitude of organic species,[5] Littler and Waters have shown that most, if not all, such reactions proceed *via* a free-radical mechanism wherein V(V) undergoes only a one-electron reduction. Thus these reactions appear to occur according to the sequence

$$V(V) + R \rightarrow V(IV) + R\cdot$$

$$R\cdot + V(V) \rightarrow V(IV) + P \quad \text{(rapid)}$$

where R, R·, and P represent the reductant, a free radical, and the oxidized product, respectively. The alternative sequence

$$V(V) + R \rightarrow V(III) + P$$

$$V(III) + V(V) \rightarrow 2V(IV) \quad \text{(rapid)}$$

wherein V(V) undergoes two-electron reduction, followed by rapid V(V) oxidation of the V(III) intermediate to V(IV) was ruled out by detection of the free-radical intermediate.

Littler and Waters have also studied the stoichiometry and kinetics of V(V) reduction by pinacol,[5] cyclopentanone,[6] and cyclohexanone.[6] In all cases indirect evidence for a free radical was observed, and the one-electron reduction of V(V) to V(IV) was demonstrated. The rate of V(V) reduction by cyclopentanone was observed to be first order with respect to hydrogen ion concentration in perchlorate media at an ionic strength of 6.0 *M*. The rate of V(V) oxidation of pinacol in sulfate media showed virtually no hydrogen ion dependence below 1.0 *M* in hydrogen ion. Above this level an increase in the electron-transfer rate was ascribed to either a more reactive form of V(V), possibly $V(OH)_3^{2+}$ or a vanadium(V) sulfate complex such as $[V(OH)_3HSO_4]^+$.

Wells and Kuritsyn have suggested[7] that the reduction of V(V) by hydroquinone (QH_2) may proceed *via* an inner-sphere mechanism, giving the products V(IV) and *p*-benzoquinone. The rate is first order in [V(V)] overall but becomes less than first order in [QH_2] at higher concentrations of the reductant, suggesting complexation of V(V) prior to the electron-transfer step. The rate increases with increasing hydrogen ion concentration, further suggesting that the equilibrium constant for complexation is dependent upon [H^+].

Cooper, *et al.*, have studied[8] the reduction of V(V) by hypophosphorous acid, which also involves complexation

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prior to the electron-transfer process. It is well known that, below pH 1, the dominant vanadium(V) species is VO_2^+,[7,8] which is therefore the species involved in complex formation. Electron transfer was slow enough in this study to enable the determination of the stability constant for the VO_2^+-$H_2PO_2^-$ complex, the value of which was found to be $16.6 \pm 2.2\ M^{-1}$. The observed rate law for electron transfer was rationalized on the basis of kinetic significance of several V(V)-P(I) complexes in various states of protonation. Indirect evidence for a free-radical intermediate was also observed in this system.

Experimental Section

Materials. Stock solutions of vanadium(V) perchlorate were prepared by dissolution of either recrystallized sodium vanadate hydrate or Fisher Certified vanadium pentoxide in dilute perchloric acid. Total vanadium in each solution was determined spectrophotometrically as the V(V)-H_2O_2 complex.[9] The concentration of V(V) in each solution was determined titrimetrically[10] with Fe(II) in 5 M H_2SO_4. Total vanadium and [V(V)] agreed within 1%. Free acid concentration in each solution was calculated from the known initial acid concentration and the final V(V) concentration. The free acid in the stock vanadium(V) perchlorate solutions contributed negligibly to the total acid in the kinetic runs. Stock solutions of L-ascorbic acid were prepared just prior to use from material obtained from Schwartz/Mann. Perchloric acid solutions were prepared by dilution of Baker and Adamson 70% $HClO_4$ and were standardized by titration with NaOH to the phenolphthalein end point. A lithium perchlorate stock solution was prepared by neutralization of analytical reagent grade lithium carbonate with $HClO_4$, followed by boiling to eliminate CO_2. The concentration of Li^+ was determined by passage of aliquots of the stock solution through a Dowex 50W-X2 (H^+) cation-exchange column, followed by titration of the liberated hydrogen ion. Distilled water used in all experiments was obtained in polyethylene containers from Belmont Springs Co., Belmont, Mass.

Kinetics Studies. All kinetics studies were carried out at 425 nm using the stopped-flow spectrophotometer which has been described previously.[11] The output of the photomultiplier tube was recorded on a Biomation 610B transient recorder, which was triggered by a leaf switch on the collecting syringe. The 255 channels of voltage *vs.* time data which were obtained for each run were recorded on paper tape using a 33ASR Teletype unit equipped with a Pivan B103 interface. In all experiments [V(V)] was sufficiently large to ensure that all reactions were pseudo first order. Total transmittance changes were 5% or less for all reactions studied, allowing the approximation that the value of the excess transmittance $(T_t - T_\infty)$ at each point is proportional to the concentration of unreacted material. Values of k_{obsd}, the pseudo-first-order rate constants, were obtained by least-squares analysis of transmittance *vs.* time data according to the function $-\ln[(T_t - T_\infty)/(T_0 - T_\infty)] = k_{obsd}t$. The relative transmittance at infinite time was computed from the final 15 channels of information. Weights for each data point at time t were proportional to the value of the excess transmittance $(T_t - T_\infty)$ at each respective point. Ionic strength was maintained at unity by addition of $LiClO_4$. Kinetics studies conducted with the aim of determining the spectrum of the intermediate species were carried out using a storage oscilloscope to monitor the output of the photomultiplier tube. Photographs were taken of the image stored on the cathode ray tube. The absorbance of the intermediate species was calculated from the observed transmittances, extrapolated to the time of flow stop (±5 msec). All kinetics studies were conducted in the presence of air, which was shown to have no detectable effect on the observed rate constants.

Stoichiometry. To establish the stoichiometric change in metal, 2.00 ml 0.175 M V(V) was added to excess (approximately 4.0 g) L-ascorbic acid in 50 ml of 1 M $HClO_4$. The resultant blue solution was charged onto a Dowex 50W-X2 (H^+) ion-exchange column, followed by elution with 3 M $HClO_4$. The [V(IV)] was determined spectrophotometrically at 750 nm.[12] Amount of V(IV) for V(V) → V(IV): calcd, 0.350 mmol; found, 0.338 mmol. The overall stoichiometry was determined as follows: 2.00 ml of 0.175 M V(V) was added to 0.142 mmol of L-ascorbic acid in 1 M $HClO_4$, and the [V(IV)] produced was determined as above. Amount of V(IV) for $C_6H_8O_6 + 2V(V) \rightarrow C_6H_6O_2 + 2V(IV) + 2H^+$: calcd, 0.284 mmol; found, 0.297 mmol.

Polymerization. A series of reactions between V(V) and ascorbic acid were carried out in deaerated vials at 25° in the presence of 5% v/v acrylonitrile. The initial concentrations of V(V) and $HClO_4$ were 1.0×10^{-3} and 1.0 M, respectively. Ascorbic acid concentrations were 0.008, 0.014, and 0.031 M. A cloudy suspension formed within a few minutes after addition of V(V). A large amount of precipitate was observed after a lapse of 30 min. Blank experiments from which either V(V) or ascorbic acid were excluded gave no detectable polymerization during this time. While these experiments do not serve to identify free-radical species, they do indicate that the reaction between V(V) and ascorbic acid produces species which are capable of the initiation of acrylonitrile polymerization.

Results and Discussion

The Intermediate. When acidic solutions of L-ascorbic acid and V(V) are mixed, a readily distinguishable brown color appears rapidly and then disappears, giving way to the blue of V(IV). A $5.26 \times 10^{-3}\ M$ solution of V(V) in 1.0 M $HClO_4$ was mixed with a $6.49 \times 10^{-4}\ M$ solution of L-ascorbic acid in the stopped-flow spectrophotometer. Absorbance as a function of time was obtained at 25-nm intervals from 350 to 625 nm. The initial absorbance at all wavelengths was greater than that of either V(V) or L-ascorbic acid. No absorbance changes were detected after 500 msec from the time of mixing. From the value of the absorbance at the time of mixing, corrected for absorbance due to excess V(V), the spectrum of the intermediate was determined, and is shown in Figure 1. The spectrum exhibits a single maximum at 425 nm. Discussion of the calculation of the value of the molar absorptivity of the intermediate species will be deferred until the value of the equilibrium constant for intermediate formation is described below.

Kinetics Studies. The pseudo-first-order rate constants for the reduction of V(V) by L-ascorbic acid at 25.0° are presented in Table I. Each kinetics experiment was first order in [ascorbic acid]. However, the data do not fit a second-order rate law but exhibit a saturation of the pseudo-first-order rate constant as the concentration of V(V) increases. For instance, at $[H^+] = 1.0\ M$, k_{obsd} increases by only a factor of 4.5 for a 30-fold increase in [V(V)]. Further treatment of the data showed that a plot of $1/k_{obsd}$ *vs.* $1/[V(V)]$ is linear. This result is consistent with a rate law for which the observed rate constant can be expressed[13,14] as $k_{obsd} = kK[V(V)]/(1 + K[V(V)])$ where k is a first-order rate constant for the decomposition of an intermediate complex described by the stability quotient, K.

The data in Table I have been analyzed by a nonlinear least-squares program,[15] which minimizes the squared deviations of the parameters a and b for the function $y = abx/(1 + bx)$ where a, b, x, and y represent k, K, [V(V)], and k_{obsd}, respectively (*vide* Figure 2). The values of k and K obtained in this manner are $12.1 \pm 0.2\ sec^{-1}$ and $488 \pm 28\ M^{-1}$, respectively.[16] The adequacy of fit is demonstrated by the agreement between k_{obsd} and k_{calcd} appearing in Table I. The absence of a significant $[H^+]$ dependence of

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[16] Errors are standard deviations. All data points were weighted equally.

Table I. Kinetic Data for the Reduction of V(V) by L-Ascorbic Acid (25.0°, Ionic Strength = 1.0 *M* (ClO_4^-))

$[H^+]$, *M*	$10^3[V(V)]$, *M*	10^5[L-Ascorbic acid], *M*	k_{obsd},[a] sec^{-1}	k_{calcd},[b] sec^{-1}
1.00	0.580	1.75	2.68 ± 0.30 (10)	2.67
1.00	0.702	1.62	3.30 ± 0.22 (6)	3.09
1.00	1.404	1.62	5.12 ± 0.28 (5)	4.92
1.00	2.106	1.62	6.06 ± 0.28 (5)	6.13
1.00	2.808	1.62	6.75 ± 0.21 (5)	6.89
1.00	3.506	1.62	8.19 ± 0.12 (5)	7.63
1.00	3.506	6.49	8.36 ± 0.10 (3)	7.63
1.00	7.012	6.49	9.45 ± 0.13 (3)	9.36
1.00	10.52	6.49	10.41 ± 0.11 (3)	10.12
1.00	14.02	6.49	10.71 ± 0.21 (2)	10.55
1.00	17.53	6.49	11.01 ± 0.32 (3)	10.83
1.00	17.53	1.62	10.45 ± 0.18 (4)	10.83
0.50	0.580	1.75	2.65 ± 0.35 (11)	2.67
0.20	0.580	1.75	2.57 ± 0.30 (10)	2.67
0.20	0.871	1.44	3.70 ± 0.14 (5)	3.61
0.20	1.161	1.44	4.52 ± 0.20 (5)	4.38
0.20	1.741	1.44	4.94 ± 0.27 (5)	5.56
0.20	2.320	1.44	6.36 ± 0.45 (5)	6.42
0.20	2.902	1.44	6.43 ± 0.27 (5)	7.09
0.20	5.804	1.44	8.81 ± 0.22 (5)	8.94
0.20	11.61	1.44	9.92 ± 0.18 (5)	10.28

[a] Error is standard deviation. Figure in parentheses is number of individual runs. [b] Calculated as $k_{calcd} = kK[V(V)]/(1 + K[V(V)])$, where $k = 12.1\ sec^{-1}$ and $K = 488\ M^{-1}$ (see text).

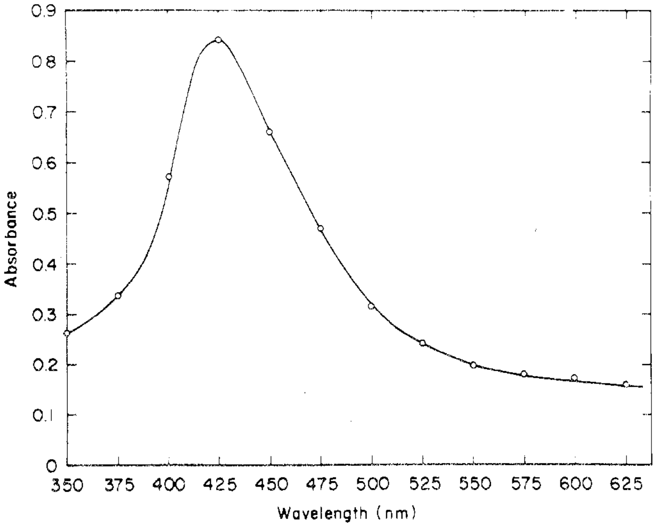

Figure 1. Optical spectrum of the reaction intermediate. A 5.26 × 10^{-3} *M* solution of V(V) was mixed with a 6.49 × 10^{-4} *M* solution of L-ascorbic acid in the stopped-flow spectrophotometer. Perchloric acid concentration was 1.0 *M*. Absorbance at the time of flow stop was obtained by extrapolation as described.

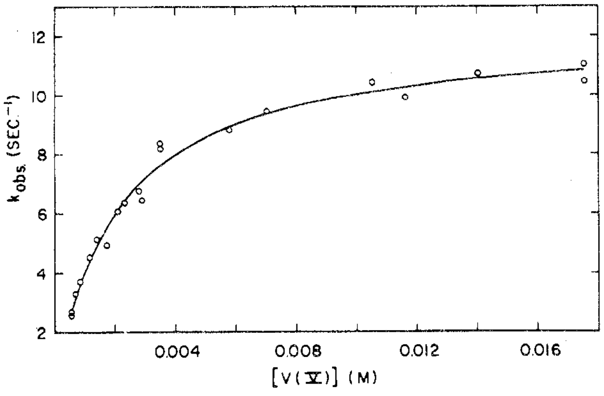

Figure 2. Plot of k_{obsd} *vs.* total [vanadium(V)]. The curve drawn through the data points satisfies the equation given in the text.

either *k* or *K* is seen in the evaluation of the parameters *a* and *b* at each hydrogen ion concentration. At $[H^+] = 1.0$ *M*, *a* and *b* are calculated to be 12.1 ± 0.2 sec^{-1} and 524 ± 36 M^{-1}, while at $[H^+] = 0.20$ *M*, *a* and *b* are 11.7 ± 0.4 sec^{-1} and 487 ± 45 M^{-1}, respectively. The value of the molar absorptivity of the intermediate at 425 nm, calculated using $l = 1.1$ cm and $K = 488 \pm 28\ M^{-1}$, is then found to be $4.31 \pm 0.12 \times 10^3\ M^{-1}\ cm^{-1}$.

We conclude that the most plausible mechanism for the reduction of V(V) by L-ascorbic acid (H_2A) involves rapid complexation of the metal ion by the reductant, followed by the inner-sphere transfer of one electron; V(IV) and a radical, R·, are thereby generated. The radical is rapidly oxidized by V(V), producing V(IV) and the product, dehydroascorbic acid, A.

$$V(V) + H_2A \overset{rapid}{\rightleftarrows} [V^VH_2A]$$

$$[V^VH_2A] \xrightarrow[determining]{rate} V(IV) + R\cdot$$

$$R\cdot + V(V) \xrightarrow{rapid} V(IV) + A$$

The two-electron reduction mechanism can be ruled out for the following reasons. The simplest representation of this mechanism would be

$$V(V) + H_2A \overset{rapid}{\rightleftarrows} [V^VH_2A]$$

$$[V^VH_2A] \xrightarrow[determining]{rate} V(III) + A$$

$$V(III) + V(V) \rightarrow 2V(IV)$$

Under the conditions of these experiments ($[H^+] = 1.0$ *M* (ClO_4^-) ≈ ionic strength, 25.0°) the rate constant for the V(III) + V(V) → 2V(IV) reaction has been determined[17] by Daugherty and Newton to be 243 M^{-1} sec^{-1}. At the lowest concentration of V(V) employed in our studies, 5.8×10^{-4} *M*, the pseudo-first-order rate constant for the V(III)-V(V) reaction would be 0.14 sec^{-1}, corresponding to a half-time of 5 sec. The observed half-time for electron transfer under these conditions is 0.25 sec. If it is assumed that neither unreacted ascorbic acid nor dehydroascorbic acid is capable of mediating the reaction between V(III) and V(V), then this reaction occurs roughly 20 times too slowly to account for the observed rate of formation of V(IV). Furthermore, the rate law for reduction of V(V) by V(III) is predominantly dependent upon $[H^+]^{-1}$. No such behavior is observed in the ascorbic acid system.

In the solutions studied, VO_2^+ and H_2A are the dominant uncomplexed reactants.[7,8,18] Direct complexation of VO_2^+ by H_2A is indicated by the lack of a pH dependence for *K*, the intermediate complex formation constant. The electron-transfer rate constant is likewise pH independent, indicating that only a single intermediate complex is important. A plausible, although not exclusive, mechanism consistent with these results is the direct decomposition of this intermediate to yield products. This conclusion is analogous to that known for the vanadium(V)-pinacol reaction;[5] in the sulfuric acid medium employed in that study the $[H^+]$ dependence appears only above 1.0 *M*, where protonated V(V) cations may become involved.

As noted above, the major fraction of vanadium in ascid-

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ians is found as V(III) within the vanadocytes. It is interesting, however, that even such powerful two-electron reductants as L-ascorbic acid do not readily reduce V(V) to the trivalent state. Indeed, since the exact nature of the reducing species in ascidians remains unclear, ascorbic acid may not be a meaningful model system for the *in vivo* reduction of V(V). On the other hand, it has been observed[19] that, given sufficient time, ascorbic acid will reduce V(IV), apparently to V(II). The residence time of V(V) at the site of reduction in ascidians would have to be sufficiently long for such a slow reduction to occur. Experiments designed to measure the rate of assimilation and loss of V(V) from ascidians will enable the determination of the residence time of the element within the animal. Such experiments are now being conducted in this laboratory.

Registry No. Vanadium, 7440-62-2; L-ascorbic acid, 50-81-7.

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Association of Cadmium(II) and Bromide in Anhydrous Molten Mixtures of Calcium Nitrate with Sodium Nitrate or Potassium Nitrate and the Effect of Water[1]

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Association constants of Cd^{2+} with Br^- to form $CdBr^+$ and $CdBr_2$ have been calculated from potentiometrically determined activity coefficients in the solvents molten anhydrous 2:1 KNO_3-$Ca(NO_3)_2$ at 200, 240 and 280° and in 2:1 $NaNO_3$-$Ca(NO_3)_2$ at 260°. From these results, the Cd^{2+}–Br^- pair association constant has been estimated in the hypothetical pure supercooled $Ca(NO_3)_2$ and compared with previously reported association constants in hydrous melts of $Ca(NO_3)_2$. The dependence of the association constant on water activity suggests the possibility that the hydration equilibrium of Cd^{2+} may involve two water molecules.

Introduction

The solution chemistry of aqueous electrolytes shows marked changes when the water content is reduced below 4-8 mol of water per mol of salt.[3,4] In this region of low water content there is insufficient water to provide complete hydration shells around the ions and the continuous dielectric continuum through which the ions are assumed to interact in the primitive model of electrolyte solutions. The behavior of these highly concentrated solutions or *hydrous melts* approaches that of molten salts, and models must take into account the competition among ion–ion, water–water, and ion–water interactions.

We have been studying association equilibria[5,6] and other thermodynamic properties[7] in anhydrous molten salts and in concentrated aqueous electrolytes in order to determine the effect of water on electrolyte interactions. A modified quasilattice model was developed to describe competitive hydration and association equilibria of dilute solute ions such as Cd^{2+} and Br^- and was shown to be applicable to the association data in the range between the anhydrous molten salt and about 50 mol % water in $LiNO_3$-KNO_3 as solvent.[8] The model has been applied also to the effect of water on association equilibria of Ag^+,[9] Cd^{2+},[10] or Pb^{2+} [10] with Cl^- or Br^- in molten ammonium nitrate melts.

A meaningful test of the model in hydrous melts requires independent knowledge of the association constants in the absence of water. Although association constants of $CdBr^+$ have been reported in hydrous $Ca(NO_3)_2$ melts, the association constants of $CdBr^+$ in anhydrous calcium nitrate are not known; furthermore, the quasilattice model does not yield physically reasonable association constants on extrapolation from the measured association constants of Cd^{2+}–Br^- in the hydrous solvents $Ca(NO_3)_2$-H_2O or KNO_3-$Ca(NO_3)_2$-H_2O.[5] It is therefore the purpose of this paper to present the results of measurements of association constants in the anhydrous molten salt solvents 2:1 KNO_3-$Ca(NO_3)_2$ and 2:1 $NaNO_3$-$Ca(NO_3)_2$ at several temperatures and to estimate a value in anhydrous $Ca(NO_3)_2$. The results are compared with previous results in the hydrous melts $Ca(NO_3)_2 \cdot 4H_2O$ and $Ca(NO_3)_2 \cdot 6H_2O$ and their mixtures with KNO_3.[5,6b,c] Making use of recent water activity data in these hydrous melts[11] we show that one possible interpretation of the water activity dependence of the ion-pair equilibria is the pairwise rather than stepwise association of water molecules with Cd^{2+} ions in the solvent $Ca(NO_3)_2$. We also present equations for analysis of association equilibria in charge unsymmetric solvent mixtures, *i.e.*, solvents containing different numbers of cations and anions, in terms of the Temkin ion ratios.

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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