TRANSPORT IN AQUEOUS BATTERY SYSTEMS

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The purpose of this program is to measure the four diffusion coefficients of the $ZnCl_2$–KCl–H_2O system. These data are needed for proper modeling and optimization of Zn–chlorine battery systems. Literature discrepancies for the diffusion coefficients of the limiting binary $ZnCl_2$–H_2O system need to be resolved, and data need to be collected for higher and lower concentrations than are presently available.

In the previous contract period, the diffusion coefficients D_v for dilute aqueous $ZnCl_2$ measured by Agnew and Paterson were rather scattered and about 1 percent lower than those found in this study. Variations in pH showed no significant effect. However, a possible source of the discrepancy could have been the poor quality of the supposedly analytical reagent grade $ZnCl_2$ used, which contained nearly 1 percent of alkali metal and alkaline earth impurities. Three compositions were redone so far this year using $ZnCl_2$ made from 99.994 percent pure ZnO (Table 1). These new D_v values are about 0.3 percent lower than those from the impure $ZnCl_2$, but still substantially higher than Agnew and Paterson's. Seven densities have also been measured at various compositions of this purer $ZnCl_2$ and are systematically higher than the data for the impure salt. The lower D_v and higher densities for the pure $ZnCl_2$ are consistent with the expected contributions of the impurities in the less pure salt.

In the previous contract period, we obtained diffusion coefficients for three compositions of the $ZnCl_2$–KCl–H_2O system, whose mean concentrations $\bar{c}_1$ and $\bar{c}_2$ are (0.5, 2.0), (1.5, 2.0), and (2.5, 2.0). In all three systems, the cross-term diffusion coefficients were small. If the cross-term D_{ij} were small at all compositions, modeling of this system would be greatly simplified. However, thus far in the study, D_{ij} was measured for the composition (0.5, 0.5), which has a nontrivial positive value of D_{21}. Moreover, preliminary results for the composition (0.5, 4.0) indicate a large, negative value of D_{21}. It appears that the concentration dependencies of the D_{ij} are much more complicated than were indicated by last year's limited results. The

TABLE 1

Diffusion coefficient of aqueous $ZnCl_2$ at 25 °C

$\bar{c}$ (mol dm^{-3})	Δc (mol dm^{-3})	$\bar{m}$ (mol kg^{-1})	J	$10^5 D_v$ (cm^2 sec^{-1})
0.39598	0.03938	0.39982	92.16	1.0036
0.49394	0.03892	0.49986	87.18	0.9917
1.2065	0.04028	1.2494	72.99	0.9870

TABLE 2

Diffusion coefficients of $ZnCl_2$–KCl–H_2O at 25 °C ($ZnCl_2$ at 0.5 mol)

$\bar{c}_1$	$\bar{c}_2$	$10^5 D_{11}$	$10^5 D_{12}$	$10^5 D_{21}$	$10^5 D_{22}$	Comments
0.5	0.5	0.935	0.017	0.161	1.555	1982
0.5	2.0	0.954	0.041	0.047	1.542	1981
0.5	4.0	0.933	0.026	−0.700	2.003	preliminary

$\bar{c}_1$ and $\bar{c}_2$ are in mol-dm^{-3}; D_{ij} are in cm^2 sec^{-1}; 1 refers to $ZnCl_2$; 2 to KCl.

values for all D_{ij} with 0.5 M $ZnCl_2$ are given in Table 2. In addition, 22 densities at various ternary compositions have been measured.

During 1983 more binary $ZnCl_2$–H_2O D_vs will be measured with the purer $ZnCl_2$ to further check earlier measurements. Higher and lower concentrations will also be measured to characterize this salt more fully. One more ternary composition will be done to add to the grid of compositions needed to understand this exceptionally complicated system.

TRANSITION METAL OXIDE COATED TITANIUM ELECTRODES FOR REDOX BATTERIES

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The objective of this research program is to ascertain electrocatalytic activity of transition metal oxides for use as long-life redox battery electrodes. A primary motivation for this work is to produce porous electrodes (of titanium) with reproducible surface activity for experiments to corroborate predictions of porous electrode theory. An additional goal of this research program is to ascertain whether a simple one-step outer-sphere electron transfer mechanism relates to the ferric–ferrous redox reaction at high reactant/product concentrations in a strong acid chloride medium. Kinetic rate expressions of this couple under these conditions at the metal oxide surfaces are sought.

Coatings of the conductive and active rutile structure form of selected transition metal oxides (namely RuO_2, IrO_2, OsO_2) are desired. Both IrO_2 and RuO_2 coatings having the rutile structure (as confirmed by X-ray diffraction) were prepared by thermal decomposition of their respective hydrated chloride salts. In the case of OsO_2, only amorphous coatings have been achieved. Failure to obtain the rutile structure is apparently due to the conversion of OsO_2 to the volatile OsO_4 at baking temperatures. Further work with OsO_2 is not being pursued at this time.