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Note

# THERMODYNAMICS OF DIVALENT SALTS IN DIOXANE + WATER MIXTURES

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Studies of electrolytic conductance in dioxane + water media of varying dioxane content were initiated previously [1]. In the present communication an attempt is made to evaluate the thermodynamic function $\Delta G_t^0$ for the transfer of $MgSO_4$, $ZnSO_4$ and $NiSO_4$ from water to the respective dioxane + water media, which would give some information regarding ionic solvation.

## MATERIALS AND METHODS

The salts and dioxane used were of E. Merck "Extra pure" varieties. Purification of dioxane, preparation of solvents and solutions and conductance measurements have been reported earlier [1]. The conductance measurement was of an accuracy of ±2 in 1000, the concentration range was 0.02—0.002 mole $l^{-1}$, and the investigation temperature was 35 ± 0.01°C.

## RESULTS AND DISCUSSION

The plot of $\Lambda$ vs. $C^{1/2}$ was not linear, $\Lambda^0$ and $K$ were obtained using the methods of Fuoss and Krauss [2] and Shedlovsky [3], which gave the same results.

The $\Delta G^0$ values were calculated by the equation

$$\Delta G^0 = -RT \ln K$$

The standard thermodvnamic quantities ($\Delta G_t^0$) for the transfer process

TABLE 1
Free energy of transfer of salts from water to dioxane + water mixtures

| Salt | $\Delta G_t^0$ (kJ mole$^{-1}$) | | |
|---|---|---|---|
| | 10% dioxane | 20% dioxane | 30% dioxane |
| $MgSO_4$ | 2.86 | 6.02 | 8.68 |
| $ZnSO_4$ | 4.85 | 12.89 | 14.90 |
| $NiSO_4$ | 1.51 | 4.10 | 5.89 |

TABLE 2

Electrical and chemical parts of the free energy change accompanying the transfer of salts from water to dioxane + water

| Salt | $\Delta G^0_{t(el)}$ (kJ mole$^{-1}$) | | | $-\Delta G^0_{t(Ch)}$ (kJ mole$^{-1}$) | | |
|---|---|---|---|---|---|---|
| | 10% dioxane | 20% dioxane | 30% dioxane | 10% dioxane | 20% dioxane | 30% dioxane |
| $MgSO_4$ | 228.66 | 508.14 | 889.25 | 231.52 | 514.28 | 897.93 |
| $ZnSO_4$ | 193.49 | 429.97 | 752.44 | 198.34 | 442.26 | 767.73 |
| $NiSO_4$ | 134.43 | 298.74 | 492.02 | 135.34 | 305.84 | 497.91 |

(from water to 10, 20 and 30% dioxane + water mixtures) were determined by the method of Feakin and Turner [4], and are tabulated in Table 1. The probable uncertainty in $\Delta G^0_t$ is ±15 J mole$^{-1}$.

The $\Delta G^0_t$ values are observed to be positive at all solvent compositions. This indicates that the salts are in a higher free energy state in dioxane + water mixtures than in water, suggesting that water has more affinity for the salts than for the dioxane + water mixtures.

Knowing the $\Delta G^0_t$ values and the ionic radii of the cations and anions [5], $\Delta G^0_t$ was divided into two parts according to Roy et al. [6]. It consists of an electrostatic part, $\Delta G^0_{t(el)}$, corresponding to a change in the dielectric constant of the medium and another nonelectrostatic or chemical contribution, $\Delta G^0_{t(Ch)}$, arising from the specific chemical interaction between the ions and the solvent. $\Delta G^0_{t(el)}$ was calculated from Born's equation [7], and then $\Delta G^0_{t(Ch)}$ was determined. The results obtained are presented in Table 2. It is evident that the values of $\Delta G^0_{t(Ch)}$ are negative in all cases and increase with increase in dioxane content. This indicates that the transfer of salts from water to dioxane + water mixtures is favoured as far as chemical interaction agreement with viscosity results [8].

Using conductance data, the Walden product $\Lambda^0\eta_0$ has also been employed $Zn^{2+} > Ni^{2+}$; hence, the ionic solvation is of the reverse order, which is in agreement with viscosity results [8].

Using conductance data, the Walden product $\Lambda^0\eta_0$ has also been employed to study the ion—solvent interaction in a solution. $\Lambda^0\eta_0$ values of the three salts at different solvent compositions are recorded in Table 3. The plot of

TABLE 3

The Walden product, ($\Lambda^0\eta$) ($\Omega^{-1}$ cm$^2$ p), of the three salts at different solvent compositions

| Salt | 10% dioxane | 20% dioxane | 30% dioxane |
|---|---|---|---|
| $MgSO_4$ | 0.979 | 0.991 | 0.694 |
| $ZnSO_4$ | 1.091 | 1.084 | 1.069 |
| $NiSO_4$ | 0.937 | 0.971 | 0.646 |

$\Lambda^0\eta_0$ vs. solvent compositions is linear and the slope is of the order $Mg^{2+} > Ni^{2+} > Zn^{2+}$, which indicates the order of the ionic solvation [9]. There is some discrepancy between the dissociation constant obtained from $\Delta G_t^0$ and that obtained from the Walden product. The crystallographic radii of $Zn^{2+}$ and $Ni^{2+}$ are almost the same (0.72 and 0.74, respectively), so it is expected that the ionic solvation would be almost the same; hence the discrepancy between the two methods is not unnatural.

## REFERENCES

1 N.C. Das and P.B. Das, Electrochim. Acta, 23 (1978) 191.
2 R.M. Fuoss and C.A. Krauss, J. Am. Chem. Soc., 33 (1933) 476.
3 T. Shedlovsky, J. Franklin Inst., 225 (1938) 439.
4 D. Feakins and D.J. Turner, J. Chem. Soc., (1965) 4786.
5 P.P. Misra and P.B. Das, Experentia, 24 (1979) 321.
6 R.N. Roy, W. Vernon and A.L.M. Bothwell, Electrochim. Acta, 17 (1972) 5.
7 H.P. Bernets and M.M. Spetzer, J. Chem. Soc., Faraday Trans. I. (1973) 1492.
8 P.B. Das, J. Indian Chem. Soc., 54 (1977) 1193.
9 R.L. Blokhra and M.L. Parmour, J. Electrochem. Soc., 57 (1974) 117.