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The Redox Acidity Function, R_0(H) in Glycols and Their Aqueous Mixtures

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Synopsis. The variation of the redox acidity function, R_0(H), based on ferrocene redox couple has been studied at 25 °C as a function of solvent composition in diethylene glycol-water and ethylene glycol-water mixtures and compared with the H_0 variation in these solvents. Further, the redox function for sulfuric acid has been reported upto 6 molal in 50 wt% diethylene glycol-water mixture as the solvent.

The indicator acidity functions have been the most extensively studied[1] among the acidity functions. However, it has been well established in recent years,[1] that these functions are not satisfactory as an index of the proton activity of the medium as they are known to vary with the nature of the indicators employed in such measurements. Strehlow and Wendt[2] proposed an alternate acidity function, the redox function, R_0(H), based on redox systems of large size of the charge type, 0/1+, such as ferrocene couple. Although this function has been studied in aqueous solutions,[2] practically no measurements have been reported in non-aqueous media,[3] especially in amphiprotic solvents and their aqueous mixtures. In continuation of our earlier work[4—6] on this subject in glycolic solvents, the present investigation deals with a study of the variation of R_0(H) in diethylene glycol-water and ethylene glycol-water mixtures at 0.01 mol/kg perchloric acid as also the determination of R_0(H) for sulfuric acid in 50wt% diethylene glycol as solvent.

Experimental

The purification of ethylene and diethylene glycols has been described[4,7] elsewhere. Ferrocene (E. Merck) was sublimed twice under vacuum and the resulting pure orange crystals were employed. Perchloric acid (E. Merck, Proanalysi, 70 wt %) was used in measurements in aqueous mixtures involving variation of solvent composition while methanesulphonic acid (Fluka), purified by distillation, was used in the pure organic solvents. Aqueous SCE was the reference electrode in these studies. A.R. Sulfuric acid was used in measurements in 50 wt % diethylene glycol as solvent. Mercury, mercurous sulphate electrode was employed as the reference in these measurements.

The determination of R_0(H) function is based on the evaluation of the EMF of the cell.

$$\text{Pt, H}_2\text{(g, 1 atm)}\Big/\begin{matrix}\text{acid in the}\\ \text{given solvent}\end{matrix}\quad\begin{matrix}\text{FOC, FiC}^+\\ (1:1)\end{matrix}\Big/\text{Pt} \qquad (1)$$

in the solvent and water and was obtained by a combination of the polarographic $E_{1/2}$ of ferrocene *vs.* SCE or mercury, mercurous sulphate electrode as reference and the EMF of the hydrogen-calomel or hydrogen-mercury, mercurou sulphate cell using the same experimental solution for both the measurements. Further details of the determination of the EMF of the cell (1) are given[8] elsewhere.

Results and Discussion

The redox function, R_0(H), is defined by

$$R_0(\text{H}) = \frac{E_s - E^\circ_w}{2.303\,RT/F} \qquad (2)$$

where E_s refers to the EMF of the cell (1) in the solvent and E°_w is the standard EMF of the cell in water which has a value of +0.400 V at 25 °C as reported[2] earlier. The EMF's of cell (1) at 0.01 mol/kg perchloric acid in various diethylene glycol-water and ethylene glycol-water mixtures and the R_0(H) data in these media at 25 °C are recorded in Table 1. The H_0 data obtained in these solvents at 0.01 mol/kg perchloric acid according to the method described[4] previously, using *p*-nitroaniline as indicator are also recorded in this table for comparison.

Table 2 presents the EMF's of cell (1) and R_0(H) data at various molalities of sulfuric acid in 50 wt% diethylene glycol as solvent.

Assuming that the neutral component of the transfer free energy of ferricinium ion is equal to that of ferrocene and neglecting the small electrostatic transfer free energy of the ferricinium ion, which is justifiable in view of the larger size of ferricinium ion (r_{Fic^+}= 3.3 Å,)[9] the R_0(H) can be related to the proton activity of the medium by

$$R_0(\text{H}) = -\log\,(m_{\text{H}^+}\,{}_w\gamma_{\text{H}^+}) \qquad (3)$$

where m_{H^+} is the molality of the H$^+$ ion and ${}_w\gamma_{\text{H}^+}$ is the activity coefficient of the same ion on the aqueous standard state. It is seen from Table 1 that R_0(H) increases continuously with increasing additions of diethylene glycol, passes through a maximum at about 90 wt% organic solvent and then decreases. A similar result is observed in ethylene glycol-water mixtures although the maximum occurs at 95 wt% organic solvent in this case. This implies that in both organic solvent-water mixtures the proton activity of the medium initially decreases, passes through a minimum at about 90—95 wt% organic solvent and then increases. Evaluation of the proton medium effect employing the ferrocene redox couple as reference in these solvents showed[8] a variation similar to R_0(H) and thus the basicity of the medium increases with increasing addition of the organic solvent at fixed acid concentration upto 90—95 wt% organic solvent and then decreases in the pure solvent, which can be explained on the basis of the structural theory of ion solvation proposed by Feakins and Watson.[10] It is also noted from Table 1 that R_0(H) and H_0 vary similarly in these solvent mixtures with good agreement in the composition of maximum basicity region in diethylene glycol-water mixtures while it is somewhat

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TABLE 1. R_0(H) AND H_0 DATA IN DIETHYLENE GLYCOL–WATER AND ETHYLENE GLYCOL–WATER MIXTURES AT 25° C

Wt % diethylene glycol	EMF of cell(1) in V	R_0(H)	H_0	Wt % ethylene glycol	EMF of cell(1) in V	R_0(H)	H_0[a]
20.00	0.5287	2.18	2.35	30.00	0.5456	2.47	1.15
40.00	0.5635	2.77	2.42	50.00	0.5608	2.72	1.25
50.00	0.5702	2.88	—	70.00	0.5872	3.16	1.25
60.00	0.5866	3.16	2.75	90.00	0.6017	3.41	1.10
80.00	0.6469	4.18	2.80	95.00	0.6431	4.11	—
90.00	0.6607	4.41	—	100.00	0.5895	3.22	0.00
95.00	0.6548	4.31	—	—	—	—	—
100.00	0.6348	3.97	1.09	—	—	—	—

a) At 0.1 molal HCl.

TABLE 2. R_0(H) OF SULFURIC ACID IN 50 wt% DIETHYLENE GLYCOL AT 25 °C

Molality of H_2SO_4	EMF of cell (1) in V	R_0(H)
0.1178	0.4644	1.09
0.2335	0.4251	0.43
0.4710	0.4107	0.18
1.00	0.3945	−0.09
2.00	0.3553	−0.76
3.60	0.3171	−1.40
6.00	0.2155	−3.12

poor in ethylene glycol–water mixtures, Further, R_0(H) is generally greater than H_0 at a given solvent composition (from the data in diethylene glycol–water mixtures), the difference being given by

$$R_0(\mathrm{H}) - H_0 = \log \left(\frac{\gamma_{\mathrm{B}}}{\gamma_{\mathrm{BH}^+}}\right)_{\mathrm{w}} \quad (4)$$

where the γ_B and γ_{BH^+} represent the activity coefficients of the indicator base and its conjugate acid on the aqueous standard state. Equation (4) was checked in diethylene glycol–water mixtures by calculation of the activity coefficient ratio from the indicator data (unpublished results) on *p*-nitroaniline in these mixtures. For this purpose, the medium effect of the indicator was obtained from solubility measurements and that of its conjugate acid was realised through the application of the ferrocene assumption to the p*K* data on the indicator and fair agreement was indeed observed.

It is seen from Table 2 that R_0(H) of sulfuric acid in 50 wt% diethylene glycol decreases with increasing acid concentration indicating that the proton activity of the medium is enhanced with acid concentration. The R_0(H) of an aqueous sulfuric acid solution is more negative[2] than R_0(H) in 50 wt% diethylene glycol at a given acid concentration which shows that aqueous acid solutions have higher proton activity than those in 50 wt% diethylene glycol. This indicates that this solvent is more basic than water, a result in agreement[8] with the conclusions arrived from the proton medium effect in this solvent.

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