Proton Medium Effects Utilising Ferrocene Redox Couple as Reference in Propylene Glycol-Water, Methanol-Propylene Glycol and Methanol-Water Mixtures

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Utilising the ferrocene reference method, proton medium effects ($\log m\gamma\, H^+$) were determined in methanol-water, propylene glycol-water and methanol-propylene glycol mixtures of varying composition. On the basis of the ferrocene method, it was shown that all methanol-water, propylene glycol-water and methanol-propylene glycol mixtures including the pure solvents are more basic than water and these results were explained in terms of the structural theory of ion solvation proposed by Feakins and coworkers. Further, it was shown that methanol is slightly more basic than propylene glycol which is in agreement with the conclusions arrived from earlier EMF measurements.

Introduction

Studies on ion solvent interactions in non-aqueous media through the determination of the medium effects on single ions, in particular on the proton have lately received considerable attention [1–3]. Two extrathermodynamic methods for the determination of such effects, viz. the reference electrolyte method and that based on redox couples of large size of the $0/+1$ charge type appear to be most promising [1]. However, only a few studies based on redox couples of large size, such as the ferrocene redox couple, especially in amphiprotic solvents their aqueous mixtures, have been [4, 5] made despite the experimental simplicity of the method. The present work, which is a continuation of our earlier work [5], deals with a study of proton medium effects using a ferrocene redox couple as reference in two aqueous amphiprotic solvents viz. methanol-water and propylene glycol-water mixtures and also the isodielectric solvent mixture of methanol-propylene glycol of varying composition.

Experimental

Ferrocene (E. Merck) was twice purified by sublimation under vacuum and the resulting pure orange crystals were used. Perchloric acid (E. Merck, pro analysi 70 wt%) and p-toluenesulphonic acid, purified by recrystallisation from ether, were employed in the measurements involving aqueous-organic solvent mixtures and the pure organic solvents, respectively. The acids themselves served as the supporting electrolyte in polarographic measurements. It was shown from conductance measurements (unpublished results) that p-toluene sulphonic acid is practically completely dissociated in methanol and propylene glycol. A.R. (BDH) methanol was distilled twice before use. Propylene glycol (LR, BDH) was purified according to the procedure described previously [6]. Double distilled water was employed in all the measurements. A DME with a drop time of 4 sec and a mass rate of flow 1.1048 mg/sec in 0.1 M KCl without the application of a potential together with an aqueous SCE with a potassium nitrate salt bridge were used in the polarographic measurements. The half-wave potentials of the ferrocene-ferricinium couple (Vs aqueous SCE), required in this work, were determined in the various solvent mixtures in the acid concentration range 0.01 – 0.02 m with a Metrohm polarecord (E 261) and were combined with the EMF data on the hydrogen-calomel cell under identical conditions to obtain the standard potential of the ferrocene-ferricinium ion couple in water and in various organic solvent-water mixtures as described previously [5].

Results and Discussion

The difference in the standard potentials of this couple in solvent (E^0_{S}) and in water (E^0_{W}) is related [5] to the transfer free energy of the proton, $\Delta G^0_{\mathrm{H^+}}$, according to

$$F\,(E^0_{\mathrm{S}} - E^0_{\mathrm{W}}) = \Delta G^0_{\mathrm{Cell}} = \Delta G^0_{\mathrm{Fic^+(el)}} - \Delta G^0_{\mathrm{H^+}} \qquad (1)$$

where $\Delta G^0_{\mathrm{Fic^+(el)}}$ represents the electrostatic free energy of transfer of the ferricinium ion. $\Delta G^0_{\mathrm{Fic^+(el)}}$ was evaluated from the simple Born equation (using $r_{\mathrm{FiC^+}} = 3.3$ Å) [4], as it was shown earlier [7] that the use of the modified Born equation with empirical radius correction terms produces only minor changes in $\Delta G^0_{\mathrm{H^+}}$. For this purpose, the dielectric constants of methanol-water mixtures were taken from the literature [8], the dielectric constants of propylene glycol-water mixtures were determined (our unpublished results), and in the case of propylene glycol-methanol mixtures, an average value of $D = 30.92$ was assumed for all solvent compositions as they are nearly isodielectric. The average values of $\Delta G^0_{\mathrm{Cell}}$, $\Delta G^0_{\mathrm{Fic^+(el)}}$, $\Delta G^0_{\mathrm{H^+}}$ and $\log m\gamma\, \mathrm{H^+}$ for all solvent compositions in methanol-water and propylene glycol-water mixtures are recorded in Table I. A comparison of $\Delta G^0_{\mathrm{Cell}}$ from this work and that of Alfenaar and Deligny [9] in methanol-water mixtures shows fair agreement for all compositions except at 40 wt.% methanol, indicating the reliability of our results. Table II gives similar results in methanol-propylene glycol

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Table I. Proton transfer free energies and medium effects in methanol-water and propyleneglycol-water mixtures at 30 °C.

	Methanol-water mixtures				Propylene glycol-water mixtures			
Wt.% water	ΔG^0_{Cell} cal.	$\Delta G^0_{\text{Fic}^+\text{(el)}}$ cal. g. ion^{-1}	$-\Delta G^0_{\text{H}^+}$ cal. g. ion^{-1}	$-\log m\gamma H^+$	ΔG^0_{Cell} cal.	$\Delta G^0_{\text{Fic}^+\text{(el)}}$ cal. g. ion^{-1}	$-\Delta G^0_{\text{H}^+}$ cal. g. ion^{-1}	$-\log m\gamma H^+$
0	2605	925	1680	1.22	2380	1018	1362	0.98
10	3540	710	2830	2.04	3235	740	2495	1.80
20	3050	558	2492	1.80	2800	588	2212	1.60
40	2270	343	1927	1.39	1725	320	1405	1.01
60	775	189	586	0.43	957	164	793	0.57
80	72	78	−6.0	0.004	667	56	611	0.44
100	0.0	0.00	0.00	0.00	0.00	0.00	0.0	0.00

Table II. Proton transfer energies and medium effects in methanol-propylene glycol mixtures at 30 °C.

Wt.% propylene-glycol	ΔG^0_{Cell} cal.	$\Delta G^0_{\text{Fic}^+\text{(el)}}$ cal.g.ion^{-1}	$-\Delta G^0_{\text{H}^+}$ cal.g.ion^{-1}	$-\log m\gamma H^+$
0	2605	925	1680	1.22
20	2473	970	1503	1.08
40	2495	970	1525	1.10
60	2498	970	1528	1.10
80	2478	970	1508	1.09
100	2380	1018	1362	0.98

mixtures. According to this method, all methanol-water and propylene glycol-water mixtures are more basic than water, the maximum basicity region being near about 90 wt.% organic solvent, and this increase of basicity on the addition of the organic solvent to water can be explained in terms of the structural theory of ion solvation proposed by Feakins and coworkers [10]. The greater basicity of the pure solvents compared to water is most probably associated with the absence of characteristic structure (less structural order) in these solvents. Similar conclusions regarding the basicity of organic solvent-water mixtures based on the ferrocene method were reached in the case of ethylene glycol-water and diethylene glycol-water mixtures [5]. Similarly, all propylene glycol-methanol mixtures are more basic than water although the change in basicity is negligible when methanol is added to propylene glycol which indicates the absence of drastic structural changes in these solvent mixtures as compared to those when water is a constituent. Further, methanol is slightly more basic than propylene glycol because of the more negative value of the proton medium effect in this solvent than in propylene glycol. This is in agreement with the conclusions of Kundu et al.[11], reached on the basis of their EMF measurements and is reasonable in view of the fact that the electron density on the oxygens of the hydroxyl groups in propylene glycol is reduced by the considerable intramolecular hydrogen bonding effect in this molecule compared to that in methanol.

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