Solvation Free Energies of Transfer of Anion Radicals: 4-Nitroaniline Anion Radical in Acetonitrile-Water Mixed Solvent System

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THE solvation free energies of transfer ($\Delta\Delta G'$) of 4-Nitroaniline anion radical in acetonitrile-water mixed solvent system were determined using cyclic-voltammetry. The present method employed measurement of reversible $E_{\frac{1}{2}}$ (for the reduction) of 4-Nitroaniline, 1-ethyl-4-carbomethoxy pyridinium iodide and rubidium cation. Values of $\Delta\Delta G'$ obtained by using both, 1-ethyl-4-carbomethoxy pridinium iodide and rubidium ion (Pleskov method), are presented.

INTRODUCTION

THE stability of anion radicals and the reversibility of electrode processes in varying composition of solvents can be studied directly and conclusion therefrom can be made regarding the lifetime etc. of the anion radical. The solvation free energy of transfer of radical-anion cannot be inferred without having some idea about the change in liquid junction potential (in using a reference electrode). Maironovskii reported studies on the variation of $E_{\frac{1}{2}}$ of various bromothiophenes in aqueous-ethanol and aqueous-dimethyl formamide. However, no corrections for the change in composition of solvent were made. Thus no inference regarding the free-energy of solvation can be made. Peover[2] has reviewed the work on the effect of solvent on reduction and oxidation potential in pure solvents. He also made corrections for liquid junction potential but no numerical values have been given and the discussion is rather qualitative.

Nitroaromatics have been investigated electrochemically by many workers[1-6]. The reason being that nitrocompounds are easily reducible, and generally, their anion radicals are stable in aprotic solvents. Properties of these anion radicals can be investigated e. g. by ESR. In the present study we made cyclic voltammetric studies on 4-nitroaniline in acetonitrile-water mixture with the aim of investigating the stability of the anion radical, reversibility of the electrode process, the effect of solvent composition on the reduction potential and solvation free energy of transfer.

Nitroanilines had been studied in our laboratory and 4-Nitroaniline has been found to give reversible waves in acetonitrile and acetonitrile-water system[7]. This system seemed to us suitable for the present study.

The difficulty arising from using reference electrodes in various solvents (or solvent mixture) led us to search for a method which could be applied to any reversible system and in practically any solvent. We found that such a method might exist: the reduction of 1-ethyl-4-carbomethoxy pyrididum iodide and utilization of its Z-values. Another method which is somewhat established one is Pleskov's method of using rubidium cation[2,8-11]. This method has also been adopted and results obtained by the two methods are compared with the Pleskov method.

Below we present the details of our method.

Variation in reduction potentials due to change of solvent or solution composition (or for mixture of solvent) for an electrochemical process,

$$O + e \rightleftharpoons R \qquad (1)$$

where R be neutral or charged species, can be approximated as

$$\Delta E' = \frac{1}{nF}[\Delta G(0)_{s1} - \Delta G(0)_{s2}] - [\Delta G(R)_{s1} - \Delta G(0)_{s2}] + a \approx (E_{\frac{1}{2}})_{s1} - (E_{\frac{1}{2}})_{s2} = \Delta E_{\frac{1}{2}} \qquad (2)$$

where $\Delta G(X)_{s1}$ is free energy of solvation of x (ex) in solvents (s), and $E_{\frac{1}{2}}$ is the half-wave potential, all expressed in Volts.

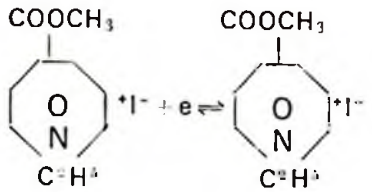
Expression (2) can be rewritten as

$$\Delta E_{\frac{1}{2}} \approx -\frac{\Delta\Delta G'}{nF} + a \qquad (3)$$

where $\Delta\Delta G' = \Delta\Delta G(R) - \Delta\Delta G(0)$; where

$$\Delta\Delta G = (\Delta G)_{s_1} - (\Delta G)_{s_2} \qquad (4,5)$$

Thus, it is seen from (3) that, to determine $\Delta\Delta G$, α has to be eliminated, or evaluated, or estimated, or replaced by some other experimentally measurable quantities. Here α is the uncertainty arising from the change in potential of reference electrode with the variation in solvent (or solution composition). The use of rubidium ion[2] (Rb^+) (Pleskov method) or Ferrocine[8] as the reference electrode to eliminate α has been attempted[8-11]. However, an alternative method, based upon the replacement of α by measureable or calculable quantities is presented. The method is based upon the electrochemical reduction of 1-ethyl-4-carbomethoxy pyridinum iodide and utilization of solvent dependence of its charge transfer spectra (Z-Values)[12]. Consider the reduction of 1-ethyl-4-carbomethoxy pyridinium iodide[13].



$$Py^+I^- + e \rightleftharpoons Py^{\cdot} + I^-$$

Thus corresponding to equation (3), we have

$$(E_{\frac{1}{2}})_{PY^+} = -\Delta\Delta G(I^-) - \Delta\Delta G(Py^-) + \Delta\Delta G(Py^+I^-) + \alpha \qquad (7)$$

in proper units.

It is observed that α of equation (3) can be replaced by the terms given in equation (7).

$\Delta E_{\frac{1}{2}}$ of equation (7) is an experimentally observed quantity. $\Delta\Delta G(Py^{\cdot})$ can be approximated to be zero, since pyridinyl radical does not interact with the solvent as evidenced by very little solvent effect on near U.V. spectra of this radical[14]. Also, there is negligible contribution due to stabilization of the ground state on the rate constant of atom tranfer reaction of pyridinyl redical as evidenced by negligible solvent effect[15]. $\Delta\Delta G(I^-)$ can be calculated, as first approximation, employing Born equation[2,8,16], while ion-dipole interaction equation can then be used as higher approximation.

$$-\Delta G = \frac{Ne^2}{2r_{(I^-)}}\left(1 - \frac{1}{\varepsilon}\right) \qquad (8)$$

N is Avogadro number, r is radius of ion and ε the dielectric constant of the solvent. Thus, $\Delta\Delta G(I^-)$ is given by

$$\Delta G_{S_1} - \Delta G_{S_2} = \Delta\Delta G(I^-)$$

$$= \frac{Ne^2}{2r_{(I^-)}}\left[\frac{1}{\varepsilon(S_1)} - \frac{1}{\varepsilon(S_2)}\right] \qquad (9)$$

$\Delta\Delta G(Py^+I^-)$ is the change in the free energy of solvation of Py^+I^- from one solvent to another (or mixed solvent) and is approximately equal to $\frac{1}{2}\Delta Z$, where Z is the solvent polarity parameter[17-19].

Thus it is clear that all the terms in (7) are either experimentally observable or else can be easily calculated. Equation (7) can be written as

$$(\Delta E_{\frac{1}{2}})_{Py^+I^-} = \frac{Ne^2}{2r_{(I^-)}}\left[\frac{1}{\varepsilon(S_1)} - \frac{1}{\varepsilon(S_2)}\right] + \frac{1}{2}\Delta Z + \alpha \qquad (10)$$

which can now be combined with (3) to give $\Delta\Delta G'$. This $\Delta\Delta G'$ can be compared with those obtained by, say, Pleskov method (Rb^+ ion method) or Ferrocene method.

Approximate values of these parameters (ε and Z-values) for mixed solvents system were obtained by the following methods

a) Δ Z-values : Z°_{12} values (*i.e.* Z-values for mixtures in absence of salt) were estimated from the components.

$Z^{\circ}_{12} = X_1 Z^{\circ}_1 + X Z^{\circ}_2$ where X's are the mole fractions.

b) ε, The dielectric constant

i) ε°_{12} was estimated as in the case of Z-values

$\varepsilon^{\circ}_{12} = X_1 \varepsilon^{\circ}_1 + X_2 \varepsilon^{\circ}_2$

RESULT AND DISCUSSION

In Table 1 electrochemical data for $P_y{}^+I^-$, RbCl and 4-nitroaniline, are collected. In Table 2, $\Delta\Delta G'$ as evaluated by the rubidium ion method (Pleskov method) and pyridium iodide method are collected for comparison. It is quite clear that the values differ substantially, but it is also remarkable that the values agree qualitatively *i.e.* they are of the same sign : both methods indicate that the 4-nitroaniline anion radical is solvated to some extent.

α also contains the variation in surface potential due to change in solvent.

TABLE 1

Electrochemical and other data for Py^+I^-, RbCl and 4NA in acetonitrile-water mixed solvent system[a].

MeCN	Z^0_{12}	ε^0_{12}	$-(E^{1}_{\frac{1}{2}})^{b,c}_{Py^+I}$	$-(E^{1}_{\frac{1}{2}})^{b,c,d}_{RBCl}$	$-(E^{1}_{\frac{1}{2}})^{b,c}_{4NA}$
Mole fraction					
1.000(X_0)	(71.3)	(36.7)	0 747	1.832	1.300
0.838(X_1)	(75.2)	(43.4)	0.800	1.836	1.106
0.634(X_2)	(79.8)	(52.0)	0.816	1.843	1.1015
0.510(X_3)	(82.7)	(57.2)	0.822	1.850	0.980

(a) With 0.1 M TBAP (b) Vs. SCE $E^{1}_{\frac{1}{2}}$ is potential corresponding to 85% of peak current (three electrode configuration) (c) The reversibility of charge transfer was established from $(E_p)_c-(E_p)_a$, $(i_p)_c/(i_p)_a$ and E_p-$E^{1}_{\frac{1}{2}}$ values (d) $E^{1}_{\frac{1}{2}}$ for zero water concentration was obtained by extrapolation

TABLE 2

Born free energies and free energies of transfer for 4-Nitroaniline Anion Radical in Acetonitrile-water mixed solvant system[a].

Transfer Process MeCN mole fraction[b]		Born Free Energies[c,d]	G (Py$^+$ Id)[e]	G (Pleskov)[d,f]
X_0	X_1	0.400	7.50	4.50
X_0	X_2	0.750	11.80	6,83
X_0	X_3	0.90	13.89	7.90

(a) with 0.1 M TBAP (b) X_i X_j means for transfer process: $\Delta\Delta G = \Delta G(X_i) - \Delta G(X_j)$ see table 1 for X_i (c) Calculated as explained in the text with radius of iodide ion = 2.16 Å (d) in Kcal/mole (e) Pyridinium iodide method (f) Pleskov method.

There are two aspects of result for $\Delta\Delta G'$ which are to be discussed: (1) $\Delta\Delta G'$, as obtained by the two methods, are significantly different from zero (b) the numerical values for $\Delta\Delta G'$ as obtained by the two methods do not agree.

Since, from both methods (Pleskov and Py^+I^- methods), the free energy of transfer of nitroaniline anion radical, going from pure acetonitrile to acetonitrile-water mixture (or one mixed solvent system to another), is found to be different from zero, we have to accept that the result obtained is not due to inaccuracies in these methods, but the nitroaniline radical ion does get solvated. This is in agreement with the work of Peover that anion radicals, in general, get solvated[9]. However, Peover did not give any numerical values for $\Delta\Delta G'$. In the present case, the nitro group of nitroaniline and the hydrogen bond of the solvent (H_2O) may be contributing a significant percentage of the total solvation energy but no attempt was made to separate these contributions.

The second aspect that the two methods give different numerical values for free energy of transfer will be discussed now.

The departure in numerical value for $\Delta\Delta G'$ as obtained from Py^+I^- method from those obtained by Rubidium ion method could have been of some significance, had we known the accuracy of Pleskov method itself. Pleskov method is not accurate and no accurate numerical values are expected. Its limitation has been discussed in the literature and need not be elaborated here[11]. We analyse possible errors involved in the pyridinium iodide method.

The main problem in evaluating free energy of transfer of radical ion is the problem of a, which we replaced by the terms in Eq. 7. for pyridinium iodide. Simplifications were introduced in the equation to make it manageable.

First of all, the solvation free energy of transfer of Py. radical (eqn. 7) is considered to be negligible. This is not drastic assumption, since, as explained above, the radical does not show large dependence on solvent (solubility, optical spectra, kinetics etc.)[14,15] (<0.01V.).

The other approximations are the use of Z-values for the solvation of the charge transfer compound of pyridinium iodide and use of Born charging energy for the solvation of iodide ion. The Z-values is the solvent polarity parameter and depends upon the mechanism of stabilization of the ground state and destablization of the excited state of the charge transfer complex (Py^+I^-) by the solvent[12]. Assumption of equal stablizing and destablizing of state leads to the solvation free energy (of transfer) for pyridinium iodide as $\frac{1}{2}\Delta Z$, as used in electron transfer reaction[20].

The third approximation, as mentioned above, is the use of Born expression for the solvation free energy of transfer for iodide ion. This means that

ion dipole etc. higher (interaction) terms are neglected. No attempt has been made to investigate the effect of higher terms. Thus the calculation presented here should be considered as a first approximation in the investigation of the phenomonon of solvation of nitroaniline radical anion.

These were the approximation in the models, we now discuss the approximations introduced in evaluating various terms.

(1) *The Born Charging Expression (a charged sphere in a dielectric continuum).* Following terms must be known : a) radius of iodide ion in all solvent system studied b) The dielectric constant of solvent system.

a) Radius of iodide ion : The radius of iodide ion has been kept constant (2.16 Å)[16] in acetonitrile and acetonitrile-water mixture. It can be easily shown that a few per cent variation in the value of 'r' the radius, will not effect the α values significantly.

b) Because of lack of experimental data of dielectric constant of the solvent available the dielectric constant of the mixture ε_{12}° is evaluated by using eqn. 12.

This expression is quite accurate as checked with the available data. The next approximation could be to make correction for the presence of salt. However the correction (due to presence of salt) in the dielectric constant amounts to about 10%. A departure of even 25% in the correction term due to presence of salt should not effect the final result to great extent.

(2) *Approximation in Z-value :* Z°_{12} was evaluated from Z-values of its components from Eqn. 11. This approximation has been checked with available data and has been found to be quite good approximation. The correction for salt, in the present study is superfluous, since a constant term is to be added to Z°_{12} which cancels out in ΔZ_{12} terms. The use of $\frac{1}{2}\Delta Z_{12}$ is justified on theoretical grounds[12]. Also it was experimentally found to be quite good[23].

Thus the errors involved in the evaluation of the various terms are small, and if our model is good enough approximation, then the results obtained by this method should be accurate enough.

We turn to the subtle problems arising from the nonzero value for $\Delta\Delta G'$. The question whether radical anions get solvated is a fundamental question[21]. Our investigations show that 4-nitroaniline radical-anion does get solvated. Is it due to the specific property of nitrogroup and hydrogen bonded solvent (H_2O) or is it general property of all anion radical, the present investigation does not answer. However further investigation is underway. The question whether the dianion also plays role *i.e.* if following equilibria :

$$2NA^{-} \rightleftharpoons NA^{-2} + NA \qquad (14)$$

$$NA^{-2} + Solv. \rightleftharpoons (NA^{-2})\ Solv. \qquad (15)$$

$$2(NA^{-})\ Solv. \rightleftharpoons (NA^{-2})\ Solv. + NA + Solvent \qquad (16)$$

also effect the solvation free energies of transfer, could be judged from the disproportionation constant (Eqn. 14). Unfortunattely the dianion of nitroanilines have not been found to be stable enough and the reversible second reduction potential $(E_{\frac{1}{2}})_2$ have not been determined. However the disproportinnation contant, if it is of the order of 10^{-5} (e.g. in case of 1,3 dinitro benzene), it can hardly effect the solvation of the monoanion radical.

EXPERIMENTAL

Experimental details have already been described[7,13,23]. 1-Ethyl-4-Carbomethoxy pyridinium iodide was crystallised three times from acetone (mp 111-112°C, Lit. 111-112 [see ref 17]) Rubidium Chloride (E. Merck) was used as source of Rb^{+}, and was used directly. Distilled water was distilled only once. Purification of solvent and and supporting electrolyte has already been described[7,13,23].

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