May, 1988] Bull. Chem. Soc. Jpn., 61, 1735—1742 (1988)

Relative Standard Electrode Potentials of I_3^-/I^-, I_2/I_3^-, and I_2/I^- Redox Couples and the Related Formation Constants of I_3^- in Some Pure and Mixed Dipolar Aprotic Solvents

Jayati Datta, Abhijit Bhattacharya, and Kiron Kumar Kundu*
Physical Chemistry Laboratories, Jadavpur University, Calcutta-700032, India
(Received February 12, 1987)

Standard potentials of I_3^-/I^- and I_2/I_3^- redox couples relative to that of aqueous saturated calomel reference electrode SCE (W), $E_{SCE(w)}$ have been determined in propylene carbonate (PC), *N,N*-dimethylformamide (DMF), acetonitrile (ACN), and their binary mixtures at 25 °C from potentiometric measurements. The results helped evaluate the standard potentials of the redox couple I_2/I^- relative to $E_{SCE(w)}$ as well as the related formation constant (K_f) of I_3^- in these solvent systems. The solvent effects on the formation equilibrium $I_2+I^- \rightleftharpoons I_3^-$ were analyzed in the light of the transfer free energies of I_2, $\Delta G_t^\circ(I_2)$, as obtained from solubility measurements of I_2 in the solvents, that of I^-, $\Delta G_t^\circ(I^-)$, as obtained earlier by use of the widely used TATB reference electrolyte assumption and that of I_3^-, $\Delta G_t^\circ(I_3^-)$, as obtained by subtracting these two contributions from the respective transfer free energies of formation equilibrium in the mixed solvents relative to a chosen reference solvent in each solvent system. The solvation behavior of these individual iodine species viz. I_2, I^-, I_3^- was interpreted in terms of involved interaction viz. Born, ion-dipole, ion-induced dipole, dispersion type soft-soft interactions, CTTS complexation and also the cavity effect as computed by the scaled particle theory (SPT).

The electrochermical behavior of the halogen/halogenide ion (X_2/X^-) redox couples in different nonaqueous media has lately become increasingly important due to their potential use in some high energy nonaqueous primary[1] and secondary batteries[1,2] and also in nonaqueous photoelectrochemical (PEC) cells.[3,4] In this context the knowledge of the intensive factor such as the standard potential (E°) of the galvanic elements X_2/X^-, and that of the involved X_3^-/X^- and X_2/X_3^- redox couples as well as the formation constant (K_f) of X_3^- in different dipolar aprotic solvents and their binary mixtures should be of particular interest. These, or at least their relative values, will be helpful to characterize the Fermi levels of these redox couples as required for the potential nonaqueous PEC cells, to elucidate their influence on the charging-discharging characteristics of the potential nonaqueous batteries and also to evaluate the kinetic parameters of the involved galvanic reactions in both the cases. This knowledge will then help judge the relative potentiality of the solvents for their use in the nonaqueous batteries or PEC cells comprising these redox couples.

Of the widely used battery fluids propylene carbonate (PC) and *N,N*-dimethylformamide (DMF) have attracted increasing attention.[5] Acetonitrile (ACN), though not so widely used, has got the distinction of being a protophobic dipolar aprotic solvent like PC, but nearly isodielectric to DMF. Very recently Kuznetsova et al.[6] reported the values of $E^\circ_{I_3^-/I^-}$ and $E^\circ_{I_2/I_3^-}$ and the formation constant K_f of I_3^- in DMF and its mixtures with PC at different temperatures. But their data, based on a potentiometric titration procedure using a reference half cell, Pt, I_2 solvent //, seems questionable, as I_2 solution without any added I^- would hardly act as a suitable redox couple. Moreover, appreciable ionization of I_2 to I^- in these aprotic solvents unlike in protic solvents like water, is somewhat doubtful, although charge transfer complex formation with these solvents cannot be ruled out. Further, the so-called electrode potential (E°) values reported, appear to be relative to the emf of the reference half-cell mentioned above. In the present paper we therefore report the standard electrode potentials (E°) of I_3^-/I^-, I_2/I_3^-, and I^-/I_2 redox couples relative to aqueous saturated calomel reference electrode SCE(w) and the related formation constant (K_f) or I_3^- in these dipolar aprotic solvents and their binary mixtures containing 25, 50, and 75 wt% of the cosolvents.

The cells used for this purpose are

$$\text{SCE(w)}//I^-(m),\ I_3^-(m),\ \text{solvent/Pt} \qquad \text{(A)}$$

$$\text{SCE(w)}//I_2(m),\ I_3^-(m),\ \text{solvent/Pt} \qquad \text{(B)}$$

where m stands for the molal concentration of I^-, I_2, and I_3^-. The emf's of the cells were measured for several values of m so that the ionic strength (μ) could be varied from 0.01 to 0.1.

Admittedly, the use of SCE(w) as the reference half-cell has resulted in the introduction of a liquid junction potential (E_j) in the final E° values of the redox couples in each solvent. While the E_j values based on TATB methods[7] are known for these pure solvents,[8] those for the mixed solvents could be estimated at least approximately by assuming linear dependence with mole per cent cosolvent composition and hence accounted for, if required (vide footnote under Table 1). Moreover, in most of the electrochemical measurements viz. cyclic voltammetry, polarography etc. the most commonly used reference half-cell is the SCE(w) itself,[9] of course with

Table 1. Standard Electrode Potentials ($E°$) (in Volt) of I_3^-/I^-, I_2/I_3^-, and I_2/I^- Redox Couples Relative to ($E_{SCE(w)}+E_j$) as well as to $E^\circ_{SHE(w)}$ in Pure Solvents PC, ACN, DMF, and Their Binary Mixtures at 25 °C

Wt% cosolvent	$E^\circ_{I_3^-/I^-}$	$E^\circ_{I_2/I_3^-}$	$E^\circ_{I_2/I^-}$	$E^\circ_{I_3^-/I^-}$	$E^\circ_{I_2/I_3^-}$	$E^\circ_{I_2/I^-}$
	relative to ($E_{SCE(w)}+E_j$)			relative to $E^\circ_{SHE(w)}$		
			PC+DMF mixture			
0	0.056	0.741	0.284	0.428	1.114	0.656
25	0.075	0.685	0.278	(0.470)	(1.079)	(0.673)
50	0.080	0.680	0.280	(0.493)	(1.693)	(0.693)
75	0.085	0.680	0.283	(0.513)	(1.107)	(0.711)
100	0.091	0.701	0.295	0.532	1.144	0.736
			PC+ACN mixture			
25	0.052	0.686	0.263	(0.409)	(1.043)	(0.620)
50	0.040	0.655	0.245	(0.387)	(1.002)	(0.592)
75	0.027	0.635	0.230	(0.368)	(0.976)	(0.571)
100	0.017	0.617	0.217	0.354	0.954	0.554
			ACN+DMF mixture			
25	0.055	0.604	0.238	(0.408)	(0.957)	(0.591)
50	0.076	0.650	0.267	(0.450)	(1.024)	(0.641)
75	0.078	0.667	0.274	(0.480)	(1.069)	(0.676)

The values in parentheses for the mixed solvents were tentatively estimated by assuming linear variation of E_j (TATB) values with mole percent cosolvent compositions in the respective solvent systems, the E_j (TATB) values for the pure solvents being known (Ref. 8). This assumption is however based on the fact that E_j (TATB) values caused by aqueous sat. KCl and 0.1 M Et_4N Pic at hetero-solvent interfaces comprising H_2O and methanol, ethanol, ACN, PC, DMSO, and DMF fall on a single straight line. Moreover, a recent study[26] reveals that E_j (TATB) values for the same system at interfaces, between H_2O/H_2O+ACN mixtures bear a fairly good linear relationship with mole percent ACN.

appropriate measure for minimizing the contamination of solvents across aqueous-nonaqueous interface. Thus, even if these E_j values are present, these are not likely to pose any serious problem at least from the operational point of view.

In the present study the derived formation constant (K_f) of I_3^- will be of course free from any uncertainty as the values of E_j as well as $E_{SCE(w)}$ will be eliminated. Moreover, the prime discussion being related to K_f values the contention derived thereof will have little effect on the uncertainties in E_j values.

In order to gain insight into the solvent effect on the formation equilibrium of I_3^-,$\delta[\Delta G^\circ(I_3^-)]$ the transfer free energies $\Delta G^\circ_t(i)$ of the involved individual species (i) from a chosen reference solvent (R) to the solvent (S) concerned are useful[10,11] as

$$\begin{aligned}\delta[\Delta G^\circ(I_3^-)] &= 2.303\,RT\,[p_S K_f(I_3^-) - p_R K_f(I_3^-)] \\ &= \Delta G^\circ_t(I_3^-) - \Delta G^\circ_t(I^-) - \Delta G^\circ_t(I_2). \qquad (1)\end{aligned}$$

To facilitate the splitting, $\Delta G^\circ_t(I_2)$ values were determined by measuring the solubilities of I_2 in the solvents, as the $\Delta G^\circ_t(I^-)$ values based on the widely used tetraphenylarsonium tetraphenylborate (TATB)[11,12] reference electrolyte assumption:

$$\Delta G^\circ_t(Ph_4As^+) = \Delta G^\circ_t(Ph_4B^-) = 1/2\Delta G^\circ_t(Ph_4\,As\,BPh_4)$$

have been evaluated earlier[13] for these solvent systems.

Experimental

PC (Koch light) was first dried over activated Molecular Sieves 4A (E. Merck) for about a week and then fractionally distilled twice under reduced pressure.[8] ACN (AR, SD) and DMF (E. Merck) were purified by methods described earlier.[8] I_2 (E. Merck) was purified by sublimation. KI (GR. E. Merck) was pretreated by heating at 150 °C for a few hours and then dried in vacuum before use.

For measuring the solubilities of I_2 in different solvents, saturated solutions of I_2 were prepared by mild shaking of the suspension of I_2 and allowed to equilibriate at $25°\pm0.1$ °C. At 2—3 d intervals aliquots of each solution were withdrawn and I_2 concentration was estimated by titrating with a standard thiosulfate solution. The operations were repeated till two successive readings agreed within ±1%.

Stock solutions of I_2 and KI were made with the pretreated I_2 and KI in solvents of different compositions, namely 100, 75, 50, 25 wt% of each binary mixture. Solutions of cell A were prepared by adding appropriate amount of I_2 solution to known amount of standard KI solution so that $m_{I^-}=m_{I_3^-}=m$ and that of cell B by adding requisite amount of KI solution to a known amount of I_2 solution, so that $m_{I_2}=m_{I_3^-}=m$. And the solutions of different ionic strengths were prepared by appropriately diluting a suitable amount of stock mixture with the solvent.

The reference SCE(w) was of Fisher calomel reference electrode (model E 6A) with a porous ceramic junction and fitted within a jacket containing the cell solution. The jacket is connected to the rest of the cell solution through a G-2 gooch junction, similar to that used by Gritzner[14] and the upper end allowed the insertion of the reference electrode through a tightly fitted Teflon stopper. The flow rate through the ceramic junction of the Fisher calomel reference electrode for 8 cm head being 1—5 μl per hour, the uncertainties possible for contamination of the solvents hardly affected the observed potential beyond the experimental error±1 mV.

The cell was essentially similar to the conventional[15] three necked polarographic/cyclic voltammetric cell and fitted with three standard joint mouths, through which the Pt-wire electrode as well as the jacketed reference electrode were introduced, keeping the third one closed by a standard joint stopper. The cell containing the working solution was fitted with the Pt-wire electrode and the stoppered jacket with the cell solution inside it. The system was first thermally equilibriated at 25 °C. The Fisher calomel reference electrode was then introduced into the jacket by replacing the stopper. The emf values were measured with a Kiethley Electrometer (Model 616). The equilibrium potential was attained within 15—20 min of dipping the reference electrode. Some of the readings were also checked by using Elico (India) calomel reference electrode (Type ER-70) and found to agree within the experimental error with those obtained with the jacketed reference electrode.

Results

In the case of cell (A) the half-cell reaction is essentially

$$I_3^- + 2e^- \longrightarrow 3I^-, \tag{2}$$

and the observed emf, E_A of cell is given by

$$\begin{aligned} E_A = {} & [E^\circ_{I_3^-/I^-} - (E_{SCE(w)} + E_j)] - \frac{RT}{2F} \ln m^3_{I^-}/m_{I_3^-} \\ & - \frac{RT}{2F} \ln \gamma^3_{I^-}/\gamma_{I_3^-}, \end{aligned} \tag{3}$$

and the extrapolation function $E^{\circ\prime}_A$ by

$$\begin{aligned} E^{\circ\prime}_A &= E_A + \frac{2.3\,RT}{F} \log m - \frac{2.3\,RT}{F} S_f \mu^{1/2} \\ &= [E^\circ_{I_3^-/I^-} - (E_{SCE(w)} + E_j)] + b\mu, \end{aligned} \tag{4}$$

where $m_{I^-}=m_{I^-}=m$, by experimental conditions, γ_i is the activity coefficient of the species i and is being computed by the limiting form of Debye-Hückel equation,[16] S_f the Debye-Hückel constant, b the emperical parameter depending upon the solvent and temperature, and the other terms are having usual significance. The extrapolation function $E^{\circ\prime}$ on extrapolation to $\mu=0$ yielded $E^\circ_{I_3^-/I^-}$ relative to $[E_{SCE(w)}+E_j]$ which on elimination of the respective E_j values as well as $E_{SCE(w)}$, furnished $E^\circ_{I_3^-/I^-}$ values in the solvents relative to $E^\circ_{SHE(w)}$.

In the case of cell (B), the half-cell reaction is essentially

$$3I_2 + 2e^- \longrightarrow 2I_3^-, \tag{5}$$

and the observed emf, E_B of the cell is given by

$$\begin{aligned} E_B = {} & [E^\circ_{I_2/I_3^-} - (E_{SCE(w)} + E_j)] - \frac{RT}{2F} \ln m^2_{I_3^-}/m^3_{I_2} \\ & - \frac{RT}{2F} \ln \gamma^2_{I_3^-}/\gamma^3_{I_2}, \end{aligned} \tag{6}$$

and the extrapolation function $E^{\circ\prime}_B$ by

$$\begin{aligned} E^{\circ\prime}_B &= E_B - \frac{2.3\,RT}{F} \log m - \frac{2.3\,RT}{F} S_f \mu^{1/2} \\ &= [E^\circ_{I_2/I_3^-} - (E_{SCE(w)} + E_j)] + b\mu, \end{aligned} \tag{7}$$

where $m_{I_3^-}=m_{I_2}=m$ and other terms are having usual significance. As before, the extrapolation of the observed linear plots of $E^{\circ\prime}_B$ vs. μ to $\mu=0$ yielded $E^\circ_{I_2/I_3^-}$ relative to $[E_{SCE(w)}+E_j]$. The $E^\circ_{I_2/I_3^-}$ relative to $E^\circ_{SHE(w)}$ are

Table 2. Values of $\log K_f(I_3^-)$, $\Delta G^\circ_f(I_3^-)$, $-\log S$, and $\delta[\Delta G^\circ_f(I_3^-)$ in Pure Solvents PC, DMF, ACN, and Their Binary Mixtures at 25 °C

Wt% cosolvent	$\log K_f(I_3^-)$ (K_f in L mol^{-1})	$\Delta G^\circ_f(I_3^-)$ kJ mol^{-1}	$-\log S$ mol kg^{-1}	$\delta[\Delta G^\circ_f(I_3^-)]$ kJ mol^{-1}
		PC+DMF mixture		
0	7.78(7.8)[a]	−44.1	0.842	0.0
25	6.87	−39.2	−0.392	4.9
50	6.76	−38.6	−0.762	5.5
75	6.70	−38.2	−0.903	5.9
100	6.89(7.0)[b]	−39.3	—	4.8
		PC+ACN mixture		
25	7.15	−40.8	0.639	3.3
50	6.93	−39.6	0.572	4.5
75	6.85	−39.1	0.512	5.0
100	6.76(6.8)[b]	−38.6	0.445	5.5
		ACN+DMF mixture		
0	6.76	−38.6	0.445	0
25	6.18	−35.3	−0.310	3.3
50	6.46	−36.9	−0.636	1.7
75	6.63	−37.8	−0.868	0.8
100	6.89	−39.3	—	−0.7

Values in parentheses are taken from a) J. Courtot-Coupez et M. L'Her, Comptes rendus, 266 series C, 1968, p. 1286; b) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1979).

then obtained in a similar manner as described earlier.

The value of formation constant (K_f) of I_3^- in these solvents which are identical with the equilibrium constant values of the reaction

$$I_2 + I^- \rightleftharpoons I_3^-. \tag{8}$$

were then obtained by the relation

$$\log K_f(I_3^-) = \frac{2}{3}\cdot\frac{F}{2.3RT}[E^\circ_{I_2/I_3^-} - E^\circ_{I^-/I_3^-}]. \tag{9}$$

The standard electrode potential $E^\circ_{I_2/I^-}$ of the redox couple I_2/I^- in these solvents relative to $E^\circ_{SHE(w)}$ were then obtained by proper coupling of the actual standard electrode potentials $E^\circ_{I_3^-/I^-}$ and $E^\circ_{I_2/I_3^-}$ relative to $E^\circ_{SHE(w)}$ with the help of the relation

$$E^\circ_{I_2/I^-} = \frac{1}{3}[2E^\circ_{I_3^-/I^-} + E^\circ_{I_2/I_3^-}] \tag{10}$$

The E° values of the three redox couples thus obtained relative to $[E_{SCE(w)}+E_j]$ and also to $E^\circ_{SHE(w)}$ are listed in Table 1. The estimated uncertainties of the values are about ± 1 mV. In Table 2 are presented the values of $\log K_f$ (I_3^-), $\Delta G^\circ_f(I_3^-)$, and $\delta[\Delta G^\circ_f(I_3^-)]$.

The transfer free energies of I_2 from the chosen reference solvent R (R=PC in PC+DMF and PC+ACN mixtures and R=ACN in ACN+DMF mixtures) to the respective solvent mixtures were computed on mole fraction scale from the measured

Table 3. Various Free Energy Transfer Parameters for I^-, I_2, and I_3^- from PC to (PC+DMF) and (PC+ACN) Mixtures and from ACN to (ACN+DMF) Mixtures at 25 °C

Wt% consolvent	mol% consolvent	$\Delta G^\circ_{t,total}$ kJ lmol^{-1} $I^{-a)}$	$\Delta G^\circ_{t,total}$ I_2	$\Delta G^\circ_{t,total}$ I_3^-	$\Delta G^\circ_{t,cav}$ kJ mol^{-1} I^-	$\Delta G^\circ_{t,cav}$ I_2	$\Delta G^\circ_{t,cav}$ I_3^-	$\Delta G^\circ_{t,Born}$ kJ mol^{-1} I^-	$\Delta G^\circ_{t,Born}$ I_3^-
				PC→PC+DMF mixture					
0	0	0	0	0	0	0	0	0	0
25	0.3177	−1.4	−6.8	−3.1	1.2	1.6	3.8	0.3	0.1
50	0.5828	−2.7	−8.7	−5.4	2.3	3.1	7.2	1.0	0.5
75	0.8074	−3.0	−9.3	−5.7	3.3	4.6	10.9	2.1	1.0
100	1.0	−2.9	—	—	4.4	6.2	14.6	3.7	1.9
				PC→PC+ACN mixture					
25	0.4533	0.5	−0.37	4.2	1.0	1.3	2.8	0.7	0.4
50	0.7133	1.6	−0.16	7.4	1.5	1.9	3.9	1.5	0.8
75	0.8819	2.1	−0.02	9.0	1.7	2.1	4.3	2.4	1.2
100	1.0	3.5	0	11.3	1.8	2.3	4.5	3.9	2.0
				ACN→ACN+DMF mixture					
0	0	0	0	0	0	0	0	0	0
25	0.1577	−1.6	−4.6	−3.2	0.5	0.8	2.0	—	—
50	0.3596	−2.8	−6.8	−8.5	1.2	1.7	4.4	—	—
75	0.6275	−5.6	−8.5	−14.3	1.9	2.8	7.2	—	—
100	1.0	−6.0	—	—	2.6	3.9	10.1	—	—

Wt% consolvent	mol% consolvent	$\Delta G^\circ_{t,i-d}$ kJ mol^{-1} I^-	$\Delta G^\circ_{t,i-d}$ I_3^-	$\Delta G^\circ_{t,i-id}$ kJ mol^{-1} I^-	$\Delta G^\circ_{t,i-id}$ I_3^-	$\Delta G^\circ_{t,int}$ kJ mol^{-1} I^-	$\Delta G^\circ_{t,int}$ I_2	$\Delta G^\circ_{t,int}$ I_3^-
				PC→PC+DMF mixture				
0	0	0	0	0	0	0	0	0
25	0.3177	3.4	1.6	−2.1	−0.5	−4.2	−8.4	−8.1
50	0.5828	6.2	3.1	−3.9	−0.9	−8.2	−11.8	−15.2
75	0.8074	8.6	4.1	−5.4	−1.2	−11.7	−13.9	−20.5
100	1.0	10.6	5.1	−6.7	−1.5	−14.9	—	—
				PC→PC+ACN mixture				
25	0.4533	1.0	1.2	1.0	0.3	−3.2	−1.3	−0.5
50	0.7133	1.6	1.9	1.6	0.4	−4.6	−1.9	0.4
75	0.8819	2.0	2.4	1.9	0.5	−5.9	−2.3	0.6
100	1.0	2.3	2.7	2.2	0.6	−6.7	−2.6	1.5
				ACN→ACN+DMF mixture				
0	0	0	0	0	0	0	0	0
25	0.1577	1.3	0.5	−2.2	−0.6	−1.2	−5.4	−5.1
50	0.3596	3.0	1.1	−5.0	−1.4	−2.0	−8.5	−12.6
75	0.6275	5.3	1.9	−8.7	−2.5	−4.1	−11.3	−20.9
100	1.0	8.4	3.1	−13.8	−3.9	−3.2	—	—

a) These values are taken from Ref. 13.

solubilities (S) (mol kg^{-1} of solvent) of I_2 in the solvents by use of Eq. 11.

$$\Delta G_t^\circ(I_2) = RT \ln {}_{R}S/{}_{S}S + RT \ln {}_{R}y_{I_2}/{}_{S}y_{I_2} + RT \ln {}_{R}M/{}_{S}M = RT \ln {}_{R}S/{}_{S}S + RT \ln {}_{R}M/{}_{S}M \qquad (11)$$

where M=molar and mean molar mass of pure and mixed solvents respectively. The activity coefficients ${}_{R}y_{I_2}$ and ${}_{S}y_{I_2}$ being referred to the corresponding states of saturated solution in the respective solvents are likely to be more or less equal and hence the activity coefficient factor $RT\ln {}_{R}y_{I_2}/{}_{S}y_{I_2}$ is assumed to be zero. The $\log S$ values are presented in Table 2 and the $\Delta G_t^\circ(I_2)$ values in Table 3.

Moreover, recently Kundu and co-workers[13] have also determined the ΔG_t° values of I^- in these solvents [vide Table 3]. So utilizing these values of I^- and those of I_2 as obtained in the present study, the corresponding values of I_3^- were computed by use of the relation (1) and are presented in Table 3.

Discussion

Variation of $\delta[\Delta G_f^\circ(I_3^-)]$ with mole percent cosolvent from PC to PC+DMF and PC+ACN mixtures are shown in Figs. 1 and 2 respectively and those from ACN to ACN+DMF mixtures in Fig. 3. While $\delta[\Delta G_f^\circ(I_3^-)]$ values are found to increase sharply at first but slowly later in PC+ACN mixtures, those for PC+DMF mixtures pass through a broad maximum as the cosolvent concentration increases. Evidently, the formation of I_3^- is less favored in both the cases, as compared to that in pure PC, the extent, however, depends upon the cosolvent composition. On the other hand, $\delta[\Delta G_f^\circ(I_3^-)]$ from ACN to ACN+DMF mixtures (Fig. 3) passes through a slight maximum around 20 mole percent DMF and gradually acquires a negative trend at high DMF content. Thus on addition of DMF to the reference solvent ACN, the equilibrium (Eq. 8) is at first shifted towards left and at higher DMF composition it is shifted towards right compared to that in ACN. Now, $\delta[\Delta G_f^\circ(I_3^-)]$ being a composite parameter, more informative, and meaningful interpretation of these results awaits the dissection of this parameter into less composite individual quantities. For this purpose the solvent effect on the formation equilibrium (Eq. 8) can be expressed as in Eq. 1.

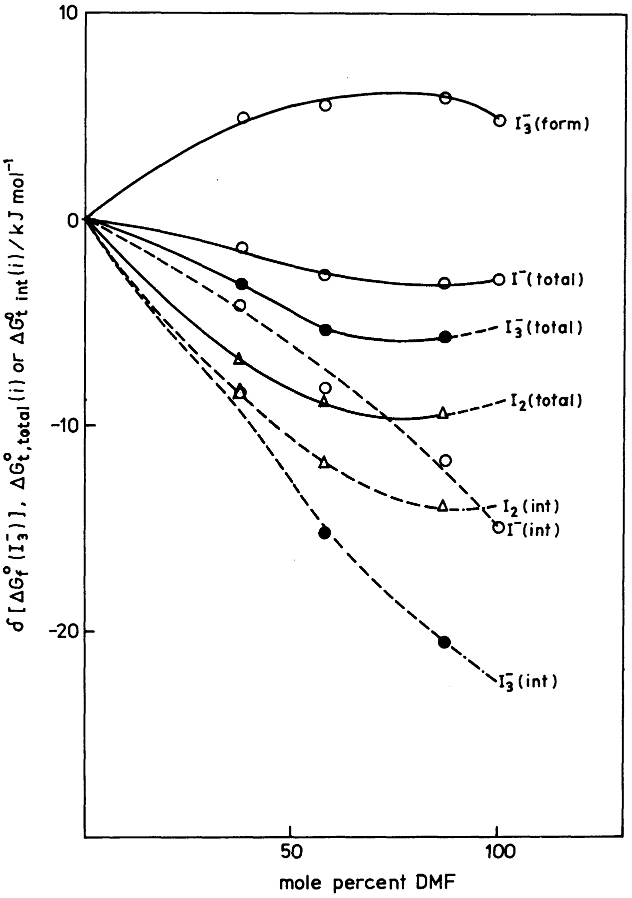


Fig. 1. Variations of $\delta[\Delta G_f^\circ(I_3^-)]$ and $\Delta G_t^\circ(i)$ [i=I^-, I_2, or I_3^-] total (solid lines) and int. (broken lines) with mole percent DMF in PC+DMF mixtures at 25 °C.

The $\Delta G_t^\circ(i)$-composition curves for PC+ACN and PC+DMF are shown in Figs. 1 and 2 respectively, whereas those from ACN to ACN+DMF mixtures in Fig. 3. Notably, all the three iodine species are stabilized with addition of DMF to either PC or ACN,

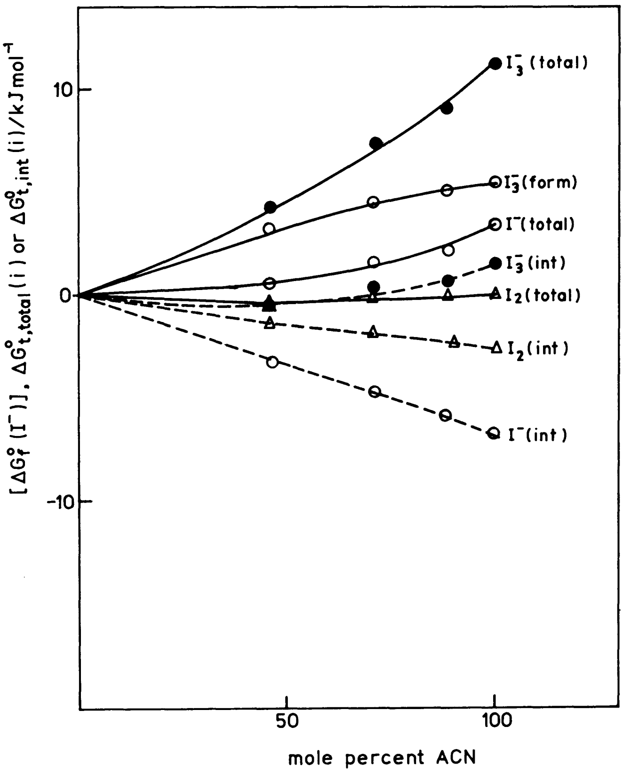


Fig. 2. Variations of $\delta[\Delta G_f^\circ(I_3^-)]$ and $\Delta G_t^\circ(i)$ [i=I^-, I_2, or I_3^-] total (solid lines) and int. (broken lines) with mole percent ACN in PC+ACN mixtures at 25°C.

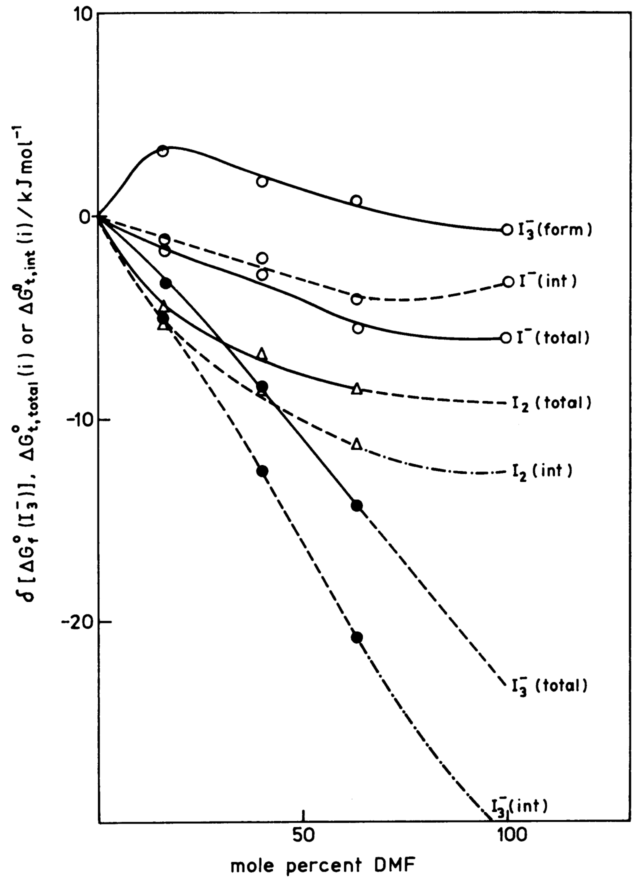


Fig. 3. Variations of $\delta[\Delta G^\circ_t(I_3^-)]$ and $\Delta G^\circ_t(i)$ [$i=I^-$, I_2, or I_3^-] total (solid lines) and int. (broken lines) with mole percent DMF in ACN+DMF mixtures at 25 °C.

the order of stabilization being $I_2>I_3^->I^-$ in PC+DMF mixtures (Fig. 1) and $I_3^->I_2>I^-$ in ACN+DMF mixtures (Fig. 3). On the other hand in PC+ACN mixtures (Fig. 2) as the ACN content increases, both I^- and I_3^- are increasingly destabilized in the order $I_3^->I^-$, and $\Delta G^\circ_t(I_2)$ passes nearly through the zero line. To rationalize the observed behavior a detailed analysis of the different forces and factors that are likely to be operative to different extents on these iodine species is in order. These are the electrostatic and nonelectrostatic contributions. The electrostatic part consists of a) Born-type electrostatic interaction,[17] corresponding transfer free energy term being designated by $\Delta G^\circ_{t,\mathrm{Born}}$, b) ion-dipole interaction[18] [$\Delta G^\circ_{t,i\text{-}d}$], c) ion-quadrupole interaction[18] [$\Delta G^\circ_{t,i\text{-}q}$], and d) ion-induced dipole interaction[18] [$\Delta G^\circ_{t,i\text{-}id}$]. All of these electrostatic contributions would be highest for I^- with highest charge density, followed by I_3^- but absent for I_2. The nonelectrostatic contributions are a) the well-known cavity effect[19] due to the formation of solvent-cage or highly ordered skin-phase inside which solute molecules are caged, b) dispersion or 'soft–soft' interaction[20] dictated by the size and polarizability of both the solute and solvent molecules. In a common solvent, the solvation behavior of the solute species may be expected to be guided by the softness of the solute itself, which is in the order of $I_3^->I_2>I^-$, c) specific complexation effects of charge transfer (CT)[21] or charge transfer to solvent (CTTS)-type.[22] I_2 with a low lying LUMO is known to be a good acceptor of charge and hence often forms stable CT-complex with donor solvents like PC, DMF, and ACN, whereas I^- and I_3^- are expected to form CTTS complexes of the type $(X^-)_{\mathrm{solv}}\rightarrow(X+e)_{\mathrm{solv}}$ in the order $I^->I_3^-$. These complexation effects are known[21] to depend on the first two nonelectrostatic factors mentioned above, apart from the electrostatic factors for the ions I^- and I_3^-.

It is apparent from the nature of $\Delta G^\circ_t(i)$-composition profiles that none of the above-mentioned factors shows a sole predominance over the others towards the observed behavior. Evidently the evaluation of the individual ΔG°_t terms related to these factors by suitable methods wherever possible may be, at least partially, rewarding in the final analysis.

The widely used simple Born-equation.[17]

$$\Delta G^\circ_{t,\mathrm{Born}}=\frac{1}{2}N_A(Z_i e)^2 r_i^{-1}(\varepsilon_S^{-1}-\varepsilon_R^{-1}) \qquad (12)$$

where N_A=Avogadro's number, $Z_i e$ is the charge, r_i=radius of the ion i and ε_S and ε_R the dielectric constant of the solvent and the reference solvent respectively, though somewhat approximate, may be used to evaluate $\Delta G^\circ_{t,\mathrm{Born}}$ values. These values in PC+DMF and PC+ACN mixtures are presented in Table 3. ACN and DMF being nearly isodielectric ($\varepsilon_{\mathrm{ACN}}=36.37$ and $\varepsilon_{\mathrm{DMF}}=36.71$)[16] $\Delta G^\circ_{t,\mathrm{Born}}$ values for the transfer from ACN to ACN+DMF mixtures are practically zero. The ion-dipole contribution $\Delta G^\circ_{t,i\text{-}d}$ may be expressed[18] as

$$\Delta G^\circ_{t,i\text{-}d}=-N_A q[\mu_S/\sigma_S^2-\mu_R/\sigma_R^2] \qquad (13)$$

where q=the charge on the ion, taken as that of electron as no appreciable shielding is presumably possible in the cases under consideration, σ=inter nuclear distance between ion and the solvent molecule, and μ=dipole moment of the solvent. The subscript 'S' stands for the solvent to which transfer is performed from the reference solvent 'R'. For mixed solvents however, $\Delta G^\circ_{t,i\text{-}d}$ values were obtained following Kim[18] by multiplying the quantity obtained above for pure solvent by X_{S_1} where,

$$X_{S_1}=X_S[\mu_S/\sigma_S^2)/(\mu_R/\sigma_R^2)] \qquad (14)$$

and X_s is the mole fraction of the cosolvent in the mixed solvent. The $\Delta G^\circ_{t,i\text{-}d}$ values thus obtained are also given in Table 3. It was not possible to estimate the magnitude of ion-quadrupole interactions due to the absence of quadrupole moment for these solvents though their significance could not be ruled out particularly for single ions. However, $\Delta G^\circ_{t,i\text{-}id}$ values were computed by using[18]

$$\Delta G^\circ_{t,i\text{-}id} = \frac{1}{2} N q^2 [(\alpha_S/\sigma_S^4) - (\alpha_R/\sigma_R^4)] \tag{15}$$

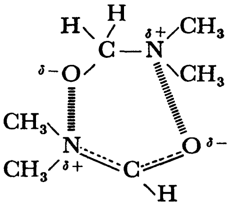
where α is the molecular polarizability of the respective solvents. And for the mixed solvents these values were obtained by multiplying the quantity obtained above for pure solvent[18] by X_{S_2} where,

$$X_{S_2} = X_S[(\alpha_S/\sigma_S^4)/(\alpha_R/\sigma_R^4)] \tag{16}$$

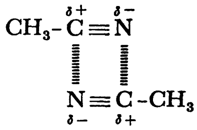
These $\Delta G^\circ_{t,i\text{-}id}$ values are also given in Table 3. Lastly, $\Delta G^\circ_{t,cav}$ values are computed following Triener's formulae[19] and are presented in the same table. The transfer free energies of the iodine species thus free from nearly all the electrostatic contributions barring ion-quadrupole interaction, and the solvent-cage effect as well, is likely to reveal the specific complexation effects along with 'soft–soft' interaction and is denoted by ΔG°_t(int) [vide Table 3]. Variations of ΔG°_t(int) with solvent compositions are depicted in Figs. 1—3 for the respective solvent systems.

From the variation of ΔG°_t(int) in Figs. 1 and 3 it is observed that all the three iodine species are increasingly stabilized with the addition of DMF to either PC or ACN, the order being $I_3^- > I_2 > I^-$ in both the cases. On the other hand, while I_3^- is slightly destabilized with addition of ACN to PC, the other two species are stabilized to some extent in the sequence $I^- > I_2$ (vide Fig. 2).

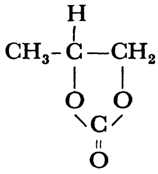
Now polarizability (α) of the pure solvents when computed from refractive index values[23] assuming monomeric solvent entities, are 4.41, 7.88, and 8.56×10^{-24} cm^3 for ACN, DMF and PC respectively. But the experimental α value of pure DMF is found to be abnormally high (11.02×10^{-24} cm^3).[24] Thus it was suggested[24] that DMF exists as dimers **A** in pure liquid, a part of which however may be converted to monomers in the mixed solvents. Similarly some dimeric species **B** are also found[25] to exist in ACN. No such evidence for dimerization is however found for PC. The dimeric entities obviously make DMF the softest among the three solvents. And α values for ACN may rise to some extent but not so as to exceed that of DMF. So on addition of DMF to either PC or ACN, all the iodine species will get stabilized in the order of their relative softness $I_3^- > I_2 > I^-$ as a result of dispersion interaction. The CT or CTTS complexation effect may also be present which will be in the order $I_2 > I^- \gg I_3^-$. The destabilization of I_3^- in PC+ACN mixtures (Fig. 2) is probably due to the difference in dispersion interaction resulting from the difference in effective polarizability between the two solvents concerned. But stabilization of I_2 and I^- though not to a greater extent, may be the result of CT or CTTS complexation or of ion-quadrupole interaction which we have failed to compute.



A



B



C

Notably, while discussions on ΔG°_t(int) are really meaningful in the cases where these values are rather large, as is the case of DMF admixtures, that for low ΔG°_t(int) values will be somewhat less meaningful because of the involved uncertainties in the computation of various ΔG°_t components, the combined effects of which may be as high as[18] ±5 kJ or more. Even then, in a complex situation, where various forces and interactions are at play, the dissection, though very tentative, helps elucidate at least a good qualitative picture of the interactions involved, as is observed in the present paper.

Thanks are due to CSIR, New Delhi for the award of a Research Associateship to J. D.

References

1) R. Jassinski, "High Energy Batteries," Plenum Press, New York (1967).

2) S. Bhattacharya, U. Mandal, J. Datta, K. Das, and K. K. Kundu, Proc. 3rd Int. Conf. on Electrochem. Sc. Tech., held at Madras, India during 10—14 Dec. 1984.

3) R. Memming, *Electrochim. Acta,* **25**, 77 (1980) and the relevant references therein.

4) K. Rajeswar, P. Singh, and J. Du Bow, *Electrochim. Acta,* **23**, 1117 (1978).

5) C. K. Mann "Electroanalytical Chemistry," A series of Advances, Vol. 3, ed by A. J. Bard, Marcell Dekker Inc., New York (1969).

6) L. M. Kuznetsova, V. P. Avdeev, and N. T. Nikurashina, *Russ. J. Phys. Chem.,* **59**, 721 (1985) Eng.

7) R. Alexander, E. C. I. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.,* **89**, 3703 (1967).

8) J. Datta, S. Bhattacharya, and K. K. Kundu, *Aust. J. Chem.,* **36**, 1779 (1983).

9) C. A. Mann and K. K. Barnes, "Electrochemical Reactions to Nonaqueous Systems," Marcel Dekker, New York (1970); J. N. Butler, *Adv. Electrochem. Eng.,* **7**, 77 (1970); J. N. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.,* **79**, 870, 1852 (1957); R. C. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.,* **82**, 3239, 3526 (1960); J. Datta, A. Bhattacharya, and K. K. Kundu, *J. Electroanalchem.,* under publication.

10) R. Alexander, A. J. Parker, J. A. Sharp, and W. E. Waghrone, *J. Am. Chem. Soc.,* **94**, 1148 (1972).

11) A. K. Das and K. K. Kundu, *J. Chem. Soc., Faraday Trans. 1.,* **70**, 1452 (1974); A. K. Das and K. K. Kundu, *J. Soln. Chem.,* **5**, 431 (1976); K. Bose, K. Das, and K. K. Kundu,

Electrochim. Acta, **26**, 479 (1981); A. Bhattacharya, A. K. Das, and K. K. Kundu, *Ind. J. Chem.*, **20A**, 347, 353 (1981).

12) O. Popovych, *Anal. Chem.*, **46**, 2009 (1974); *idem.*, *Crit. Rev. Anal. Chem.*, **1**, 73 (1970).

13) S. Bhattacharya and K. K. Kundu, *Ind. J. Chem.*, submitted.

14) G. Gritzner, *J. Electroanal. Chem.*, **144**, 259 (1983).

15) a) E. Geliadi, E. Kirowa-Eisner, and J. Pencier, "Interfacial Electrochemistry: An experimental Approach," Addison-Wesley Pub. Co. Inc., Massachusetts (1975); b) Jurgen Heinze, *Angew. Chem.*, **23**, 831 (1984) and relevant references therin.

16) A. K. Covington and T. Dickinson, "Physical chemistry of Organic Solvent Systems," Plenum Press, London (1973).

17) M. Born, *Z. Physik.*, **1**, 45 (1920).

18) J. I. Kim., A. Ceacal, H. J. Born, and E. A. Gomaa, *Zeit. fur Physik. Chem. Neue Folge, Bd.*, **110**, 5209 (1978); J. I. Kim, *J. Phys. Chem.*, **82**, 191 (1978).

19) C. Treiner, *Can. J. Chem.*, **55**, 682 (1977); A. Bhattacharya, J. Datta, K. Das, and K. K. Kundu, *Ind. J. Chem.*, **21A**, 9 (1982).

20) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

21) K. M. C. Davis "Molecular Association," ed by R. Forster, Academic Press, London (1975), Vol. 1.

22) M. C. R. Symons and M. J. Blandamer, "Hydrogen Bonded Solvent Systems," ed by A. K. Covington and P. Jones, Taylor and Francis, London (1968).

23) "Handbook of Chemistry and Physics," ed by R. C. Weast, The Chem. Rubber Co. U. S. A. (1971).

24) P. Rohdewald and M. Moldner, *J. Phys. Chem.*, **77**, 373 (1973).

25) E. L. Zukova, *Opt, Spectro.*, **4**, 750 (1958); A. M. Saum, *J. Polym. Sci.*, **42**, 57 (1960).

26) G. Senanayake, Ph. D. Thesis, Murdoch University, Australia, 1986, p. 246.