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Transfer Free Energies of Fluoride Ion in Aqueous Mixtures of Some Organic Solvents

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Standard free energies of transfer, ΔG_t°, of potassium fluoride (KF) from water to aqueous mixtures of dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), acetonitrile (ACN), 1,2-dimethoxyethane (DME), and 2-methoxyethanol (ME) have been determined at 25 °C from emf measurements performed on the double cell: Pb(Hg)–PbF_2/KF(m), solvent/K(Hg)/KF(m), water/PbF_2–Pb(Hg). ΔG_t° values of F^- were obtained from these values using the corresponding values of K^+, as obtained earlier by use of tetraphenylarsonium tetraphenylborate reference electrolyte assumption. In each solvent system $\Delta G_t^\circ(F^-)$ values are found to be increasingly positive with cosolvent composition reflecting the pronounced destabilization of F^- and their relative order : DME>DMSO≫DMF≫ACN≈ME conforms to what is expected from the relative 'aproticity' of the dipolar aprotic cosolvents and that induced in the protic ME by the possible intramolecular H-bonding. The observed larger destabilization of F^- compared to OH^- in ME–water system has been attributed to the H-bonding effect of the protic cosolvent ME and the reverse behaviour in DME–water and DMSO–water systems to the absence of such effect of these cosolvents. Moreover, tests of Feakins-type extrapolation for assigning individual ion contribution using ΔG_t°(KF) values along with those of other potassium halides, provided some important reflections on the inadequacy of such plots made without the data points of F^-.

It is well known that the dipolar aprotic solvents exert pronounced effects on the acidity functions[1] or rates of reactions involving nucleophiles. But the elucidation of the thermodynamic basis of such effects is yet far from complete. Recent years have therefore witnessed increased interests on this topic as are evidenced from various studies[2–7] on the transfer energetics of different ions based on the widely accepted tetraphenylarsonium tetraphenylborate (TATB) assumption[2–8] in various pure and mixed solvents, including some typical dipolar aprotic solvents.

Strikingly enough, although F^- is often used[9] in organic synthesis for proton abstraction reactions in dipolar aprotic solvents because of its possible pronounced "desolvation" in the solvents, transfer free energies of F^- have been reported, so far as we know, only in protic solvent D_2O.[10] So, in continuation of our previous studies[7] on transfer free energies, ΔG_t°, of different ions based on TATB assumption, we are now reporting ΔG_t° of F^- in aqueous mixtures of some dipolar aprotic cosolvents like dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), acetonitrile (ACM), and 1,2-dimethoxyethane (DME) and of a protic solvent like 2-methoxyethanol (ME). While the compositions studied in the first three cases are 20, 40, and 60 wt% cosolvents and for DME are 10, 30, and 50 wt%, those for ME are 10, 30, 50, and 70 wt % cosolvent.

For the purpose in view, we have obtained the standard free energies of transfer of potassium fluoride (KF) from water to these mixed solvents by determining the standard emf's (ΔE°) of the double cell I

$$\begin{aligned}&\mathrm{Pb(Hg)\text{-}PbF_2/KF(m),\ Solvent/K(Hg)/KF(m),}\\&\mathrm{Water/PbF_2\text{-}Pb(Hg)}\end{aligned} \qquad \text{(I)}$$

using a procedure similar to that used by Voice[10] in D_2O. These values helped evaluate $\Delta G_t^\circ(F^-)$ values as the values for K^+, based on TATB assumption, for each of the solvent systems are known from our previous studies.[7b–e] Moreover, it is well known that Feakins-type extrapolation[11] for assigning individual ion contributions to the ΔG_t° values being usually based on the adjacent data points of three larger sized halide ions, are susceptible to intrinsic limitations of long extrapolation. So, attempts have also been made to test if the inclusion of data point for F^- can improve the extrapolation procedure or not.

Experimental

The fluoride electrode consisting of a two-phase lead amalgam covered with insoluble lead(II) fluoride (PbF_2) was prepared in a manner essentially similar to that described by Voice.[10] The lead amalgam was prepared by electrolysing an aqueous solution (@ 10%) of $Pb(NO_3)_2$ (A.R., B.D.H.) using mercury (triply distilled) pool as cathode and Pt electrode as anode. The amalgam thus prepared was preserved in a sealed bottle under H_2 atmosphere. Before using it was repeatedly washed with a very dilute HNO_3 (AR., B.D.H.) to remove the ash or film, if any, and then by deionized CO_2-free water. The PbF_2 was prepared by mixing aqueous solution of $Pb(NO_3)_2$ and NaF (Merck, GR) with constant stirring. The white precipitate so obtained was filtered, washed repeatedly by magnetic stirring with CO_2- and O_2-free deionized water, and dried.

The base of the Pb(Hg)–PbF_2 electrode was a J-shaped glass tube with two limbs separated by a glass seal and connected electrically through a Pt-wire fused in the glass seal. The longer limb was fitted with a B-19 standard joint to hold the electrode in the cell vessel and the shorter limb at the other end serving as the electrode "cup" contained the electrode materials and was dipped in the cell solution. Before introducing the Pb-amalgam into cups, one eachside of the double cell, the Pb-amalgam was warmed in a closed vessel until it became mobile to attain its two phase character properly. The cooled two-phase amalgam was masked with a thick layer of PbF_2 crystals. It was observed that asymmetry potential was fairly high when a thin layer of PbF_2 was used. But it was considerably reduced if the layer of PbF_2 over Pb-amalgam become thick and was found to be practically within the range of experimental accuracy (±0.3 mV). So, the measurement of bias potential before each set of experiment was not necessary.

Preparation and preservation of K-amalgam as well as the cell design have been described elsewhere.[12] The solvents used are of the following grades: DME (Reidel), DMSO

(L.R., B.D.H.), DMF (L.R., B.D.H.), ACN (L.R., B.D.H.), and ME (E. Merck). The method of purification of DME,[7f)] DMSO,[13a)] DMF,[13b)] ACN,[13c)] and ME[7e)] were similar to those described earlier. Triply distilled and CO_2- and O_2-free water was used for the preparation of solvents as well as the cell solutions.

Anhydrous KF (Merck GR) was dried in a vacuum desiccator for about two weeks. Heating at high temperature was avoided due to the possibility of formation of insoluble material as reported earlier.[14)] Because of highly hygroscopic nature of KF, F^- concentrations of the stock solutions were checked by standard gravimetric method. Solutions of different materials were made by weight dilution of the stock solutions. General experimental procedure, including the emf measurements with the help of a Leeds Northrup K_4-potentiometer and a moving coil galvanometer (Cambridge Instrument) as a null-point detector, has been described.[12)]

The conditions for equilibrium were different for different solvents. Actually, in pure water as well as up to 50 wt% aqueous mixtures of ME the equilibrium was established within around 2 h and the constancy of emf readings to ±0.2 mV for 1 h was considered to be the criterion of equilibrium and for 70% ME–water solution the equilibrium was attained after about 4 h. In aqueous dipolar aprotic solvents, however, overnight ageing of the electrode in the respective solution was essential to get stable emf readings. The final emf readings were often checked by introducing separate fluoride electrodes or by measuring emf of the cell I taking pair of solutions having exactly same molality.

Results

The observed emf values (ΔE) of the double cell I for different molalities (m) of KF in different cosolvent–water mixtures are listed in Table 1. These were used to construct the following function.[12b)]:

$$\Delta E^{\circ\prime} = \Delta E - 2k[f_s(\mathrm{m}) - f_w\mathrm{m})] = \Delta E^{\circ}_{\mathrm{m}} - 2k\Delta bm, \quad (1)$$

where

$$f(\mathrm{m}) = -A_0B_0m^{1/2}(1+a_0B_0m^{1/2})^{-1} - \ln(1+0.002Mm). \quad (2)$$

The subscripts s and w denote the mixed solvent and water respectively, $k=RT/F$, M is the appropriate molecular weight of the solvent, a_0 is the ion-size parameter, A_0B_0 and B_0 are the Debye-Hückel constants in S.I. units as given by[13c)]

$$A_0B_0 = 1.824\times10^6 \ln 10d^{1/2}(\varepsilon_0T)^{-3/2}\,\mathrm{mol}^{-1/2}\,\mathrm{kg}^{1/2}, \quad (3)$$

$$B_0 = 50.29\times10^{10}\,d^{1/2}(\varepsilon_0T)^{-1/2}\,\mathrm{m}^{-1/2}\,\mathrm{mol}^{-1}\,\mathrm{kg}^{1/2}, \quad (4)$$

where ε_0 is the dielectric constant, d the density of the solvent, T is the temperature in absolute scale. Since alteration of a_0 values caused no significant change in $\Delta E^{\circ}_{\mathrm{m}}$ values, the values of $a_0=0$ was used in all the cases. In Eq. 1 Δb is the difference of b values in the solvent and water, which are empirical constants depending on the nature of solvent, temperature and on the assumed a_0-values.

$\Delta E^{\circ\prime}$ values were calculated by Eq. 1 and the plots of $\Delta E^{\circ\prime}$ *vs.* m were found to be linear in all the cases and when extrapolated to $m=0$ yielded the values of $\Delta E^{\circ}_{\mathrm{m}}$ as intercepts. The values of $\Delta E^{\circ}_{\mathrm{m}}$ in the respective solvents are given in Table 2 and are correct within ±0.3 mV.

Transfer free energies of *KF*, ΔG°_{t}(KF) from the standard state in water to the standard state in the respective solvents were obtained on mole fraction scale by Eq. 5

$$\Delta G^{\circ}_{t}(\mathrm{KF}) = F\Delta E^{\circ}_{\mathrm{m}} - 2RT\ln(M_s/M_w), \quad (5)$$

where M_w is the molecular weight of water. The ΔG°_{t}(KF) values are given in Table 2 and correct within ±0.03 kJ mol⁻¹.

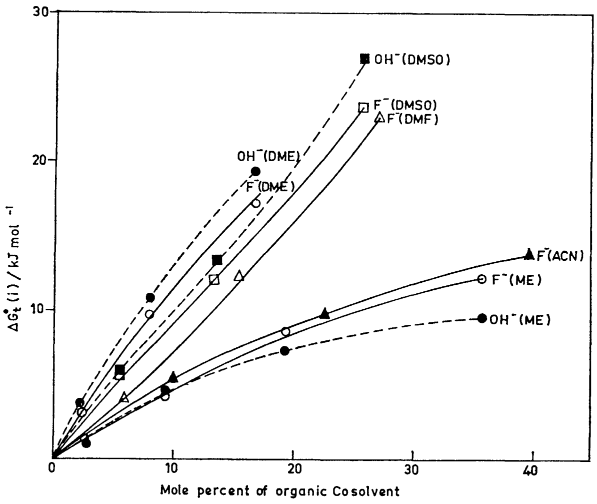


Fig. 1. Variation of $\Delta G^{\circ}_{t}(F^-)$ (solid line) and ΔG°_{t} (OH^-) (dotted line) in various aqueous-organic solvents.

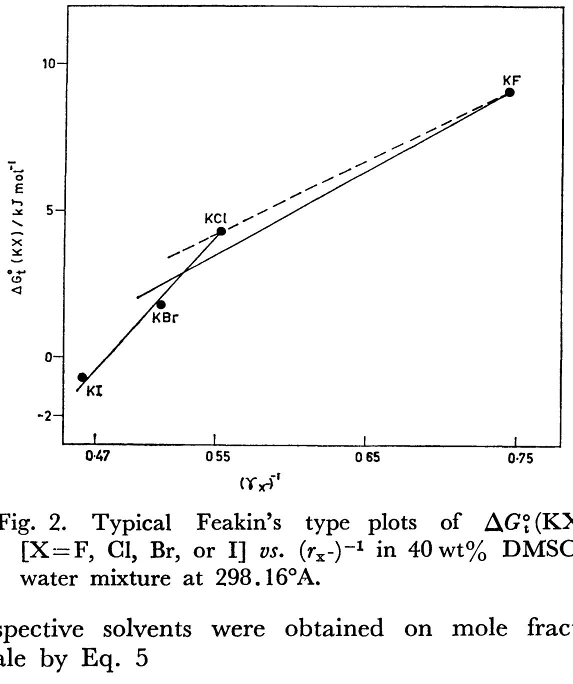


Fig. 2. Typical Feakin's type plots of ΔG°_{t}(KX) [X=F, Cl, Br, or I] *vs.* $(r_{x^-})^{-1}$ in 40 wt% DMSO-water mixture at 298.16°A.

The transfer free energies of F^-, $\Delta G^{\circ}_{t}(F^-)$, in all the solvents were evaluated from the respective ΔG°_{t} (KF) values using the corresponding ionic contributions of K^+, *i.e.* $\Delta G^{\circ}_{t}(K^+)$, taken from our earlier work based on TATB method[7b–f)] and are presented in Table 2. For the sake of comparison ΔG°_{t} (i) values of Cl^-, Br^-, and I^-[7b–f)] and OH^-[7b,g,h)] in some of the mixed solvents, are also presented in Table 2. Moreover, in order to draw important implications of the observed results, ΔG°_{t}-composition profiles of OH^- for DMSO–water,[7b)] DME–water[7h)] and ME–water[7g)] systems have also been shown in Fig. 1, where those of F^- for all the solvent systems are illustrated.

TABLE 1. EMF (ΔE) IN VOLT OF THE DOUBLE CELL (I) IN DIFFERENT AQUEOUS-ORGANIC SOLVENTS AT 25 °C

System	m/mol kg^{-1}	ΔE/V	m/mol kg^{-1}	ΔE/V	m/mol kg^{-1}	ΔE/V	m/mol kg^{-1}	ΔE/V
	20% DMSO		40% DMSO		60% DMSO			
DMSO-H_2O	0.0978	0.0434	0.0934	0.1053	0.0761	0.1970		
	0.0773	0.0447	0.0773	0.1062	0.0593	0.1974		
	0.0589	0.0456	0.0604	0.1086	0.0493	0.2013		
	0.0490	0.0473	0.0407	0.1106	0.0382	0.2024		
	0.0401	0.0478	0.0305	0.1124	0.0276	0.2032		
	0.0184	0.0495	0.0208	0.1134	0.0196	0.2019		
DMF-H_2O	0.0900	0.0459	0.0972	0.1084	0.0957	0.1956		
	0.0795	0.0464	0.0756	0.1090	0.0799	0.1958		
	0.0564	0.0468	0.0549	0.1100	0.0596	0.1977		
	0.0491	0.0474	0.0496	0.1104	0.0382	0.1991		
	0.0378	0.0476	0.0371	0.1110	0.0808	0.1990		
	0.0163	0.0478	0.0174	0.1115	0.0195	0.2002		
ACN-H_2O	0.1054	0.0390	0.0954	0.0758	0.0921	0.1231		
	0.0971	0.0404	0.0754	0.0791	0.0807	0.1245		
	0.0787	0.0410	0.0574	0.0810	0.0613	0.1275		
	0.0587	0.0414	0.0401	0.0824	0.0527	0.1291		
	0·0398	0.0424	0.0306	0.0830	0.0310	0.1325		
	0.0205	0.0430	0.0190	0.0842	0.0207	0.1358		
	10% DME		30% DME		50% DME			
DME-H_2O	0.1013	0.0253	0.1019	0.0824	0.1014	0.1403		
	0.0842	0.0256	0.0837	0.0830	0.0839	0.1418		
	0.0667	0.0266	0.0667	0.0834	0.0672	0.1452		
	0.0524	0.0270	0.0545	0.0840	0.0535	0.1472		
	0.0403	0.0276	0.0364	0.0846	0.0406	0.1480		
	0.0233	0.0285	0.0239	0.0851	0.0223	0.1474		
	10% ME		30% ME		50% ME		70% ME	
ME-H_2O	0.1218	0.0144	0.1231	0.5776	0.1259	0.1006	0.1100	0.1472
	0.1100	0.0151	0.1100	0.0583	0.1100	0.1019	0.0981	0.1484
	0.0953	0.0154	0.0982	0.0597	0.0977	0.1035	0.0870	0.1500
	0.0739	0.0180	0.0904	0.0600	0.0739	0.1038	0.0735	0.1504
	0.0546	0.0186	0.0754	0.0602	0.0594	0.1052	0.0552	0.1506
	0.0469	0.0215	0.0537	0.0606	0.0500	0.1059	0.0395	0.1510
	0.0301	0.0201	0.0350	0.0616	0.0381	0.1069	0.0303	0.1513
	0.0184	0.0213	0.0248	0.0618	0.0238	0.1071	0.0263	0.1515

Tests of Feakins-type extrapolation[11] by use of data points for all the potassium halides *i.e.* from the plots of ΔG_t°(KX) [X=F, Cl, Br, and I] *vs.* $(r_{x^-})^{-1}$ showed that no straight line was obtainable through the data points for all the four anions simultaneously in any of the solvents. Consequently, in each of the solvent systems, three values of $\Delta G_t^\circ(K^+)$ were evaluated by extrapolating the mean deviation lines through the data points for X=Cl, Br, I, and for X=F, Cl, Br, and the 'ideal' line through the data points for X=F and Cl. These value of K^+ are compared with the corresponding values obtained by TATB in Table 3. Figure 2 illustrates the plots of ΔG_t°(KX) against $(r_{x^-})^{-1}$ referred to above for 40 wt % DMSO–water system.

Discussion

As Table 2 shows, the transfer free energies of F^- from water to all the aqueous-organic solvents are increasingly positive indicating that the ion becomes increasingly destabilized as the proportion of the cosolvents increases. Thus, the observed destabilization of F^- from this thermodynamic consideration also corroborates the widely recognized phenomenon of increased "desolvation" of the anions caused by the addition of dipolar aprotic solvents. This in fact stems from the increasing loss of hydrogen-bonded stability of the anions[13c] and decreasing interactions with the mixed solvents resulting from the increased proportion of the cosolvents which either have little H-bond donating propensity or sterically shielded interacting positive charge centres. From Table 2 it is also evident that for any given solvent the extent of destabilization of halide ions (X^-) decreases with the increased size of the ions. Expectedly, this is the amalgamated effects of decreasing strength of H-bonded interactions with water on the one hand and increasing strength of "soft-soft"[14] and dispersion interactions[15] between the dipolar aprotic cosolvents and the increasing anion size on the other.

TABLE 2. VALUES OF STANDARD EMF'S $\Delta E°/V$ OF THE CELL (I) AND FREE ENERGIES OF TRANSFER ΔG_t° FOR KF AND OTHER SINGLE IONS FROM WATER TO AQUEOUS MIXTURES OF COSOLVENTS

System	Wt%	At 25°C			$\Delta G_t^\circ(\mathrm{i})/\mathrm{kJ\ mol^{-1}}$					
		Mole %	$\Delta E°/V$	$\Delta G_t^\circ(\mathrm{KF})/\mathrm{kJ}$	K^+	F^- [f]	Cl^-	Br^-	I^-	OH^-
$DMSO-H_2O$ [a]	20	5.46	0.0507	4.06	−1.6	5.7	3.3	2.1	0.8	5.9
	40	13.33	0.1144	9.22	−2.8	12.0	7.2	4.6	2.1	13.4
	60	25.70	0.2080	17.00	−6.6	23.6	14.3	10.5	5.0	27.0
$DMF-H_2O$ [b]	20	5.81	0.0479	3.81	−0.2	4.0	2.1	1.2	−0.2	—
	40	14.11	0.1109	8.92	−3.4	12.3	7.7	5.6	2.6	—
	60	27.00	0.1984	16.17	−6.6	22.8	15.9	11.0	4.9	—
$ACN-H_2O$ [c]	20	9.88	0.0429	3.55	−2.0	5.5	3.6	2.6	1.6	—
	40	22.63	0.0838	6.83	−2.6	9.4	6.4	4.7	2.0	—
	60	39.71	0.1453	11.99	−1.8	13.8	8.9	6.3	2.6	—
$DME-H_2O$ [d]	10	2.17	0.0308	2.56	−0.7	3.3	2.3	1.3	0.7	3.7 [g]
	30	7.89	0.0874	7.07	−2.6	9.7	6.9	4.8	2.8	10.9 [g]
	50	16.66	0.1448	11.44	−5.7	17.1	12.7	10.0	5.8	19.4 [g]
$ME-H_2O$ [e]	10	2.56	0.0218	1.71	0.6	1.2	0.5	0.01	−0.2	1.0 [h]
	30	9.21	0.0603	3.83	−0.3	4.2	3.1	2.0	0.6	4.6 [h]
	50	19.14	0.1019	7.45	−1.3	8.7	6.1	4.4	1.2	7.2 [h]
	70	35.59	0.01367	9.40	−2.8	12.2	9.6	7.2	2.5	9.6 [h]

a) Ref. 7b. b) Ref. 7c. c) Ref. 7d. d) Ref. 7g. e) Ref. 7e. f) Present study. g) Ref. 7h. h) Ref. 7g.

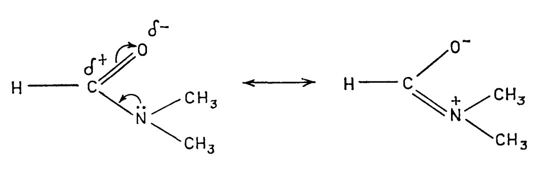
TABLE 3. VALUES OF $\Delta G_t^\circ(K^+)/\mathrm{kJ\ mol^{-1}}$ BASED ON EXTRAPOLATION AND R.E. METHODS

System	Wt%	Feakins-type extrapolation with data points of K-salts of			R.E.M. [a]
		(Cl^-, Br, I^-)	(F^-, Cl^-, Br^-)	(F^-, Cl^-)	
DMSO	20	−10.0	−6.1	−4.9	−1.6
	40	−27.2	−11.4	−8.8	−2.8
	60	−23.6	−20.0	−17.9	−6.6
DMF	20	−11.3	−4.1	−3.3	−0.2
	40	−26.6	−10.6	−8.4	−3.4
	60	−52.5	−17.0	−14.2	−6.6
ACN	20	−10.5	−4.4	−3.6	−2.0
	40	−22.1	−6.3	−4.5	−2.6
	60	−32.7	−8.6	−6.1	−1.8
DME	10	−8.1	−4.6	−3.3	−0.7
	30	−19.4	−6.3	−3.7	−2.6
	50	−29.1	−8.4	−5.4	−5.7
ME	10	−3.1	−1.4	−1.0	0.6
	30	−11.5	−1.7	−0.4	−0.3
	50	−21.2	−4.2	−2.5	−1.3
	70	−27.6	−4.0	−0.7	−2.8

a) R.E.M.: Reference electrolyte method on TATB assumption (Refs. 7b, c, d, e, f).

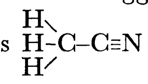
It is interesting to note, as $\Delta G_t^\circ(F^-)$-composition profiles for the solvents (Fig. 1) show, that at any composition the destabilizing capacity of the cosolvents decreases in the order DME>DMSO$\geqslant$DMF$\gg$ACN$\approx$ME. Significantly enough, similar order has also been observed[1] in the enhancement of H_- function by these dipolar aprotic cosolvents, excepting DME, when added to 0.1 m disodium 1,2-ethanediolate solution in 1,2-ethanediol, which of course chiefly reflects the relative destabilization of the 1,2-ethanediolate anion.

As this order reflects the effects of relative "aproticity" of the cosolvents resulting chiefly from the combined effects of relative magnitudes and approachability of the positive charge centres of the cosolvents, these results appear to suggest that the "aproticity" of DMF is slightly less than that of DMSO. Although it is difficult at this stage to differentiate the relative percentages of the two possible forms of DMF: A and B[17] one may wonder if the slightly less destabilization of F^- and other X^- ions relative to those in DMSO–water arises from the weak H-bonding effect of H-atom attached to the positively charged C atom of the form A. Alternatively, the formal positive charge on S atom in

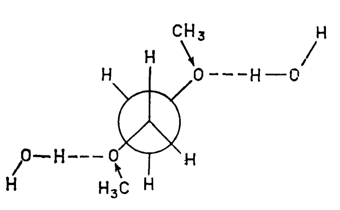


A B

DMSO molecule appears to be sterically more unapproachable than that in DMF molecule, affecting the ion-dipole interactions. Either of these effects will be of course more predominant in the cases of pure solvents than in the mixed solvents as has been observed.[2)]

On the other hand, the relatively less destabilization of F^- and other X^- ions in ACN–water mixtures compared to those in DMSO or DMF–water mixtures is indicative of the fact that "aproticity" of ACN is smaller than that of the other two dipolar aprotic solvents as is expected from its relatively smaller size, less shielded positive charge centre and also weak H-bonding propensity.[18)] Besides, this is also expected, if, as has been suggested by Kebarle *et al.*,[19)] X^- approaches  $H_3C{-}C{\equiv}N$ molecule along the C_3-axis of the latter and bonding occurs symmetrically through all 3H atoms. Since the overall strength of such H-bonds should increase as the X^- becomes larger and more accommodative,[20)] $\Delta G^\circ_t(F^-) \gg \Delta G^\circ_t(Cl^-) > \Delta G^\circ_t(Br^-) > \Delta G^\circ_t(I^-)$, as has been observed.

But strikingly enough, in spite of the fact that ME is a protic solvent with a relatively strong H-bonding centre compared to ACN, the observed comparable destabilization of F^- in these two solvent systems suggests that the inductive effect of CH_3^- group in ME possibly imparts "aproticity" comparable to that of ACN through intramolecular H-bonding[21)] or alternatively, makes the protic character of the hydroxylic H atom fairly less than that of pure water. On the other hand, the observed pronounced destabilization of F^- in DME–water system is indicative of the effect of pronounced "aproticity" of DME which results from the absence of any localized positive charge centres suitable for anion solvation. Also, the enhanced negative charge density on the O atoms of two methoxyl groups will also help destabilization of F^-. Apart from these, the DME–water complexes C in water-rich composition which are capable of anion solvation, are likely to be replaced by complexes of the type D in water deficient composition thus imparting decreasing acidity to the mixed solvents. Moreover, the inductive effect of two CH_3^- groups relayed through co-operative hydrogen bonded structures, diminishes the proticity of the hydrogen-bonded water in the water–cosolvent complexes. All these together are likely to result in the decreasing acidity of the mixed solvents.



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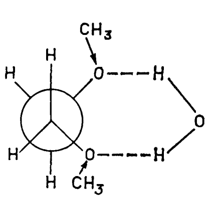

D

It is interesting to note that while in DMSO–water and DME–water mixtures the ΔG°_t-composition profiles for OH^- lie above the corresponding profiles for F^-, the reverse is true in ME–water system (Fig. 1). This larger destabilization of OH^- compared to F^- in DMSO–water and DME–water mixtures can be attributed to its pronounced stabilization in water because of its intrinsic protophilicity and natural propensity of fitting in water structures[13b)] and the relatively poor H-bond denating capacity of the aqueous DMSO and DME solutions. But the observed reverse behaviour of OH^- compared to F^- in ME–water system indicates that ME being itself a protic solvent stabilizes the protophilic OH^- through H-bonding more than F^-. Thus, the present results suggest that while the stability of OH^- is governed more by H-bond donating capacity of water and the protic cosolvents, that of F^- is dictated partly by H-bond donating capacity and partly by "aproticity" of the cosolvents, which is chiefly guided by the magnitudes and the location of formal positive charges of the cosolvent dipoles.

Tests of Feakins-type extrapolation using $\Delta G^\circ_t(KF)$ values along with the corresponding values of other potassium halides (Fig. 2) reveral that the "ideal plots' of $\Delta G^\circ_t(KX)$ *vs.* $(r_{x^-})^{-1}$ through the data points of KF and KCl yield single-ion contributions (Table 3) that are nearer to those obtained by TATB method.[7b–e)] But those obtained from the mean deviation lines drawn through the data points of KF, KCL, and KBr or of KCl, KBr, and KI are increasingly far off from the respective values by TATB method, indicating that the superimposed soft-soft interactions[20)] on Br^- and I^- make the latter plots more untenable.

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