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Activity Coefficients of Ferrocenium Iodide in Aqueous-Organic Salt Solutions

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Abstract—Potentiometric titration at 298.2 was used to measure electrode potentials and to estimate standard EMFs and unified activity coefficients for ferrocenium iodide in aqueous–acetone and aqueous–ethanol solutions of various salt compositions.

Ferrocene (Fc) does not form stable complexes in solutions. Unstable complexes with a number of organic and inorganic ligands are known, whose nature has not been reliably established. The ferrocene molecule is apolar, diamagnetic, highly symmetrical, and close in principal physicochemical characteristics to aromatic hydrocarbons [1]. Solvation of ferrocene and its derivatives, as well as interamolecular interactions play a decisive role in solution of these compounds in various solvents.

The oxidized form of ferrocene, the ferrocenium cation (Fc^+), like ferrocene, does not form stable complexes with acido ligands and resemble in its behavior in aqueous solutions alkali metal cations [2]. There is some information in the literature on the formation of unstable compounds of Fc^+ with anions [3, 4]. The structure of these associates has not been firmly established. The complex-formation constants of Fc^+ with the anions CH_3COO^- [5], Cl^- [6], $HCOO^-$ [7], ClO_4^- [8], and some other acido ligands were determined. Association of the ferrocenium cation with the perchlorate anion in aqueous-dioxane solvents with constant and varied ionic strengths was studied [9, 10], as well as the behavior of Fc^+ in aqueous–2-propanol solvents with varied salt compositions.

The formation of unstable complexes changes the activity coefficient of the «microform» in accordance with the composition of the salt background, and also changes the physicochemical properties of the mixed aqueous-organic solvents. At present, there are different theories of ionic interactions in aqueous-organic solvents (for instance, of Fuoss and Bjerrum and of Winstein) [11–15]. Common to all the theories is the use of the “rigid sphere” model [16], and their validity is commonly tested by finding linear dependences between experimental logarithms of association constants ($\log K_{as}$) and the reciprocals of the dielectric constants of solvents ($1/\varepsilon$). Attempts to analyze the equilibrium constants of complex formation in mixed aqueous-organic solvents with varied water contents were undertaken in [17, 18].

Belevantsev and Aseeva [19] reasoned that variations of the complex-formation constants with the contents of organic components in mixed solvents are more expedient and valid in terms of dependences like (1):

$$\log K^*_{c,i} = a_i - b_i \log [H_2O]^*. \tag{1}$$

Here $K^*_{c,i}$ is the association constant of the *i*th component on the molality scale; a_i is a constant; b_i is a value that differs from *i* and most commonly is an noninteger slope; $[H_2O]^*$ is the equilibrium concentration of water.

Further this equation was brought to the forms (2) and (3):

$$\log K^*_{c,i} = \log K^0_{c,i} - n \log [H_2O]^*, \tag{2}$$

$$\log K^*_{c,i} = \log K^0_{c,i} - b^*_i \log ([H_2O]^*/[H_2O]^0). \tag{3}$$

Here $K^0_{c,i}$ is the equilibrium constant of the *i*th component on the molality scale, extrapolated to the zero content of the organic component; n is an integer value and corresponds to the stoichiometric coefficient in the equilibrium equation for complex formation in mixed solvents; b^*_i is the fitting parameter of the linear regression; and $[H_2O]^0$ is the molar concentration of water (55.56 M).

In [20, 21], an approach was developed, according to which the variation in the stability of complex ions with varied composition of the aqueous-organic solvent is determined by three factors: decreasing concentration of water in the mixed solvent with increasing concentration of the organic solvent (dilution factor); change in the solvation contribution in the ΔG^0 (standard Gibbs energy) of complex formation (medium effect); and entering of organic molecules into the inner coordination sphere of the central ion.

The effect of the first and last factors can be accounted for via the corresponding equilibrium constants which can then be used to find experimental stability constants. Thus, at present there are different approaches to interpretation of experimental data for complex formation in mixed aqueous-organic solvents.

The aim of the present work was to study the effect of the composition of the salt background in aqueous and aqueous-organic solvents on the unified activity coefficients of ferrocenium iodide, determined by measuring the EMFs of galvanic cells without transport, to calculate on their basis of the complex-formation constants between the ferrocenium cation and the anions of the salt background, to examine different published approaches, and to interpret the dependence of K_c on the composition of the mixed solvent.

The uinified activity coefficients of ferrocenium iodide $u_{\pm}$(FcI) were determined in mixed aqueous-organic solvents with the molar fraction N_2 of the organic component, on the background of lithium, sodium, and potassium chlorides and bromides. The dependence of the coefficients on the concentration of salt background is characteristic of 1,1 electrolytes, i.e. the coefficients decrease in the concentration range where prevailing are electrostatic long-range interactions between ions and increase in the concentration range where prevailing are solvation and association of ions.

The unified activity coefficients $u_{\pm}$(FcI) determined on the background of lithium, sodium, and potassium iodides, as well as of lithium and sodium perchlorates monotonically decrease with increasing background concentration.

One of the possible reasons for the gap between experimental values and estimated by equations based on the Debye–Huckel theory is that this theory neglects interactions of ions with solvent and association of ions in solution. At equal concentrations of salts with the same anion, the salt with a smaller cation has a higher activity coefficient, which is explained by weakened hydration of larger alkali metal cations [22]. The same is true of the $u_{\pm}$(FcI) values determined on the background of alkali metal salts, which decrease in the order $Li^+ > Na^+ > K^+$. This result is nicely consistent with the notion of the effect of cations on the properties of solvents [23]. The mutual effect of cations and anions, that similarly affect water structure, reduces $u_{\pm}(Fc^+$ and $M^+)$. By contrast, cations and anions, that oppositely affect water structure (structuring anions and structure-destructuve Fc^+), increase these coefficients [23].

Thus, the dependence of the $u_{\pm}$(FcI) values (“microforms”) on the nature of the cations of the background salt, like the dependence of the mean ionic activity coefficients of alkali metal salts, agree well with the Frank–Henry theory, as well as with the theory of positive and negative ionic hydration [24].

Most of the background salt anions and the ferrocenium cation are classed with structure-destructive ions and similarly affect water structure. Therefore, $u_{\pm}$(FcI) should decrease in the order $Cl^- > Br^- > ClO_4^- > I^-$. However, the $u_{\pm}$(FcI) values determined on the background of alkali metal chlorides and bromides at background salt concentrations no higher that 1 M fit the respective values estimated in the framework of the second-order Debuy–Huckel theory, whereas the $u_{\pm}$(FcI) values determined on the background of alkali metal iodides and perchlorates monotonically decrease over the entire range of background salt concentrations. These results suggest that the mixed solvents studied the ferrocenium cation is associated with the iodide and perchlorate anions. According to [25], at concentrations up to 0.2 molar fraction, the organic component play the role of dilutor (dilution factor) and its molecules do not enter the inner sphere of the central ion. Thus, the process of formation of complex ion $[Fc^+L^-]$ can be represented by the following scheme:

$$Fc(H_2O)^+_{n\,\mathrm{solv}} + L^-_{\mathrm{solv}} = Fc(H_2O)^+_{n-x}L^-_{\mathrm{solv}} + xH_2O_{\mathrm{solv}}. \quad (4)$$

Here L = ClO_4 and I; $x = 1$ or 2.

The step complex-formation constants were calculated from the complexation degrees [26]. For the standard state we used the final-in-concentration solutions of the lithium, sodium, and potassium chloride background salts [27] [Eq. (5)]:

$$\phi = y_{\pm}(MCl)/y_{\pm}(ML) = K_1[L^-] + K_2[L^-]^2. \quad (5)$$

Here ϕ is the complexation degree; $y_{\pm}$ are the activity coefficients of ferrocenium iodide on different backgrounds; M = Li, Na, K; L = I, ClO_4; and K_1 and K_2 are the concentration formation constants of complexes ML and ML_2^-.

As follows from the constants calculated by Eq. (5), the complex formation of Fc^+ with I^- and ClO_4^- in aqueous-ethanol and aqueous-acetone solvents is described by two constants K_1 and K_2, and, therewith,

Table 1. Concentration formation constants K for complexes ML and ML_2^-

Parameter	K value for N_2 of acetone						K value for N_2 of ethanol					
	0	0.0101	0.0324	0.0578	0.0952	0.1406	0	0.0127	0.0404	0.0716	0.1169	0.1707
$K_1(LiClO_4)$	0.358	0.381	0.449	0.538	0.690	0.993	0.361	0.375	0.412	0.524	0.631	0.691
$K_2(LiClO_4)$	0.005	0.006	0.006	0.006	0.005	0.005	–	–	0.016	0.016	0.017	0.016
$K_1(NaClO_4)$	0.563	0.686	0.737	0.865	1.020	1.290	0.529	0.589	0.675	0.778	1.078	1.422
$K_2(NaClO_4)$	0.481	0.461	0.449	0.451	1.040	1.900	0.056	0.073	0.078	0.075	0.078	0.095
$K_1(LiI)$	0.941	1.060	1.320	1.970	3.110	5.440	0.985	1.030	1.140	2.060	3.840	5.560
$K_2(LiI)$	0.158	0.221	0.368	0.631	0.718	1.050	0.161	0.217	0.409	0.641	0.768	1.030
$K_1(NaI)$	1.190	1.210	1.770	2.220	3.280	5.440	1.0280	1.320	1.610	2.180	4.180	5.570
$K_2(NaI)$	0.362	0.508	0.511	0.598	1.080	1.520	0.322	0.489	0.527	0.611	1.070	1.510
$K_1(KI)$	3.640	3.750	3.910	4.630	6.890	9.030	3.780	4.040	4.180	4.710	6.570	9.070
$K_2(KI)$	0.328	0.341	0.368	0.371	0.379	0.488	0.321	0.320	0.341	0.347	0.341	0.376

the value of $F_1\{F_1 = (\phi - 1)/[L^-]\}$ increases from Li^+ to K^+, which agrees with the trend in variation of the mean ionic activity coefficients of ferrocenium iodide $u_\pm(FcI)$ with the cation of the salt background. Therewith, the K_2 value reflects the effect of variation in activity coefficients (secondary effect of nonideality of aqueous-organic salt solutions). Practically constant K_2 values are observed, independent of N_2, for $LiClO_4$ and KI in the mixed solvents studied for salts in which the cation and anion similarly affect water structure. At the same time, for LiI and NaI a certain dependence of K_2 on N_2 takes place. For all the salts K_1 varies with molar fraction of the organic component in the mixed solvent.

Thus, the above findings firmly establish the formation of complex compound $[Fc^+L^-]$ ($L = I^-$, ClO_4^-) in the systems studied. The K_1 and K_2 values are listed in Table 1.

The effect on K_1 and K_2 on the nature of the cation of the salt background is consistent with the effect of cations on $u_\pm(FcI)$, considered above.

In a general form, the dependence of the formation constant of $[Fc(C_5H_5)_2^+L^-]$ on the composition of the mixed solvent can be described by the correlation equation $\log K = \log K^0 + BX$ {K^0 is the constant extrapolated to (measured in) a solution with the zero fraction of the organic component ($N_2 = 0$); B is a value whose meaning is described in [19]; X is a parameter depending to the fraction N_2 of the organic component in the mixed solvent}. We examined principal approaches to interpreting the dependence of the complex-formation constant of the ferrocenium cation with the perchlorate and iodide anions on the composition of the mixed solvents. The correlations $\log K$–$1/\varepsilon$, $\log K$–N_2, and $\log K$–$\log [H_2O]^*$ were considered. The resulting parameters of the correlation equations are listed in Table 2.

Most of the equilibria studied exhibit a fair $\log K$–$1/\varepsilon$ correlation.

The b value decreases in the order $Li^+ > Na^+ > K^+$, which is consistent with the Bjerrum's concept of ion pair formation in nonequeous solutions [12].

The dependence of the logarithm of the formation constant of $[Fc^+L^-]$ on the equilibrium concentration of water in mixed solvents ($\log [H_2O]^*$) or on $\log ([H_2O]^*/[H_2O]^0)$ call for finding fitting parameters to obtain constant logarithms of the formation constants of monoligand complexes [FcL], extrapolared to the zero contents of the organic components ($\log K^\phi$), i.e. a value independent of the composition of the mixed solvent. Such approach is probably useful when one deals with complicated equilibria and is basically of practical rather than of theoretical value.

As seen from Table 2, the b values span the range from 2 to 5. The number of water molecules in the material balance of reaction (4), estimated from the $b_i - i$ relation [19], is 1–4. However, if the association of the ferrocenium cation with the perchlorate anion involves formation of a complex with $x = 1$, then the complex formation of Fc^+ with I^- (Table 2) may involve formation of two complexes: $[Fc^+I^-]$ and $[Fc^+I_2]^-$. Such ionic interaction may result in liberation from the solvation shells of the ions of up to 3 water molecules. Evidence for this assumption comes from Table 3 which lists the formation constants of $[Fc^+L^-]$, corrected for the packing term ($\log([H_2O]^*)$) in the material balance of reaction (4).

The account for the packing term in the material balance equation gave best results for the complex

Table 2. Parameters of correlation equations for aqueous-organic solvents

Parameter[a]	Value of the parameter for background electrolyte in the water–acetone system				
	$LiClO_4$	$NaClO_4$	LiI	NaI	KI
	$\log K_1$–N_2				
b	3.096 ± 0.282	2.543 ± 0.196	5.452 ± 0.446	4.945 ± 0.423	4.247 ± 0.422
$\log K_1^0/N_{2\to 0}$	–0.437 ± 0.021	–0.239 ± 0.016	–0.018 ± 0.016	–0.054 ± 0.034	0.545 ± 0.035
r	0.986	0.992	0.989	0.988	0.984
	$\log K_1$–$1/\varepsilon$				
b–10^{-2}	3.056 ± 0.028	2.509 ± 0.099	5.342 ± 0.107	4.737 ± 0.128	4.092 ± 0.106
$-\log K_1^0/1/\varepsilon \to 0$	4.266 ± 0.036	3.382 ± 0.129	6.706 ± 0.140	5.865 ± 0.168	4.570 ± 0.138
r	0.999	0.997	0.999	0.998	0.999
	$\log K_1$–$\log [H_2O]^*$				
$-b$	1.991 ± 0.133	1.645 ± 0.086	3.488 ± 0.207	3.089 ± 0.206	2.660 ± 0.206
$\log K_1^0/\log [H_2O]^*_{\to 0}$	3.027 ± 0.221	2.621 ± 0.142	6.054 ± 0.343	5.444 ± 0.341	5.186 ± 0.342
$-r$	0.991	0.995	0.993	0.991	0.988
	$\log K_1$–$\log [H_2O]^0/\log [H_2O]^*$				
b	1.991 ± 0.133	1.645 ± 0.086	3.488 ± 0.207	3.083 ± 0.138	2.660 ± 0.206
$-\log K_1^0/(\log [H_2O]^0/\log [H_2O]^*_{\to 0})$	–0.446 ± 0.016	–0.248 ± 0.010	–0.032 ± 0.025	0.047 ± 0.017	0.543 ± 0.025
r	0.991	0.995	0.993	0.996	0.988
	$\log K_1$–N_2				
b	2.170 ± 0.115	2.484 ± 0.099	5.396 ± 0.114	5.263 ± 0.314	2.176 ± 0.349
$\log K_1^0/N_{2\to 0}$	–0.455 ± 0.011	–0.270 ± 0.010	–0.053 ± 0.013	0.009 ± 0.031	0.541 ± 0.035
r	0.995	0.997	0.999	0.994	0.960
	$\log K_1$–$1/\varepsilon$				
b	2.192 ± 0.110	2.581 ± 0.092	5.415 ± 0.134	5.126 ± 0.297	2.142 ± 0.264
$\log K_1^0/1/\varepsilon \to 0$	–3.185 ± 0.144	–3.493 ± 0.121	–6.793 ± 0.176	–6.351 ± 0.390	–2.119 ± 0.348
r	0.995	0.997	0.999	0.993	0.971
	$\log K_1$–$\log [H_2O]^*$				
$-b$	1.637 ± 0.077	1.926 ± 0.067	4.036 ± 0.145	3.800 ± 0.312	1.576 ± 0.237
$\log K_1^0/\log [H_2O]^*_{\to 0}$	2.402 ± 0.128	3.085 ± 0.110	6.999 ± 0.239	6.671 ± 0.518	3.303 ± 0.392
$-r$	0.996	0.997	0.997	0.987	0.958
	$\log K_1$–$\log [H_2O]^0/\log [H_2O]^*$				
b	1.636 ± 0.077	1.926 ± 0.067	4.036 ± 0.145	3.800 ± 0.313	1.576 ± 0.237
$-\log K_1^0/(\log [H_2O]^0/\log [H_2O]^*_{\to 0})$	0.453 ± 0.009	0.276 ± 0.008	0.043 ± 0.017	–0.041 ± 0.037	–0.552 ± 0.028
r	0.996	0.998	0.997	0.987	0.958

[a] (r) Correlation coefficient of linear regression, and (b) slope of the linear dependence $\log K$–$1/\varepsilon$, $\log K$–N_2, or $\log K$–$\log [H_2O]^*$.

formation between the ferrocenium cation with the perchlorate anion in the mixed aqueous-organic solvents. At the same time, for the iodide complexes $[Fc^+I^-]$ on the background of potassium iodide, too, a fair $\log K^{\phi}$–N_2 correlation is observed.

Thus, the $\log K$–$1/\varepsilon$ dependence is best founded among the correlations considered. This suggests formation in the mixed aqueous-organic solvents studied of associates like ion pairs which, according to the commonly accepted classification, are unstable complex compounds. Some confusion arising when weak interactions in solution are classed as one or another type of ionic complex formation is also as-

Table 3. Formation constants of $[Fc^+L^-]$ corrected for the packing term

Electrolyte	log $[H_2O]$					
	1.745	1.727	1.689	1.648	1.590	1.523
	Acetone					
$LiClO_4$	1.299	1.308	1.341	1.437	1.429	1.400
$NaClO_4$	1.495	1.507	1.516	1.585	1.599	1.630
LiI	1.718	1.752	1.809	1.942	2.083	2.258
NaI	1.821	1.810	1.879	2.058	2.106	2.259
KI	2.306	2.301	2.339	2.508	2.530	2.630
	Ethanol					
$LiClO_4$	1.303	1.301	1.304	1.367	1.390	1.363
$NaClO_4$	1.468	1.497	1.518	1.539	1.623	1.676
LiI	1.738	1.739	1.870	1.962	2.174	2.392
NaI	1.852	1.848	1.896	1.987	2.211	2.455
KI	2.323	2.333	2.310	2.321	2.336	2.478

sociated with the fact that electrostatic interactions, unlike bond formation, have no effect on the electronic structure of ions, and this makes the resulting experimental data difficult to interpret.

Therefore, in our opinion, the state of the ferrocenium ion in mixed aqueous-acetone and aqueous-ethanol solvents of various salt composition (in our case, halides and perchlorates of certain alkali metals) can be described in terms of either the unified activity coefficients of ferrocenium iodide or interactions of the ferrocenium cation with the iodide and perchlorate ions at appropriate choice of the standard state.

EXPERIMENTAL

The $u_{\pm}$(FcI) values [27] were determined at 298.2 K by potentiometric titration using galvanic cell without transport.

$$\mathrm{Pt(Fc)/FcI}(5\times10^{-3},\ \mathrm{M}),\ (CH_3)_2CO(C_2H_5OH)\ (N_2);$$
$$H_2O(1-N_2);\ \mathrm{ML}\ (c,\ \mathrm{M})/\mathrm{AgI,\ Ag}.$$

Here M = Li, Na, K; L = Cl, Br, I, ClO_4; N_2 is the molar fraction of acetone or ethanol; and c is the concentration of background salt, M.

The electrode reversible with respect to the ferocenium cation was prepared by the known procedure [28]. For the iodide-selective electrode was used an EM-I-01 electrode. The galvanic system met the maintained for constant EMF in all the systems to an accuracy of ±1.0 mV. The analytical concentration of ferrocenium iodide in the electrolytic cell was measured from 5×10^{-3} to 5×10^{-2} M, which ensured stable operation of the galvanic element. The molar fraction of acetone in mixed solvent was measured from $N_2 = 0$ (water) to $N_2 = 0.1406$, and the molar fraction of ethanol, from 0 to 0.1707. The concentration of background salt was measured from 0.5 to 6.0 M, depending on its solubility in mixed solvent.

Potentiometric titration gave constant formal electrode potentials E^0_{f}. The slope of the E(mV)–log [FcI] dependence fitted the theoretical value over the entire ranges of N_2 and c, which gave evidence for the reversibility of the galvanic element in the systems studied.

The standard EMFs (E^0) were obtained by the least-squares method. The unified activity coefficients of ferrocenium iodide were calculated by the equation in [29].

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