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REACTION ENTROPY FOR THE ELECTROREDUCTION OF 2-PHENYL-3-ARYLIMINO-3*H*-INDOLES IN VARIOUS APROTIC SOLVENTS

G. MARROSU, F. RODANTE * and A. TRAZZA

Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia, Università "La Sapienza", Via del Castro Laurenziano 7, 00161 Roma (Italy)

L. GRECI

Dipartimento di Scienze dei Materiali e della Terra, Facoltà di Ingegneria, Università di Ancona, Via delle Brecce Bianche, 60131 Ancona (Italy)

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ABSTRACT

The entropy and free energy of the one-electron reduction of some 2-phenyl-3-arylimino-3H-indole derivatives in dimethylformamide, acetonitrile and dimethylsulphoxide have been determined using a non-isothermal cell arrangement. The observed correlation between the values of $\Delta S_r^{\ominus}$ and the solvent acceptor number reveals that the electroreduction process is affected principally by the degree of structuring of the solvent, while the contribution of the substituents arising from the spin density of radical anions, as evaluated by the Hückel–McLachlan molecular orbital method, is negligible.

INTRODUCTION

Variations in the solvent medium are generally expected to alter the thermodynamics and kinetics of electron transfer reactions. The origins of observed solvent effects are frequently manifold, arising out of alterations in the chemical nature of the reacting species as well as in the reactant–solvent interactions in both the ground reactant and transition states [1–3]. This diversity of possible influences can severely hamper a fundamental understanding of the observed effects in terms of electrochemical processes. For these reasons, much attention has been given to thermodynamic studies of simple electron transfer processes at electrodes, and in particular, to reversible one-electron reductions of organic molecules.

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* Author to whom correspondence should be addressed.

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The number of solvent effects can be further diminished by studying the reduction process from a neutral molecule to a stable radical anion. Particular attention has been given to the study of molecules including heteroatoms, as in the case of quinones [3], phenazines [4], and nitromesitilene [5], by virtue of the well defined reaction centre for electron change.

Radical anions possessing localized charge interact strongly with molecules of aprotic solvents, and for a given radical anion, the various interactions with different solvents can be related to an acidic property of solvents of i.e. acceptor number (AN).

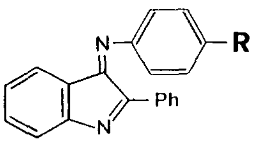
Entropy is the most commonly used thermodynamic property for this purpose, since its variation $\Delta S_r^{\ominus} = S_{red}^{\ominus} - S_{ox}^{\ominus}$ is related to energy solvation of radical anions and molecules. The use of a non-isothermal cell offers the possibility of absolute estimation of entropy difference [6–17] by the relation $\Delta S_r^{\ominus} = nF\,dE_f^{\ominus}/dT$, where F denotes the Faraday constant, n the number of electrons transferred, and $dE_f^{\ominus}/dT$ the temperature variation in the formal potentials in various solvents.

The thermodynamic potential $E_f^{\ominus}$ depends mainly on interactions with the solvent, for which two models of "solvent effects" can be considered. The first ascribes the solvation of ions to the type of solvent as well as to the solute properties; the second is concerned with specific short-range interactions described by empirical solvent scales [18,19]. In the latest view, an empirical correlation analysis can be applied to relate the thermodynamic potential (or better, the entropy variation) to specific parameters of the solvent (e.g. Lewis acidity).

The aim of the present work is to study solvent effects upon the thermodynamics of electroreduction of 2-phenyl-3-arylimino-3*H*-indoles **1a**–**1f** in aprotic media.

In a previous paper [20] we reported that the reduction of indoles **1a**–**1f** in dimethylformamide takes place, at a mercury dropping electrode, in two one-electron steps. In every case, the first step is reversible and produces a species (radical anion) which is stable during the time of the voltammetric measurements.

In the present paper we report the $\Delta S_r^{\ominus}$ values related to the first one-electron reduction of **1a**–**1f** in dimethylformamide, acetonitrile and dimethylsulphoxide obtained using a non-isothermal cell in the range 0–60 °C. Free energy values for the same process at 20 °C are also evaluated.



a: R = H
b: R = Me
c: R = OMe
d: R = NMe_2
e: R = Cl
f: R = Br

2-Phenyl-3-arylimino-3*H*-indoles **1a**–**1f**

EXPERIMENTAL

2-Phenyl-3-arylimino-3H-indoles **1a–1f** were prepared according to reported methods [21].

Dimethylformamide (DMF, Merck Uvasol) and dimethylsulphoxide (DMSO, Merck Uvasol) were twice distilled under reduced pressure after drying first over 4A molecular sieves and then over neutral alumina. Acetonitrile (ACN, Merck Uvasol) was purified by distillation over CaH_2, P_2O_5 and then CaH_2 again. Tetraethylammonium perchlorate (Et_4NClO_4, Carlo Erba, RS grade) was vacuum dried at 60 °C for 4 days and used as supporting electrolyte at 0.1 M concentration.

The voltammetric measurements were performed using an AMEL 471 multipolarograph in a conventional three-electrode cell maintained at varied temperature (0–60 °C), controlled with an accuracy of ± 0.1 °C. A semi-stationary long-lasting sessile-drop mercury electrode [22] was used as the working electrode. The other electrodes were: a platinum wire as a counter electrode and a reference electrode Hg/Hg_2Cl_2, NaCl(satd. aq.) | agar–NaCl(aq.) | agar (1.5% w/v) DMF (or DMSO)–water (40% v/v) Et_4NClO_4 (satd.) | methylcellulose (5% w/v) DMF (or DMSO)–Et_4NClO_4 (satd.) | sintered-glass disk [20], or a silver wire dipped in a 0.1 M $AgClO_4$–ACN | sintered-glass disk | 0.1 M Et_4NClO_4–ACN | sintered-glass disk, maintained at a constant temperature (20 °C). Solutions were deoxygenated by means of a stream of pure argon, which was maintained above the solutions during the voltammetric measurements.

According to Yee et al. [16], the reaction entropy $\Delta S_r^{\ominus}$ for the one-electron reversible process under consideration can be evaluated from measurements of the temperature coefficient $\mathrm{d}E_f^{\ominus}/\mathrm{d}T$ using a non-isothermal cell, since the contributions of the temperature gradients across the liquid junction and of the mercury in the working electrode can be neglected. Moreover, we assume that the formal potential $E_f^{\ominus}$ is equal to the corresponding half-wave potential $E_{1/2}$, since the ratio value diffusion coefficient of (**1a–1f**)/diffusion coefficient of $(\mathbf{1a{-}1f})^{\dot{-}}$ is close to unity.

The half-wave potentials for the first one-electron reduction of compounds **1a–1f** at about 10^{-3} M concentration were determined from polarographic curves recorded by sampled DC polarography (dropping time 2 s, sweep rate 5 mV s^{-1}). The cyclic voltammetric curves of the compounds in different solvents, recorded with a potential scan limited to the first reduction step, show a clear reversible, diffusion-controlled, one-electron cathodic–anodic system, in which the reduction product (radical anion) is stable even at moderate scan rates (0.05–0.1 V s^{-1}). All reported half-wave potentials are referred to the ferrocinium–ferrocene (Fc^+/Fc) reduction potential, as suggested by Strehlow [23].

McLachlan spin density distributions were calculated by a computer program with the following values: $h_N(N=C) = 0.5$; $K_{CN} = 1.0$; $K_{CN}(N_{10}$–

$C_{11}) = 0.8$; $K_{CC} = 1.0$; $K_{CC}(C_2–C_{17}) = 0.8$; $K_{CC}(C–Me) = 0.7$; $h_{Me} = 2.0$; $K_{CO}(C_{14}–O_{23}) = 0.8$; $h_{\ddot{O}Me} = 2.0$; $K_{CCl} = 0.4$, $h_{Cl} = 2.0$; $K_{CBr} = 0.3$; $h_{Br} = 1.5$; $K_{CNMe_2} = 0.8$; $h_{\ddot{N}}(NMe_2) = 1.5$; $\lambda = 1.2$.

RESULTS AND DISCUSSION

Features of the solvents considered are reported in Table 1.

ACN and DMSO have similar acceptor number values but very different degrees of structuring in particular, ACN is "unstructured", and DMSO is "very structured". (DMF shows an intermediate degree of structuring.) The solvent dipolar moments, which greatly influence radical anions solvation and therefore entropy values, are very similar for all three solvents. Therefore, the parameters which contribute to differentiation of the solvent effects in the electroreduction of 2-phenyl-3-arylimino-3*H*-indoles **1a–1f** are:

(i) the different dielectric constant value of DMSO;

(ii) the different AN value of DMF;

(iii) the different degree of structuring of ACN.

The chosen solvents can be used to emphasize the varying influence of the substituent (R) upon the electron distribution of the corresponding ion radical skeleton. The electric charge distribution of the solute is tightly linked to solute–solvent interactions, which in turn are a function of the different acidity (AN) and the different degree of structuring of the solvents. Such studies are usually carried out using entropy quantity, the variation of which, $\Delta S_r^{\ominus}$, owing to solute–solvent interactions, can be considered as a sum of two terms:

(i) a structure-making effect describing an entropy decrease caused by ordering of the solvent dipoles around the radical ions;

(ii) a structure-breaking effect which accounts for an entropy increase from the disordering of structured solvents.

The solvent effects on the electroreduction of the indole derivatives **1a–1f** can be examined from the following points of view:

(a) behaviour of the same derivative as a function of solvent variation;

(b) behaviour of different derivatives in the same solvent.

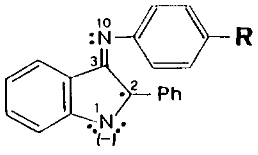
TABLE 1

Solvent properties: dielectric permittivity (*D*) [24], acceptor number (AN) [19], and dipole moment (*m*) [25]

	D	AN	*m* (Debye)
DMF	36.71	16.0	3.82
ACN	37.00	18.9	3.92
DMSO	45.00	19.3	3.96

TABLE 2

McLachlan spin density distributions

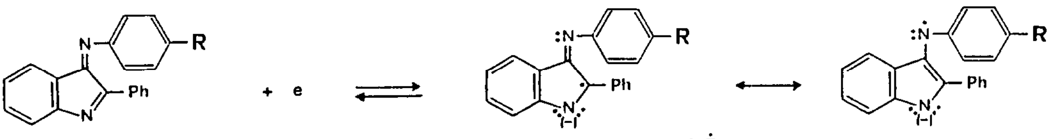


(**1a–1f**)$^{\dot{-}}$.

Compound	N_1	C_2	C_3	N_{10}	Σq^0 [a]
(a) R ≡ H	0.0973	0.1410	0.0323	0.4579	0.7285
(b) R ≡ Me	0.0948	0.1427	0.0256	0.4667	0.7298
(c) R ≡ OMe	0.0941	0.1431	0.0238	0.4690	0.7300
(d) R ≡ NMe_2	0.0934	0.1435	0.0221	0.4705	0.7295
(e) R ≡ Cl	0.0965	0.1416	0.0300	0.4610	0.7291
(f) R ≡ Br	0.0967	0.1414	0.0307	0.4601	0.7289

[a] Σq^0 is the sum of the spin densities at N_1, C_2, C_3, N_{10}.

The first reversible one-electron reduction process of **1a–1f** in aprotic media can be represented by Scheme 1



Scheme 1. **1a–1f** (**1a–1f**)$^{\dot{-}}$

in which the anion radical formulae (**1a–1f**)$^{\dot{-}}$ indicate high spin densities at C_2 and N_{10} with a fully developed charge at endocyclic nitrogen N_1. The spin density values at N_1, C_2, C_3, N_{10}, calculated by the Hückel–McLachlan molecular orbital method, are reported in Table 2.

The $E_{1/2}$ values relating to the first reduction process of the compounds under study in the three solvents at different temperatures are represented in Fig. 1: (a) DMF, (b) ACN and (c) DMSO. The linear coefficients $dE_{1/2}/dT$ with the corresponding correlation coefficients of linear regression are reported in Table 3. The calculated free energy $\Delta G^{\ominus}$ and entropy $\Delta S_r^{\ominus}$ values are reported in Table 4. Finally, the behaviour of each derivative in the three different solvents is shown in Figs. 2 and 3, which represent the quantities $\Delta G^{\ominus}$ (Fig. 2) and $\Delta S_r^{\ominus}$ (Fig. 3) as a function of the solvent acceptor number (AN).

It can be seen that from the free energy point of view, reduction of all of the indole derivatives **1a–1f** is hindered less with increasing values of solvent AN (Fig. 2). In every case, going from electron-donating to electron-withdrawing substituents, the free energy decreases according to the scale NMe_2 > OMe > Me > H > Cl > Br, and this results in reduced hindrance of the reduction process. The compounds **1a** (R ≡ H) and **1b** (R ≡ Me) are

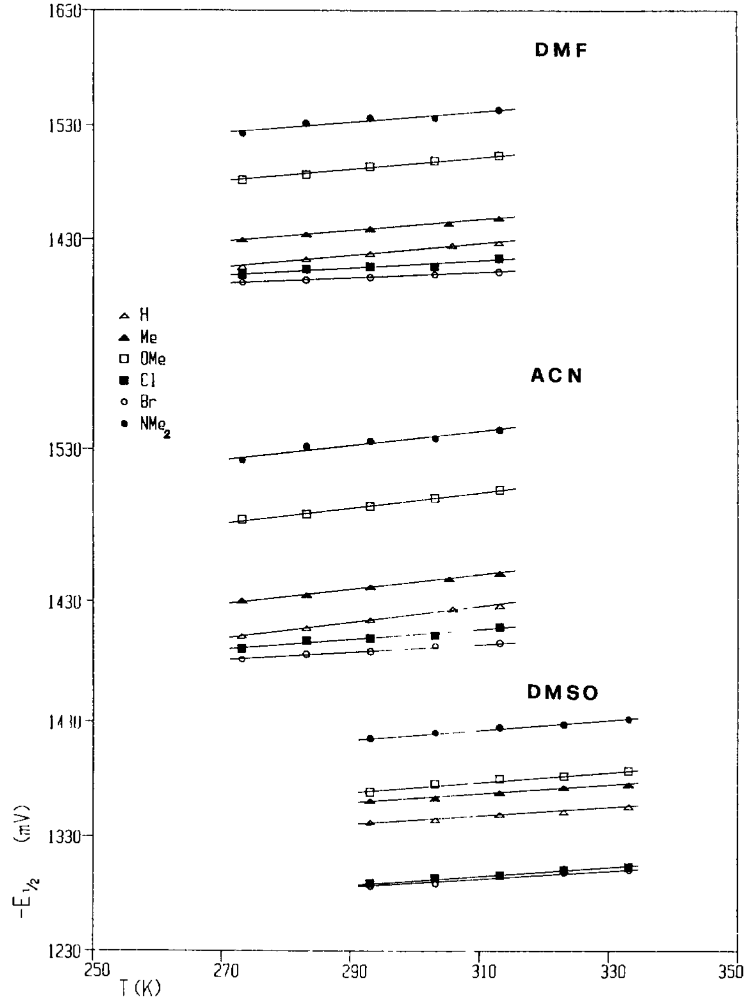


Fig. 1. $E_{1/2}$ vs. T (K) for the first reduction process of indoles **1a–1f** in DMF (a), ACN (b) and DMSO (c) (see text).

TABLE 3

Slope and correlation coefficient values of $E_{1/2}$ vs. T (see Fig. 1)

Compound	DMF		ACN		DMSO	
	– Slope	– r	– Slope	– r	– Slope	– r
(a) R ≡ H	5.13	0.998	5.77	0.997	3.75	0.995
(b) R ≡ Me	4.79	0.999	5.36	0.999	3.90	0.991
(c) R ≡ OMe	5.00	0.999	4.40	0.997	4.45	0.982
(d) R ≡ NMe_2	4.60	0.972	3.90	0.980	4.30	0.992
(e) R ≡ Cl	3.20	0.977	3.40	0.990	3.90	0.997
(f) R ≡ Br	2.35	0.999	2.60	0.991	3.40	0.975

TABLE 4

Free energy and entropy values of indoles **1a–1f** in the three solvents

Compound	$\Delta G^{\ominus}$ (kJ mol^{-1})			$-\Delta S_r^{\ominus}$ (J mol^{-1} K^{-1})		
	DMF	ACN	DMSO	DMF	ACN	DMSO
(a) R ≡ H	136.77	130.84	129.53	49.52	48.67	36.18
(b) R ≡ Me	138.84	132.32	131.42	46.26	45.42	37.63
(c) R ≡ OMe	144.01	132.96	131.99	48.24	42.45	42.94
(d) R ≡ NMe_2	148.16	136.24	136.53	44.38	37.63	41.49
(e) R ≡ Cl	135.71	125.48	124.28	30.88	32.81	37.63
(f) R ≡ Br	134.84	124.95	124.23	22.67	25.09	32.81

influenced to a lesser extent by solvent variation, as can be seen from the small slopes of their straight lines (Fig. 2).

As regards the entropy quantity (Fig. 3), the behaviour of the indole derivatives **1a–1f** can be divided into the results of inductive (I) and mesomeric (M) effects of the substituents: Cl and Br (electron-withdrawing with $I^- > M^+$), OMe and NMe_2 (electron-donating with $I^- < M^+$), and finally Me (for which I^+ and M^+ are very small). It can be seen (Fig. 3) that for the compounds containing Cl (**1e**) or Br (**1f**), the entropy decreases with increasing AN, whereas for the compounds containing OMe (**1c**) or NMe_2 (**1d**), the entropy increases with increasing AN. For the compounds containing Me (**1b**) or H (**1a**), going from DMF (AN = 16.0) to ACN (AN = 18.9), the entropy value changes only a little, whereas a remarkable increase takes place going from ACN to DMSO (AN = 19.3).

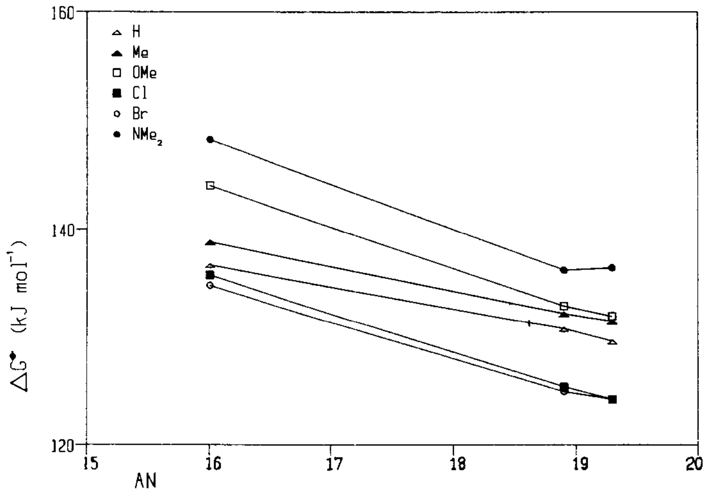


Fig. 2. Free energy vs. acceptor number (AN) for the reduction of indoles **1a–1f** in the three solvents.

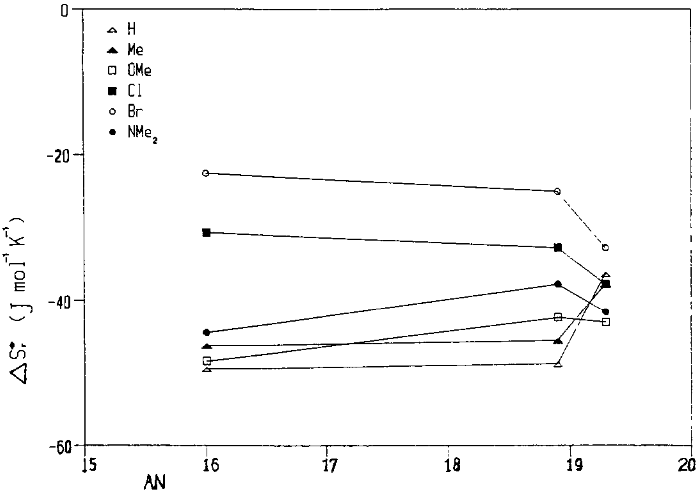


Fig. 3. Entropy vs. acceptor number (AN) for the reduction of indoles **Ia–If** in the three solvents.

The slope of the correlation $\Delta S_r^\ominus$ vs. AN, i.e. $d\Delta S_r^\ominus/dAN$, represents the sensitivity of the entropic quantity (for each compound) to the solvent effect described in terms of Lewis acid. According to the short-range donor–acceptor model, the interaction between the radical anions and the molecules of solvent (represented by the parameter $d\Delta S_r^\ominus/dAN$) should be related to electron density, and thus to spin density, as these two quantities are empirically related [3,8,10,26,27]. In fact, considering the relationship $[(d\Delta S_r^\ominus/dAN)_R - (d\Delta S_r^\ominus/dAN)_H]$ vs. $\Sigma q(0)$ (where the quantity in square brackets is the difference between the slopes of $\Delta S_r^\ominus$ vs. AN for each substituent R and the corresponding slope for H, and Σq^0 is the sum of the

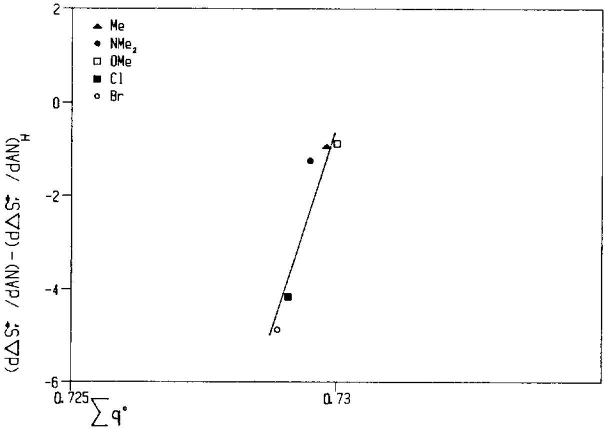


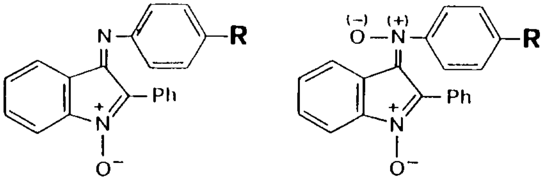
Fig. 4. Slope of $\Delta S_r^\ominus$ vs. AN relative to the same slope of the unsubstituted compound (R = H) vs. total spin density Σq^0 (see Table 2).

spin densities at N_{10}, C_3, C_2, N_1 reported in Table 2), it can be observed (Fig. 4) that a fairly good fit ($r = 0.945$) is obtained for all substituents. A better correlation still ($r = 0.988$) is obtained if one excludes the compound **1d** ($R \equiv NMe_2$).

The substituents under consideration do not noticeably affect the electronic distribution of either endo (N_1) or exo (N_{10}) nitrogens, as can be seen from the negligible difference between the calculated spin density values (Table 2). However, the Hückel–McLachlan molecular orbital calculations show that for the radical ions **(1a–1f)**$^{\dot{-}}$, a higher spin density value is found at the exo than at the endo nitrogen atom, which indicates that the radical–solvent interactions are mainly determined by the charge located on the exocyclic nitrogen atom.

The variation in the behaviour of the indole derivatives **1a–1f** as shown in Fig. 3 seems to be mainly due to the solvent effect rather than the substituent effect. On varying the solvent, electron-withdrawing substituents ($R \equiv Cl$ or Br) show increased ordering (structure-making effect) and a reduced hindrance to the reduction process. By contrast, for the electron-donating substituents ($R \equiv OMe$ or NMe_2), the structure-breaking effect plays a role, with a corresponding entropy increase and a simultaneously increased hindrance to the reduction process.

As regards the compounds **1b** ($R \equiv Me$) and **1a** ($R \equiv H$), it can be observed that while there is a slight variation of the entropy quantity going from DMF to ACN, a more remarkable change occurs going from ACN to DMSO, i.e. when there is a shift from the least to the most structured solvent. In this case, the structure-breaking effects are clearly prevailing. We have been able to confirm this trend through a study of the solvent effect on the one-electron reversible reduction of other indole derivatives, namely 2-phenyl-3-arylimino-3H-indole-*N*,*N*′-dioxides (**2a–2f**) and 2-phenyl-3-arylimino-3H-indole-1′-oxides (**3a–3f**) in the same three solvents [28].



2-Phenyl-3-arylimino-3*H*-indole-N,N′-dioxides **2a–2f** (left) and 2-phenyl-3-arylimino-3*H*-indole-1′-oxides **3a–3f** (right).

Because of the great sensitivity of entropy to variation of solvent structure, the order of the substituents' favouring of the electroreduction of **1a–1f** in a given solvent is different to that obtained for the free energy quantity (see Figs. 3 and 2). A levelling effect can, however, be observed when the reduction process takes place in DMSO (Fig. 3).

The behaviour of the various derivatives in a given solvent can be

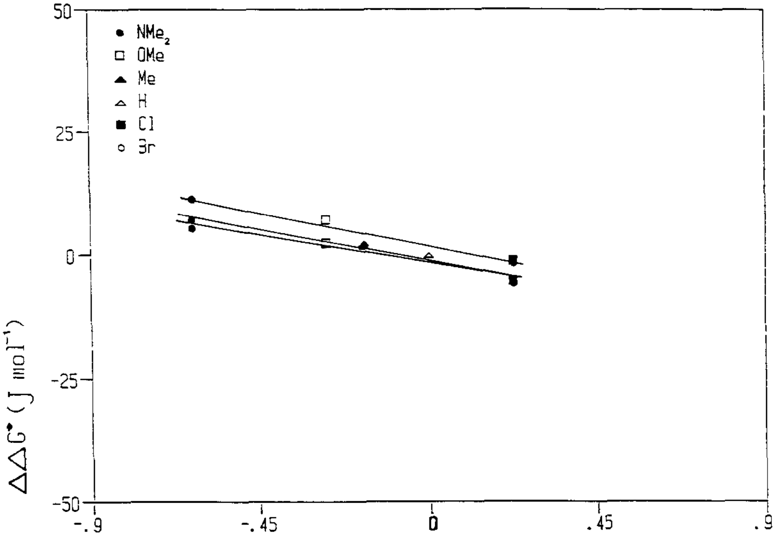


Fig. 5. Free energy variation vs. $-\rho\sigma_R$ for the reduction of indoles **1a–1f** in the three solvents ($\rho_{DMF} = -0.15$; ρ_{ACN} -0.13; $\rho_{DMSC} = -0.14$).

evaluated in terms of the Hammett equations $\Delta\Delta G^{\ominus} = -\rho\sigma_R$ (where ρ is the reaction constant expressing the susceptibility of the reduction process to the polar effects of substituents, and σ_R is the Hammett constant of the substituent R [29]). As expected, the reduction process of **1a–1f** is favoured going from electron-donating to electron-withdrawing substituents (Fig. 5). Moreover, the function linearity shows that there is no great change in the reduction process for any of the three solvents considered.

Further investigations are in progress, extending the study both to other solvents with lower acceptor number (e.g. dimethylacetamide, hexamethylphosphoramide), and to compounds **2a–2f** and **3a–3f**, which have structures very similar to that of the indole derivatives examined in the present work.

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