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Determination of Standard Gibbs Energies of Transfer of Organic Anions across the Water/Nitrobenzene Interface

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The oxidation of decamethylferrocene dissolved in a nitrobenzene droplet and attached to a graphite electrode that is immersed in an aqueous electrolyte solution provides the basis to determine the standard Gibbs energies of transfer of simple organic anions, such as those of aliphatic and aromatic mono- and dicarboxylic acids, and phenols. The data are rationalized on the basis of the constitution of the compounds.

Introduction

Standard Gibbs energies of transfer of compounds across the interface of immiscible solvents are highly important thermodynamic data. They are a measure of their lipophilicity and allow assessing their biological activity, membrane permeability, intra- and intermolecular interactions, and so forth.[1−3] Standard Gibbs energies of transfer of ions play an exceptional role in phase transfer catalysis.[1,4] It is rather surprising that these fundamental data are not known for most of the simple organic anions, for example, the anions of the aliphatic and aromatic acids, phenols, and so forth.[5] The reason for this situation is a considerable lack of precise methods to determine these values. The state of the art is to measure the ion transfer across the interface of two immiscible solutions with the help of a four-electrode potentiostat under the provision that the organic phase contains a very hydrophobic supporting electrolyte and the water phase contains a very hydrophilic supporting electrolyte.[6,7] The potential window that can be utilized is very small, usually 400−600 mV, and it can be extended only in some cases, either by coupling solution equilibria[8−10] or by using microhole arrangements.[1,11] Utilizing the four-electrode arrangement Reymond et al.[12−14] recently have studied the transfer of weak acids and bases at the liquid/liquid interfaces and used ionic partition diagrams. Recently, we have reported a methodology to determine standard Gibbs energies of ion transfer by coupling the ion transfer across a liquid/liquid interface with an electron transfer across an (solid) electrode/organic solution interface.[15−17] This three-phase arrangement (cf. Scheme 1) (i) allows us to avoid the supporting electrolyte in the organic phase, (ii) needs only a three-electrode potentiostat, and (iii) allows us to expand considerably the potential window. With the help of a microelectrode probe, it was shown that the reaction indeed starts at the three-phase junction and advances into the nitrobenzene droplet.[18] Here we report for the first time that this methodology is very effective to determine standard Gibbs free energies of transfer of important organic ions, and we show how these thermodynamic data are related to the constitution of the compounds.

Experimental Section

A 0.1 mol dm^{-3} solution of decamethylferrocene (dmfc) was prepared by dissolving dmfc (Acrös Organics) in water saturated nitrobenzene. 2 μL of this solution was attached as a droplet to the surface of a paraffin impregnated graphite electrode (PIGE) with the help of an Eppendorf-type pipet. The fabrication of the PIGE is described elsewhere.[19] The electrode with the attached droplet was immersed into an aqueous electrolyte solution, and the electrochemical oxidation of dmfc in that three-phase arrangement was studied utilizing a three-electrode potentiostat. The PIGE was a graphite rod with 0.5 cm diameter and an exposed surface area of 0.2 cm^2. The approximate radius of the hemispherical droplet was 0.1 cm. Square-wave (SW) voltammetry was used because it is a fast technique providing a precise

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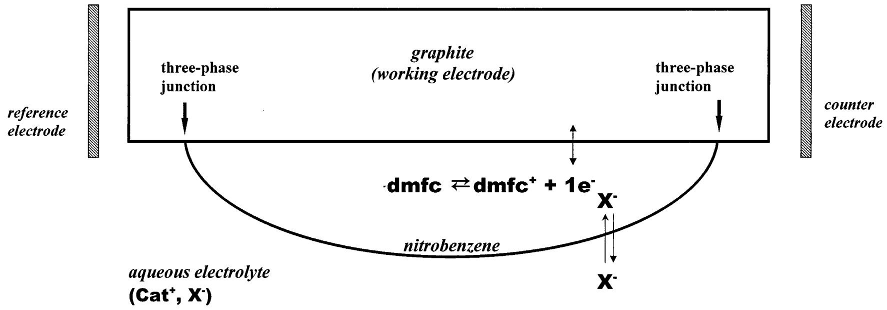
Scheme 1



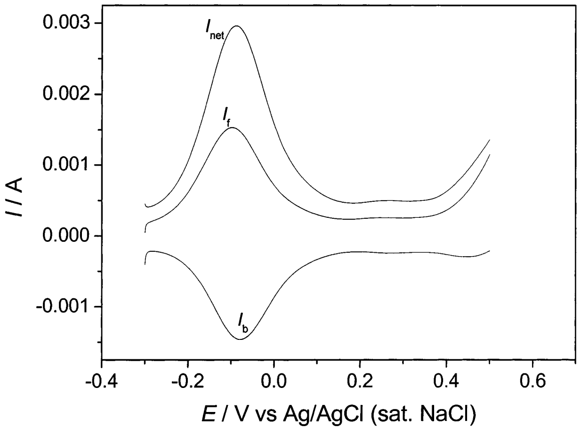


Figure 1. Forward (I_f), backward (I_b), and net (I_{net}) components of the square-wave voltammetric response of a nitrobenzene droplet with a volume of 2 μL containing 0.1 mol dm^{-3} dmfc attached to a paraffin impregnated graphite electrode which is immersed in a 1 mol dm^{-3} aqueous KSCN solution. The experimental conditions were SW frequency $f = 100$ Hz, SW amplitude $E_{sw} = 50$ mV, scan increment d$E = 0.15$ mV, and starting potential $E_s = -0.30$ V.

measurement of the peak potential, that is, the formal potential of the system. Because of the short measurement time, the nitrobenzene droplet was stable and neither a significant distortion nor a change of the color of the droplet was observed. SW voltammograms were recorded using the commercial electrochemical measuring system AUTOLAB (Eco-Chemie, Utrecht, Netherlands). Typical measuring parameters were as follows: SW frequency $f = 100$ Hz, SW amplitude $E_{sw} = 50$ mV, scan increment d$E = 0.15$ mV, and starting potential $E_s = -0.50$ V vs Ag/AgCl. An Ag/AgC//saturated NaCl solution reference electrode ($E = 0.200$ V vs SHE) was used, and a platinum wire served as auxiliary electrode. All salts for preparation of the electrolyte solutions were used as purchased. All aqueous solutions were saturated with nitrobenzene. All chemicals used were of analytical grade. The water used was Millipore Q. All experiments were carried out at 25 °C.

The aqueous phase contained the alkali salts of the compounds in a concentration of 1 mol dm^{-3}. When the concentration was varied, the solutions contained a potassium hydrogenphthalate buffer of a pH that maintained the anions in a concentration that was practically equal to their analytical concentration (i.e. protonation was kept negligible).

Results and Discussion

Coupling an Electron and Ion Transfer by Oxidation of Decamethylferrocene at a Three-Phase Arrangement. The oxidation of dmfc to dmfc$^+$ in nitrobenzene in a three-phase arrangement, electrode/nitrobenzene/water (E|NB|W), gives rise to a well-defined SW voltammetric response with a peak potential depending on the type and concentration of anions in the aqueous phase. Figure 1 shows all components of a typical SW voltammetric response recorded in a 1 mol dm^{-3} KSCN aqueous solution. The forward (oxidation) and backward (reduction) components of the SW voltammetric response are bell-shaped curves with virtually equal peak heights and a peak potential separation of 28 mV. By increasing the SW frequency from 30 to 350 Hz, the half-peak width and peak potential remained almost unchanged, scattering slightly around the average value within ±8 and ±10 mV, for peak potential and half-peak width, respectively. The voltammetric properties of the oxidation of dmfc in the three-phase arrangement are typical for a reversible electrode mechanism, implying that the voltammetric data can be related to the thermodynamic properties of the system under study.

The electron transfer reaction occurring at the electrode/nitrobenzene interface has to be accompanied by an ion transfer across the water/nitrobenzene interface to preserve the electroneutrality of the organic phase (cf. Scheme 1). For this reason, the potential of the response is strongly dependent on the type and concentration of ions present in the aqueous phase.

The overall electrode process of dmfc oxidation in the E|NB|W three-phase arrangement can be described by the following reaction:

$$\mathrm{dmfc}_{(NB)} + \mathrm{X}^{-}_{(W)} \rightleftarrows \mathrm{dmfc}^{+}_{(NB)} + \mathrm{X}^{-}_{(NB)} + \mathrm{e}^{-} \qquad \mathrm{(I)}$$

(see Scheme 1). The following form of the Nernst equation applies to this reaction:[15]

$$E^{\theta'}{}_{c} = E^{\theta}{}_{dmfc^{+}{}_{(NB)}|dmfc_{(NB)}} + \Delta_{W}^{NB}\varphi^{\theta}{}_{X^{-}} - \frac{RT}{T}\ln(a_{X^{-}{}_{(W)}}) + \frac{RT}{F}\ln\left(\frac{a^{*}{}_{dmfc_{(NB)}}}{2}\right) + \frac{RT}{F}\ln\frac{a_{dmfc^{+}{}_{(NB)}}}{a_{dmfc_{(NB)}}} \qquad (1)$$

where the formal potential $E^{\theta'}{}_{c}$ can be defined as

$$E^{\theta'}{}_{c} = E^{\theta}{}_{dmfc^{+}{}_{(NB)}|dmfc_{(NB)}} + \Delta_{W}^{NB}\varphi^{\theta}{}_{X^{-}} - \frac{RT}{T}\ln(a_{X^{-}{}_{(W)}}) + \frac{RT}{F}\ln\left(\frac{a^{*}{}_{dmfc_{(NB)}}}{2}\right) \qquad (2)$$

Here, $E^{\theta}{}_{dmfc^{+}{}_{(NB)}|dmfc_{(NB)}}$ is the standard potential of the dmfc$^+$/dmfc redox couple in nitrobenzene, $\Delta_{W}^{NB}\varphi^{\theta}{}_{X^{-}}$ is the standard potential of the transfer of X$^-$ from water to nitrobenzene, and $a^{*}{}_{dmfc}$ is the initial activity of dmfc in the organic phase. Knowing the standard transfer potential of the anion, one can calculate the standard Gibbs energy of transfer across the water/nitrobenzene interface using the following equation:[6]

$$\Delta G^{\theta}{}_{X^{-}(W\rightarrow NB)} = -zF\Delta_{W}^{NB}\varphi^{\theta}{}_{X^{-}} \qquad (3)$$

(for monovalent anions, z is -1). The Galvani potential

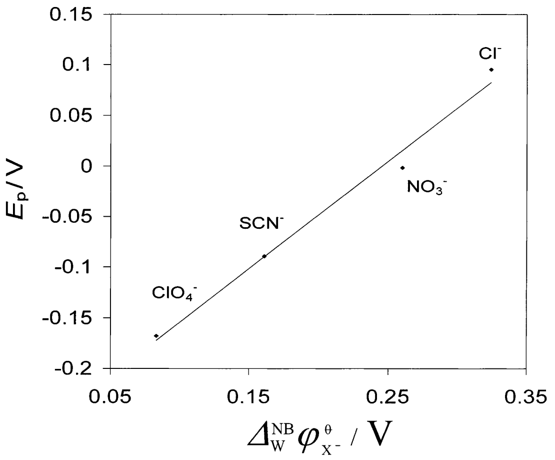


Figure 2. Dependence of the peak potential of the net SW voltammetric response of a nitrobenzene droplet, containing a 0.1 mol dm^{-3} dmfc solution recorded in different aqueous electrolyte solutions, on the standard potentials of transfer across the water/nitrobenzene interface of respective anions. The concentration of the aqueous electrolytes was 1 mol dm^{-3}. All other conditions were the same as those in Figure 1.

difference $\Delta_W^{NB}\varphi^\theta{}_{X^-}$ is defined as $\Delta_W^{NB}\varphi^\theta{}_{X^-} = \phi^{NB} - \phi^{W}$, where ϕ^{NB} and ϕ^{W} are the inner potentials of nitrobenzene and water, respectively. For this purpose, the value of the standard redox potential of the dmfc$^+$/dmfc redox couple in nitrobenzene is needed. This value can be determined by studying the oxidation process of dmfc in the presence of different anions, for which the energies of transfer across the water/nitrobenzene interface are already known. Figure 2 shows the dependence of the peak potential of the response, recorded in the presence of different anions, on their standard potentials of transfer across the water/nitrobenzene interface. The values of the standard potential of transfer have been taken from the literature.[5] The dependence is linear, which is in agreement with eq 2. According to eq 2, the intercept of the dependence E_p versus $\Delta_W^{NB}\varphi^\theta{}_{X^-}$ is equal to

$$E^\theta{}_{\mathrm{dmfc^+_{(NB)}|dmfc_{(NB)}}} - \frac{RT}{F}\ln(a_{\mathrm{X^-(W)}}) + \frac{RT}{F}\ln\left(\frac{a^*{}_{\mathrm{dmfc_{(NB)}}}}{2}\right)$$

which serves as the basis for estimation of the standard redox potential of the dmfc$^+$/dmfc couple in nitrobenzene. The equation obtained by a linear regression analysis of the data presented in Figure 2 reads $E_p/\mathrm{V} = 1.059\ \Delta_W^{NB}\varphi^\theta{}_{X^-}/\mathrm{V} - 0.259$ ($R^2 = 0.99$). Approximating the activity of the species with their concentrations, and taking into account the concentration of X$^-$ in the aqueous phase ($c_{\mathrm{X^-(W)}} = 1$ mol dm^{-3}) together with the concentration of dmfc in the organic phase ($c_{\mathrm{dmfc_{(NB)}}} = 0.1$ mol dm^{-3}), the standard potential of the dmfc$^+$/dmfc redox couple in nitrobenzene is $E^\theta{}_{\mathrm{dmfc^+_{(NB)}|dmfc_{(NB)}}} = -0.184$ V vs Ag/AgCl. It is also important to note that the slope of the line in Figure 2 is close to 1, which is in accordance with eq 2. Therefore, knowing the standard redox potential of the dmfc$^+$/dmfc couple in NB, the energy of transfer of other ions following the general electrode mechanism (I) can be determined.

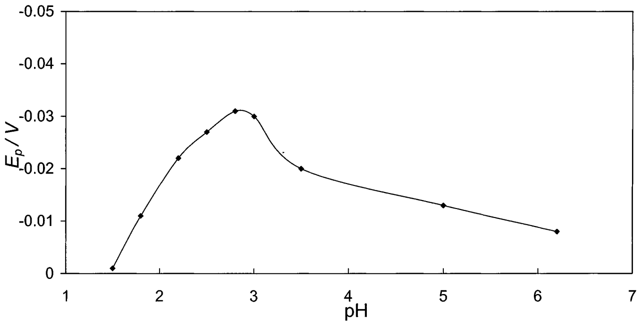


Figure 3. Dependence of the peak potential of the net SW voltammetric response of a nitrobenzene droplet, containing a 0.1 mol dm^{-3} dmfc solution recorded in a 1 mol dm^{-3} aqueous solution of hydrogenmaleate, on the pH of the aqueous medium. All other experimental conditions were the same as those in Figure 1.

However, it is important to note that strongly hydrophilic anions, requiring higher energy of transfer from water to nitrobenzene than the energy of transfer of dmfc$^+$ in the opposite direction, cannot be studied by the proposed method. For instance, in 1 mol dm^{-3} Na_2SO_4 or NaF aqueous solutions, the peak potential of the response is $E_p = 0.150$ V vs Ag/AgCl, being independent of both type and concentration of the supporting electrolyte. Under such conditions, the electroneutrality of the organic phase is maintained by an expulsion of dmfc$^+$ into the aqueous phase, and the electrode mechanism occurs according to the reaction

$$\mathrm{dmfc_{(NB)}} \rightleftarrows \mathrm{dmfc^+{}_{(W)}} + e^- \qquad \text{(II)}$$

Therefore, the potential of 0.150 V vs Ag/AgCl is the positive limit of the potential window of the proposed method. On the other side, the negative limit of the available potential window is determined by the ascending current due to the reduction of nitrobenzene. When the potential limit on the negative side is defined as that potential where the current caused by nitrobenzene reduction equals that of the dmfc response, the limit is −0.75 at pH 1 and −0.63 at pH 13. Calculating the standard Gibbs energies accessible within the available potential window of the method, the following intervals were found: -33.80 kJ mol^{-1} $\leq \Delta G^\theta{}_{\mathrm{X^-(W\to NB)}} \leq +37.21$ kJ mol^{-1} and -41.08 kJ mol^{-1} $\leq \Delta G^\theta{}_{\mathrm{X^-(W\to NB)}} \leq +37.21$ kJ mol^{-1}, for pH 13 and 1, respectively.

Standard Gibbs Energies of Transfer of the Monoanions of Aliphatic Dicarboxylic Acids across the Water/Nitrobenzene Interface. The first group of studied ions comprises the monoanions of the following dicarboxylic acids: oxalic, malonic, maleic, succinic, citraconic, and glutaric acid. An attempt has been also made to study the transfer of fumarate ions (monoanion); however, irreproducible results have been observed because of the low solubility of the acid.

In the presence of the alkali salts of dicarboxylic acid in the aqueous phase, the voltammetric properties of reaction I are strongly sensitive to the pH of the medium. Within the range $\mathrm{p}K_{a,1} < \mathrm{pH} < \mathrm{p}K_{a,2}$ ($K_{a,1}$ and $K_{a,2}$ are the first and second acidity constants, respectively), the monoanionic form is the predominant species in the aqueous solution. At pH < p$K_{a,1}$ and pH > p$K_{a,2}$, the undissociated and dianionic forms of the acid prevail, respectively. Figure 3 represents the effect of pH on the peak potential of the response in the presence of maleic acid. The dependence exhibits a maximum positioned within the interval 2.5 < pH < 4.0. As the pK_a values of maleic acid are p$K_{a,1} = 1.83$ and p$K_{a,2} = 6.07$, this result is reasonable, although the shape of the curve cannot be easily explained. At pH < 2.5 and pH > 4.0, the concentration of the monoanion strongly decreases, causing a shift of the peak potential in a positive direction, as predicted by eq 2. At a constant pH of the medium (i.e. pH = 3.4), the dependence of the peak potential on the logarithm of the hydrogenmaleate concentration is a linear function with a slope of −60.8 mV.

Table 1. Properties of the Net SW Voltammetric Responses and the Estimated Values of the Standard Gibbs Free Energies of Transfer of the Monoanionic Forms of the Aliphatic Dicarboxylic Acids[a]

monoanion of dicarboxilic acid	formula	slope of the dependence E_p vs $\log(c)$ in mV	E_p/V vs Ag/AgCl	$\Delta G^{\theta}_{X^-(W\to NB)}$ [b]/ kJ mol^{-1}	pH	p$K_{a,1}$	p$K_{a,2}$
hydrogenoxalate	$C_2HO_4^-$	−60.8	0.05	28.17	2.2	1.23	4.19
hydrogenmalonate	$C_3H_3O_4^-$	−68.0	0.004	24.02	4.0	2.83	5.69
hydrogenmaleate	$C_4H_3O_4^-$	−62.3	−0.037	20.26	3.4	1.83	6.07
hydrogensuccinate	$C_4H_5O_4^-$	−57.2	−0.024	21.42	4.8	4.16	5.61
hydrogencitraconate	$C_5H_5O_4^-$	−58.7	−0.043	19.68	5.0	3.85	5.43
hydrogenglutarate	$C_5H_7O_4^-$	−51.0	−0.037	20.26	4.8	4.31	5.41

[a] Experimental conditions were the same as those in Figure 1. [b] The values of $\Delta G^{\theta}_{X^-(W\to NB)}$ are estimated using the calibration line in Figure 2.

A corresponding analysis of the SW voltammetric response on pH and concentration of the acid has been carried out for all studied monoanions. In all cases, the SW voltammetric response is a well-defined peak, enabling a precise measurement of the peak potential and determination of the standard Gibbs energy of transfer across the water/nitrobenzene interface. Table 1 summarizes the relevant data of the voltammetric measurements, together with the calculated values of the standard Gibbs energies of transfer of the monoanions of dicarboxylic acids across the water/nitrobenzene interface, using the calibration line in Figure 2. For these and all following compounds, the dependence of the peak potentials on the concentration of the anions has been checked. In most cases it was found that there is a linear dependence within the range 0.1−1 mol dm^{-3}. If there was a measurable scattering of the values around the straight line, the intercept of the linear fitting line was used. Activity coefficients have been taken into account for neither the aqueous nor the nonaqueous phases, as is usual practice in these studies. In a very strict way, the determined data are conditional Gibbs free energies. Further, it must be said that all reported data are based on the Grunwald assumption of identical standard Gibbs free energies of transfer of tetraphenylborate anions and tetraphenylarsonium cations[21] because the used calibration data are already based on this extrathermodynamic assumption.

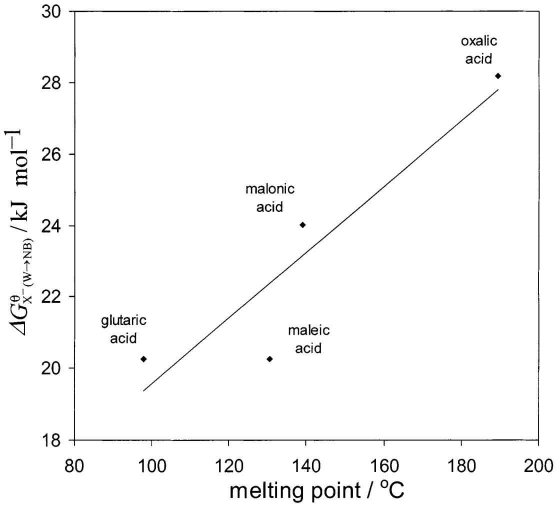


Figure 4. Correlation of the estimated standard Gibbs energies of transfer of the monoanionic forms of dicarboxylic acids across the water/nitrobenzene interface with the melting points of the acids. The data for the melting points are taken from ref 29.

From the estimated $\Delta G^{\theta}_{X^-(W\to NB)}$ values, one can conclude that the lipophilicity of the anions increases proportionally to the number of carbon atoms, which is an expected trend. It is very interesting to note that the monoanionic forms of the unsaturated acids, such as maleic and citraconic acid, have a lower energy of transfer than the monoanionic forms of the corresponding saturated acids, that is, succinic and glutaric acid. This behavior can be attributed to the negative inductive effect of the double bond. To understand this phenomenon, it is instructive to recall that the standard Gibbs energy of transfer of an ion between two immiscible solvents is caused by the difference between the solvation energies in both solvents. Although the standard Gibbs energy of transfer is a complex quantity depending on a series of physicochemical parameters of the system, its dominating component is of electrostatic nature, depending on both the charge and size of the transferred ion. According to the electrostatic Born theory,[1] the energy of transfer is proportional to the square of the charge of the ion. Therefore, the atomic group with a negative inductive effect in an organic anion decreases the energy of transfer from water to an organic solvent by delocalization of the electron density and decreasing the effective charge of the anion. For the same reason, maleic and citraconic acids are stronger electrolytes, with respect to the first dissociation step, than the corresponding saturated succinic and glutaric acids, which can be seen from the p$K_{a,1}$ values given in Table 1. Moreover, the $\Delta G^{\theta}_{X^-(W\to NB)}$ values correlate well with the melting points of the acids (see Figure 4).

Standard Gibbs Energies of Transfer of the Anions of Ortho-Substituted Phenols across the Water/Nitrobenzene Interface. The transfer process of a series of nitrophenolate anions across the water/dichlorethane interface has been studied by Chopineaux-Courtois et al.[22] The data of the standard Gibbs energy of transfer across the water/nitrobenzene interface are only available for 2,4-dinitrophenolate, 2,6-dinitrophenolate, and 2,4,6-trinitrophenolate (picrate) anions.[23]

Ortho-substituted phenols are highly toxic compounds primarily because of their ability to uncouple the cellular energy production. It is known that 2-nitrophenol increases the ATPase activity of mammalian skeletal muscles in the presence of different cations.[24] Moreover, phenol itself and its halogen derivatives are well-known carcinogenic substances. In general, a phenol-type compound may be transported across the skin barrier by diffusion through the appendages, hair follicles, or by diffusion through the stratum corneum.[25] For all these reasons, the knowledge of the lipophilicity of these

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Table 2. Properties of the Net SW Voltammetric Responses and the Estimated Values of the Standard Gibbs Free Energies of Transfer of the Anionic Forms of the Ortho-Substituted Phenols[a]

anion of ortho-substituted phenol	formula	slope of the dependence E_p vs log(c) in mV	E_p/V vs Ag/AgCl	$\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}{}^{b}$/ kJ mol^{-1}
o-nitrophenolate	$C_6H_4ONO_2^-$	−70	−0.101	14.37
o-chlorophenolate	$C_6H_4OCl^-$	−64	−0.08	16.34
phenolate	$C_6H_5O^-$	−67	−0.035	20.45
o-methylphenolate	$C_6H_4OCH_3^-$	−45	−0.016	22.18

[a] The pH of the aqueous medium was 12.8. The other conditions were the same as those in Figure 1. [b] The values of $\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}$ are estimated using the calibration line in Figure 2.

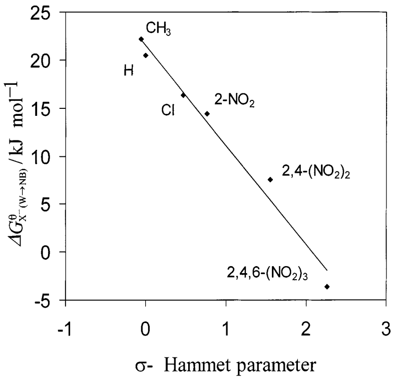

Figure 5. Correlation of the estimated standard Gibbs energies of transfer of the ortho-substituted phenolate anions across the water/nitrobenzene interface with the σ-Hammett constants of the atomic groups in the ortho position. The data of σ-Hammett constants are taken from ref 26.

Table 3. Peak Potentials of the Net SW Voltammetric Response, Standard Potential Differences at the W/NB Liquid Interface, and the Standard Gibbs Energies of the Transfer of the Anions of Aliphatic and Aromatic Monocarboxylic Acids[a]

anion	E_p/mV vs Ag/AgCl	$\Delta_W^{NB}\varphi^{\theta}{}_{X^-}{}^{b}$/ mV	$\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}{}^{b}$/ kJ mol^{-1}
	Monocarboxylic Aliphatic Acids		
formiate	49.00	291.40	28.07
acetate	60.00	301.80	29.14
propionate	40.30	283.16	27.30
butyrate	46.33	288.86	27.86
valeriate	35.00	278.14	26.82
capronate	−7.70	237.74	22.94
oenanthate	−63.00	185.43	17.88
caprylate	−103.00	142.85	13.78
pelargonate	−116.00	135.28	13.02
caprinate	−119.70	131.78	12.71
	Monocarboxylic Aromatic Acids		
benzoate	−29.70	216.70	20.94
salicylate	−124.30	127.72	12.32
acetylsalicylate	−142.00	110.70	10.68

[a] The concentration of the anions in the aqueous phase was 1 mol dm^{-3}. All other conditions were the same as those in Figure 1. [b] The values of $\Delta_W^{NB}\varphi^{\theta}{}_{X^-}$ and $\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}$ are estimated using the calibration line in Figure 2.

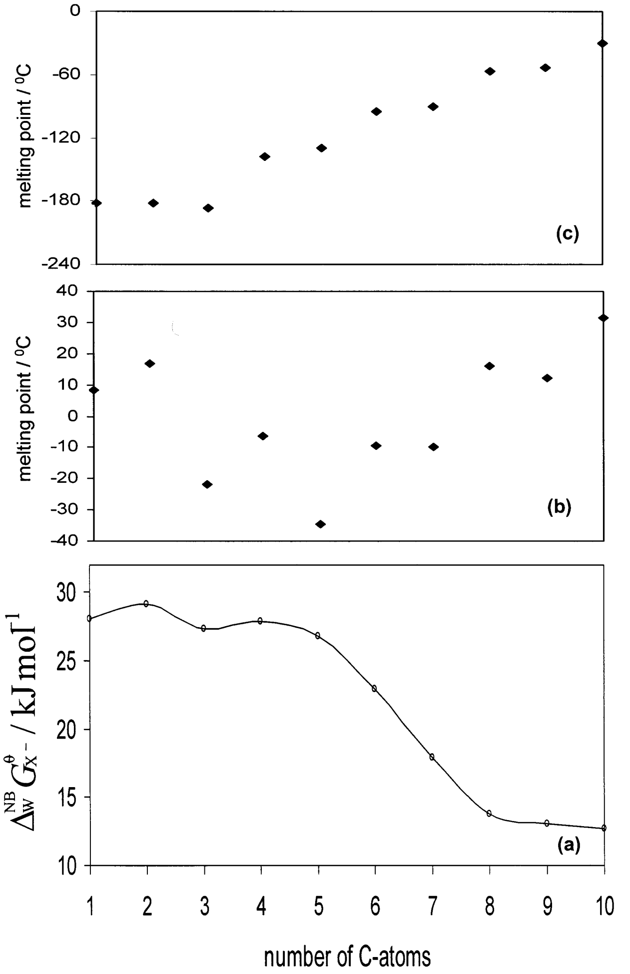

Figure 6. Correlation of the estimated standard Gibbs energies of transfer of the anionic forms of the aliphatic monocarboxylic acids (a), melting points of the acids (b), and melting points of alkanes (c) with the number of carbon atoms.

compounds is of particular importance for pharmacy and medicine.

During measurements, the aqueous phase contained a 1 mol dm^{-3} solution of a respective phenol in a 2 mol dm^{-3} NaOH solution, providing a complete dissociation of the studied phenols. The relevant parameters collected by SW voltammetry, together with the estimated values of the standard Gibbs energies of transfer across the W/NB interface, are summarized in Table 2.

Analyzing the data of $\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}$ presented in Table 2, one can note that the lipophilicity of the ortho-substituted phenolate anions increases in proportion to the increasing negative inductive effect of the atomic group bonded in the ortho-position. The larger the negative inductive effect of the atomic group in the ortho-position, the lower the effective charge at the oxygen atoms of the phenolate ion, which causes the energy of transfer from water to nitrobenzene to decrease. Shown in Figure 5 is the dependence of the standard Gibbs energies of transfer on the respective σ-Hammett constants. In this correlation the $\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}$ values of 2,4-dinitrophenolate and picrate anions are also included, which have been determined by different electrochemical methods,[23] and the σ-Hammett constants are taken from ref 26. A fairly good linear relationship between $\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}$ and the σ-Hammett constants is observed ($R^2 = 0.981$). The fact that the values of $\Delta G^{\theta}{}_{X^-(W\rightarrow NB)}$ determined by different electrochemical methods fit well together in a single correlation analysis supports the validity and consistency of these data.

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Standard Gibbs Energies of Transfer of the Anions of Aliphatic and Aromatic Monocarboxylic Acids across the Water/Nitrobenzene Interface. The last group of studied compounds contains a series of anions of aliphatic and aromatic monocarboxylic acids, which are listed in Table 3. All measurements have been carried out using a 1 mol dm^{-3} aqueous solution of a potassium salt of a particular acid. The aqueous solution has been prepared by titration of an aqueous solution of the respective acid with a KOH solution until reaching the equivalent point of the titration. Under such conditions, the concentration of the undissociated acid is negligible. After titration, the concentration of the acidic anions was adjusted to 1 mol dm^{-3}.

The oxidation of dmfc in the three-phase arrangement in the presence of monocarboxylate anions proceeds according to the general reaction pathway described by reaction I. The voltammetric properties of the response confirmed the reversibility of the electrode mechanism.

The correlation of the standard Gibbs energies of transfer with the number of carbon atoms is depicted in Figure 6. As expected, the overall trend is that the lipophilicity of the anions increases by increasing the number of carbon atoms. However, from C_1 to C_5, the data alternate in the same way as the melting points of the acids and also of the alkanes (see Figure 6). The latter fact is usually explained by the so-called transoidal structure of the alkanes with an even number of carbon atoms and the cisoidal structure of those with uneven numbers.[27] Transoidal means that the methyl groups at both ends have the largest possible distance from each other, whereas cisoidal means that they are facing each other. In the case of aliphatic carboxylate anions, the standard Gibbs free energies of transfer are slightly depressed in the case of uneven number of carbon atoms in the range C_1 to C_5. The cisoidal structure seems to facilitate the transfer from water to nitrobenzene. Since the cisoidal structure is more compact than the transoidal one, it may be assumed that the solvation of the alkyl chain by water is also less, as hence are the standard Gibbs free energies of transfer. Figure 6 shows that the standard Gibbs energies of anion transfer are relatively independent of the chain length for C_1 to C_5 and above C_8, obviously because for the short chains the charge contribution dominates, whereas for the long chains the charge independent contribution dominates. This agrees well with an analysis of charge dependent and charge independent contributions to the Gibbs energies of transfer of ions made by Osaki et al.[28]

Conclusions

This study shows that the recently developed methodology for the determination of standard Gibbs energies of ion transfer can be successfully applied for determining these data of organic anions of variable lipophilicity. The systematic study of some series of homologous compounds revealed the importance of the charge delocalization for the size of the Gibbs energies of transfer.

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