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Inclusion of the Regioisomeric Nitrobenzene Derivatives and Ferrocene Guests by β-Cyclodextrin Polymer and Their Transport through the Polymer Matrix*

DARIUSZ KORADECKI and WŁODZIMIERZ KUTNER**
Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

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Abstract. Host–guest equilibria have been investigated involving inclusion sites of the microparticulate amorphous β-cyclodextrin polymer, β-CDP-25, and a range of redox guests comprising regioisomeric nitrobenzene derivatives and ferrocene. The equilibria were studied by the batch method. Inclusion-governed, Langmuir-type sorption equilibria occurred in the β-CDP-25/guest systems studied in 1 : 1 (v/v) aqueous methanolic solutions. A 1 : 1 (host inclusion site)/guest stoichiometry was found and sorption equilibrium constants were determined. The values of the constants changed by a factor of 20 between the most weakly and strongly included guests. Regioselective discrimination of β-CDP-25 was most pronounced with respect to nitrophenols. Transport phenomena of guest moelcules in the β-CDP-25 matrix have also been studied. The apparent diffusion coefficients of guest molecules were determined in the β-CDP-25 matrix by chronamperometry at the (β-CDP-25)–PTFE–carbon composite electrodes. These diffusion coefficients were almost four orders of magnitude lower than the corresponding coefficients of guest molecules in solution in the absence of β-CD. The diffusion mechanism was postulated for the guest molecules in the β-CDP-25 matrix, which invoked hopping of the molecules between inclusion sites.

Key words. Inclusion complexes, β-cyclodextrin host, β-cyclodextrin polymer host, ferrocene guest, 2-, 3-, 4-nitroaniline guests, 2-, 3-, 4-nitrotoluene guests, 2-, 3-, 4-nitrophenol guests, 3,4- and 3,5-dinitrotoluene guests, 2-, 3-, 4-chloronitrobenzene guests, 2- and 4-nitrobenzoic acid guests, chemically modified (β-cyclodextrin polymer)–PTFE–carbon composite electrode, hopping mechanism of diffusion of a guest species between polymer inclusion sites.

1. Introduction

A nonreducing cyclic oligosaccharide, β-cyclodextrin (β-CD), composed of seven 1,4-linked α-D-glucose units, is an effective complexing agent for the inclusion, among others, of aromatic molecules of the size of benzene [1]. It is also a second sphere molecular receptor for the inclusion of transition metal complexes bearing hydrophobic ligands [2, 3]. Complexes of 1 : 1 stoichiometry are then predominantly formed [4]. β-CD inclusion systems have been studied in aqueous [1] and non-aqueous [5, 6] solutions as well as in the solid state [7–9].

We present here studies, which are rather scarce in the literature [10–12], on the inclusion properties of polymerized β-CD. The insoluble, microparticulate, exten-

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** Author for correspondence.

sively crosslinked β-cyclodextrin polymer, β-CDP-25, and a range of electrochemically active guests, was used to study the heterogeneous inclusion equilibria involving the polymer and the redox guest in solution. Insoluble β-CD polymers are used for selective sorption [11, 12] and release [13] of a broad range of organic guests. The β-CDP-25 polymer has been utilized as a column packing material both for liquid [14–19] and gas [20] chromatography for separation of, for instance, racemic mixtures. A mixed retention mechanism was postulated [20] which comprised adsorption and inclusion complex formation.

Due to its catalytic properties β-CD has been exploited, with an appropriate guest included, as a model system of hydrolytic enzymes [21, 22]. Also, β-CD has been extensively used as a modifier of electrode reactions [23]. In the present paper we describe the electrochemical behavior of the β-CDP-25/(redox guest) system as well as the transport phenomena inside the β-CDP-25 matrix with the ultimate goal of evaluating β-CDP-25 as a membrane-type material. Compression moulded graphite–polyfluorohydrocarbon composite electrodes were used, being quite common, nowadays, in electroanalysis [24]. Electrodes containing guest preloaded β-CDP-25 polymer as the third component of the electrode mixture were used in the hope of developing a useful tool suitable for studying the (polymer host)/(redox guest) system. The ferrocene guest was chosen to probe the system because its inclusion by β-CD is strong [2]. Moreover, it reveals a simple, reversible, one-electron electrode behavior and for this reason it has often been used to probe polymer modified electrodes [25]. We also examined a range of nitrobenzene regioisomeric derivatives, which were already partially exploited in the β-CD/host systems both in the studies of solution equilbria [26–30] and in electrochemistry [31–33].

2. Experimental

2.1. MATERIALS

The β-CDP-25 material was a generous gift from Professor J. Szejtli of Cyclolab, Cyclodextrin Research and Development Laboratory, Budapest, Hungary. The polymer was prepared by exhaustive crosslinking of the β-cyclodextrin monomer with epichlorohydrine and poly(vinyl alcohol) [34, 35]. It contained 58 wt % of β-cyclodextrin and 0.3 wt % of poly(vinyl alcohol). The polymer was used in the form of microparticulate beads which were *ca.* 20 μm in dia. Beads were purified before use, primarily from traces of toluene [36], by prolonged washing on a sintered glass frit with several milliliter portions of a 1 : 1 (v/v) aqueous methanolic solution until the filtrate was free from UV-light absorbing impurities. Reagent grade ferrocene (Merck, Darmstadt, R.F.G.) was resublimated before use. Nitro compounds (P.O.Ch., Gliwice, Poland) were of analytical or reagent grade. They were purified prior to use by distillation under reduced pressure in the case of liquids, or by recrystallization from aqueous methanolic solutions in the case of solids. Triply distilled water was used to prepare the solutions for electrochemical experiments; the third distillation was carried out in a quartz still. The PTFE powder (Aldrich, Milwaukee, WI, U.S.A) and Ultra Superior Purity graphite powder (Ultra Carbon Corp., Bay City, MI, U.S.A.) were used for fabrication of the moulded composite electrodes.

2.2. APPARATUS AND METHODS

2.2.1. *Spectroscopy*

UV spectra in solution and IR spectra in the solid state (KBr pellets) were recorded with a Carl Zeiss (Jena, G.D.R.) Model Specord UV VIS and a Beckman Model IR 4240 spectrophotometer, respectively. Raman spectra were recorded with a Varian Model Cary 82 spectrophotometer.

The small angle X-ray scattering (SAXS) experiments were performed with the A. Paar (Princeton, NJ, U.S.A.) X-ray camera. Filtered CuK_α X-ray radiation analyzed in the range 3.4′ to 58.7′ was applied to a 2 mm thick powder sample, which was placed between Mylar foil windows.

2.2.2. *Thermochemical Techniques*

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed by means of a Dupont Model 951 and 910 apparatus, respectively. A 10 mg sample of the guest saturated β-CDP-25 polymer was heated in a nitrogen atmosphere with a scanning rate of 10 K min^{-1} in the 300 to 600 K temperature range.

2.2.3. *Electrochemistry*

An Elpan (Lubawa, Poland) electrochemical set-up composed of a Model EP-20 potentiostat, and a Model EG-20 linear sweep generator and a home-made rotating disk electrode (RDE) set-up were used. Electrochemical experiments were performed in a conventional three-electrode water-jacketed cell with a Pt wire as the counter electrode and the NaCl-saturated calomel electrode (SSCE) as the reference electrode. A glassy carbon electrode (GCE) was used as the working electrode, which was a PTFE-shrouded GC-30 glassy carbon rod (Tokai Carbon, Inc., Japan), 0.301 cm in diameter polished to a mirror finish with 1 μm Metadi II diamond paste (Buehler, Switzerland). The (β-CDP-25)–PTFE–carbon composite electrode (see below) was used as the working electrode. Potentials cited are referred to the SSCE.

2.2.4. *Inclusion Equilibria Studies*

A Premed (Warszawa, Poland) universal shaker, type 327 and a Model MPW-300 (Mechanika Precyzyjna, Warsaw, Poland) bench top centrifuge were used for wet loading of the β-CDP-25 beads with guest compounds. In the batch method used here typically a 2 mL sample of the loading solution was equilibrated in a shaker with a 20 mg portion of β-CDP-25. After *ca.* 10 min of shaking the inclusion equilibrium was reached and the polymer was separated by centrifugation. The concentration of the guest in the β-CDP-25 phase was determined by UV spectroscopy as the lowering of the guest concentration in solution. An air thermostat was used for temperature stabilization during the equilibration.

For preparation of the composite electrodes (see below) the guest loaded polymer beads were washed from the solute adsorbed on the bead surface with a few milliliter portion of the blank loading solution and then air-dried to constant mass.

All experiments were carried out at 20 ± 0.5°C, unless stated otherwise.

2.2.5. *Fabrication of Composite Electrodes*

The composite electrodes were prepared by a simplified procedure developed in Ref. [24]. A dry powder mixture of β-CDP-25 (polymer density 1.0 g cm^{-3}), wet loaded with the guest compound, graphite (density 1.7 g cm^{-3} [37]), and PTFE (pressed material density 2.3 g cm^{-3}), in a 10 : 30 : 60 per cent by weight ratio, was thoroughly ground in a mortar. (The mixture could not be prepared from suspension in an organic solvent for better bead dispersion, as recommended in Ref. [24], without affecting the inclusion equilibria involved.) The ratio of components used was chosen from the optimum range recommended for low residual currents and electrode resistance on the one hand and high mechanical stability on the other [24]. Typically, 100 mg of the dry powder mixture was transferred to a stainless-steel pellet press die in which a 12 mm long piece of thick-walled PTFE tubing was placed to provide a shroud for the pellet. The die was operated by a rotary torque wrench. The pressure applied for moulding of the pellet, *ca.* 2.1 GPa, was much higher than that used before [24]. Such a high pressure allowed moulding of the pellet at room temperature. Heating of the die to higher temperatures might affect the inclusion system during moulding. The PTFE shrouded pellet, *ca.* 4 mm thick and 4.5 mm in diameter, was removed from the die and fit mounted to the end of a heavy-walled glass tube. Electric contact was provided by a mercury drop and a tantalum wire. The mean electrode resistance of the composite electrodes through the pellet body was (15 ± 5) Ω as determined with an ohmmeter by contacting both sides of the pellet with mercury. The electrode surface was occasionally renewed by a razor blade cut. The electrodes remained mechanically stable after immersion in aqueous electrolytes because of the rather small swelling ability of β-CDP-25 [12]. By analogy to the Sephadex G-25 gel (Pharmacia Fine Chemicals, Uppsala, Sweden) for gel chromatography, the β-CDP-25 is a polymer with a water swelling capacity of about 2.5 mL/g dry material. Conventional carbon paste electrodes (CPE) doped with the redox substance loaded polymer beads [38] proved useless in the present study because the liquid binder of the paste, e.g. the Nujol mineral oil, not only extracted the guest from the β-CDP-25 phase but was also prone to dissolve in the aqueous methanolic test solutions, which lead to decomposition of the paste.

In the early stage of the present work we tried to produce β-CDP-25 films on PTFE shrouded Pt or glassy carbon disk electrodes. The β-CDP-25 is practically insoluble in any organic solvent. So, we tried to dissolve β-CDP-25 in water by prolonged heating in a PTFE autoclave at extreme temperature and pressure conditions, i.e. at *ca.* 1 GPa and 100°C. The resulting solution was unstable with respect to β-CDP-25 precipitation on a day time scale. Therefore the electrode surfaces were dip-coated immediately after the dissolving procedure was completed. However, the inclusion properties of the resulting films were rather poor so, eventually, the procedure was abandoned.

3. Results

3.1. β-CDP-25 STRUCTURAL CHARACTERISTICS

Transport of a guest molecule through the solid host material is greatly dependent on the structure of the material. This is why we attempted to determine the structural properties of β-CDP-25. The β-cyclodextrin monomer is known to form crystals with a variety of molecular packings [7]. We performed SAXS experiments with β-CDP-25. The only conclusion that could be reasonably drawn from the resulting data was that β-CDP-25 forms a predominantly non-crystalline phase. Nevertheless, there is a pronounced long-range structural organization of the polymer which manifests itself by the presence of spherical aggregates of 40 to 60 nm in diameter of an increased density.

Also, IR and Raman spectra were recorded for the β-CD crystalline monomer and for the β-CDP-25 polymer versus the respective 2-nitroaniline guest inclusion systems. Unfortunately, the spectra obtained were not very informative. Although there are significant differences between the IR and Raman spectra of the monomer and polymer (the β-CD monomer spectra are much richer in bands compared with the polymer spectra, which reveal broad unresolved peaks), no appreciable changes were observed in the spectra of the 2-nitroaniline guest before and after encapsulation both in the monomer and polymer solid hosts, similar to the behavior of the β-CD/4-nitrophenol system [28].

3.2. INCLUSION EQUILIBRIA

Inclusion properties of both the monomer and polymer of β-cyclodextrin were estimated by studying the respective inclusion equilibria.

3.2.1. *The (β-CDP-25)/Guest Inclusion Equilibria*

In order to quantify the inclusion properties of β-CDP-25 against ferrocene and a range of nitro compounds the inclusion induced polymer/solution sorption equilibria were examined and the sorption equilibrium constants, β_{pol}, determined. Also the free energy changes due to sorption, $\Delta G^{\circ}_{\mathrm{pol}} = -RT\ln\beta_{\mathrm{pol}}$, were calculated. For that purpose a series of 1 : 1 (v/v) aqueous methanolic solutions of varying concentration of each guest compound was prepared and the guest was wet loaded into the β-CDP-25 matrix. Methanol was chosen as the organic solvent component of the solution in order to enhance the solubility of the guest compound. There are only minor interactions between methanol and β-CD, $\beta_{\mathrm{sol}}(\beta\text{-CD/methanol}) = 0.4 \pm 0.1$ [39], and the included methanol is easily substituted by the studied guests.

In Figure 1 plots of typical sorption data are shown, by way of example, for nitrophenols in the log–log representation, as the ratio of the fraction of guest occupied to unoccupied inclusion sites, $\theta/(1-\theta)$, of β-CDP-25 against the equilibrium guest concentration in solution $[G]_{\mathrm{sol}}$, for over two decades of $[G]_{\mathrm{sol}}$. We estimated the population of the inclusion sites in the β-CDP-25 phase, $C^{\infty}_{\mathrm{pol}} = 0.8$ M, based on the concentration of β-CD toruses in the polymer net, which was calculated by assuming that all hydroxyl groups of β-CD participate in the polymer net formation. If the 1 : 1 inclusion complex is formed then the

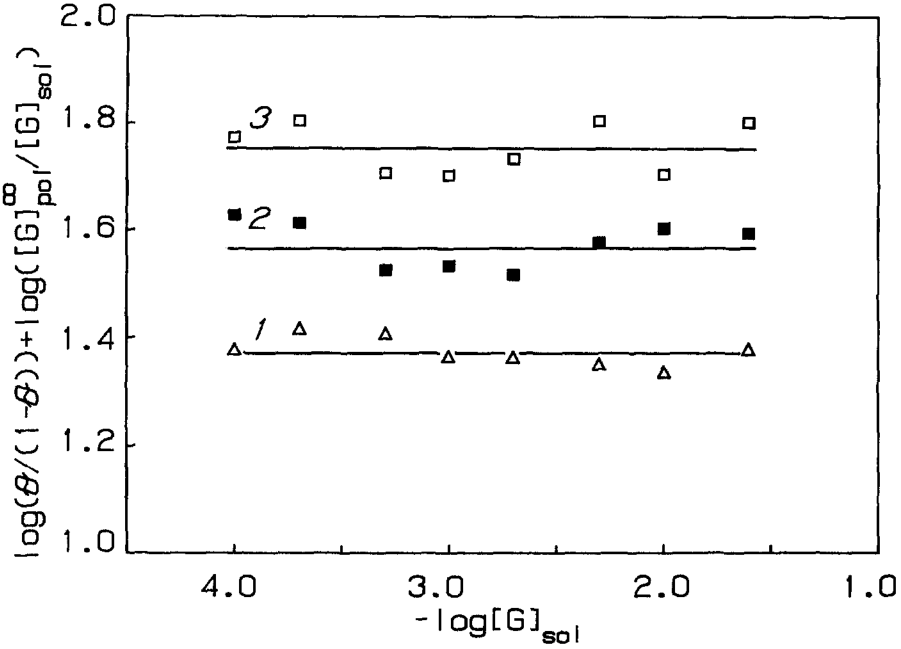

Fig. 1. Sorption isotherms in a log–log representation of the ratio of the fraction of the guest occupied to unoccupied inclusion sites, $\theta/(1-\theta)$, as a function of the equilibrium guest concentration, $[G]_{sol}$, in the 1 : 1 (v/v) aqueous methanolic solution for: *1* – 2-nitrophenol, *2* – 3-nitrophenol, and *3* – 4-nitrophenol.

maximum guest concentration, $[G]_{pol}^{\infty}$, is equal of course to C_{pol}^{∞}, provided that the guest molecules are located mostly at the inclusion sites. All sorption data appeared to be well described by the Langmuir type isotherm

$$[G]_{sol}\beta_{pol} = \theta[G]_{pol}^{\infty}/(1-\theta) \qquad (1)$$

where $\theta = [G]_{pol}/[G]_{pol}^{\infty}$ and $[G]_{pol}$ are the fraction of the guest occupied inclusion sites and the guest concentration in the β-CDP-25 phase, respectively. Straight lines parallel to the abscissa were obtained for all nitrophenols (Figure 1) as well as for all other systems studied (not shown). The calculated β_{pol} and ΔG_{pol}° values are summarized in Table I. For some systems studied θ approaches, but by no means exceeds, unity. Furthermore, analysis of Equation 1 in a linear representation, i.e. $\theta/(1-\theta)$ vs $[G]_{sol}$ (not shown), leads to straight lines with zero plot intercepts for all systems. (The scatter of intercept values does not exceed the scatter of the β_{pol} values). Hence, the complex stoichiometry is independent of the guest concentration and only 1 : 1 inclusion complexes are indeed formed.

Contrary to the coulometric method developed [40] for determination of the partition coefficient of a redox cation, which is ion exchanged into the Nafion film, the β_{pol} values were determined in the present work by using a total amount of the guest molecules wet loaded into the polymer, which was equilibrated with the solution phase. The coulometric method accounts only for that portion of the redox ions present in the polymer phase, which is accessible for charge transfer.

Table I. Sorption equilibrium constants, β_{pol}, standard free energies of sorption, ΔG^{o}_{pol}, and apparent diffusion coefficients of guests in the β-CDP-25 matrix, $D_{app,pol}$. (Standard free energies of formation of the corresponding inclusion complexes in solution, ΔG^{o}_{sol}, recalculated from literature data, are given in parentheses).

Guest Compound	β_{po} ± s.d.	ΔG^{o}_{pol} ± s.d. kJ mol^{-1}		$10^7 \times D^{a}_{app,pol}$ cm^2 s^{-1}
Ferrocene	144.3 ± 15.9	− 12.3 ± 0.6	(− 20.3[b][47], − 11.8[c][50], − 18.7[d])	0.027
2-Nitroaniline	13.1 ± 2.0	− 6.8 ± 0.9		1.8
3-Nitroaniline	11.4 ± 1.1	− 6.0 ± 0.6		0.4
4-Nitroaniline	24.2 ± 2.7	− 7.9 ± 0.6	(− 11.3 ± 1.1[e][27])	
2-Nitrotoluene	13.8 ± 1.7	− 6.5 ± 0.7		3.4
3-Nitrotoluene	12.5 ± 1.4	− 6.3 ± 0.6		9.6
4-Nitrotoluene	14.8 ± 1.2	− 6.7 ± 0.5		25
1-Chloro-2-nitrobenzene	16.0 ± 3.5	− 6.9 ± 1.2	(− 13.8[f][31])	4.7
1-Chloro-3-nitrobenzene	14.8 ± 1.9	− 6.7 ± 0.8	(− 12.3[f][31])	8.4
1-Chloro-4-nitrobenzene	11.8 ± 0.9	− 6.1 ± 0.4	(− 12.5[f][31])	35
2-Nitrophenol	11.3 ± 0.8	− 6.0 ± 0.4	(− 12.2 ± 0.8[g][27])	
3-Nitrophenol	16.6 ± 1.5	− 6.8 ± 0.5	(− 12.0 ± 0.9[h][27])	
4-Nitrophenol	26.2 ± 2.0	− 8.1 ± 0.6	(− 12.0 ± 1.4[i][27], − 14.1[j][26], − 14.6[k][28], − 17.2 ± 9.6[l][29], − 13.5[m][30])	
3,4-Dinitrotoluene	10.8 ± 3.8	− 5.9 ± 2.0		
3,5-Dinitrotoluene	15.2 ± 2.9	− 6.7 ± 1.1		
2-Nitrobenzoic acid	10.5 ± 3.3	− 5.8 ± 1.8		
4-Nitrobenzoic acid	7.4 ± 1.2	− 5.0 ± 1.0		
Nitromethane	0.0 ± 2.0	0.0 ± 1.0		57
2-Nitronaphthalene	0.0 ± 2.0	0.0 ± 0.9		0.14

[a] the β-CDP-25 phase was equilibrated with an excess of 1 mM guest solution (1 : 1 (*v*/*v*) water/methanol).

[b] RP-8 HPLC, 25% ethanol, phosphate buffer pH 6, (20 ± 2)°C.

[c] Optical rotation, methanol, 20°C.

[d] RDE, 0.1 M $NaClO_4$, 1 : 1 (*v*/*v*) water/methanol, (20 ± 0.5)°C, the present paper.

[e] UV spectroscopy, hydrochloric acid pH 0.31, (23 ± 2)°C.

[f] dc polarography, phosphate buffer pH 7 ($I = 0.5$ M), 25°C.

[g] UV spectroscopy, phosphate buffer pH 6.8, (23 ± 2)°C.

[h] UV spectroscopy, phosphate buffer pH 7.6, (23 ± 2)°C.

[i] UV spectroscopy, phosphate buffer pH 6.4 (23 ± 2)°C.

[j] Gel chromatography, 0.01 M CH_3COONa pH 4.3.

[k] IR spectroscopy, phosphate buffer pH 3.5 ($I = 0.25$ M), 23°C.

[l] Calorimetry, water (25 ± 0.1)°C.

[m] NMR spectroscopy, phosphate buffer pH 6, 20°C.

It is interesting to note that the concentration in the polymer phase of a non-included guest, e.g. nitromethane or 2-nitronaphthalene, is at most equal to the concentration of the guest in the loading solution, since no concentration decrease in the solution was observed upon wet loading. However, the partition coefficient, $P = [G]_{pol}/[G]_{sol}$, (determined as the slope of the linear, rising portion of the $[G]_{pol}$

vs $[G]_{sol}$ plot, not shown), varies in the range $(12 \pm 1) \leq P \leq (99 \pm 2)$ for 4-nitrobenzoic acid and ferrocene, i.e. the most weakly and strongly included guests, respectively (Table I). Hence, one may infer that the guest molecules occupy predominantly the inclusion sites of the β-CDP-25 matrix. So, the calculated β_{pol} and ΔG^{o}_{pol} values may be regarded as stability constants and free energy changes, respectively, of the β-CDP-25/guest inclusion complexes formed and the isotherms constructed as inclusion isotherms [41].

3.2.2. *The (β-CD)/Guest Inclusion Equilibria in Solution*

To compare inclusion properties of the polymer and monomer forms of β-CD, the ΔG^{o}_{pol} values obtained in the present work were compared with the correponding literature values of the standard free energy change due to the formation of the inclusion complex, ΔG^{o}_{sol} (Table I). Additionally, in the present paper the stability constant of inclusion complex formation in 1 : 1 (v/v) aqueous methanolic solution, β_{sol}, was determined and ΔG^{o}_{sol} calculated for the β-CD/ferrocene system. For that purpose the RDE experiments were performed in the $900 \leq f \leq 4900$ rpm range at the GCE. By using the Levich equation:

$$i_l = 0.620\, n\, F\, A\, D^{2/3}_{app,sol} \omega^{1/2} \nu^{-1/6}\, C_{sol} \tag{2}$$

the $D_{app,sol}$ values of the apparent guest diffusion coefficient in solution was determined (n, F, and A denote the number of electrons transferred, the Faraday constant and the electrode surface area, respectively; ν is the kinematic viscosity of the 1 : 1 (v/v) aqueous methanolic solution and ω the rotation frequency in rad s^{-1}). In Figure 2 Levich plots are shown of the limiting current, i_l, of the ferrocene oxidation against the square root of rotation frequency (in rpm), $f^{1/2}$, for the β-CD/ferrocene system for a range of analytical β-CD concentrations, $C_{\beta\text{-CD},sol}$. Straight lines with zero plot intercepts were obtained, which is typical of mass transport-controlled charge transfer. This indicates that the rates of the inclusion complex equilibria involved are too high to affect limiting currents. The apparent diffusion coefficient of ferrocene obtained in the present work, $D_{G,sol} = 5.6 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ is more than twice as large as that in acetonitrile, $D = 2.4 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ [42], whereas one would rather expect an inverse correlation in view of the lower kinematic viscosity of acetonitrile. The discrepancy may result from the different experimental conditions used. Nevertheless the data obtained in the present study are consistent within the experimental series and are useful for comparison purposes. The $D_{G,sol}$ value for ferrocene is ca. 5 times larger than the apparent diffusion coefficient of its β-CD inclusion complex, $D_{G\text{-}(\beta\text{-CD}),sol}$. Astonishingly, the latter is larger than the diffusion coefficient of β-CD itself, which is $D_{\beta\text{-CD}} = 3.3 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$ [43], as determined by using the Stokes–Einstein relation. Since the apparent diffusion coefficient is inversely proportional to the effective radius of the diffusing species, the radius of the solvated β-CD/ferrocene complex is ca. 5 times higher than the ferrocene radius. The presence of β-CD in aqueous solution affects only slightly the kinematic viscosity of solution [33] and therefore β_{sol} could be determined by using the equation [44–46]:

$$\beta_{sol} = (D_{app,sol} - D_{G,sol})/((D_{G\text{-}(\beta\text{-CD}),sol} - D_{app,sol})[\beta\text{-CD}]_{sol}) \tag{3}$$

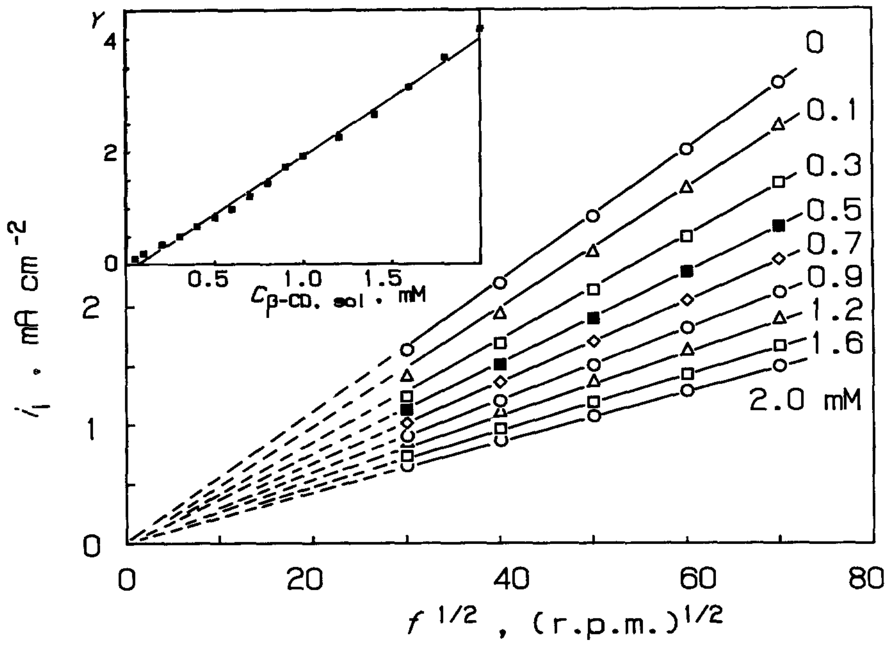

Fig. 2. Levich plots of density of the limiting oxidation current of 1 mM ferrocene, i_l against the square root of the rotation frequency, $f^{1/2}$, in 0.1 M $NaClO_4$, 1 : 1 (v/v) water/methanol, for different analytical concentrations of β-CD, $C_{\beta\text{-CD,sol}}$, indicated by numbers by each curve; inset is a $Y = (D_{\text{app,sol}} - D_{\text{G,sol}})/(D_{\text{G,(}\beta\text{-CD),sol}} - D_{\text{app,sol}})$ dependence on $C_{\beta\text{-CD,sol}}$ (Equation 3).

which holds for rapid exchange of a guest between its free and bound forms. The solid line in the inset of Figure 2 is computed by the best fit of the $D_{\text{app,sol}}$ data to Equation 3. The high value of the correlation coefficient obtained, $r = 0.995$, indicates, in addition to the result of the Levich analysis, that Equation 3 adequately accounts for the data over the entire β-CD concentration range and makes the assumption about the rapid guest exchange justified. The calculated value of β_{sol}(β-CD/ferrocene) $= (2.1 \pm 0.04) \times 10^2\ M^{-1}$ is close to that obtained by liquid chromatography [47] (Table I).

Besides the decrease of the RDE limiting current with the increase of the β-CD concentration a 20 mV shift was observed in the half wave potential, $E_{1/2}$, of the RDE step when the β-CD concentration was increased from zero to 2 mM. Assuming that neither the β-CD complex of ferrocene nor of the ferricenium cation is electroactive and their diffusion coefficients are similar, charge is also transferred to the free guest, and the guest exchange is fast one may calculate the stability constant of the β-CD/(ferricenium cation) complex, $\beta_{+\text{sol}}$, by using the equation [49]:

$$\Delta E_{1/2} = (RT/F)\ln(\beta_{+\text{sol}}/\beta_{\text{sol}}) \tag{4}$$

After correcting the $\Delta E_{1/2}$ value for ohmic potential loss the value of $\beta_{+\text{sol}} = 950\ M^{-1}$ was calculated.

The RDE method, which worked so well for the β-CD/ferrocene system, appeared impractical for determining the stability constants of the inclusion complex formation in the β-CD/(nitro compound) systems. For instance,. based on the literature value of β_{sol} for 4-nitrophenolate, which is ca. $10^3\ \mathrm{M}^{-1}$ [33], one could expect a 65% decrease (well beyond the 3% r.s.d. experimental error) of the RDE limiting current in the 4-nitrophenolate solution, pH 10, saturated with β-CD, as compared with the β-CD free solution. However, no measurable decrease of the limiting current of the four-electron reduction step was observed after addition of β-CD to the basic solution of a nitro compound, even after saturation with β-CD was reached. Moreover, the observed limiting currents were time dependent. Presumably, the slow chemical equilibria involved are superimposed on the charge transfer.

The literature values of β_{sol} for the regioisomers studied vary in the same order as the values of the sorption equilibrium constants, β_{pol}, calculated in the present paper for inclusion complexes in the polymer phase (Table I). Hence, one may infer that the mechanism of complex formation and the factors which affect the complex stability are similar for the monomeric and polymeric β-cyclodextrin forms and the contribution of the polymer network to the complex equilibria is fairly small.

3.3. THERMAL CHARACTERISTICS OF THE β-CDP-25/GUEST SYSTEM

In the solid monomer β-CD/guest system the tightly bound guest molecule is either not liberated upon heating [4, 50] or is liberated [9] just before the thermal degradation of β-CD at ca. 573 K.

In our TGA and DSC experiments on the β-CDP-25 polymer, ferrocene and 2-nitroaniline were chosen as probing guests. Ferrocene forms the most stable inclusion complex with the β-CDP-25 studied in the present work and 2-nitroaniline may be regarded as a representative guest of nitro compounds.

Similarly to the behavior of the monomer system, in the polymer system besides a rapid mass loss below 373 K (TGA), accompanied by heat absorption (DSC, ca. 17 J per gram of the sample), which was presumably due to the water release, we did not observe any significant heat exchange and mass decrease below ca. 573 K, i.e. before thermal degradation of the β-CDP-25 polymer occurred.

3.4. ELECTROCHEMISTRY OF THE β-CPD-25/GUEST INCLUSION SYSTEMS

The study of the electrochemical characteristics of the β-CDP-25/guest inclusion system was performed by cyclic voltammetry, CV, at the (β-CDP-25)–PTFE–carbon composite electrode preloaded with a guest. The CV behavior of ferrocene in such a system in the ferrocene free solution (Figure 3) is similar to the behavior of ferrocene at GCE with ferrocene present in solution. No differences in the formal potentials are observed and the peaks have a diffusion-tailed shape. The linear dependence of the anodic, i_{pa}, (and cathodic, i_{pc}, not shown) peak current versus the square root of the potential scan rate, $v^{1/2}$, in the $10 \leq v \leq 200\ \mathrm{mV\ s}^{-1}$ range with zero plot intercept (Figure 3, inset) and the scan rate-independent 75 mV difference of the anodic and cathodic peak potentials (fairly close to the theoretical 59 mV value), point to a semi-infinite diffusion control. The positive deviation of

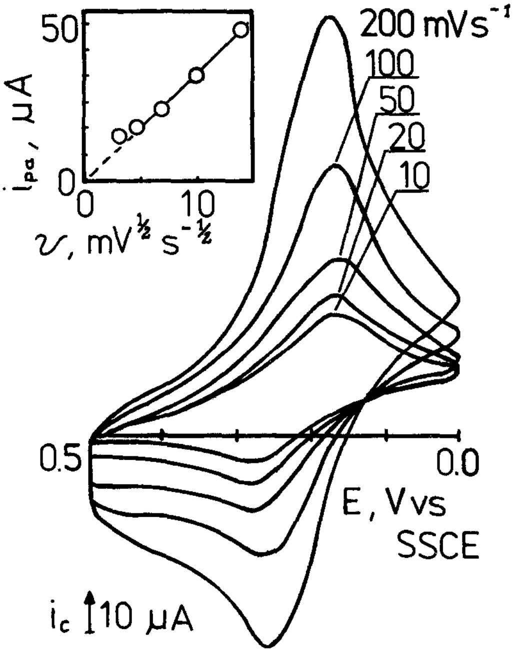

Fig. 3. Cyclic voltammograms at the ferrocene loaded (β-CDP-25)–PTFE–carbon composite electrode in 0.1 M $NaClO_4$, 1 : 1 (v/v) water/methanol; ferrocene concentration in the polymer phase, $[G]_{pol} = 0.8$ M. The electrode was kept at the initial potential, $E_i = 0.5$ V, until oxidation current decayed to zero. Potential scan rate is indicated by numbers by each curve. Inset is the plot of the anodic peak current, i_{pa}, against the square root of the potential scan rate, $v^{1/2}$.

the data at small v values from the straight line (inset) may be ascribed to the sphericity of diffusion inside the bead, which has been reported before for other systems [38]. The apparent diffusion coefficients of ferrocene and of the ferricenium cation in the polymer matrix, $D_{app,pol}$, were calculated by using the Randles–Sevcik equation:

$$i_p = 2.69 \times 10^5 n^{3/2} A_{eff} D_{app,pol}^{1/2} v^{1/2} [G]_{pol} \tag{5}$$

where n and A_{eff} are the number of electrons transferred and the effective electrode surface area (see below), respectively. Note that the diffusion coefficient of the ferricenium cation is larger by the factor of 1.4 than that of ferrocene. The calculated value of $D_{app,pol}$ for ferrocene is close to the one determined by chronoamperometry (see below), which is presented in Table I.

There was no leakage of ferrocene to the solution, which was checked in the multi-scan CV experiment at the ferrocene preloaded composite electrode in which a ferrocene-free background solution was vigorously stirred. The peak currents of successive CV curves were independent of the scan number.

The pattern of cyclic voltammetry curves in a guest free supporting electrolyte at the (β-CDP-25)–PTFE–carbon composite electrode, loaded preliminarily with a nitro compound, differed substantially from the corresponding curves recorded at the GCE with the guest present in the test solution. Illustrative is Figure 4 in which

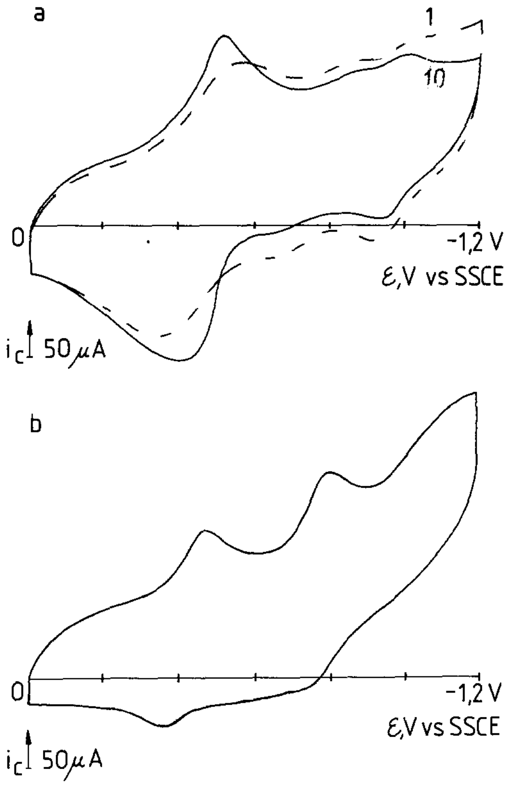

Fig. 4. Cyclic voltammogram at the 50 mV s^{-1} potential scan rate (a) at the 3-nitroaniline loaded (β-CDP-25)-PTFE-carbon composite electrode in 0.1 M $NaClO_4$, 0.1 M NaOH, 1 : 1 (*v*/*v*) water/methanol (concentration of 3-nitroaniline in the β-CDP-25, $[G]_{pol} = 0.1$ M, scan number at each curve), and (b) of 1 mM 3-nitroaniline in 0.1 M $NaClO_4$, 0.1 M NaOH, 1 : 1 (*v*/*v*) water/methanol at GCE.

cyclic voltammograms are shown, by way of example, for the 3-nitroaniline-loaded electrode. In contrast to the solution behavior, which is independent of the scan number (Figure 4b), upon multiple cycling in the 0 to -1.2 V potential range the redox peak currents of the system at the most positive potentials grows at the expense of the currents at the most negative ones. The former corresponds to the reversible one-electron reduction to the respective nitro anion radical [51]. A similar behavior is observed, although to a different extent, for each nitro compound system studied. Obviously, stabilization of the free radical takes place in the β-CDP-25 environment and this requires further scrutiny [52].

3.5. GUEST TRANSPORT THROUGH THE β-CDP-25 MATRIX

Transport phenomena occurring in the β-CDP-25/guest system were evaluated by determining the apparent diffusion coefficients of the guest compounds in the β-CDP-25 matrix. Chronoamperometry was used for that purpose at the (β-CDP-25)-PTFE-carbon composite electrodes loaded before with a guest compound.

Experiments were peformed in the guest free, 1 : 1 (v/v) aqueous methanolic background solution, which was 0.2 M in $NaClO_4$ and 0.1 M in NaOH. At such a solution composition the CV voltammograms obtained for all preloaded composite electrodes were the best developed. Chronoamperometric current transients were obtained after the application of potential steps of 0 to 0.5, 0.1 to −0.5, and 0.1 to −1.0 V for ferrocene, nitroaniline and other nitro compound systems, respectively. Working potentials applied for the nitro compound analyses were more negative than respective reduction peaks at the most negative potentials. Since no qualitative differences were observed at cyclic voltammograms (at least at first scans) for β-CD/guest systems in solution at GCE and for loaded composite electrodes in a guest free solution a four-electron charge transfer for the latter was adopted, similar to the case for the former [51]. Figure 5 shows a set of typical i vs $t^{-1/2}$ plots for the (β-CDP-25)/nitrotoluene systems. For $0.8 \le t \le 4.0$ s straight lines with zero plot intercepts were obtained, as predicted for diffusion-controlled processes by the Cottrell equation:

$$i = n\,F\,A_{\text{eff}} D_{\text{app,pol}}^{1/2} [G]_{\text{pol}} / (\pi^{1/2} t^{1/2}). \tag{6}$$

The calculated $D_{\text{app,pol}}$ values are summarized in Table I. These values are to be considered merely as rough approximations because there are at least two perceivable apparent sources of discrepancy in the $D_{\text{app,pol}}$ calculation.

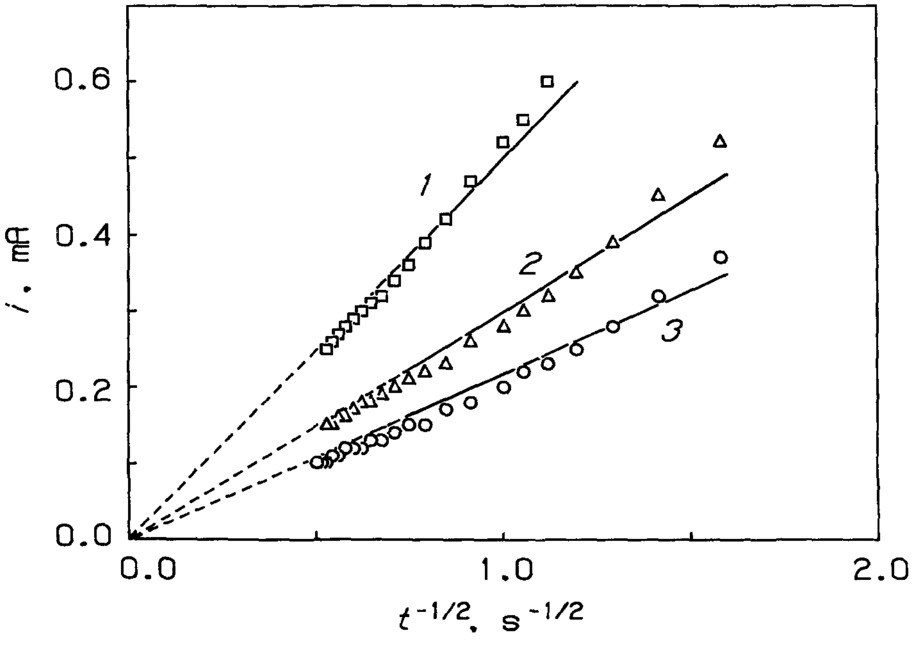

Fig. 5. Cottrell plots of the four-electron reduction at the guest preloaded (β-CDP-25)–PTFE–carbon composite electrodes in 0.2 M $NaClO_4$, 0.1 M NaOH, 1 : 1 (v/v) water/methanol solution of *1* – 4-nitrotoluene, $[G]_{\text{pol}} = 16$ mM, *2* – 3-nitrotoluene, $[G]_{\text{pol}} = 14$ mM, and *3* – 2-nitrotoluene, $[G]_{\text{pol}} = 16$ mM. The potential step applied was from 0.1 to −1.0 *V*.

(i) The value of $[G]_{\text{pol}}$ may be too high because it corresponds to the total guest content in the polymer phase (see above) rather than that accessible for charge transfer.

(ii) The effective surface area of the composite electrode was approximated as $A_{\text{eff}} = 0.33\ \text{cm}^2$. The assumption adopted here was [38] that A_{eff} is equal to that fraction of the 0.196 cm^2 overall electrode area which corresponds to the cross-sectional area of the spherical polymer microparticles exposed to solution. The implication is that the heterogeneous charge exchange takes place at the polymer/graphite boundary of contact, which is accessible to solution. The calculation of A_{eff} was based on the relative wt % composition of the composite electrode. The polymer swelling was taken into account in these estimations by invoking the factor of 2.5 by which the volume of the polymer being in contact with solution is higher than that of the dry one.

Measurements were also performed on the dependence of $D_{\text{app,pol}}$ on the ferrocene concentration in β-CDP-25. They revealed that the $D_{\text{app,pol}}$ value, obtained by the Cottrell analysis at the composite electrode decreases by more than one order of magnitude with the increase of $[G]_{\text{pol}}$ in the $0.01 \leq [G]_{\text{pol}} \leq 0.8$ M concentration range (Figure 6).

The Arrhenius analysis of $D_{\text{app,pol}}$ was performed in the 0 to 40°C range for the ferrocene preloaded composite electrode

$$D_{\text{app,pol}} = D_{0,\text{pol}} \exp(-E_a/RT) \tag{7}$$

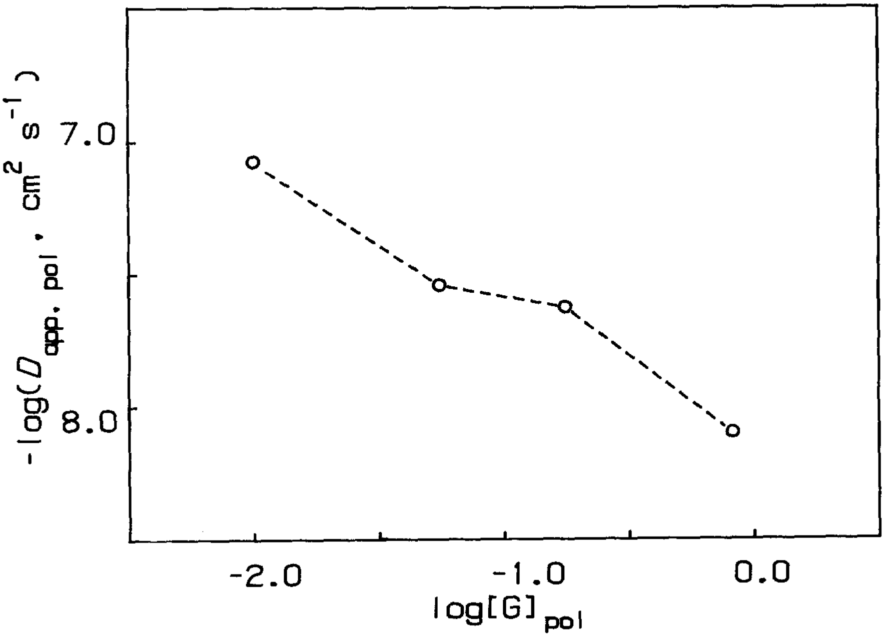

Fig. 6. Log–log dependence of the apparent diffusion coefficient of ferrocene in the β-CDP-25/ferrocene system, $D_{\text{app,pol}}$, on the ferrocene concentration in the β-CDP-25 phase, $[G]_{\text{pol}}$, as determined by the Cottrell analysis at the (β-CDP-25)–PTFE–carbon composite electrode in 0.1 M NaClO_4, 1 : 1 (v/v) water/methanol.

to determine the activation energy of diffusion, E_a. The dependence of the logarithm of $D_{app,pol}$ (determined for ferrocene by the Cottrell analysis) on the reciprocal of absolute temperature was linear (not shown). The ferrocene concentration range was $0.01 \leq [G]_{pol} \leq 0.8$ M. The mean value of E_a found from the slope of the straight lines obtained was equal to 13 ± 3 kJ mol^{-1}. This value is on the one hand comparable with ΔG^0_{pol} of the (β-CDP-25)/ferrocene system (Table I) and on the other much higher than the E_a value for charge transport in redox conducting polymers [53].

4. Discussion

The β-CDP-25 polymer preserves the ability of the β-CD monomer to form inclusion complexes. Strong host–guest interactions were confirmed by our thermal analysis experiments. It is misleading to compare directly the change of the standard free energy of formation of an inclusion complex in solution and that in the polymer phase since their standard states of reference are different. Sorption of nitroanilines by β-CDP-25 increases in the order *3-*, *2-*, *4-*, which is the same as that of β-CD polyurethane resins [11]. Generally, *4-* isomers give the largest sorption equilibrium constants (Table I) as they usually penetrate farthest into the β-CD cavity [54].

Apparently, one might expect more stable complexes to be formed by the β-CD-25 polymer because of the physical sorption by the polymer net, which accompanies inclusion and additionally increases the guest content in the β-CDP-25 phase. However, this sorption effect does not seem to be significant. For instance, a dextrin polymer phase is prone to sorb only negligible amounts of a guest [10]. Also, no enrichment of the β-CDP-25 polymer phase was observed for guests which are not included, e.g. 2-nitronaphthalene and nitromethane (Table I). The molecule of 2-nitronaphthalene is simply too big and the nitromethane one too small to give rise to the stabilization energy due to the van der Waals interactions of the guest with the β-CD torus, which is 0.60–0.64 nm in inner diameter [55]. (The approximate diameter of 2-nitronaphthalene and nitromethane is 0.8 and 0.3 nm, respectively as estimated by using the literature values of bond lengths [56, 57]. Because of steric hindrance, there is also practically no inclusion of some naphthalene methyl derivatives by β-CD [58].

The β-CDP-25/guest inclusion data are well described by the Langmuir isotherms for all systems. Hence, no extra-thermodynamic parameters are necessary to account either for the guest mutual interactions or for the accessibility of sorption (inclusion) sites. Therefore, one may infer that mutual interactions of guest molecules in the polymer matrix are apparently absent. We have recently confirmed this conclusion by the ESR spectroscopy of free radical guests entrapped in the β-cyclodextrin polymer [52]. We found that radical guest molecules were well isolated from one another because there was practically no spin exchange between the radicals occupying the inclusion sites, even at high guest loads. Moreover, we have shown by Mösbauer spectroscopy that the ferrocene molecules are molecularly dispersed in the β-CDP-25 matrix and exercise rather high vibrational mobility at inclusion sites [59]. Also, it was shown by ^{2}H-NMR spectroscopy [60] that 4-nitrophenol is mobile in the cavity of β-CD and this motion is mostly rotation about its polar C1–C4 axis, which is an axis common with that of β-CD.

Hence, microscopically, the charge propagation through the β-CDP-25 phase may be perceived as being accomplished either by electron exchange between guest molecules located at adjacent inclusion sites or by hopping of guest molecules between inclusion sites. The dependence of $D_{\mathrm{app,pol}}$ on the guest concentration in the polymer seems to be decisive in that respect. The increase of $D_{\mathrm{app,pol}}$ with the increase of $[G]_{\mathrm{pol}}$ is expected for the former mechanism [25, 61]. The opposite dependence, which was observed herein for ferrocene, may point to the latter mechanism. Therefore we propose, by analogy to the hopping mechanism of electron transport in conducting polymers of fixed redox sites [62], to assume that the charge diffusion through the β-CDP-25 matrix invokes hopping of a guest molecule between neighboring occupied and unoccupied inclusion sites. Obviously, this diffusion is accompanied by the back diffusion of ions produced at the charge exchange site and diffusion of counter ions, which are introduced and removed from the polymer phase for charge compensation. The hopping, driven by the concentration gradient, is quite rapid since the apparent diffusion coefficients, $D_{\mathrm{app,pol}}$, are rather large as for solids. The value of the Arrhenius energy barrier is in harmony with the change of free energy of dissociation of the β-CDP-25/ferrocene inclusion complex and may indicate that the energy of the host–guest bond breaking is the main contribution to the activation energy barrier of the guest diffusion in the system.

The β-CDP-25 polymer seems promising for membrane-type applications because it is fairly selective, chemically inert and insoluble both in protic and in aprotic solvents. Besides it provides a fairly fast guest transport. Moreover, the diffusion coefficients found for different regioisomers are different. For instance, for nitrotoluenes and chloronitrobenzenes they decrease by a factor of ca. 6 in the order from *4*- through *3*- to *2*- isomers.

Acknowledgments

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