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ORIGINAL ARTICLE

The response behavior of PPy-DB18C6 electrode to terbium(III) in acetonitrile and its thermodynamic application



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Abstract Polypyrrole modified electrode prepared by electropolymerization of pyrrole in the presence of a complexing ligand, dibenzo-18-crown-6(DB18C6), was prepared and investigated as a Tb^{3+} -selective electrode in acetonitrile. The potentiometric response of the electrode was linear within the Tb^{3+} concentration range 1×10^{-5} – 1×10^{-2} M with a Nernstian slope of 20.9 mV decade⁻¹ in AN. The electrode was applied to study the complexation of the terbium(III) ion in acetonitrile with such other basic aprotic solvent molecules (*D*) as dimethyl sulfoxide, *N,N*-dimethyl formamide, propylene carbonate and pyridine. The successive complex formation constant (β_i) and Gibbs energies of transfer (ΔG_{tr}) of Tb^{3+} in AN in relation to such *D* were obtained. © 2012 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

1. Introduction

Most chemical reactions proceed in solution, and solvation has a strong effect on the reactivity of compounds. Using non-aqueous solvents instead of aqueous systems results in significant differences in both the solubility of hydrophobic compounds and the dissociation of electrolytes, and also in

both the activities and Gibbs energies of ions. Since the thermodynamic data obtained from ion–solvent complex formation are very important for estimating and predicting such effects as those mentioned above, many investigations (Fawcett, 2004; Ahrand, 1978; Gutmann, 1978; Burger, 1983; Mamantov and Popov, 1994; Izutsu, 2002; Marcus, 1985, 1997, 1998) have been carried out by means of analytical methods, such as IR, NMR, Raman spectroscopies, conductometry, potentiometry, and calorimetry. Among these methods, the potentiometric method is preferable because of its preciseness. Ion-selective electrodes can be used directly to trace activity changes of ions in solution. The application of ion-selective electrodes in non aqueous and mixed solvents to thermodynamic studies was reviewed by Pungor et al. (1983). Studies that aimed to determine the successive complex formation constants between a monovalent cation and solvent molecules using a monovalent cation sensitive glass electrode

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(Beckman Co., Ltd.) were reported (Nakamura et al., 1990, 1994, 1999; Izutsu et al., 1980). Also, the thermodynamic response ability of the electrode not only to activity change due to an alteration in its concentration, but also to that due to a change of the solvent was confirmed (Nakamura, 1975). These studies certified the effectiveness of an ion-selective electrode for investigating the ion-solvent complex formation reactions.

Conducting polymers, due to their imprinting and templating ability, have been widely used for the development of highly selective sensors (Lange et al., 2008; Gupta et al., 2006). Polypyrrole (PPy) is one of the most extensively used conducting polymers in the design of chemical sensors. This polymer has good stability, facile synthesis, higher conductivity and versatility compared to many other conducting polymers (Ansari, 2006; Wang et al., 2001). Further, PPy can be easily coated as thin adherent films on various metal or carbon substrates by electropolymerization from aqueous or organic solvents. These characteristics make PPy highly suitable for various electrochemical applications including voltammetric (Shiu and Chan, 1995; Arrigan and Lowens, 1999; Song and Shiu, 2001; An et al., 2002), potentiometric (Blaz et al., 2000; Vazquez et al., 2005; Alvarez-Romero et al., 2007; Sahin et al., 2008), amperometric (Sode et al., 2003) and impedimetric (Giroud et al., 2009; Cortina-Puig et al., 2007) techniques for the determination of various cationic, anionic and neutral molecular species.

Terbium is an important member of the rare earth family and is used in cathode ray tubes, magnets optical computer memories and magnetostrictive alloys. Nowadays, determination of terbium is considered necessary because of the increasing interest in bioinorganic and inorganic chemistry, increased industrial use and also its increased discharge toxic properties and other adverse effects. A number of investigations into the development of terbium selective electrodes in aqueous solutions have been reported in the literature (Ganjali et al., 2005; Zamani et al., 2006; Gupta et al., 2008), but in this work, for the first time we have reported a Polypyrrole modified based terbium-ion-selective electrode for use in nonaqueous solutions such as acetonitrile for thermodynamic investigations. In nonaqueous solvents, such measurements have been largely limited to membrane electrodes using glass or crystalline sensing elements (Izutsu et al., 1980; Cox et al., 1974; Nakamura et al., 1982) because of possible damage to or dissolution of electrode components by organic solvents. But this electrode has both time stability and well-defined potentiometric behavior.

2. Experimental

2.1. Materials and reagents

Dibenzo18-crown-6 (Fluka), Pyrrole (>97%, Merck) and terbium(III) nitrate (Merck) were used without further purification. Tetraethylammonium perchlorate was purchased from Aldrich Chemical Co. The solvents: acetonitrile, dimethyl formamide, dimethyl sulfoxide, propylene carbonate and pyridine all from Merck Company were used with the highest purity.

2.2. Apparatus

The electrochemical polymerization of pyrrole was performed using a μ Autolab electrochemical system (Eco-Chemie,

Utrecht, The Netherlands) equipped with NOVA software (Eco-Chemie, Utrecht, The Netherlands). The electrochemical cell was assembled with a conventional three-electrode system; an Ag/AgCl/KCl (3.5 M) reference electrode (Metrohm, Herisau, Switzerland) and a platinum wire as a counter electrode. The working electrode, to be covered with PPy/DB18C6 film, was a graphite disk electrode with an area of about 2 mm². The potentiometric measurements were carried out on a Metrohm Model 692 digital pH/Ion Meter. All experiments were typically conducted at 25 ± 2 °C. The electronic absorption spectra of solutions were recorded in acetonitrile solvent in the region of 200–700 nm using an Agilent UV-Vis spectrophotometer and a quartz cell of 1.0 cm path length.

2.3. PPy film electrode preparation

A graphite disk electrode was fabricated from a graphite rod, and housed in a Teflon body. The surface of the disk electrode (2 mm diameter), was polished with a SiC paper. The electrode was rinsed with water and allowed to dry. Two milligram modifier (DB18C6) was dissolved in 1 ml of pyrrole. Then a volume 0.5 μ l of this solution was syringed at the end of the disk. Copper wire contacted to the other end, providing the electric contact. The electrode was placed in a solution containing 0.025 M pyrrole and 0.1 M NaNO₃, and polypyrrole formed electrochemically on the electrode by the cyclic voltammetry method. Fig. 1 shows the voltammograms recorded during the polymerization of Py. In this procedure, the potential was scanned from -0.7 to 1.3 V at the scan rate of 50 mVs⁻¹ three times. The electrode was then conditioned in dry acetonitrile containing 1.0 × 10⁻³ M Tb(NO₃)₃ and 0.01 M Et₄NClO₄ for 2 h.

2.4. Potentiometric measuring system

The potentiometric response of the electrode to Terbium cation was investigated by measuring Cell 1. All compartments of Cell 1 were freshly prepared each time. Steady state potentials were read to ± 1 mV.

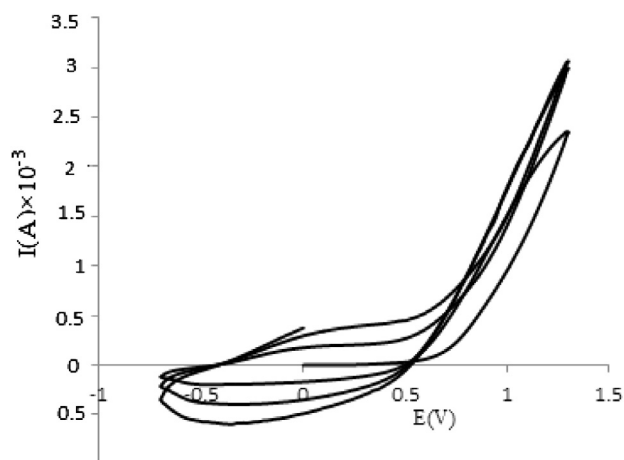


Figure 1 Repetitive CVs for the polymerization of Py in a solution containing 0.025 M pyrrole and 0.1 M NaNO₃, Scan rate: 50 mVs⁻¹.

Ag|10 mM AgNO₃
 + 10 mM Et₄NClO₄(AN)||50 mM Et₄NClO₄(AN)|| c Tb(NO₃)₃
 + 10mM Et₄NClO₄(AN)|PPy
 – [DB18C6]membrane|graphite electrode Cell 1

where c is the concentration in mol dm⁻³ of Tb(NO₃)₃, which was added by a microburet. The change in the liquid-junction

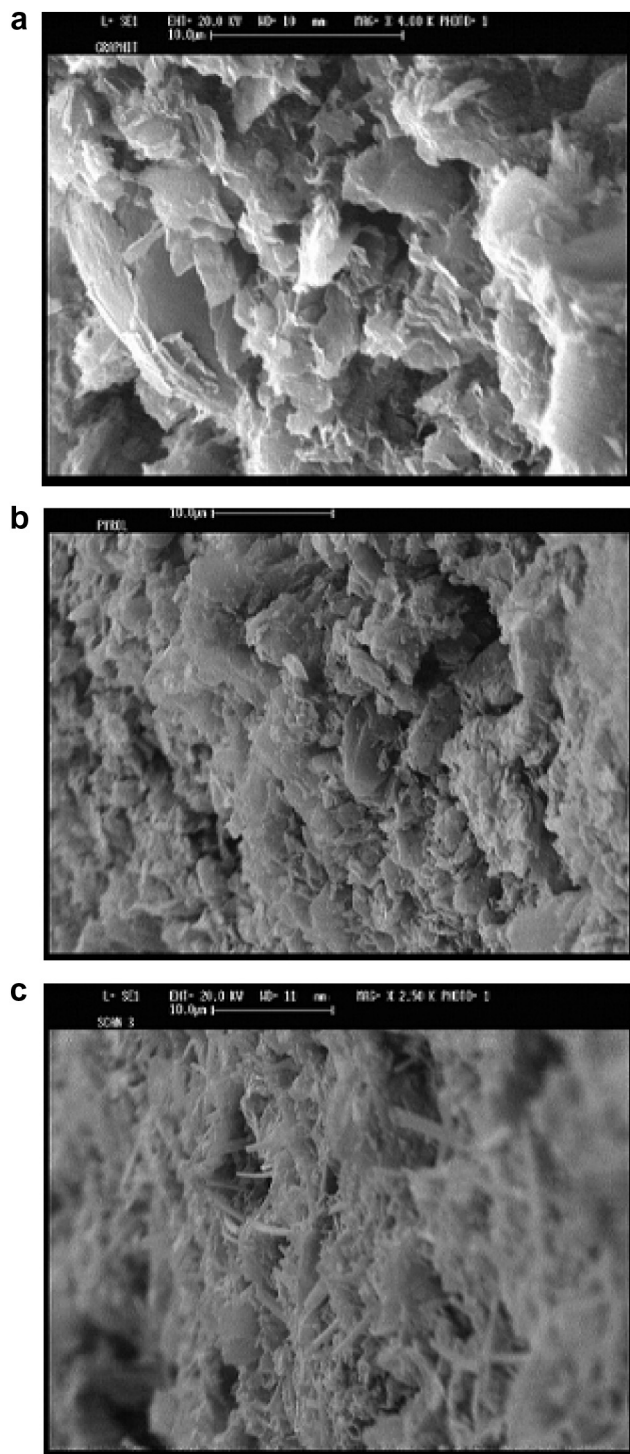


Figure 2 SEM images of GDE (A), PPy-GDE (B) and PPy/DB18C6-GDE (C).

potentials of Cell 1 during emf measurements was negligible in the experiment (Izutsu et al., 1991).

2.5. Determination of the successive complex formation constants and Gibbs energy of transfer

The EMFs of Cell 2 were measured,

Ag|10 mM AgNO₃
 + 10 mM Et₄NClO₄(AN)||50 mM Et₄NClO₄(AN)||Tb(ClO₄)₃
 + 10 mM Et₄NClO₄(AN + D)|PPy
 – [DB18C8]membrane|graphite electrode Cell 2

Where D denotes DMF, DMSO, PC and Py. AN was used in the experiments as reference solvent (R). Small amounts of solvent D were added stepwise into the cell to obtain successive complex formation constants. The steady-state potential was obtained within 2 min and the emf change was recorded to 1 mV.

3. Results and discussion

3.1. SEM Images of GDE (graphite disk electrode), PPy-GDE and PPy/DB18C6-GDE

The typical morphology of GDE and PPy-GDE is shown in Fig. 2a, b. The image of PPy/DB18C6-GDE is shown in Fig. 2c, compared to PPy-GDE, the surface of PPy/DB18C6-GDE is hybrid of poly pyrrole and submicron-scale particle of DB18C6.

3.2. Spectrophotometric measurement

Trivalent lanthanide ions have the outer shell electronic configuration as [Xe] 4f⁽¹⁻¹⁴⁾ 5d¹6s². The bonds between lanthanum ion and the macrocyclic DB18C6 ionophore are mainly ion-dipole and non-directional, and are similar to those between alkali metal ions and crown ethers since the 4f electrons are effectively shielded. Thus, in order to understand the peculiar selective response ability of the electrode, UV-Vis spectrophotometric investigations in AN were carried out. A solution of Tb(NO₃)₃ in AN was titrated by stepwise addition to AN solution which contained a constant concentration of DB18C6 (2.0×10^{-5}). The UV-Vis spectra of these solutions are shown in Fig. 3. The spectrum of the original solution of DB18C6 in AN had a high peak at about 215 nm, then it decreased with increasing Tb³⁺. These results indicate that DB18C6 interacts with Tb³⁺. It is reasonable to consider that the experimental observation of Nernstian response to Tb³⁺ indicated that stable complex formation and ion-distribution between the sensor membrane and the solution may occur.

3.3. Conductometric measurement

The equilibrium constant and the thermodynamic parameters for complex formation of dibenzo-18-crown-6 with La⁺³ cation have been determined by conductivity measurements in acetonitrile. Fig. 4 shows the changes in the conductance of 20 ml of 1×10^{-4} M solution of Tb³⁺, by the addition of a 2×10^{-3} M of DB18C6 in AN. The results showed that, the ligand to cation mole ratio is 1, indicating the formation of

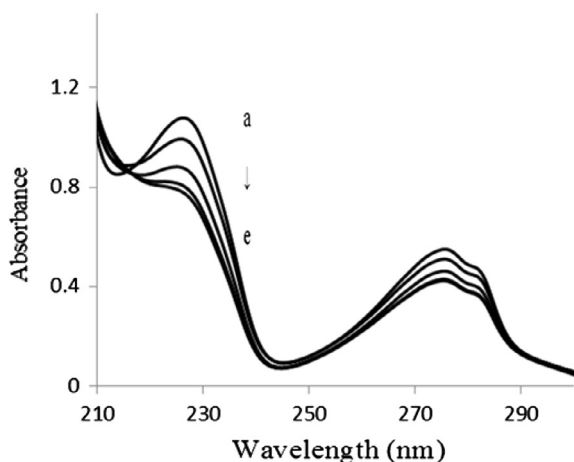


Figure 3 UV-Vis spectra of the interaction between DB18C6 and terbium ion in acetonitrile. All of the solutions contained 2×10^{-5} M DB18C6. Concentration of Tb^{3+} : (a) 0; (b) 1×10^{-6} ; (c) 1×10^{-5} ; (d) 5.5×10^{-4} ; (e) 1×10^{-3} M.

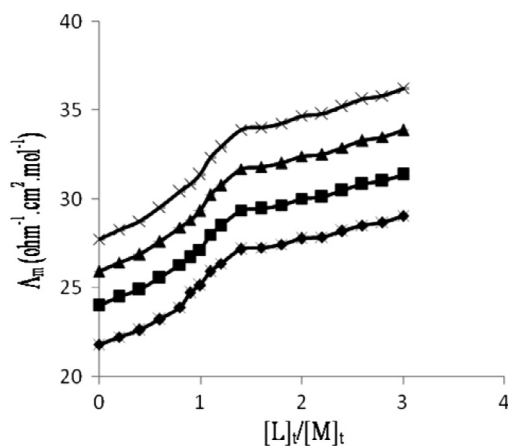


Figure 4 Molar conductance-mole ratio plots for $(DB18C6.Tb)^{3+}$ complex in AN at different temperatures ($\diamond = 15^\circ C$, $\blacksquare = 25^\circ C$, $\blacktriangle = 35^\circ C$, $\times = 45^\circ C$).

stable 1:1 complex between DB18C6 and the Tb^{3+} cation used. The formation constant, K_f , of the resulting 1:1 complex were evaluated by computer fitting of the molar conductance-mole ratio data to appropriate equations (Nakamura and Mongi, 1997; Ganjali et al., 1998). The changes in standard enthalpy (ΔH_c°) for complexation reaction were obtained from the slope of the Van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The

changes in standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 293.15\Delta S_c^\circ$. The results are summarized in Table 1. The results show that the value ΔS_c° of the complexation reaction between DB18C6 with Tb^{3+} cation in AN is positive, therefore, the complexation reaction is entropy stabilized. Since during the complexation of the cation by a macrocyclic ligand, most of the coordinated solvent molecules are replaced by the donor atoms of the ligand, even when the cation-macrocycle binding is weak, the increased degree of freedom, because of the desolvation of cation, may result in positive entropic gain.

3.4. Calibration curve

The modified electrode reached steady-state potentials within 2 min in response to changes in Tb^{3+} concentration. The plot of EMF vs $-\log[\text{terbium}]$ shown in Fig. 5, indicates that the sensor has a nernstian response to the activity change caused by the concentration change of the analyte ion over a wide concentration ranges of (1.0×10^{-5}) – (1.0×10^{-2}) M of terbium(III) cation in AN. The respective slopes of the resulting calibration graphs for electrode are 20.9 ± 0.4 mV decade $^{-1}$. In contrast, the electrode coated with polypyrrole alone yielded a sluggish response to Tb^{3+} with response times in excess of 5 min (Table 2). This confirms our feeling that the presence of the carrier in the membrane serves to stabilize the electrode potential and to improve the reproducibility and dynamic behavior.

3.5. Static response time of the electrode

In order to evaluate the practical static response time of the electrode, the average time required to achieve a potential within ± 1 mV of the final steady-state potential was measured by recording the potential-time plots of two different concentrations of Tb^{3+} and the results are shown in Fig. 6. The results clearly indicate that the electrode exhibits a constant and stable potential within 40 s.

3.6. Determination of the successive complex formation constants of Tb^{3+} with some organic solvent molecules and Gibbs energy of transfer

From the nernstian response of the electrode mentioned above it has been found that the electrode has the necessary condition to proceed with the experiment in order to obtain the successive complex formation constants (β_i) and Gibbs energies of transfer (ΔG_{tr}) of Tb^{3+} in AN in relation to such D, which are estimated by the same method described previously (Shamsipur and Hassani, 1994). From the emf measurements of cell 2, the complex formation constants can be calculated as:

Table 1 Log K_f values and thermodynamic parameters for $(DB18C6.Tb)^{3+}$ complex in AN.

	Log K_f (\pm SD) ^a	$-\Delta G_c^\circ$ (25 °C), KJ mol $^{-1}$	$-\Delta H_c^\circ$, KJ mol $^{-1}$	$-\Delta S_c^\circ$, KJ mol $^{-1}$
15 °C	3.86 \pm 0.04			
25 °C	3.76 \pm 0.03	22 \pm 1	1.4 \pm 0.7	69 \pm 3
35 °C	3.77 \pm 0.03			
45 °C	3.79 \pm 0.03			

^a Standard deviation.

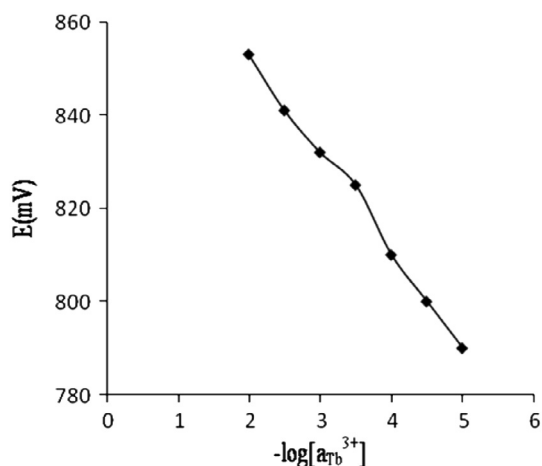


Figure 5 Calibration curve for Tb^{3+} in AN at a PPy-[DB18C6] electrode (25°C).

Table 2 Responses of polymer membrane electrodes to Tb^{3+} in AN at 25°C.

Electrode	Slope (mV per decade)	Linear range (M)	R^2
PPy	-17.8 ± 0.6	$1 \times 10^{-5} - 5 \times 10^{-3}$	0.928
PPy-[DB18C6]	-20.92 ± 0.4	$1 \times 10^{-5} - 1 \times 10^{-2}$	0.994

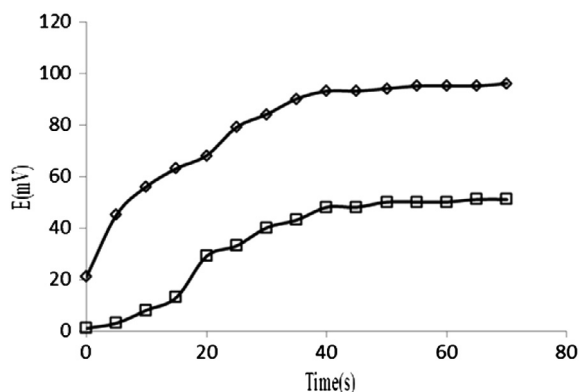


Figure 6 Potential-time plots of two different terbium concentrations in AN: (◇) 1.0×10^{-2} , and (□) 1.0×10^{-3} .

$$R = \{10^{\Delta E/19.72} - 1\}/[D] = \beta_1 + \beta_2[D] + \beta_3[D]^2 + \dots$$

Fig. 7 shows an example of the relation between R and $[D]$ for the case in which D was DMSO. From the intercept and the slope of the line, β_1 and β_2 are obtained. The results of the β_i of Tb^{3+} in AN with some basic solvent molecules are summarized in Table 3. From these results, we can see that except for pyridine, the ability of Tb^{3+} with other solvents increases with the solvent basicity, as predicted by DN. In Fig. 8, $\log \beta_1$ values for Tb^{3+} are represented as a function of Gutmann's donor number (DN) of the solvents. The small β_1 values for pyridine in the present work may be due to the small dielectric constant of pyridine.

The Gibbs energy of transfer of an ion, Y , from a reference solvent, R , to another solvent, D , was defined, and detailed

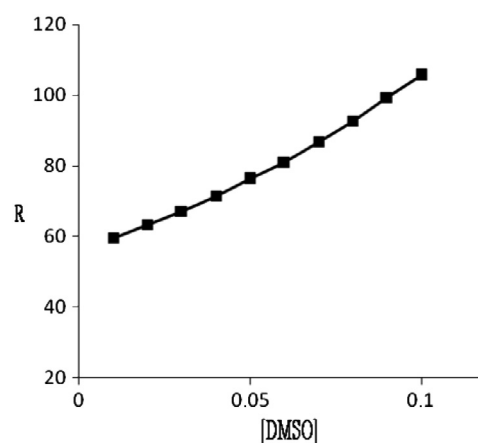


Figure 7 The relation between R vs. $[\text{DMSO}]$ for the terbium ion in acetonitrile.

Table 3 Successive complex formation constants and the Gibbs energy of transfer, $\Delta G_{\text{tr}}(\text{Tb}^{3+}, \text{AN} \rightarrow \text{D})$ in KJ mol^{-1} , of Tb^{3+} in AN with some basic solvent molecules at 25°C.

	Solvent			
	PC	DMF	DMSO	Py
Donor number	15	26.6	29.8	33.1
$\text{Log } \beta_1$	1.04	1.55	1.7	1.26
$\text{Log } \beta_2$	2.03	2.76	2.85	2.75
$\text{Log } \beta_3$	2.97	3.71	3.79	–
$-\Delta G_{\text{tr}}(\text{Tb}^{3+}, \text{AN} \rightarrow \text{D})$	28.95	129.68	141.83	103.34

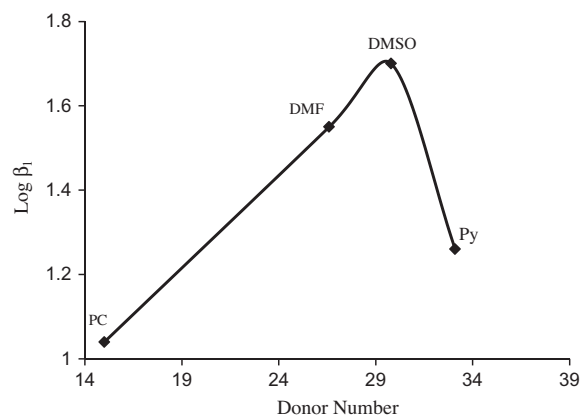


Figure 8 The relation between $\log \beta_1$ and donor numbers of solvents for the terbium ion in acetonitrile.

descriptions have been given in previous papers (Izutsu, 2002; Nakamura and Mongi, 1997). The emf change, ΔE , which is the potential difference between the initial and steady potentials obtained at each addition of quite a small volume of other solvents, was analyzed by a method proposed by Cox et al. (Cox et al). The results are summarized in Table 3. The negative values of $(\Delta G_{\text{tr}})(\text{Tb}^{3+})$ indicate that $\text{Tb}(\text{III})$ is more strongly solvated in the mixtures under study than in pure AN. It is observed from Fig. 9 that a rapid favorable change in the

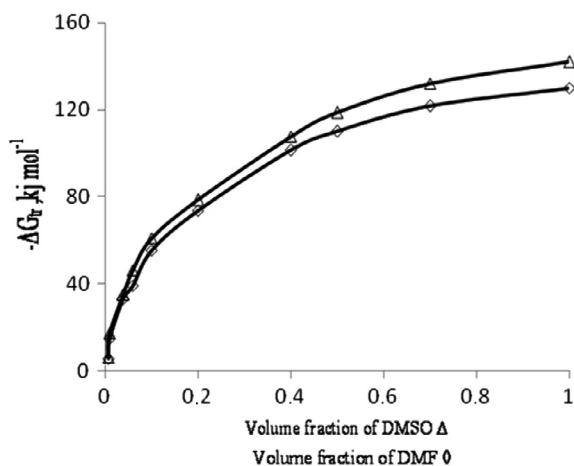


Figure 9 Free energy of transfer of Tb^{3+} from AN to (\diamond) AN-DMF mixtures vs. DMF content and (Δ) AN-DMSO mixtures vs. DMSO content.

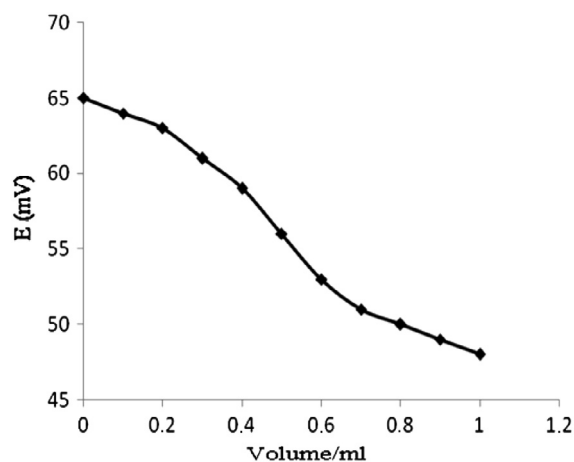


Figure 10 Titration curve for 10 ml of 0.1 mM $Tb(NO_3)_3$ versus 2 mM DB18C6 in an acetonitrile solution with a PPy-[DB18C6] electrode.

free energy of Tb (III) takes place when small amounts of DMF or DMSO (about 1 vol%) are added to the system, indicating preferential coordination of Tb (III) by these solvents. These results are in agreement with expectations based on the DN of the solvents used. Further, it is observed that the change in the ΔG_{tr} of Tb (III) is greater up to ca. 15 vol% D; above this level a more gradual change takes place.

3.7. Analytical applications

The proposed Tb (III) selective electrode was found to work well under laboratory conditions. It was used as an indicator electrode in potentiometric titration of 10 ml terbium ion solution (1.0×10^{-4} M) with a 0.002 M DB18C6 solution. The resulting titration curve is shown in Fig. 10. As can be seen in the inset of Fig. 10, the potential response after each addition of DB18C6 to $Tb(NO_3)_3$ in AN was fairly fast, and a steady state potential was achieved.

4. Conclusions

PPy-[DB18C6] membrane-based ion-selective electrode was applied for thermodynamic investigations in nonaqueous solutions. This electrode was confirmed to be applicable for obtaining the successive complex formation constants and the Gibbs energy of transfer of Tb^{3+} in AN in relation to some other basic solvent molecules. The Nernstian response ability of the electrode has been confirmed to be the result of heterogeneous selective complex formation reactions between the analyte ion in the solution and HOST immobilized at the membrane. It was successfully used as a Tb^{3+} indicator electrode for the chemical reaction of Tb^{3+} with DB18C6 in AN solution.

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