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## ORIGINAL ARTICLE

# A PPy-B15C5 modified lanthanum (III) electrode 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, benzo-15-crown-5 (B15C5), was prepared and investigated as a $La^{3+}$-selective electrode in acetonitrile. The potentiometric response of the electrode was linear within the $La^{3+}$ concentration range $1 \times 10^{-4}$ to $1 \times 10^{-1}$ M with a Nernstian slope of 19.5 mV decade$^{-1}$ in AN. The electrode was applied to study the complexation of the lanthanum (III) ion in acetonitrile with other basic solvent molecules (D) such as dimethyl sulfoxide, N,N-dimethylformamide, propylene carbonate, N,N,Diethylaniline and methanol. The successive complex formation constant ($\beta_i$) and Gibbs energies of transfer ($\Delta G_{tr}$) of $La^{3+}$ in AN in relation to such D were obtained.
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## 1. Introduction

Conducting polymers, due to their imprinting and templating ability, have been widely used for the development of highly selective sensors (Kriz et al., 1997; Haupt, 2001). 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 (Svenson and Nicholls, 2001; 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; Wanekaya and Sadik, 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 (Cortina-Puig, 2007) techniques for the determination of various cationic, anionic and neutral molecular species.

Lanthanum is an important member of this family whose compounds are used widely in various applications. Developing the industrial uses of lanthanum compounds as well as their enhanced discharge into the nature, have increased the demand for monitoring of trace amount of lanthanum in real samples. A number of investigations into the development of

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lanthanum selective electrodes in aqueous solutions have been reported in the literature (Mittal et al., 2004; Gupta et al., 2003; Ganjali et al., 2003), but in this work, for the first time we have reported a Polypyrrole modified lanthanum-ion-selective electrode for use in non aqueous solutions such as acetonitrile for thermodynamic investigations.

Using nonaqueous 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 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; Marcus, 1997; Marcus, 1998; Gritzner, 1988) have been carried out by means of analytical methods, such as IR, NMR, Raman spectroscopy, conductometry, potentiometry, and calorimetry. Among these methods, the potentiometric method is preferable because of its preciseness. Ion-selective electrodes can be used to directly 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 (Beckman Co. Ltd.) were reported (Nakamura, 1975; Izutsu et al., 1980). Also, the ability of the electrode to thermodynamically respond 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 ion–solvent complex formation reactions.

In nonaqueous solvents, such measurements have been largely limited to membrane electrodes using glass or crystalline sensing elements (Izutsu et al., 1980; Nakamura et al., 1982; Cox et al., 1979) because of possible damage to or dissolution of electrode components by organic solvents. But in this work, we have reported a Polypyrrole modified based lanthanum-ion-selective electrode that has both time stability and well-defined potentiometric behaviour.

## 2. Experimental

### 2.1. Materials and reagents

Benzo15-crown-5 (Fluka), Pyrrole (>97%, Merck) and Lanthanum (III) nitrate (Merck) were used without further purification. Tetraethyl ammonium perchlorate was purchased from Aldrich Chemical Co. The solvents: acetonitrile, dimethyl formamide, dimethyl solfoxide, propylene carbonate, N,N, Diethyl aniline and methanol all from Merck company were used with the highest purity.

### 2.2. Apparatus

The electrochemical polymerization of pyrrole was performed using a μAutolab 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;
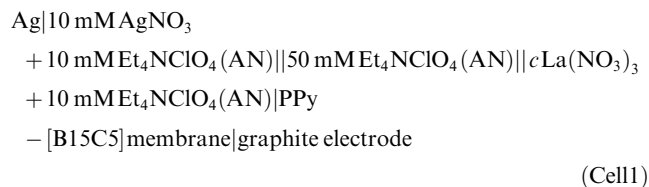
an Ag/AgCl/KCl (3.5 M) reference electrode (Metrohm, Herisau, Switzerland) and a platinum wire as a counter electrode. The working electrode, to be covered with PPy/B15Crown5 film, was a graphite disk electrode with an area of about 2 mm$^2$. The potentiometric measurements were carried out on a Metrohm Model 692 digital pH/Ion Meter. All experiments were typically conducted at 25 ± 2 °C.

### 2.3. Polypyrrole modified 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. 2 mg of modifier (B15C5) was dissolved in 1 mL of pyrrole. Then 0.5 μl of this solution was syringed at the end of the disk. Copper wire was 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 LiClO$_4$, 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 mV s$^{-1}$ three times. The electrode was then conditioned in dry acetonitrile containing $1.0 \times 10^{-3}$ M La(NO$_3$)$_2$ and 0.01 M Et$_4$NClO$_4$ for 2 h.

### 2.4. Potentiometric measuring system

The potentiometric response of the electrode to Lanthanum cation was investigated by measuring Cell 1. All compartments of Cell 1 were freshly prepared each time. Steady state potentials were read to ±0.1 mV.

Ag|10 mM AgNO$_3$

$+$ 10 mM Et$_4$NClO$_4$ (AN)||50 mM Et$_4$NClO$_4$ (AN)|| $c$ La(NO$_3$)$_3$

$+$ 10 mM Et$_4$NClO$_4$ (AN)|PPy

$-$ [B15C5] membrane|graphite electrode

(Cell 1)

where $c$ is the concentration in mol dm$^{-3}$ of La(NO$_3$)$_3$, which was added by a microburet. The change in the liquid-junction potentials of Cell 1 during emf measurements was negligible in the experiment (Izutsu et al., 1991).
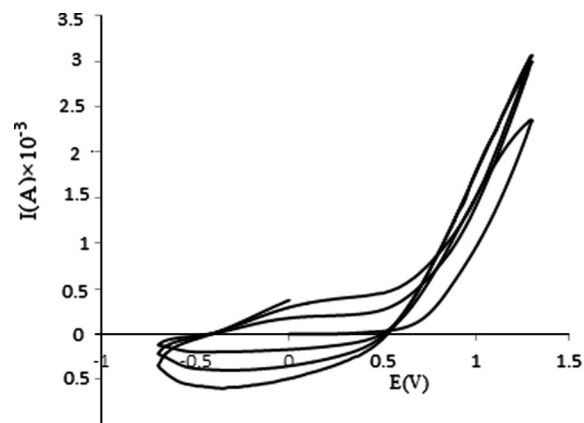


**Figure 1** Repetitive CVs for the polymerization of Py in a solution containing 0.025 M pyrrole and 0.1 M LiClO$_4$, Scan rate: 50 mVs$^{-1}$.

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

The emfs of Cell 2 were measured,

Ag|10 mM AgNO$_3$

  + 10 mM Et$_4$NClO$_4$(AN)||50 mM Et$_4$NClO$_4$(AN)||La(NO$_3$)$_3$

  + 10 mM Et$_4$NClO$_4$(AN + D)|PPy

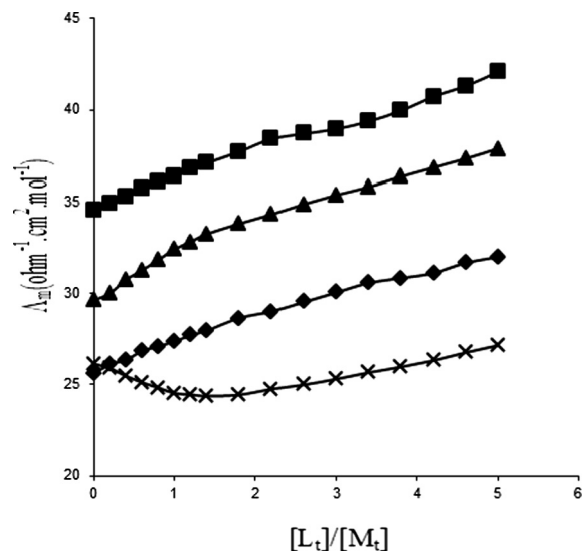  − [B15C5]membrane|graphite electrode

(Cell2)
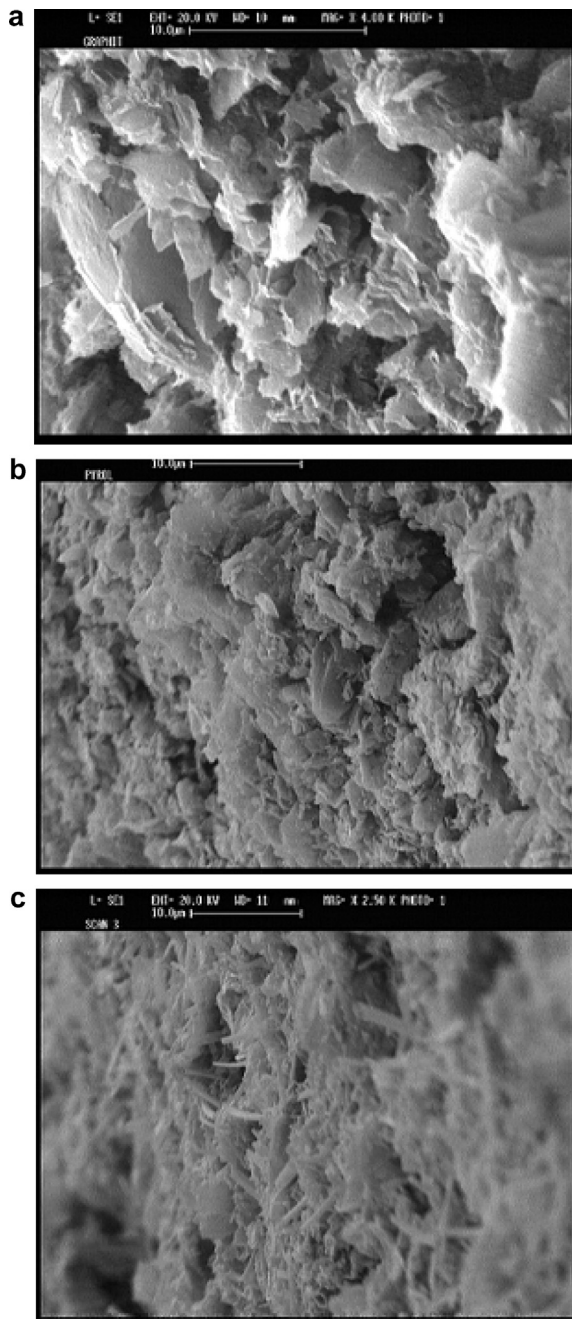


**Figure 3** Molar conductance-mole ratio plots for (B15C5.La)$^{3+}$ complex in AN at different temperatures (♦ = 15 °C, ■ = 25 °C, ▲ = 35 °C, × = 45 °C).

where D denotes DMF, DMSO, PC, DEA, and MeOH. 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, PPy-GDE and PPy/B15C5-GDE

The typical morphology of GDE and PPy-GDE is shown in Fig. 2a and b. The image of PPy/B15C5-GDE is shown in Fig. 2c, compared to PPy-GDE, the surface of PPy/B15C5-GDE is hybrid of poly pyrrole and submicron-scale particle of B15C5.

### 3.2. Conductometric measurement

The equilibrium constant for complex formation of benzo-15-crown-5 with La$^{3+}$ cation has been determined by conductivity measurements in acetonitrile. Fig. 3 shows the changes in the conductance of 20 ml of $1 \times 10^{-4}$ M solution of La$^{3+}$, by the addition of a $2 \times 10^{-3}$ M of B15C5 in AN. The results showed that, addition of B15C5 ligand to La$^{3+}$ solution at 30 °C, 40 °C and 50 °C, shows an increase in molar conductivity with an increase in ligand concentration. This indicates that the (B15C5.La)$^{3+}$ complex is more mobile than free solvated La$^{3+}$ cation in acetonitrile. The ligand to cation mole ratio at 30 °C and 40 °C is 1, indicating the formation of stable 1:1 complex between B15C5 and the La$^{3+}$ cation used. The formation constant, $K_f$, of the resulting 1:1 complex was evaluated by computer fitting of the molar conductance-mole ratio data to appropriate equations (Nakamura and Mongi, 1997; Ganjali et al., 1998) (Table 1). In 50 °C, the ligand to cation mole ratio is 2, indicating the formation of stable 1:2 complex between B15C5 and the La$^{3+}$ cation used. A very
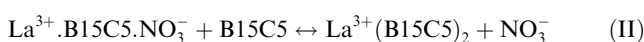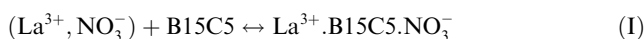


**Figure 2** SEM images of GDE (A), PPy-GDE (B) and PPy/B15C5-GDE (C).

**Table 1**  Log $K_f$ values for (B15C5.La)$^{3+}$ complex in AN.

| Log $K_f$ ($\pm$ SD)[a] | 20 °C | 30 °C | 40 °C | 50 °C |
|---|---|---|---|---|
| | [b] | 3.07 $\pm$ 0.07 | 3.40 $\pm$ 0.08 | [b] |

[a] Standard deviation.
[b] The data can not be fitted in equation.

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

| Electrode slope | (mV per decade) | Linear range | (M) $R^2$ |
|---|---|---|---|
| PPy | $-13.8 \pm 0.5$ | $1 \times 10^{-3}$–$5 \times 10^{-1}$ | 0.981 |
| PPy-[DB18C6] | $^-19.5 \pm 0.3$ | $1 \times 10^{-4}$–$1 \times 10^{-1}$ | 0.991 |

different behaviour was observed for complexation of La$^{3+}$ cation with B15C5 in acetonitrile in 20 °C. It is seen in Fig. 2 that addition of B15C5 to solution of La$^{3+}$ cation in 20 °C, causes the molar conductivity to initially decrease until the molar ratio reaches to 1:1 and then to increase. Such behaviour may be described according to the following equilibria:

$$(La^{3+}, NO_3^-) + B15C5 \leftrightarrow La^{3+}.B15C5.NO_3^- \qquad (I)$$

$$La^{3+}.B15C5.NO_3^- + B15C5 \leftrightarrow La^{3+}(B15C5)_2 + NO_3^- \qquad (II)$$

It seems that addition of the ligand to La$^{3+}$ cation solution results in the formation of a relatively stable 1:1 complex which is present as an ion-pair (), then addition of the second ligand to ion-pair complex causes formation of a stable 1:2 complex with a sandwich structure () which results in dissociation of ion-pair, therefore, the conductivity increases.

### 3.3. Calibration curve

The modified electrode reached steady-state potentials within 20 s in response to changes in La$^{3+}$ concentration. The plot of EMF vs. −log [Terbium] shown in Fig. 4, 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 range of $(1.0 \times 10^{-4})$–$(1.0 \times 10^{-1})$ M of Lanthanum (III) cation in AN. The respective slopes of the resulting calibration graphs for electrode are 19.5 $\pm$ 0.3 mV decade$^{-1}$. In contrast, the electrode coated with polypyrrole alone yielded a sluggish response to La$^{3+}$ with response times in excess of 10 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 behaviour.
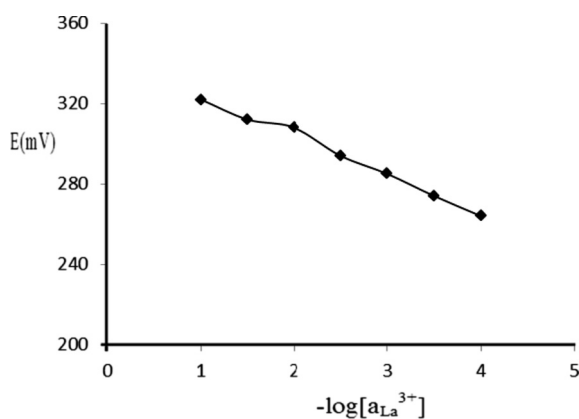
**Figure 4**   Calibration curve for La$^{3+}$ in AN at a PPy-[DB18C6] electrode (25 °C).
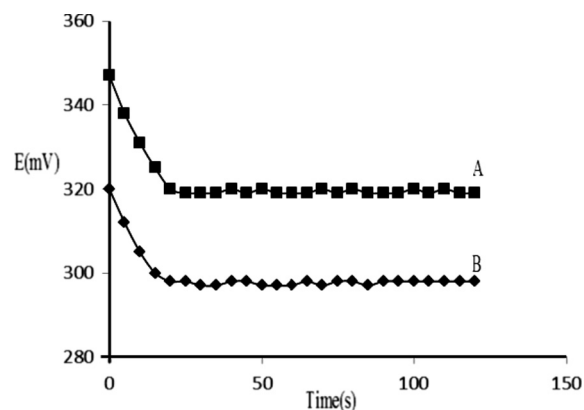
**Figure 5**   Potential-time plots of two different lanthanum concentrations in AN: (A) $1.0 \times 10^{-2}$ and (B) $1.0 \times 10^{-3}$.

### 3.4. 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 $\pm 1$ mV of the final steady-state potential was measured by recording the potential-time plots of two different concentrations of La$^{3+}$ and the results are shown in Fig. 5. The results clearly indicate that the electrode exhibits a constant and stable potential within 20 s.

### 3.5. Lifetime study

The electrodes worked as well as the freshly prepared electrodes, after preparation and dry storage at room temperature for 1 month.

### 3.6. Determination of the successive complex formation constants of La$^{3+}$ 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 conditions to proceed with the experiment in order to obtain the successive complex formation constants ($\beta_i$) and Gibbs energies of transfer ($\Delta G_{tr}$) of La$^{3+}$ 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:

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

Fig. 6a and b show examples of the relation between R and [D] for the case in which D were PC and DMSO, respectively. From the intercept and the slope of the line, $\beta_1$ and $\beta_2$ are obtained. The results of the $\beta_i$ of La$^{3+}$ in AN with some basic

**Figure 7** The relation between $\log \beta_1$ and donor numbers of solvents for the lanthanum ion in acetonitrile.

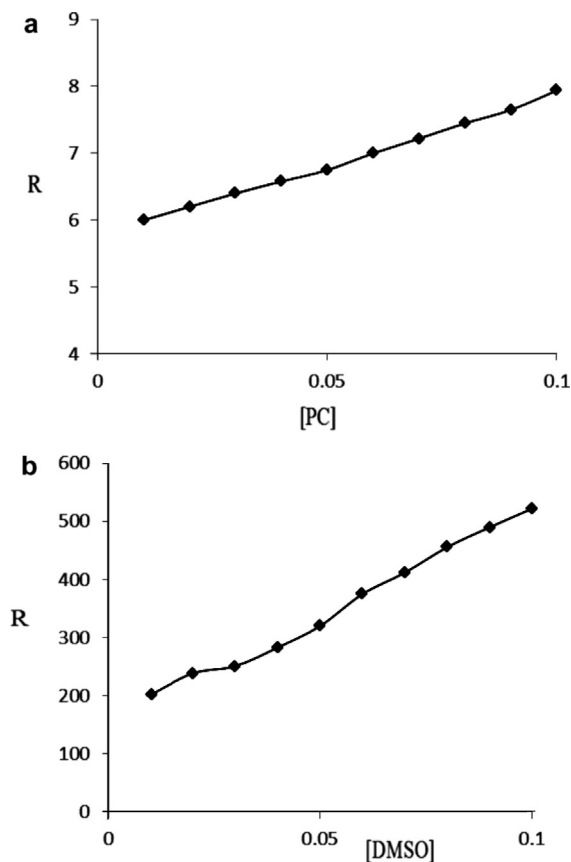**Figure 6** The relation between R vs. [PC] for the lanthanum ion in acetonitrile (a) and the relation between R vs. [DMSO] for the lanthanum ion in acetonitrile (b).

solvent molecules are summarized in Table 3. From these results, we can see that except for pyridine, the ability of La$^{3+}$ with other solvents increases with the solvent basicity, as predicted by DN. in Fig. 7, $\log \beta_1$ values for La$^{3+}$ are represented as a function of Gutmanns donor number (DN) of the solvents.

The Gibbs energy of transfer of an ion, Y, from a reference solvent, R, to another solvent, D, was defined, and detailed descriptions have been given in previous papers (Izutsu, 2002; Nakamura and Mongi, 1997). The emf change, $\Delta E$, which is the potential difference between the initial and steady potentials obtained at each addition of quite a small volume of other solvents, was analysed by a method proposed by Cox et al. (1974). The results are summarized in Table 3. The neg-
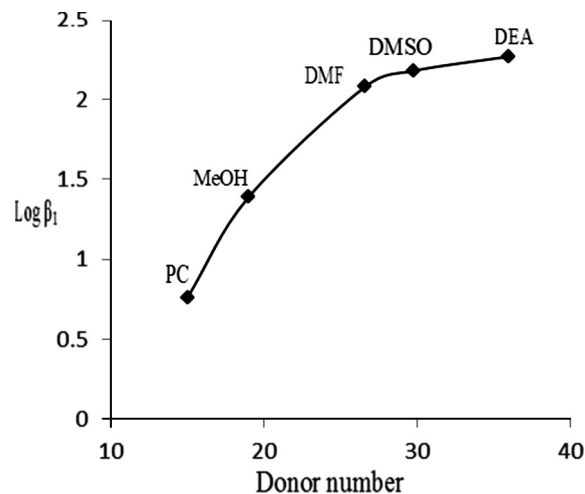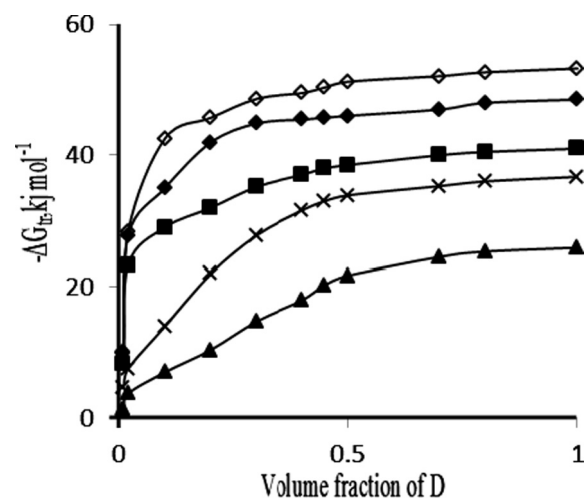


**Figure 8** Free energy of transfer of La$^{3+}$ from AN to (▲) AN–PC mixtures vs. PC content, (×) AN–MeOH mixtures vs. MeOH content, (■) AN-DMF mixtures vs. DMF content, (♦) AN–DMSO mixtures vs. DMSO content, and (◊) AN–DEA mixtures vs. DEA content.

ative values of $(\Delta G_{tr})$ (La$^{3+}$) indicate that La (III) is more strongly solvated in the mixtures under study than in pure AN. It is observed from Fig. 8 that a rapid favourable change

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

|  | Solvent | | | | |
|---|---|---|---|---|---|
|  | PC | MeOH | DMF | DMSO | N,N,Diethylaniline |
| Donor number | 15 | 19 | 26.6 | 29.8 | 36 |
| Log $\beta_1$ | 0.76 | 1.39 | 2.08 | 2.18 | 2.27 |
| Log $\beta_2$ | 1.32 | 2.50 | 3.21 | 3.57 | 3.62 |
| Log $\beta_3$ | 2.27 | 3.43 | 4.15 | 4.51 | 4.56 |
| $\Delta G_{tr}$ (Tb$^{3+}$, AN → D) | 25.9 | 36.7 | 41 | 48.5 | 53.3 |

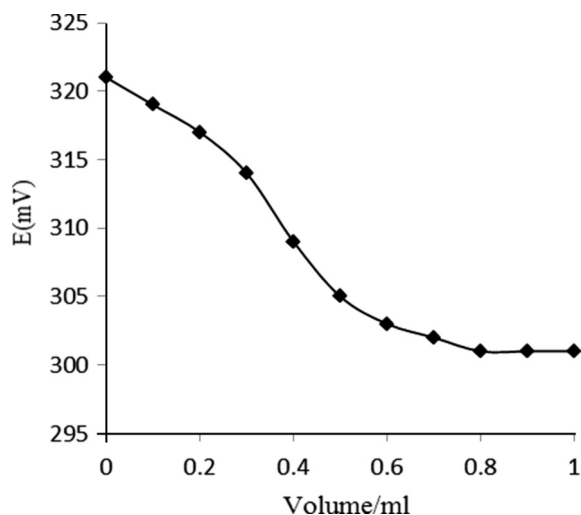**Figure 9**  Titration curve for 10 mL of 0.1 mM $La(NO_3)_3$ vs. 2 mM B15C5 in a acetonitrile solution with a PPy-[B15C5] electrode.

in the free energy of La (III) takes place when small amounts of D (about 1 vol%) are added to the system, indicating preferential coordination of La (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 $\Delta G_{tr}$ of La (III) is greater up to ca. 15 vol% D; above this level a more gradual change takes place.

*3.7. Determination of the complex formation constant of $(B15C5. La)^{3+}$*

The PPy-[B15C5] electrode was successfully used as a $La^{3+}$ indicator electrode for the chemical reaction of $La^{3+}$ with B15C5 in AN solution. As can be seen in the inset of Fig. 9, the potential response after each addition of B15C5 to $La(NO_3)_3$ in AN was fairly fast, and a steady state potential was achieved. From the titration, the complex formation constant obtained by using the PPy-[B15C5] electrode was 1194 that is in satisfactory agreement with the determined value with conductometric method.

**4. Conclusions**

PPy-[B15C5] 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 $La^{3+}$ 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 $La^{3+}$ indicator electrode for the chemical reaction of $La^{3+}$ with B15C5 in AN solution.

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