

# THERMOCHEMISTRY OF INTERACTIONS OF Na<sup>+</sup> WITH BENZO-15-CROWN-5 ETHER IN ACETONITRILE-WATER MIXTURES AT 298.15 K

H. Piekarski and Malgorzata Józwiak

Department of Physical Chemistry, University of Łódź, Pomorska 165, 90-236 Łódź, Poland

(Received March 28, 1996)

## Abstract

Enthalpies of dissolution of benzo-15-crown-5 ether (B15C5) in mixtures of acetonitrile with water and in solutions of NaI and NaBPh<sub>4</sub> ( $I=0.05 \text{ mol dm}^{-3}$ ) in these mixtures were measured at 298.15 K. From the obtained results and appropriate literature data, the thermodynamic functions of B15C5/Na<sup>+</sup> complex formation in acetonitrile-water mixtures were determined. The enthalpies of transfer of the complex B15C5/Na<sup>+</sup> from pure acetonitrile to the examined mixtures were calculated and are discussed.

**Keywords:** acetonitrile-water mixtures, benzo-15-crown-5 ether/Na<sup>+</sup> complex, complex solvation, dissolution enthalpy, thermodynamic functions of complex formation

## Introduction

Inorganic cation complexes with macrocyclic ligands have been intensively examined in recent decades. In these studies, attention was focused primarily on the ligand selectivity and the complex stability in different solvents. Information on the thermal effects of interactions between the macrocyclic ligands and cations in solution, and particularly in mixed solvents, is very scarce. In this paper we present the results of thermochemical studies on the system containing benzo-15-crown-5 ether (B15C5) and Na<sup>+</sup> in acetonitrile-water mixtures. We examined the effect of the mixed solvent composition on the B15C5 dissolution enthalpy in the chosen mixtures without and with a dissolved sodium salt. B15C5 is known to form a complex of 1:1 type with Na<sup>+</sup> [1-3]. The literature gives some information on the stability of the complex B15C5/Na<sup>+</sup> in pure acetonitrile [4-11]. Gholivand and his co-workers published values of the B15C5/Na<sup>+</sup> complex formation constants,  $K$ , in acetonitrile-water mixtures [7]. We therefore expected that the experimental data obtained in this work would allow an analysis of the thermodynamic functions of complex formation and complex solvation in mixtures of acetonitrile with water. In order to examine a possible effect of the nature of the anion on the investigated process, we performed the dissolution experiments with two different sodium salts, NaI and NaBPh<sub>4</sub>. Such a choice of salts was a consequence of our earlier observation of the

different values of the B15C5/Na<sup>+</sup> complex formation enthalpies in methanol when these two salts were used [12].

## Experimental

Benzo-15-crown-5 ether was synthesized and purified at the Chemical Faculty of the Technical University of Gdańsk (*mp*: 352–352.5 K; literature: 352–352.5 K [13]). Sodium iodide (POCh-Gliwice, Poland) was purified and dried as previously [14]. Sodium tetraphenylborate (Fluka) purified as proposed by Cox *et al.* [15] was dried under reduced pressure at 373 K. Acetonitrile (Fluka) was purified by the method described in the literature [16].

The water-acetonitrile mixtures were prepared by mass. The salt solutions (with ionic strength  $I=0.05 \text{ mol dm}^{-3}$ ) were obtained by dissolving an appropriate amount of each salt in freshly prepared solvent.

All measurements were performed at 298.15 K, with an 'isoperibol' type calorimeter as described in our earlier report [17]. The uncertainties in the measured enthalpies did not exceed  $\pm 0.7\%$  of the measured value.

The measurements of the B15C5 dissolution enthalpy were performed within the range 10–100 mol% acetonitrile. The solubility of B15C5 in pure water and in the mixtures with very high water contents was so small that precise calorimetric measurements were impossible.

## Results

Six to eight independent measurements were performed on each investigated mixture. The final concentration of the B15C5 solutions ranged from 0.002 to 0.01 mol dm<sup>-3</sup>. No concentration dependence (outside the error limits) of the enthalpies of dissolution was observed, and consequently the measured enthalpies were regarded as the standard values,  $\Delta_{\text{sol}}H^\circ$ .

Table 1 Standard enthalpies of solution of B15C5 ( $\Delta_{\text{sol}}H^\circ$ ), in AN-water and AN-water-electrolyte (NaI, NaBPh<sub>4</sub>) systems at 298.15 K

mol% of water	$\Delta_{\text{sol}}H^\circ/\text{kJ mol}^{-1}$		
	AN	AN-NaI	AN-NaBPh <sub>4</sub>
0	23.67±0.04	0.90±0.07	—
10	18.62±0.03	7.07±0.06	6.92±0.07
20	16.07±0.04	8.16±0.04	8.47±0.04
30	14.49±0.02	9.21±0.02	9.49±0.04
40	13.50±0.03	10.66±0.02	10.10±0.08
50	12.57±0.04	11.00±0.02	10.99±0.04
60	11.55±0.03	10.73±0.05	10.50±0.02
70	10.80±0.02	9.96±0.02	10.10±0.02
80	9.80±0.02	9.32±0.04	9.33±0.02
90	10.24±0.01	10.01±0.03	10.01±0.04

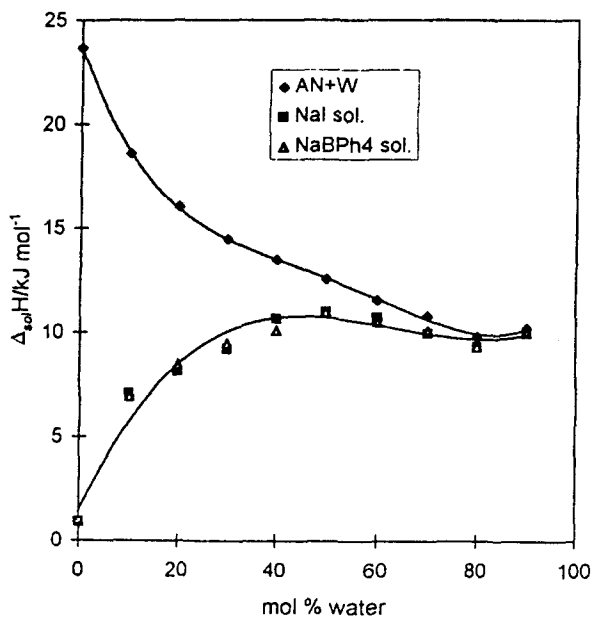


Fig. 1 Dissolution enthalpies of B15C5 in acetonitrile–water mixtures and in solutions of NaI and NaBPh<sub>4</sub> in these mixtures at 298.15 K

The values of  $\Delta_{\text{sol}}H^\circ$  for B15C5 in the acetonitrile–water mixtures, and in the mixtures with the dissolved salts are listed in Table 1 and plotted in Fig. 1 as a function of the mole percentage of water.

## Discussion

### Enthalpies of solution

The effect of dissolution of B15C5 is endothermic in all the investigated mixtures and depends strongly on the mixed solvent composition. The B15C5 dissolution enthalpy in pure acetonitrile is  $\Delta_{\text{sol}}H^\circ = 23.67 \text{ kJ mol}^{-1}$ . It is less endothermic than that of B15C5 dissolution in pure methanol,  $32.07 \text{ kJ mol}^{-1}$  [12], as acetonitrile is a less structured solvent than methanol, and the energy loss necessary for cavity formation in the solvent structure in order to locate a solute molecule is smaller in acetonitrile.

The addition of water to acetonitrile makes the dissolution of B15C5 less endothermic.  $\Delta_{\text{sol}}H^\circ$  decreases as the amount of water in the mixed solvent is increased, and it passes through a minimum at ca. 80 mol% water.

It may be supposed that, despite the relatively high dipole moment of the acetonitrile molecule ( $\mu = 3.44$  [18]), B15C5 in pure acetonitrile is weakly solvated. This is so as the positive charge centre of the acetonitrile molecule dipole is not easily accessible for the B15C5 molecule. The decrease in  $\Delta_{\text{sol}}H^\circ$  as water is added to acetonitrile is probably connected with the preferential solvation of B15C5 by water

molecules and with water-B15C5 hydrogen bonds formation. The strongest effect of solvation is observed in the mixture containing ca 80 mol% water, where the minimum of  $\Delta_{\text{sol}}H^\circ$  appears. It is noteworthy that the position of this minimum corresponds to the range of the acetonitrile-water mixture composition where the inhomogeneity of the system is postulated [19]. Further elevation of the water content of the mixed solvent, beyond the  $\Delta_{\text{sol}}H^\circ$  minimum position, causes an increase in the B15C5 dissolution enthalpy (and a significant decrease in its solubility), due to the formation of a highly ordered solvent structure.

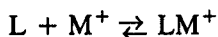
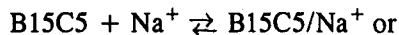
Within the whole investigated composition range, the dissolution enthalpies of B15C5 in the acetonitrile-water mixtures containing added sodium salt are less endothermic than those in the mixtures without electrolyte. This phenomenon is connected with B15C5/Na<sup>+</sup> complex formation. The observed negative (exothermic) shift is the highest in pure acetonitrile and it decreases as the water content in the mixed solvent increases (Fig. 1). Water is a solvent of high solvating ability (DN=33 [18]), which can compete strongly with the ligands for cations. Therefore, the addition of water to acetonitrile, which is a low donicity solvent (DN=14.1 [18]), will decrease the extent of interaction between the ligand donor atoms and the cations. It is noteworthy that the shapes of the  $\Delta_{\text{sol}}H^\circ=f(x)$  function within the range of high water content in the mixtures with and without the electrolyte are similar to each other. This observation confirms a strong influence of the solvation capability of water on the thermal effects of the processes occurring in the solution.

The dissolution enthalpies of B15C5 in NaI solution are the same, within the error limits, as those in NaBPh<sub>4</sub> solution. Thus, the effect of the nature of the anion on the B15C5/Na<sup>+</sup> complex formation in the investigated system seems to be negligible.

### *B15C5/Na<sup>+</sup> complex formation*

As mentioned earlier, the literature contains values of the equilibrium constant of B15C5/Na<sup>+</sup> complex formation in acetonitrile-water mixtures [7]. With the necessary calorimetric data now at our disposal, we are able to calculate the enthalpy and entropy of B15C5/Na<sup>+</sup> complex formation in the investigated mixtures. The salts NaX (X=Cl<sup>-</sup>, Br<sup>-</sup>, NCS<sup>-</sup>, Pic<sup>-</sup>, BPh<sub>4</sub><sup>-</sup>) are known to form complexes of 1:1 type with B15C5 [4-11]. There is no evidence of the formation of 2:1 (ligand to metal ion) complexes between Na<sup>+</sup> and B15C5 in acetonitrile or in solvents of larger donicities [5].

The reaction of 1:1 complex formation can be expressed by the equation



with the corresponding equilibrium constant:

$$K = f_{\text{C}}[\text{LM}^+]/f_{\text{L}}[\text{L}]f_{\text{M}}[\text{M}^+] \quad (1)$$

The activity coefficient of the ligand,  $f_{\text{L}}$ , can be assumed to be equal to unity; the ionic activity coefficients of the given ion and complex ( $f_{\text{M}}$  and  $f_{\text{C}}$ , respectively) can

be calculated on the basis of the Debye and Hückel theory. However, in the opinion of some authors (e.g. [19]), the corrections due to neglect of the activity coefficients are within the experimental error limits. If the thermal effects resulting from the solvent structure change in response to the dissolved electrolyte are neglected, the heat of dissolution of crystalline B15C5 in the solution of the electrolyte can be presented as follows:

$$n_L \Delta_{\text{sol}} H_2^0 = n_L \Delta_{\text{sol}} H_1^0 + V[\text{LM}^+] \Delta H_{(\text{s})} \quad (2)$$

where  $n_L$  is the number of moles of B15C5;  $\Delta_{\text{sol}} H_2^0$  is the molal enthalpy of B15C5 dissolution in the solution of the electrolyte;  $\Delta_{\text{sol}} H_1^0$  is the molal enthalpy of B15C5 dissolution in the pure solvent;  $V$  is the volume of solution in the calorimeter;  $[\text{LM}^+]$  is the concentration of the complex in  $\text{mol dm}^{-3}$ ; and  $\Delta H_{(\text{s})}$  is the enthalpy of complex formation in solution.

From expression (2), we obtain

$$n_L \Delta_{\text{sol}} H_2^0 - n_L \Delta_{\text{sol}} H_1^0 = V[\text{LM}^+] \Delta H_{(\text{s})} \quad (3)$$

The total numbers of moles of B15C5 ( $n_L$ ) and electrolyte ( $n_E$ ) can be expressed as

$$n_L = V([\text{L}] + [\text{LM}^+]) \quad (4)$$

$$n_E = V([\text{M}^+] + [\text{LM}^+]) \quad (5)$$

Combination of Eqs (1), (3), (4) and (5) gives a possibility for calculation of the complex formation enthalpy in solution. The equilibrium constant values,  $K$  for B15C5/ $\text{Na}^+$  complex formation in each investigated mixture, necessary for these calculations, were determined by interpolation of the earlier literature data [7]. The  $\log K$  values appeared to be a linear function of the molal composition of the acetonitrile-water mixtures (Eq. 6), which made the interpolation easy:

$$\begin{aligned} \log K &= 0.4433 + 0.031916 X_{\text{AN}} \\ r &= 0.9999 \end{aligned} \quad (6)$$

where  $X_{\text{AN}}$  is the mole percentage of acetonitrile.

The entropy of complex formation,  $\Delta S_{(\text{s})}$ , was then calculated from the well-known thermodynamic relation

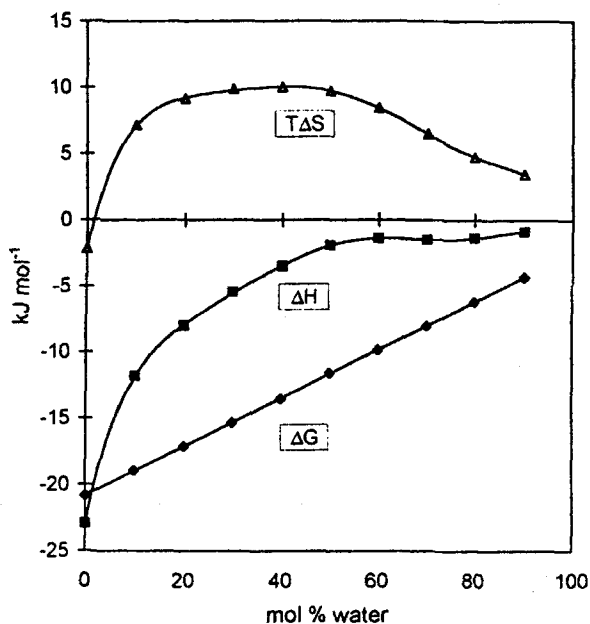
$$\Delta G_{(\text{s})} = -RT \ln K = \Delta H_{(\text{s})} - T \Delta S_{(\text{s})} \quad (7)$$

The thermodynamic functions for B15C5/ $\text{Na}^+$  complex formation in acetonitrile-water mixtures are presented in Table 2 and Fig. 2 as a function of the mixed solvent composition. They were calculated by using the  $\Delta_{\text{sol}} H_2^0$  data for NaI as dissolved electrolyte.

It is seen from these data that an increase of the water content in the mixed solvent causes a decrease in the complex stability [7] and makes the complex forma-

**Table 2** Thermodynamic parameters for B15C5/Na<sup>+</sup> complex formation in AN-water mixtures and the enthalpy of transfer of the complex from AN to AN-water mixtures at 298.15 K

mol% of water	$\Delta G/$	$\Delta H_{(s)}/$	$T\Delta S/$	
	kJ mol <sup>-1</sup>			
0	-20.8	-22.93±0.01	-2.13	0
10	-19.0	-11.79±0.01	7.21	-2.6
20	-17.01	-7.98±0.01	9.12	-0.6
30	-15.3	-5.44±0.01	9.86	
40	-13.5	-3.49±0.01	10.01	2.4
50	-11.6	-1.96±0.01	9.64	
60	-9.82	-1.40±0.01	8.42	2.4
70	-7.99	-1.50±0.01	6.49	
80	-6.16	-1.39±0.01	4.77	4.6
90	-4.34	-0.89±0.01	3.45	16.5

**Fig. 2** Thermodynamic functions of B15C5/Na<sup>+</sup> complex formation in acetonitrile-water mixtures

tion enthalpy less exothermic. These illustrated by the  $\Delta G$  complex stability changes in the acetonitrile-rich region (0–20 mol% water) of the mixed solvent composition are caused by both enthalpy and entropy changes. In the range

20–60 mol% water, the  $\Delta G$  changes are enthalpy-driven, while in the range of high water content they reflect the entropy variation. This clearly illustrates the important influence of the mixed solvent properties [20–24] and the solute-solvent interactions in the complexation reactions.

The enthalpy of complex formation in solution,  $\Delta H_{(s)}$ , can be presented as

$$\Delta H_{(s)} = \Delta H_{(g)} + (\Delta_{\text{solv}}H - \Delta_{\text{solv}}H_L - \Delta_{\text{solv}}H_{M^+}) \quad (8)$$

where  $\Delta H_{(g)}$  is the enthalpy of complex formation in the gas phase, while  $\Delta_{\text{solv}}H$ ,  $\Delta_{\text{solv}}H_L$  and  $\Delta_{\text{solv}}H_{M^+}$  denote the enthalpies of solvation of the complex, ligand and cation, respectively.

Unfortunately, lack of the  $\Delta H_{(g)}$  and  $\Delta_{\text{solv}}H_L$  data makes it impossible to calculate the complex solvation enthalpy for the investigated mixtures. However, it is possible to analyse the effect of the mixed solvent composition on the  $\Delta_{\text{solv}}H$  values. With the notations (AN) for the functions relating to solutions in pure acetonitrile, and (M) for those in acetonitrile–water mixtures, Eq. (8) can be rewritten:

$$\begin{aligned} \delta\Delta H_{(s)} = \Delta H_{(s)}(M) - \Delta H_{(s)}(AN) = [\Delta_{\text{solv}}H(M) - \Delta_{\text{solv}}H(AN)] - \\ - [\Delta_{\text{solv}}H_L(M) - \Delta_{\text{solv}}H_L(AN)] - [\Delta_{\text{solv}}H_{M^+}(M) - \Delta_{\text{solv}}H_{M^+}(AN)] \end{aligned} \quad (9)$$

The difference:  $[\Delta_{\text{solv}}H_x(M) - \Delta_{\text{solv}}H_x(AN)]$  is the enthalpy of transfer of substance  $x$  from pure acetonitrile to the acetonitrile–water mixtures. It can be calculated as the difference of the dissolution enthalpies of solute  $x$  in the mixture and in pure acetonitrile:

$$\begin{aligned} \Delta_{\text{solv}}H_x(M) - \Delta_{\text{solv}}H_x(AN) = \Delta_{\text{tr}}H_x(AN \rightarrow M) \\ = \Delta_{\text{solv}}H_x(M) - \Delta_{\text{solv}}H_x(AN) \end{aligned} \quad (10)$$

Thus:

$$\delta\Delta H_{(s)} = \Delta_{\text{tr}}H(AN \rightarrow M) - \Delta_{\text{tr}}H_L(AN \rightarrow M) - \Delta_{\text{tr}}H_{M^+}(AN \rightarrow M) \quad (11)$$

and

$$\Delta_{\text{tr}}H(AN \rightarrow M) = \delta\Delta H_{(s)} + \Delta_{\text{tr}}H_L(AN \rightarrow M) + \Delta_{\text{tr}}H_{M^+}(AN \rightarrow M) \quad (12)$$

With use of the dissolution enthalpies of B15C5 and the B15C5/Na<sup>+</sup> complex formation enthalpies determined in this work and the literature data for the transfer enthalpies of Na<sup>+</sup> [25], the enthalpies of transfer of the complex B15C5/Na<sup>+</sup> from pure acetonitrile to acetonitrile–water mixtures were calculated. The results are given in Table 2 and Fig. 3 as a function of the mixed solvent composition. For the sake of comparison, the enthalpies of transfer of Na<sup>+</sup> for the same mixtures are also presented in Fig. 3.

The observed similarity in shape of the  $\Delta_{\text{tr}}H=f(x)$  curves indicates that, despite the partial shielding of the complexed Na<sup>+</sup>, its interaction with the surrounding sol-

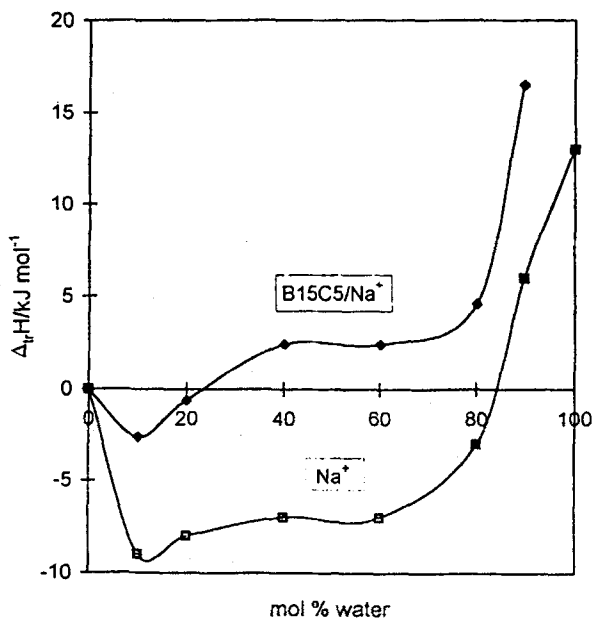


Fig. 3 Enthalpies of transfer of  $\text{Na}^+$  [25] and  $\text{B15C5/Na}^+$  from acetonitrile to acetonitrile-water mixtures

vent makes a major contribution to the complex solvation enthalpy changes in acetonitrile-water mixtures.

## References

- 1 J. J. Christensen, D. J. E. Eatough and R. M. Izatt, *Chem. Rev.*, 74 (1974) 351.
- 2 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb and J. J. Christensen, *Chem. Rev.*, 85 (1985) 271.
- 3 R. M. Izatt, K. Pawlak and J. S. Bradshaw, *Chem., Rev.*, 91 (1991) 1721.
- 4 Y. Jayathirtha and V. Krishnan, *Indian J. Chem., Sect. A*, 18A (1979) 311.
- 5 J. D. Lin and A. I. Popov, *J. Am. Chem. Soc.*, 103 (1981) 3773.
- 6 A. Hofmanova, J. Koryta, M. Brezina and M. Mittal, *Inorg. Chim. Acta*, 28 (1978) 73.
- 7 M. B. Gholivand and M. Shamsipur, *Inorg. Chim. Acta*, 121 (1986) 53.
- 8 H.-J. Buschman, *J. Solution Chem.*, 17 (1988) 277.
- 9 N. N. Strakhova, V. P. Solov'ev and O. A. Reavskii, *Koord. Khim.*, 15 (1989) 483.
- 10 Y. Takeda and T. Kumazawa, *Bull. Chem. Soc. Jpn.*, 61 (1988) 655.
- 11 K. M. Tawarah and S. A. Mized, *J. Inclusion Phenom.*, 6 (1988) 583.
- 12 H. Piekarski, S. Taniewska-Osińska and J. F. Biernat, *Inorg. Chim. Acta*, 124 (1986) 115.
- 13 C. J. Pedersen, *J. Am. Chem. Soc.*, 89 (1967) 7017.
- 14 S. Taniewska-Osińska and M. Józwiak, *J. Chem. Thermodynamics*, 18 (1986) 339.
- 15 B. G. Cox, G. R. Hedwig, A. J. Parker and D. W. Watts, *Aust. J. Chem.*, 27 (1974) 477.
- 16 J. F. Coetzee, *Pure Appl. Chem.*, 13 (1966) 429.
- 17 H. Piekarski and D. Waliszewski, *Thermochim. Acta*, 258 (1995) 67.
- 18 Y. Marcus, in 'Ion solvation' ed. by J. Wiley and Sons 1985, pp. 140, 143, 186.



- 19 M. H. Abraham, in 'Thermochemistry and its application to chemical and biological systems' (NATO ASI Ser., Ser. C) Reidel, 1984, pp. 275-287.
- 20 D. A. Armitage, M. J. Blandamer, M. J. Foster, N. J. Hidden, K. W. Morcom, M. C. R. Symons and M. J. Wootten, *Trans. Faraday Soc.*, 64 (1968) 1193.
- 21 C. Moreau and G. Douhéret, *J. Chem. Thermodyn.*, 8 (1976) 403.
- 22 C. Moreau and G. Douhéret, *Thermochim. Acta*, 13 (1975) 385.
- 23 D. F. Grant-Taylor and D. D. MacDonald, *Can. J. Chem.*, 54 (1976) 2813.
- 24 C. De Visser, W. J. M. Heuvelsland, L. A. Dunn and G. Somsen, *J. Chem. Soc. Faraday Trans. 1*, 74 (1978) 1159.
- 25 K. Miyaji and K. Morinaga, *Bull. Chem. Soc. Jpn.*, 56 (1983) 1861.