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Influence of solvent on thermodynamic parameters and stability of some multicomponent polymer complexes involving an acrylic polymer, poly (ethylene imine) and poly (vinyl pyrrolidone)

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Summary

Stability constant and thermodynamic parameters (e.g. ΔH^0 and ΔS^0) have been determined at several temperatures for some multicomponent complexes of varying composition involving poly (acrylic acid) (PAA), poly (vinyl pyrrolidone) (PVP) and poly (ethylene imine) (PEI) in aqueous medium and water-DMSO mixture. It has been observed that the stability constant and thermodynamic parameters of the interpolymer complexes change due to presence of organic solvent in the medium. Some of these observations have been attributed to the change in the degree of solvation of component polymers, reduced hydrophobic interaction and dielectric constant of the medium.

Introduction

Processes of interpolymer complexes (IPC) formation are the subject of the intensive research during the last decades. These complexes have not only provided new polymer materials, but they can also be tailored to special uses in technology and medicine [1-22]. Interactions between non-ionic polymers and polyelectrolytes have been extensively reported in the literature [2,7,10]. However most of the information available on intermacromolecular complexes is qualitative in nature because of the lack of a suitable theory to interpret the experimental observations [5,23]. Moreover, very little information is available regarding the formation and stability of multicomponent intermacromolecular complexes. In our recent publications a stepwise destabilization of some multicomponent interpolymer complexes in aqueous medium has been reported [24-27]. The complex formation process in aqueous solutions depend on the structure and hydrophobicity of interacting macromolecules i.e. pH and ionic strength of solutions temperature [28-31]. Keeping this in mind, it was considered of interest to prepare some-three component intermacromolecular complexes involving poly (acrylic acid) (PAA), poly (ethylene imine) (PEI) and poly (vinyl pyrrolidone) (PVP) in pure aqueous medium and water-DMSO mixture. PAA is known to interact with PEI through electrostatic interactions to form a poly electrolyte complex [1-5,23,27]. It is also well known, that this poly carboxylic acid interacts with PVP through hydrogen bonding and ion-dipole interactions to form an interpolymer complex [1-5,27]. The composition of the interpolymer complexes can be varied by changing the relative proportions of the respective components. These systems are interesting in view of the fact, that the specific contribution from different interaction forces (e.g. electrostatic, hydrogen bonding and ion-dipole interactions) will depend on the composition of the intermacromolecular complexes. In aqueous medium the stabilization of complexes are mainly through hydrophobic interactions [1-5,33,34]. In organic solvents, one can expect considerable weakening of hydrophobic interactions, and hence stability constant and thermodynamic parameters (e.g. change in entropy ΔS^0 and enthalpy ΔH^0) of the interpolymer complexes are most likely to be affected in such media [2,8,35]. However, the solvent effect is considered to be one of the most important controlling factors during interpolymer complexation, because some solvents can interact with polymer via hydrogen bonds [2,36-38]. Thus complex formation can regarded as a three-component system involving a proton donating polymer, a proton accepting polymer, and a solvent. In less polar solvents like methanol, ethanol, DMSO, the interaction due to poly carboxylic acid (e.g. PAA) and solvent is considerable, thereby reducing its interaction with other polymer. Therefore, in a mixed solvent like water-DMSO mixture, the extent of ionization of poly carboxylic acid will depend on the composition of the medium.

Though considerable data are available in the literature regarding the role of solvent on interpolymer complexation but there seems to be no mention on stability and related thermodynamic parameters of multicomponent complexes of PAA, PEI and PVP in water-DMSO mixture. The main aim of this investigation was to find out the role of dielectric constant and reduced hydrophobic interactions on the stability and thermodynamic parameters of interpolymer complexes.

Experimental

Poly (acrylic acid) (PAA)

Purified acrylic acid (distilled twice in vacuo, b. p. 63°C, 12mmHg) was polymerized with benzoyl peroxide as an initiator in a moist dioxane-methanol mixture [26-27]. The polymerization time was 2.5h in nitrogen at 50°C. The reaction mixture was dissolved in methanol and reprecipitated twice with ethyl acetate. The polymer was dried to constant weight in vacuo at 110°C. The viscosity average molecular weight of the polymer was calculated from intrinsic viscosity of polymer in 2 M NaOH aqueous solution at a constant temperature of 25°C using the Mark-Houwink equation $[\eta] = KM_\eta^\alpha$ [34,39,40]. The constant K and α in the above equation were equal to 42.2×10^{-3} ml g^{-1} and 0.64, respectively. The viscosity average molecular weight $\overline{M_\eta}$ $=4.0 \times 10^5$.

Poly (ethylene imines) (PEI)

PEI was supplied by BDH Chemical Ltd (Poole.UK) in the form of a 50% viscous aqueous solution, with number average molecular weight $\overline{M_n} = 1.5 \times 10^5$.

Poly (vinyl pyrrolidone) (PVP)

PVP was supplied by Fluka Switzerland in the form of a white crystalline powder. The weight average molecular weight ($\overline{M_w}$) of the polymer was calculated from viscosity measurements using the following equation:

$$[\eta] = 6.76 \times 10^{-2} M^{0.55} \text{ (in aqueous medium at 25°C)} \quad \textbf{(1)}$$

Where [η] is intrinsic viscosity and $\overline{M_\eta} = 2.4 \times 10^4$ (*g/mol*) [27,34,40].

Solvent

Double distilled water and analytical grade dimethyl sulfoxide (DMSO) were used for the mixed solvent for all the measurements.

Measurement of pH

The pH measurement of solutions of the polymer or complex was carried out in a water jacketed cell by ATI ORION pH meter (model 525A), using a combination electrode (ORION pH Triode 91-57) with auto calibration for buffers 1.68, 4.01, 7.00, 10.01 and 12.46 within a range of ± 0.01 pH units.

Table 1: pH data for PAA and PAA-PEI-PVP complex systems at various temperatures in aqueous medium

System	Composition (unit mole)	pH						
		20°C	30°C	40°C	45°C	50°C	55°C	60°C
I	1.0 PAA	5.165	5.190	5.265	5.302	5.364	5.437	5.483
II	1.0 PAA + 0.8 PEI + 0.2 PVP	5.651	5.891	6.359	6.687	6.582	5.507	5.942
III	1.0 PAA + 0.6 PEI + 0.4 PVP	5.674	5.730	5.900	5.906	5.862	5.160	5.927
IV	1.0 PAA + 0.4 PEI + 0.6 PVP	5.211	5.709	5.856	5.896	5.525	5.492	5.622

Two points standard calibration was performed at the beginning of each day measurements and also with one standard every two hours to compensate for possible electrode drift. In all experiments the temperature was thermostatically controlled within ± 0.05°C by circulating water through jacketed glass cell, and the sample solution was continuously stirred using a magnetic stirrer. The pH of PAA solution was measured at a polymer concentration of 1×10^{-3} mol/l in the absence and presence of stoichiometric concentration of PEI and PVP. Complexes did not precipitated at this concentration. In every system the amount of PAA was kept constant as the amount of PEI and PVP was varied during each experiment.

Table 2: pH data for PAA and PAA-PEI-PVP complex systems at various temperatures in H_2O-DMSO solvent mixture

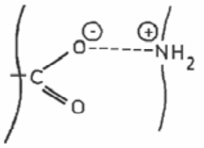
System	Composition (unit mole)	pH						
		20°C	30°C	40°C	45°C	50°C	55°C	60°C
I	1.0 PAA	5.984	5.430	5.450	5.496	5.492	5.565	5.560
II	1.0 PAA + 0.8 PEI + 0.2 PVP	6.220	5.755	5.838	5.898	5.835	5.882	5.891
III	1.0 PAA+ 0.6 PEI + 0.4 PVP	6.174	5.670	5.742	5.755	5.741	5.800	5.800
IV	1.0 PAA+ 0.4 PEI + 0.6 PVP	6.131	5.596	5.705	5.651	5.610	5.680	5.680

Result and discussion

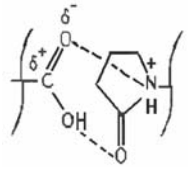
In order to study the role of dielectric constant and reduced hydrophobic interactions on the stability and thermodynamic parameters of interpolymer complexes, several three component interpolymer complexes have been prepared by mixing PAA with stoichiometric quantities of PEI and PVP in pure aqueous medium and in a mixed solvent (i.e. 75% H_2O + 25% DMSO).

II) 1.0 unit mole PAA + 0.8 unit mole PEI + 0.2 unit mole PVP
III) 1.0 unit mole PAA + 0.6 unit mole PEI + 0.4 unit mole PVP
IV) 1.0 unit mole PAA + 0.4 unit mole PEI + 0.6 unit mole PVP

It is known that the PAA interact with PEI through electrostatic interactions to form a polyelectrolyte complexes [1-5,23,24,27], whereas complex formation of PAA with PVP is attributed to hydrogen bonding and ion-dipole interactions as is shown below [1-5,24,25].



PAA-PEI



PAA-PVP

Therefore, the three component complex of PAA, PEI and PVP is likely to be formed as a result of three interacting forces, e.g. electrostatic, hydrogen bonding and ion-dipole interaction [1-5,14,15,27]. The stability of these three component interpolymer complexes at higher temperature is likely to be influenced by the relative amount of PEI and PVP present. This is in view of the fact that coulomb forces are only slightly changed at elevated temperature, where as hydrogen bonding breaks up beyond a certain temperature [1-5,27].

In addition to the above mentioned interacting forces, hydrophobic interactions play a significant role in the stability of interpolymer complexes. It is known that hydrophobic interactions are reinforced with increasing temperature in an aqueous medium [25-27]. Moreover the effect of hydrophobic interactions on stabilization of hydrogen bond containing complexes may be stronger than on the stabilization of the polyelectrolyte complexes [1-5,25-27,33]. In organic solvents, one can expect considerable weakening of hydrophobic interactions and hence stability constant ***K*** and thermodynamic parameters (e.g. change in entropy ΔS^0 and enthalpy ΔH^0) of the interpolymer complexes are most likely to be affected in such media [2-5,35]. In less polar solvents like DMSO, the interaction due to poly carboxylic acid (e.g. PAA) and solvent is considerable, thereby reducing its interaction with other polymer. Therefore, in a mixed solvent like water-DMSO mixture the extent of ionization of poly carboxylic acid will depend on the composition of the medium [2-5,8,36-38].

It is expected that these facts will be reflected in the temperature dependence studies of ***K*** of these three component interpolymer complexes. We have determined the stability constant (***K***), degree of linkage (***θ***), and other related thermodynamic parameters (e.g. ΔH^0 and ΔS^0) for the complexation systems (II-IV) by using Osada's method [2,24-27,41]. The method involves determination of degree of linkage (***θ***), which is defined as the ratio of binding groups to the total number of potentially interacting groups. The stability (***K***) is related to ***θ*** by;

$$\theta = 1 - \left([H^+]/[H^+]_0\right)^2 \qquad (\mathbf{2})$$

$$K = \frac{\theta}{C_0(1-\theta)^2} \qquad (\mathbf{3})$$

Where C_0 is the initial concentration of poly carboxylic acid (mol. L^{-1}) and $[H^+]$ and $[H^+]_0$ are proton concentration in the poly carboxylic acid solution in the presence and absence of proton accepting polymer, respectively. The values of ***θ*** for the complexes systems studied are given in Table 3 and 4.

Table 3: Degree of the linkage of complexes at various temperatures in aqueous media

System	Composition of complex (unit mole)	Degree of linkage (θ)						
		20°C	30°C	40°C	45°C	50°C	55°C	60°C
II	1.0 PAA + 0.8 PEI + 0.2 PVP	0.354	0.573	0.705	0.743	0.731	0.714	0.712
III	1.0 PAA + 0.6 PEI + 0.4 PVP	0.521	0.563	0.583	0.611	0.607	0.547	0.487
IV	1.0 PAA + 0.4 PEI + 0.6 PVP	0.168	0.141	0.149	0.1468	0.157	0.088	0.057

Table 4: Degree of the linkage of complexes at various temperatures in H_2O-DMSO mixed solvent

System	Composition of complex (unit mole)	Degree of linkage (θ)						
		20°C	30°C	40°C	45°C	50°C	55°C	60°C
II	1.0 PAA + 0.8 PEI + 0.2 PVP	0.688	0.770	0.826	0.841	0.791	0.770	0.781
III	1.0 PAA + 0.6 PEI + 0.4 PVP	0.590	0.673	0.739	0.711	0.686	0.677	0.970
IV	1.0 PAA + 0.4 PEI + 0.6 PVP	0.498	0.521	0.683	0.521	0.429	0.424	0.426

The corresponding plots of LnK versus reciprocal of temperature for system II-IV in pure aqueous medium and in water-DMSO mixture are shown in figures 1-4.

It can be seen from the figures that for all the complex systems (i.e. II-IV) in aqueous and in a water-DMSO solvent mixture there is an initial increase up to 45°C and then there is a fall beyond this temperature. Also stability of all the complex systems in mixed solvent are more as compared to aqueous medium. It is evident from table 3, 4 and Fig. 1-3 that the relative stability of complex system II is much greater compared to other systems in both solvents.

This could be anticipated in view of the fact, that the complex system II has a relatively higher proportion of electrostatic interaction compared to other systems due to the higher proportion of PEI. In pure aqueous medium at elevated temperature ***K*** of the complex system II increases due to reinforced hydrophobic interactions, whereas coulomb forces are only slightly affected. In a mixed solvent due to presence of DMSO, poly acrylic acid is more dissociated and results stronger electrostatic interactions as compared to aqueous medium [2-5], hence the stability of this complexes will be more in a mixed solvent.

In complex system III and IV, the relative proportions of hydrogen bonding and ion-dipole interactions are expected to be large due to presence of higher proportion of the PVP in these complexes. Since temperature has a pronounced influence on hydrogen bonding complexes, ***K*** for these complexes has been found to be relatively small. However, the effect of hydrophobic interaction is likely to stabilize the hydrogen bonding containing more than the polyelectrolyte complex [2,33], and will partly compensate for the temperature effect in aqueous medium.

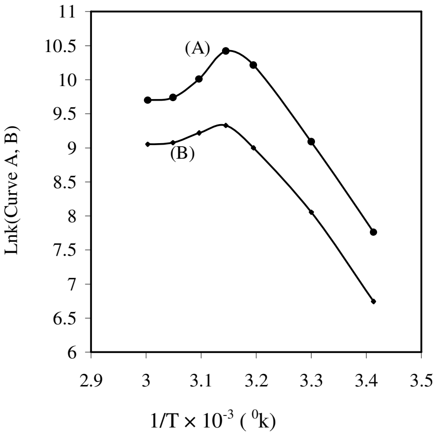


Fig 1: Relationship of Ln K versus 1/ T for complex system II, (A) water-DMSO, (B) aqueous medium

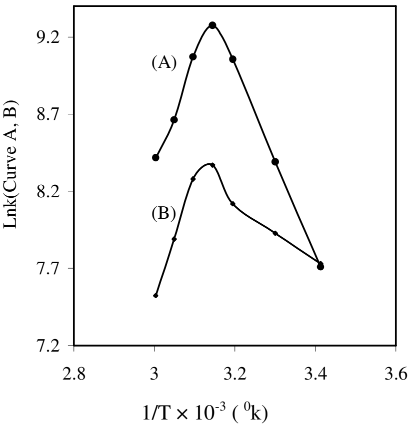


Fig 2: Relationship of Ln K versus 1/ T for complex system III, (A) water- DMSO, (B) aqueous medium

The higher stability of the complex systems III and IV in mixed solvent as compared to aqueous medium are due to presence of PEI in these systems which are more dissociated in DMSO, results stronger electrostatic interactions which reinforced hydrogen bonding.

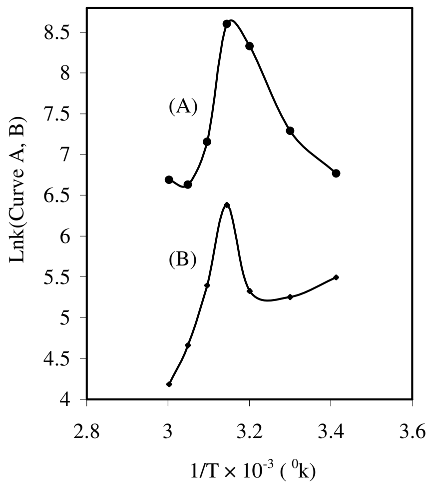


Fig 3: Relationship of Ln K versus 1/ T for complex system IV, (A) water-DMSO, (B) aqueous medium

The thermodynamic Parameters (e.g. ΔH^0 and ΔS^0) can be calculated from the temperature dependence of stability constant (***K***) of the complexes, by using the following relationships [2,24-27,32,41].

$$\Delta G^0 = -RTLnK \qquad \textbf{(4)}$$

$$\mathrm{d(LnK)}/\mathrm{d(1/T)} = -\Delta \mathrm{H}^0/\mathrm{R} \qquad \textbf{(5)}$$

$$\Delta S^0 = -(\Delta G^0 - \Delta H^0)/T \qquad \textbf{(6)}$$

Where ΔG^0 is the change in standard free energy and (*R*) is the molar gas constant.

The standard enthalpy and entropy change for complexation system (II to IV) have been calculated on the basis of the above equations at several temperatures and the corresponding plots have been shown in figures 4-7.

The net enthalpy change (ΔH^0) and overall change in entropy (ΔS^0) during interpolymer complex formation consist of three basic steps e.g. (1) desolvation (2) complex formation by electrostatic, ion-dipole and hydrogen bonding interactions and (3) conformational changes involving complex formation. Therefore, the overall change in ΔH^0 and ΔS^0 are the sum of these contributions [2-5,24,26]. Since the contribution to each step will be different for various systems, different values for ΔH^0 and ΔS^0 are understandable, on comparing ΔH^0 *vs* T and ΔS^0 vs T curves for all complex systems in aqueous and in a water-DMSO solvent mixture, three distinct peaks can be seen (cf. Fig 4-9).

Fig. 4 and 7 show variation of ΔH^0 and ΔS^0 vs T for complex system II in pure aqueous medium and water-DMSO solvent mixture. It can be seen that the first peak which is observed at 30-35°C is higher for mixed solvent. This perhaps indicates release of more ions due to presence of DMSO in this medium, which get more solvated and result more ΔH^0 and ΔS^0 of solvation. The second peak observed is greater for aqueous medium. This may attributed to reinforcement of electrostatic interaction between PAA and PEI as a result of hydrophobic interaction in this medium. The third peak is observed at 48°C for aqueous medium and for mixed solvent. Also it can be seen the fall in ΔH^0 and ΔS^0 vs T curves in the case of mixed solvent (i.e. curve A) is more, this may be assigned to weaker hydrogen bonding and hydrophobic interactions in water-DMSO solvent mixture which result destabilization of the complex. The plots of variation of ΔH^0 and ΔS^0 vs T for complex system III in aqueous and water-DMSO solvent mixture are depicted in Fig. 5 and 8 and for complex system IV in Fig. 6 and 9 respectively.

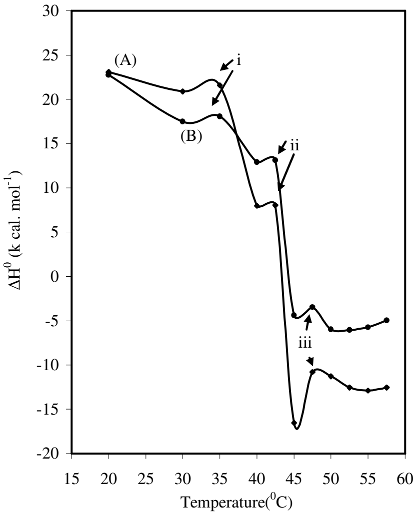


Fig 4: Temperature dependence of standard enthalpy changes ΔH^0 for complexation system II, (A) water-DMSO, (B) aqueous medium

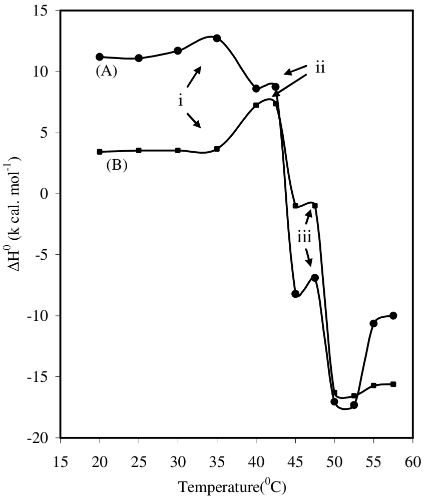


Fig 5: Temperature dependence of standard enthalpy changes ΔH^0 for complexation system III, (A) water-DMSO, (B) aqueous medium

On comparing ΔH^0 and ΔS^0 values of these complexes together (cf. Fig. 5,6,8,9) and with those in complex system II. It can be seen that the similar trends are observed except, the second peak for complex system III and IV in mixed solvent is higher, this is again may be due to more dissociated PAA which result stronger electrostatic interactions with PEI in addition to hydrogen bonding interaction in this medium, the remaining parts of graph and temperature at which they were observed can possibly explained, on the basis of reasons mentioned earlier for complex system II. Except the relatively more stable interacting pairs e.g. PAA-PEI in water-DMSO get destabilized at higher temperature i.e. 50°C (cf. Fig. 6 and 9 Curve B).

In conclusion it can be said that in the presence of DMSO in the medium, though the hydrogen bonding and hydrophobic interactions decreases but the stability constant of the interpolymer complexes increases due to more ionization of PAA in presence of DMSO which result stronger electrostatic interaction. In presence of DMSO in the solvent mixture, the values of ΔH^0 and ΔS^0 during complexation are entirely different from those observed in aqueous medium.

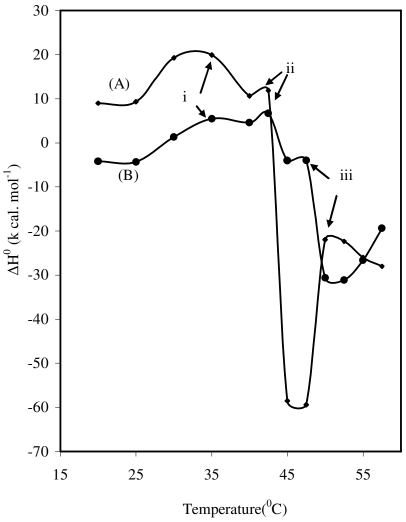


Fig 6: Temperature dependence of standard enthalpy changes ΔH^0 for complexation system IV, (A) water-DMSO, (B) aqueous medium

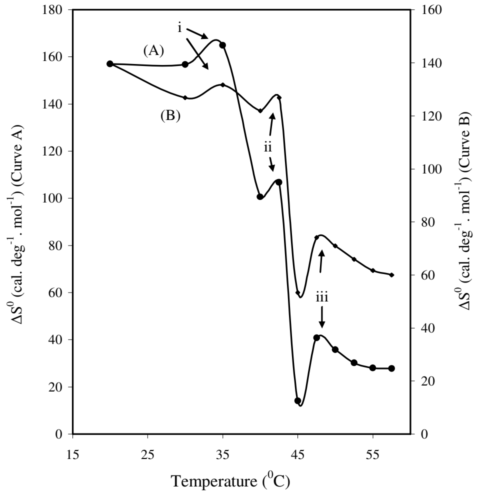


Fig 7: Temperature dependence of standard entropy changes ΔS^0 for complexation system III, (A) water-DMSO, (B) aqueous medium

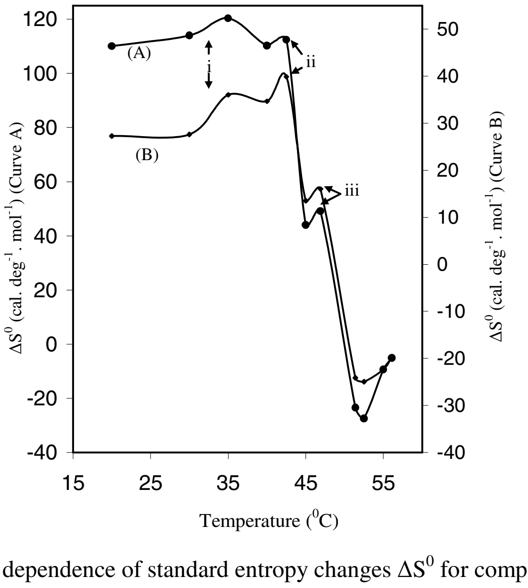


Fig 8: Temperature dependence of standard entropy changes ΔS^0 for complexation system III, (A) water-DMSO, (B) aqueous medium

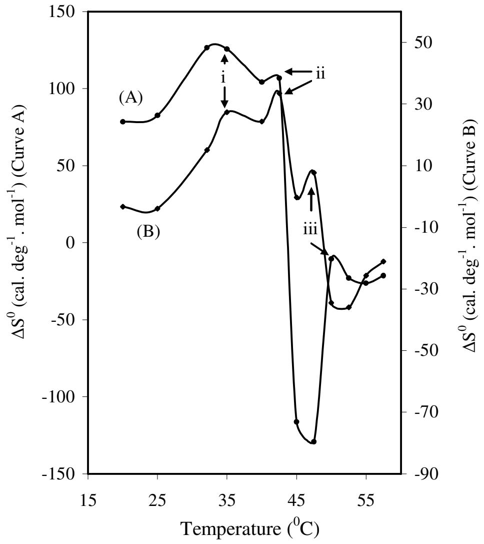


Fig 9: Temperature dependence of standard entropy changes ΔS^0 for complexation system IV, (A) water-DMSO, (B) aqueous medium

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