

Studies on the Kinetics of Alkali Catalysed Solvolysis of Substituted Valerate Ester in Aquo-Dipolar Aprotic Solvent Reaction Media

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ABSTRACT

The kinetics of the alkali catalysed hydrolysis of Ethyl Iso-valerate (substituted iso- valerate) were studied in aquo- aprotic solvent systems (aquo-DMSO) and the specific rate constants of the reaction were found decreasing with increasing concentration of the organic content (DMSO) of the media. It is inferred that dielectric effect and the solvation changes are the causes of depletion in the rate of the reaction.

The Iso-composition activation energy (E_C) and the Iso-dielectric activation energy (E_D) of the reaction were found to increase and decrease respectively and from this, it is inferred that the transition state of the reaction is desolvated and its initial state is solvated.

From the depletion observed in the solvation number of the water content of the aquo-DMSO solvent systems with increase in the temperature of the reaction, it is inferred that unimolecular mechanistic path of the reaction is changed to bimolecular mechanistic path. Increase observed in free energy of activation with simultaneous increase in the values of both the ΔH^* and ΔS^* , it is inferred that in the presence of DMSO with reaction media, the reaction becomes enthalpy dominating and entropy controlled.

From the evaluated values of iso-kinetic temperature of the reaction which comes to be 330.0, it is concluded the Barclay-Butler rule is obeyed by the

reaction and there is strong solvent-solute interaction in presence of DMSO in the reaction media

KEYWORDS: Iso-valerate ester, Dipolar aprotic solvent, Iso – kinetic temperature, Iso-composition and Iso-dielectric activation energy, Transition state, Entropy controlled, Enthalpy dominating, Solvent-Solute Interaction.

INTRODUCTION

The kinetics of alkali catalysed hydrolysis of Ethyl Iso-valerate in aquo-DMSO media has been planned to be carried out, as this reaction is very useful from commercial as well as from the hygienic points of views and also because it has not been paid adequate attention by the researchers so far.

The solvolysis of the said ester was studied in aquo-DMSO media having varying concentration of DMSO from 20-80% (v/v) at five different temperatures, i.e., 20,25,30,35 and 40°C.

EXPERIMENTAL

Export quality Ethyl iso-valerate ester packed in Switzerland and SISCO grade of DMSO were taken in to use. The kinetics of alkali catalysed hydrolysis of Ethyl Iso-valerate were studied using earlier reported process¹⁻³ keeping the strength of alkali and esters as 0.1 M and 0.05 M respectively. The concentration of the organic solvent DMSO was varied from 20 to 80% (v/v) and hydrolysis was carried out at five different temperatures at 20,25,30,35 and 40°C. The reaction was found to follow second order kinetic

equation and the evaluated values of the specific rate constants were enlisted in Table-I. The evaluated values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) have been recorded respectively in Table -II and III. From the slopes of the plots of $\log k$ value versus $\log [H_2O]$ (values as recorded in Table-IV), the evaluated values of number of water molecules associated with the activated complex of the reaction have been tabulated in Table-V. The three thermodynamic activation parameters namely ΔH^* , ΔG^* and ΔS^* were calculated by applying Wynne-Jones and Eyring equation⁴ and their values are synchronised in Table -VI.

Results and Discussion:

Solvent Effect on the Rate of Reaction:

Table-I shows that the specific rate constant values of the reaction decrease with increasing proportion of DMSO in the reaction media. On plotting $\log k$ values against mol % of DMSO, it is obvious that rates of reaction go on depleting with gradual addition of DMSO in the reaction media. The depletion in the rate follows smooth depleting path. From the plots of $\log k$ versus mol% of DMSO in the reaction media, two intersecting straight lines having different values of slopes are obtained. The decrease in the rate with increasing mol % of DMSO at all the five temperatures are found to follow deep depletion path up to 19.50 mol% of the DMSO in the reaction media and after its 19.50 mol % in the reaction media, the rate of depletion becomes slow. It is clear that sharpness in the depletion of the rate becomes slow with increase in temperature of the reaction. This decreasing trend in the values of the rate constants needs to be discussed in the light of Hughes and Ingold⁵ predictions and the theory of Laidler and Landskroener⁶. The values of dielectric constant of the reaction media

go on decreasing with gradual addition of DMSO. So our findings are fully in accordance with the qualitative prediction of Hughes and Ingold⁵.

However, our findings are also in agreement with the qualitative prediction and views of Singh & Jha *et al.*^{7,8} and recent reports of Singh & Singh *et al.*⁹ and Hafizee & Singh¹⁰, who predicted that the rate of ion dipolar reaction decreases partly with decrease in the dielectric constant values of the reaction media and partly due to the solvation changes taking place in the reaction media.

Solvent effect on the Iso-composition Activation Energy (E_C) of the reaction:

The values of iso-composition activation energy (E_C) of the reaction were evaluated from the slopes of Arrhenius plots of $\log k$ values of the reaction against $10^3/T$ and have been tabulated in Table-II. The plots of $\log k$ versus $10^3/T$ were sketched.

From Table-II, it is obvious that E_C values go on increasing from 97.01 kJ/mol to 134.16 kJ/mol with increase in concentration of DMSO from 20 to 80% (v/v) in reaction media. This change is probably due to solvation changes taking place either at initial state level or at the transition state level or at the level of both the states as reported earlier by several researchers^{9,10} in this field. Considering the extent of solvation to be a dominant factor, The following three factors seem to be responsible for increase in E_C values with gradual addition of DMSO in the reaction media:-

- (i) The initial state is solvated and the transition state is desolvated,
- (ii) The initial state is solvated more than the transition state, and
- (iii) The transition state is desolvated more than initial state.

The transition state being large anion (ester +OH) not available more for

solvation by DMSO molecule than the initial state, so the first factor seems to be operative in this case and it also gets support when the values of entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*) go on increasing with concentration of DMSO as shown in Table-VI. Such observations and inferences have been supported earlier by Singh & Priyanka *et al.*¹¹ and recently by Verma¹².

Solvent Effect on the Iso-dielectric Activation Energy (E_D) of the Reaction:

On perusal of the data of Table-III, it is found that iso-dielectric energy (E_D) values of the reaction are decreasing from 149.70 kJ/mol to 118.09 kJ/mol with increase in dielectric constant values of the reaction media from $D = 60$ to $D = 75$ respectively. Since D values of the aquo-DMSO reaction media go on decreasing with gradual addition of DMSO to it, hence it may also be concluded that like E_C values, E_D values are also increasing with decrease in D values of the reaction media or with adding more and more DMSO to it. Thus it also may be inferred that E_C and E_D values of the solvolysis reactions are complimentary to each other.

Such findings and their interpretations have been found in support of the past views of Elsemongy *et al.*¹³, Woford¹⁴ and are also supported by the recent reports of Narendra & Singh *et al.*¹⁵.

Effect of Solvent on the Solvation number and on the Mechanistic pathways of the reaction:

The solvation number i.e. the number of water molecules involved in the formation of the activated complex of the reaction were evaluated from the slopes of the plots of $\log k$ values of the reaction against $\log[H_2O]$ values of the reaction media. By using Robertson¹⁶ equation which is –

$$\log k = \log k' + n \log[H_2O]$$

where 'n' is the solvation number.

The $\log k$ and $\log [H_2O]$ are enlisted in Table-IV and their plots are drawn during the study period and the numerical values of the slopes of the plots have been enlisted in Table-V.

Robertson *et al.*¹⁷ have established that the numerical value of solvation number 'n' i.e. the number of water molecules associated with the activated complex in its formation are fairly high for reaction following unimolecular mechanistic pathway and are low for reaction following bimolecular mechanistic pathway.

From the values recorded in Table-V, it is clear that at all the temperatures of the reaction, the plots of $\log k$ versus $\log[H_2O]$, there are two straight lines having different slopes which meet at $\log [H_2O]$ value 1.480 which corresponds to 54.40% of water in aquo-DMSO media.

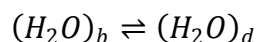
From the evaluated values of slopes as recorded in Table -V, it is clear that before $\log [H_2O]$ value 1.480 which corresponds to 54.40% of water concentration in the reaction media, their values are decreasing from 0.888 to 0.342 with rise in temperature of the reaction from 20 to 40°C. Similarly, after $\log [H_2O]$ values 1.480 i.e. above 54.40% of water in the reaction media, the numerical values of the slopes i.e. the number of water molecules associated with the activated complex in its formation decrease from 1.792 to 0.606 with increase in temperature from 20 to 40°C.

Overall, it may be concluded that number of water molecules associated with the activated complex of the reaction in the formation decrease from 1.792 to 0.342.

Thus, on the guidelines of Robertson *et al.*¹⁷, it may be inferred that with rise in temperature of the reaction, the mechanistic pathways of the reaction is

changed from unimolecular to bimolecular in presence of DMSO in the reaction media.

About the change in the structure of water in presence of DMSO and with rise in temperature of the reaction, water components of the reaction media changes its structure from its bulky form to dense form at equilibrium.



Such observations and inferences have earlier been reported by Singh & Singh *et al.*¹⁸ and in recent years by Kumar & Singh¹⁹.

Effect of Aquo-DMSO solvent system on the Thermodynamic Parameters of the Reaction:

The three thermodynamic activation parameters namely ΔH^* , ΔG^* and ΔS^* of the alkali catalysed hydrolysis of Ethyl Iso-valerate were evaluated using Wynne-Jones and Eyring equation³ and their values have been synchronised in Table-VI.

From Table -VI, it is clear that out of the three thermodynamic activation parameters ΔH^* , ΔG^* and ΔS^* , all of them are found increasing with increasing mol % of DMSO in the reaction media.

For better understanding of the effect of solvent DMSO on these three thermodynamic activation parameters, their values were plotted against mol % of the solvent DMSO which have been shown in Fig. 1,2 and 3 showing the variation in ΔH^* , ΔG^* and ΔS^* respectively with mol % of DMSO in the reaction media.

The reasonable and considerable increase in ΔG^* values (from 81.81 to 84.24 kJ/mol at 30°C) as found in Table -VI and non-linear variation in ΔH^* , ΔG^* and ΔS^* with mol% of DMSO as shown in Fig. 4, 5 and 6 respectively are indication of specific solvation taking place in the process of activation as reported by Saville and Hudson²⁰, Tommila *et al.*²¹

and Hyne *et al.*²². Enhancement observed in both the ΔH^* and ΔS^* values also justifies that transition state of the reaction is desolvated and the initial state of the reaction is solvated. Simultaneous increase in ΔG^* values with increase in ΔH^* and ΔS^* values is only possible when the extent (degree) of enhancement in ΔH^* values is more than that of ΔS^* values and from this, it may be inferred that alkali catalysed hydrolysis of Ethyl Iso-valerate is entropy suppressing or controlled and enthalpy dominating reaction. Such findings and interpretations have earlier been reported by Singh & Kumari *et al.*²³, Monalisa & Singh *et al.*²⁷ and recently Sabita and Singh²⁵ have also reported similar observations and inferences.

Solvent effect on Iso-kinetic Temperature and Solvent-Solute Interaction:

This reaction is found to obey Barclay and Butler²⁶ rule and straight line is obtained when ΔH^* values of the reaction is plotted against ΔS^* as shown in Fig. 4 and from their values tabulated in Table-VI.

The Barclay and Butler equation is

$$\delta m (\Delta H^*) = \beta \delta m (\Delta S^*)$$

It is a relation between enthalpy (ΔH^*) and entropy (ΔS^*) of activation values of the reaction and ' β ' is called iso-kinetic temperature of the relation which is also called Leffer-Grunwald solvent stabilizer operator²⁷. From the values of slope of the plot, the values of Iso-kinetic temperature was evaluated which came to be 330.02 \approx 330.0.

In the light of Leffler's²⁸ guidelines, from the values of iso-kinetic temperature which is greater than 300, it is inferred that there is a considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to appreciably strong interaction between the solvent and the solute present in the reaction media. The structural changes

with increasing proportion of DMSO in aquo-DMSO reaction media are responsible for the depletion observed in the values of the specific rate constant of the reaction.

Earlier Singh & Singh *et al.*²⁹ and Singh & Kumari *et al.*³⁰ and in recent years Prashansa & Singh *et al.*³¹ and Rakesh & Singh *et al.*³⁹ have also reported similar conclusions about the solvent-solute interaction in the reaction media.

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Table – I

Specific rate constant values of Alkali catalysed hydrolysis of Ethyl Iso-valerate in water-DMSO media
 $k \times 10^3$ in (dm)³ mole⁻¹ min⁻¹

Temp in °C	% of DMSO (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20°C	88.11	69.74	53.41	42.48	33.58	26.84	18.96
25°C	169.79	137.15	111.25	91.96	75.25	61.12	46.51
30°C	323.67	272.14	231.79	197.83	168.81	143.02	114.18
35°C	602.28	523.48	450.56	407.47	360.25	316.15	262.30
40°C	1105.10	999.54	914.32	834.07	766.13	687.23	613.06

Table - II

Evaluated values of Iso-composition Activation Energy (E_C or E_{exp}) of the reaction in water-DMSO media.

% of DMSO	20%	30%	40%	50%	60%	70%	80%
E_C values in kJ/mol	97.01	102.97	109.17	113.96	119.34	125.28	134.16

Table - III

Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at Different-Desired 'D' values of water-DMSO media.

D values	D= 60	D = 62.5	D = 65	D =67.5	D = 70	D = 72.5	D = 75
E_D values in kJ/mol	149.70	139.84	136.45	129.61	126.27	122.09	118.09

Table – IV

Variation of log k values of the reaction with log[H₂O] values of water-DMSO media at different temperatures.

% of DMSO (v/v)	% of H ₂ O	log[H ₂ O]	3+ log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.9450	2.2299	2.5101	2.7798	3.0434
30%	70%	1.5898	1.8435	2.1372	2.4348	2.7189	2.9998
40%	60%	1.5229	1.7276	2.0463	2.3651	2.6614	2.9611
50%	50%	1.4437	1.6282	1.9636	2.2963	2.6101	2.9212
60%	40%	1.3468	1.5861	1.8765	2.2274	2.5560	2.8843
70%	30%	1.2218	1.4288	1.7862	2.1554	2.4999	2.8371
80%	20%	1.0458	1.2778	1.6675	2.0576	2.4188	2.7875

Table - V

Values of the slopes of the plots of log k versus log [H₂O] values at different temperatures

Temperature in °C	Slope - I Where log [H ₂ O] value is below 1.480	Slope – II where log [H ₂ O] value is above 1.480
20°C	0.888	1.792
25°C	0.730	1.487
30°C	0.590	1.181
35°C	0.495	1.027
40°C	0.342	0.606

Table- VI
Consolidated Values of Thermodynamic Activation Parameters (ΔH^* , ΔG^* and ΔS^*) of the reaction in water-DMSO solvent system at different temperatures.
 ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mol

% of DMSO (v/v)	Mol% of DMSO	ΔH^* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20%	5.94	95.25	88.01	45.20	81.83	45.06	81.81	45.02	81.41	44.94	81.20	44.91
30%	9.77	99.55	85.58	57.84	82.35	57.62	82.05	57.68	81.77	57.65	81.46	57.73
40%	14.40	104.94	83.23	74.09	82.87	74.04	82.46	74.20	82.11	74.11	81.73	74.15
50%	20.17	112.31	87.79	97.33	83.34	97.21	82.85	97.23	82.41	97.08	81.93	97.06
60%	27.49	117.05	84.36	111.56	83.84	111.42	83.25	111.54	82.73	111.42	82.15	111.49
70%	37.09	122.71	84.91	129.02	84.36	128.70	83.67	128.83	83.06	128.72	82.43	128.68
80%	50.27	131.12	86.02	154.10	85.03	154.83	84.24	154.88	83.54	154.64	82.73	154.76

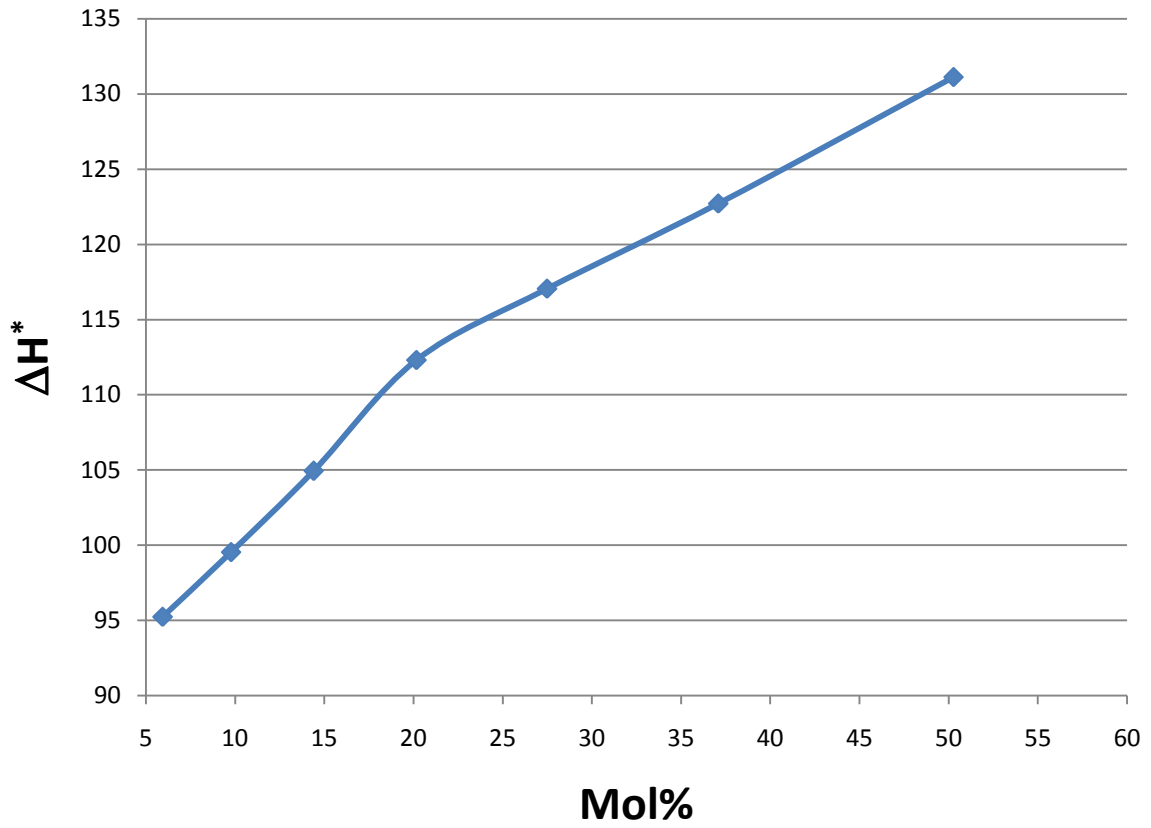


Fig. 1

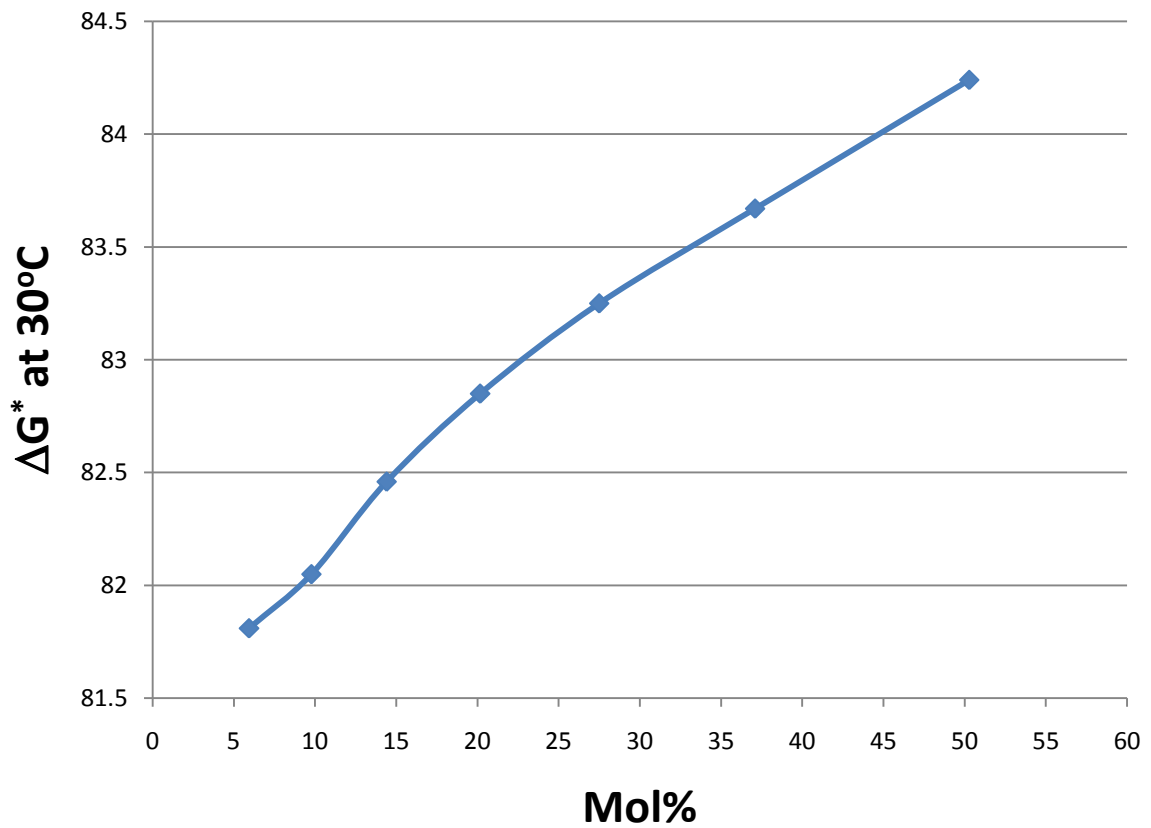


Fig. 2

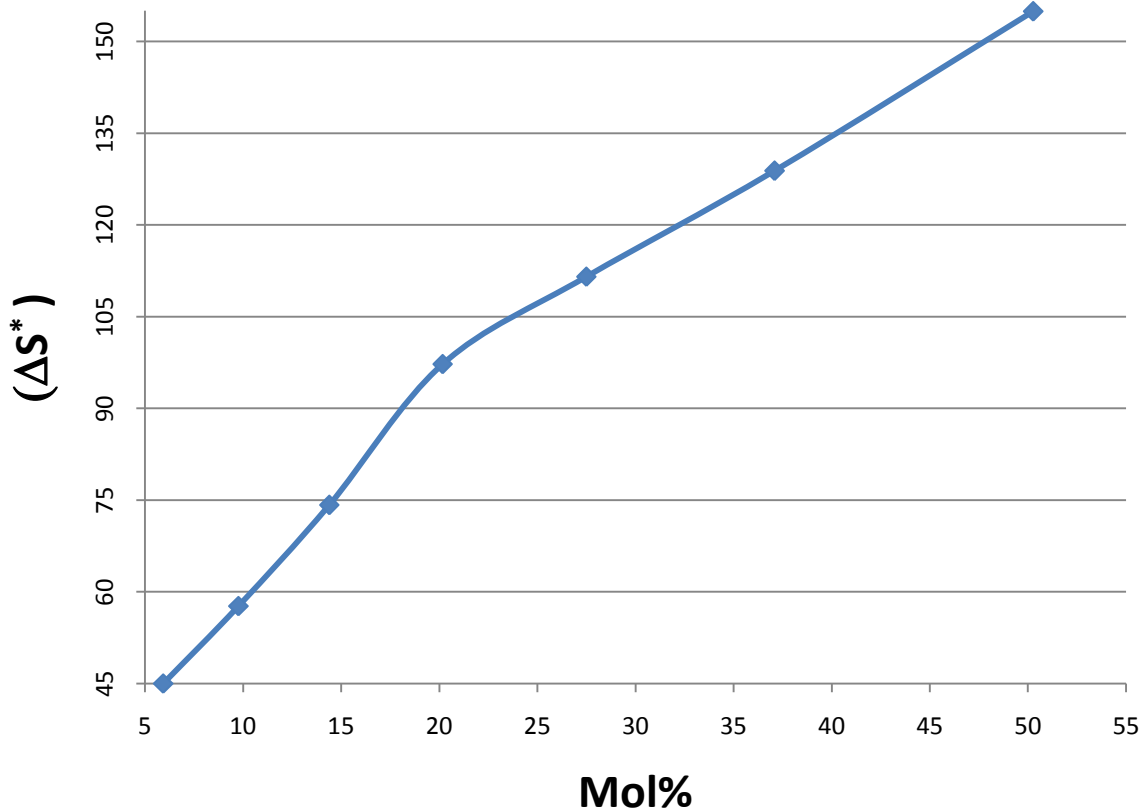


Fig. 3

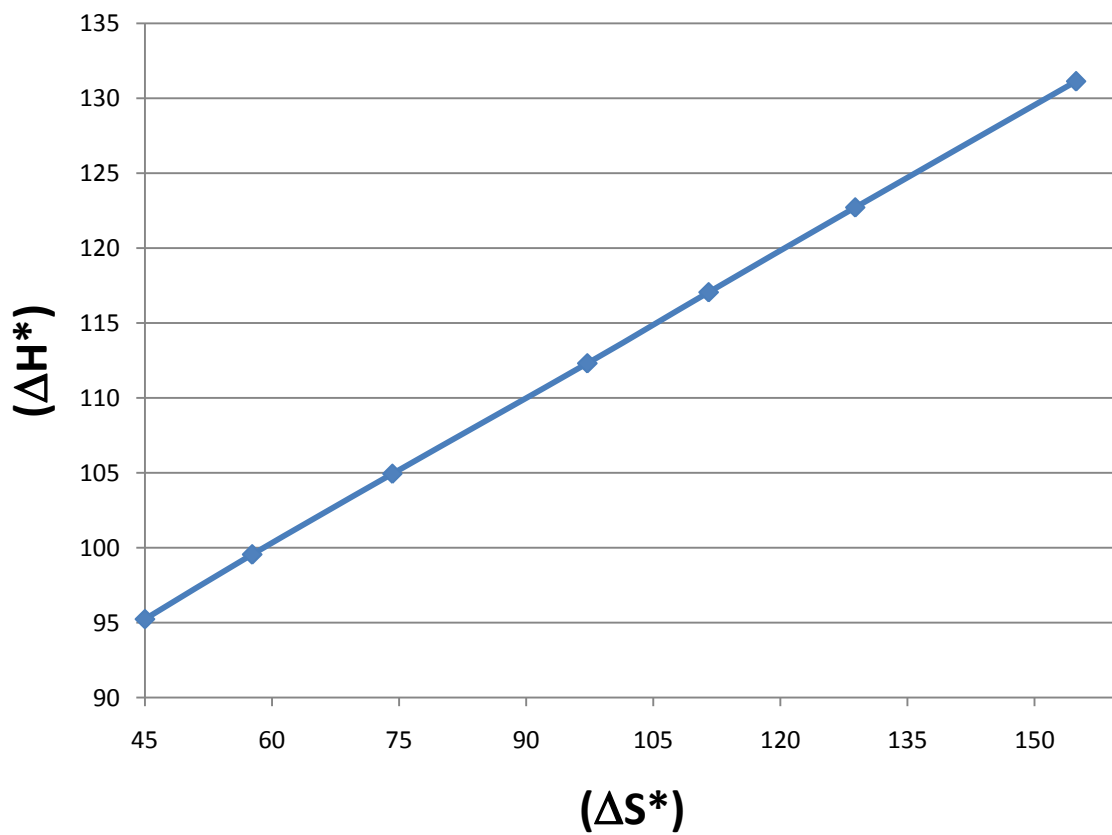


Fig. 4