Dr. Kumari Priyanka, 2025, 13:6
ISSN (Online): 2348-4098
ISSN (Print): 2395-4752

International Journal of Science, Engineering and Technology
An Open Access Journal

A Kinetic Study of the Solvent Effect of Aquo-1-Butanol Solvent Systems on The Kinetic and Thermodynamic Parameters of The Catalysed Solvolysis of Methyl Caprate

Dr. Kumari Priyanka
Department of Chemistry, K. B. Jha College, Katihar
Purnea University Purnea

Abstract- The solvent effect of t-butanol on the alkali catalysed solvolysis of Methyl caprate was studied by carrying out the hydrolysis of the ester in water-t-butanol media of varying composition consisting of 30 to 80% 1-butanol (v/v) at different temperatures ranging from 20 to 40°C. The specific rate constant values of the reaction were found to decrease with increasing concentration of t-butanol in the reaction media. The iso-composition and iso-dielectric activation energies (E_c and E_d) of the reaction were found to increase and decrease respectively with increasing concentration of the solvent (t-butanol) in the reaction media and with increasing the dielectric constant values of the reaction media. From these findings, it is inferred that the transition and initial states of the reaction are desolvated and solvated respectively with the addition of t-butanol in the reaction media. It was found that number of water molecules associated with the activated complex decreases from 1.506 to 0.424 with increasing temperature from 20°C to 40°C and this tells us that with addition of t-butanol in the reaction media, the mechanistic path followed by the reaction is changed from unimolecular to bimolecular. Form simultaneous enhancement in values of all the three thermodynamie activation parameters ie in ΔG* ΔH* and ΔS*, it has been concluded that in presence of t-butanol the reaction is enthalpy dominating and entropy controlled and specific solvation is taking place in the water-t-butanol media. From the values of iso-kinetic temperature, i.e. 331.42, it may be concluded that the reaction in water-t-butanol media obeys Barclay-Butler rule and there is strong solvent-solute interaction in the reaction media.

Keywords: Enhancement, Unimolecular, Activation Parameters, Enthalpy Dominating. Entropy Controlled, Desolvation, Iso-kinetic Temperature, Associated, Barclay-Butler Rule. Solvent-Solute Interaction.

I. INTRODUCTION

The studies on the kinetics of alkali catalysed hydrolysis of Methyl caprate in water-t-butanol media were proposed as the study of solvent effect of tertiary alcohol on the hydrolysis of caprate ester has not been paid adequate attention by the kineticists so far. It has been planned to perform the reaction in water-t-butanol media having varying concentration of t-butanol at 5 different temperatures i.e. at 20, 25, 30, 35 and 40°C in order to establish the mechanism of the reaction and also to study about the solvent-solute interaction in the reaction media.

Experimental:

Export quality of Methyl caprate of Fluka ΔG* grade packed in Switzerland and Merck grade of t-butanol were used. The kinetics of the reaction were studied as usual[1-3] by keeping the strength of alkali M/10 and that of the ester M/20 in the reaction mixture. The reaction was found to obey the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table-1. From the recorded values of log k and $10^3/T$, in Table - II log k values were plotted against $10^3/T$.

The values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_d) have been mentioned in Table- III and IV respectively. The log k values were plotted against log [H_2O] from their values recorded in Table V, the evaluated values of the slopes of these plots have been noted in Table -

VI. The consolidated values of the thermodynamic activation parameters, ie. ΔH*, ΔG* and ΔS* were calculated by using Wynne-Jones and Eyring[4] relation are enlisted in Table - VII.

Effect of Solvent on the Specific Rate Constant values of the Reaction:

From the survey of the data recorded in Table - I, it is obvious that the rate of the reaction decreases regularly with gradual addition of t-butanol in the reaction media at all the temperatures at which the kinetics of the reaction has been studied.

In order to study the variation in rate constant values with increasing concentration of 1-butanol in the reaction media, the log k values have been plotted against mol% of t-butanol content in the reaction media as shown in Fig. 1.

Figure 1 shows that the rate of reaction go on decreasing having different slopes due to two intersecting straight lines in the plots at about 17.35 mol % of t-butanol in the reaction media. From Fig. 1, it is also apparent that with increase in temperature, the degree of depletion in the rate become shallow (slow). Such decrease in the rate with increasing proportion of the organic co-solvent like t-butanol is not new, but a number of researchers like Laidler-Landskroener[5] and recently Singh & Mishra[6] have also reported such observation about the depletion in rate with increasing concentration of the organic co-solvent in the reaction media. However, the possible rate depleting factors in the rate may be listed as follows:
(i) decrease in the bulk dielectric constant of the medium,
(ii) decreasing the polarity of the reaction media on adding less polar t-butanol.

The above noted two rate depleting factors are quite in operation and this is in support of the recent reports of Kumar & Singh et al[7] that the rate ought to decrease with decreasing dielectric constant value of the reaction media with addition of t-butanol to it.

Table - I

Specific rate constant values of Alkali catalysed hydrolysis of Methyl caprate in water-t-butanol media

$k \times 10^3$ in $(dm)^3\ mol^{-1}\ min^{-1}$

Temp in °C	% of t-butanol (v/v)					
	30%	40%	50%	60%	70%	80%
20° C	49.41	37.33	29.39	23.29	17.34	12.22
25° C	94.65	77.11	61.83	49.20	39.36	28.25
30° C	187.15	162.22	126.04	119.97	89.55	72.79
35° C	354.65	309.39	268.60	229.67	199.43	155.53
40° C	684.07	601.31	523.72	476.47	407.47	352.37

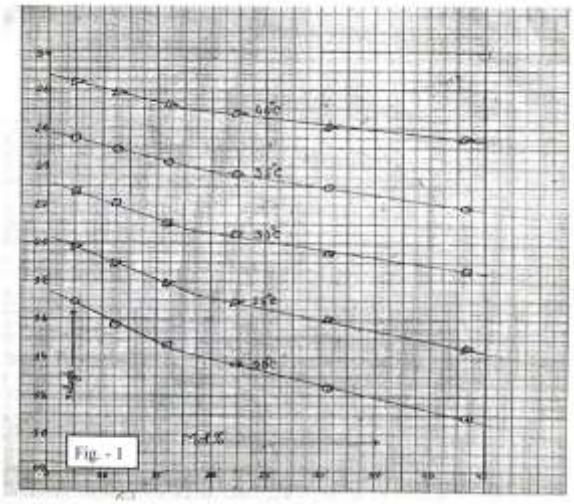

Fig. - 1 : Variation of log k values with mol % of t-butanol in water-t-butanol media

Solvent Effect on the Iso-composition Activation Energy:

From the slopes of the Arrhenius plots of log k values against $(10^3) / T$ from their values enlisted in Table - II) as shown in Fig. 2, the iso-composition activation energy (E_C) of the reaction were evaluated and mentioned in Table - III.

From the values recorded in Table-III, it is obvious that E_C or E_{exp} values go on increasing with increasing concentration of 1-butanol in reaction mediaThis trend 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 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 t-butanol in the reaction media:-

- The initial state is more solvated than the transition state,
- The initial state is less desolvated than the transition state, and
- The transition state is desolvated and the initial state is solvated.

The transition state being large anion (ester + OH^-) available less for solvation by t-butanol molecule than the initial state, so the third 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 increasing concentration of t-butanol (Table-VII).

Similar interpretations for enhancement in the values of activation energy of the reaction with gradual addition of the organic content in the reaction media have also been reported recently by various researchers[3,6,10,11]

Effect of Solvent on the Isodielectric -Activation Energy (E_D) of the reaction:

On perusal of the data of Table IV, it is observed that the iso-dielectric activation energy (E_D) values of the reaction go on decreasing from 124.91 kJ/mol to 104.93 kJ/mol with increase in D values from D = 20 to D = 50 respectively. Such depletion in E_D values with increase in D values of the reaction media are in accordance with the increase in

Table-II

Variation of log k values of the reaction with (10^3) / T in water-t-butanol media.

Temp. °C	$10^3/T$	3 + log k values at different % of t-butanol (v/v)					
		30%	40%	50%	60%	70%	80%
20°C	3.413	1.6938	1.5728	1.4682	1.3672	1.2391	1.0872
25°C	3.356	1.9761	1.8871	1.7912	1.6920	1.5951	1.4510
30°C	3.300	2.2722	2.2101	2.1005	2.0491	1.9521	1.8621
35°C	3.247	2.5498	2.4905	2.4291	2.3610	2.2998	2.1917
40°C	3.195	2.8351	2.7791	2.7191	2.6781	2.6101	2.5497

Table - III

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

% of t-butanol (v/v)	30%	40%	50%	60%	70%	80%
E_c in kJ/mol	101.75	106.56	110.37	115.88	121.57	128.24

Table - IV

Evaluated values of Iso-Dielectric Energy (E_D) of the reaction at different desired 'D' values of water-t-butanol media.

D values	D = 20	D =25	D = 30	D = 35	D = 40	D = 45	D = 50
E_D values in kJ/mol	124.91	119.84	116.28	112.72	110.81	109.02	104.93

E_C values with increasing concentration of the organic content (t-butanol) in the reaction media.

Since D values of the reaction media decreases with addition of organic solvent in it, so it can also be concluded that E_D values of this reaction also increases like E_C values with decrease in D values of the reaction media.

However, these findings and interpretations regarding change (decrease) in E_D values with increase in D values of the reaction media are in support of the past views of Elsemongy[8] and Wolford[12] and have also been recently supported by Singh & Namrata[3] Singh & Perween[10], Singh & Hafizee et al.[11] and Kumar & Singh[13].

Effect of Solvent on the Mechanistic Pathways of the Reaction:

For establishing the mechanistic pathways of the reaction, Robertson[14] gave an idea of solvation number 'n' which is the solvation number or the number of water molecules involved in the formation of the activated complex and for its evaluation he proposed the equation:

$$\text{Log } k = \log k_o + n \log[H_2O]$$

Robertson et al[15]. have established the principle that the values of solvation number (n) for the reaction following unimolecular mechanistic pathway is fairly high but for the reaction following bimolecular path it will be low.

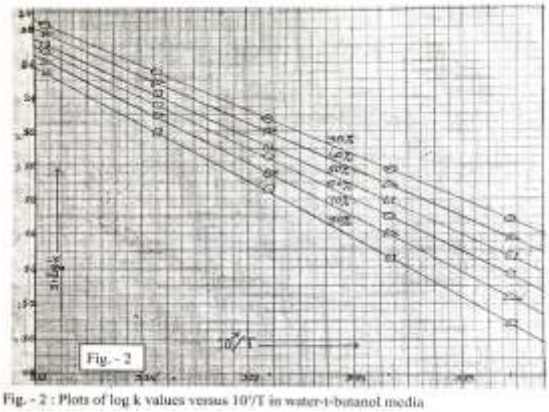

Fig. - 2 : Plots of log k values versus $10^3/T$ in water-t-butanol media

The number of water molecules 'n' involved in the formation of the activated complex of the reaction were determined by plotting log k values against log [H_2O] value for alkali catalysed hydrolysis of Methyl caprate in water-t-butanol media. The value of log k and log [H_2O] have been tabulated in Table - V and their plots have been pictured in Fig. -3. The numerical values of the slopes of plots have been recorded in Table - VI.

From Fig. 3, it is clear that at each temperature of the reaction, the plots of log k versus log [H_2O], two intersecting straight lines having different values of slopes are obtained at log [H_2O] value at about 1.425 which corresponds to 47.90% of water in water-t-butanol media.

From the values recorded in Table - VI, it is clear that below log [H_2O] value 1.425, which corresponds to 47.90% of water in the reaction media, the number of water molecules associated with the activated complex decreases from 0.930 to 0.424 with rise in temperature of the reaction from 20 to 40°C. Similarly, in case of above 47.90% of water concentration in the reaction media, the values of slopes decreases from 1.506 to 0.800 with increase in temperature from 20 to 40°C of the reaction. Overall, it may be inferred that number of water molecules associated with the activated complex in its formation decreases from 1.506 to 0.424.

In the light of guidelines of Robertson et al[15] from the decreasing number of water molecules from 1.506 to 0.424 involved in the formation of the activated complex, it

Table - V

Variation of log k values of the reaction with log [H_2O] values of water-t-butanol system (media) at different temperatures

% of t-butanol	% of water	log [H_2O]	3 + log k				
			20°C	25°C	30°C	35°C	40°C
30%	70%	1.5898	1.6938	1.9761	2.2722	2.5498	2.8351
40%	60%	1.5229	1.5720	1.8871	2.2101	2.4905	2.7791
50%	50%	1.4437	1.4682	1.7912	2.1005	2.4291	2.7191
60%	40%	1.3468	1.3672	1.6920	2.0491	2.3610	2.6781
70%	30%	1.2218	1.2396	1.5951	1.9521	2.2998	2.6101
80%	20%	1.0458	1.0872	1.4510	1.8621	2.1912	2.5491

Table - VI

Values of the slopes of the plots of log k versus log [H_2O] at different temperatures

Temperature in °C	Slope I when log [H_2O] value is below 1.425	Slope II when log [H_2O] value is above 1.425
20°C	0.930	1.506
25°C	0.809	1.350
30°C	0.596	1.082
35°C	0.579	0.831
40°C	0.424	0.800

may be inferred that the mechanistic pathway followed by the reaction is changed from unimolecular to bimolecular in presence of t-butanol in the reaction media and with increase in temperature of the reaction from 20 to 40 deg * C

Regarding the changes in the structure of water, it is obvious that in presence of t-butanol and with rise in temperature, water components of the reaction media, changes its structure from bulky to dense form.

$$(H_2O)_b \rightleftharpoons (H_2O)_d$$

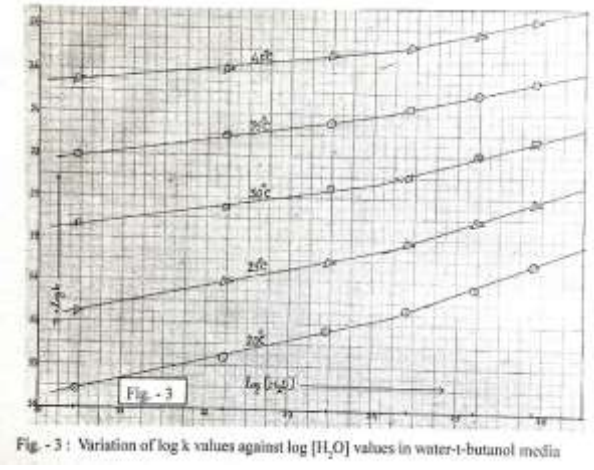

Fig. - 3 : Variation of log k values against log [H_2O] values in water-t-butanol media

Such findings and inferences have also been recently supported by Singh & Kumari[16]

Solvent effect on Thermodynamic Activation Parameters of the Reaction:

For better study of the effects of solvent, the thermodynamic activation parameters, such as enthalpy of activation ΔH* entropy of activation ΔS* and free energy of activation ΔG* were taken into account as they have great significance. These parameters

evaluated using Wynne-Jones and Eyring[4] equation have been recorded in Table- VII. In order to highlight the effect of solvent concentration on these thermodynamic parameters more clearly, ΔH*, ΔG* and ΔS* values were plotted against mole % of t-butanol as shown in Fig. 4, 5 and 6 respectively.

The values of ΔG* recorded in Table-VII obviously indicate that the variation in ΔG* is small and it increases from 88.82 to 91.18 kJ/mol with change of proportion of t-butanol from 30% to 80% (v/v) at 30°C slowly with gradual addition of the organic content in water. The small but considerable increase in ΔG* and non-linear variation in ΔH* and ΔS* curves with the increasing mol % of t-butanol are indication of specific solvation taking place in the process of activation as already reported by Saville & Hudson[17] and Tomilla et al[18].

Table - VII

Consolidated Values of the Thermodynamic Activation Parameters (ΔH*, ΔG* and ΔS*) of the reaction in in water-t-butanol solvent system at different temperatures

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of t-butanol (v/v)	Mol % of t-butanol	ΔH* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*
30%	7.52	98.78	89.03	32.28	88.98	32.88	88.80	32.95	88.67	32.83	88.44	33.04
40%	11.23	103.89	89.71	48.39	89.49	48.33	89.16	48.62	89.02	48.29	88.77	48.30
50%	15.95	107.65	90.29	59.22	90.03	59.10	89.79	58.92	89.38	59.31	89.13	59.14
60%	22.15	112.94	90.86	75.37	90.60	74.98	90.09	75.43	89.78	75.21	89.40	75.29
70%	30.68	116.92	91.58	86.48	91.15	86.47	90.65	86.69	90.14	86.94	89.79	86.69
80%	43.15	126.59	92.43	116.59	91.98	116.16	91.18	116.89	90.78	116.27	90.15	116.43

Simultaneous increase in ΔG*, ΔH* and ΔS* values with increas in mol% of t-butanol in the reaction media are only possible when the extent (degree) of enhancement in ΔS* values is less than that in ΔH* values and from this, it may be inferred that in alkali catalysed hydrolysis of Methyl caprate in water-t-butanol media, t-butanol acts as entropy controller

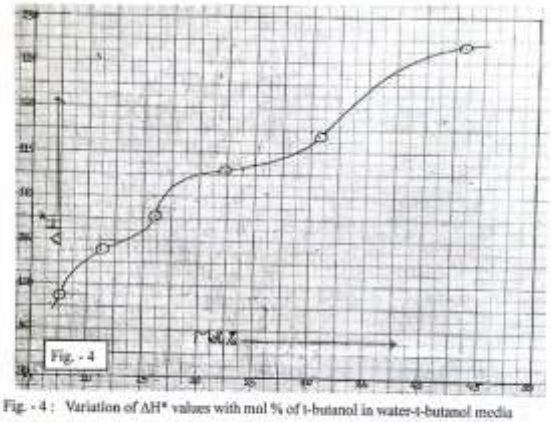

Fig. - 4 : Variation of ΔH* values with mol % of t-butanol in water-t-butanol media

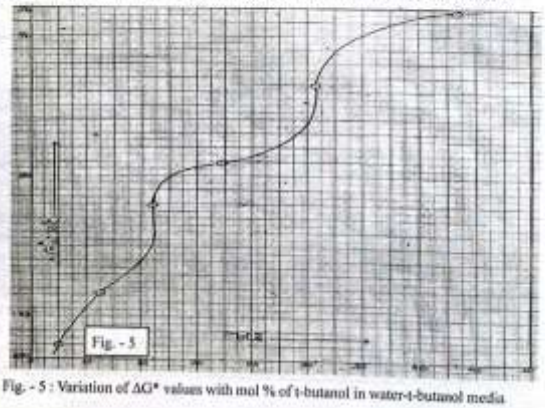

Fig. - 5 : Variation of ΔG* values with mol % of t-butanol in water-t-butanol media

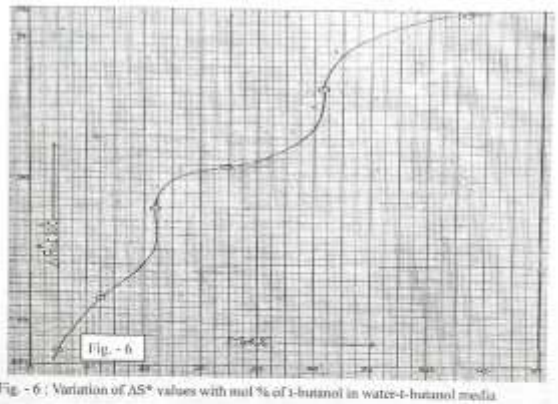

Fig. - 6 : Variation of ΔS* values with mol % of t-butanol in water-t-butanol media

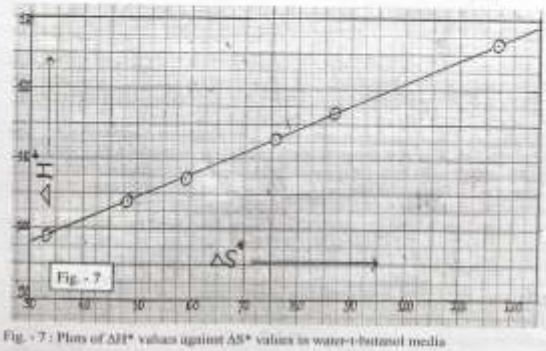

Fig. - 7 : Plots of ΔH* values against ΔS* values in water-t-butanol media

and enthalpy dominating solvent. Such inferences have also been supported by the views of Sharma & Singh et al[21] and recently by Kumar & Singh et al[7]. and Singh et al[20].

Obedience of Barclay-Butler relationship:

This reaction is found to obey Barclay-Butler[21] relationship as a straight line is obtained when ΔH* values are plotted against ΔS* at 30°C (values mentioned in Table-VII) as shown in Fig. 7. From the value of the slope of the plot, the values of iso-kinetic temperature of the reaction comes to be 331.42. In the light of the reports of Leffler[22], high and considerable values of iso-kinetic temperature shows that in presence of t-butanol, there is appreciably strong solvent-solute interaction in the reaction media (water-t-butanol). Similar reports have also been communicated in recent days by Singh & Namrata[3] Singh & Perween et al[10], Kumar & Singh[13] and Singh & Kumari et al[23]

REFERENCES

1. Singh, R. T., Kumari, R., Singh, P. and Kumari, Anjula: ARJ Phys. Sci., 14, No. (1-2). 127-135,2011
2. Singh, R. N., Smriti, Kumar, S. and Singh, R. T.: NIRJ Sci. 12, 67-76, 2013
3. Singh, R T., Kumari, M., Chaudhary, K. K. and Namrata: ARJ Phy. Sci. 13. Nos. (1-2), 105-115, 2013
4. Wynne-Jones W. F. K. and Eyring, H.: J. Chem. Phys., 3, 492, 1953
5. Laidler, K. J. and Landskroener, P. A.: Trans. Faraday Soc. 1956, 52, 200
6. Singh, R.T., Mishra, S. K., Singh, S. B. and Singh, S.: ARJ Phys. Sci., 15, No. (1-2), 141-150, 2012
7. Kumar, S., Mishra, S. K., Dubey, R. and Singh, R. T.: NIRJ Sci. 15, 29-88, 2014
8. Elsemongy, M. M.: Z. Physik, Chem., (Neue Folge) 1975, 94, 295
9. Singh, Lallan., Singh, R. T. and Jha, R. C. J. Indian. Chem.. Soc., 1981, 58, 566
10. Singh, R. T., Kumar, S., Perween, Z. and Singh, R. 1.: ARJ Phy. Sci. 16, No. (1-2), 117-128, 2013
11. Singh, RT., Navendu, K. S. Henry, W. and Hafizee, N. K.: NIRJ Sci. 14,53-61,2013
12. Wolford, R. K. J. Phys. Chem.,. 68, 3392, 1964
13. Kumar, P., Rai, R.M., Rai, C. L.. and Singh, R.T: NIRJ Sei. 15, 59-63, 2014
14. Robertson, R. E.: Prog. Phy. Org. Chem., 4, 213, 1967
15. Robertson, R. E., Heppolitile, R. L. and Scott, J. M.: Canad. J. Chem. Soc., 37, 803, 1959
16. Singh, R. T., Kumar, A., Singh, R. and Kumari, V.: NIRJ Sci. 12, 53-65, 2013
17. Saville, B. J. and Husdan, R.F. and M. N. H. Moussa: J. Chem. Soc., 20, 120,1955, 95,215
18. Tomilla, E., and Mevikallio, E.: Somun Kemi, 26C, 79, 1953
19. Sharma, S. P., Rai, C.L., Singh, A. K. and Singh, R.T.: NIRJ, Sci., 5, 121-126, 2010
20. Singh, S K., Kumari, S., Prasad, R. J. and Singh, R. T.: ARJ Phy. Sci. 14, No. (1-2), 115-125, 2011
21. Barclay, I. M. and Butler: Trans. Faraday Soc. 1938, 34, 1445 J. A. V.
22. Leffler, J. E.: J. Org. Chem., 20, 1201, 1955
23. Singh, R. T., Kumari, V., Singh, M. and Kumari, N. NIRJ Sci. 13, 59-63, 2013