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Applicability of pH measurement method for monitoring non-aqueous solvent based reaction rates

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ABSTRACT

UV-VIS absorbance measurement is a widely used and well established monitoring method for the kinetic study of various chemical reactions. The present study is carried out to evaluate applicability of pH measurement method, specially, for monitoring non-aqueous mediated chemical reactions along with UV-VIS absorbance measurement method. The rate constant values obtained by pH measurement were moderately in agreement with that by absorbance measurement method, which suggests that pH measurement could be used to monitor the reactions to get preliminary information about the kinetic aspect of the reactions.

Keywords: kinetic study, monitoring methods, rate constant, C.A.N.

INTRODUCTION

The kinetic study provides valuable information about mechanism and rate of chemical reactions [1]. Monitoring of progress of any industrial reaction is important to check the course of the reaction to get desired product with expected yield. Various monitoring methods like measurement of Absorbance [2-4], Electrical conductance [5], pH measurement [6], titrimetric method [7-9] etc are practiced as check-in processes. Each method has its own advantages and disadvantages, but, Spectrophotometric method is widely used in chemical and pharmaceutical analyses due to some specific features like selectivity, easy applicability and sensitivity [10].

The pH measurement could be a monitoring method if H^+ ions are reacting or being produced during a reaction [11]. This method could be a simple one in most of the cases, but may have certain limitations like applicability in non aqueous solvent, low degree of dissociation of some reacting species. To evaluate the applicability of pH measurement for monitoring of rate of such type of reactions, the present work, wherein, simultaneous measurements of pH and absorbance are carried out for the oxidation of 7- methyl- 2- chloro- 3-formyl quinoline by C.A.N. (ceric ammonium. nitrate).

MATERIALS AND METHODS

Synthesis of substrate 7- methyl- 2- chloro- 3-formyl quinoline was carried out by using Vilsmeier-Haack Reagent reaction [12]. Oxidation of 7- methyl- 2- chloro- 3-formyl quinoline was carried out by C.A.N., taking equimolar conc (0.01M) and the progress of reaction was monitored by measurement of pH and absorbance simultaneously at regular interval of time. The chemicals used were of AR grade, the pH measurement was carried out by using Elico

LI 120 pH meter and the absorbance was measured on Shimadzu UV 1800 spectrophotometer. Same reaction was carried out at four different temperatures.

RESULTS

Table 1.1, 1.2, 1.3 and 1.4 show K values at 50, 60, 70 and 80 °C by pH measurement. Table 1.5, 1.6, 1.7 and 1.8 show K values by OD measurement, while, the table 1.9 shows mean K values by pH and OD measurements.

Table 1.1: K values by pH at 50 °C

Time (t)	pH	x	a-x	1/a-x	K s ⁻¹
0	6.5	--	--	--	--
5	4.94	1.148E-05	0.0049885	200.46	0.001534395
10	3.91	0.000123	0.004877	205.045	0.008408691
15	3.69	0.0002042	0.0047958	208.515	0.009460717
20	3.42	0.0003802	0.0046198	216.459	0.013715908
25	3.18	0.0006607	0.0043393	230.452	0.020301045
30	3.09	0.0008128	0.0041872	238.825	0.021569345
35	2.99	0.0010233	0.0039767	251.464	0.024506828
40	2.97	0.0010715	0.0039285	254.551	0.022729722
45	2.98	0.0010471	0.0039529	252.981	0.019622464
50	2.99	0.0010233	0.0039767	251.464	0.01715478

Table 1.2: K values by pH at 60 °C

Time (t)	pH	x	a-x	1/a-x	K s ⁻¹
0	6.12	--	--	--	--
5	4.7	1.995E-05	0.00498	200.801	0.002671008
10	3.81	0.0001549	0.0048451	206.393	0.010655513
15	3.62	0.0002399	0.0047601	210.079	0.011198759
20	3.31	0.0004898	0.0045102	221.719	0.018098847
25	3.1	0.0007943	0.0042057	237.774	0.025182762
30	3.01	0.0009772	0.0040228	248.585	0.026991876
35	2.92	0.0012023	0.0037977	263.315	0.030149907
40	2.93	0.0011749	0.0038251	261.431	0.025596211
45	2.92	0.0012023	0.0037977	263.315	0.023449928
50	2.92	0.0012023	0.0037977	263.315	0.021104935

Table 1.3: K values by pH at 70 °C

Time (t)	pH	x	a-x	1/a-x	K s ⁻¹
0	5.7	--	--	--	--
5	3.1	0.0007943	0.0042057	237.774	0.12591381
10	2.86	0.0013804	0.0036196	276.272	0.127120701
15	2.74	0.0018197	0.0031803	314.436	0.127150922
20	2.68	0.0020893	0.0029107	343.56	0.119632926
25	2.61	0.0024547	0.0025453	392.882	0.128588248
30	2.57	0.0026915	0.0023085	433.188	0.129549028
35	2.54	0.002884	0.002116	472.597	0.129808013
40	2.51	0.0030903	0.0019097	523.641	0.134850502
45	2.51	0.0030903	0.0019097	523.641	0.119867113
50	2.5	0.0031623	0.0018377	544.152	0.114717281

Table 1.4: K values by pH at 80 °C

Time (t)	pH	x	a-x	1/a-x	K s ⁻¹
0	4.49	--	--	-	--
5	2.75	0.0017783	0.0032217	310.393	0.367977164
10	2.57	0.0026915	0.0023085	433.188	0.388647084
15	2.5	0.0031623	0.0018377	544.152	0.382390938
20	2.47	0.0033884	0.0016116	620.517	0.35043114
25	2.44	0.0036308	0.0013692	730.343	0.353562077
30	2.42	0.0038019	0.0011981	834.651	0.352583703
35	2.41	0.0038905	0.0011095	901.267	0.333936884
40	2.39	0.0040738	0.0009262	1079.68	0.366534855
45	2.38	0.0041687	0.0008313	1202.93	0.371454163
50	2.38	0.0041687	0.0008313	1202.93	0.334308747

Table 1.5: K values by OD at 50 °C

Time (t)	OD	x	a-x	1/a-x	K s ⁻¹
0	0.013	--	--	--	--
5	0.112	0.001008	0.003992	250.501	0.16833667
10	0.198	0.001782	0.003218	310.752	0.1845867
15	0.243	0.002187	0.002813	355.4924	0.17276929
20	0.276	0.002484	0.002516	397.4563	0.1645469
25	0.299	0.002691	0.002309	433.0879	0.15539194
30	0.329	0.002961	0.002039	490.4365	0.1613536
35	0.351	0.003159	0.001841	543.1831	0.1634205
40	0.369	0.003321	0.001679	595.5926	0.16483026
45	0.388	0.003492	0.001508	663.13	0.17152962
50	0.397	0.003573	0.001427	700.7708	0.16692362

Table 1.6: K values by OD at 60 °C

Time (t)	OD	x	a-x	1/a-x	K s ⁻¹
0	0.019	--	--	--	--
5	0.127	0.001143	0.003857	259.2689	0.19756287
10	0.197	0.001773	0.003227	309.8853	0.18314224
15	0.253	0.002277	0.002723	367.242	0.18582446
20	0.301	0.002709	0.002291	436.4906	0.19707551
25	0.338	0.003042	0.001958	510.7252	0.20715015
30	0.352	0.003168	0.001832	545.8515	0.19213974
35	0.381	0.003429	0.001571	636.5372	0.20787487
40	0.396	0.003564	0.001436	696.3788	0.20682451
45	0.406	0.003654	0.001346	742.9421	0.20108965
50	0.416	0.003744	0.001256	796.1783	0.19872611

Table 1.7: K values by OD at 70 °C

Time (t)	OD	x	a-x	1/a-x	K s ⁻¹
0	0.021	--	--	--	--
5	0.156	0.001404	0.003596	278.0868	0.26028921
10	0.243	0.002187	0.002813	355.4924	0.25915393
15	0.306	0.002754	0.002246	445.236	0.27248442
20	0.343	0.003087	0.001913	522.7392	0.26894929
25	0.381	0.003429	0.001571	636.5372	0.29102482
30	0.398	0.003582	0.001418	705.2186	0.28067701
35	0.417	0.003753	0.001247	801.9246	0.28663077
40	0.434	0.003906	0.001094	914.0768	0.29753199
45	0.443	0.003987	0.001013	987.1668	0.29154327
50	0.449	0.004041	0.000959	1042.753	0.28091762

Table 1.8: K values by OD at 80 °C

Time (t)	OD	x	a-x	1/a-x	K s ⁻¹
0	0.029	--	--	--	--
5	0.254	0.002286	0.002714	368.4598	0.56153279
10	0.359	0.003231	0.001769	565.2911	0.60881854
15	0.399	0.003591	0.001409	709.7232	0.56635912
20	0.423	0.003807	0.001193	838.223	0.53185247
25	0.449	0.004041	0.000959	1042.753	0.56183525
30	0.459	0.004131	0.000869	1150.748	0.52819333
35	0.469	0.004221	0.000779	1283.697	0.51604621
40	0.483	0.004347	0.000653	1531.394	0.55474732
45	0.489	0.004401	0.000599	1669.449	0.5442404
50	0.493	0.004437	0.000563	1776.199	0.52539964

Table 1.9: Mean K values by pH and OD measurement

Temp	Mean K by pH	mean K by OD
50	0.0159	0.1673
60	0.0195	0.1977
70	0.1117	0.2789
80	0.2582	0.5499

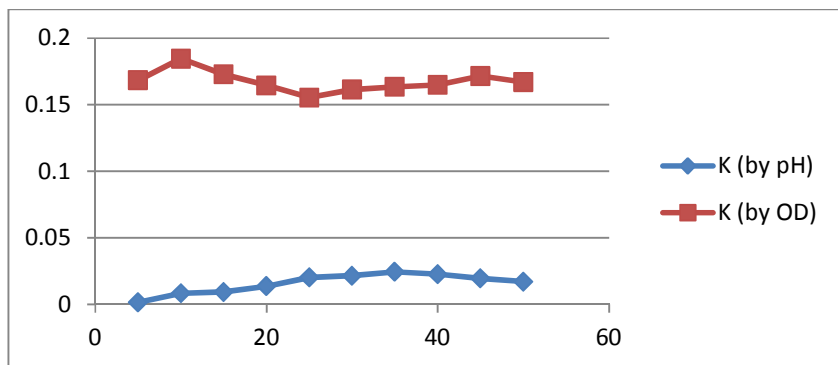


Fig. 1.1: K values by pH and OD measurement vs time at temp 50 °C

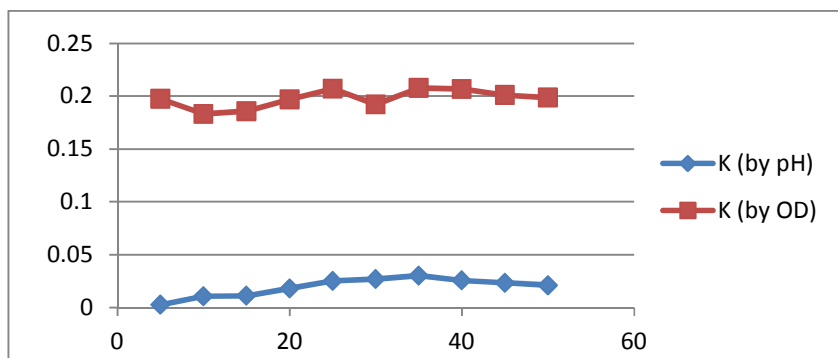


Fig. 1.2: K values by pH and OD measurement vs time at temp 60 °C

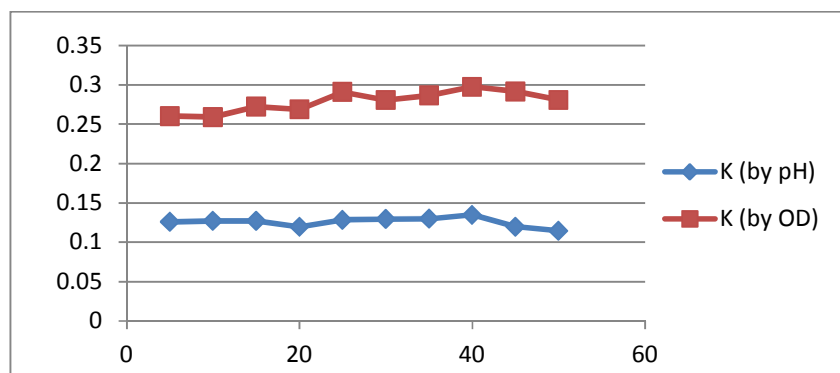


Fig. 1.3: K values by pH and OD measurement vs time at temp 70 °C

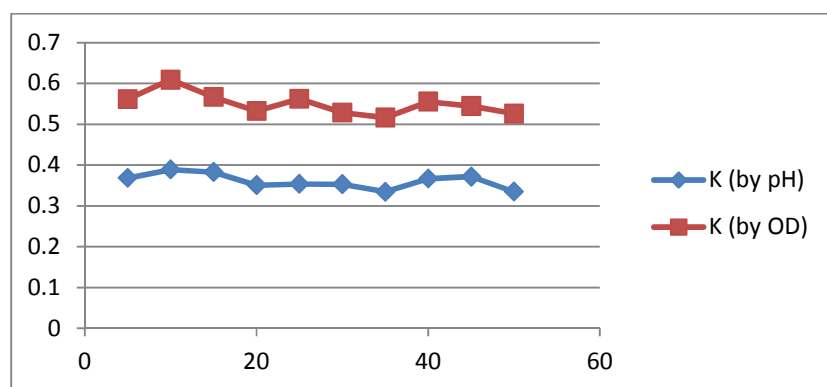


Fig. 1.4: K values by pH and OD measurement vs time at temp 80 °C

DISCUSSION

From fig.1.1 to 1.4, it appears that there is a moderate agreement between k values calculated by pH measurements and by OD measurements. But there is a good agreement between these two monitoring methods as far as the trend of the reaction, especially, the rate of change of reaction rate is considered.

CONCLUSION

Moderate agreement between K values (by pH and by OD measurement) shows that the pH measurement method could be suitable for reactions carried in aqueous solvents and involving strong acidic or basic reactants and may not be suitable to that extent for non-aqueous solvents and for weak acids and bases, but is useful for easy and rapid monitoring of progress of any reaction; whereas monitoring by absorbance measurements is more applicable to variety of solvents and also weak acids and bases. pH measurement method would be useful to get a preliminary information about the trend of reaction rate. Also, for real verification, the researchers should not rely on any single monitoring method, but, it is better to monitor any process by more than one testing methods (cross verification).

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