New measurements and modeling of electrical conductivity and pH of n-propanethiol and n-butanethiol in *N*-methyldiethanolamine + piperazine (MDEA-Piperazine) Aqueous solution at 306 K and 1atm.

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Abstract:

In this work new measurements of electrical conductivity (µS.cm^{-1}) and pH of n-propanethiol and n-butanethiol in *N*-methyldiethanolamine (MDEA) + piperazine aqueous solution at 306 K and atmospheric pressure. The experiments were performed at three 2.5 ml, 3.0 ml and 5.0 ml volumes of n-propanethiol and n-butanethiol in 45 wt % and 18 wt % MDEA aqueous solutions. The piperazine concentration has been kept constant by 4 wt % in all the experiments. The changes in electrical conductivity (EC) with time have been related to the change in concentration of ionic species and change of pH has been related to the acid-base neutralization reaction.

Keywords: electrical conductivity, kinetics of thiols, acid-base neutralization, thiol removal, organic sulfur species

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1. Introduction:

The standard state properties, equilibrium constant, Gibbs free energy, chemical potential and enthalpy of reaction for the organic sulfur species like thiols (RSH) (also known as thiols) in gas phase, liquid phase and in aqueous phase are highly required properties for the optimized process design in oil and gas Industry. Unfortunately limited or no information about the kinetics and phase behavior is available in open literature [1]. The natural gas and petroleum industries are dealing with raw materials containing variable concentrations of acid gases (CO_2, H_2S) and traces of organic sulfur species (OSS) like thiols and dimethyl disulfide , and many others. Treatment processes have to remove not only H_2S and CO_2 but also (thiols) thiols and prohibited compounds because worldwide regulations for environmental protection are forcing the petroleum industry to decrease the sulfur content in petroleum fluids[1]. Mercaptan belong to thiol-group of compound which contain an –SH group bound to a radical R. Mercaptan properties are governed to a large extent by the length of this radical [1,2] .

In this work a new cell has been constructed for the simultaneous measurements of electrical conductivity ($\mu S.cm^{-1}$) and pH of n- propanethiol and n-butanethiol in 45 wt % and 18 wt % MDEA and 4 wt % piperazine aqueous solution at 306 K and atmospheric pressure. It was observed that, as the mercaptan ions moves in MDEA and piperazine aqueous solution; electrical current flows through solutions and electrical conductivity increases with the increase in ionic concentration. The change in electrical conductivity of n-propanethiol and n-butanethiol in *N*-Methyldiethanolamine and piperazine aqueous solutions has been related to the change in the concentrations of ions formed inside the solution. The change in pH of n-Propanethiol and n-butanethiol in *N*-methyldiethanolamine and piperazine aqueous solutions has also been studies. The reaction is acid-base neutralization so the change of pH has been related to the acid-base neutralization reaction. This information is further helpful to calculate the aforementioned properties and solubility due to chemical reaction[1].

2. Electrical Conductivity Model:

2.1 Chemical Reaction:

The chemical reaction of n-propanethiol and n-butanethiol in *N*-Methyldiethanolamine + piperazine aqueous solution can be written as a function of concentrations and ionic charges.

$$RSH + H_2O \rightarrow RH^- + H_3O \tag{1}$$

$$RSH + R_3N \text{ (or } R_4N) \rightarrow RS^- + RNH^+ \tag{2}$$

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{3}$$

$$PZH^+ + H_2O \rightarrow PZ + H_3O^+ \tag{4}$$

$$PZ + RSH + H_2O \rightarrow PZRS^- + H_3O^+ \tag{5}$$

$$PZRS^- + RSH + H_2O \rightarrow {}^-SRPZRS^- + H_3O^+ \tag{6}$$

$$EC = F^2 \sum (z_i^2) \Theta_i C_i \tag{7}$$

$$\Theta_i = \frac{D_L}{RT}\frac{mol\ cm^2}{J.s} \tag{8}$$

F = 96500 coulombs, and z_i = ionic charge

Where, D_L (cm^2/s) is the diffusivity of thiols in aqueous solutions. *R* (atm dm^3/mol K), is the general gas constant. *T* (K) is the temperature in Kelvin. In case of RS-ions the value of $z_i$is (-1). In general the co-relation can be written as

$$EC = f(c_i, z_i) \tag{9}$$

The main idea is to correlate the change in electrical conductivity as a function of time and thiol concentration as shown in equation (9).

3 Experimental Section:

3.1 Materials

The apparatus and materials used for the experiments with specifications and supplier are provided in the figure 1 and Table (1). Distilled water was used and no further purification was made.

[Table 1]

3.2 Apparatus and Experimental setup

The experiments are performed with two different compositions of MDEA *i.e* 45 wt % and 18 wt % + 4 wt % piperazine aqueous solutions. The amount of n-propanethiol and n-butanethiol were added individually *i-e* (2.50 ml, 3.0 ml and 5.0 ml).The change in electricity conductivity (µS/cm) and pH with time at 306 K and atmospheric pressure have been studies. First of all the 70 grams of 45 wt % MDEA aqueous solution was added followed by the recalculated quantity of piperazine. The n-propanethiol and n-butanethiol were added with three different concentrations *i.e* 2.5 ml, 3.0 ml and 5.0 ml respectively. The same procedure was performed with different concentration of 18 wt % MDEA and 4 wt % piperazine aqueous solution by using 2.5 ml,3.0 ml and 5.0 ml of n-propanethiol and n-butanethiol respectively. Our literature review reveals that up to now no experimental data points about the electrical conductivity of thiols containing systems are available in the literature; therefore no comparison is possible.

[figure 1]

The schematic diagram of the apparatus design is presented in figure 1. The electrical conductivity meter and pH meter probes have been placed in the center of the cell, as shown in figure 1. The change in electrical conductivity and pH has been measured with time. Only the electrical conductivity of n-propylmercaptan into MDEA aqueous solution is reported by Awan *et al.* [1] and the ionization constants for thiols were reported by Yabroff and White [3]. At first MDEA and piperazine aqueous solution was prepared gravimetrically under vacuum. A known quantity of MDEA and piperazine aqueous solution (140 cm^3) was loaded into the cell, which already contains magnetic stirrer for stirring. Once Electrical conductivity and pH values are stable then n-propanethiol or n-butanethiol were introduced into the cell through a special injector arrangement. Finally, the cell is placed inside a liquid water bath where temperature is maintained at 306 K. The probes of the electrical conductivity meter, pH meter and temperature were placed inside the cell, through a Teflon cap, inside it a special type of O-ring to avoid entrance of air. A vacuum connection to the cell was used for removing air from the cell. It was observed as the mercaptan ions moves in MDEA and piperazine aqueous solution. Electrical current flows through solutions and electrical conductivity increases with the increase in ionic concentration. The change in electrical conductivity of n-propanethiol and n-butanethiol in *N*-

Methyldiethanolamine and piperazine aqueous solutions is due to the change in the concentrations of ions formed inside the solution. The change in electrical conductivity (EC) with time is due to the change in concentration of ionic species and change of pH is due to related to the acid-base neutralization reaction. This information is further helpful to calculate the thermo physical properties and solubility due to chemical reaction.

3.3 Calibration of Equipments:

The 4 electrodes ADWA 310 conductivity meter and pH meter were calibrated according to the standards mentioned in their manual books. Electrical conductivity meter probe ADWA 310 (4electrodes) was calibrated with 0.1*N* KCl solution. pH meter was also calibrated with buffer solution having pH 4, 7 and 10.0 at 303.15 K. The calibration readings of electrical conductivity and pH are presented in tables S1 and S2 of supporting document. The calibration curves are shown in figures S1 and S2 of supporting document. The values of pH and electrical conductivity with their respective uncertainties can be obtained using the two following four equations (10 to 13):

$$pH = apH_{Exp} + b \tag{10}$$

$$EC = cEC_{Exp} + d \tag{11}$$

$$\mathrm{u(pH)} = \sqrt{\mathrm{u(b)}^2 + \mathrm{pH}_{\mathrm{Exp}}\,\mathrm{u(a)}^2} \tag{12}$$

$$\mathrm{u(EC)} = \sqrt{\mathrm{u(d)}^2 + \mathrm{EC}_{\mathrm{Exp}}\,\mathrm{u(c)}^2} \tag{13}$$

With $a=1.285$, $b=-1.025$, $u(a)=0.126$, $u(b)=0.841$, $c=0.720$, $d=436$, u(c)=0.038 and $u(d)=61$.

4. Results and Discussions:

The electrical conductivity and pH measurements of n-propanethiol and n-butanethiol in *N*-Methyldiethanolamine and piperazine aqueous solution are presented in this work (Tables 2 -7). As no other data has been found in open literature, comparison was not possible. Only the electrical conductivity of n-PM in MDEA aqueous solution has been discussed by Awan *et al.*[1]. Correlations between the electrical conductivity, pH and the change in ionic concentration with time have been suggested. First the composition of the MDEA and piperazine aqueous solution were kept constant *i.e.* 50 wt % and 5 wt % respectively and the composition of n-propanethiol and n-butanethiol vary from 2.5 ml, 3.0 ml to 5.0 ml. Similarly the same procedure was performed for 18 wt % MDEA and 5 wt % piperazine aqueous solutions by using 2.5 ml, 3.0 ml and 5.0 ml of n-propanethiol and n-butanethiol.

[Tables 2 to 7]

It is observed that initially electrical conductivity (EC) and the value of pH increases in *N*-Methyldiethanolamine + piperazine aqueous solution (no thiols has been added to cell). After the addition of thiols the electrical conductivity (EC) decreases and pH starts increasing for some time till equilibrium is achieved as shown in figures (see figures 2-9). The decrease in electrical conductivity might be due to the physical solubility phenomenon and increase in electrical conductivity might be due to the chemical reaction *i.e*. formation of ionic species and the decrease in pH is due to the acid-base neutralization reaction. However the results of electrical conductivity of n-propanethiol / n-butanethiol (5.0 ml) in MDEA-piperazine aqueous solution as a function of time did not show the initial decrease in electrical conductivity(EC) values (see figure 2,3,4,5).

[Figures 2 to 9]

This might be due to the bigger value of chemical solubility in comparison to the physical solubility; as the common observation does support with the hypothesis that there is a physical as well as chemical solubility of n-propanethiol and n-butanethiol in MDEA and piperazine aqueous solutions by using different composition small change in the data was observed. The change in electrical conductivity and pH of 18 wt % was low as compared to the 45 wt % MDEA and 4 wt % piperazine aqueous solution as shown in the following figures (8, 9).

[figure 8]

[figure 9]

According to these experiments, we can confirm the existence of a chemical reaction between n-propanethiol and n-butanethiol in MDEA and piperazine aqueous solution. However more experiments must be performed in a Lewis type kinetic cell, for better understanding of the phenomenon. Electrical conductivity of n-PM in pure water has been reported in literature [2] showing that electrical conductivity in pure water is higher with respect to pure MDEA. In the literature there is no or limited information is available about the kinetics of thiols in water and/or MDEA-piperazine aqueous solution. Only the ionization constants for thiols were reported by Yabroff and White [3]. The equilibrium constant of n-butyl mercaptan (n-BM) at alkaline conditions in water at 301K, $K_{eq}=K_a/K_w=2489$ was reported by Matsis *et al.*[4]. This value indicates a minor dissociation of n-propanethiol and n-butanethiol in aqueous solution. The permittivity of a solvent like alkanol amine may affect the reaction rate between the solvent itself and thiols, as discussed by Yakupov *et al.*[5].The solvent may therefore also affect the rate of dissociation of mercaptan. The solubility of thiols in MDEA has been discussed by Bedel land Miller[6] as the sum of physical and chemical solubility on the basis of the acid-base neutralization approach in an alkanol amine solution. Methyl mercaptan and ethyl mercaptan (EM) are weak acids, but higher thiols behave like hydrocarbons as the alkyl group increases[7,8,9]. According to these experiments, we have confirmed the existence of a chemical reaction between n-propanethiol and n-butanethiol in MDEA-piperazine aqueous solutions. It was not possible to give an indication of the possible mechanism of the chemical reaction; just we can confirm that ions are produced with time before the equilibrium is achieved. Moreover during their action, negative and positive charged ions are created. The negative charge is supposed to be on sulfur atom (CH_3-CH_2-CH_2-S^-), CH_3-CH_2-CH_2-CH_2-S^-). It is also concluded that organic part ($CH3$-$CH2$-$CH2^+$) carries hydrophobic and (S^-) part carries hydrophilic properties. Similarly in the case of pH, at higher value of thiols (*i-e* 5.0 ml) the solutions show more acidic behavior. So, there is a chance of fast chemical reaction and there will be greater rate constant. Consequently n-propanethiol and n-butanethiol molecules group together to form a drop. This drop has a negative global charge. So all the drop push away together (they don't collapse together)

5 Conclusions:

Electrical conductivity and pH measurements of n-propanethiol and n-butanethiol in *N*-Methyldiethanolamine and piperazine aqueous solution at 306 K and atmospheric pressure have been presented and discussed. The existence of chemical reaction between n-propanethiol /n-butanethiol in MDEA-piperazine aqueous solutions has been highlighted. The changes in electrical conductivity (EC) with time have been related to the change in concentration of ionic species and change of pH has been related to the acid-base neutralization reaction.

Supporting Information: In the supporting document tables S1 and S2 presents calibration of 4 electrodes ADWA 310 electrical conductivity temperature range from 303.15 K to 310.15 K and calibration of pH meter at 303.15 K respectively. The figures S1 and S2 presents Calibration curve; the theoretical electrical conductivity of standard solution 0.1 *N* KCl solution as a function of experimental electrical conductivity at 303.15 K and 1 atm and Calibration curve; experimental (pH) of 4, 7 and 10 buffer solution is plotted as a function of theoretical pH at 303.15 K and 1 atm respectively.

6. References:

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Tables:

Table 1: CAS numbers, purities, and suppliers of materials

Chemical Name	**CAS No.**	**Purity %**	**Supplier**
N-Methyldiethanolamine (MDEA)	107-03-9	99 + GC	SIGMA-ALDRICH
piperazine	110-808-3	≥ 98 ,0%	SIGMA-ALDRICH
n-butanethiol	109-79-5	99%	SIGMA-ALDRICH
n-propanethiol	107-03-9	99%	SIGMA-ALDRICH

Table 2: Electrical conductivity and pH of n-propanethiol and n-butanethiol (2.5 ml by vol.) in 45 wt% *N*-Methyldiethanolamine+ 4 wt% piperazine aqueous solution at 306K and atmospheric pressure.

No. of data points	Time/min	n-propanethiol			n-butanethiol		
		pH	EC $_{\text{Experimental}}$ (μS/cm)	EC $_{\text{Theoretical}}$ (μS/cm)	pH	EC $_{\text{Experimental}}$ (μS/cm)	EC $_{\text{Theoretical}}$ (μS/cm)
1	0	10.63	1606.5	934.5	10.56	1555.5	1098.0
2	10	10.73	1570.8	742.3	10.66	1504.5	872.1
3	20	10.83	1581	589.6	10.72	1514.7	759.6
4	30	10.7	1596.3	795.4	10.52	1514.7	1204.0
5	40	10.46	1591.2	1382.1	10.5	1504.5	1260.7
6	50	10.45	1586.1	1414.6	10.49	1484.1	1290.1
7	60	10.44	1581.1	1447.6	10.49	1479.1	1290.1
8	70	10.43	1581.1	1481.3	10.48	1479.1	1320.1
9	80	10.38	1591.2	1662.1	10.46	1479.1	1382.4
10	90	10.38	1591.2	1662.1	10.45	1484.1	1414.6
11	100	10.37	1601.4	1700.1	10.45	1484.1	1414.6
12	110	10.36	1616.7	1740.4	10.43	1489.2	1481.3
13	120	10.36	1632.0	1740.4	10.43	1499.4	1481.3
14	130	10.37	1647.3	1700.8	10.42	1509.6	1515.8
15	140	10.37	1652.4	1700.8	10.39	1535.1	1624.2
16	150	10.35	1652.4	1780.9	10.39	1555.5	1624.2
17	160	10.34	1657.5	1822.4	10.37	1606.5	1700.8
18	170	10.34	1662.6	1822.4	10.35	1683.1	1780.9
19	180	10.34	1667.7	1822.4	10.34	1759.5	1822.4
20	190	10.34	1672.8	1822.4	10.34	1769.7	1822.4

The standard uncertainties u are u(T, k=2) = 0.03 K , u(pH, k=2) = 0.05, u.(σ, k=2)=0.1; where σ stands for electrical conductivity

Table 3: Electrical conductivity and pH of n-propanethiol and n-butanethiol (3.0 ml by vol.) in 45 wt% *N*-Methyldiethanolamine+ 4 wt% piperazine aqueous solution at 306K and atmospheric pressure.

No. of data points	**Time** (min)	**n-propanethiol**			**n-butanethiol**		
		pH	**EC$_{\text{Experimental}}$ (μS/cm)**	**EC$_{\text{Theoretical}}$ (μS/cm)**	**pH**	**EC$_{\text{Experimental}}$ (μS/cm)**	**EC$_{\text{Theoretical}}$ (μS/cm)**
1	0	10.78	1650.1	1102.6	10.98	1060.8	927.5
2	10	11.02	1600.1	1050.5	11.27	958.8	475.6
3	20	11.05	1580.1	1475.3	11.3	907.8	443.9
4	30	10.46	1530.9	1728.0	11.35	851.7	395.6
5	40	10.45	1479.2	1768.3	11.35	836.4	395.6
6	50	10.44	1479.3	1809.5	11.12	918	671.9
7	60	10.43	1479.2	1851.6	10.84	831.3	1280.4
8	70	10.4	1484.1	1984.1	10.75	1009.8	1575.3
9	80	10.38	1500.9	2077.6	10.66	1229.1	1938.2
10	90	10.37	1550.5	2126.0	10.61	1484.1	2174.7
11	100	10.37	1675.4	2126.0	10.55	1698.3	2496.9
12	110	10.36	1775.2	2175.5	10.5	1892.1	2501.7
13	120	10.37	1874.6	2126.0	10.49	2126.7	2566.9
14	130	10.36	1974.2	2175.5	10.49	2254.2	2566.9
15	140	10.35	2073.8	2226.2	10.48	2386.8	2633.7
16	150	10.34	2173.4	2278.1	10.48	2463.3	2633.7
17	160	10.34	2273.1	2278.1	10.48	2524.5	2633.7
18	170	10.33	2372.6	2331.1	10.47	2550	2642.9
19	180	10.33	2372.2	2331.1	10.47	2565.3	2642.1
20	190	10.32	2373.5	2385.5	10.47	2565.3	2642.1
21	200	10.32	2380.6	2385.5	10.46	2565.3	2652.0
22	210	10.32	2385.7	2385.5	10.46	2565.3	2652.0
23	220	10.32	2388.8	2385.5	10.46	2565.3	2652.0
24	230	10.32	2391.9	2385.5	10.46	2565.3	2652.0
25	240	10.32	2395.7	2385.5	10.46	2565.3	2652.0
26	250	10.32	2398.1	2385.5	10.46	2565.3	2652.0
27	260	10.32	2398.1	2385.5	10.46	2565.3	2652.0
28	270	10.32	2399.2	2385.5	10.46	2565.3	2653.0
29	280	10.32	2400.2	2385.5	10.46	2565.3	2653.0

The standard uncertainties u are u(T, k=2) = 0.03 K , u(pH, k=2) = 0.05, u.(σ, k=2)=0.1; where σ stands for electrical conductivity

Table 4: **Electrical conductivity and pH of n-propanethiol and n-butanethiol (5.0 ml by vol.) in 45 wt% *N*-Methyldiethanolamine+ 4 wt% piperazine aqueous solution at 306K and atmospheric pressure.**

No. of data points	**Time** (min)	**n-propanethiol**			**n-butanethiol**		
		pH	**EC** $_{\textbf{Experimental (μS/cm)}}$	**EC** $_{\textbf{Theoritical (μS/cm)}}$	**pH**	**EC** $_{\textbf{Experimental (μS/cm)}}$	**EC** $_{\textbf{Theoritical (μS/cm)}}$
1	0	10.63	1800.2	1214.9	10.34	1953.1	1214.9
2	10	10.88	1708.5	683.1	10.67	1973.7	568.2
3	20	11	1545.3	518.1	10.73	1861.5	494.9
4	30	10.8	1519.8	821.3	10.76	1846.2	461.8
5	40	10.7	1514.7	1034.0	10.76	1836.2	461.8
6	50	10.63	1504.5	1214.9	10.65	1779.9	594.9
7	60	10.57	1524.9	1394.0	10.6	1718.7	667.6
8	70	10.55	1580.1	1460.7	10.54	1718.7	766.5
9	80	10.53	1620.2	1529.5	10.49	1739.1	860.0
10	90	10.51	1660.5	1601.6	10.44	1769.7	965.0
11	100	10.49	1700.1	1677.2	10.39	1774.8	1082.8
12	110	10.47	1740.2	1756.2	10.34	1785.1	1214.9
13	120	10.45	1780.3	1839.00	10.29	1790.1	1363.2
14	130	10.43	1820.5	1925.7	10.24	1810.5	1529.6
15	140	10.41	1860.6	2016.4	10.19	1846.2	1716.3
16	150	10.39	1900.7	2111.5	10.14	1912.5	1925.7
17	160	10.37	1940.7	2211.1	10.09	1963.5	2160.8
18	170	10.35	1980.3	2315.2	10.07	2014.5	2262.6
19	180	10.33	2020.2	2424.4	10.07	2080.8	2262.6
20	190	10.31	2138.5	2538.7	10.06	2157.3	2315.3
21	200	10.31	2155.7	2538.7	10.06	2218.5	2315.3
22	210	10.31	2255.7	2538.7	10.05	2359.3	2469.3
23	220	10.31	2227.6	2538.7	10.05	2384.8	2569.3
24	230	10.31	2300.7	2538.7	10.05	2400.1	2569.3
25	240	10.31	2350.9	2538.7	10.05	2450.1	2688.3
26	250	10.31	2476.1	2538.7	10.05	2505.2	2701.3
27	260	10.31	2505.2	2538.7	10.04	2690.3	2724.5
28	270	10.31	2510.2	2538.7	10.04	2710.3	2724.5
29	280	10.31	2510.5	2538.8	10.04	2710.3	2724.5

The standard uncertainties u are u(T, k=2) = 0.03 K , u(pH, k=2) = 0.05, u.(σ, k=2)=0.1; where σ stands for electrical conductivity

Table 5: Electrical conductivity and pH of n-propanethiol and n-butanethiol (2.5 ml by vol.) in 18 wt% *N*-Methyldiethanolamine+ 4 wt% piperazine aqueous solution at 306K and atmospheric pressure.

No. of data points	**Time** (min)	**n-propanethiol**			**n-butanethiol**		
		pH	**EC $_{\text{Experimental}}$ (μS/cm)**	**EC $_{\text{Theoretical}}$ (μS/cm)**	**pH**	**EC $_{\text{Experimental}}$ (μS/cm)**	**EC $_{\text{Theoretical}}$ (μS/cm)**
1	0	10.63	1606.5	1012.8	10.56	1555.5	1098.0
2	10	10.73	1570.8	742.3	10.66	1504.5	872.2
3	20	10.83	1581.1	589.6	10.72	1514.7	759.6
4	22	10.83	1606.5	589.6	10.72	1509.6	759.6
5	24	10.83	1596.3	589.6	10.72	1509.6	759.6
6	26	10.83	1596.3	589.6	10.62	1509.6	956.3
7	30	10.7	1596.3	795.4	10.52	1514.7	1204.0
8	40	10.46	1591.2	1382.4	10.5	1504.5	1260.8
9	50	10.45	1586.1	1414.6	10.49	1484.1	1290.1
10	60	10.44	1581.2	1447.6	10.49	1479.1	1290.1
11	70	10.43	1581.1	1481.3	10.48	1479.2	1320.2
12	80	10.38	1591.2	1662.1	10.46	1479.3	1382.4
13	90	10.38	1591.2	1662.1	10.45	1484.1	1414.6
14	100	10.37	1601.4	1700.8	10.45	1484.1	1414.6
15	110	10.36	1616.7	1740.4	10.43	1489.2	1481.3
16	120	10.36	1632.2	1740.4	10.43	1499.4	1481.3
17	130	10.37	1647.3	1700.8	10.42	1509.6	1515.8
18	140	10.37	1652.4	1700.8	10.39	1535.1	1624.2
19	150	10.35	1652.4	1780.9	10.39	1555.5	1624.2
20	160	10.34	1657.5	1822.4	10.37	1606.5	1700.8
21	170	10.34	1662.6	1822.4	10.35	1683.3	1780.9
22	180	10.34	1667.7	1822.4	10.34	1759.5	1822.4
23	190	10.34	1672.8	1822.4	10.34	1769.7	1822.4

The standard uncertainties u are u(T, k=2) = 0.03 K , u(pH, k=2) = 0.05, u.(σ, k=2)=0.1; where σ stands for electrical conductivity

Table 6: Electrical conductivity and pH of n-propanethiol and n-butanethiol (3.0 ml by vol.) in 18 wt% *N*-Methyldiethanolamine + 4 wt % piperazine aqueous solution at 306 K and atmospheric pressure.

No. of data points	**Time** (min)	**n-propanethiol**			**n-butanethiol**		
		pH	**EC** **Experimental** **(μS/cm)**	**EC** **Theoretical** **(μS/cm)**	**pH**	**EC** **Experimental** **(μS/cm)**	**EC** **Theoretical** **(μS/cm)**
1	0	10.23	2167.5	1950.08	10.45	1693.2	1414.0
2	10	10.42	1856.4	1757.90	10.6	1540.2	1001.4
3	20	10.52	1744.2	1602.00	10.61	1509.6	978.6
4	30	10.52	1713.6	1602.00	10.6	1504.5	1001.4
5	40	10.3	1734.1	1699.16	10.6	1509.6	1001.4
6	50	10.15	1744.2	1711.44	10.55	1519.8	1123.6
7	60	10.1	1759.5	1883.70	10.5	1504.4	1260.7
8	70	10	1779.9	1993.84	10.45	1494	1414.6
9	80	9.94	1800.3	2289.29	10.35	1514.7	1780.9
10	90	9.94	1810.5	2289.29	10.35	1565.7	1780.9
11	100	9.93	1810.5	2342.63	10.29	1616.7	2044.8
12	110	9.93	1938.2	2342.63	10.29	1667.7	2044.8
13	120	9.92	2065.5	2397.20	10.28	1772.8	2092.5
14	130	9.92	2193.2	2397.20	10.28	1877.9	2092.5
15	140	9.92	2320.5	2397.20	10.22	1981.8	2402.6
16	150	9.91	2376.6	2453.05	10.21	2086.8	2458.6
17	160	9.91	2376.6	2453.05	10.21	2191.8	2458.6
18	170	9.91	2376.6	2453.05	10.2	2191.8	2515.8

The standard uncertainties u are u(T, k=2) = 0.03 K , u(pH, k=2) = 0.05, u.(σ, k=2)=0.1; where σ stands for electrical conductivity

Table 7: Electrical conductivity and pH of n-propanethiol and n-butanethiol (5.0 ml by vol.) in 18 wt% *N*-Methyldiethanolamine+4 wt% piperazine aqueous solution at 306K and atmospheric pressure.

No. of data points	**Time** (min)	**n-propanethiol**			**n-butanethiol**		
		pH	**EC $_{\text{Experimental}}$ (μS/cm)**	**EC $_{\text{Theoretical}}$ (μS/cm)**	**pH**	**EC $_{\text{Experimental}}$ (μS/cm)**	**EC $_{\text{Theoretical}}$ (μS/cm)**
1	0	10.63	1545.3	1401.5	10.98	1892.1	1765.5
2	10	10.88	1519.8	1200.2	11.27	1856.4	1655.2
3	20	11.0	1514.7	1175.4	11.3	1836.0	1544.9
4	30	10.8	1504.5	1125.3	11.35	1836.0	1564.7
5	40	10.78	1524.9	1175.4	11.35	1744.2	1424.4
6	50	10.7	1540.2	1125.3	10.75	1775.7	1425.3
7	60	10.67	1560.6	1077.6	10.66	1850.0	1526.2
8	70	10.64	1581.0	1193.1	10.61	1924.3	1627.1
9	80	10.61	1596.3	1278.4	10.55	1998.6	1728.1
10	90	10.58	1650.0	1369.9	10.5	2072.9	1828.9
11	100	10.55	1703.7	1467.9	10.49	2147.2	1929.8
12	110	10.52	1757.4	1572.9	10.49	2221.5	2030.8
13	120	10.49	1811.1	1685.4	10.48	2295.8	2131.7
14	130	10.46	1864.8	1806.0	10.42	2370.1	2232.6
15	140	10.43	1918.5	1935.1	10.32	2444.4	2250.2
16	150	10.4	1972.2	2073.6	10.22	2518.7	2267.8
17	160	10.4	2025.9	2221.9	10.13	2593.0	2285.5
18	170	10.4	2179.6	2380.7	10.12	2667.3	2325.5
19	180	10.4	2279.6	2480.8	10.1	2667.3	2365.5
20	190	10.4	2379.6	2580.5	9.98	2667.3	2545.5
21	200	10.4	2379.6	2580.5	9.98	2667.3	2595.6
22	210	10.4	2479.6	2580.8	9.97	2667.3	2645.6
23	220	10.4	2479.6	2580.8	9.97	2667.3	2645.6

The standard uncertainties u are u(T, k=2) = 0.03 K , u(pH, k=2) = 0.05, u.(σ, k=2)=0.1; where σ stands for electrical conductivity

Figures:

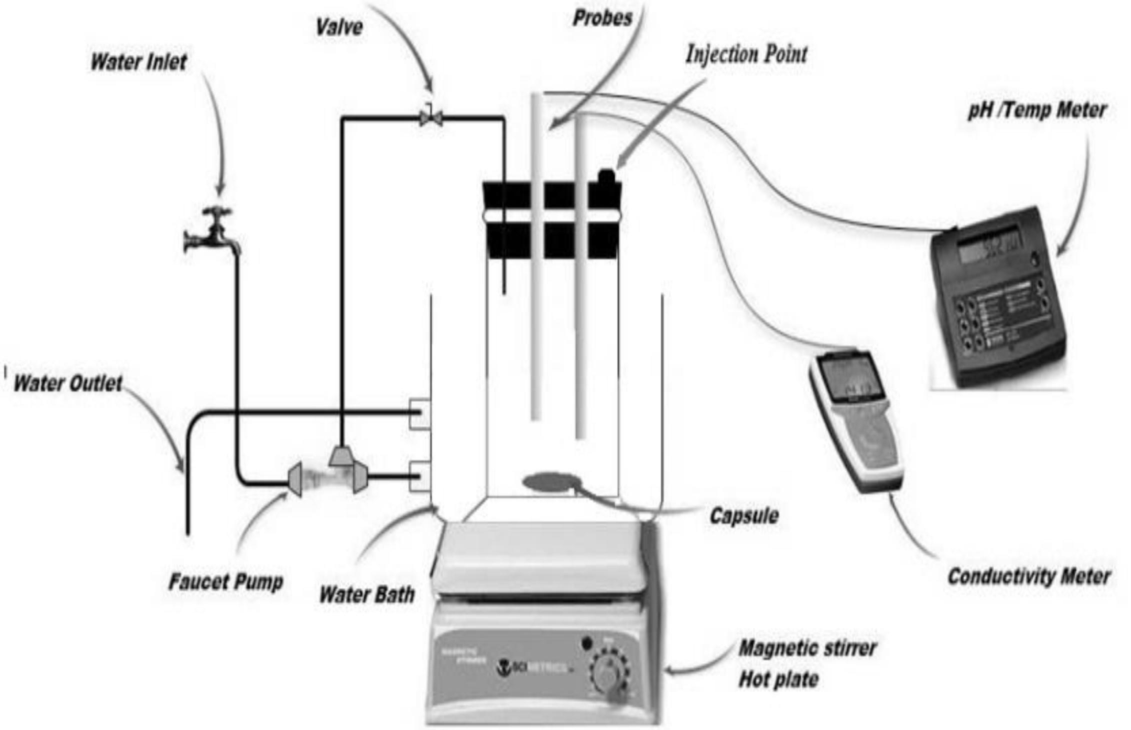

Figure 1: Schematic diagram of experimental setup.

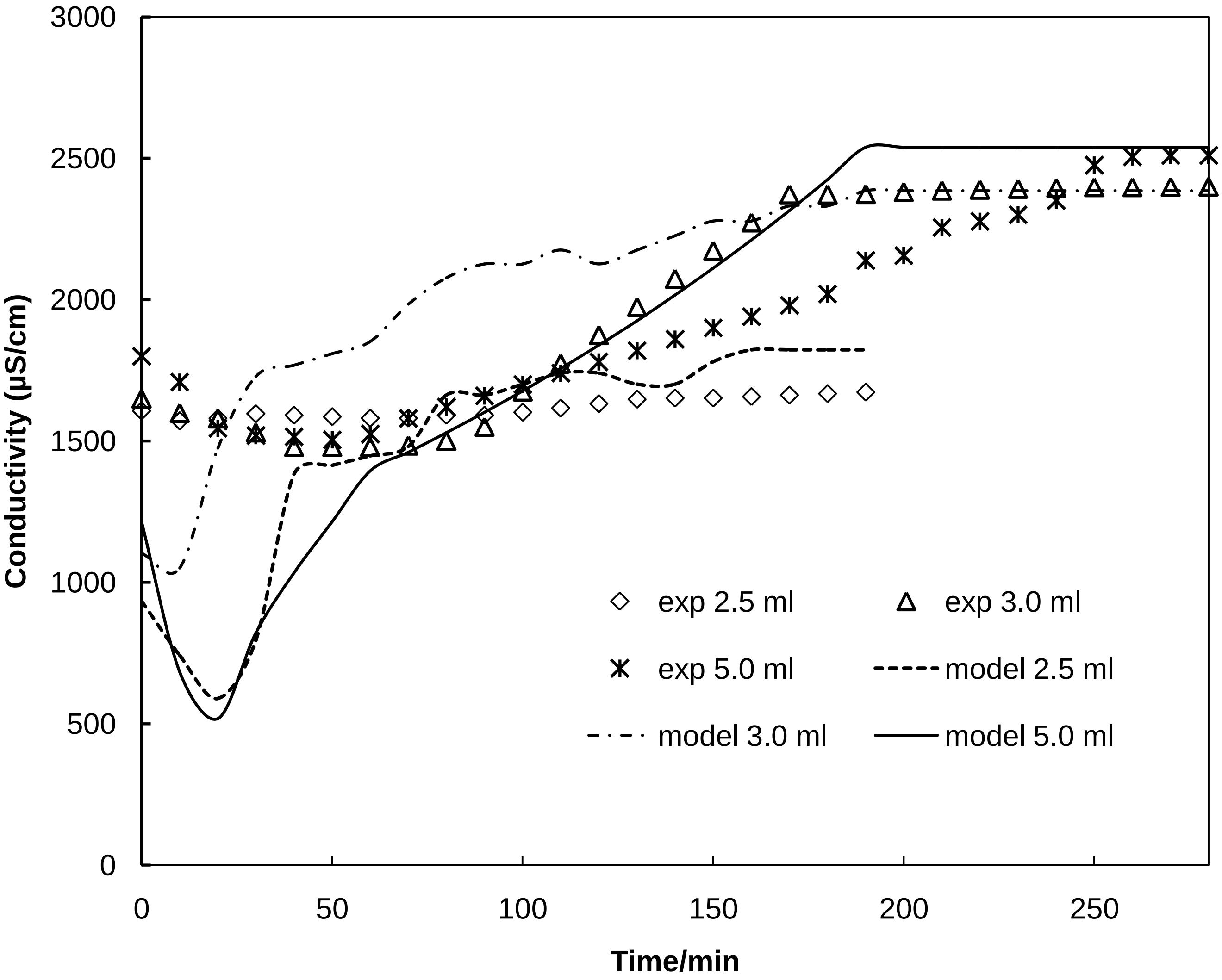

Figure 2: Electrical conductivity of n-propanethiol in 45 wt % MDEA + 4 wt % piperazine aqueous solution at 306K and 1 atm.

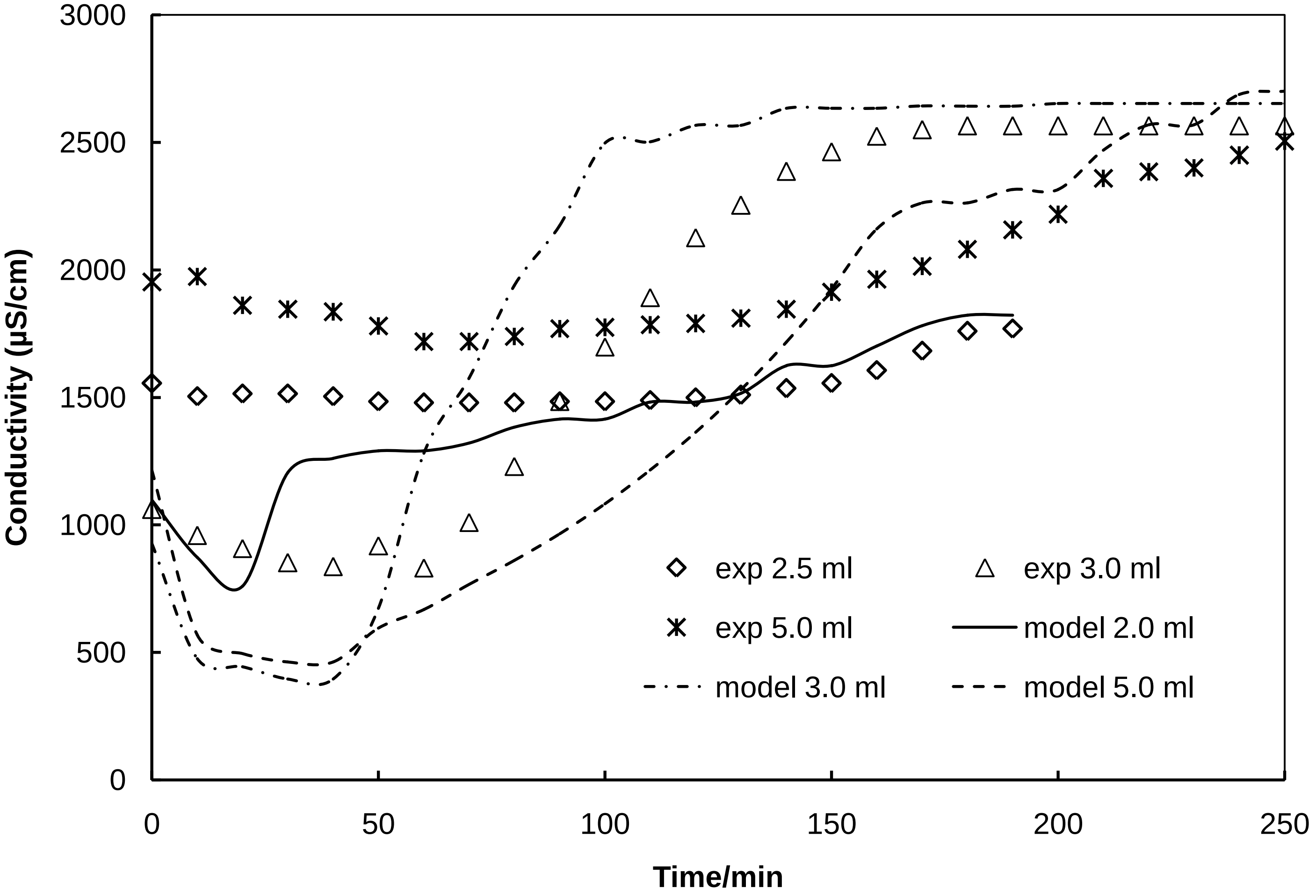

Figure 3:Electrical conductivity of n-butanethiol in 45 wt % MDEA + 4 wt % piperazine aqueous solution at 306 K and 1 atm.

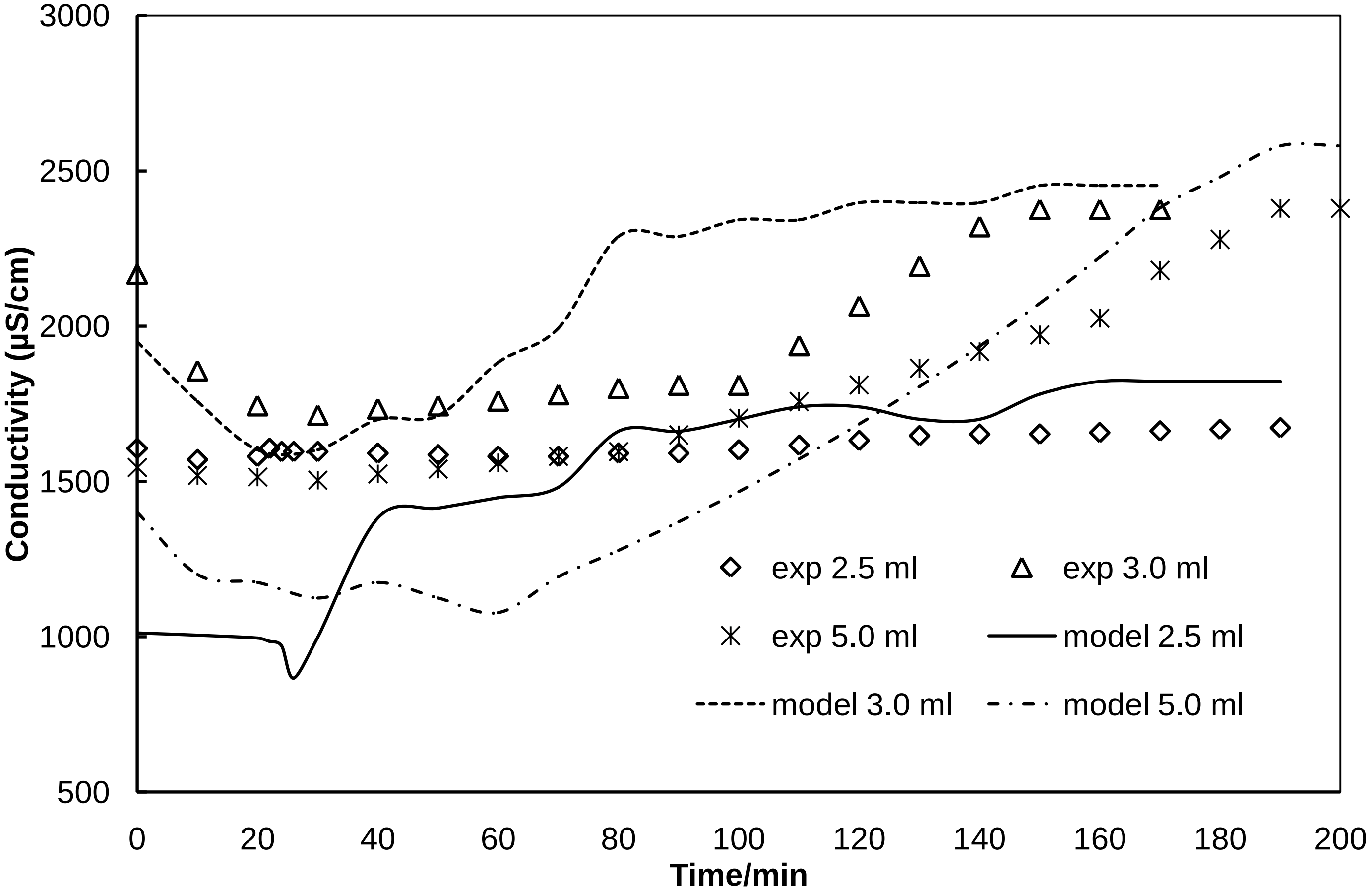

Figure 4: Electrical conductivity of n-propanethiol in 18 wt % MDEA + 4 wt % piperazine aqueous solution at 306 K and 1 atm.

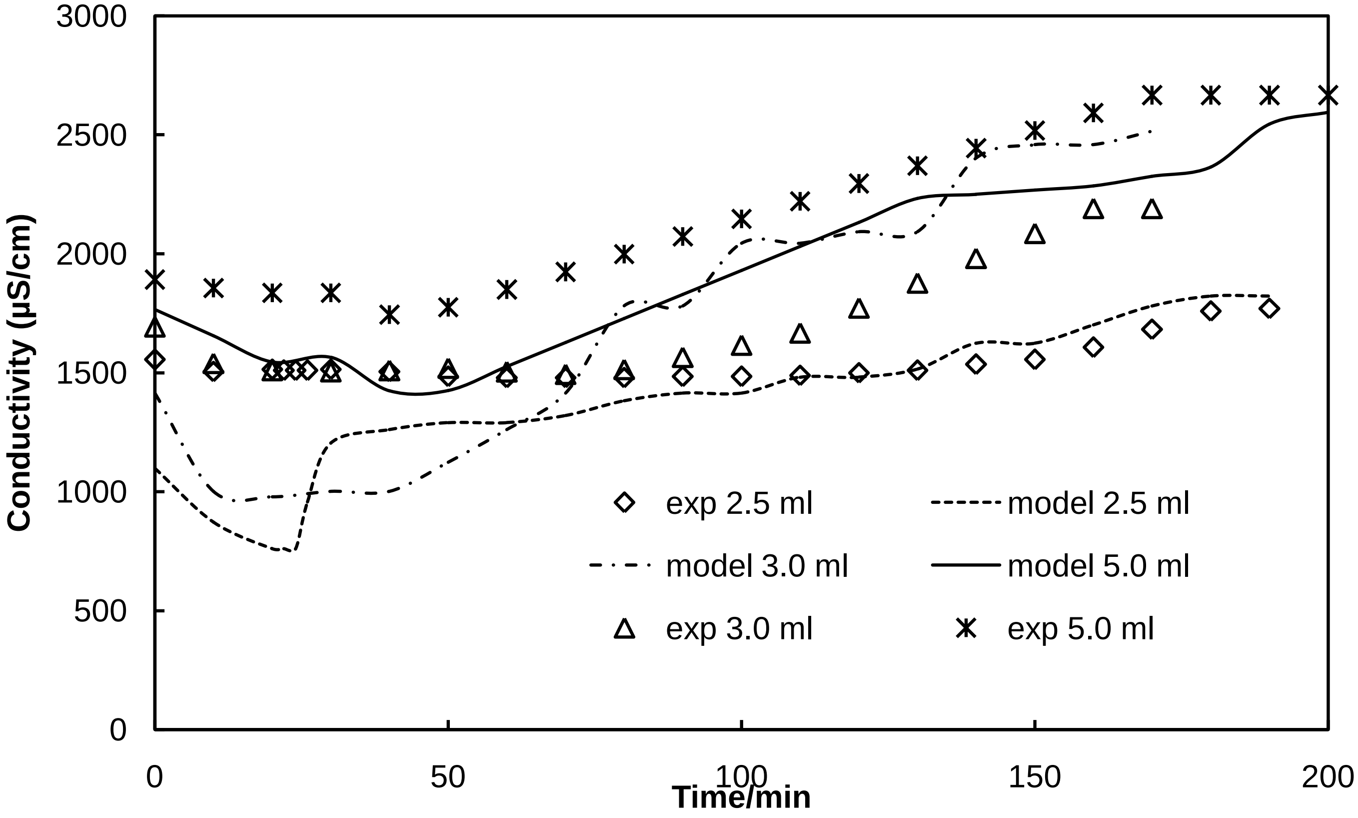

Figure 5: Electrical conductivity of n-butanethiol in 18 wt % MDEA + 4 wt % piperazine aqueous solution at 306 K and 1 atm.

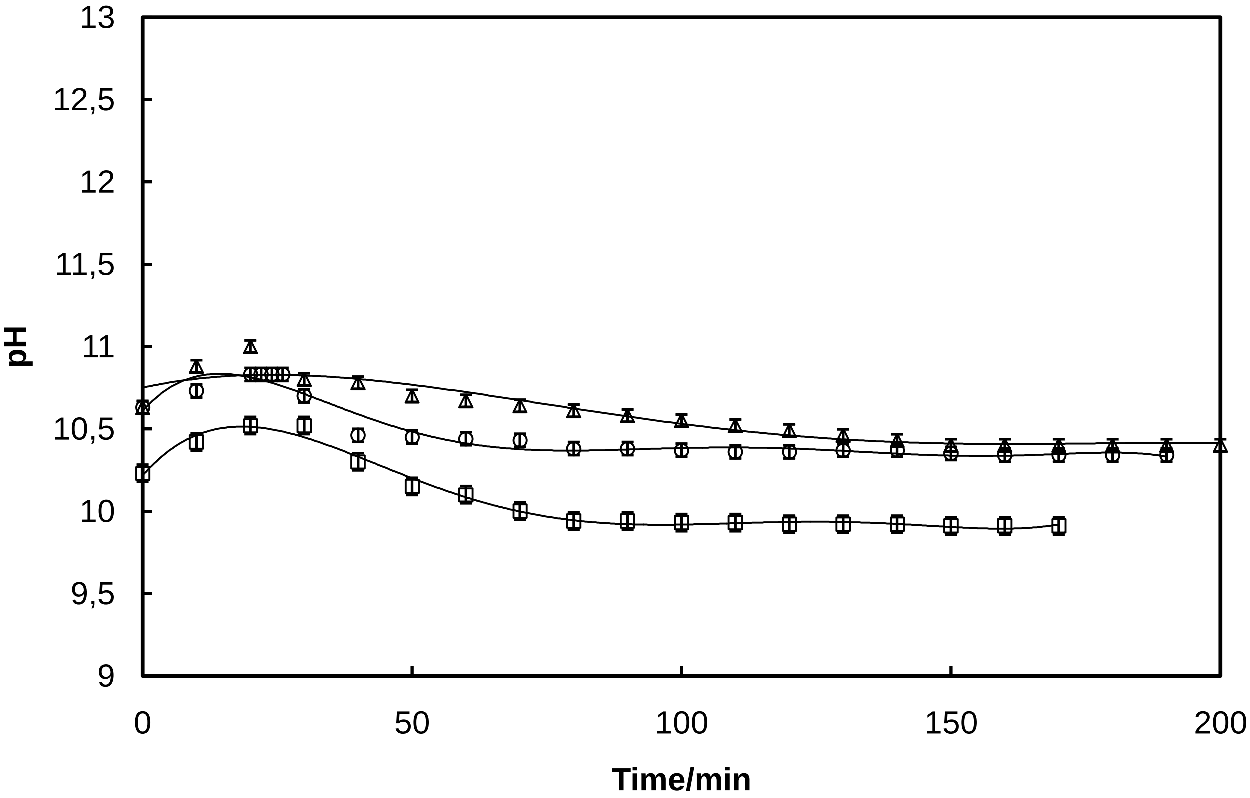

Figure 6: The pH of n-propanethiol in 45 wt % *N*-Methyldiethanolamine + 4 wt% piperazine aqueous solution at 306 K and 1 atm. where symbols presents experimental data: □; 2.5 ml n-propanethiol, o; 3.0 ml n-propanethiol, Δ; 5.0 ml n-propanethiol added. the solid lines show the trend lines. Error band; ± 5 % experimental uncertainty.

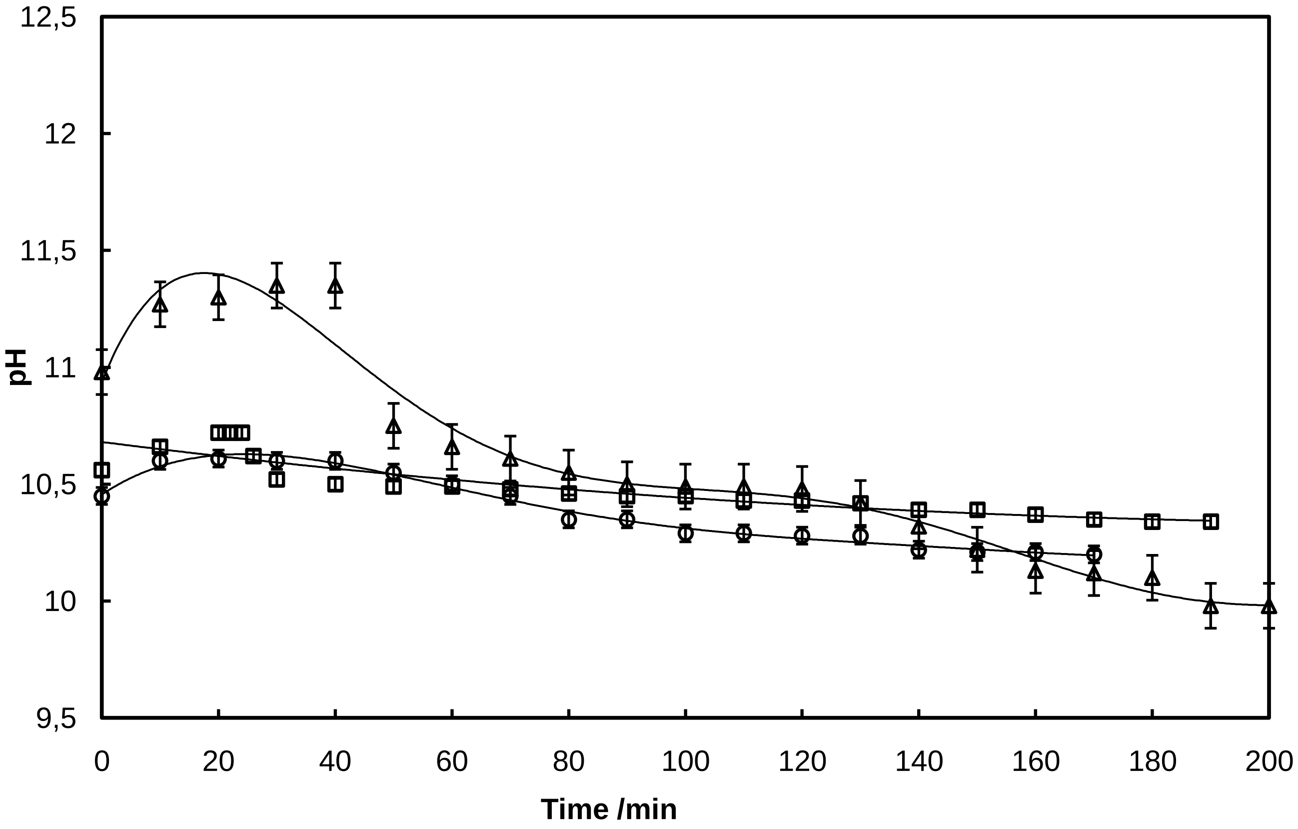

Figure 7 : The pH of n-butanethiol in 45 wt % *N*-Methyldiethanolamine + 4 wt% Piperazine aqueous solution at 306 K and 1 atm. where symbols presents experimental data: o; 2.5 ml n-propanethiol, □; 3.0 ml n-propanethiol, Δ; 5.0 ml n-propanethiol added. the solid lines show the trend lines. Error band; ± 5 % experimental uncertainty.

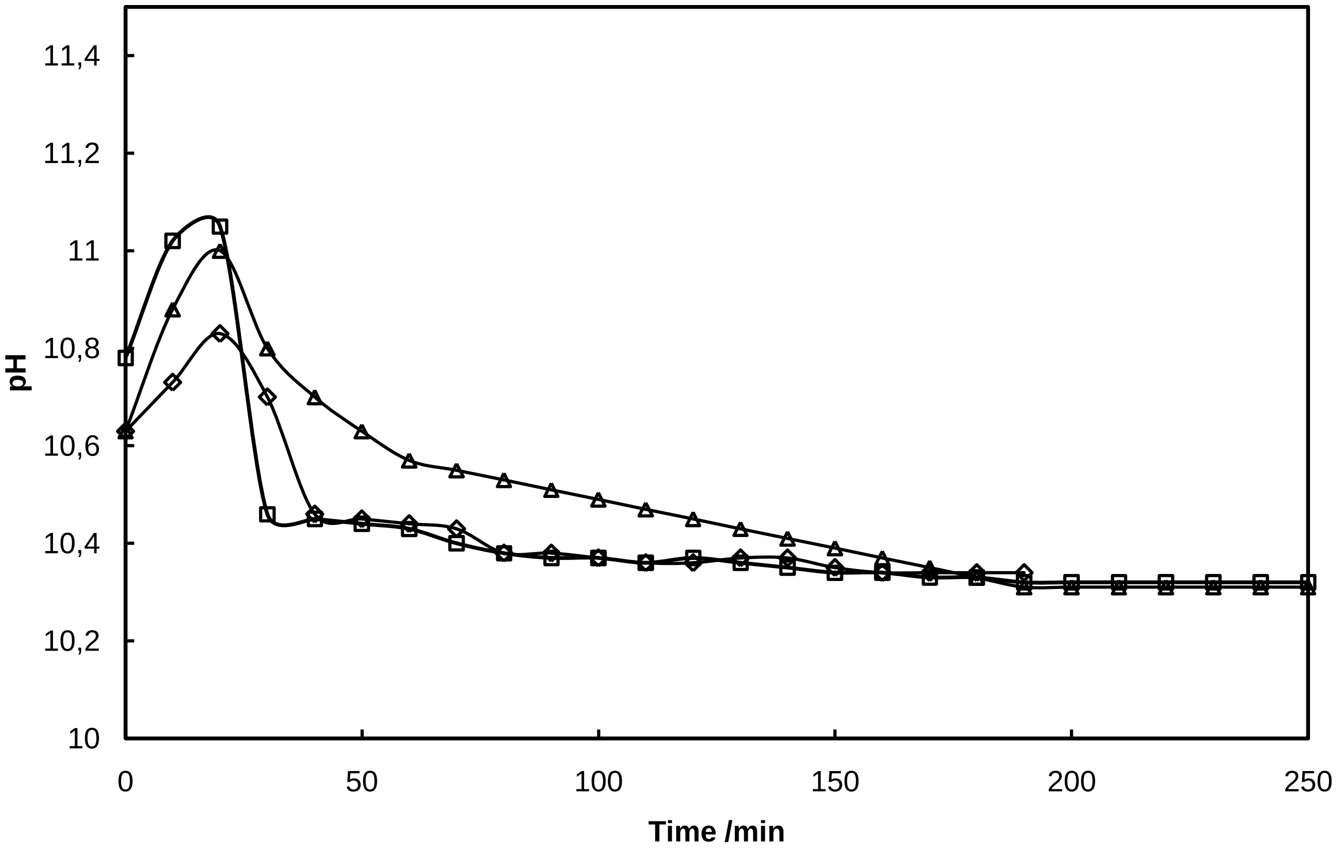

Figure 8 : The pH of n-propanethiol in 18 wt % *N*-Methyldiethanolamine + 4 wt% piperazine aqueous solution at 306 K and 1 atm. where symbols presents experimental data: ◊; 2.5 ml n-propanethiol, □; 3.0 ml n-propanethiol, Δ; 5.0 ml n-propanethiol added. the solid lines show the trend lines. Error band; ± 5 % experimental uncertainty.

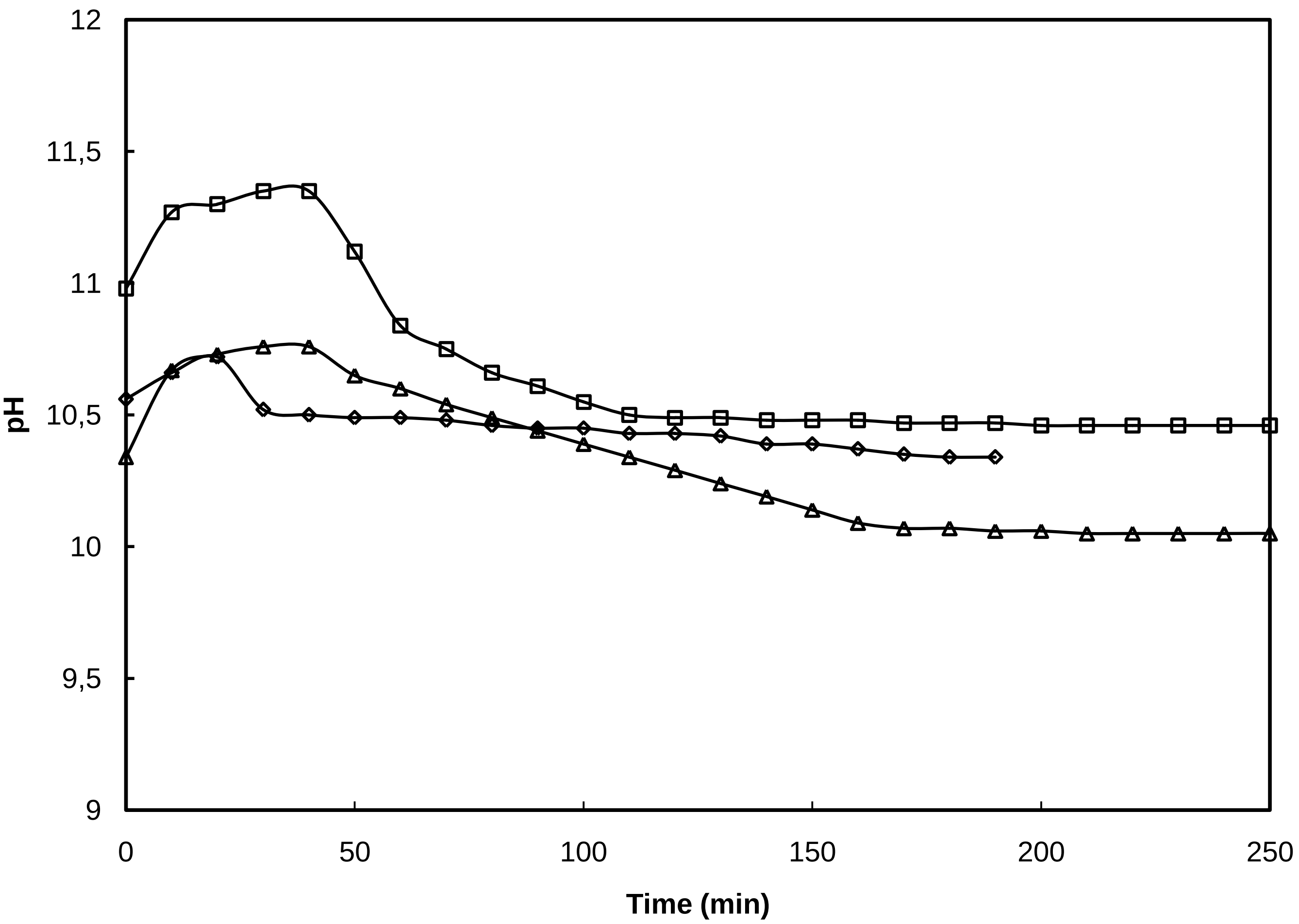

Figure 9: The pH of n-butanethiol in 18 wt % *N*-Methyldiethanolamine + 4 wt% piperazine aqueous solution at 306 K and 1 atm. where symbols presents experimental data: ◊; 2.5 ml n-propanethiol, □; 3.0 ml n-propanethiol, Δ; 5.0 ml n-propanethiol added. the solid lines show the trend lines. Error band; ± 5 % experimental uncertainty.