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Filter Paper Salt Bridge in Potentiometric Titrations: An Undergraduate Laboratory Chemical Education Article

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Abstract It is essential in an electrochemistry laboratory to use salt bridge in electrochemical cells while measuring the emf. This provides a means of eliminating "liquid junction potential" between two half cells. It was indicated laconically without any experimental details (https://en.wikipedia.org/wiki/Salt_bridge#cite_ref-1) that the salt bridges can also be made using laboratory filter paper soaking in a suitable inert salt solution. In this article we have made a detailed potentiometric experimental study on four representative titrations viz. strong acid (HCl) versus strong base (NaOH), weak acid (CH_3COOH) versus strong base (NaOH), ferrous iron (Fe^{2+}) versus dichromate ($Cr_2O_7^{2-}$), and chloride ion (Cl^-) versus silver ion (Ag^+) using filter paper salt bridge and compared the results with those obtained using Agar-Agar salt bridge.

Keywords: *salt bridge, Filter paper salt bridge, Potentionmetric titrations*

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1. Introduction

In Daniell cell at the junction, the following situation is observed [1,2]:

$$\begin{array}{rr|ll} & Zn^{2+} & Cu^{2+} & \\ (1.0\ M) & & & (1.0\ M) \\ & SO_4^{\ 2-} & SO_4^{\ 2-} & \end{array}$$

If a small current is passed through the cell from left to right it is carried across the junction by Zn^{2+} ions and by SO_4^{2-} ions. Similarly if a small current is passed from right to left it is carried across the junction by Cu^{2+} ions and by SO_4^{2-} ions. Thus the cell is not reversible. Reversibility can be applied only after the elimination of 'liquid junction potential'. Generally this is successfully achieved by a device called 'salt bridge'. Thus the cell is denoted as:

$$Zn(s)\left|ZnSO_4(aq)\right|\left|CuSO_4(aq)\right|Cu(s)$$

A double vertical line || denotes an interface for which it is assumed that the 'liquid junction potential' is eliminated. Similarly a concentration cell is represented as:

$$Pt\left|H_2(g)\right|HCl(aq, m_1)\left|\right|HCl\ (aq, m_2)\left|H_2(g)\right|Pt$$

It is needless to mention here about the details of reversibility of electrochemical cell as the aim of the present article is solely on electrochemical laboratory practice and on the emphasis of the construction and the successful use of 'low cost filter paper salt bridge'. The conductivity depends on several factors: concentration of electrolyte solution, the consistency of pores of the filter paper and the other is the absorbing capacity of the filter paper. Usually a filter paper with soft texture and high absorbing capacity leads to higher conductivity. Therefore absolute measurements are not possible with filter paper salt bridge like estimating some standard physical properties: dissociation constants of weak acids (K_a), hydrolysis constants (K_h) of the salts of weak acid and strong base or weak base and a strong acid and solubility product (K_{sp}) of sparingly soluble salts in aqueous solution, yet the data obtained using low cost filter paper salt bridge is certainly useful in estimating the unknown concentrations of the solutions used.

The present article is an excellent practice in an undergraduate physical chemistry laboratory. This helps the students to record the potentiometric titrations experimental data, construction of figures in different ways viz. sigmoid plots, first and second derivative plots and interpretation of the final results.

2. Experimental

A detailed procedure for construction of a salt bridge is available in literature [3,4,5]. A low cost filter paper salt bridge could be made as follows: First we need a U-shaped glass tube. This could be made in a glass blowing work shop [6]. Even a U-shaped cool-drink straw will do its job perfectly! Now a filter paper could be rolled as shown in Figure 1.

The rolled filter paper could be slowly insinuated in to the U-shaped glass tube or U-shaped cool-drink straw as shown in Figure 2.

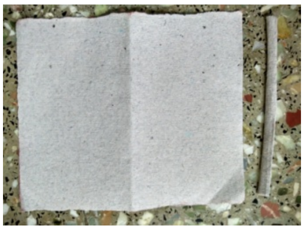

Figure 1.

Figure 2.

All the required stock solutions were prepared using laboratory grade chemicals in the distilled water. All the figures were done using KaleidaGraph software version 4.1, supplied by Synergy Software, Reading, PA, USA.

3. Results and Discussion

Acid base titrations were carried out using quinhydrone electrode. The redox titration was carried out using platinum electrode. The precipitation titration was carried out using silver electrode. In the entire three titrations standard calomel electrode was used as the reference electrode.

The rolled filter paper inserted in to U-shaped tube is placed in a suitable salt solution of specified concentration usually of KCl or KNO_3. The reason for choosing KCl or KNO_3 is that the transport numbers of both cation and anion of the salts are almost same so that they carry same amount of current [1,7]. The rolled filter paper will now be wetted with the salt solution as shown in Figure 3.

Figure 3.

Figure 4 shows a typical potentiometric experimental set-up.

Figure 4.

No gelification agent is required because the filter paper itself serves as medium of conduction. This can be used as salt bridge. U-shaped glass tube or U-shaped cool-drink straw is meant for giving the mechanical strength to the wetted rolled filter paper. Otherwise each time a new rolled filter paper has to be used for every new titration. This devise exactly replaces the Agar-Agar salt bridge constructed using salt solution gellified with Agar-Agar. The preparation of the Agar-Agar salt bridge is time consuming, tedious and little expensive. It needs Agar-Agar, usage of gas burner, and quite bit of the suitable salt either KCl or KNO_3. Whereas the filter paper salt bridge needs a piece of filter paper and 10-15 ml of dilute salt solution. Thus the zero or filter paper salt bridge reduces the cost and saves the time. The titration of a strong acid (HCl, 0.1 M) with strong base (NaOH, 0.1 M), weak acid (CH_3COOH, 0.1 M) with strong base (NaOH, 0.1 M), titration of ferrous iron (Fe^{2+}, 0.1 M) with dichromate ($Cr_2O_7^{2-}$, 0.0167 M) and titration of chloride (Cl^-, 0.05 M) with silver ion (Ag^+, 0.05 M) were performed using the Agar-Agar salt bridge and zero or filter paper salt bridge. The results were tabulated in Table 1 and Table 2 and explained by suitable Figure 5-Figure 16.

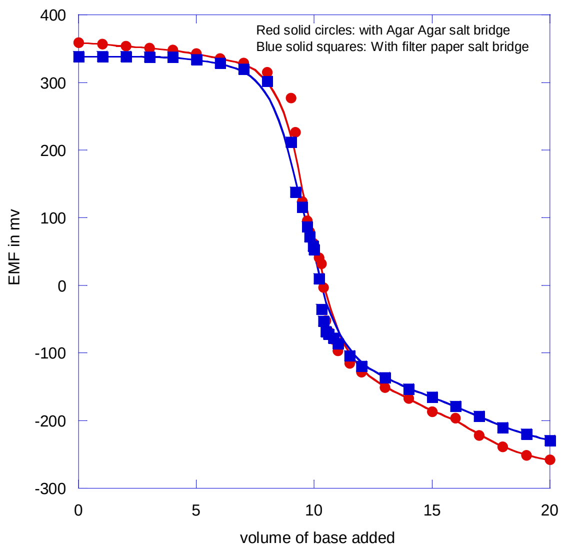

Figure 5A. Plot of the titration of strong acid (HCl= 0.1M) with strong base (NaOH=0.1M)

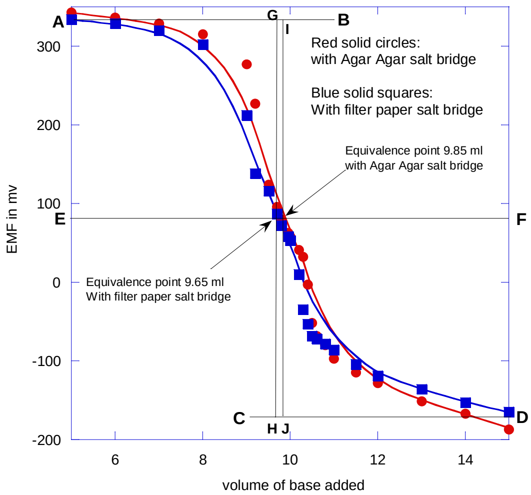

Figure 5B. Plot of the titration of strong acid (HCl= 0.1M) with strong base (NaOH=0.1M)

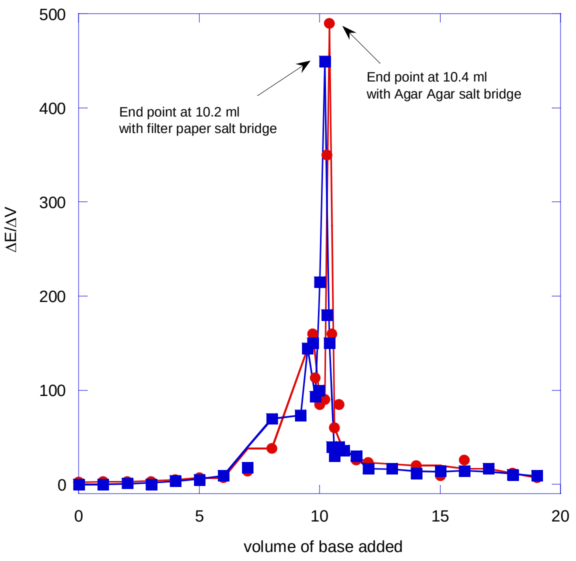

Figure 6. First derivative plot of the titration of strong acid (HCl= 0.1M) with strong base (NaOH=0.1M)

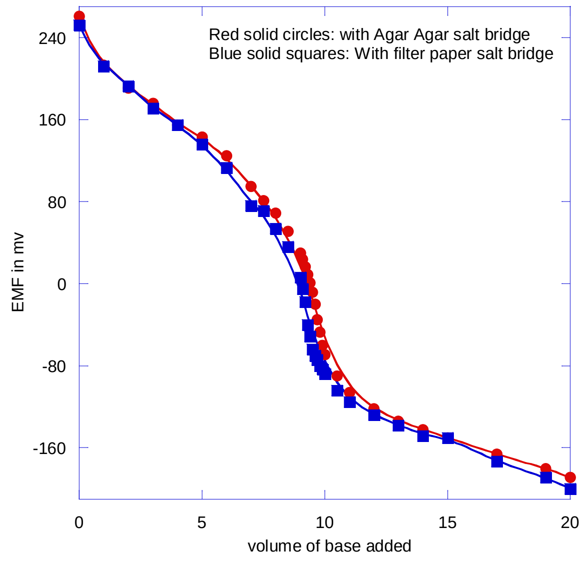

Figure 8A. Plot of the titration of weak acid (CH_3COOH= 0.1M) with strong base (NaOH=0.1M)

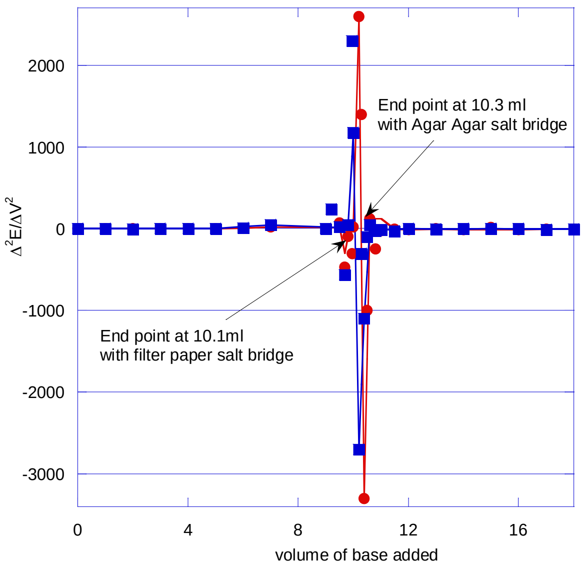

Figure 7A. Second derivative plot of the titration of strong acid (HCl= 0.1M) with strong base (NaOH=0.1M)

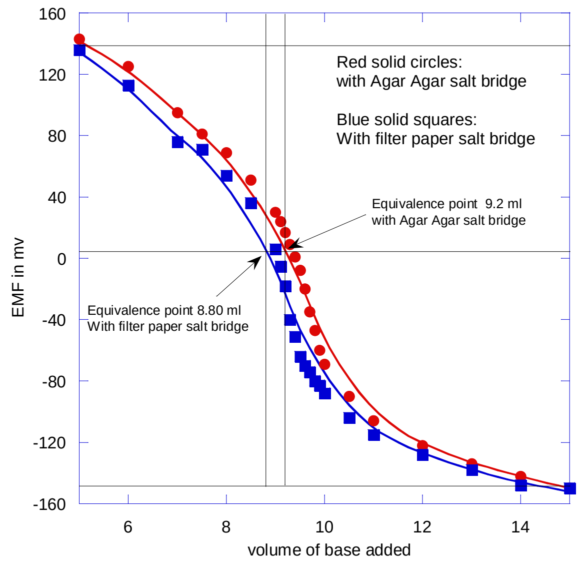

Figure 8B. Plot of the titration of weak acid (CH_3COOH= 0.1M) with strong base (NaOH=0.1M)

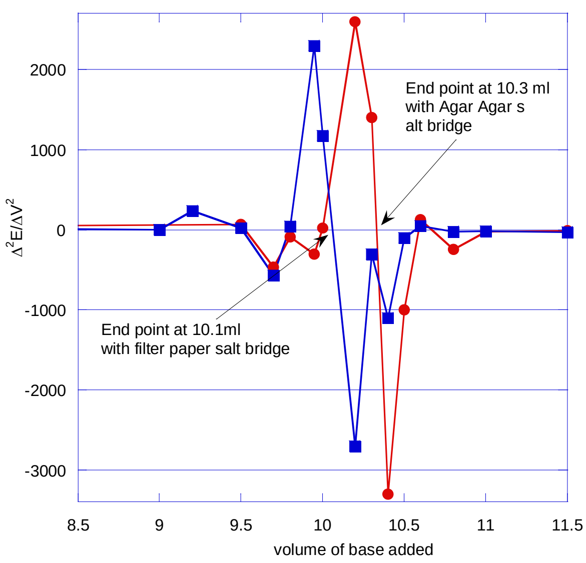

Figure 7B. Second derivative plot of the titration of strong acid (HCl= 0.1M) with strong base (NaOH=0.1M)

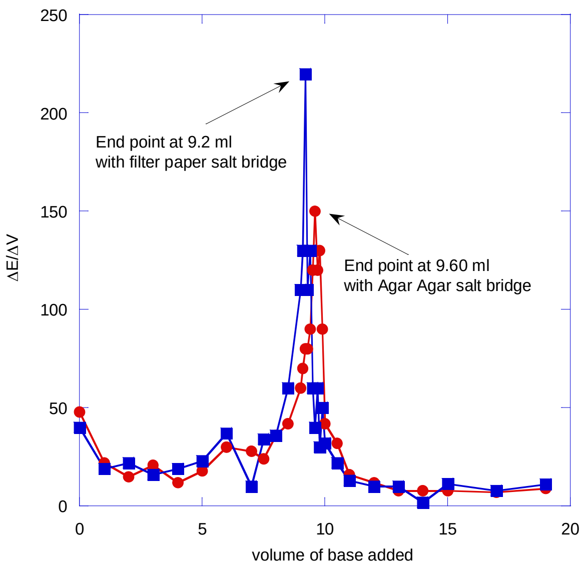

Figure 9. First derivative plot of the titration of weak acid (CH_3COOH= 0.1M) with strong base (NaOH=0.1M)

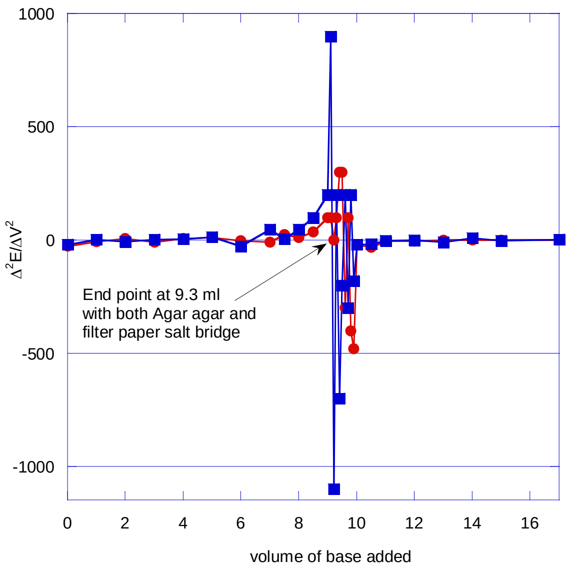

Figure 10A. Second derivative plot of the titration of weak acid (CH_3COOH= 0.1M) with strong base (NaOH=0.1M)

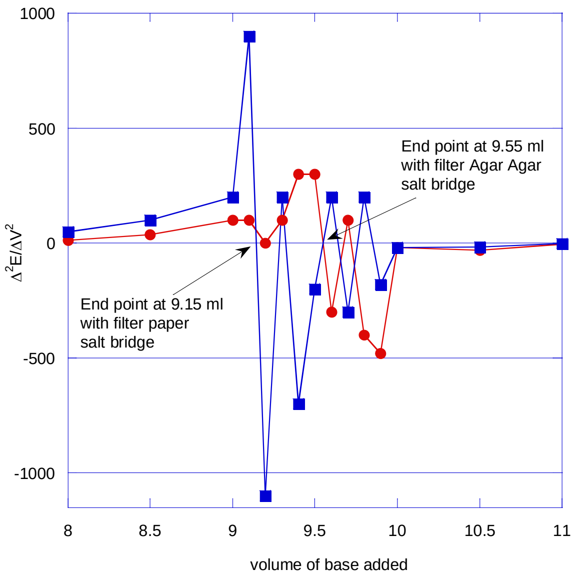

Figure 10B. Second derivative plot of the titration of weak acid (CH_3COOH= 0.1M) with strong base (NaOH=0.1M)

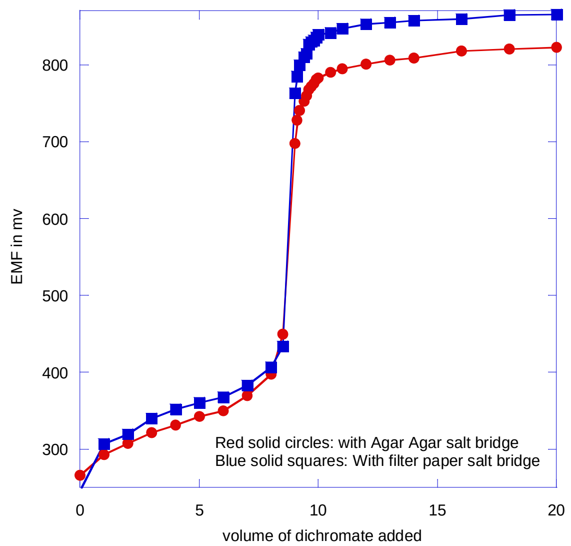

Figure 11A. Plot of the titration of Ferrous Iron (Fe^{2+}=0.1M) with dichromate ($Cr_2O_7^{2-}$=0.067M)

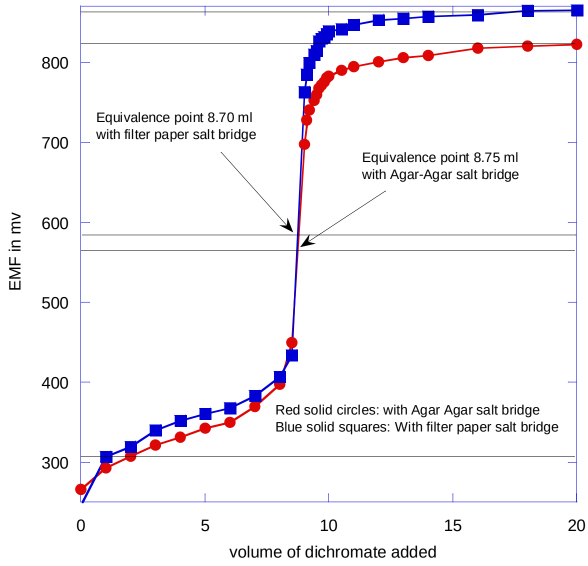

Figure 11B. Plot of the titration of Ferrous Iron (Fe^{2+}=0.1M) with dichromate ($Cr_2O_7^{2-}$=0.067M)

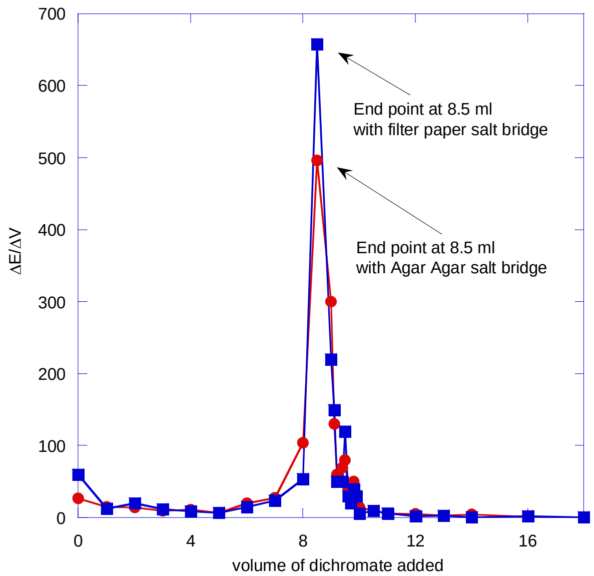

Figure 12. First derivative plot of the titration of Ferrous Iron (Fe^{2+}=0.1M) with dichromate ($Cr_2O_7^{2-}$=0.067M)

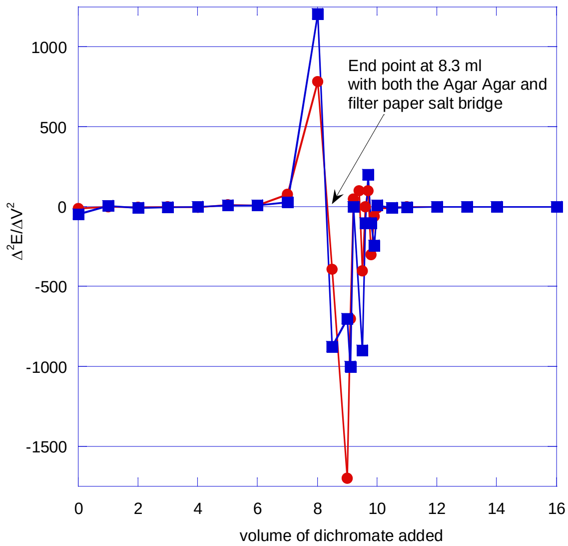

Figure 13. First derivative plot of the titration of Ferrous Iron (Fe^{2+}=0.1M) with dichromate ($Cr_2O_7^{2-}$=0.067M)

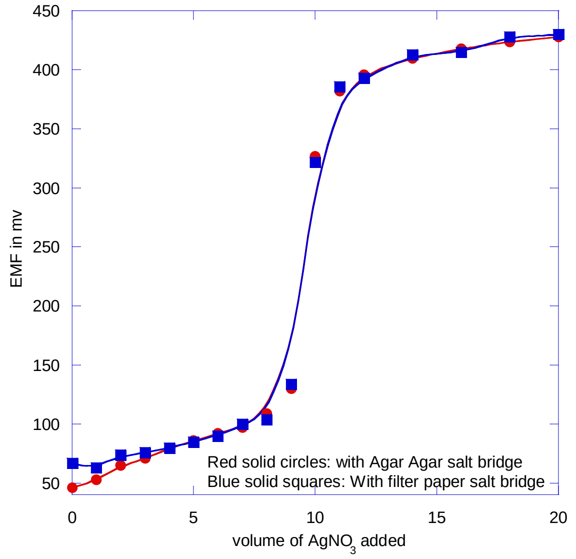

Figure 14A. Plot of the titration of chloride ion (0.05M) with Ag^+ (0.05M)

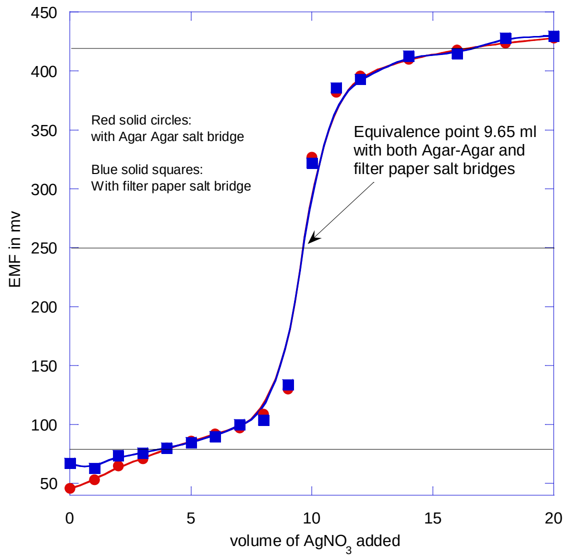

Figure 14B. Plot of the titration of chloride ion (0.05M) with Ag^+ (0.05M)

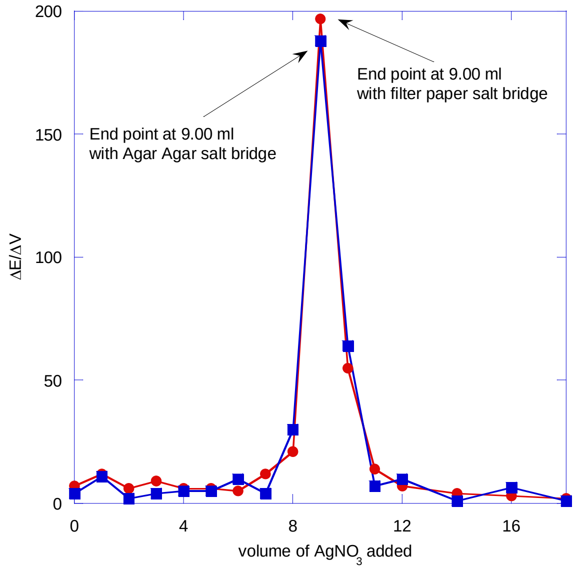

Figure 15. First derivative plot of the titration of chloride ion (0.05M) with Ag^+ (0.05M)

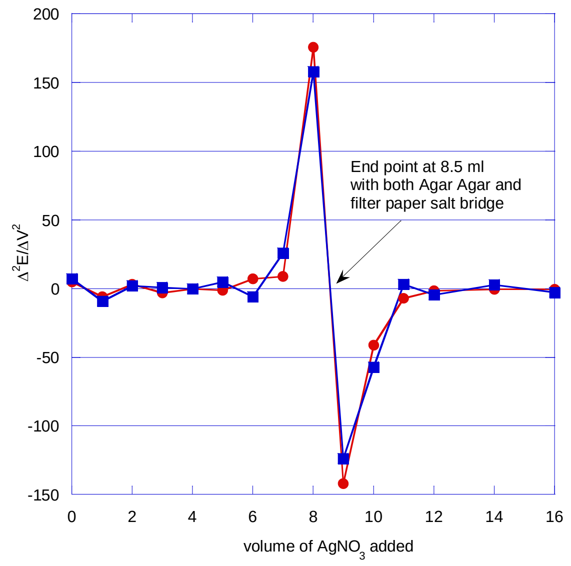

Figure 16. Second derivative plot of the titration of chloride ion (0.05M) with Ag^+ (0.05M)

Results of the titration of strong acid vs strong base with Agar-Agar salt bridge and zero or filter paper salt bridge is given Table 1 and Figure 5, Figure 6 and Figure 7. Results of the titration of weak acid vs strong base with Agar-Agar salt bridge and zero or filter paper salt bridge are given in Table 1 and Figure 8, Figure 9 and Figure 10. Results of the titration of Fe^{2+} vs $Cr_2O_7^{2-}$with Agar-Agar salt bridge and zero or filter paper salt bridge is given in Table 2 and Figure 11, Figure 12 and Figure 13. Results of the titration of Cl^- vs Ag^+ with Agar-Agar salt bridge and zero or filter paper salt bridge (soaked in KNO_3 solution) is given in Table 2 and Figure 14, Figure 15 and Figure 16. Figure 5, Figure 8, Figure 11 and Figure 14 show that though the absolute potentials differ to a smaller extent in both the measurements using the two salt bridges, yet the trend in the equivalence point are unmistakable. Figure 6, Figure 9, Figure 12 and Figure 15 show the equivalence points from 1st derivative plots. Similarly Figure 7, Figure 10, Figure 13 and Figure 16 show the equivalence points from 2nd derivative plots.

The final results are given in Table 3. The results are compared and found promising within 3-6 % experimental error except in the case of precipitation titration explains the importance and advantage of zero or filter paper salt bridge. Even that 10% error in the precipitation titration is only from sigmoid plot Figure 14B. Table 3 column-2 gives the equivalence points from direct titration using chemical method with suitable indicators. Figure 5B is an expanded version of the Figure 5A. Approximately two parallel lines AB and CD were drawn in the beginning and at the end of the titration in Figure 5B. A parallel line EF to X-axis is drawn midway between AB and CD. Another two perpendicular lines GH and IJ were drawn parallel to y-axis. At the points of intersection of EF with GH and IJ gives the equivalence points of the titration. Similarly Figure 8B, Figure 11B and Figure 14B were constructed. The results were tabulated in table-3. Figure 7B is an expanded version of the Figure 7A on X-axis in order to see the equivalence point clearly on the second derivative plot. Similarly the Figure 10B is an expanded version of the Figure 10A. The equivalence points from double derivative plots are found from the points of intersection of the x-axis and the straight locus joining the two points which are away at a maximum distance from the X-axis.

Table 1. Data for the titration of strong acid (HCl; 0.1 M) and weak acid (CH_3COOH; 0.1 M) with strong base (NaOH; 0.1M)

Strong acid (HCl) vs Strong base (NaOH)			Weak acid (CH_3COOH) vs Strong base (NaOH)		
Vol. of base in ml	EMF in mv		Vol. of base in ml	EMF in mv	
	Agar-Agar salt bridge	Filter paper salt bridge		Agar-Agar salt bridge	Filter paper salt bridge
0	359	339	0	261	252
1	357	339	1	213	212
2	354	339	2	191	193
3	351	338	3	176	171
4	348	338	4	155	155
5	343	334	5	143	136
6	336	329	6	125	113
7	329	320	7	95	76
8	315	302	7.5	81	71
9	277	212	8	69	54
9.2	227	138	8.5	51	36
9.5	124	116	9	30	6
9.7	96	87	9.1	24	-5
9.8	80	72	9.2	17	-18
9.95	63	58	9.3	9	-40
10	58	53	9.4	1	-51
10.2	41	10	9.5	-8	-64
10.3	32	-35	9.6	-20	-70
10.4	-3	-53	9.7	-35	-74
10.5	-52	-68	9.8	-47	-80
10.6	-68	-72	9.9	-60	-83
10.8	-80	-78	10	-69	-88
11	-97	-86	10.5	-90	-104
11.5	-115	-104	11	-106	-115
12	-128	-119	12	-122	-128
13	-151	-136	13	-134	-138
14	-167	-153	14	-142	-148
15	-187	-165	15	-150	-150
16	-196	-179	17	-166	-173
17	-222	-193	19	-180	-189
18	-239	-210	20	-189	-200
19	-251	-220			
20	-258	-229			

Table 2. Data for the titration of Fe^{2+} (0.1 M) vs dichromate (0.0167 M) and Chloride (0.05 M) vs Ag^+ (0.05 M)

Fe^{2+} vs dichromate			Chloride vs Ag^+		
Vol. of Dichromate in ml	EMF in mv		Vol. of Ag^+ in ml	EMF in mv	
	Agar-Agar salt bridge	Filter paper salt bridge		Agar-Agar salt bridge	Filter paper salt bridge
0	266	247	0	46	67
1	293	307	1	53	63
2	308	320	2	65	74
3	322	340	3	71	76
4	332	352	4	80	80
5	343	361	5	86	85
6	350	368	6	92	90
7	370	383	7	97	100
8	398	407	8	109	104
8.5	450	434	9	130	134
9	698	763	10	327	322
9.1	728	785	11	382	386
9.2	741	800	12	396	393
9.4	753	810	14	410	413
9.5	760	815	16	418	415
9.6	768	827	18	424	428
9.7	772	830	20	428	430
9.8	776	832			
9.9	781	836			
10	783	839			
10.5	790	842			
11	795	847			
12	801	853			
13	806	855			
14	809	858			
16	818	860			
18	821	865			
20	823	866			

Table 3. Final results and their comparison

system	Equiva-lence point from direct titration	Equivalence point from sigmoid plot		Equivalence point from $\Delta E/\Delta V$ plot		Equivalence point from $\Delta E^2/\Delta V^2$ plot		% error					
		With Agar-Agar salt bridge	With filter paper salt bridge	With Agar-Agar salt bridge	With filter paper salt bridge	With Agar-Agar salt bridge	With filter paper salt bridge	In sigmoid plot		In $\Delta E/\Delta V$ plot		In $\Delta E^2/\Delta V^2$ plot	
								d	e	d	e	d	e
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Strong acid (HCl) vs strong base (NaOH)	10.20[(a)]	9.85	9.65	10.4	10.2	10.35	10.05	3.4	5.4	-2.0	0.0	-1.5	1.5
Weak acid (CH_3COOH) vs strong base (NaOH)	9.40[(a)]	9.20	8.80	9.60	9.20	9.55	9.15	2.1	6.4	-2.1	2.1	-1.6	2.7
Ferrous iron (Fe^{2+}) vs dichromate ($Cr_2O_7^{2-}$)	8.40[(b)]	8.75	8.70	8.50	8.50	8.30	8.30	-4.2	-3.6	-1.2	-1.2	1.2	1.2
Chloride ion (Cl^-) vs silver ion (Ag^+)	8.75[(c)]	9.65	9.65	9.00	9.00	8.50	8.50	-10	-10	-2.9	-2.9	2.9	2.9

[a]using phenolphthalein indicator; [b]using diphenylamine indicator; [c]using potassium chromate indicator; [d]Agar-Agar salt bridge; [e]Filter paper salt bridge.

4. Conclusions

The present work provides a comprehensive study of potentiometric titrations, plotting the results and their interpretation to an undergraduate physical chemistry laboratory class-room. Instead of a glass tube a U-shaped ordinary plastic tube will work perfectly. Even one can use a U-shaped cool-drink straw available in bakeries for this purpose! The use and practice of KaleidaGraph (Synergy Software, Reading, PA, USA) is very user friendly to undergraduate students and easily practicable, hence advised to buy for every college/university.

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