CHAPTER 4

MICROELECTROPHORESIS MEASUREMENTS WITH IODOBENZENE EMULSIONS

4.1. Introduction :

In the present chapter we describe the results obtained from electrophoretic mobility measurements with iodobenzene droplets. Again, the condition ζ = constant has been tried to be maintained by keeping the electrolyte and its concentration constant. Particles of varying sizes were used, so that the effect of variation of κa on electrophoretic mobility could be conveniently studied.

4.2. Materials used, the preparation of emulsions and experimental procedure :

All chemicals etc. used were similar as described in the case of Nujol emulsion. Iodobenzene was prepared from freshly distilled aniline by diazotisation, the product was purified by vacuum distillation, and finally a small quantity of the middle fraction boiling at $185\pm0^{\circ}C$ was collected. The emulsion in double distilled water was prepared by mechanical dispersion, as described in the case of Nujol emulsions. Emulsion:electrolyte mixtures were prepared as before. The electrolytes used were KCl, $BaCl_2$ and $LaCl_3$.

The experimental procedure, and all details, e.g. the cleaning of the cell and glassware, avoidance of contamination, etc. were exactly similar as before. Measurements were made in the conventional electrophoresis cell only, at room temperature ($28^{\circ}\pm2^{\circ}C$).

4.3. Calculations :

Particle size correction due to diffraction of light was made by the method described already, using Figs.(3.6, 3.7, 3.9).

The ζ potentials were calculated by the W.L.O.method. The results, together with the values of the parameters used are given in Tables (4.1-4.10), and shown in Figs. (4.1-4.4). In the case of unsymmetrical electrolytes, again, the method of calculation was similar as in the case of Nujol droplets in $BaCl_2$ and $LaCl_3$ solutions. The procedure for ionic mobility correction for the 1-1 as also 2-1 and 3-1 electrolytes was similar as described earlier.

Finally, choosing a suitable average value for the ζ potential of each system ($\zeta_{W.L.O.(av)}$) the electrophoretic mobilities were recalculated by the W.L.O.method. These are shown in Tables (4.11-4.14) and in Figs.(4.5-4.6) together with the experimental values.

CALCULATION OF ζ POTENTIAL OF IODOBENZENE DROPLETS BY THE W.L.O.METHOD

Diameter $\times 10^4$ (cm)	Time(sec)		$-U \times 10^4$ (cm^2/sec/V)	$a \times 10^4$ (cm)	$\log \kappa a$	Corrected E'					E'_{expt}	$y_{0(expt)}$	$-\zeta_{W.L.O.}$ (mV)
	R_t	L_t				$y_0=1$	2	3	4	5			

Table 4.1 Iodobenzene in distilled water (27^oC)

$\kappa = 9.714 \times 10^4 cm^{-1}$; $\sigma = 3.535 \times 10^{-6}$ mho/cm; $i = 42.5 \times 0.2 \times 10^{-6}$ amp; $d = 105.0 \times 10^{-4}$ cm; $m_+ = 0.0393$; $m_- = 0.3057$; $E'_{expt} = 0.7202 \times 10^4 xU$; $\zeta_{W.L.O.} = 25.87 y_{0(expt)}$ (mV)

0.569	5.5	5.5	1.999	0.284	0.4413	1.056	1.975	2.53	2.89	3.038	1.439	1.45	37.53
0.810	5.0	4.9	2.170	0.405	0.5939	1.086	2.037	2.61	2.87	2.973	1.563	1.50	38.82
2.516	4.0	4.0	2.686	1.258	1.0871	1.206	2.307	3.01	3.31	3.14	1.929	1.60	41.40
2.942	3.9	3.9	2.820	1.471	1.1547	1.252	2.416	3.114	3.46	3.254	2.030	1.65	42.70
3.784	3.3	3.3	3.256	1.892	1.2641	1.273	2.482	3.27	3.65	3.40	2.344	1.85	47.87
4.770	3.2	3.2	3.358	2.385	1.365	1.304	2.584	3.357	3.812	3.652	2.415	1.94	50.20
6.301	3.0	3.0	3.666	3.151	1.485	1.325	2.626	3.528	4.069	4.408	2.640	2.05	53.06
7.875	2.9	2.9	3.792	3.937	1.582	1.356	2.638	3.734	4.327	4.079	2.729	2.10	54.34
10.50	2.5	2.5	4.099	5.250	1.707	1.407	2.74	3.80	4.694	4.91	2.950	2.17	56.15

Table 4.2 Iodobenzene in 1.11×10^{-5} N KCl (30^oC)

$\kappa = 1.093 \times 10^5 cm^{-1}$; $\sigma = 4.861 \times 10^{-6}$ mho/cm/ $i = 58.0 \times 0.2 \times 10^{-6}$ amp; $d = 105 \times 10^{-4}$ cm; $m_+ = 0.1732$; $m_- = 0.1681$; $E'_{expt} = 0.6747 \times 10^4 xU$; $\zeta_{W.L.O.} = 26.13 y_{0(expt)}$ (mV)

0.5688	4.5	4.5	2.586	0.284	0.4925	1.06	2.00	2.62	3.00	3.14	1.745	1.75	45.58
0.8098	3.9	4.0	2.946	0.405	0.6471	1.10	2.10	2.70	3.02	3.12	1.988	1.95	50.79
1.0590	3.8	3.9	3.020	0.529	0.7625	1.10	2.15	2.76	3.08	3.20	2.038	1.92	50.01
2.516	3.7	3.7	3.148	1.258	1.1383	1.27	2.42	3.18	3.60	3.75	2.124	1.95	50.79
3.348	3.4	3.4	3.417	1.674	1.2624	1.25	2.50	3.35	3.85	3.35	2.306	1.85	48.19
4.770	3.0	3.1	3.772	2.385	1.4161	1.30	2.56	3.60	4.05	4.10	2.545	1.97	51.33
7.350	2.8	2.8	4.167	3.675	1.6039	1.38	2.68	3.75	4.50	4.84	2.812	2.15	53.40
10.50	2.5	2.5	4.662	5.250	1.7588	1.40	2.75	3.90	4.90	5.40	3.147	2.30	59.91

CALCULATION OF ζ POTENTIAL OF IODOBENZENE DROPLETS BY THE W.L.O.METHOD (Contd.)

Diameter $x10^4$(cm)	Time(sec) R_t	Time(sec) L_t	$-Ux10^4$ (cm^2/sec/V)	$ax10^4$ (cm)	log κa	Corrected E' y_0=1	2	3	4	5	E'_{expt}	$y_{0(expt)}$	$-\zeta_{W.L.O.}$ (mV

Table 4.3 Iodobenzene in $3.33x10^{-5}$N KCl (30°C)

κ =$1.903x10^5 cm^{-1}$; σ=$8.362x10^{-6}$ mho/cm; i=$14.5x10^{-6}$ amp; d=$105x10^{-4}$ cm; m_+=0.1732; m_-=0.1681; E'_{expt}=$0.6747x10^4$ xU; $\zeta_{W.L.O.}$=$26.13y_{0(expt)}$ (mV)

0.5688	4.0	4.1	3.768	0.2844	0.7331	1.11	2.17	2.79	3.10	3.22	2.543	2.50	65.21
0.8098	3.9	3.4	3.873	0.4049	0.887	1.16	2.25	2.92	3.30	3.38	2.613	2.50	65.21
2.516	3.3	3.3	4.562	1.258	1.3789	1.30	2.58	3.42	4.0	4.10	3.079	2.52	65.61
2.942	3.2	3.2	4.689	1.471	1.4465	1.34	2.60	3.55	4.14	4.34	3.163	2.55	66.40
3.784	2.9	3.0	5.192	1.892	1.5564	1.36	2.68	3.70	4.45	4.80	3.504	2.75	71.01
5.770	2.7	2.7	5.682	2.385	1.6567	1.40	2.73	3.86	4.70	5.30	3.834	2.77	72.14
7.875	2.5	2.5	6.122	3.9375	1.8744	1.42	2.80	4.00	5.02	5.75	4.131	3.12	81.28
10.50	2.3	2.3	6.313	5.250	1.9994	1.43	2.90	4.17	5.34	6.20	4.260	3.05	79.45

Table 4.4 Iodobenzene in $9.99x10^{-5}$N KCl (30°C)

κ =$3.296x10^5 cm^{-1}$; σ=$1.994x10^{-5}$ mho/cm; i=$34x10^{-6}$ amp; d=$105x10^{-4}$ cm; m_+=0.1732; m_-=0.1681; E'_{expt}=$0.6747x10^4$ xU; $\zeta_{W.L.O.}$=$26.13y_{0(expt)}$ (mV)

0.5688	3.5	3.6	4.552	0.284	0.9719	1.20	2.30	3.00	3.40	3.45	3.072	3.15	82.06
0.8098	3.3	3.3	4.698	0.405	1.1265	1.24	2.42	3.15	3.60	3.70	3.171	3.05	79.45
1.0390	3.1	3.1	4.998	0.529	1.2419	1.24	2.50	3.30	3.85	3.85	3.365	3.10	80.76
2.516	3.0	3.0	5.174	1.258	1.6177	1.40	2.68	3.75	4.50	5.50	3.491	2.87	75.01
3.348	2.7	2.7	5.604	1.674	1.7418	1.40	2.85	3.92	4.90	5.43	3.783	2.85	74.23
5.770	2.6	2.6	5.932	2.385	1.8955	1.42	2.84	4.07	5.10	5.75	4.003	2.92	76.07
6.301	2.5	2.5	6.189	3.150	2.0163	1.42	2.90	4.14	5.35	6.20	4.177	3.01	78.41
10.50	2.3	2.3	6.724	5.250	2.2382	1.45	2.93	4.25	5.57	6.57	4.538	3.17	79.97

CALCULATION OF ζ POTENTIAL OF IODOBENZENE DROPLETS BY THE W.L.O.METHOD (Contd.)

Diameter $x10^4$(cm)	Time(sec) R_t	Time(sec) L_t	$-Ux10^4$ (cm^2/sec/V)	$\alpha x10^4$ (cm)	log κa	Corrected E' $y_0 = 1$	2	2.5	3	E'_{expt}	$y_{0(expt)}$	$-\zeta_{W.L.O.}$ (mV)

Table 4.5 Iodobenzene in $1.044x10^{-5}$ N $BaCl_2$ (27^oC)

$\kappa = 1.302x10^5 cm^{-1}$; $G = 4.861x10^{-6}$ mho/cm; $i = 58x0.2x10^{-6}$ amp; $d = 105x10^{-4}$ cm; $m_+ = 0.3968$; $m_- = 0.1717$; $E'_{expt} = 0.7202x10^4 xU$; $\zeta_{W.L.O.} = 25.87 y_{0(expt)}$ (mV)

0.5688	6.2	6.2	1.802	0.2844	0.5684	0.99	1.62	1.55	1.47	1.298	1.42	36.74
0.8098	6.0	6.1	2.21	0.4049	0.7219	1.03	1.62	1.57	1.50	1.592	1.50	39.16
2.942	5.0	4.9	2.523	1.4710	1.2821	1.20	1.90	1.96	1.90	1.817	1.80	46.57
3.348	4.9	4.9	2.600	1.674	1.3382	1.23	1.95	2.03	1.96	1.873	1.85	47.86
4.158	4.8	4.8	2.923	2.079	1.4324	1.266	2.066	2.166	2.100	2.105	2.10	54.33
6.301	3.5	3.6	3.142	3.1505	1.6128	1.300	2.30	2.5	2.45	2.262	2.15	58.44
7.875	3.0	3.0	3.715	3.9375	1.7097	1.36	2.40	2.67	2.67	2.675	2.50	64.68
10.50	2.8	2.9	3.912	5.250	1.8347	1.40	2.55	2.90	3.10	3.06	3.35	86.66

Table 4.6 Iodobenzene in $3.132x10^{-5}$ N $BaCl_2$ (27^oC)

$\kappa = 2.259x10^5 cm^{-1}$; $G = 7.936x10^{-6}$ mho/cm; $i = 84x0.2x10^{-6}$ amp; $d = 105x10^{-4}$ cm; $m_+ = 0.3968$; $m_- = 0.1717$; $E'_{expt} = 0.7202x10^4 xU$; $\zeta_{W.L.O.} = 25.87 y_{0(expt)}$ (mV)

0.5688	7.2	7.2	1.742	0.2844	0.8078	1.05	1.63	1.60	1.53	1.254	1.25	32.33
0.8098	6.0	6.0	2.092	0.4049	0.9613	1.10	1.68	1.68	1.63	1.506	1.29	33.50
2.516	4.8	4.9	2.562	1.258	1.4535	1.27	2.10	2.20	2.14	1.853	1.67	43.20
3.348	4.0	4.0	3.149	1.674	1.5776	1.30	2.23	2.40	2.33	2.268	2.05	53.04
4.770	3.2	3.2	3.743	2.385	1.7314	1.37	2.43	2.70	2.71	2.639	2.3	59.50
6.301	2.9	3.0	4.362	3.1505	1.8522	1.40	2.57	2.93	3.13	3.042	2.70	69.85
7.875	2.5	2.5	4.998	3.9375	1.9491	1.40	2.66	3.05	3.36	3.299	2.82	72.95
9.452	2.5	2.5	4.998	4.7260	2.0284	1.42	2.72	3.18	3.56	3.599	3.05	78.91

CALCULATION OF ζ POTENTIAL OF IODOBENZENE DROPLETS BY THE W.L.O.METHOD (Contd.)

Diameter $x10^4$(cm)	Time(sec) R_t	Time(sec) L_t	$-Ux10^4$ (cm^2/sec/V)	$ax10^4$ (cm)	log κa	Corrected E' y_0=1	2	2.5	3	E'_{expt}	$y_{0(expt)}$	$-\zeta_{W.L.O.}$ (mV)

Table 4.7 Iodobenzene in $8.352x10^{-5}$N $BaCl_2$ (27^oC)

κ =$3.684x10^5 cm^{-1}$; σ=$1.587x10^{-5}$ mho/cm; i=$28.0x10^{-6}$ amp; d=$105x10^{-4}$ cm; m_+=0.3943; m_-=0.1717; E'_{expt}=$0.7202x10^4$ xU; $\zeta_{W.L.O.}$=$25.87 y_{0(expt)}$ (mV)

0.5688	6.5	6.5	2.305	0.2844	1.0202
0.8098	5.1	5.1	2.960	0.4049	1.1737
1.059	4.5	4.5	3.345	0.5295	1.2902
2.942	3.5	3.5	4.291	1.471	1.7339
3.348	3.2	3.2	4.714	1.674	1.7900
3.784	3.0	3.0	5.002	1.892	1.8432
4.770	2.8	2.8	5.372	2.385	1.9438
7.875	2.5	2.5	6.032	3.9375	2.1615
10.50	2.2	2.2	6.840	5.250	2.2865

Table 4.8 Iodobenzene in $1.11x10^{-5}$N $LaCl_3$ (27^oC)

κ =$1.551x10^{-5} cm^{-1}$; σ=$5.555x10^{-6}$ mho/cm; i=46.5x0.2x10^{-6} amp; d=$105x10^{-4}$ cm; m_+=0.5267; m_-=0.1717; E'_{expt}=$0.7202x10^4$ xU; $\zeta_{W.L.O.}$=$25.87 y_{0(expt)}$ (mV)

0.5688	12.1	12.1	1.312	0.2844	0.6445
0.8098	11.0	11.1	1.443	0.4049	0.7980
1.0590	7.6	7.6	2.083	0.5295	0.9145
2.516	6.6	6.7	2.386	1.258	1.2903
3.348	5.5	5.6	2.853	1.674	1.4143
3.784	5.0	5.0	3.172	1.892	1.4675
4.770	4.2	4.2	3.763	2.385	1.5681
6.301	3.8	3.8	4.172	3.1505	1.6889

CALCULATION OF ζ POTENTIAL OF IODOBENZENE DROPLETS BY THE W.L.O.METHOD (Contd.)

Diameter $x10^4$(cm)	Time(sec) R_t	Time(sec) L_t	$-Ux10^4$ (cm^2/sec/V)	$\alpha x10^4$ (cm)	log κa	Corrected E' $y_0 = 1$	Corrected E' $1\frac{2}{3}$	Corrected E' 2	E'_{expt}	$y_{O(expt)}$	$-\zeta_{W.L.O.}$ (mV)

Table 4.9 Iodobenzene in $3.33x10^{-5}$N $LaCl_3$ (27^oC)

$\kappa = 2.687x10^5 cm^{-1}$; $\sigma = 8.563x10^{-6}$ mho/cm; $i = 19.5x10^{-6}$ amp; $d = 105x10^{-4}$ cm; $m_+ = 0.5267$; $m_- = 0.1717$; $E'_{expt} = 0.7202x10^4 xU$; $\zeta_{W.L.O.} = 25.87 y_{O(expt)}$ (mV)

0.5688	9.7	9.7	1.194	0.2844	0.8831	0.93	1.04	1.01	0.8598	0.90	23.28
0.8098	8.3	8.3	1.382	0.4049	1.0366	0.98	1.10	1.05	0.9954	1.025	26.48
1.059	6.9	6.9	1.652	0.5295	1.1531	1.03	1.17	1.10	1.190	1.10	28.44
2.516	6.6	6.6	1.733	1.258	1.5289	1.21	1.53	1.53	1.248	1.05	27.16
3.784	5.2	5.2	2.192	1.892	1.7059	1.30	1.77	1.83	1.579	1.30	33.61
6.301	5.1	5.1	2.240	3.1505	1.9275	1.38	2.00	2.20	1.613	1.20	31.05
10.50	4.4	4.4	2.582	5.250	2.1494	1.43	2.22	2.50	1.859	1.375	35.57
3.676	6.0	6.2	2.090	1.8380	1.6936	1.30	1.71	1.80	1.505	1.12	30.33

Table 4.10 Iodobenzene in $8.88x10^{-5}$N $LaCl_3$ (27^oC)

$\kappa = 4.387x10^5 cm^{-1}$; $\sigma = 1.897x10^{-5}$ mho/cm; $i = 35x10^{-6}$ amp; $d = 105x10^{-4}$ cm; $m_+ = 0.5267$; $m_- = 0.1717$; $E'_{expt} = 0.7202x10^4 xU$; $\zeta_{W.L.O.} = 25.87 y_{O(expt)}$ (mV)

0.5688	12.8	12.8	1.112	0.2844	1.0961	1.00	1.13	1.08	0.8007	0.75	19.40
0.8098	11.0	11.0	1.297	0.4049	1.2496	1.07	1.17	1.27	0.9342	0.825	21.34
1.059	10.0	10.0	1.426	0.5295	1.3661	1.12	1.35	1.30	1.027	0.88	22.77
2.942	8.4	8.4	1.693	1.471	1.8098	1.35	1.90	2.00	1.219	0.90	23.28
4.770	7.6	7.6	1.872	2.385	2.0197	1.41	2.10	2.33	1.348	0.95	24.58
6.301	7.0	7.4	2.030	3.1505	2.1405	1.44	2.20	2.50	1.462	1.02	26.38
7.350	6.4	6.4	2.212	3.6750	2.2075	1.45	2.25	2.57	1.593	1.11	28.72
9.452	6.0	6.0	2.363	4.7260	2.3166	1.47	2.33	2.70	1.702	1.175	30.40

ELECTROPHORETIC MOBILITIES OF IODOBENZENE DROPLETS

Calculation of U by W.L.O. method using $\zeta_{(av)}$

$a \times 10^4$ (cm)	$\log \kappa a$	E	$U_{W.L.O.} \times 10^4$ ($cm^2/sec/V$)

Table 4.11 1.044×10^{-5} N $BaCl_2$ (27°C)

$\kappa = 1.302 \times 10^5 cm^{-1}$; $\zeta_{W.L.O.(\bar{a}v)} = 54.0$ mV; $y_0 = 2.084$

0.284	0.5680	1.60	2.222
0.405	0.7219	1.65	2.292
1.471	1.2821	1.92	2.666
1.674	1.3382	2.00	2.777
2.079	1.4324	2.10	2.916
3.151	1.6128	2.30	3.268
3.937	1.7097	2.48	3.444
5.250	1.8347	2.63	3.653

Table 4.12 3.13×10^{-5} N $BaCl_2$ (27°C)

$\kappa = 2.259 \times 10^5 cm^{-1}$; $\zeta_{W.L.O.(av)} = 57.0$ mV; $y_0 = 2.199$

0.2844	0.8078	1.62	2.250
0.4049	0.9613	1.70	2.360
1.258	1.4535	2.15	2.985
1.674	1.5776	2.35	3.263
2.385	1.7314	2.57	3.569
3.151	1.8522	2.72	3.778
3.937	1.9491	2.85	3.958
4.726	2.0284	2.92	4.055

Table 4.13 3.33×10^{-5} N $LaCl_3$ (27°C)

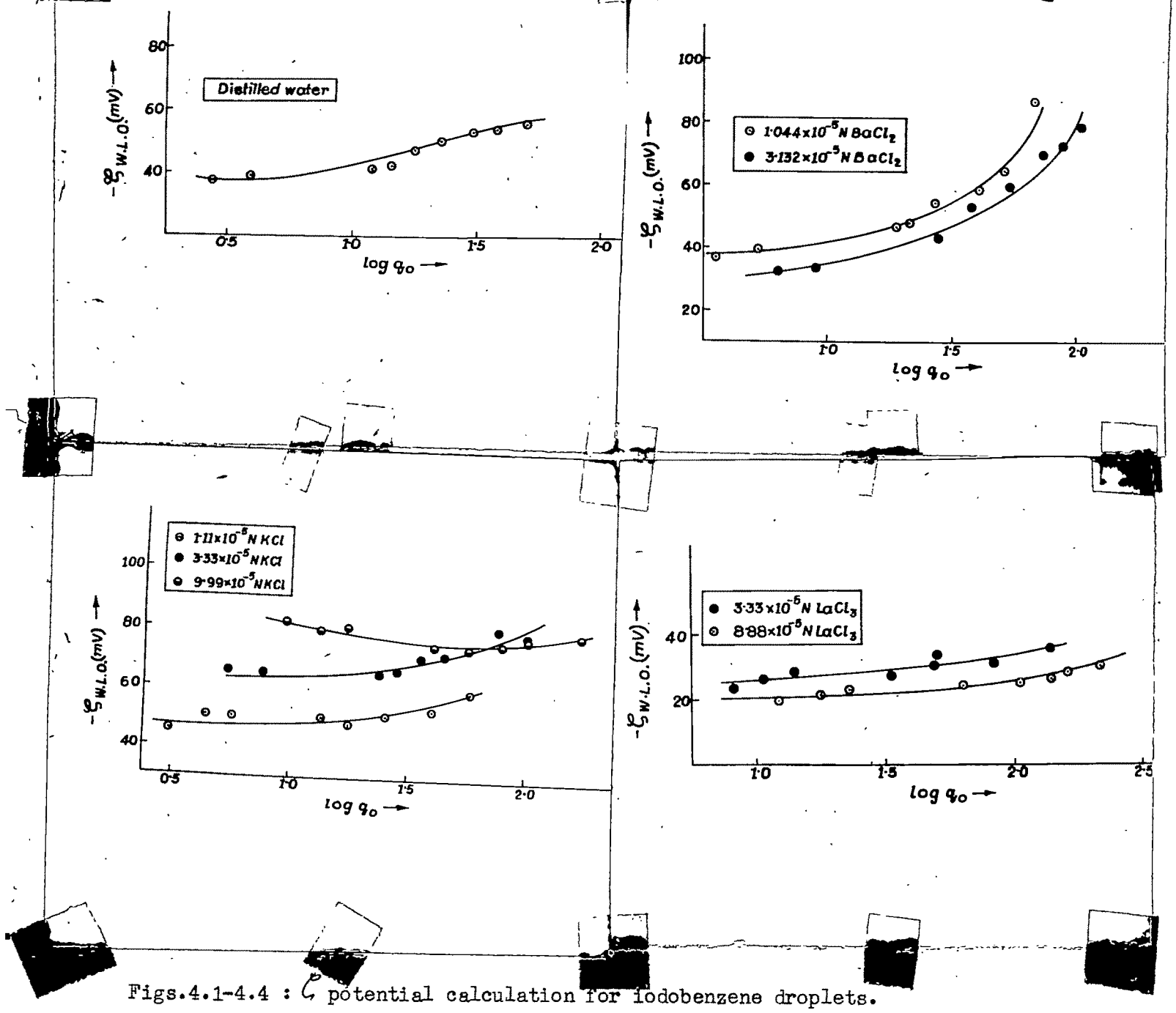
$\kappa = 2.687 \times 10^5 cm^{-1}$; $\zeta_{W.L.O.(av)} = 27.0$ mV; $y_0 = 1.043$

0.2844	0.8831	0.94	1.305
0.4049	1.0366	1.00	1.389
0.5295	1.1531	1.05	1.458
1.258	1.5289	1.25	1.736
1.892	1.7059	1.32	1.833
3.1505	1.9275	1.35	1.918
5.250	2.1494	1.43	1.986
1.838	1.6936	1.45	2.061

Table 4.14 8.88×10^{-5} N $LaCl_3$ (27°C)

$\kappa = 4.387 \times 10^5 cm^{-1}$; $\zeta_{W.L.O.(av)} = 23.3$ mV; $y_0 = 0.90$

0.2844	1.0961	0.925	1.284
0.4049	1.2496	1.000	1.389
0.5295	1.3661	1.04	1.444
1.471	1.8098	1.22	1.694
2.385	2.0197	1.27	1.764
3.151	2.145	1.30	1.801
3.675	2.2075	1.32	1.833
4.726	2.3166	1.32	1.876



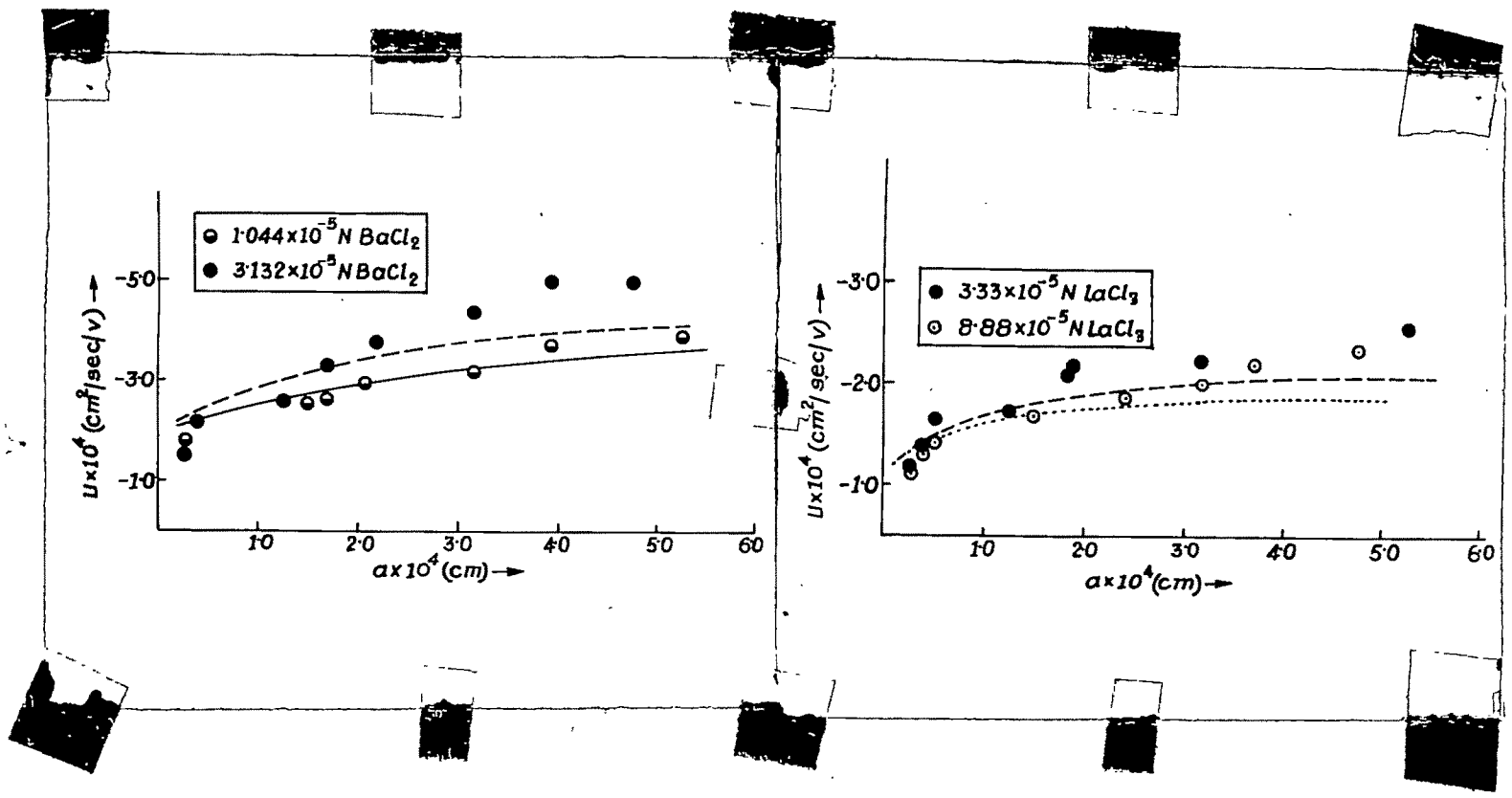
Figs.4.1-4.4 : ζ potential calculation for iodobenzene droplets.

Fig.4.1. Distilled water (27°C).

Fig.4.2. KCl solutions: ⊙ : 1.11×10^{-5}N(30°C), ● : 3.33×10^{-5}N(30°C), ⊙ : 9.99×10^{-5}N(30°C).

Fig.4.3. $BaCl_2$ solutions: ⊙ : 1.044×10^{-5}N(27°C), ● : 3.132×10^{-5}N(27°C).

Fig.4.4. $LaCl_3$ solutions: ⊙ : 8.88×10^{-5}N(27°C), ● : 3.33×10^{-5}N(27°C).



Figs.4.5-4.6: Theoretically calculated electrophoretic mobilities for iodobenzene droplets by the W.L.O. method.

Fig.4.5. $BaCl_2$ solutions [--- 3.132×10^{-5}N; —— 1.044×10^{-5}N].

Fig.4.6. $LaCl_3$ solutions [--- 3.33×10^{-5}N; ··· 8.88×10^{-5}N].

4.4. Discussion of the results of mobility measurements with Nujol and Iodobenzene droplets :

The experimentally determined electrophoretic mobilities of both Nujol and Iodobenzene droplets, in distilled water as also in electrolyte solutions (Figs.3.15, 3.16, and 4.5-4.6, for $BaCl_2$ and $LaCl_3$ solutions only) are seen to increase steadily with increase in particle size. Earlier measurements by other workers[27,58,70] have also shown an unambiguous trend of increase of electrophoretic mobility with increase in particle size in media of constant electrolyte concentration.

The effect of electrolytes, in general, is to maintain the same trend. With increase in concentration of electrolytes the mobility generally increases for the same particle size; (most marked for lower valent counter-ions); however, as the counter-ion valency increases this trend is suppressed; and for La^{+3}, as counter-ion the mobility eventually decreases (e.g., for the Iodobenzene emulsion) for particles of same size.

As the ionic composition and concentration of the medium has not been allowed to change in the above experiments (variation of mobility with particle size), so it is logical to assume that the surface characteristics of the particle, e.g., its electrostatic potential difference with respect to the bulk solution, or its charge-density also remain unaltered. In fact, the condition of constant ionic composition and concentration had deliberately been imposed in order to secure the above, simplifying situation, namely constant ζ potential or constant surface charge density*. The advantage accruing here from in regard to the simplification of the theoretical calculations (e.g. of ζ potentials) have already been mentioned.

The ζ potentials have been calculated from the electrophoretic mobility results only by the W.L.O. method, as the limitations etc. of the alternative analytical approximations are already known (Chapter 2) and present no further interest. The calculated ζ potentials have been shown for both the systems in all the solutions in Figs.(3.11-3.14) and (4.1-4.4).

The most important result which is manifest from these figures is that the ζ potential does not remain constant, but shows a steady increase with particle size. This is true both of the distilled water as also of the electrolyte solution systems. The same result has also been noted (Chapter 2) in case of Mooney's electrophoretic mobility data for oil droplets, and has also been reported earlier[69] in case of Stckelberg et al's mobility measurements.

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*Over the κa range involved, the relation between the two is nearly linear (ref.39); therefore the constancy of one implies that of the other.

This result is in contradiction with our basic assumption that in systems of constant electrolyte concentration and composition the ζ potential of the particles remains constant. As the computer calculation method gives, so to say, a rigorous solution of the equations of the theory, therefore, the above contradiction can not be attributed to possible approximations in the method of calculation (as it could have been, in the case of the analytical approximations of Overbeek and Booth). Thus, the said contradiction may be due either to (i) the simplifications inherent in the theoretical treatments, viz., the neglect or overlooking of some possible complicating factors, or the invalidity of some of the basic assumptions made in the theories, etc., or to (ii) a genuine change of the ζ potential with particle size, even in media of constant electrolyte concentration. The effect of particle curvature in this respect has been investigated.[87)]

The change in ζ potential with the electrolyte concentration and valency of the counter-ions parallels the corresponding change in mobility. ζ increases with electrolyte concentration for particles of same size; this being most marked for KCl and almost absent or reversed for $LaCl_3$. For Iodobenzene droplets the reversal occurs already in the case of $BaCl_2$.

The calculation of electrophoretic mobility on the assumption of a suitable average (constant) ζ value for each system, and the comparison of the theoretically calculated mobilities with the experimental values is of some interest (Figs.3.15-3.16 and 4.5-4.6). This has been done for the case of the polyvalent counter-ions (Ba^{++} and La^{+++}) only. The calculations are not in very good agreement with the experimental results, as could have been anticipated on the basis of the fact that the findings from the calculation of ζ itself in the first instance, was in poor agreement with the assumption of a constant ζ for each system. It is seen from the figures that the observed increase of mobility with particle size is steeper than predicted by theory (the discrepancy is more marked for Ba^{++} than for La^{+++}).