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Application of Lee-Wheaton equation for some ionic surfactants in aqueous solution

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ABSTRACT

This paper reports conductmetric investigations of some ionic surfactants using Lee-Wheaton equation. Two sets of electrical conductivities of aqueous solutions of anionic sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfate (SDBS) and cationic cetyltrimethylammonium bromide (CTAB), below and above critical micelle concentrations (CMC) have been measured at different temperatures. At concentrations below than CMC application of Kohlrausch's model show abnormal relationships for all surfactants and application of Lee-Wheaton equation cannot proceed. While, at concentrations over CMC, Lee-Wheaton model is applicable with no logical results. It was concluded that Lee-Wheaton equation does not recognizes the formation of micelles and care should be taken for treating self assembly compounds using this equation.

KEYWORDS

Lee-Wheaton equation;
Surfactants;
Sodium dodecyl sulfate (SDS);
Dodecyl benzene sulfate (SDBS);
Cetyltrimethylammonium bromide (CTAB).

INTRODUCTION

The dual nature of surfactants molecules; both hydrophilic and hydrophobic characteristics in a single molecule having significant affects in outcoming useful and interest solution properties. It is apparent that the employment of these ampliphilic molecules in enormous aspects increases day by day[1-3]. The significance importance of these molecules become as attracting factor for scientist to do more investigations using their special facilities. For example, ionic surfactants (sodium dodecyl sulfate; SDS and cetyltrimethylammonium bromide; CTAB) have been explored by Huibers using quantum mechanical calculations[4].

Whatever, the relatively long chain of hydrophobic group may play a good role in the electrolytic behavior of ionic kind of surfactants molecules. Furthermore, it was proposed by most scientists that these chains are responsible for the self assembly of surfactants in aqueous solution. On the other hand, Lee-Wheaton equation considered to be the most advanced model dealing with ions in solution[5]. The equation describes ionic transports in solution containing any number of ionic species of any valancy type, and hence is suitable for use with symmetrical, asymmetrical or mixed electrolytes[6]. Most applications of Lee-Wheaton equation have been captured to inorganic salts and complexes[7]. No employments of this equa-

tion to surfactants or even long chain molecules have been found in literatures. Therefore, it seems interesting to investigate the common ionic surfactants (anionic SDS, sodium dodecyl benzene sulfate; SDBS and cationic CTAB) by this equation in order to get information which might be useful for elucidation the behavior of surfactants in aqueous solution.

EXPERIMENTAL

Materials and measurements

All used surfactants were analytical grade commercial products. Conductivity water was used for preparation of all solutions with specific conductance of 3-5 $\mu S.cm^{-1}$. All conductivity measurements were carried out using HANNA EC 214 conductivity meter with accuracy of $\pm 0.01\ \mu S.cm^{-1}$. In order to control the temperature within $\pm 0.1\ C^{o}$, a water circular thermostat Thermo Hakke K20 was used. A closed Jacket Cell connected to the thermostat using isolated rubber tubes was used. All measurements was carried out after stirring for a while using magnetic stirrer instead of nitrogen gas. The latter causing bubbles due to presence of surfactants which therefore avoided. 0.1 M of used surfactants was freshly prepared as stock solution. In order to make the measurements more accurate, the volumes of all measured solutions have been estimated through weight instead of direct volumetric determination. This due to the fact that the produced bubbles due to presence of surfactants particularly at the top of solution would definitely disturb the observation of solution level. 35 ml of water was placed in conductimetric cell and then the stock solution was added using plastic syringe. After each addition the solution was mixed using magnetic stirrer.

Theoretical calculations

The used surfactants in presented work are considered to be as 1:1 symmetrical electrolyte[6]. The latter obey to the simplest form of Lee-Wheaton equation in the form described by Pethybridge and Taba[8]:

$$\Lambda = \gamma\Lambda_s^o[1 + C_1(\beta\kappa) + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3] - \frac{\rho\kappa}{(1+\kappa d)}[1 + C_4(\beta\kappa) + C_5(\beta\kappa)^2 + \kappa d/12] \quad (1)$$

Where Λ is the experimental molar (equivalent) conductivity ($S.\ cm^2.mol^{-1}$), γ is the fraction of free (unassociated) ions, Λ_s^o is the limiting molar conductivity of surfactant, all other symbols are well defined and illustrated in Ref. 6.

RESULTS AND DISCUSSION

It is well known that surfactants molecules tend to make micelles at certain concentrations called as critical micelle concentration (CMC). Such phenomenon attracts us in order to investigate the electrochemical behaviors of this kind of molecules at concentration below than CMC. In other word, no one certain about the state of existence of surfactants molecules; i.e. surfactants molecules exist in a single state in the water-air interface at pre-micellization process? Therefore, concentrations range $1.6x10^{-5}$- $5x10^{-4}$M (under CMC) of used surfactants has been employed for conductmetric measurements at different temperatures. Figures 1-3 exhibit the results of application Kohlrausch's for SDS, SDBS and CTAB at 25°C respectively. Indeed, these show abnormal relationships in contrast to these well known of common strong and weak electrolytes. However, practically we have found that Lee-Wheaton equation cannot treat these data in addition to others which have been measured at different temperatures (10, 15, 20 and 30°C). The reason for this may be attributed to the following two factors which arisen from some special characters of these molecules. The molecules will be at the surface in order to reduce the free energy caused by the repulsion of hydrophobic tail of surfactant with water molecules. The second is may be related to the formation of dimmer, trimmer, tetramer and so on under CMC.

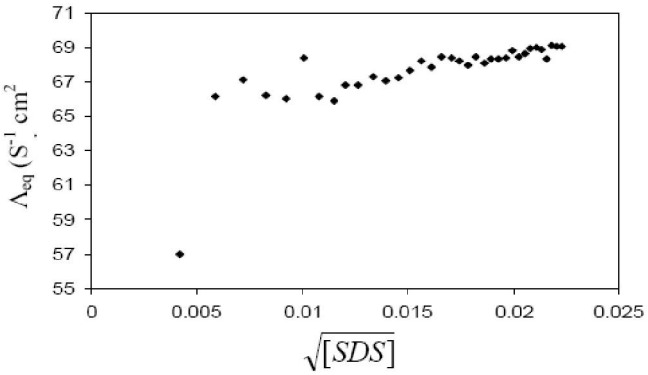

Figure 1 : Plot of the equivalent conductivity against the square rote of molar concentration of SDS at different temperatures.

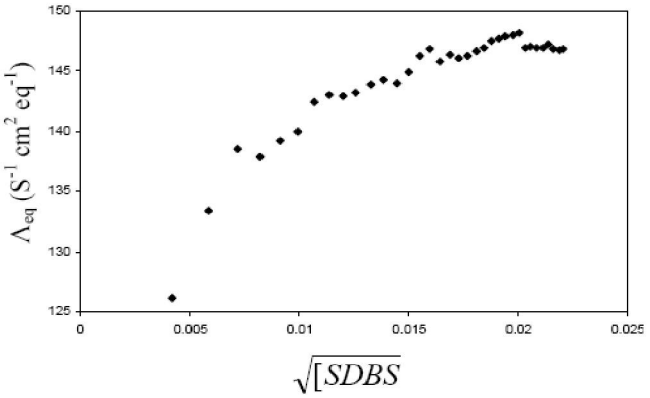

Figure 2 : Plot of the equivalent conductivity against the square rote of molar concentration of SDBS at different temperatures.

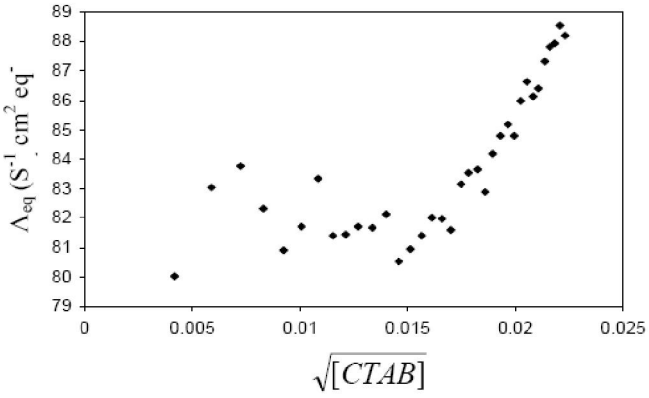

Figure 3 : Plot of the equivalent conductivity against the square rote of molar concentration of CTAB at different temperatures.

In order to get more information about the applicability of Lee-Wheaton equation on surfactants molecules, Concentrations over CMC were taken under our investigations. TABLES 1-3 list the equivalent conductivities as function of concentrations at different temperatures for SDS, SDBS and CTAB respectively, While, Figures 4-6 present the application of these results to the Kohlrausch's model. The latter Figures show apparently that the results over CMC are more applicable to Kohlrausch's law in contrast to these of Figures 1-3. Interestingly, the results of TABLES 1-3 were found to be applicable to Lee-Wheaton equation as given in TABLES 4, 5 and 6 for SDS, SDBS and CTAB respectively. In other word, the relative small values of what have calculated using equation 2 indicate the good applicability of Lee-Wheaton equation for such treatment[5].

TABLE 1 : The equivalent conductivities (S. cm^2.mol^{-1}) with the molar concentration for SDS in different temperatures.

293.16 °K		298.16 °K		303.16 °K		208.16 °K		313.16 °K		318.16 °K	
$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ
0.087	43.595	0.084	49.972	0.082	56.217	0.086	60.414	0.087	68.504	0.086	72.887
0.171	43.066	0.168	46.718	0.170	65.488	0.170	58.201	0.175	66.070	0.172	68.393
0.257	42.153	0.253	46.907	0.258	53.558	0.253	58.617	0.259	64.372	0.256	70.826
0.340	41.780	0.346	47.573	0.344	60.079	0.336	58.607	0.339	63.008	0.338	68.920
0.420	41.665	0.428	46.667	0.428	53.282	0.412	57.985	0.420	64.006	0.418	69.775
0.603	41.639	0.612	47.204	0.616	52.605	0.595	57.642	0.598	62.846	0.599	68.543
0.780	40.860	0.789	45.514	0.794	50.827	0.770	56.513	0.772	62.963	0.774	68.050
0.950	37.444	0.958	41.534	0.967	46.504	0.937	52.820	0.939	58.576	0.942	64.750
1.114	34.453	1.123	38.371	1.132	42.736	1.098	48.897	1.100	54.170	1.103	59.705
1.273	32.037	1.280	35.761	1.291	40.431	1.253	45.892	1.255	51.078	1.259	56.748
1.427	30.273	1.434	33.819	1.437	38.465	1.404	43.445	1.405	48.112	1.409	53.900
1.575	28.885	1.581	32.312	1.575	36.676	1.551	41.585	1.551	46.156	1.555	51.360
1.775	27.255	1.784	30.663	1.779	34.737	1.751	39.239	1.750	43.537	1.758	49.026
1.966	25.626	1.977	29.433	1.970	33.384	1.941	37.557	1.939	41.714	1.949	46.887
2.151	25.148	2.163	28.199	2.156	32.410	2.112	36.412	2.121	40.497	2.132	45.156
2.327	24.359	2.338	27.450	2.332	31.290	2.286	35.569	2.296	39.634	2.306	43.922
2.497	23.782	2.507	26.845	2.503	30.638	2.450	34.531	2.461	38.345	2.472	42.661
2.659	23.312	2.668	26.274	2.666	29.852	2.610	33.871	2.620	37.699	2.631	41.868
2.813	22.783	2.821	25.874	2.821	29.305	2.762	33.244	2.773	36.960	2.784	41.190
2.963	22.507	2.969	25.396	2.971	28.971	2.908	32.572	2.918	36.319	2.931	40.515
3.106	22.182	3.111	25.168	3.114	28.385	3.048	32.055	3.058	35.863	3.072	40.289

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TABLE 2 : The equivalent conductivities (S. cm^2.mol^{-1}) with the molar concentration for SDBS in different temperatures.

293.16 °K		298.16 °K		303.16 °K		208.16 °K		313.16 °K		318.16 °K	
Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ
0.057	88.680	0.056	100.716	0.059	118.377	0.062	112.815	0.059	130.219	0.059	149.236
0.113	84.928	0.114	103.329	0.117	117.117	0.116	123.039	0.119	135.910	0.117	150.476
0.172	88.231	0.170	99.279	0.171	121.910	0.172	122.012	0.176	135.264	0.175	147.017
0.230	86.836	0.225	98.537	0.229	114.197	0.230	118.439	0.234	132.912	0.232	149.134
0.286	86.580	0.281	98.163	0.287	113.373	0.284	116.360	0.293	131.873	0.289	146.718
0.396	84.229	0.388	95.139	0.396	108.998	0.396	114.351	0.403	129.535	0.398	141.762
0.503	82.598	0.491	93.485	0.498	104.867	0.502	110.848	0.509	124.970	0.504	137.345
0.607	81.697	0.594	92.154	0.601	102.744	0.605	110.488	0.613	122.265	0.610	135.452
0.706	79.570	0.697	90.480	0.701	101.657	0.708	108.524	0.716	119.786	0.708	131.606
0.803	78.599	0.797	88.533	0.799	99.023	0.809	107.582	0.815	117.299	0.806	130.352
0.900	77.816	0.893	87.634	0.896	97.478	0.906	105.467	0.912	117.392	0.903	128.172
0.997	76.903	0.988	86.237	0.992	97.185	1.003	106.257	1.008	115.193	0.998	127.577
1.158	75.790	1.149	84.719	1.154	94.316	1.165	101.964	1.170	113.382	1.158	124.164
1.313	74.057	1.304	83.259	1.309	93.282	1.321	101.080	1.326	114.078	1.311	122.769
1.463	73.674	1.453	82.626	1.461	92.122	1.472	99.731	1.476	110.732	1.463	120.075
1.606	72.747	1.597	81.553	1.606	91.483	1.616	98.442	1.623	109.692	1.609	119.278
1.747	71.740	1.737	80.999	1.747	90.590	1.756	97.410	1.764	107.544	1.750	119.273
1.883	71.245	1.871	80.111	1.883	89.512	1.892	96.188	1.900	108.297	1.886	118.142
2.015	70.632	2.001	79.435	2.014	88.863	2.024	96.185	2.032	107.655	2.017	117.400
2.144	70.173	2.129	78.819	2.141	88.450	2.152	96.079	2.160	106.630	2.145	116.003
2.266	69.928	2.251	78.519	2.264	87.905	2.276	95.679	2.283	106.312	2.270	115.337

TABLE 3 : The equivalent conductivities (S. cm^2.mol^{-1}) with the molar concentration for CTAB in different temperatures.

293.16 °K		298.16 °K		303.16 °K		208.16 °K		313.16 °K		318.16 °K	
Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ	Mx10^2	Λ
0.088	53.713	0.079	58.731	0.092	67.474	0.089	76.094	0.087	82.484	0.087	90.209
0.178	36.784	0.161	44.272	0.180	47.486	0.174	59.797	0.172	62.850	0.173	69.869
0.263	29.410	0.250	34.443	0.264	39.033	0.258	44.265	0.257	55.941	0.259	58.651
0.346	25.293	0.336	30.056	0.347	34.654	0.340	39.144	0.340	44.738	0.342	50.373
0.430	22.973	0.422	27.602	0.431	31.688	0.421	35.180	0.421	40.965	0.424	45.645
0.611	19.789	0.604	23.415	0.610	27.947	0.604	31.472	0.601	36.197	0.606	40.852
0.788	18.039	0.777	21.411	0.785	24.962	0.779	29.275	0.776	33.481	0.781	37.850
0.958	16.814	0.944	20.042	0.955	23.711	0.948	26.699	0.944	31.528	0.949	35.258
1.120	16.111	1.106	19.123	1.119	22.646	1.110	25.680	1.108	30.212	1.113	33.760
1.275	15.512	1.263	18.576	1.277	21.655	1.267	24.789	1.265	29.230	1.269	33.072
1.427	15.035	1.416	18.121	1.448	20.819	1.419	23.967	1.416	28.290	1.420	31.951
1.572	15.042	1.564	17.809	1.592	20.505	1.565	23.397	1.563	27.752	1.566	31.459
1.770	14.889	1.766	17.421	1.792	20.060	1.765	22.726	1.763	26.982	1.767	30.538
1.950	14.743	1.953	17.181	1.984	19.737	1.956	22.395	1.954	26.398	1.958	29.966
2.131	14.665	2.132	17.151	2.165	19.469	2.138	22.217	2.135	26.025	2.141	29.361
2.305	14.596	2.301	17.016	2.338	19.352	2.312	22.018	2.310	25.701	2.315	28.847
2.472	14.460	2.466	16.854	2.504	19.192	2.478	21.915	2.477	25.418	2.480	28.413
2.624	14.347	2.624	16.829	2.664	19.084	2.637	21.768	2.637	25.209	2.639	28.138

293.16 °K		298.16 °K		303.16 °K		208.16 °K		313.16 °K		318.16 °K	
$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ	$Mx10^2$	Λ
2.776	14.284	2.776	16.697	2.817	18.975	2.790	21.652	2.791	24.821	2.792	27.891
2.922	14.150	2.922	16.619	2.962	18.859	2.937	21.522	2.938	24.701	2.933	27.847
3.052	14.039	3.062	16.412	3.102	18.743	3.078	21.476	3.079	24.446	3.071	27.704

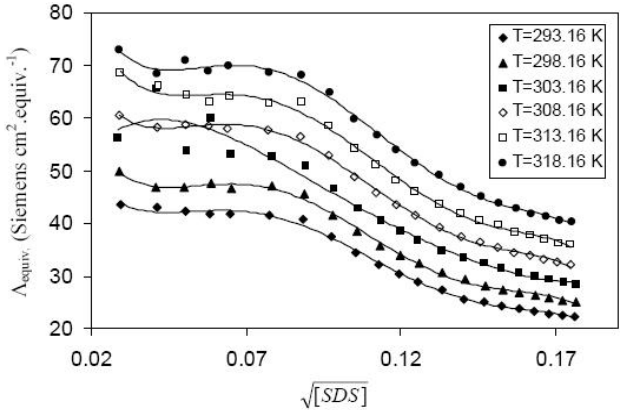

Figure 4 : Plot of the equivalent conductivity against the square rote of molar concentration of SDS at different temperatures.

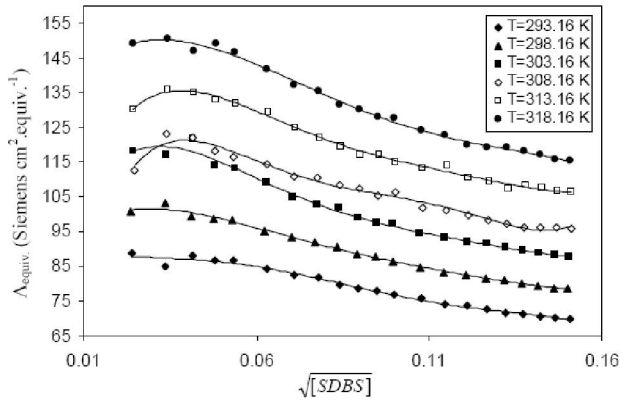

Figure 5 : Plot of the equivalent conductivity against the square rote of molar concentration of SDBS at different temperatures.

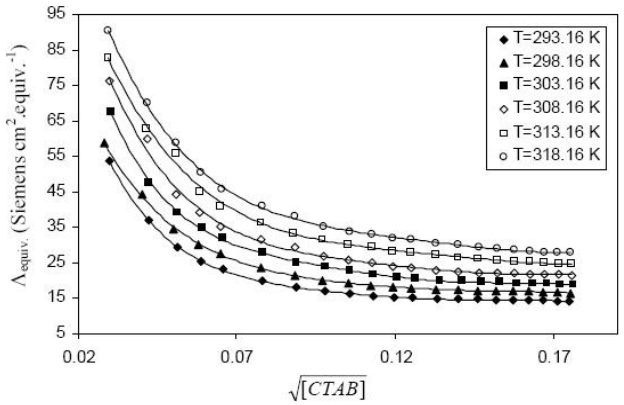

Figure 6 : Plot of the equivalent conductivity against the square rote of molar concentration of CTAB at different temperatures.

TABLE 4 : The best fit parameters of analysis of conductance data for SDS solution at different temperatures.

Temp. (°K)	K_A	Λ_o	R (A°)	σs (Λ)
293.16	59.831	50.157	29	0.020
298.16	70.392	58.159	29	0.020
303.16	241.573	89.78	29	0.008
308.16	57.1413	69.382	29	0.024
313.16	48.380	76.193	29	0.025
318.16	42.4688	81.801	29	0.025

TABLE 5 : The best fit parameters of analysis of conductance data for SDBS solution at different temperatures.

Temp. (°K)	K_A	Λ_o	R (A°)	σs (Λ)
293.16	30.46	91.28	19	0.008
298.16	29.16	105.17	19	0.008
303.16	25.24	122.63	19	0.019
308.16	19.16	124.06	19	0.019
313.16	18.99	140.85	19	0.014
318.16	17.12	156.32	19	0.016

TABLE 6 : The best fit parameters of analysis of conductance data for CTAB solution at different temperatures.

Temp. (°K)	K_A	Λ_o	R (A°)	σs (Λ)
293.16	948.11	69.21	29	0.024
298.16	910.12	74.79	29	0.023
303.16	800.66	86.80	29	0.006
308.16	750.23	100.34	29	0.031
313.16	619.01	103.44	29	0.029
318.16	520.82	109.08	29	0.032

$$\sigma_S = \left[\frac{\sum_{i=1}^{n}(\Lambda_{i(cal)} - \Lambda_{i(exp)})^2}{n-2}\right]^{1/2} \quad (2)$$

It is apparent the values of R which represent the distance between anion and cation (TABLES 4-6) show equal values for SDS and CTAB in contrast to that of SDBS. But this contradicts the fact that both SDS and SDBS have the same polar head group in contrast to that of cationic CTAB. It should be noted that the analysis of the obtained values of R denote that the cations and anions are separated by many water molecules. In addition, the values of association constants K_A for SDS

Full Paper

and CTAB show maxima with temperature which may be also considered as not logical results. In general, the results indicate that Lee-Wheaton equation does not recognize the formation of micelles and therefore it is not valid for surfactants molecules.

CONCLUSIONS

On the basis of our investigations one could conclude that Lee-Wheaton equation in the form described by Pethybridge and Taba is not applicable for surfactants molecules which give not logical results from physical point of view. Therefore, attention should be taken into account for the application of the latter model for molecules having tendency for self-assembly process.

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