A STUDY OF WATER ADSORPTION IN DIMETHYLSULFOXIDE BY A. C. POLAROGRAPHY

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Differential double layer capacity measurements were done with addition of water on dimethylsulfoxide (DMSO) with 0.1 M tetraethyl ammonium perchlorate as the supporting electrolyte, by a.c. polarography This study was required as the a.c. polarograph of the supporting electrolyte alone, showed a small, unusual hump requiring interpretation. DMSO showed water adsorption-desorption at — 2 37 volts vs silver reference electrode (AgR). Effect of water on the kinetic parameters, namely Cot $\emptyset$ ($\emptyset$ = phase angle), faradaic current and heterogenous rate constant (K_s) values of some alkali metals were determined. There was an increase in the values of Cot $\emptyset$, K_s and the faradaic current, with lithium showing the most and Cesium the least. Possible interpretations are given.

Dimethylsulfoxide (DMSO) is a dipolar aprotic solvent and this class of solvent has attracted the attention of workers partly because of their peculiar properties[1—6]. DMSO is highly hygroscopic and it has a pronounced degree of solvation. Considerable work has been done on DMSO in the pharmacological and medical field because of its usefulness in medicine[7—10]. Butler[11] has given a well documented study of DMSO electrochemistry in relation to conductance studies and polarography.

In the course of the investigation of the reaction kinetics of the alkali metals in DMSO[12] a small hump was noticed in the a.c. polarographic study of the supporting electrolyte alone. Tetraethyl ammonium perchlorate (TEAP was used as the supporting electrolyte. This observation necessitated the water study and its effect on the kinetic parameters. The water adsorption and its effect on the value of heterogenous rate constant (Ks), phase angle (cot θ), faradaic current, double layer admittance and differential double layer capacity (C_L) at different frequencies for both the supporting electrolyte in DMSO and some alkali metals in DMSO are reported here. As DMSO is highly hygroscopic, this research was undertaken to study the effect throughly with controlled water addition upto 80 mM. This study helps in understanding how far the water adsorption in DMSO can lead to erroneous data.

EXPERIMENTAL

Materials : Commercial DMSO was obtained from Fisher Chemicals Co. It was purified by double distillation with vacuum dried molecular sieves in the vacuum of a rotary at 30°C. The water content of the solvent (DMSO) was ascertained by Karl Fisher titration method using Precision Scientific Co. Auto Aquatrator. Solvent samples with more than 10 mM water concentration were redistilled. Solvent was held in dry molecular sieves in sealed vessels before use. The water content was 2—4 mM.

The TEAP [Molecular formula — $(C_2H_5)_4NClO_4$], obtained from Eastman Organic Chemicals Co. was recrystallized from ethyl alcohol. The final product was dried in a vacuum oven at 55°C. The solvent and the supporting electrolyte showed no trace of impurities when tested polarographically. Lithium and cesium perchlorates obtained from K and K labs. were dried in a vacuum oven at 60°C for 24 hours.

Nitrogen gas (AIR products Co.) purified, 99.97% pure containing 0.001% oxygen and 0.0012% water was dried over anhydrous magnesium perchlorate and passed over hot copper filings (for removal of trace O_2) before use.

Apparatus : A square platinum electrode Sargent model S—30515 D) was used as the counter electrode. Silver electrode in 0.1 M $AgClO_4$ in DMSO was used as the reference electrode (AgR) The junction between the electrolysis vessel and the reference electrode was an asbestos fibre sealed in a glass tube. The polarographic cell was a water jacketted model QA 876-5 supplied by Brinkmann and Co., and a

three electrode configuration was used. Sargent S—84880 circulating constant temperature water bath was used. The temperature was kept at 30°C ± 0.1°C.

Princeton Applied Research Model 170 Electrochemistry system was used for a.c. polarography and for recording current voltage curves. It has a phase sensitive measurement system in all the four quadrants and it is provided with IR compensation facility[13].

Procedure : The preparation of solutions was done in a glove box in a dry nitrogen atmosphere and the solutions were mixed throughly in an electrical shaker. The experiments were done in a nitrogen atmosphere in a glove box. Additional IR compensation was used. The phase adjustment was done at the initial potential to compensate for the phase of the double layer current. The in phase and out of phase measurements were done at the phase control setting of 90° and 180° respectively. Exact details of operation are given elsewhere[13]. Cell resistance (R) and double layer admittance (Y) were previously determined[12]. Addition of water in the range of 10 mM, 20 mM, 40 mM and 80 mM were made using a fine calibrated syringe. The study was done at 50, 100 and 1000 Hz in the case of supporting electrolyte in DMSO and at three different frequencies in the case of metal salts in DMSO. Data reduction was done using IBM 7090.

RESULTS AND DISCUSSION

The parameters i_i, i_o, f, Epeak (E_{dc} max.), m, t, were measured and d, $E_{\frac{1}{2}}$, and ω were calculated. Here, the symbols are

i_T = Total alternating current ($\mu\alpha$)
i_o = Out of phase current ($\mu\alpha$)
i_i = in phase current ($\mu\alpha$)
i_c = double layer current ($\mu\alpha$)
θ = phase angle between the faradaic current and the applied potential
β, α = transfer coefficient
ω = angular frequency ($2\pi f$)
f = frequency (Hz)
K_s = heterogenous rate constant
$E_{\frac{1}{2}}$ = half wave potential
E_{peak} = d.c. potential at cot θ maximum (E_{dc} max.)
m = rate of flow of mercury
t = drop time (seconds)

The data reduction was done as follows[15,16].

$$i_T^2 = (i_o^2 + i_i^2) \quad \text{—— (1)}$$

with IR compensation,

$$\text{Cot } \phi = \frac{i_i}{(i_T^2 + i_c^2 - 2i_c i_o - i_i^2)^{\frac{1}{2}}} \quad \text{—— (2)}$$

substituting for i_T as in Eq.1, Eq.2 reduces to,

$$\text{Cot } \phi = \frac{i_i}{(i_o - i_c)} \quad \text{—— (3)}$$

For the fundamental harmonic a.c. polarographic wave,

$$E_{dc\ max} = E_{\frac{1}{2}} + \frac{RT}{nF} \ln (\alpha/\beta) \quad \text{—— (4)}$$

$$1-\beta = \alpha = \frac{e^{\frac{E_{peak} - E_{\frac{1}{2}}}{(RT/nF)}}}{1 + e^{\frac{E_{peak} - E_{\frac{1}{2}}}{(RT/nF)}}} \quad \text{—— (5)}$$

$$\text{Cot } \varphi = \frac{1 + (2\omega_D)^{\frac{1}{2}}}{K_s[(\alpha'\beta)^{-\alpha} + (\alpha/\beta)\beta]} \quad \text{—— (6)}$$

The plot of cot θ vs $\omega^{\frac{1}{2}}$ and cot θ vs F_{dc} (Eq. 3 and Eq. 6) provide the insight into the reaction kinetics in a qualitative way. A Cot θ = 1 in the plot of cot θ vs $\omega^{\frac{1}{2}}$ is indicative of a diffusion controlled process. A plot of cot θ vs $\omega^{\frac{1}{2}}$ with a positive slope and intercept of unit on the ordinate suggests a simple quasi-reversible system. Further details are given elsewhere [15,16]. A quasi reversible model is used here on the basis of cot θ vs $f^{\frac{1}{2}}$ and cot θ vs E_{dc} data.

The plot of differential double layer capacity (C_L) vs potential for three different frequencies for the supporting electrolyte with 10 mM water addition is shown in Fig. 1. The capacity decreases with increase in frequency and shows a peak at —2.37 volts. Figure 1 also shows the plot of C_L vs potential for 20 mM water addition. The trend is same as for 10mM, but the curve in 10 mM at 1000 Hz is more flat and slightly higher. Figure 2 shows the plot of C_L vs potential of the same system for 10 mM 20 mM, 40 mM and 80 mM water at one frequency (100 Hz). The data of 10 mM and 20 mM at 50 Hz is superimposed in Fig. 2 for comparison. The peak value of capacity occurs at —2.37 volts for all frequencies, and shows increase with increasing concentration of water but decreases with increasing frequency, agreeing with the data in Fig. 1. generally.

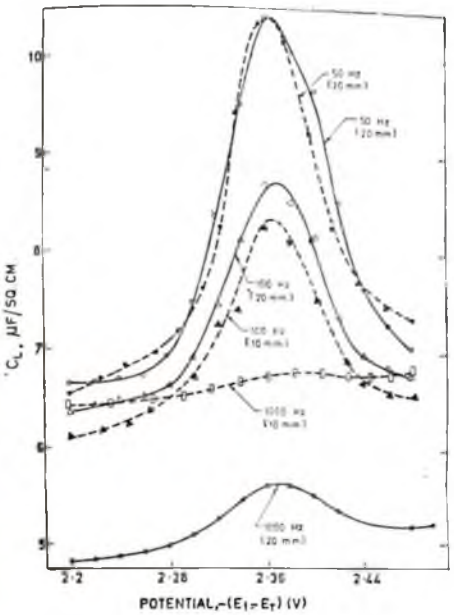


Fig. 1. Water study Differential double layer capacity vs potential 0.1 M TEAP+DMSO + 10, 20 mM water.

Table—1. Water study in DMSO with supporting electrolyte alone. Conditions : Supporting electrolytic was 0.1 M $(C_2H_5)_4NClO_4$ in DMSO; Temp. = 30°C; height = 37 cm.

Frequency Hz	Conc. of water, mM.	Peak capacity μ F	Successive difference. μ F
100	10	8.4	
100	20	8.8	(0.4)
100	30	8.875	(0.075)
100	40	9.375	(0.5)
50	10	10.4	
50	20	10.53	(0.13)
50	20	10.55	
100	20	8.7	(—1.85)
1000	20	5.65	(—3.05)
50	10	10.3	
100	10	8.2	(—2.1)
1000	10	6.8	(—1.4)
1000	10	6.8	
1000	20	5.675	(—1.125)

At low frequency, the general trend is increasing C_L with increasing concentration. Table 1 shows the peak differential double layer capacity for various concentrations and various frequencies. The successive difference in values are shown in bracket, for clarity. There is a general decrease of C_L with increase in frequency. At low frequencies (50, 100 Hz) C_L increases with concentration, where as at high frequency (1000 Hz) there is a slight decrease. In the first two sets and the last set the concentration is varied at a constant frequency. In the third and fourth set, it is vice versa. It should be noted there is reproducibility though the readings were taken separately.

Previous work on these aspects was done by Payne[4]. He has measured the double layer capacity for a number of inorganic electrolyte in DMSO. He has studied specific desorption of certain anions by differential double layer capacity measurements. The height of C_L at the peak for 100 Hz at 10, 20, 40 and 80 mM concentration (Fig. 2.0) are 2, 2.375, 2 5 and 3μF respectively from the base. It is directly proportional to the concentration of water. The same trend is seen at low frequency. This affords a method of determining the unknown concentration of water from the height of C_L at the peak. Using least square method one finds a value of 1.986 for the intercept and 0.012 as the slope for a straight line fit. The concentration of water is taken as X and C_L values are Y in the fit.

Effect of addition of water on cot Ø, faradaic current and K_s:

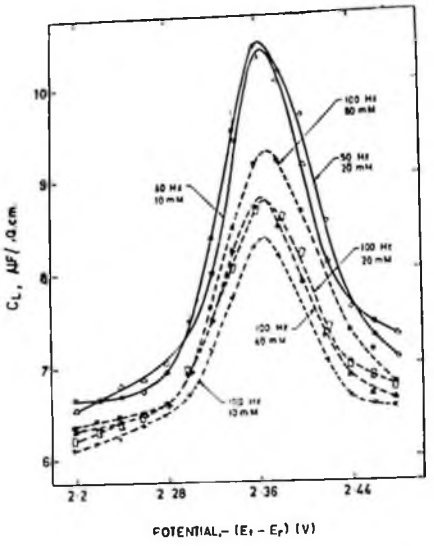


Fig. 2. Water study Differential double layer capacity vs potential 0.1 M TEAP + DMSO + Water (10, 20, 40, 80 mM) at 50, 100 Hz.

The effect of addition of water in very small quantities in the values of faradaic current, cot Ø and cot Ø (max) for $LiClO_4$ and $CsClO_4$ is shown in Figures 3 to 6. The faradaic current data for different frequencies for lithium show an increase with increasing frequency (Fig. 3). The cesium data in Fig. 4 also show the same trend but the peak is not as sharp as for Lithium (Fig. 3). Figure 5 shows cot Ø vs potential for lithium and the same for Cesium is shown in Fig. 6. The cot Ø values using corrected and uncorrected values of double layer admittance are plotted side by side for comparison. The former value is less than the latter as expected, but the cot Ø values are still higher than that of the metal alone, as seen below.

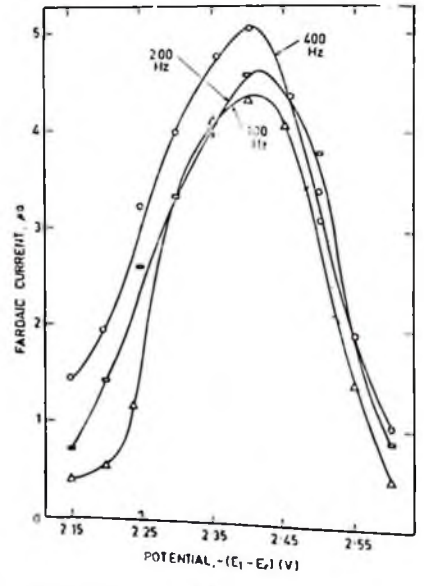
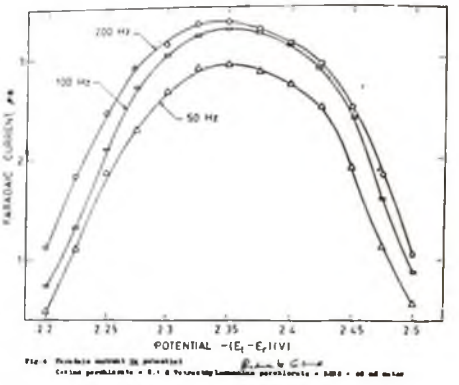


Fig. 3. Faradaic current vs potential Lithium perchlorate + 0.1 M Tetraethylammonium perchlorate + DMSO + 20 mM water.



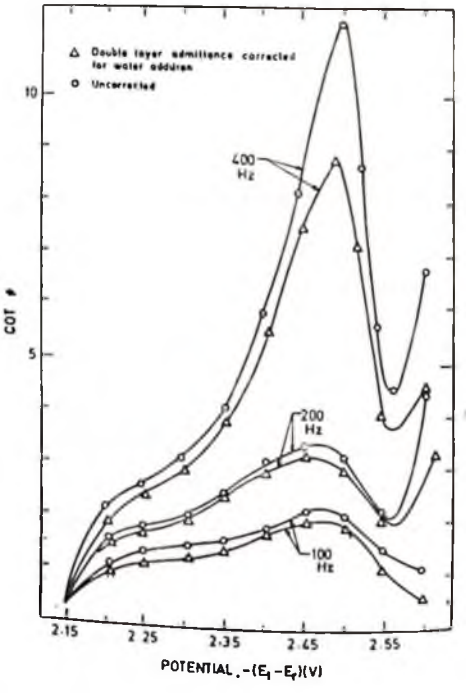


Fig. 5. Cot Ø vs potential Lithium perchlorate + 0.1 M Tetraethylammonium perchlorate + DMSO + 20 mM water (no I.R.)

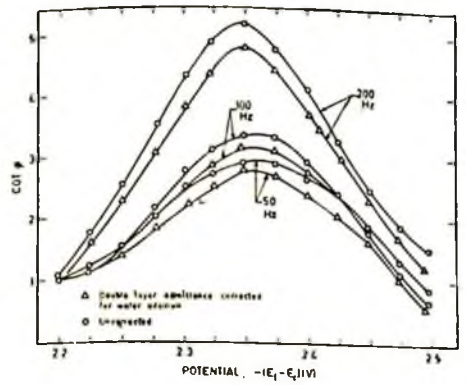


Fig. 6 Cot Ø vs potential Cesium perchlorate + 0.1 M Tetraethylammonium perchlorate + DMSO + 40 mM water (no I R)

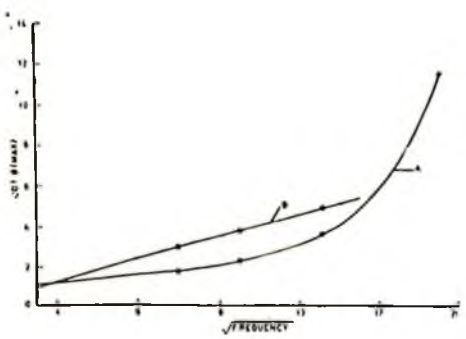


Fig. 7. Cot Ø max) vs frequency Alkali metal perchlorate + 0.1 M Tetraethylammonium perchlorate + DMSO + water

A = Li perchlorate + 20 mM water
B = Cs perchlorate + 40 mM water

Tables 2, 3 and 4 show the comparison of cot Ø, faradaic current and K_s values for the two metal ions and metal ions with addition of very small quantities of water. In Table 2 it is shown that addition of water has a definite effect on the phase angle (cot Ø). Table 3 shows there is a general increase in faradaic current with the addition of water for both lithium and cesium. The increase in faradaic current as a percentage change is small but the increase in cot Ø values are remarkable, especially for lithium with lithium showing the effect more. (See table 2). The percentage increase in faradaic current in both cases is not appreciable. The K_s values are compared in Table 4. The same trend is seen. In the cot Ø (max) vs frequency (Table 2) data the increase in cot Ø (max) with water addition

Table – 2. Comparison of cot Ø (max) for Metal and Metal Ion with addition of water. Conditions : Supporting electrolyte was 0.1 M $(C_2H_5)_4NClO_4$ in DMSO; Temp. = 30°C; height = 37 cm; Concentrations were near 2×10^{-3} M. of electroactive species; Cot Ø values obtained using corrected double layer admittance are given in brackets.

Frequency Hz	$LiClO_4$	$LiClO_4$ + 20 mM H_2O
100	0.4	2.2 (2 0)
200	0.7	3.5 (3.3)
400	4.8	10.8 (9.0)

Frequency Hz	$CsClO_4$	$CsClO_4$ + 40 mM H_2O
50	2.4	2.9 (2.7)
100	2.6	3.3 (3.1)
200	3.0	5.25 (4.8)

Table—3. Comparison of Faradaic Current (max.) for Metal Ion and Metal Ion with addition of Water. Conditions : Supporting electrolyte was 0.1 M $(C_2H_5{}_4NClO_4$; Temp. = 30°C; height = 37 cm; Concentrations were near 2×10^{-3} M of electroactive species.

Frequency Hz	$LiClO_4$	$LiClO_4$ + 20 mM H_2O
100	4 0	4.3
200	4.4	4.6
400	4.6	5.2

Frequency Hz	$CsClO_4$	$CsClO_4$ + 40 mM H_2O
50	2.8	2 9
100	2.8	3.3
200	3.2	3.5

Table—4. Comparison of Ks values ($cm/sec \times 10^{-2}$) for Metal Ion and Metal Ion with addition of water. Conditions same as Table 3.

Frequency Hz	$LiClO_4$	$LiClO_4$ + 20 mM H_2O
100	—6.3	10.34
200	—5.4	43.0
400	1.0	21.6

Frequency Hz	$CsClO_4$	$CsClO_4$ + 40 mM H_2O
50	2.963	3.6
100	1.323	1.70
200	1.435	2.7

is more pronounced in the case of lithium than cesium. The same trend for deviation from reversibility was there with lithium showing a slope of 0.110 and Cesium a slope of 0.067[12] in the $\log \frac{(i_d - i_i)}{i}$ vs potential plot,[12] in D.C. polarography. In A.C. polarography, cesium showed an intercept of unity in the cot Ø (max) vs $f^{1/2}$ data where as for lithium it is much less than unity[12]. Figure 7 shows cot Ø (max) vs $f^{1/2}$ for both the metals with very small amounts of water added. Cesium shows a straight line behaviour with an intercept of unity. In the case of lithium, it is not linear but the intercept is unity. The results show the effect of water absorption is very pronounced in the case of lithium and shows to some extent in the case of cesium. The reaction kinetics is affected.

In the heterogenous rate constant (K_s) data cesium showed a reasonable consistency (order of 10^{-2}) with a slight decrease with increasing frequency and a similar behaviour was observed for lithium[12]. In water study here the same trend is seen but the variation is more marked in the case of lithium (See Table 4). The values are considerably higher than that of metal alone. In the water study lithium gets most affected and cesium the least. From the solvation point of view, lithium is highly solvated[17] while cesium is less solvated, from charge density considerations.

The possible interpretations can be : 1. Experimental error; 2. Water desorption, adsorption process at the electrode interface; 3. Inappropriate model, (i.e.) the effect is real and the quasi-reversible model is not appropriate.

Water adsorption-desorption at —2.37 volts is of significance as it is in the immediate vicinity of the potential of interest. In both cases of lithium and cesium there is a marked deviation in K_s values. Smith[15] has shown that adsorption process at the electrode can lead to intercepts less than unity. Payne[4] has reported from double layer capacity studies in DMSO that there is no adsorption of cations at the electrode interface while there is adsorption of ClO_4^- ion at the interface near zero potential. Cogley and Butler[18] have reported there is no adsorption of Li^+ at the electrode interface at low concentrations. Imai and Delahay[19] have reported no specific adsorption of Li^+,Rb^+. Therefore adsorption process of cations at the electrode interface can be ruled out from the above results.

If we can ascribe the kinetic behaviour to an inappropriate model, i e , the model assumed from the data trends is incorrect (also assuming the experimental results are essentially correct and not influenced by some arti fact such as the desorption of water) the most obvious difference between two metal ions is the degree of solvation. One may be actually be seeing what one sets out to find, a kinetic process heavily influenced by the solvent. If this is the case, the most reasonable assumption is that some chemical step is involved. That chemical reaction interferes with the reaction kinetics of metal ions, with lithium being the most affected.

The water adsorption-desorption occurs at —2.37 volts and as such its effect on the reaction kinetics may or may not prove important. A study of the kinetics of the reaction with different concentrations of electroactive species may clarify this

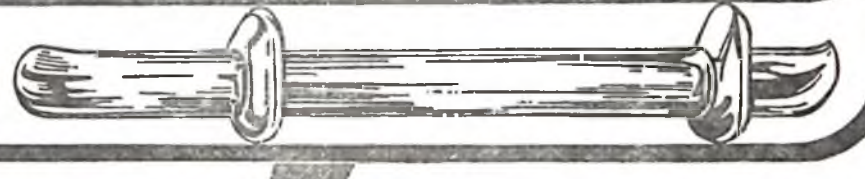
point. The necessity of perfectly dry atmosphere in these area of research is of prime importance as shown. Further work on lithium and other alkali metals in a dry, vacuum conditions, eliminating the last traces of water will be helpful. Similar work on sulfolane, a dipolar aprotic solvent, may be of interest. The error in cot β data is estimated to be $\pm 12.5\%$ by input of simulated errors of $\pm 5\%$ in the input data. To that extent there is uncertainty but the effect is real.

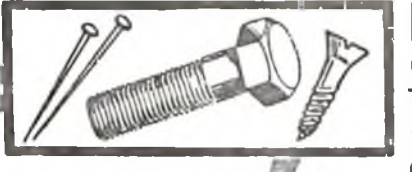
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