DIFFERENTIAL CAPACITY CURVES FOR MERCURY IN 0·1M-LiCl–ACETONE–WATER SYSTEM

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Differential capacity and potential of zero charge were measured on a dropping mercury electrode in 0·1M-LiCl in acetone–water mixtures. On the basis of a generalized model of the electrode double layer, constants characterizing the adsorption of acetone on mercury were calculated. From these values, theoretical electrocapillary and capacity curves for solutions containing up to 50 vol. % acetone were obtained.

In the previous work[1], we studied the electrocapillary curves for mercury in 0·1M--LiCl–acetone–water system. Since from these curves the parameters characterizing adsorption of acetone cannot be determined with sufficient accuracy, we decided to perform capacity measurements. The mentioned system was already previously studied[2], but the capacity measurements were not used to obtain data characterizing adsorption of acetone, and since the results were presented only graphically we could not use them in theoretical calculations.

RESULTS AND DISCUSSION

The differential capacity curves (Fig. 1a) in the acetone–water mixtures show adsorption–desorption peaks whose height increases with increasing concentration of acetone up to 95 vol.%. At still higher concentrations of acetone (Fig. 1b) the cathodic peaks become smaller and are shifted to more anodic potentials. Instead of anodic peaks, we observed in the medium of concentrated acetone only a sharp increase of capacity. From the behaviour of cathodic peaks in this medium it can be concluded that acetone ceases to function as a surface active substance with respect to water. This is substantiated by electrocapillary measurements[1], namely by the course of the dependence of the relative surface excess on potential (Fig. 2). The relative surface excesses decrease at higher concentrations of acetone than 95 vol. % to negative values.

Charge curves were calculated from the differential capacity curves by numerical integration (Fig. 3). For equations see Appendix. The integration was performed from the zero charge potential, E_0, of mercury in 0·1M-LiCl.

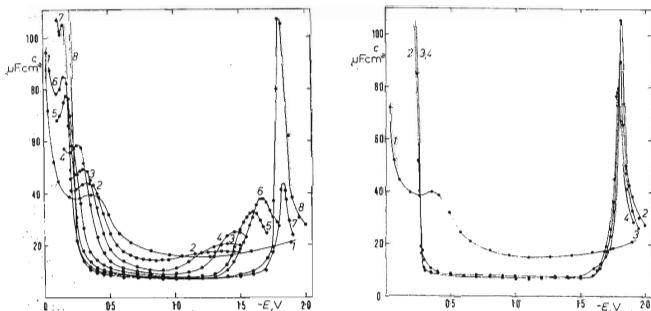| vol. % acetone	0	1	2	5	10	25	50	75	90	95	98	99	99·5
$-E_0$, mV	519	501	479	455	395	344	301	290	282	271	322	352	374

FIG. 1

Dependence of Differential Capacity on Potential for 0·1M-LiCl in Water–Acetone Mixtures
    a) Vol. % acetone: 1 0; 2 2; 3 5; 4 10; 5 25; 6 50; 7 75; 8 95.
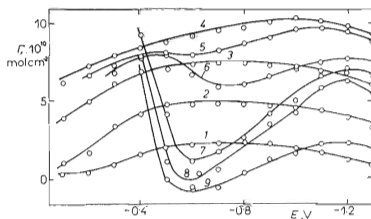   b) Vol. % acetone: 1 0; 2 85; 3 98; 4 99·5.

FIG. 2

Dependence of Relative Surface Excess Γ_r on Potential
    Experimental data in ref.[1]. 0·1M-LiCl; vol. % acetone: 1 3·7; 2 11; 3 20; 4 40; 5 60; 6 80; 7 90; 8 95; 9 98.

The charge curves have a normal course, their intersection with the charge curve for a solution without acetone remains approximately constant up to 75 vol. % acetone and is shifted somewhat to more anodic potentials at higher concentrations. The theoretical calculation of the capacity curves is based on a generalized model of the electrode double layer[3]. To this purpose, we first calculated seven constants characterizing the adsorption of acetone on mercury. Since they cannot be calculated directly from the generalized model we used as a first approximation the model of two parallel capacitors according to Frumkin as in ref.[4]. First we determined the coefficient of mutual interaction of adsorbed acetone molecules, a, for potentials at which the maximum adsorption occurs and for potentials corresponding to such concentrations of acetone at which the coverage in the peak is about 0·5. In addition, the capacity, C', for unit coverage with acetone was determined. The equations for the calculation are given in Appendix. The obtained dependence of the coefficient a on potential is moderately concave (Fig. 4). It was further assumed that the dependence of the interaction coefficient a does not vary when the Frumkin model is replaced by the generalized one. From this dependence the constants n and k characterizing its form were calculated. The constants E_N and B_0 were obtained as shown in Appendix. They were corrected together with the constant A to obtain values corresponding to the generalized model of the double layer as shown in Appendix.

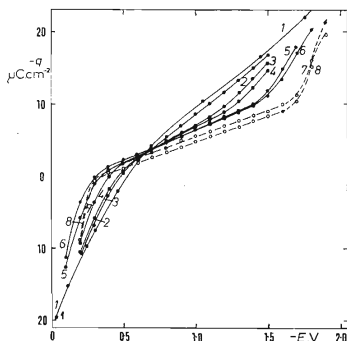Thus, we obtained all seven constants from which the theoretical electrocapillary

Fig. 3

Dependence of Surface Charge Density on Potential for 0·1M-LiCl in Water–Acetone Mixtures Vol. % acetone: *1* 0; *2* 2; *3* 5; *4* 10; *5* 25; *6* 50; *7* 98; *8* 99·5.

and capacity curves were calculated with the use of the values of the capacity, charge and surface tension for solutions without acetone[5] as shown in Appendix. It is seen from Fig. 5 that the agreement between theoretical and experimental curves is good, whereby the obtained adsorption parameters are confirmed.

Our calculations involved the molar activity of acetone[6]. The condition of constant chemical potential of LiCl was not fulfilled since the activity coefficients for the mixed media used are not known. Besides that, at concentrations of acetone higher than 95 vol. %, the association of Li^+ and Cl^- ions plays a significant role[7], which probably influences the course of the capacity curves and causes inconstancy of the diffusion potentials. We therefore calculated the theoretical electrocapillary and capacity curves only for solutions of up to 50 vol. % acetone. The value of the capacity at full coverage, C', is not quite accurate since it was obtained by extrapolation of the curved dependence. The influence of this inaccuracy on the theoretical curves is, however, small. The interaction coefficient, a, for the positively charged interface is influenced by simultaneous adsorption of Cl^- ions. Hence, it will be somewhat different if another, e.g. nonadsorptive electrolyte is used. The constant A is little dependent on the acetone concentration. Since it corresponds to the maximum surface concentration of acetone ($A = RT\Gamma_m$), we took in further calculations its maximum value obtained for acetone concentrations $50 - 75$ vol. %.

It follows from the constants, especially B_0, characterizing adsorption of acetone that acetone is less surface active than diethylketone, propyl alcohol and propionic acid:

Substance	a_0	n	k	C'	E_N	A	B_0	ref.
$(CH_3)_2CO$	0·68	0·93	0·70	6·6	0·49	1·59	0·92	—
C_2H_5COOH	0·70	0·91	0·21	6·5	0·24	1·25	2·86	3
$C_2H_5CH_2OH$	1·11	1·0	1·16	4·85	0·33	1·40	3·00	9
$(C_2H_5)_2CO$	1·61	1·0	1·02	5·75	0·51	0·99	12·25	10

The dependence of a on E is curved similarly as with propionic acid (it is characterized
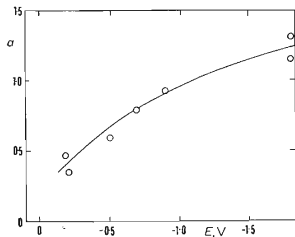

FIG. 4

Dependence of Interaction Constant a on Potential

by the values of n and k). With respect to the small value of a_0 (ref.[3]) and small differences in adsorption parameters between water and acetone, the system under study is fitted rather by the single-layer model[3], from which the dependences of D/δ and μ/δ on coverage Θ were calculated according to the equations in Appendix. These dependences are shown in Fig. 6, from which the deviations of the system under study from the Frumkin model are obvious.
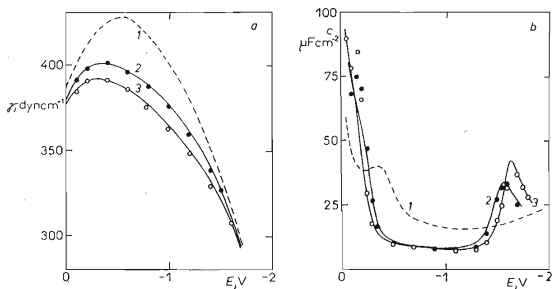

FIG. 5

Comparison of Theoretical and Experimental Electrocapillary (*a*) and Capacity (*b*) Curves
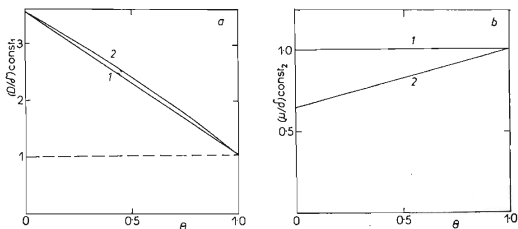 Vol. % acetone: *1* 0; *2* 25; *3* 50.

FIG. 6

Dependence of D/δ (*a*) and μ/δ (*b*) on Relative Adsorption Θ
  1 Frumkin model ($n = k = 1$); *2* system under study ($n = 0.93$, $k = 0.70$). Equations used are in Appendix.

EXPERIMENTAL

The basic circuit and the apparatus used for the measurement of the differential capacity and zero charge potential are shown in Figs 7 and 8.

The differential capacity was measured on a dropping mercury electrode located in the center of a cylindrical platinum counter electrode of a large surface area. The tip of the glass capillary was drawn out so as to prevent screening of the drop with the glass. The measurement was carried out with a commercial impedance bridge (Tesla BM 400) enabling to measure capacity in the range 10 pF—10 μF with an accuracy of $\pm 0.1\%$. This bridge was adapted for our purpose; its operating voltage of a frequency of 800 c.p.s. was lowered by a transformer to 5 mV and a resistance box (R1 — to terminals c_x) was connected in parallel to the capacity standard C2 in one branch of the bridge. When the loss angle indicator was set to zero, the resistance and capacity components of the electrode system in the other branch of the bridge (connected to terminals c_N) could be compensated.

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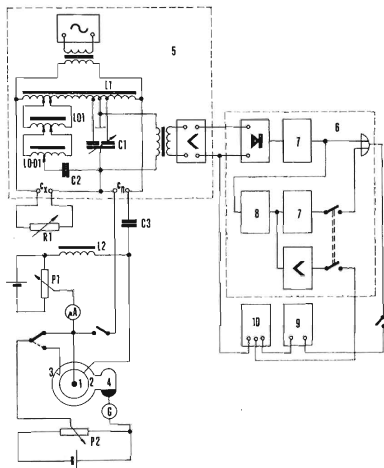
Basic Circuit for Measurement of Differential Capacity and Zero Charge Potential

1 Dropping mercury electrode; 2 Pt electrode of large surface area; 3 streaming mercury electrode; 4 normal calomel electrode; 5 impedance bridge Tesla BM 400; 6 timer; 7 Schmidt circuit; 8 monostable flip-flop circuit; 9 electronic counter Tesla BM 363; 10 oscilloscope with a slow time base Tesla OPD 280 M.

The electrodes were polarized with a d.c. voltage taken from an LP 55 type polarograph (P1 in Fig. 7). A large capacitor of 200 μF (C3) was connected in series with the measured cell capacity to prevent flow of direct current through the bridge. A choke L2 in the d.c. circuit prevented flow of alternating current through the d.c. source. The error due to the additional capacity lies within the range of experimental errors. All a.c. leads were screened, their screening was connected to one point and grounded. The electrode system was not grounded but screened with a metal sheet. The potential of the dropping mercury electrode with respect to a calomel electrode filled with 1M-LiCl was measured with a QTK compensator (P2; Metra, Blansko). During the capacity measurement, the circuit for measurement of the d.c. potential was switched off. We assumed that the diffusion potential in the stopcock leading to the calomel electrode was constant and reproducible. The time between breaking off of the drop and equilibrating the bridge was measured by means of a timer in connection with an oscilloscope with a slow time base and an electronic counter. The accuracy of the time measurement on the cathode ray tube was ± 0.02 s. By means of the timer it was possible to choose a time that was exactly by 1 s shorter than the time between breaking off of the drop and equilibrating the bridge. A simple streaming electrode was dipped into the solution under study and its potential (measured against the same calomel electrode as the potential of the dropping electrode) was considered equal to the zero charge potential.

The solution was deaerated by bubbling for an hour with nitrogen which was freed from oxygen by the catalytic action of copper (I), and dried by its passing through a column of P_2O_5. Wash bottles with the same solution as the measured one were placed before the reaction vessel to prevent any changes in the composition of the solution under examination. The nitrogen outlet was closed by a water siphon. The vessel was thermostated at 20·0°C. Lithium chloride of reagent
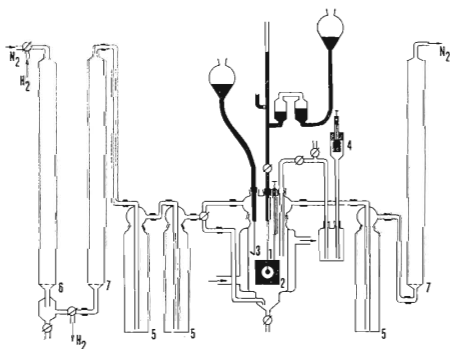

FIG. 8

Apparatus for Measurement of Differential Capacity and Zero Charge Potential

1 Dropping mercury electrode; 2 Pt electrode of large surface area; 3 streaming mercury electrode; 4 normal calomel electrode; 5 wash bottles with the same solution as the measured one; 6 catalytic column for removal of oxygen; 7 columns with P_2O_5.

grade was heated for 5 h in a platinum dish at 600°C, recrystallized twice from conductivity water and dried at 120°C to constant weight. It was stored in an exsiccator over P_2O_5. Acetone of reagent grade was dried by a molecular sieve and rectified twice on a column apparatus of 20 theoretical plates. Water was tripple distilled, for the third time in a quarz glass apparatus. The solutions were always freshly prepared. Mercury was distilled twice.

The correctness and exactness of the capacity measurements were checked on a model of a capacity and resistance in series as well as in solutions of 0·1M-LiCl and KCl, where the capacity values are known[5]. The measured values of the parallel resistance and capacity were recalculated for the case of a resistance and capacity in series. The average error in the determination of the differential capacity was $\pm 0.5\%$. The value of the zero charge potential in 0·1M-LiCl (ref.[5]) was also checked.

APPENDIX

Equations Used

1) Numerical integration according to Simpson's rule beginning from the potential of zero charge.

2)
$$\Theta = (C_0 - C)/(C_0 - C'), \qquad (IV.11)*$$

C' is obtained by extrapolation of the dependence of $1/C$ on $1/c$ to $c \to \infty$.

3) The value of E_m is obtained as the intersection of the charge curve without acetone with that in the presence of 95% acetone.

4) From the Frumkin equation

$$y = c/c_{\Theta = 0.5} = (\Theta/(1 - \Theta)) \exp(a(1 - 2\Theta)) \qquad (IV.13)$$

the value of a was calculated as

$$e^a = (dy/d\Theta)_{\Theta = 0}. \qquad (IV.15a)$$

5) The value of A was calculated from experimental values of surface tension for solutions of $50-75$ vol.% acetone:

$$A = (\gamma_0 - \gamma)/[\ln(1 - \Theta) + a\Theta^2]. \qquad (IV.48)$$

6) The value of Θ_{max} was calculated from the equation

$$\frac{(K^{max} + \Theta_{max})^2 (1 - 2\Theta_{max})}{\Theta_{max}^2 (1 - \Theta_{max})^2} = 6\alpha[E_{max} - E_m]^2, \qquad (IV.30)$$

where $K_{max} = (C_{max} - C_0)/(C_0 - C')$, $\alpha = (C_0 - C')/2A$.

Use was made of the capacity curves for solutions of $95-98$ vol.% acetone (for cathodic peaks) and 75 vol.% acetone (anodic peaks).

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* Reference is made to Eq. (IV.11) in ref.[8]; analogously below.

Calculation of Constants n and k

The value of n was calculated from Eq. (22) in ref.[3]:

$$\frac{8n(n-1)}{(n+1)^3} = \frac{E_1(a_2 - a_0) - E_2(a_1 - a_0)}{E_1\, f(E_2) - E_2\, f(E_1)},$$

$$E_1 < 0, \quad E_2 > 0, \quad f(E) = A^{-1}[\Delta\gamma_0 + C'E(E_N - \tfrac{1}{2}E)].$$

The value of k was calculated from Eq. (21) in ref.[3]:

$$a = a_0 + [8n/A(n+1)^3]\,[(n-1)\,(\Delta\gamma_0 - \tfrac{1}{2}C'E^2) + (kn-1)\,C'E_N E].$$

Calculation of Constants E_N and B_0

The value of E_N was obtained by extrapolation of the charge curve for 95 vol. % acetone to $q = 0$. Further we have

$$B_0 = (e^{-a_0}/c_{\Theta=0.5}) \exp\left[-\frac{(C'E_N)^2}{2A(K_0 - C')}\right], \qquad (IV.\,57)$$

where $K_0 = q_0/E_m$.

Correction of A, E_N and B_0 to Obtain Values Corresponding to the Generalized Model

$$A = A^* \frac{4n}{(n+1)^2}; \quad E_N = E_N^* \frac{4}{4 - (n-1)\,(k-1)}; \quad B_0 = B_0^*/n.$$

The superscript * denotes values calculated from the Frumkin theory of two parallel capacitors. The above equations are from ref.[3].

Calculation of Capacity Curves

First the potentials E_1 and E_2 were calculated for given Θ at a given concentration of acetone from Eq. (10a) in ref.[3]:

$$(A/n)\,(1 + n\Theta - \Theta)^2\,[\ln(B_0 c) - \ln(\Theta/(1-\Theta)) + 2a_0\Theta] +$$
$$+ C'E_N[(n-1)\,(k-1)\,\Theta^2 + 2(k-1)\,\Theta - k]\,E = \Delta\gamma_0 - \tfrac{1}{2}C'E^2.$$

To these values, the values of γ_0, q_0 and C_0 were assigned. The capacity curve was calculated from Eq. (14) in ref.[3]:

$$C = \frac{1}{1 + (n-1)\,\Theta}\left[C_0(1 - \Theta) + nC'\Theta + \frac{\alpha}{\beta}\right],$$

$$\alpha = n^2\Theta(1 - \Theta)\,[q_0 - C'E + C'E_N(k - (n-1)\,(k-1)\,\Theta^2 - 2(k-1)\,\Theta]^2,$$
$$\beta = A[1 - 2a_0\Theta(1 - \Theta)]\,(1 + n\Theta - \Theta)^3 - 2n\Theta(1 - \Theta)\,[(n-1)\,(\Delta\gamma_0 - \tfrac{1}{2}C'E^2) +$$
$$+ (kn-1)\,C'E_N E].$$

Calculation of the electrocapillary curve from Eq. (13), ref.[4]:

$$\gamma = \gamma_0 \div A\left[\ln(1-\Theta) + a_0\Theta^2 + \right.$$

$$\left. + \frac{(n-1)(\Delta\gamma_0 - C'E^2/2) + (kn-1)C'E_\mathrm{N}E}{1 + n\Theta - \Theta^2} n\Theta^2\right].$$

The dependence of D/δ on coverage Θ calculated from Eq. (30), ref.[3]:

$$4\pi C'D/\delta = [p - (p-n)\Theta]/[1 + (n-1)\Theta]; \quad p = \overline{C}_0/C'.$$

The dependence of μ/δ on Θ from Eq. (31), ref.[3]:

$$(\mu/\delta)\,\Gamma_\mathrm{m}N_\mathrm{A}/C'E_\mathrm{N} = [kn - (k-1)n\Theta]/[1 + (n-1)\Theta].$$

LIST OF SYMBOLS

γ	surface tension (dyn/cm)
C	differential capacity (F/cm^2)
q	charge of electrode (C/cm^2)
γ_0	surface tension of solution without acetone (dyn/cm)
$\Delta\gamma_0$	decrease of γ_0 due to electrolyte (dyn/cm)
q_0	charge of electrode in solution without acetone (C/cm^2)
C_0	differential capacity of solution without acetone (F/cm^2)
$\overline{C}_0$	integral capacity of solution without acetone (F/cm^2)
E	electrode potential with respect to zero charge potential in solution without acetone (V)
E_0	zero charge potential in solution without acetone with respect to N.C.E. in 1M-LiCl (V)
$E_{\text{(N.C.E.)}}$	potential with respect to N.C.E. in 1M-LiCl
E_N	difference of zero charge potentials at zero and total coverages of electrode with acetone (V)
E_m	potential of maximum adsorption (V)
E_max	potential of the capacity peak (V)
C'	differential capacity at full coverage of electrode with acetone (F/cm^2)
Θ	coverage
c	concentration of acetone (mol/l)
y	relative concentration of acetone, $c/c_{\Theta=0.5}$
a	interaction constant of adsorbed molecules
a_0	value of a at potential E_0
B_0	equilibrium adsorption constant at potential E_0 (l/mol)
n, k	constants characterizing the dependence of a on E
Γ_m	maximum surface concentration of acetone (mol/cm^2)
A	constant equal to $RT\Gamma_\mathrm{m}$ (J/cm^2)
Γ_r	relative surface excess of acetone (mol/cm^2)
Γ_a	surface concentration of acetone (mol/cm^2)
Γ_v	surface concentration of water (mol/cm^2)
$x_\mathrm{a}, x_\mathrm{v}$	molar fractions of acetone and water

D	dielectric constant (F/cm)
δ	thickness of double layer (cm)
μ	component of dipole moment perpendicular to electrode surface (C cm)
N_A	Avogadro number

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