

## ADSORPTION OF METHYL ETHYL KETONE ON MERCURY

O. FISCHER, S. STANDARA

*Department of Theoretical and Physical Chemistry,  
Purkyně University, 611 37 Brno*

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Adsorption parameters of methyl ethyl ketone on mercury were calculated on the basis of a generalized model of the electrode double layer from electrocapillary data measured previously. The correctness of these parameters is demonstrated by calculated theoretical electrocapillary curves which are in accord with the experimental ones. The results agree with values of the adsorption parameters obtained by differential capacity measurements.

Partridge and coworkers<sup>1</sup> measured electrocapillary curves of mercury in aqueous 0.1M-MgSO<sub>4</sub> with added methyl ethyl ketone (MEK) up to a concentration of 1M. From the dependence of the surface tension on concentration of MEK they calculated the relative surface excess of MEK.

We used in our work their data (read from their magnified diagrams) to calculate the adsorption parameters of MEK by the method of Damaskin, Frumkin and Čižov<sup>2</sup>, and we compared our results with the adsorption constants of MEK obtained meanwhile<sup>3</sup> from measurements of the differential capacity of mercury in 1N-Na<sub>2</sub>SO<sub>4</sub>. Numerical differentiation of the electrocapillary curves gave charge curves (Fig. 1), from which the potential of maximum adsorption,  $E_m = -0.61$  V vs NCE, was determined as the intersection of the charge curves without and with 1M-MEK. The difference of the zero charge potentials at unit and zero surface coverages,  $E_N$ , was determined by extrapolation of the zero charge potentials from Fig. 1 to zero reciprocal concentration of MEK (Table I). The differential capacity  $C'$  corresponding to full coverage of the electrode was calculated from the slope of the tangent to the charge curve for 1M-MEK in the point where this slope is lowest<sup>4</sup>. In calculating the coverage  $\theta = \Gamma/\Gamma_m$ , the surface concentrations were set equal to the relative surface excesses from ref.<sup>1</sup> and  $\Gamma_m$  to the maximum relative surface excess. The latter is constant at potentials near to the maximum adsorption potential at MEK concentrations down to 0.4M. The difference between the surface concentration and relative surface excess of MEK is small at low concentrations of MEK and largest at 1M-MEK. It is therefore possible that the value of  $\Gamma_m$  is somewhat lower than the surface concentration of MEK at maximum coverage. The value of  $A = RT\Gamma_m$  was calculated from the maximum surface concentration.

The constant of mutual interaction,  $a$ , of adsorbed MEK molecules (Fig. 2) was calculated from the experimental adsorption isotherms at different potentials,  $E$ , by the method of Damaskin<sup>5</sup> and coworkers using the Frumkin model of adsorption. The following equation was used to this purpose:  $c/c_{\theta=0.5} = [\theta/(1-\theta)] \exp \cdot [a(1-2\theta)]$ . In contrast to the results obtained from the differential capacity curves<sup>3</sup>, the  $a$ - $E$  dependence is linear with a small negative slope. We assume that the results from the electrocapillary curves are more correct than those from the capacity curves, analogously to similar dependences for fatty acids<sup>6</sup>. For propionic acid, the dependence of  $a$  on  $E$  is similar as with acetone<sup>7</sup>, for MEK it can be expected to be linear as with butyric acid. The value of the constant  $n$  (which together with  $k$  characterizes the  $a$ - $E$  dependence) is equal to one,  $k$  is close to one ( $k = 1 + A\beta/C'E_N$  according to ref.<sup>2</sup>, where  $\beta$  is the slope of the  $a$ - $E$  dependence). The deviations between the constants calculated from the Frumkin and generalized models are small. The values of  $A$ ,  $E_N$  and the equilibrium adsorption constant  $B_0$  were corrected for the generalized model with the use of the equations in ref.<sup>2</sup>:

$$B_0 = (e^{-a_0}/c_{\theta=0.5}) \exp [-(C'E_N)^2/2A(q_0/E_m - C')], \quad (\text{see ref.}^8),$$

where  $q_0$  denotes charge density in solutions without MEK at the potential of maximum adsorption,  $a_0$  value of  $a$  at the zero charge potential in solution without MEK.

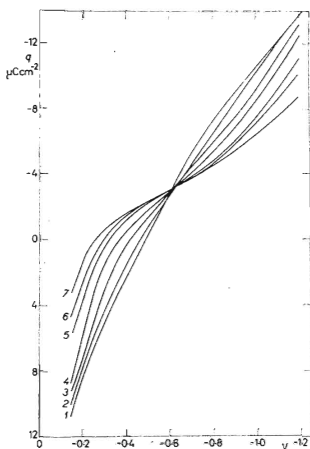


FIG. 1

Dependence of Surface Charge Density,  $q$ , on Potential

Solution of 0.1M-MgSO<sub>4</sub> with added methyl ethyl ketone of concentration: 1 0; 2 0.05M; 3 0.1M; 4 0.2M; 5 0.4M; 6 0.65M; 7 1.0M. According to Partridge and coworkers<sup>1</sup>.

FIG. 2  
Dependence of Interaction Constant,  $a$ ,  
on Potential  
1 Acetone<sup>7</sup>, 2 methyl ethyl ketone, 3  
diethyl ketone<sup>9</sup>.

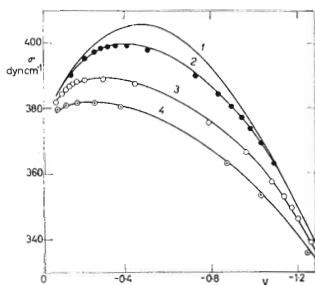
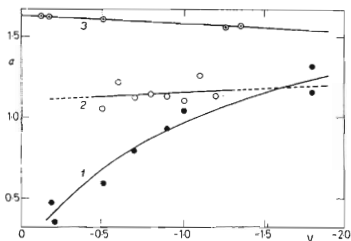


FIG. 3  
Comparison of Theoretical and Experimental  
Electrocapillary Curves for MEK  
Curves according to ref.<sup>1</sup>, points calculated  
according to ref.<sup>2</sup> Concentration of MEK:  
1 0; 2 0.1M; 3 0.4M; 4 1.0M.

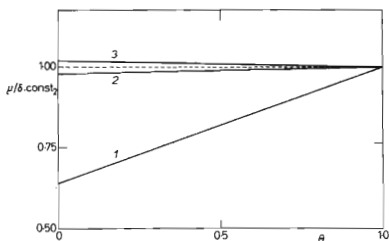


FIG. 4  
Dependence of  $\mu/\delta$  on Coverage  $\theta$   
1 Acetone<sup>7</sup>, 2 methyl ethyl ketone, 3 diethyl ketone<sup>9</sup>. Calculation according to ref.<sup>2</sup>, dashed  
curve corresponds to the Frumkin model ( $n = k = 1$ ).

TABLE I  
Values of Adsorption Parameters for the Studied Ketones

Compound	$t$ °C	$a_0$	$n$	$k$	$C'$ $\mu\text{F}/\text{cm}^2$	$E_N$ V	$A$ $\mu\text{J}/\text{cm}^2$	$\Gamma_m \cdot 10^{10}$ $\text{mol}/\text{cm}^2$	$B_0$ l/mol	Ref.
Acetone	25	0.68	0.93	0.70	6.60	0.49	1.59	6.41	0.92	7
MEK	15	1.00	1.062	1.25	6.22	0.48	1.1	4.62	6.62	3
	35	1.02	1.067	1.51	6.40	0.30	1.2	4.64	4.56	3
	20	1.12	1.00	0.98	6.50	0.36	0.92	3.71	6.22	—
DEK	25	1.61	1.00	1.02	5.75	0.51	0.99	3.99	12.25	9

See also ref.<sup>10</sup> which appeared after the present paper had been submitted for publication.

The constants characterizing adsorption of MEK (Table I) were used to calculate the theoretical electrocapillary curves by the known method<sup>2</sup> (Fig. 3). The agreement between theoretical and experimental electrocapillary curves is very good. The adsorption parameters calculated from the electrocapillary curves are close to those from the capacity curves except for the constant  $k$ . It should be considered that the constants  $C'$  and  $E_N$  obtained from the charge curves are in this case subject to a larger error since the charge curves were obtained by numerical differentiation, which is less accurate than integration. The disagreement between the values of  $k$  remains unclear; it cannot be attributed to the difference in the base electrolyte (0.1M-MgSO<sub>4</sub> and 1N-Na<sub>2</sub>SO<sub>4</sub>).

Similarly as with alcohols and fatty acids, with increasing length of the carbon atoms chain the interaction constant  $a$  and adsorption equilibrium constant  $B_0$  increase and the values of  $C'$ ,  $E_N$  and  $A$  decrease. The decrease of  $A$  is related to enlargement of the surface area available per one adsorbed molecule. It is seen from the dependence<sup>2</sup> of the ratio of  $\mu/\delta$  on coverage  $\theta$  ( $\mu$  denotes dipole moment component perpendicular to the electrode surface,  $\delta$  thickness of the double layer) for acetone<sup>7</sup>, MEK and diethyl ketone<sup>9</sup> (Fig. 4) that the properties of MEK are intermediate between those of the other two compounds. Whereas with acetone the ratio of  $\mu/\delta$  rises, with MEK it is almost constant and with diethyl ketone it diminishes indicating probably that the double layer thickness increases more rapidly than the dipole moment component.

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