
**ADSORPTION AT ELECTRODES:
ISOTHERM PARAMETERS FOR ALKYL ALCOHOLS
IN VARIOUS ELECTROLYTES**

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Frumkin-isotherm parameters are reported for 1-butanol, 1-pentanol, and cyclohexanol, in solutions containing 0.05, 0.1, or 1M-concentrations of KF, KCl, NaClO₄, or Na₂SO₄, over a range of potentials. The nature and concentration of the electrolyte, as well as the potential, influence the magnitudes of the interaction parameter and of the adsorption coefficient. These effects are in qualitative accord with known facts about the adsorbabilities of the alcohols and electrolytes. The Frumkin isotherm describes the data well, except in the presence of fairly strongly specifically adsorbed anions.

The adsorption of uncharged surfactants (*e.g.*, alcohols) at electrodes in the presence of electrolytes is a process that involves competition for the available surface between the alcohol and the ions as well as the solvent. Yet, work to the present time has been concerned almost entirely with the presumed adsorptive properties of the surfactant, ignoring possible effects of the solvent and the electrolyte. In this article, the influence of various electrolytes (KF, KCl, NaClO₄, Na₂SO₄) on the adsorptive behavior of several alcohols (1-butanol, 1-pentanol, cyclohexanol) is examined.

Results were obtained by measurement of the capacity of the double layer under a.c. conditions. Systematic measurements are reported for the potential region in which adsorption of the alcohols prevails.

EXPERIMENTAL

Double-layer capacities were measured by a non-automatic technique described previously¹, with the modification that phase-angle measurements (between cell voltage and current) were

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made by means of an Ad-Yu Phase-Vector Voltmeter Type 248 A. A dropping mercury electrode was used; measurements were made at the end of the naturally falling drop, and the results recalculated to take into account the variation of the area of the drop under changing conditions (potential, alcohol concentration).

In the region of prevailing adsorption, measured capacities were independent of the frequency of the applied signal. This indicated that adsorption equilibrium was established under our conditions. Further evidence in this direction came from the fact that measured surface coverages were independent of drop time of the electrode down to the shortest drop-times used. As a result of these findings, the majority of subsequent experiments were performed at a single frequency, *viz.* 115 Hz.

All chemicals used in this study were analytical grade, obtained from commercial sources and used without further purification. The purity of the alcohols was ascertained by gas chromatography.

Surface coverages from double-layer-capacity depressions were measured at potentials of -0.45 , -0.50 , -0.55 , -0.60 , -0.65 and -0.70 V *vs.* s.c.e., *i.e.*, within approximately 0.150 V of the point of zero charge on both anodic and cathodic sides. All experiments were carried out at $24 \pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

Isotherm Assignment

The fraction, θ , of the electrode covered by alcohol was calculated from the often used approximation that

$$C_{d1} = (1 - \theta) C_0 + \theta C_s, \quad (1)$$

where C_{d1} is the measured capacity and C_0 , C_s are the capacities for $\theta = 0$ and $\theta = 1$ respectively.

The variation of θ with alcohol concentration, C , at a fixed electrode potential gave, in almost all systems, an excellent fit to the Frumkin isotherm²

$$BC = [\theta/(1 - \theta)] \exp(-2a\theta), \quad (2)$$

where B is an adsorption coefficient and a an interaction parameter (attraction between adsorbed molecules).

Isotherms for the three alcohols used (1-butanol, 1-pentanol, cyclohexanol) were obtained in solutions containing KF, KCl, NaClO₄, or Na₂SO₄; in each system, salt concentrations of 0.05, 0.1, and 1M were used. For each system, measurements were made at 50 mV intervals in the potential range -0.45 to -0.70 V *vs.* s.c.e. Amongst the 216 isotherms obtained under these varying conditions, the fit to equation (2) was excellent in most cases: average deviation of individual points from the curve no greater than 2–5% (for $0.05 < \theta < 0.90$). In approximately 30 cases, the fit was not good. These cases were systems which showed one or more of the

following features: potential far from the point of zero charge (*i.e.*, at -0.45 or -0.70 V vs s.c.e.); concentrated electrolyte (*i.e.*, 1M rather than 0.05 or 0.1M); specific adsorption of electrolyte (*i.e.*, KCl rather than the other electrolytes used); apparent value of the interaction constant, a , comparatively large (*i.e.*, approaching or greater than 2). Fig. 1a shows the fit of experimental points to the calculated isotherm for a system typical of the c. 180 showing a "good fit" (average deviation of experimental points, 3%); Fig. 1b shows one of the cases of a bad fit, illustrative of c. 10 cases where a approaches the value of 2.

The "best fit" values of B and a were obtained by computer calculations of several types: simultaneous solution of all possible pairs of equations from a given set of data; conventional least-squares fit; progressive variation of a and B to minimize the average normal distance from the experimental points to the calculated curve. For "bad" fits, computer-based plots of possible curves were compared with the data. In the large majority of cases, all methods yielded essentially identical values for B and a , even though the relative weighting given by the calculations to points for low and high θ were not the same in the different calculations. We concluded that the fit of points to the isotherm is no better, in general, in any one given range of θ values than in any other range.

Another adsorption isotherm, intended to take into account competitive adsorption between solute and solvent, is the Flory-Huggins isotherm³

$$BC = [\theta/r(1 - \theta)^r] \exp(-2a\theta). \quad (3)$$

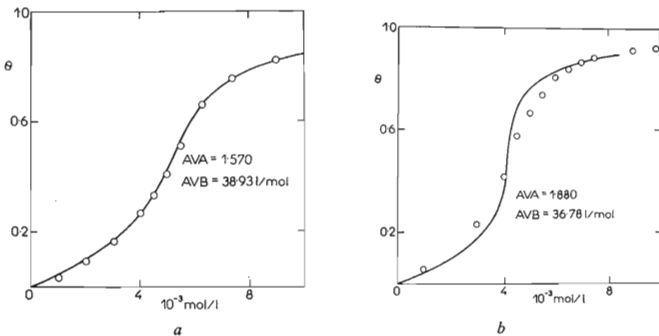


FIG. 1

Adsorption of Cyclohexanol *a* in Fluoride 0.1M-KF, -700 mV; *b* in Chloride 0.1M-KCl, -500 mV

Here, r is the number of solvent molecules (or "clusters") displaced by each molecule of adsorbed solute. We attempted to fit our experimental data to equation (3), using a least-squares computer calculation. In about 25% of the systems, equation (3) gave a better fit than equation (2); in the other cases, the fit was not sensibly different (and, as one would then expect, r was close to unity).

Since equation (3) contains 3 adjustable parameters, and equation (2) only 2, one would expect a better fit with equation (3), at least in those cases where equation (2) appears to be an unsatisfactory description of the data. However, use of equation (3) rather than equation (2) implies that the additional parameter (r) has some physical significance. We could find no evidence for this in the values of r obtained; in the majority of systems, r was close ($\pm 20\%$) to unity. The values showed no obvious trends in terms of potential, electrolyte, or alcohol (Table I). Moreover, the average

TABLE I
Values of Parameter r of Equation (3)

$E(\text{s.c.e.})$ V	KF			Na_2SO_4			NaClO_4			KCl		
	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M
1-Butanol												
-0.45	1.24	1.05	0.95	0.89	0.84	0.85	1.08	1.19	2.20	0.85	0.73	0.68
-0.50	1.05	1.06	0.88	0.99	1.03	0.89	0.84	0.83	1.31	0.75	0.62	0.97
-0.55	1.12	1.13	0.91	0.97	1.11	0.88	0.86	0.86	1.07	0.85	0.73	0.86
-0.60	1.03	1.10	0.89	1.27	0.99	0.89	0.97	0.94	1.01	0.94	0.71	0.87
-0.65	1.11	1.12	1.00	1.07	0.94	0.90	1.07	0.90	0.99	1.00	1.05	0.83
-0.70	1.15	0.98	1.15	1.36	0.79	1.09	0.99	0.79	0.98	1.10	0.95	0.56
1-Pentanol												
-0.45	1.35	1.15	1.01	1.26	1.33	1.17	1.59	1.39	1.16	0.97	2.72	0.67
-0.50	1.22	0.89	0.91	1.10	1.31	1.00	0.97	1.04	1.02	0.88	0.85	0.93
-0.55	1.24	0.99	0.93	1.17	1.44	1.31	0.97	0.85	0.94	0.97	0.92	0.99
-0.60	1.17	0.92	1.13	1.17	1.61	1.80	0.88	0.91	0.90	1.08	0.95	0.90
-0.65	1.22	1.01	1.09	1.21	1.78	2.69	1.02	0.98	0.89	1.13	1.02	0.86
-0.70	1.35	0.91	1.49	1.18	0.48	8.41	0.71	1.14	0.95	1.30	0.92	0.78
Cyclohexanol												
-0.45	1.00	1.06	0.84	0.89	0.80	0.88	1.06	1.18	1.53	0.74	0.68	0.61
-0.50	1.00	0.99	0.78	0.90	0.82	0.84	0.88	0.92	1.27	0.50	0.63	0.64
-0.55	0.87	0.88	0.77	0.84	0.83	0.98	0.78	0.83	1.10	0.73	0.58	0.72
-0.60	0.76	0.87	0.91	0.81	0.93	1.05	0.75	0.83	0.91	0.80	0.69	0.74
-0.65	0.73	0.88	0.97	0.82	1.21	1.29	0.71	0.87	0.86	0.80	0.71	0.74
-0.70	0.75	1.01	0.98	0.87	1.66	1.82	0.74	1.01	0.87	0.68	0.74	0.76

of all values of r is 1.033; or, neglecting the value of 8.41 (pentanol 1M-Na₂SO₄, -0.70 V), the average is 0.998. An obvious inference is that r , in these systems, is randomly distributed about unity and has no physical significance. Therefore, we decided to restrict interpretation of the data to examination of a and B values obtained by fitting to the Frumkin isotherm, equation (2). It is worth noting, however, for the single alcohol-electrolyte combination of cyclohexanol in potassium chloride, the Frumkin isotherm gave an unsatisfactory fit in many cases (see Tables II, III), while the Flory-Huggins equation not only gave a better fit for this whole set of systems (6 potentials, 3 electrolyte concentrations) but also the value of r was appre-

TABLE II

Values of the Interaction Parameter, a

$E(\text{s.c.e.})$ V	KF			Na ₂ SO ₄			NaClO ₄			KCl		
	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M
1-Butanol												
-0.45	1.43	1.39	1.59	1.38	1.37	1.64	1.68	1.60	1.60 ^a	1.55	1.70	1.98
-0.50	1.41	1.38	1.51	1.28	1.35	1.49	1.51	1.45	1.56 ^a	1.41	1.53	2.10 ^a
-0.55	1.33	1.30	1.40	1.24	1.25	1.39	1.39	1.33	1.50	1.29	1.38	1.77
-0.60	1.24	1.20	1.32	1.20	1.19	1.28	1.29	1.25	1.40	1.23	1.24	1.52
-0.65	1.20	1.16	1.29	1.17	1.12	1.28	1.17	1.16	1.29	1.16	1.18	1.31
-0.70	1.20	1.16	1.39	1.15	1.20	1.34	1.14	1.15	1.25	1.14	1.18	1.20 ^a
1-Pentanol												
-0.45	1.50	1.49	1.52	1.46	1.46	1.62	1.67	1.69	1.64	1.67	1.74 ^a	2.05 ^a
-0.50	1.45	1.47	1.47	1.45	1.42	1.50	1.54	1.56	1.61	1.56	1.62	2.05 ^a
-0.55	1.44	1.41	1.36	1.39	1.30	1.38	1.44	1.45	1.66	1.44	1.44	1.81 ^a
-0.60	1.39	1.36	1.28	1.34	1.33	1.32	1.36	1.36	1.59	1.40	1.36	1.63
-0.65	1.35	1.32	1.27	1.27	1.24	1.37	1.32	1.27	1.52	1.30	1.27	1.36
-0.70	1.30	1.29	1.40 ^a	1.28	1.30	1.98 ^a	1.23	1.29	1.49	1.32	1.33	1.34
Cyclohexanol												
-0.45	1.66 ^a	1.65	1.77	1.60	1.71	1.84 ^a	1.86 ^a	1.90 ^a	1.58 ^a	1.76 ^a	1.93 ^a	2.79 ^a
-0.50	1.69	1.70	1.72	1.66	1.66	1.67	1.76 ^a	1.85 ^a	1.68 ^a	1.73 ^a	1.87 ^a	2.40 ^a
-0.55	1.68	1.69	1.69	1.62	1.64	1.69	1.71	1.76 ^a	1.75	1.65	1.81 ^a	2.20 ^a
-0.60	1.62	1.60	1.68	1.62	1.59	1.60	1.64	1.67	1.77	1.61	1.73 ^a	1.97 ^a
-0.65	1.57	1.58	1.59	1.57	1.52	1.52	1.56	1.58	1.65	1.52	1.63	1.82 ^a
-0.70	1.56	1.57	1.69	1.55	1.60	1.54	1.58	1.59	1.61	1.49	1.55	1.68

^a Unsatisfactory fit to isotherm — average deviation of experimental points from best-fit curve exceeds 5%.

ciably different from unity and, if not constant, at least restricted to a reasonably narrow range of values. Clearly, the possible applicability of an isotherm such as equation (3), in systems of the type on which we report here, requires further study.

Salting Influence on Alcohol Activity

Comparison of B values amongst different systems must take into account the variation of the activity coefficient of the alcohol in the presence of the various electrolytes at the various concentrations used ("salting-out" or "salting-in" effect); otherwise,

TABLE III

Values of the Adsorption Coefficient B_a

In units of litres mol⁻¹; concentrations corrected for salting effects as in equation (4).

$E(\text{s.c.e.})$ V	KF			Na ₂ SO ₄			NaClO ₄			KCl		
	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M
1-Butanol												
-0.45	5.14	5.80	4.45	6.47	6.77	4.49	3.99	3.93	3.30 ^a	5.27	4.66	1.95
-0.50	5.87	6.58	5.36	7.76	7.34	5.69	6.11	5.96	4.21 ^a	7.30	6.82	2.28 ^a
-0.55	7.14	7.65	6.04	8.44	8.33	6.14	7.59	7.59	5.47	8.48	8.21	4.51
-0.60	8.14	8.40	6.07	8.73	8.53	6.24	8.27	8.28	6.69	8.76	9.11	6.32
-0.65	7.99	7.90	5.14	8.09	8.09	5.02	8.67	8.28	7.17	8.48	8.10	7.09
-0.70	6.69	6.53	3.49	7.16	6.02	3.51	7.62	6.82	6.22	7.36	6.47	6.07 ^a
1-Pentanol												
-0.45	30.5	31.8	28.0	33.8	32.7	25.1	24.9	23.8	16.8	29.4 ^a	25.1 ^a	11.1 ^a
-0.50	36.0	32.1	32.7	37.2	36.6	30.1	34.8	32.8	22.5	37.4	33.9	13.4
-0.55	38.3	41.0	36.5	40.6	41.2	33.1	41.1	41.0	23.9	42.4	43.0	22.1 ^a
-0.60	41.2	41.7	34.6	41.6	37.7	29.8	44.8	43.7	26.5	41.7	43.9	27.8
-0.65	38.9	39.3	27.8	39.6	33.2	22.8	42.3	42.4	25.6	42.2	41.7	33.7
-0.70	35.2	33.1	17.2 ^a	32.3	24.8	12.3 ^a	39.5	33.0	21.1	33.8	31.3	25.7
Cyclohexanol												
-0.45	35.3 ^a	36.5	32.1	42.0	35.8	32.4 ^a	26.2 ^a	22.9 ^a	26.6 ^a	36.3 ^a	29.1 ^a	5.3 ^a
-0.50	37.9	38.6	37.4	42.3	41.2	39.0	35.4 ^a	30.2 ^a	30.1 ^a	41.0 ^a	35.8 ^a	14.1 ^a
-0.55	42.1	41.4	38.6	45.6	42.9	36.4	41.3	37.6 ^a	32.5	46.8	38.4 ^a	20.6 ^a
-0.60	45.4	45.1	34.6	44.8	42.1	36.3	44.2	41.9	32.3	46.2	39.5 ^a	27.9 ^a
-0.65	44.5	40.6	32.1	43.8	39.3	34.0	44.4	41.5	34.4	46.0	39.3	28.3 ^a
-0.70	39.4	35.8	22.5	37.7	29.1	26.1	37.4	35.3	29.6	38.3	34.3	27.0

^a Unsatisfactory fit to isotherm—average deviation of experimental points from best-fit curve exceeds 5%.

as demonstrated previously⁴, the relative values of the adsorption coefficients are anomalous. Consequently, all values of B reported here are based on the equation

$$B_a C(S_0/S) = [\theta/(1 - \theta)] \exp(-2a\theta), \quad (4)$$

where S , S_0 are the solubilities of the relevant alcohol in the relevant electrolyte and in water respectively. The term (S_0/S) represents an activity coefficient that allows for the salting effect. Values of this coefficient for the solutions of interest have been reported elsewhere⁵.

Tables II and III show the values of a and B_a , respectively, obtained in this work. Values marked by asterisks indicate systems where the fit to equation (4) was "not good", a subjective choice since there is obviously no particular place in the spectrum of "goodness-of-fit" that divides "good" from "bad"; however, if *only* the systems marked by asterisks had been examined, we would have concluded that the Frumkin isotherm was inapplicable. Considering the whole range of systems studied, on the other hand, it appears that this isotherm is applicable under a wide range of conditions, including some where the electrolyte is effectively competing for available surface, as evidenced by a decrease in the apparent adsorption coefficient of the alcohol as compared to the value in absence of electrolyte.

In the following sections, qualitative interpretations of variations in values of a and B_a are made and discussed. In the development⁶ of equation (2), B had the usual connotation of an adsorption coefficient — a measure of excess concentration at the surface as compared to the bulk solution; and a was regarded as reflecting mutual interaction of adsorbed molecules, by analogy with the van der Waals' equation of state for gases. The present discussion will be based on this interpretation of the Frumkin isotherm.

The Interaction Parameter

The results in Table II show a number of regularities and patterns. In all cases, a decreases as the potential becomes more cathodic. In 0.05M electrolyte, the values are probably not very different from those in total absence of electrolyte (*cf.* generally small differences between 0.05 and 0.1M solutions, as found also for the values of B , Table III; however, see later in this section) and therefore one needs to seek an interpretation in terms of the properties of the alcohol itself, or of the competition between alcohol and water at the surface. In support of the latter possibility, one might note that the (percentage) decrease in a values, in 0.05M electrolyte, over the potential range is greater for butanol than for pentanol, and greater for the latter than for cyclohexanol. This parallels the order of absolute magnitudes of a (as well as of B), *i.e.*, one might say that the more strongly adsorbed the alcohol, and the greater the attraction between adsorbed molecules, the slighter become effects due to com-

TABLE IV
Comparison of Values of Interaction Parameter for Different Alcohols

E(S.C.E.) V	KF			Na ₂ SO ₄			NaClO ₄			KCl		
	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M	0.05M	0.1M	1M
Ratio a(pentanol)/a(butanol)												
-0.45	1.05	1.07	0.96	1.06	1.07	0.99	0.99	1.60	— ^a	1.08	— ^a	— ^a
-0.50	1.03	1.07	0.97	1.13	1.05	1.01	1.02	1.08	— ^a	1.11	1.06	— ^a
-0.55	1.08	1.09	0.97	1.12	1.04	0.99	1.04	1.09	1.11	1.12	1.04	— ^a
-0.60	1.12	1.13	0.97	1.12	1.12	1.03	1.05	1.08	1.14	1.14	1.10	1.07
-0.65	1.12	1.14	0.98	1.09	1.11	1.07	1.13	1.10	1.18	1.12	1.08	1.04
-0.70	1.80	1.11	— ^a	1.11	1.08	— ^a	1.08	1.12	1.19	1.16	1.13	— ^a
Ratio a(cyclohexanol)/a(pentanol)												
-0.45	— ^a	1.11	1.17	1.10	1.17	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
-0.50	1.17	1.16	1.17	1.14	1.17	1.11	— ^a	— ^a	— ^a	— ^a	— ^a	— ^a
-0.55	1.17	1.20	1.24	1.17	1.26	1.22	1.19	— ^a	1.06	1.15	— ^a	— ^a
-0.60	1.17	1.18	1.31	1.21	1.20	1.21	1.21	1.23	1.11	1.15	— ^a	— ^a
-0.65	1.16	1.20	1.25	1.24	1.23	1.11	1.18	1.24	1.09	1.17	1.28	— ^a
-0.70	1.20	1.22	— ^a	1.21	1.23	— ^a	1.28	1.23	1.08	1.13	1.17	1.25
Average values for all salts Ratio a(cyclohexanol)/a(butanol)												
	0.05M			0.1M			1M					
-0.45	1.05 ± 03			1.07 ± 01			0.98 ± 02					
-0.50	1.07 ± 05			1.07 ± 01			0.99 ± 02					
-0.55	1.09 ± 03			1.07 ± 03			1.02 ± 06					
-0.60	1.11 ± 03			1.11 ± 02			1.05 ± 05					
-0.65	1.12 ± 01			1.11 ± 02			1.07 ± 06					
-0.70	1.11 ± 03			1.11 ± 02			1.19					
Ratio a(cyclohexanol)/a(pentanol)												
-0.45	1.10 ^b			1.14 ± 03 ^c			— ^a					
-0.50	1.16 ± 02 ^c			1.17 ± 01 ^c			1.14 ± 03 ^c					
-0.55	1.17 ± 01			1.23 ± 03 ^c			1.17 ± 08					
-0.60	1.19 ± 03			1.20 ± 02			1.21 ± 07					
-0.65	1.19 ± 03			1.24 ± 02			1.15 ± 07					
-0.70	1.21 ± 04			1.21 ± 02			1.17 ± 09 ^c					

^a Values uncertain because of poor isotherm fit, ^b only one value; ^c two values only.

petitive adsorption of water. Such an interpretation would then imply that water molecules are more effective in decreasing the attraction of adsorbed molecules at cathodic than at anodic potentials; a possible physical model for such an effect has not, however, occurred to us.

In the solutions of low electrolyte concentration, there is a consistent difference between a values for the three alcohols at a given potential in a given electrolyte; the relevant values are given in Table IV. These would again be consistent with an interpretation in terms of intermolecular attraction, greater for cyclohexanol than for pentanol, and markedly greater for both of these than for butanol.

Increase in the concentration of electrolyte leads to increased values of a (the handful of exceptions corresponds to systems where the fit to the isotherm is not good).

TABLE V
Effect of Electrolyte on Adsorption Coefficient
Average values of B_a for all salts. Values from poor isotherm fits excluded.

$E(\text{s.c.e.})$	0.05M	0.1M	1M
1-Butanol			
-0.45	5.22 ± 12%	5.29 ± 24%	3.63 ± 31%
-0.50	6.76 ± 11%	6.68 ± 6%	5.53 ± 3%
-0.55	7.91 ± 7%	7.94 ± 4%	5.54 ± 10%
-0.60	8.48 ± 3%	8.58 ± 3%	6.33 ± 3%
-0.65	8.31 ± 3%	8.09 ± 1%	6.11 ± 17%
-0.70	7.28 ± 3%	6.46 ± 3%	4.41 ± 27%
1-Pentanol			
-0.45	29.7 ± 8%	29.4 ± 13%	23.3 ± 18%
-0.50	36.4 ± 3%	33.9 ± 3%	28.4 ± 13%
-0.55	40.6 ± 3%	41.6 ± 2%	31.2 ± 15%
-0.60	42.3 ± 3%	42.7 ± 5%	29.7 ± 8%
-0.65	40.8 ± 4%	39.1 ± 8%	27.5 ± 12%
-0.70	35.2 ± 6%	30.6 ± 9%	23.4 ± 10%
Cyclohexanol			
-0.45	42.0 ^a	36.2 ± 1%	32.1 ^a
-0.50	40.1 ± 5%	38.8 ± 1%	38.2 ± 2%
-0.55	44.0 ± 5%	42.2 ± 2%	35.8 ± 6%
-0.60	45.2 ± 2%	43.0 ± 3%	34.3 ± 4%
-0.65	44.7 ± 2%	40.2 ± 2%	33.5 ± 3%
-0.70	38.2 ± 2%	33.6 ± 7%	26.3 ± 8%

^a One value only.

This could be interpreted as an increased intermolecular attraction resulting from a greater concentration of ions at the surface, "sequestering" a greater portion of the water there and thus "salting out" the alcohol at or near the surface.

Despite the apparent invariance of a values with electrolyte concentration below 0.1M, the actual values are not the same in the different electrolytes: the magnitudes are consistently greater in KCl and NaClO₄ than in KF and Na₂SO₄. A possible partial explanation lies in variations of the potential of zero charge amongst the various solutions; the p.z.c. is more negative in the former solutions than in the latter, and if the a values were compared at equivalent *rational* potentials (*i.e.*, potential *vs.* p.z.c.), the noted differences would become smaller and might become insignificant. However, this argument is based on p.z.c. values for pure electrolytes; the values in presence of adsorbed films are not available, and are notoriously difficult of estimation. In addition, the similarity in a and B_a values at electrolyte concentrations of 0.05 and 0.1M may be illusory: one would like to have data for considerably more dilute solutions. Measurements under those conditions involve large corrections for the solution resistance, and it remains to be seen whether satisfactory accuracy can be achieved by the technique used in this work.

A second difficulty is that some effects are apparently peculiar to a given combination of electrolyte and alcohol. Thus, KCl appears to affect a values for cyclohexanol to a greater extent than for pentanol. These features, however, are uncertain in view of the comparatively poor fit of the isotherm in these cases.

TABLE VI

Relative Adsorbabilities of Alcohols

$E(\text{s.c.e.})$	0.05M	0.1M	1M
Average $B_a(\text{Pentanol})/\text{Average } B_a(\text{Butanol})$			
-0.45	5.7	5.6	6.4
-0.50	5.4	5.1	5.1
-0.55	5.1	5.2	5.6
-0.60	5.0	5.0	4.7
-0.65	4.9	4.8	4.5
-0.70	4.8	4.7	5.3
Average $B_a(\text{Cyclohexanol})/\text{Average } B_a(\text{Pentanol})$			
-0.45	1.41	1.23	1.38
-0.50	1.11	1.14	1.34
-0.55	1.08	1.01	1.15
-0.60	1.07	1.01	1.16
-0.65	1.10	1.03	1.22
-0.70	1.09	1.10	1.12

Adsorption Coefficient

In all systems, the apparent adsorption coefficient of the alcohol (Table III) showed a maximum value near the p.z.c., and decreased at both anodic and cathodic polarizations; this is the typical behavior for uncharged surfactants.

In most cases, the B_a values did not differ by a great deal in electrolyte solutions of 0.05 and 0.1M concentration. These values can then be taken to be indicative of the "intrinsic" adsorption from pure aqueous solution, and would be expected to be independent of the nature of the electrolyte (however, see above). This is approximately the case (see Table V); the variations can be ascribed to poor fit to the isotherm and resultant "experimental" errors. In addition, as in the case of the a values, one would expect variations when comparisons are made at fixed potentials with respect to the reference electrode rather than at given rational potentials. The latter, however, are not estimable with satisfactory precision in the presence of adsorption, and this also prevents comparison at fixed *charge*, rather than potential, of the electrode since knowledge of the p.z.c. is necessary for both types of calculation. Within the validity of the present data, the comparison at given potentials *vs.* s.c.e. is qualitatively consistent with expectation, B_a values for cyclohexanol being c. 10% greater than for pentanol, and the latter approximately five times as great as for butanol (Table VI).

Increase in the concentration of supporting electrolyte decreases the apparent adsorption coefficient of the alcohol. Table VII shows the percentage decrease in B_a as the electrolyte concentration is increased from 0.05 to 1M. These percentages are approximately constant for a given electrolyte at a given potential; this could indicate that the work of adsorption of the alcohol is changed by a given amount. In fact, one would expect that this work could change by an amount that depends on the charge displaced in 1M, as opposed to 0.05M electrolyte, when adsorption takes place. Within the limits of the present data, this could lead to the approximate constancy observed (Table VII).

Different electrolytes lead to different changes in B_a as the electrolyte concentration is varied. The results at -0.70 V are anomalous, but at other potentials these changes are in keeping with expectations based on the specific adsorbabilities of the ions involved; increased amounts of KF decrease adsorption of alcohol to the smallest extent, of KCl to the greatest extent; NaClO_4 and Na_2SO_4 show intermediate changes.

Competitive Adsorption of Alcohols, Electrolytes and Solvent

As indicated in the previous sections, much of the data is explicable in terms of present knowledge, albeit only in a qualitative way. For interpretation of adsorption coefficients, it is essential that salting effects in the bulk of the solution be taken into account (use of equation (4) rather than equation (2)), as discussed more fully elsewhere⁴.

Then, variation of B_a values with potential, nature of alcohol, concentration of electrolyte, and nature of electrolyte, is in accord with qualitative expectation.

Quantitative interpretation would require a detailed knowledge of the points of zero charge in the various solutions which do not seem to be accessible with adequate precision since the surface tension changes so little with changing potential in the presence of adsorbed films.

Magnitudes of the "interaction constant" can be partly explained in terms of intermolecular attraction, but problems remain as indicated earlier. Some indication of the role of the solvent may be found from the variation of a with potential under conditions where electrolyte is essentially absent.

TABLE VII

Electrolyte Effect on Adsorption of Alcohol

Percentage decreases in B_a values as electrolyte concentration increases from 0.05 to 1M.

	$E(\text{s.c.e.})$ V	Butanol	Pentanol	Cyclohexanol	Average
KF	-0.45	13%	8%	9% ^a	10 ± 2
	-0.50	9%	9%	1%	6 ± 4
	-0.55	15%	5%	8%	9 ± 4
	-0.60	25%	17%	24%	22 ± 3
	-0.65	36%	29%	28%	31 ± 3
	-0.70	50%	51% ^a	43%	48 ± 3
Na ₂ SO ₄	-0.45	31%	26%	23% ^a	27 ± 3
	-0.50	27%	19%	8%	18 ± 7
	-0.55	27%	18%	20%	22 ± 4
	-0.60	29%	28%	19%	25 ± 4
	-0.65	38%	42%	22%	34 ± 8
	-0.70	51%	62% ^a	31%	48 ± 11
NaClO ₄	-0.45	24% ^a	32%	— ^b	28 ± 4
	-0.50	31% ^a	35%	— ^b	33 ± 2
	-0.55	28%	42%	21%	30 ± 8
	-0.60	19%	41%	27%	29 ± 8
	-0.65	17%	39%	23%	26 ± 8
	-0.70	18%	47%	21%	29 ± 2
KCl	-0.45	63%	62% ^a	— ^b	63 ± 1
	-0.50	69%	64% ^a	— ^b	67 ± 3
	-0.55	47%	48% ^a	56% ^a	50 ± 4
	-0.60	28%	33%	40% ^a	34 ± 3
	-0.65	16%	20%	38% ^a	25 ± 9
	-0.70	18%	24%	30%	24 ± 4

^a One B_a value from poor isotherm fit, ^b both B_a values from poor isotherm fits.

A question remains concerning the physical significance of the isotherm parameters, in particular if some systems (*e.g.*, cyclohexanol in chloride solutions) show a better fit to some other isotherm — *e.g.*, the Flory-Huggins. The values of the interaction parameter depend on which isotherm is used (Table VIII). As stated earlier, we based our discussions on the Frumkin model in view of the preponderant fit of data to that equation and the apparent lack of physical significance of the values obtained for the Flory-Huggins parameter r . However, the fact that data fit an equation does not necessarily mean that the parameters have the physical significance assumed in the derivation of the equation; thus, an alternative interpretation of a in the Frumkin isotherm is possible⁷.

TABLE VIII
"Interaction Parameter" a and Isotherm Choice (Cyclohexanol, Potassium Chloride)
Values of a .

$E(\text{s.c.e.})$ V	From Frumkin isotherm			From Flory-Huggins isotherm		
	0.05M	0.1M	1M	0.05M	0.1M	1M
-0.45	1.76	1.93	2.79	1.37	1.43	1.46
-0.50	1.73	1.87	2.40	0.90	1.22	1.60
-0.55	1.65	1.81	2.20	1.27	1.04	1.70
-0.60	1.61	1.73	1.97	1.35	1.17	1.49
-0.65	1.52	1.63	1.82	1.29	1.14	1.34
-0.70	1.49	1.55	1.68	1.08	1.23	1.30

From the point of view of studying the details of the adsorption process, which does involve displacement of ions and solvent by surfactant, data such as that reported above is not particularly enlightening. Though the outlined interpretations could perhaps be taken further and made more quantitative, the fact remains that changes of electrolyte (nature and concentration) change the magnituder of the isotherm parameters by amounts that are not sufficiently large as to offer, for instance, any expectation that one might use such data to compare the specific adsorbabilities of perchlorate and sulfate ions. The possibility of making such comparisons, as a means of investigating the double layer at solid electrodes, was a primary aim in the present investigation, in view of the fact that direct methods (surface-tension or capacity measurements) have not been successfully applied to solid electrodes. Consequently, other ways of obtaining this information are desirable.

It turns out that the characteristics of the adsorption-desorption peaks are considerably more sensitive to changes in the nature of the system than are the magnitudes of the isotherm parameters. This is not surprising, since a.c. measurements at the peaks are influenced by the kinetics of the adsorption process as well as by the energies involved, whereas the isotherm parameters reflect only the latter. Further studies are therefore being made of the capacity peaks, and of the harmonics of the alternating signal produced⁸ in the region of the peaks.

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REFERENCES

1. Bauer H. H., Britz D., Foo D. C. S.: *J. Electroanal. Chem.* 9, 481 (1965).
2. Frumkin A. N., Damaskin B. B.: *Modern Aspects of Electrochemistry* (J. O'M Bockris, B. E. Conway, Eds), p. 149. Butterworths, London 1964.
3. Lawrence J., Parsons R.: *J. Phys. Chem.* 73, 3577 (1969).
4. Bauer H. H., Campbell H. R., Shallal A. K.: *J. Electroanal. Chem.* 21, 45 (1969).
5. Campbell H. R., Shallal A. K., Bauer H. H.: *J. Chem. Eng. Data* 15, 311 (1970).
6. Frumkin A. N.: *Z. Physik. Chem.* 116, 466 (1925).
7. Mohilner D. M.: Personal communication.
8. Bauer H. H., Shallal A. K.: *Nature* 214, 381 (1967).