118. *Adsorption at the Surface of Solutions. Part IV. Adsorption Constants in Solutions containing Two Solutes.*

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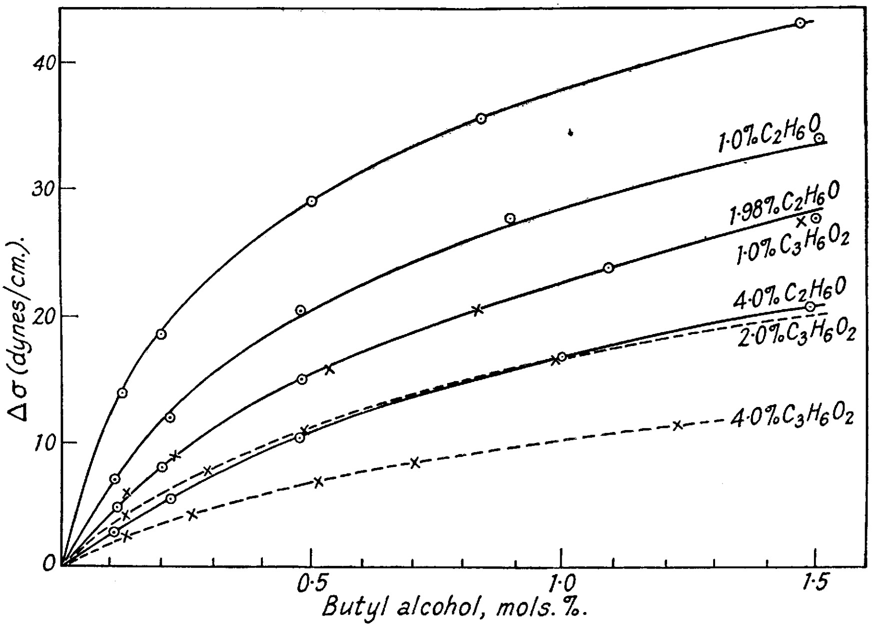
COMPARATIVELY few measurements have been made of the surface tensions of solutions containing two surface-active solutes. Butler and Ockrent (*J. Physical Chem.*, 1930, **34**, 2297, 2841; where references to previous work are given) examined aqueous solutions of ethyl and propyl alcohols, and of propyl alcohol and phenol, and found good agreement with the theoretical relation deduced by them (see below). These measurements, which were made in the course of an investigation of the electrocapillary curves of similar solutions, were not very extensive, and it appeared that a more thorough examination was desirable. We have therefore determined the surface tensions of aqueous solutions of (1) ethyl alcohol and *n*-butyl alcohol; (2) *n*-propionic acid and *n*-butyl alcohol.

EXPERIMENTAL.

The substances were carefully purified and the solutions prepared by weight. Since the activities in the ternary solutions are unknown, it has been thought best to express the concentration as the molar fraction of each constituent in the solution. The surface tensions were determined at 25° by the capillary-rise method, as previously described (Part II, J., 1932, 2098), the proper corrections being applied : the maximum bubble-pressure method appeared to be unsuitable, because the surfaces of these ternary solutions take longer to come to equilibrium than the corresponding binary solutions. The densities of the solutions were determined in a silica pyknometer at 25°.



Surface-tension lowerings of butyl alcohol in water and solutions of ethyl alcohol and propionic acid.

Tables I and II give the observed values, and in the fig. are plotted the surface-tension lowerings produced by butyl alcohol in solutions containing constant molar fractions of ethyl alcohol or propionic acid. In the case of the ethyl alcohol solutions the smooth curves represent the values calculated by the method described below.

TABLE I.

Surface tensions of aqueous ethyl alcohol–butyl alcohol solutions.

EtOH, mols. %.	BuOH, mols. %.	$D_{4^\circ}^{25^\circ}$.	σ.	σ (calc.).	EtOH, mols. %.	BuOH, mols. %.	$D_{4^\circ}^{25^\circ}$.	σ.	σ (calc.).
0·00	0·00	0·9971	71·97	(72·0)	1·98	0·0000	0·9886	55·46	55·6
	0·1243	0·9964	58·18	57·9		0·1125	0·9881	50·84	50·9
	0·2000	0·9959	53·47	53·4		0·2018	0·9876	47·57	47·6
	0·5000	0·9942	43·09	43·0		0·4775	0·9863	40·61	40·7
	0·8375	0·9922	36·38	36·4		1·0916	0·9831	31·83	31·9
	1·4790	0·9897	28·90	28·8		1·5498	0·9808	27·76	27·4
1·00	0·0000	0·9929	61·58	61·5	4·00	0·0000	0·9812	48·16	48·2
	0·1075	0·9922	54·67	54·5		0·1096	0·9808	45·32	45·4
	0·2181	0·9916	49·64	49·2		0·2186	0·9803	42·72	42·7
	0·4802	0·9901	41·34	41·6		0·4767	0·9891	37·82	37·9
	0·8997	0·9876	34·09	34·3		0·9994	0·9761	31·44	31·4
	1·5080	0·9844	27·63	27·9		1·4910	0·9710	27·52	27·7

TABLE II.

Surface tensions of aqueous propionic acid–butyl alcohol solutions.

$C_3H_6O_2$, mols. %.	BuOH, mols. %.	$D_{4^\circ}^{25^\circ}$.	σ.	$C_3H_6O_2$, mols. %.	BuOH, mols. %.	$D_{4^\circ}^{25^\circ}$.	σ.	$C_3H_6O_2$, mols. %.	BuOH, mols. %.	$D_{4^\circ}^{25^\circ}$.	σ.
1·00	0·0000	1·0003	54·07	2·00	0·0000	1·0042	47·40	4·00	0·0000	1·0097	40·54
	0·1334	0·9995	48·10		0·1299	1·0033	43·36		0·1278	1·0088	38·29
	0·2259	0·9989	45·32		0·2926	1·0022	39·74		0·2604	1·0079	36·46
	0·5308	0·9971	38·34		0·4850	1·0009	36·58		0·5104	1·0063	33·81
	0·8268	0·9953	33·76		0·9839	0·9979	30·86		0·7031	1·0050	32·15
	1·4710	0·9916	27·36		1·7336	0·9931	26·29		1·2252	1·0012	29·16

DISCUSSION.

If the adsorption of each solute is proportional to (1) its concentration in the solution, (2) the fraction of the total surface which is unoccupied by any adsorbed molecules, the adsorption will be determined by the following equations

$$A_1\Gamma_1 = k_1N_1(1 - A_1\Gamma_1 - A_2\Gamma_2);\ A_2\Gamma_2 = k_2N_2(1 - A_1\Gamma_1 - A_2\Gamma_2),$$

where Γ_1, Γ_2 are amounts of the two solutes in the surface layer, which in dilute solutions can be taken as equal to the Gibbs adsorption ($\Gamma_{H_2O} = 0$); A_1, A_2 are their areas per molecule in the surface, and $(1 - A_1\Gamma_1 - A_2\Gamma_2)$ is thus the fraction of the surface unoccupied by any solute. When $A_1 = A_2 = A$, it was shown by Butler and Ockrent (*loc. cit.*) that these equations lead to the relation

$$\sigma = \sigma_0 - kT/A \,.\, \log(1 + k_1N_1 + k_2N_2) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the corresponding equations for the single solutions being in the form given by Szyszkowski (*Z. physikal. Chem.*, 1908, **64**, 385), *viz.*,

$$\sigma = \sigma_0 - kT/A \,.\, \log(1 + k_1N_1);\ \sigma = \sigma_0 - kT/A \,.\, \log(1 + k_2N_2).$$

Similar equations involving the activities of the solutes were deduced on thermodynamical grounds by Butler (*Proc. Roy. Soc.*, 1932, **135**, 348), but since the activity coefficients of the mixed solutions are unknown, we shall discuss our observations in terms of the simpler equations given above. If the two solutes do not interfere with each other in the surface layer, except in so far as each solute reduces the surface area available to the other, equation (1) should be capable of reproducing the surface tensions of the mixed solutions, when k_1 and k_2 are given the same values as hold for the single solutions. On the other hand, if it is impossible to reproduce the surface tensions with constant values of k_1 and k_2, it may be inferred that some kind of interaction takes place between the adsorbed substances.

Butyl Alcohol–Ethyl Alcohol Solutions.—It was found that the best value of the constant $2{\cdot}303kT/A$ for the whole series of solutions was 32·3. This compares reasonably well with that found by Butler (34·8) for butyl alcohol solutions (*loc. cit.*), activities being used instead of molar concentrations. Taking this value of the constant, it was found that constant values of k_1 and k_2 were obtained for each series of solutions (N_1 constant), but slightly different values of k_1 and k_2 were required for the different concentrations of ethyl alcohol. The following values of the constants were found to be in best agreement with the data.

		Ternary solutions.		
	Water.	$N_1 = 1$.	$N_1 = 2$.	$N_1 = 4$.
k_1	1·12	1·00	1·01	1·07
k_2	13·9	14·1	13·3	12·7

The values of the surface tension calculated by (1) with these constants are given in Table I. With the exception of one or two points, the agreement is excellent. It is thus evident that the interaction between the ethyl and butyl alcohol molecules in the surface layer is comparatively small.

Butyl Alcohol–Propionic Acid Solutions.—With the same value of kT/A, good agreement with (1) is obtained for the propionic acid solutions of $N_1 = 1$, the following constant values of k_1 and k_2 being used.

	Water.	Propionic acid, $N_2 = 1$.
k_1	—	2·59
k_2	13·9	14·0

In the solutions containing a greater concentration of propionic acid, marked deviations from (1) occur, and it is impossible to assign constant values to k_1 and k_2. The nature of these variations is indicated by the figures given on p. 535, which show the variation of k_2 calculated on the assumption that k_1 is constant.

Propionic acid, mols. %.		2·0.		4·0.	
		k_1.	k_2.	k_1.	k_2.
Butyl alcohol, mols. %.	0·1	2·4	14·8	2·1	13·0
	0·5	—	13·8	—	11·4
	0·8	—	13·4	—	10·8
	1·2	—	13·0	—	9·8
	1·7	—	11·8	—	—

Some part of this variation may be due to appreciable changes of the activity coefficients in the ternary solutions, but it is unlikely that it could be entirely accounted for in this way. It thus appears that in the solutions containing the greater concentrations of propionic acid, the two solutes interact in the surface layer in such a way as materially to change their adsorption constants. Surface-tension measurements do not provide any clear evidence of the nature of this interaction, but it may be well to point out the sense in which it acts. Since the observed surface tensions are somewhat lower than those predicted by (1), using the constants of the binary solutions, it is apparent that the presence of propionic acid reduces the adsorption of butyl alcohol to a somewhat greater extent than corresponds with the area it occupies. This is the reverse of what might be expected if ester formation occurred.

SUMMARY.

1. Measurements have been made of the surface tensions of aqueous solutions of (1) ethyl alcohol and *n*-butyl alcohol; (2) *n*-propionic acid and *n*-butyl alcohol.

2. In case (1) good agreement is obtained with the equation $\sigma = \sigma_0 - kT/A \,.\, \log (1 + k_1N_1 + k_2N_2)$, only small variations of the constants k_1 and k_2 being required to reproduce the whole of the data; in case (2) a considerably greater variation of k_1 and k_2 is found. Hence, although in (1) the two solutes do not materially affect one another's adsorption constants when present in the surface layer together, yet in (2) appreciable interaction takes place.

We thank the Chemical Society for a grant.

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[*Received, March 8th,* 1934.]