THE INTERFACIAL TENSIONS BETWEEN HEXANE AND AQUEOUS SALT SOLUTIONS.

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The interfacial tension between two liquids is affected, in general, more or less by a third component which is added to this system. In the system of water and hydrocarbon oil each component has actually no mutual solubility and the added inorganic salt is only soluble in the water phase. Therefore the change of the interfacial tension caused by the concentration change of the salt solution should run parallel to that of the surface tension of the salt solution.

But an unexpected result was obtained in the experiment of McLewis on the interfacial tension of hydrocarbon oil against aqueous solution of metallic salt, namely the lowering of the interfacial tension occurred by the addition of $CuCl_2$, $AgNO_1$, or KCl.⑴ Since each of these substances raises the surface tension of water against air, and does not influence that of the organic liquid, so that the interfacial tension might be expected to be raised.

As McLewis used a dynamical method, while the present experiment was undertaken in order to repeat it statically.

Experimental.

Material. "Normal hexane from petroleum" from Kahlbaum has been used after distillation, the boiling point of which being 68.5°C. and the density 0.6691.

⑴ McLewis, *Phil. Mag.*, (6) **17** (1909), 466.

Surface Tension of Aqueous Salt Solution. Ordinary capillary rise method was used, and the capillary rise was read by means of a cathetometer. Calculations were made by the following formula.

$$\alpha = \frac{1}{2} r\, g\, h\, (d - d')$$

where α denotes the surface tension, r radius of the capillary, g gravity constant, h capillary rise, d density of the liquid and d' density of the air.

Meniscus correction for the reading of h was neglected considering the accuracy of the present experiment. For the density of air 0.0012 (at 20°C. under 760 mm. Hg) was taken into calculation. The results are shown in Table 1.

Table 1. at 20°C.

Solute	C (gram-mol per litre)	d	$r = 0.0415$ cm. h (cm.)	α (dyne/cm.)
$BaCl_2$	0	0.9982	3.535	71.7
,,	0.01	1.0000	3.525	71.8
,,	0.05	1.0074	3.510	72.0
,,	0.1	1.0162	3.495	72.2
,,	0.3	1.0532	3.400	72.8
$BaBr_2$	0.01	1.0008	3.530	71.8
,,	0.05	0.0112	3.510	72.0
,,	0.1	1.0241	3.410	72.2
,,	0.3	1.0842	3.335	72.8
NaCl	0.01	0.9986	3.535	71.8
,,	0.05	1.0003	3.535	71.9
,,	0.1	1.0024	2.530	72.0
,,	0.3	1.0095	3.520	72.2
,,	0.4	1.0146	3.515	72.5
KCl	0.01	0.9985	3.535	71.8
,,	0.05	1.0008	3.535	71.9
,,	0.1	1.0030	3.530	72.0
,,	0.2	1.0075	3.515	72.1
,,	0.3	1.0122	3.505	72.2
KBr	0.01	0.9991	3.535	71.8
,,	0.05	1.0039	3.530	71.9
,,	0.1	1.0067	3.515	72.0
,,	0.2	1.0150	3.495	72.1
,,	0.3	1.0233	3.460	72.2

Table 1.—(*Concluded*)

Solute	C (gram-mol per litre)	d	$r = 0.0415$ cm. h (cm.)	α (dyne/cm.)
KI	0.01	0.9985	3.535	71.8
,,	0.05	1.0043	3.525	71.9
,,	0.1	1.0104	3.505	72.0
,,	0.3	1.0345	3.440	72.2
$CuCl_2$	0.01	0.9994	3.530	71.8
,,	0.05	1.0043	3.515	72.0
,,	0.1	1.0100	3.515	72.2
,,	0.2	1.0222	3.480	72.4
,,	0.3	1.0343	3.469	72.8
$AgNO_3$	0.01	0.9995	3.535	71.8
,,	0.05	1.0053	3.525	72.0
,,	0.1	1.0120	3.505	72.2
,,	0.3	1.0401	3.420	72.4
$Ba(NO_3)_2$	0.01	1.0004	3.530	71.8
,,	0.05	1.0090	3.510	72.0
,,	0.1	1.0195	3.485	72.2
,,	0.2	1.0395	3.425	72.4
$[Co(NH_3)_6]Cl_3$	0.01	0.9995	3.530	71.8
,,	0.05	1.0046	3.520	72.0
,,	0.1	1.0106	3.510	72.1
,,	0.2	1.0232	3.485	72.2

Some of the above data are protted on curves in Fig. 1.

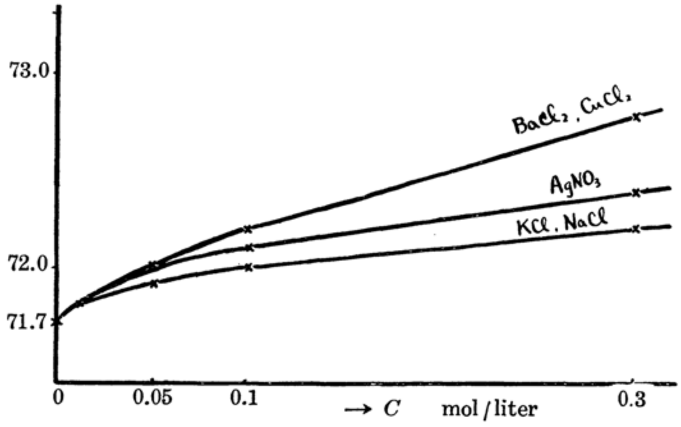

Fig. 1.

The Interfacial Tension. Determinations of the interfacial tensions were made by F. E. Bartell and F. L. Miller's method.(1) The apparatus used is shown in Fig. 2. One of the advantages of this apparatus is that the diameter of the capillary need not be stictly uniform throughout. Calibration of the capillary is necessary only for a given point. It consists of two cups A and B, about 4 cm. in diameter and 10 cm. in height, and these are connected with a U-tube, one arm of which is a capillary of 0.0385 cm. radius.

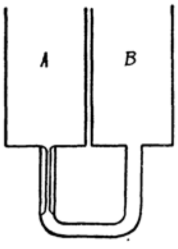

Fig. 2.

The aqueous solution is put into the cup B filling the U-tube. Then oil hexane is introduced into the cup A so that an interface is formed at the top of the capillary. More oil is added drop by drop until the interfacial meniscus is forced back just to the calibrated point. The heights of the liquid in A and B respectively, above the meniscus of the oil, say h and h', are read by means of a cathetometer. The following condition must be fulfiled in equilibrium.

$$\pi r^2 h d g = \pi r^2 h' d' g + 2\pi \alpha r$$

where d and d' denote the densities of the liquid in A and B respectively, α the interfacial tension, r the radius of the capillary and g the gravity constant. Therefore

$$\alpha = {}^1/_2\, r\, g\, (h\, d - h' d')$$

The results of the experiment are given in Table 2 and also shown by curves in Fig. 3.

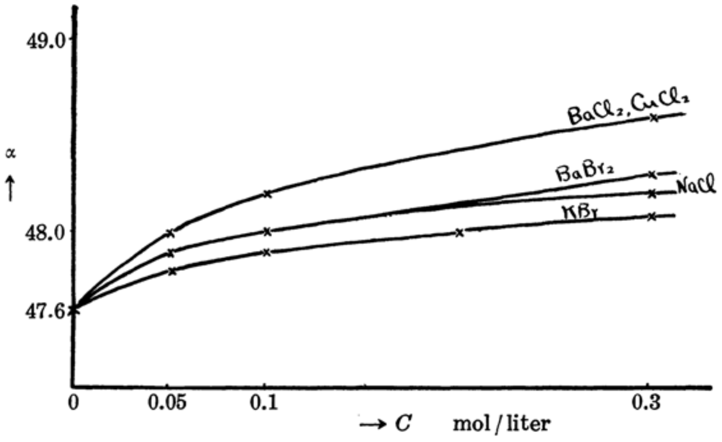

Fig. 3.

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(1) F. E Bartell and F. L. Miller, *J. Am. Chem. Soc.*, **50** (1928), 1961.

Table 2.

Solute	$C \left(\begin{matrix}\text{gram-mol} \\ \text{per litre}\end{matrix}\right)$	h (cm.)	h' (cm.)	$h\,d - h'\,d'$	α (dyne/cm.)
$BaCl_2$	0	10.290	4.355	2.539	47.6
,,	0.05	9.350	3.670	2.559	48.0
,,	0.1	9.070	3.445	2.567	48.2
,,	0.3	8.885	3.180	2.590	48.6
$BaBr_2$	0.01	8.807	3.345	2.545	47.8
,,	0.05	8.510	3.115	2.549	47.9
,,	0.1	8.290	2.290	2.557	48.0
,,	0.3	8.810	3.090	2.572	48.3
NaCl	0.05	7.905	2.735	2.552	47.9
,,	0.1	8.615	3.195	2.558	48.0
,,	0.3	9.370	3.670	2.566	48.2
,,	0.4	8.615	3.145	2.573	48.3
KCl	0.05	8.855	3.370	2.554	47.9
,,	0.1	10.080	4.170	2.559	48.0
,,	0.2	9.632	3.855	2.561	48.1
,,	0.3	9.775	3.915	2.566	48.2
KBr	0.05	8.885	3.410	2.545	47.8
,,	0.1	9.175	3.665	2.551	47.9
,,	0.2	7.665	2.525	2.559	48.0
,,	0.3	8.990	3.375	2.561	48.1
KI	0.05	8.795	3.330	2.541	47.7
,,	0.1	9.375	3.690	2.543	47.8
,,	0.3	8.925	3.300	2.558	48.0
$CuCl_2$	0.05	8.560	3.155	2.559	48.0
,,	0.1	9.645	3.850	2.568	48.2
,,	0.2	8.930	3.335	2.570	48.3
,,	0.3	8.685	3.115	2.589	48.6
$Ba(NO_3)_2$	0.05	8.425	3.055	2.555	48.0
,,	0.1	9.270	3.570	2.564	48.2
,,	0.2	9.720	3.785	2.572	48.3
$AgNO_3$	0.05	8.525	3.140	2.548	47.9
,,	0.1	9.515	3.655	2.554	48.0
,,	0.3	9.185	3.445	2.566	48.2
$Co(NH_3)_6Cl_3$	0.05	9.490	3.790	2.543	47.8
,,	0.1	8.630	3.185	2.556	48.0
,,	0.2	9.010	3.385	2.566	48.2

As we see from the table, the results indicate that, on the contrary to that of McLewis, the interfacial tension of aqueous salt solutions against hexane increase by the increase in concentration of the former, and that the interfacial tension runs approximately parallel to that of the surface tension of the salt solution against air.

Dynamical Measurement of the Interfacial Tension. Drop number method was also tried for the measurement of the interfacial tension to compare the results with that of the statical method. Results obtained by two types of dropping pipette coincided to each other and nearly coincided to that obtained by statical method as shown in Table 3. Calculations were made by the following formula.

$$\alpha = \alpha_0 \frac{n_\omega(d-d_0)}{n(d_\omega-d_0)}$$

where α_0: interfacial tension between water and hexane; n_ω: drop number of water in hexane; n: drop number of solution in hexane; d_ω: density of water; d: density of solution; d_0: density of hexane.

Table 3.

Solute	$C\left(\begin{smallmatrix}\text{gram-mol}\\ \text{per litre}\end{smallmatrix}\right)$	n	α (dynamical)	α (statical)
$BaCl_2$	0	294	47.6	47.6
,,	0.05	301	47.8	48.0
,,	0.1	309	48.0	48.2
,,	0.3	338	48.4	48.6
$BaBr_2$	0.05	303	47.7	47.9
,,	0.1	317	47.9	48.0
,,	0.3	359	48.2	48.3
$CuCl_2$	0.05	297	47.7	48.0
,,	0.1	302	47.9	48.2
,,	0.3	325	48.2	48.6
NaCl	0.1	297	47.8	48.0
,,	0.4	305	48.1	48.3
KBr	0.2	306	47.8	48.0
,,	0.3	316	48.0	48.1

The writer wishes to thank Professor J. Sameshima, under whose kind suggestion this work was carried out.

Summary.

The interfacial tensions between aqueous inorganic salt solutions and hexane have been measured by both statical and dynamical method. Results indicate that the interfacial tensions increase by the increase in concentration of the salt solutions, being nearly parallel to the surface tension of the salt solutions.

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