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INTERFACIAL TENSION IN SYSTEMS INVOLVING TBP IN DODECANE, NITRIC ACID, URANYL NITRATE AND WATER

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Abstract:

The interfacial tension was measured at 25°C in the systems TBP - _n_-dodecane/nitric acid - water and TBP - _n_-dodecane/nitric acid - uranyl nitrate - water. Empirical equations describing the interfacial tension as a function of the concentration of TBP in the starting organic phase and of uranium(VI) and nitric acid in the equilibrium aqueous phase were suggested. In the absence of uranium(VI), the interfacial tension can also be correlated with the concentration of water in the equilibrium organic phase. Free TBP, hydrated or nonhydrated, and hydrated TBP solvates of nitric acid are interfacially active. Anhydrous TBP solvates of nitric acid and the TBP solvate of uranyl nitrate, which neither is hydrated, do not exhibit any visible interfacial activity.

Grenzflächenspannung in TBP in Dodekan, Salpetersäure, Uranylnitrat und Wasser enthaltenden Systemen

Zusammenfassung:

Die Grenzflächenspannung in den Systemen TBP - _n_-Dodekan/Salpetersäure - Wasser und TBP - _n_-Dodekan/Salpetersäure - Uranylnitrat - Wasser wurde bei 25°C gemessen. Empirische Gleichungen werden vorgeschlagen, die die Grenzflächenspannung als eine Funktion der Anfangskonzentration von TBP in der organischen Phase und der Gleichgewichtskonzentrationen von Uran(VI) und Salpetersäure in der wässrigen Phase beschreiben. Bei Abwesenheit von Uran(VI) kann ein Zusammenhang zwischen der Grenzflächenspannung und der Gleichgewichtskonzentration von Wasser in der organischen Phase formuliert werden. Freies, hydratisiertes oder nicht hydratisiertes TBP und hydratisierte TBP-Solvate von Salpetersäure sind oberflächlich aktiv. Nicht hydratisierte TBP-Solvate von Salpetersäure und Uranylnitrat weisen keine messbare oberflächliche Aktivität aus.

INTRODUCTION

Available data /1-4/ show that the interfacial tension in a system involving TBP in an alkane diluent and an aqueous solution of uranyl nitrate and nitric acid strongly decreases with increasing TBP concentration and decreasing loading of the organic phase with uranium(VI). On the other hand, the concentration of nitric acid seems to have a less significant effect. It has been concluded /2/ that in the presence of uranium(VI) the interfacial tension is predominantly determined by the concentration of TBP not bound to uranium(VI), and a corresponding semilogarithmic correlation has been suggested. The published data are limited to rather high uranium(VI) concentrations and do not allow to recognize any eventual interfacial activity of uranyl nitrate solvated by TBP. Moreover, the role of nitric acid has probably been underestimated. Complexes formed by TBP with nitric acid in a system involving benzene diluent are claimed to be interfacially active /5/. In this work the interfacial tension was measured in broad ranges of uranium(VI) and nitric acid concentrations in the organic phase. The aim of the study was to make it possible to calculate the interfacial tension as a function of the concentrations of uranium(VI) and nitric acid, in ranges relevant to the Purex process, and to obtain information about the behaviour of TBP solvates of nitric acid and uranyl nitrate on the phase boundary.

EXPERIMENTAL

Chemicals: *n*-Dodecane (Fluka, olefine free), TBP, uranyl nitrate and nitric acid (all Merck, reagent grade) were used as received.

Analyses were performed by the analytical department of the Institute of Hot Chemistry: Uranium(VI) was determined by the x-ray fluorescence method or, at low concentrations, spectrophotometrically with benzoylacetone as reagent. Nitric acid was titrated by a sodium hydroxide solution after masking uranium(VI) by a mixture of sodium fluoride and ammonium oxalate.

Measurements of the interfacial tension were made by the standard du Nouy ring method with a model K 8600 supplied by Krüss, Berlin, and equipped with a Pt-Ir-ring. An aqueous solution containing appropriate amounts of uranyl nitrate and nitric acid was shaken with an initially barren solution of TBP in dodecane. Preliminary experiments had shown that a 24 h shaking was sufficient for obtaining reliable values of the interfacial tension. The phases were separated by gravity and equal volumes (15 ml) of the phases were placed into the measurement vessel of the apparatus, thermostated at $(25.0 \pm 0.1)^{\circ}C$. The vessel and the ring were carefully cleaned before each measurement by rinsing with acetone, drying and heating to about $500^{\circ}C$.

SYMBOLS

γ is the interfacial tension. $\underline{C}_U$ and $\underline{C}_H$ are the concentrations of uranium(VI) and nitric acid respectively in the equilibrium aqueous phase or, if printed with a bar above the letter $\underline{C}$, in the equilibrium organic phase. $\overline{\underline{C}}_W$ is the concentration of water in the equilibrium organic phase. $\overline{\underline{C}}_{T,init}$ is the analytical concentration of TBP in the starting organic phase. All concentrations are expressed in mol/l. $\underline{S}$ is the error square sum,

$$\underline{S} = \sum_{i=1}^{N} (\gamma_{i,exp} - \gamma_{i,calc})^2$$

with N being the total number of measurements.

RESULTS

Data on the system without uranium(VI) are shown in Fig. 1 and those obtained in the presence of uranium(VI) are gathered in Table 1. The initial TBP concentration was varied between 0.094M (2.5 vol.%) and 1.096M (30 vol.%) in the absence of uranium(VI) and was kept constant at 1.096M in the presence of uranium(VI). Low concentrations of nitric acid in the organic phase (<0.05M) could not be determined directly in the presence of large amounts of uranium(VI) and were calculated from empirical model equations /6/.

DISCUSSION

Interfacial Tension in the Absence of Uranium(VI)

The interfacial tension does not change monotonously with the concentration of nitric acid (Fig. 1). To find a mathematical description, we started with a purely empirical approach: we expressed the interfacial tension as a function of the most accessible variables, namely the equilibrium concentration of nitric acid in the aqueous phase and the starting analytical concentration of TBP in the organic phase. A power series

$$\gamma = \sum_{i=0}^{N} \sum_{j=0}^{M} a_{i,j} \underline{C}_{H}^{i} \, \underline{C}_{T,init}^{j} \qquad (1)$$

was applied which, however, needs rather high values of N and M and an inacceptably high number of parameters $a_{i,j}$ for reaching an error square sum lower than one. Unfortunately, even a compromise between an acceptable number of parameters and an appropriately low error square sum represents an equation which is not very suitable for practical use: $\underline{S} = 1.64$ was attained with $N = 3$ and $M = 4$ and with as many as 10 parameters. The parameters were found by a least square computer treatment of the data and are:

i,j	$a_{i,j}$	i,j	$a_{i,j}$
0,0	23.05	0,2	143.31
1,0	-2.3667	0,3	-154.97
2,0	1.0388	0,4	60.206
3,0	-0.13923	1,1	1.3121
0,1	-61.714	1,4	-0.46516

The fit of the calculated γ vs. log $\underline{C}_H$ curves at different analytical concentrations of TBP with the experimental points is illustrated in Fig. 1.

To obtain information about the nature of species adsorbed on the phase boundary, an attempt was made to correlate the measured interfacial tension with concentrations of components of the organic phase. Polar species which could most strongly be adsorbed on the interface are TBP hydrates and hydrated complexes of TBP with nitric acid. There is really a remarkable coherence between the interfacial tension as a function of the organic concentration of nitric acid on one side and the water concentration in the organic phase, as taken from /7/, on the other side. The water concentration in the organic phase reaches a maximum at moderate nitric acid concentrations in the system and just at those $\underline{C}_H$ values at which the interfacial tension approximately reaches a minimum. The complex $HNO_3.H_2O.TBP$ has been suggested /7/ to be formed at the corresponding organic concentrations of nitric acid and this complex could also be responsible for the lowering of the interfacial tension at $\underline{C}_H$ = 0.1 to 1M (Fig. 1), i.e. at $\overline{\underline{C}}_H$ = 0.001 to 0.1M. At higher organic concentrations of nitric acid, the γ value increases with the $\overline{\underline{C}}_H$ value. Here nitric acid replaces water from the organic phase /7/ and it can be concluded that anhydrous complexes of TBP with nitric acid exhibit a low interfacial activity. At very low acid concentrations in the organic phase, the fraction of TBP bound to nitric acid is negligible and the interfacially active species are hydrated or nonhydrated molecules of TBP.

To be able to correlate quantitatively the interfacial tension with the concentration of water in the organic phase, we needed a possibility of calculating the water concentration as a function of the analytical concentration of TBP in the starting organic phase and the equilibrium concentration of nitric acid in the aqueous phase. For this purpose we smoothed data of Davis /7/ with the aid of an empirical equation, with as many as 15 parameters, valid for $\underline{\overline{C}}_{T,init} \leqslant 1.096M$. The data of Davis /7/ have been obtained with kerosene diluent which alone dissolved a probably not equal, but similar amount of water as dodecane. The difference in the water solubility in the absence of TBP should not play any significant role, because under the conditions of our experiments the amount of water hydrating TBP was essentially higher than the amount of water dissolved by dodecane itself: the lowest water concentration in the organic phase was in our work 0.013M, while the solubility of water in pure dodecane is 0.0026M /8/.

The Gibbs adsorption equation correlates the interfacial tension with the logarithm of the concentration of an interfacially active component. Thus, we started with a simple equation $\gamma = a + \log \underline{\overline{C}}_W$. However, it turned out that the interfacial tension was a nonlinear function of the organic water concentration and the role of water was dependent on the organic concentration of nitric acid. Finaly, a rather complicated equation resulted, namely

$$\gamma = a + \log (\underline{\overline{C}}_W^b + c\underline{\overline{C}}_W^d) + \log \left(1 + \frac{e\underline{\overline{C}}_H^f}{1 + g\underline{\overline{C}}_W^h}\right) - \log (1 + m\underline{\overline{C}}_H) \qquad (2)$$

with the parameters being

a	8.68	f	2.532
b	-3.64	g	79.6
c	4.486×10^{-11}	h	3.50
d	-10.56	m	220
e	3580		

Neglecting any role of nitric acid, i.e. setting the parameters e to m equal to zero, gave an unsatisfactory fit with $\underline{S} = 7.30$. Regarding a role of nitric acid but without any connection with water, i.e. setting $g = h = 0$, improved the fit to $\underline{S} = 2.76$. A connection of the role of nitric acid with the role of water, i.e. setting also the two parameters g and h different from zero, improved the fit further to $\underline{S} = 2.26$. The necessity to connect the roles of water and nitric acid in eqn (2) implies that the species $TBP.H_2O$ and $HNO_3.H_2O.TBP$ have both a comparable interfacial activity.

Since there is a defined relation between the $\overline{C}_W$ and $\overline{C}_H$ values, it is possible to calculate theoretical curves of $\gamma = f(\log \overline{C}_H)$. Graphically presented together with experimental points (see Fig. 2), they are perhaps more illustrative than curves of $\gamma = f(\log \overline{C}_W)$ would be.

Eqn (2) indirectly correlates the interfacial tension also with the concentration of TBP. We calculated the dependence $\gamma = f(\log \overline{C}_{T,init})$ at zero concentration of nitric acid (Fig. 3). The dependence is nonlinear and this can be ascribed to an inconstancy of the activity coefficients of TBP and its hydrate at $\overline{C}_{T,init} > 0.2M$. The maximum slope of the dependence at $\overline{C}_{T,init} = 0.12$ to $0.2M$ is -10.5 and, substituted into the Gibbs adsorption equation, yields a value of about 90 Å for the area occupied on the phase boundary by the molecule of an adorbed TBP species. The same value has been reported in /9/.

As a comparison with the data of Sargent et al. /9,10/ shows, neither eqn (1) nor eqn (2) can be used for the calculation of the interfacial tension at TBP concentrations lying outside of the range 0.09 to 1.1M. Both equations give quite incorrect γ values at $\overline{\underline{C}}_{T,init} < 0.09M$ and eqn (1) also at $\overline{\underline{C}}_{T,init} > 1.1M$. Eqn (2) could be used for a rough estimation of the interfacial tension at high TBP concentrations: for the system undiluted TBP - water it gives γ = 7.3 mN/m, while γ = 7.9 mN/m has been found experimentally /10/. Both eqn (1) and (2) are valid for $\underline{C}_H \leq 3.7M$.

Interfacial Tension in the Presence of Uranium(VI)

Like in the absence of uranium(VI), also in its presence we first tried to describe the interfacial tension empirically with a power series. Since the analytical concentration of TBP was constant (1.096M) in all measurements, the interfacial tension was expressed as a function of the readilly accessible equilibrium concentrations of nitric acid and uranium(VI) in the aqueous phase,

$$\gamma = \sum_{i=0}^{N} \sum_{j=0}^{M} b_{i,j}\, \underline{C}_H^{i}\, \underline{C}_U^{j} \qquad (3)$$

with $b_{i,j}$ denoting parameters. To keep the mathematical model consistent with the description of the interfacial tension in the absence of uranium(VI), we set

$$b_{0,0} = a_{0,0}+1.096a_{0,1}+(1.096^2)a_{0,2}+(1.096^3)a_{0,3}+ \\ +(1.096^4)a_{0,4} = 10.40,$$

$$b_{2,0} = a_{2,0} \text{ and } b_{3,0} = a_{3,0}, \text{ and}$$

$$b_{1,0} = a_{1,0}+1.096a_{1,1}+(1.096^4)a_{a,4} = 1.600.$$

To extend the range of the aqueous equilibrium concentration of uranium(VI), we treated mathematically our results together with results taken from the chinese paper /4/ which appeared after the finishing of our experimental work. A least square computer treatment yielded the following parameters:

i,j	$b_{i,j}$	i,j	$b_{i,j}$
0,1	12.110	1,2	-29.432
0,3	-4.6148	2,2	0.8182
0,4	1.2926	1,3	19.503
1,1	16.775	1,4	-4.5639
2,1	-1.8125		

Also here an adequately low error square sum could only be reached with a high number of parameters, as many as 13, and the practical utility of eqn (3) is somewhat limited.

Theoretical dependences of $\gamma = f(\log \underline{C}_U)$, as calculated from eqn (3) for different constant concentrations of nitric acid in the aqueous phase, are shown in Fig. 4. The fit of the calculation with the experiment cannot be shown graphically, because neither the $\underline{C}_U$ nor the $\underline{C}_H$ values were kept strictly constant in a series of experiments in our work (keeping one of the variables strictly constant desires pre-equilibration of the organic phase with the aqueous phase and is time consuming).

We have no explanation for the maximum on the curves $\gamma = f(\log \underline{C}_U)$ at high concentrations of nitric acid, exhibited by the results taken from /4/. The increase of the interfacial tension with the uranium(VI) concentration up to $\underline{C}_U \sim 1M$ can be ascribed to a decrease of the concentration of hydrated or anhydrous free molecules of TBP, which can be expected to be the most interfacially active species in the organic phase. It is known /11/ that the extracted uranium(VI) complex, $UO_2(NO_3)_2.2TBP$, is anhydrous and with increasing loading of the organic phase with uranium(VI), as the concentration of free TBP decreases, water initially bound to free TBP is displaced from the organic phase.

A direct correlation of the interfacial tension with the water concentration in the organic phase is not possible, because no data on the water concentration as function of the organic concentrations of uranium(VI) and nitric acid are available for initially 1.096 M TBP. We therefore tried an indirect correlation. We subtracted the concentration of TBP bound to uranium(VI), equal to $2\underline{\overline{C}}_U$, from the analytical TBP concentration, in order to obtain the concentration of "free" TBP which is partly really free and partly bound to nitric acid. Assuming that only "free" TBP can be hydrated, we calculated the water concentration in the organic phase from the empiric equation used in the treatment of the data obtained in the absence of uranium(VI). Then we calculated the interfacial tension from eqn (2). It turned out that at $\underline{\overline{C}}_U > 0.1M$ the calculated γ values were systematically lower than the experimental γ values. The difference was as high as 2.7 mN/m at the highest organic uranium(VI) concentration reached in our work (0.46M). This could implie that large amounts of uranium(VI) present in the system enhance the interfacial tension. However, no definitive conclusions are justified, because two possible effects of large amounts of uranium(VI) on the properties of the organic phase were neglected: changes of the volume and, subsequently, of the concentrations (up to 4% of the starting volume) and changes of activity coefficients of "free" TBP. Moreover, "free" TBP cannot be determined directly and the above subtraction yield inaccurate results at high organic uranium(VI) concentrations, at which there is only a small difference between the values of $\underline{\overline{C}}_{T,init}$ and $2\underline{\overline{C}}_U$.

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TABLE 1

The interfacial tension in the system TBP - n-dodecane - uranyl nitrate - nitric acid - water at 25°C. The data were ordered by a computer and the number of the decimal places is determined by a printing procedure and not by the accuracy of the analysis.

Expt. No.	$\underline{C}_U$	$\underline{\bar{C}}_U$	$\underline{C}_H$	$\underline{\bar{C}}_H$	γ
0 TO 0.071M NITRIC ACID					
1	.00045	.00004	.052	.0012	10.40
62	.00405	.00045	.056	.0015	10.10
63	.00580	.00126	.054	.0015	10.00
2	.00871	.00172	.061	.0020	10.10
64	.01092	.00227	.052	.0016	9.70
3	.01723	.00542	.065	.0027	9.80
4	.03710	.01845	.070	.0040	9.50
36	.09580	.07269	.050	.0039	10.75
37	.17605	.17815	.040	.0034	12.10
39	.17941	.18992	.070	.0059	12.10
40	.31975	.30378	.050	.0036	14.40
0.071 TO 0.16M NITRIC ACID					
6	.00039	.00011	.096	.0040	10.30
65	.00337	.00113	.098	.0043	10.10
66	.00529	.00197	.095	.0042	9.90
7	.00672	.00235	.102	.0049	10.00
67	.00945	.00349	.093	.0043	9.70
8	.01555	.00803	.110	.0063	9.20
9	.03164	.02353	.120	.0083	9.20
10	.04664	.04580	.150	.0123	9.80
5	.04958	.03899	.110	.0080	9.60
38	.08655	.07647	.090	.0073	10.80
41	.43782	.37647	.100	.0061	15.60

TABLE 1 (continued)

Expt. No.	$\underline{c}_U$	$\underline{\overline{c}}_U$	$\underline{c}_H$	$\underline{\overline{c}}_H$	γ
0.16 TO 0.55M NITRIC ACID					
11	.00012	.00033	.450	.0670	9.90
69	.00172	.00508	.460	.0700	9.60
68	.00194	.00336	.470	.0730	9.70
12	.00214	.00651	.450	.0660	10.10
70	.00311	.00996	.450	.0680	9.50
13	.00550	.01765	.450	.0700	9.35
14	.01353	.04143	.460	.0700	9.20
15	.02197	.06681	.480	.0700	9.50
42	.04664	.10378	.420	.0500	11.10
43	.13571	.22143	.370	.0300	12.50
44	.26807	.34370	.520	.0200	14.90
45	.41008	.39622	.380	.0100	15.70
0.55 TO 1.1M NITRIC ACID					
16	.00007	.00039	.850	.1720	9.70
71	.00020	.00151	.830	.1700	9.50
72	.00052	.00399	.870	.1700	9.70
73	.00092	.00592	.840	.1700	9.65
17	.00110	.00769	.830	.1600	10.20
74	.00139	.01130	.820	.1600	9.40
18	.00294	.01975	.850	.1600	9.20
19	.00731	.04706	.850	.1500	9.40
20	.01487	.08445	.880	.1400	9.70
46	.02786	.10966	.740	.1000	10.70
47	.10084	.25126	.720	.0600	12.60
48	.22227	.37269	1.070	.0500	15.20
49	.37941	.43235	.980	.0300	16.40
1.1 TO 2M NITRIC ACID					
21	.00008	.00041	1.675	.3700	10.40
75	.00010	.00185	1.670	.3700	10.00
76	.00022	.00399	1.680	.3700	10.00
77	.00050	.00630	1.660	.3700	9.80
22	.00052	.00824	1.620	.3500	10.55
78	.00092	.01210	1.660	.1420	9.70
23	.00143	.02109	1.640	.3500	9.50
24	.00303	.04345	1.640	.3300	9.60
25	.00605	.07941	1.640	.2900	10.10
50	.01466	.13151	1.500	.1900	11.25
51	.06303	.28067	1.430	.1150	13.20

TABLE 1 (continued)

Expt. No.	$\underline{c}_U$	$\underline{\bar{c}}_U$	$\underline{c}_H$	$\underline{\bar{c}}_H$	γ
2 TO 3M NITRIC ACID					
26	.00002	.00041	2.590	.5400	11.20
79	.00005	.00189	2.300	.5560	10.65
80	.00019	.00420	2.550	.5500	10.45
27	.00029	.00819	2.460	.5200	11.10
81	.00036	.00630	2.540	.5500	10.40
82	.00050	.01269	2.500	.5200	10.50
28	.00084	.02155	2.490	.5100	10.10
29	.00172	.04336	2.450	.5000	10.70
87	.00176	.03697	2.030	.5300	10.50
88	.00223	.05126	2.570	.5100	10.60
89	.00307	.06807	2.570	.4900	10.70
30	.00391	.08193	2.460	.4400	10.70
54	.00908	.13529	2.350	.2900	11.80
59	.03004	.28739	2.740	.2700	15.40
55	.04412	.29496	2.160	.1900	13.40
52	.18655	.40630	2.150	.0900	16.30
53	.34496	.45756	2.280	.0600	18.00
57	.36471	.46387	2.590	.0700	18.20
3 TO 5M NITRIC ACID					
31	.00002	.00042	3.290	.6500	11.60
83	.00007	.00189	3.380	.7100	11.20
84	.00014	.00416	3.350	.7100	11.20
32	.00023	.00828	3.270	.6600	11.80
86	.00032	.01210	3.300	.6600	11.20
85	.00035	.00647	3.340	.7000	11.30
33	.00059	.02164	3.270	.6500	10.80
34	.00097	.04378	3.240	.6200	11.40
90	.00105	.03735	3.570	.6700	11.20
92	.00206	.07101	3.350	.6100	11.40
91	.00239	.05000	3.370	.6400	11.30
35	.00395	.08151	3.230	.6700	11.40
58	.00647	.13866	3.090	.4900	12.30
60	.17269	.42647	4.520	.1500	18.00
56	.17731	.42479	3.240	.1100	17.30
61	.35420	.46303	4.290	.0800	18.30

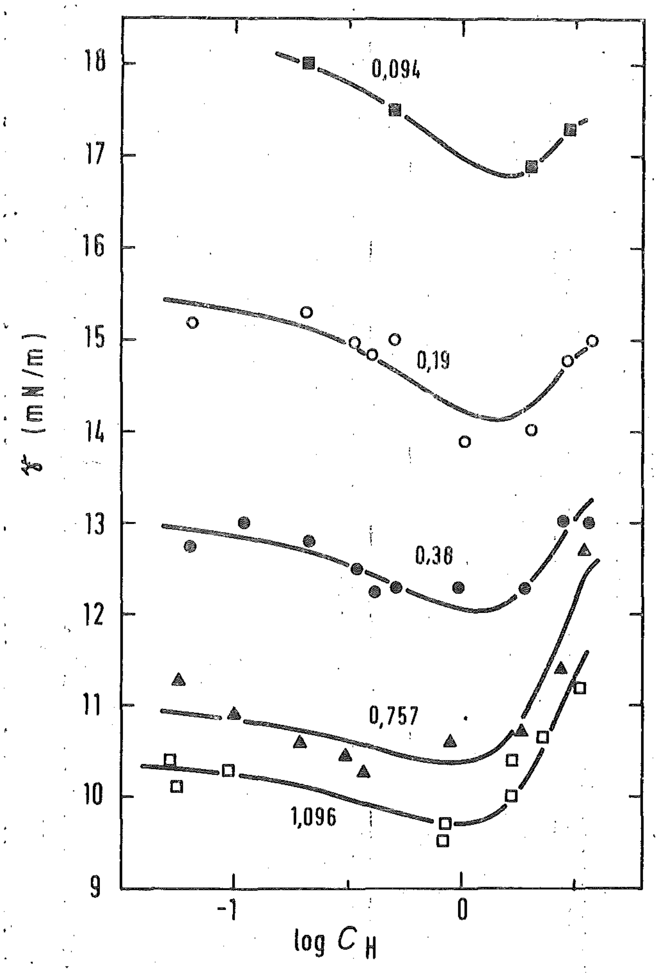

Fig. 1

The interfacial tension in the absence of U(VI) as a function of the equilibrium concentration of HNO_3 in the aqueous phase at different analytical concentrations of TBP in the organic phase (see numerals on the curves, molar scale). The solid curves were calculated from eqn (1) with the parameters given in the text.

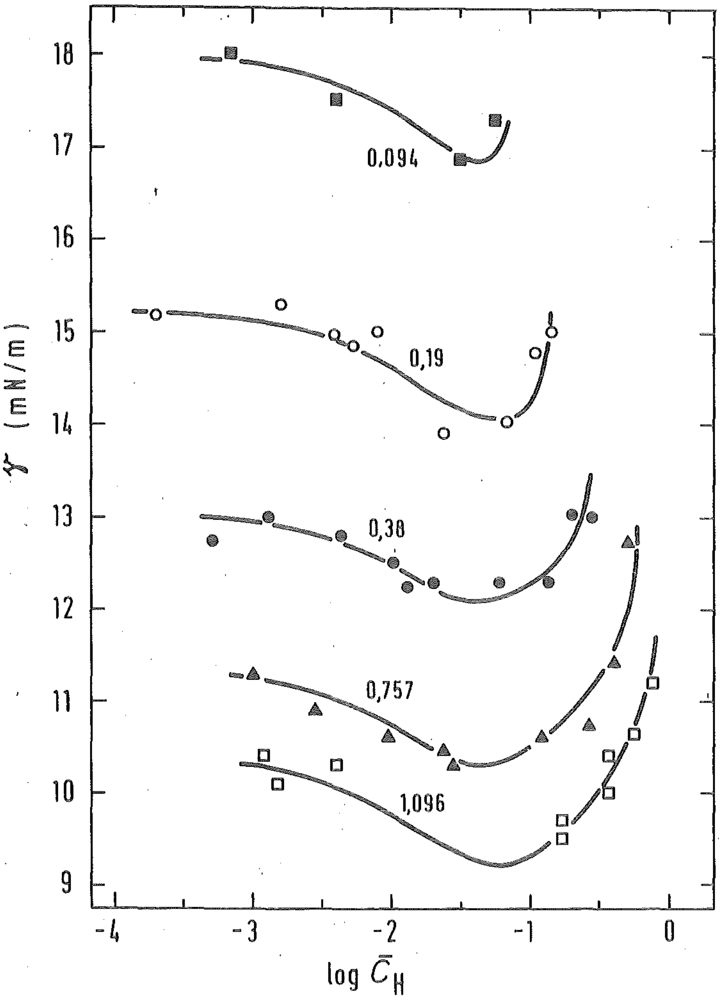

Fig. 2

The interfacial tension in the absence of U(VI) as a function of the equilibrium concentration of HNO_3 in the organic phase at different analytical concentrations of TBP (see numerals on the curves, molar scale). The solid curves were indirectly calculated from eqn (2) with the parameters given in the text.

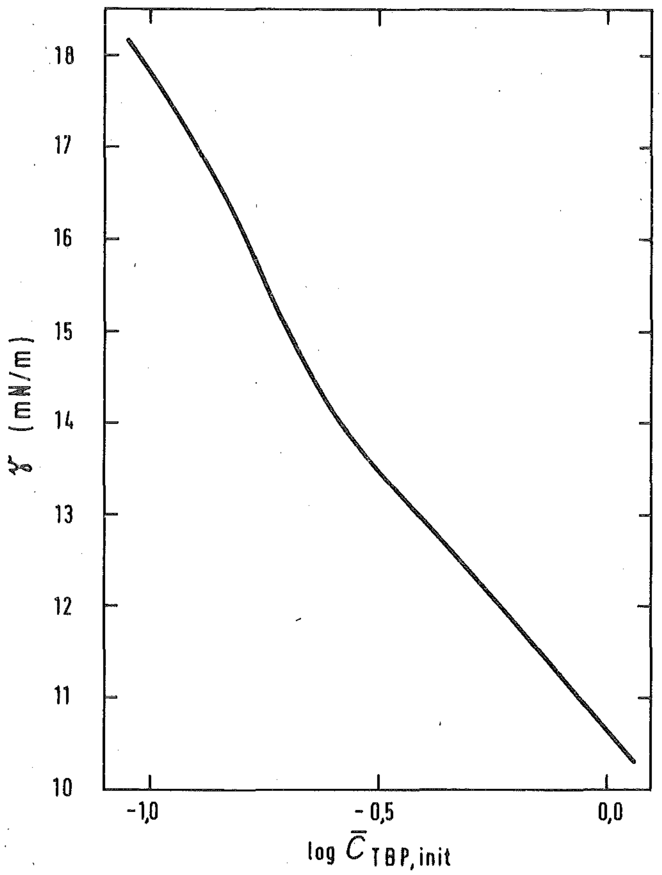

Fig. 3

The interfacial tension in the absence of U(VI) and HNO_3 as a function of the analytical concentration of TBP in the organic phase, indirectly calculated from eqn (2).

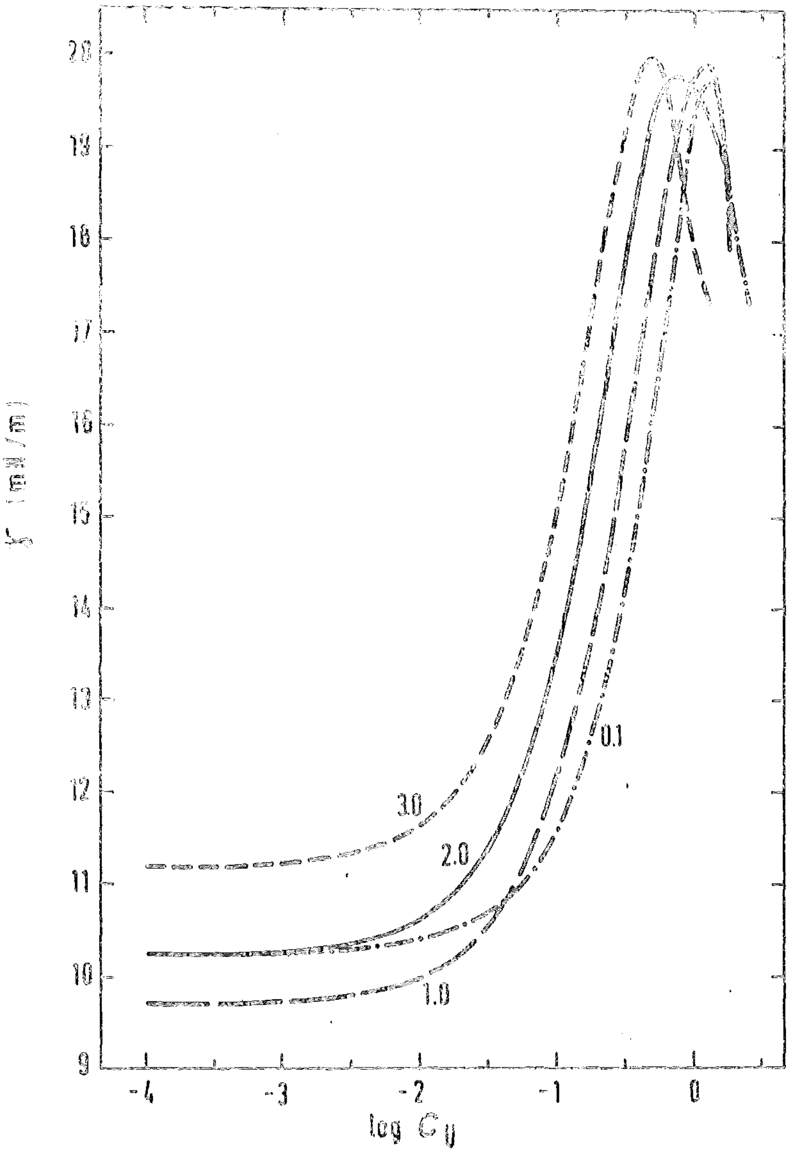

Fig. 4

The interfacial tension as a function of the equilibrium aqueous concentration of U(VI) at different equilibirum aqueous concentrations of HNO_3 (see numerals on the curves, molar scale), calculated from eqn (3) with the parameters given in the text.