INTERFACIAL TENSION IN SYSTEMS: A BINARY SOLUTION OF NONPOLAR ORGANIC COMPOUNDS–WATER

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The dependence of the interfacial tension in ten systems of the type binary mixture of nonelectrolytes–water on the composition of the solution was measured in the whole concentration range at 20°C by determining the volume of the drop. The measured values were compared with those calculated according to a relation derived in our earlier work.

In our earlier work[1] we have derived a relation for calculation of interfacial tension in a ternary system composed of water and a solution of two organic substances perfectly immiscible with water. For the case when intermolecular forces acting between particles of water and both components of the solution are approximately equal to one another, this relation simplifies to

$$\sigma_i^{AB-C} = x_A \sigma_i^{A-C} + x_B \sigma_i^{B-C} + \sigma^{AB} - x_A \sigma^A - x_B \sigma^B , \qquad (1)$$

where σ_i^{AB-C} is interfacial tension, x_A and x_B are mole fractions of the organic components in the solution, σ_i^{A-C} and σ_i^{B-C} are the interfacial tensions of pure organic substances with respect to water, σ^{AB} is the surface tension of the solution and σ^A, σ^B are the surface tensions of pure components A and B. Eq. (1) enables one to calculate the interfacial tension of the solution from its surface tension and from the surface tensions of pure components.

To be able to verify agreement between this equation and experiment, the interfacial tension was measured in ten ternary systems of the type discussed above; the systems were selected so that they possibly conform to the given assumptions. The method of measuring the drop volume was chosen for determining the interfacial tension which was then computed from the relation

$$\sigma = VgF \, \Delta d / r , \qquad (2)$$

where V is the average volume of one drop, Δd the difference between densities of both

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phases, g acceleration due to gravity, r diameter of the capillary and F a correction factor, which is tabulated in the literature[2,3] as a function of $r/V^{1/3}$.

EXPERIMENTAL

Materials Used

Benzene (thiophene-free, Urxovy závody), chlorobenzene, pure (Lachema) and hexane, A.R. grade (Lachema) were dried on a 5A molecular sieve and fractionated on a 1 m-long column packed with Berl's saddles. Cyclohexane, A.R. grade (Lachema), was rectified on a 60-plate bubble cap column (Jena). Purity of toluene, UV spectroscopy grade (Lachema) and tetrachloromethane, A.R. grade (Lachema), was satisfactory. Besides the normal boiling points, refractive indices and densities of all examined substances were measured and compared with literature data[4] (Table I).

Apparatus

The employed apparatus is outlined on Fig. 1. Its main part is a thick-walled capillary 1 whose one end is ground and its other end is fused with the storage flask 2 of the volume of ~3 ml and with microburette 3 of the volume of 5 ml. The preliminary calibrated microburette is connected with a 10 ml syringe 4 whose piston is fixed by the attached spring 6 and may be shifted by screw 5. Through this arrangement, an extremely sensitive control of the formation of the drop is achieved. The ground capillary is sealed into the metal lid 7, whose connection with the external vessel 8 is waterproof. A second capillary passing through the metal lid serves for the pressure compensation during the measurement. The ground end of the capillary reaches into a smaller vessel 9, which is placed into the external vessel during the measurement. The whole apparatus is attached to a holder, which is firmly connected with the microscope stand. This allows one to push the apparatus into the thermostat without any vibrations and without changing the horizontal position of the ground end of the capillary. The constant temperature of 20°C was maintained by a water thermostat whose temperature was controlled with an accuracy of $\pm 0.1°C$.

TABLE I

Physical Constants of Employed Substances

Substance	Refractive index		Density	
	experimental	literature	experimental	literature
Benzene	1·4978	1·4978	0·8790	0·8789
Toluene	1·4938	1·4940	0·8670	0·8669
Chlorobenzene	1·5248	1·5246	1·1065	1·1061
Tetrachloromethane	1·4600	1·4602	1·5936	1·5940
Cyclohexane	1·4234	1·4235	0·7784	0·7785
Hexane	1·3740	1·3730	0·6618	0·6595

The ground end of the capillary constitutes the most important part of the whole apparatus. The magnitude of the drop is determined by the radius of the ground area. During the measurement of the interfacial tension, the drop grows either from the outer boundary of the thick-walled capillary — similarly to surface tension measurements[5] — or from its inner boundary, according to which of both phases wets better the glass surface. It was found that it is necessary for the sake of accuracy and reproduciblity of the measurements that the drop grow always from the outer boundary of the capillary. Thus, the capillary had to be filled with the aqueous phase in all the examined cases; this phase was in some cases lighter, in others heavier than the organic phase. Two apparatus were therefore employed for the measurements. After several tests with capillaries of different outer and inner diameters, the two following variants were selected: one with a straight capillary whose ground end had 0·11 cm I.D. and 0·656 cm O.D. for measuring systems where the heavier phase is dropping into the lighter one and the other with a bent capillary whose ground end was turned upwards and had 0·11 cm I.D. and 0·647 cm O.D. for the case when the capillary is filled with the lighter phase.

Technique

Even though the organic substances were selected so that they might not be possibly miscible with water, it was necessary to prepare the equilibrium phases by shaking the weighed solution of organic compounds with water in a separating funnel before the measurement. After 24 h of standing, both phases were separated and their density was determined by Reischauer's pycnometer of the volume of 25 ml at 20°C; each value was measured 4 times.

During the measurement of the interfacial tension, the capillary with the microburette filled with the aqueous phase was submerged at its ground end into the solution of organic substances in the inner vessel. The capillary surface must be wetted with water before submersion into the organic phase, so that a smooth meniscus may form over the entire surface of the ground end. In all experiments, the inner vessel was being filled to the same height even though it was found that the depth of submersion of the ground capillary end affects the volume of the resulting drop only little. Because during the actual measurements the height of the liquid surface in the inner vessel rose by less than 2 mm, the change of the height of the liquid column over the capillary end was negligible. The apparatus was then closed and placed into the thermostat. After 30—45 min of thermostating, the production of drops started with the help of the syringe. For better ac-
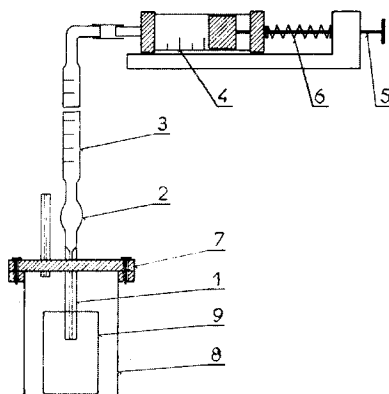

FIG. 1

Apparatus (for the description see the text)

curacy it is necessary that the drop arise extremely slowly so that equilibrium conditions at the interface may establish and the drop tears off only due to the gravity. It was established that the drop volume does not depend on the time of its formation if this time is longer than 3 min. It was produced so many drops as made possible by the volume of the microburette, and the average drop volume was calculated from the difference between the liquid levels. Each measurement was repeated at least 4 times.

The described technique was used for determining the dependence of the interfacial tension on the composition of the organic phase in the whole concentration range at 20°C for the following systems: benzene–cyclohexane–water, toluene–cyclohexane–water, benzene–chlorobenzene–water, toluene–chlorobenzene–water, benzene–tetrachloromethane–water, toluene–tetrachloromethane–water, chlorobenzene––tetrachloromethane–water, benzene–toluene–water, toluene–hexane–water, and cyclohexane–hexane–water. The average spread of experimental points was 0·5 to 0·8 erg/cm^2, which corresponds to an $1-2\%$ error. We have also determined densities of both equilibrium phases in these systems with an accuracy of $\pm 0·0002$ g/cm^3. The meassured values in individual systems are on Fig. 2 and in Table II. This table also contains differences between densities of both phases, wherefrom the region of applicability of the given experimental method may be deduced.
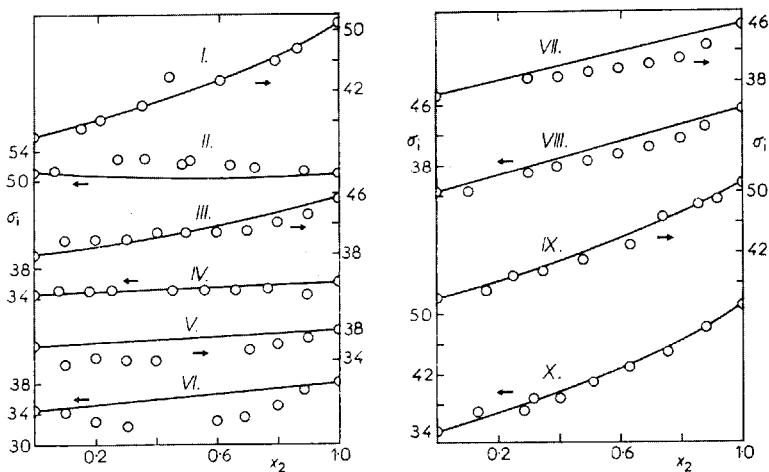

FIG. 2

Comparison of Curves Calculated According to Eq. (*1*) with Experimental Values of the Interfacial Tension in the Systems: Toluene–Hexane–Water(*I*), Cyclohexane–Hexane–Water(*II*), Chlorobenzene–Tetrachloromethane–Water(*III*), Benzene–Toluene–Water(*IV*), Toluene–Chlorobenzene–Water(*V*), Benzene–Chlorobenzene–Water(*VI*), Toluene–Tetrachloromethane–Water(*VII*), Benzene–Tetrachloromethane–Water(*VIII*), Toluene–Cyclohexane–Water(*IX*), Benzene––Cyclohexane–Water(*X*)

x_2 mole fraction of the second component.

TABLE II

Interfacial Tension σ_i (erg/cm^2) and Density Differences Between Both Phases Δd (g/cm^3) at 20°C in the Ternary Systems

x_1	Δd	σ_i	x_1	Δd	σ_i
cyclohexane(1)–benzene(2)–water			cyclohexane(1)–toluene(2)–water		
0·0000	0·1191	34·5	0·0000	0·1308	36·1
0·1358	0·1361	37·0	0·1645	0·1508	37·2
0·2836	0·1485	37·2	0·2491	0·1599	39·0
0·3141	0·1591	38·8	0·3475	0·1609	39·7
0·4062	0·1648	38·7	0·4778	0·1828	40·9
0·5136	0·1776	40·9	0·6322	0·1950	42·9
0·6304	0·1888	42·9	0·8389	0·2101	46·8
0·7599	0·2004	44·9	0·8676	0·2116	48·4
0·8834	0·2108	48·1	0·9219	0·2139	49·1
1·0000	0·2788	51·1	1·0000	0·2788	51·1
benzene(1)–chlorobenzene(2)–water			toluene(1)–chlorobenzene(2)–water		
0·0000	0·1075	38·0	0·0000	0·1075	38·0
0·1131	0·0856	37·1	0·0979	0·0836	37·0
0·2040	0·0654	34·8	0·1975	0·0586	36·6
0·3107	0·0436	33·6	0·2909	0·0369	35·5
0·4005	0·0242	33·0	0·4043	0·0049	—
0·4963	0·0045	—	0·4952	0·0131	—
0·6069	0·0201	—	0·6026	0·0384	34·0
0·6988	0·0439	32·6	0·6978	0·0645	34·1
0·7952	0·0651	32·9	0·7969	0·0857	34·6
0·8929	0·0904	34·1	0·8917	0·1066	33·6
1·0000	0·1191	34·5	1·0000	0·1308	36·1
benzene(1)–tetrachloromethane(2)–water			toluene(1)–tetrachloromethane(2)–water		
0·0000	0·5874	45·5	0·0000	0·5874	45·5
0·1202	0·5144	43·0	0·1145	0·5031	42·8
0·2037	0·4584	41·7	0·2023	0·4337	41·1
0·3042	0·3891	40·6	0·3029	0·3603	40·3
0·4060	0·3180	39·6	0·4002	0·2850	39·6
0·5059	0·2468	38·7	0·5018	0·2087	39·2
0·6090	0·1737	37·8	0·5986	0·1405	38·7
0·7005	0·1065	37·2	0·6986	0·0726	38·5
0·7959	0·0352	—	0·7986	0·0071	—
0·8948	0·0394	34·6	0·8982	0·0709	—
1·0000	0·1192	34·5	1·0000	0·13	36·1

TABLE II

(*Continued*)

x_1	Δd	σ_i	x_1	Δd	σ_i
benzene(1)–toluene(2)–water			tetrachloromethane(1)–chloroben-zene(2)–water		
0·0000	0·136	36·1	0·0000	0·1075	38·0
0·1024	0·1298	34·4	0·1007	0·1512	39·9
0·2354	0·1284	35·4	0·1985	0·2001	40·4
0·3413	0·1268	35·4	0·3032	0·2500	40·7
0·4418	0·1260	35·2	0·4012	0·2970	41·0
0·5485	0·1250	35·4	0·4997	0·3450	41·1
0·7461	0·1225	35·2	0·6001	0·3938	41·2
0·8197	0·1214	34·8	0·6998	0·4431	41·6
0·9219	0·1203	34·9	0·7997	0·4920	42·4
1·0000	0·1191	34·5	0·9006	0·5431	43·7
			1·0000	0·5874	45·5
cyclohexane(1)–hexane(2)–water			hexane(1)–toluene(2)–water		
0·0000	0·3309	51·0	0·0000	0·13	36·1
0·1104	0·3234	51·4	0·1543	0·1745	37·3
0·2722	0·3066	51·8	0·2178	0·1866	38·1
0·3535	0·2962	52·2	0·3550	0·2181	40·1
0·4866	0·2806	52·7	0·4467	0·2359	44·0
0·5102	0·2801	52·2	0·6114	0·2686	43·6
0·6338	0·2655	52·1	0·7928	0·3002	46·2
0·7233	0·2548	52·9	0·8685	0·3132	47·7
0·9311	0·2280	51·5	1·0000	0·3309	51·0
1·0000	0·2188	51·1			

DISCUSSION

It is obvious from Eq. (2) that if the difference between densities of the organic phase and water approaches zero, the drop volume grows to infinity and the interfacial tension cannot be determined by the outlined method. This case occurs in a certain concentration region in systems where the density of one organic compound is higher and that of the other lower than the density of water. Of the examined systems, four were of this type: benzene–chlorobenzene–water, toluene–chlorobenzene–water, benzene–tetrachloromethane–water, and toluene–tetrachloromethane––water.

Measured values of the interfacial tension were compared with curves calculated according to Eq. (1) (Fig. 2). The surface tensions of pure components, σ^A, σ^B, interfacial tensions of pure components with respect to water, σ_i^{A-C}, σ_i^{B-C}, and surface tensions of solutions, σ^{AB}, are for the examined substances either known from the literature[6-8] or they had been measured and published in earlier works[5,9].

As it is obvious from the figures, Eq. (1) approximates well the actual course of the interfacial tension in the benzene–cyclohexane–water, toluene–cyclohexane––water, benzene–toluene–water, and toluene–hexane–water systems. Calculated and experimental curves coincide within the range of experimental error. In all these cases, both components of the binary solution are hydrocarbons. The cyclohexane––hexane–water system is an exception because its experimental dependence of the interfacial tension exhibits a maximum whereas the calculated curve is almost linear. The maximum deviation between calculated and experimental values amounts to 5% for this system.

Concentration dependences of the interfacial tension in the benzene–tetrachloro-methane–water, toluene–tetrachloromethane–water, and chlorobenzene–tetrachloro-methane–water systems display a weak inflection point. Calculated curves do not reflect this characteristic shape even though the maximum deviations between experimental and calculated value are 4% for the benzene–tetrachloromethane–water and chlorobenzene–tetrachloromethane–water systems and 8% for the toluene–tetra-chloromethane–water system.

Curves of the interfacial tension in the benzene–chlorobenzene–water and toluene––chlorobenzene–water systems have distinct minima, whereas concentration dependences of the surface tension are almost linear. These systems exhibit largest differences between the calculated and experimental curve.

These results agree rather well with assumptions upon which Eq. (1) had been derived. The best agreement between experimental and calculated values is observed in systems where it may be assumed that both components of the binary solution behave similarly with respect to water and, on the contrary, largest deviations are found in systems where affinities of both organic compounds towards water differ considerably. In deriving Eq. (1), another assumption had also been made, namely that both phases are perfectly immiscible. This assumption was not fulfilled in any of the examined systems. As it has been stated earlier[1], it might be the reason for a relatively large change of the interfacial tension.

Even though no general conclusions can be drawn from such a small number of examined systems, we may say that Eq. (1) is suitable for estimation of interfacial tension in systems satisfying approximately assumptions on which it had been derived.

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