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Effect of Pressure on Interfacial Tension between Oil and Water

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Synopsis. The interfacial tension of hexane, octane, carbon tetrachloride and benzene against water was measured as a function of pressure up to 150 MPa at 303.15 K, using a newly designed apparatus. The interfacial tension showed definite increase with pressure and positive volume change was found on interface formation.

Several experimental studies have been carried out on the effect of pressure on interfacial tension between oil and water, but no coincidence of the results has been exhibited because of the lack of precaution for precise measurement.[1-6] It is necessary for the thermodynamic study of the interface to measure the exact pressure dependence of interfacial tension.

Experimental

A pendant drop method was adopted for measuring interfacial tension. This method is very satisfactory for the accurate evaluation of the interfacial tension between oil and water, but some precaution should be kept for precise measurement. We have newly designed an apparatus suitable for organic liquid/water interface. A schematic diagram of the apparatus designed here is shown in Fig. 1. The pressure vessel is a cylinder of stainless steel (SUS 27) 110 mm in o.d., 25 mm in i.d., and 420 mm in height, in which two quartz windows 12 mm thick and 20 mm in diameter are installed so that we can take the picture of pendant drop profiles by the camera. In order for the pendant drop cell to be free from contamination, which is caused by desorption of surface active impurities from the vessel, the cell is made of quartz, which consists of the syringe, the barrel shaped optical part, the drop forming tip, and the cylinder. The capacity of the cell is about 20 cm^3; the syringe and cylinder are filled out with water and organic liquid, respectively; and the pendant drop is formed by making use of the difference on their isothermal compressibility. Pressure was generated by means of a high pressure hand-pump and measured with a Heise bourdon gauge. Temperature was kept constant at 303.15 K by circulating thermostated water in the jacket of the pressure vessel.

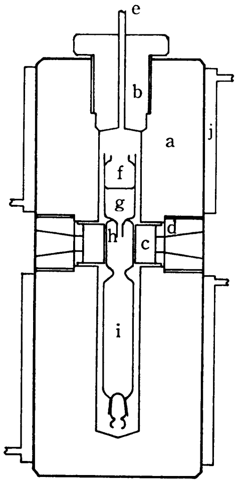

Fig. 1. Schematic diagram of the apparatus. a) Cylinder; b) flange; c) quartz window; d) window plug; e) pressure tubing with which the pressure pump and bourdon gauge are connected; f) plunger; g) syringe in which water is filled; h) drop forming tip; i) cylinder in which oil is filled; j) jacket.

Water used was refluxed with $KMnO_4$ and distilled. Organic liquids were purified by the usual method and the purity was checked by evaluating the interfacial tension at the atmospheric pressure. Water and organic liquids were stored together so that mutual solubilities were attainable.

Since the mutual solubilities of water–organic liquid systems are negligibly small, we used the density and compression data of pure water and organic liquids for the calculation of interfacial tension.[7-11]

The pendant drop cell was filled with water and organic liquid before it was set in the pressure vessel. Measurements of the interfacial tension were made under the condition of increasing pressure. For each rise in pressure, the apparatus was allowed to stand for 30 min so as to remove errors brought about by the adiabatic compression. Then the enlarged photograph of pendant drop was taken by the camera at each pressure. The dimensions of profile were determined to a precision of μm by Nikon Measurescope. The interfacial tension was calculated by using an equation proposed by Andreas *et al.*[12] and Fordham's correction factor was applied within a precision of ± 0.1 mN m^{-1}.[13]

Results and Discussion

The interfacial tension-pressure (γ-p) curves observed for organic liquid–water system are shown in Fig. 2. It is seen that the interfacial tension increases with an

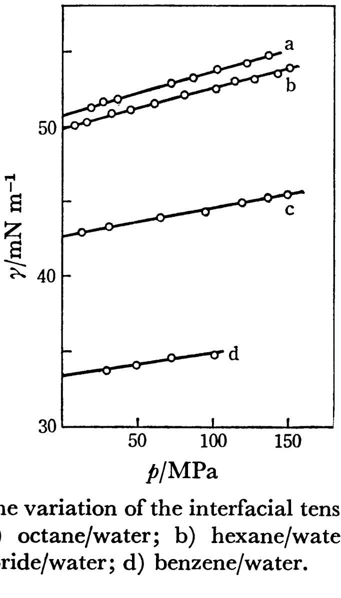

Fig. 2. The variation of the interfacial tension with pressure. a) octane/water; b) hexane/water; c) carbon tetrachloride/water; d) benzene/water.

increase in pressure and the slope of the curve is almost constant all over the pressure range investigated. The experimental equation expressing the interfacial tension as a function of the pressure is then formulated as

$$\gamma = a + bp \qquad (1)$$

The constants *a* and *b* were determined by the method of least squares. The values of *a* and *b* evaluated are given in Table 1. It is apparent that the slope of γ-p curve varies regularly with the value of interfacial tension, which is known to be correlated directly with the mutual solubility between organic liquid and water.[14] Some of these systems have been studied by several investigators. For benzene–water system, Hassan *et al.* observed for the slope to be negative,[3] Michaels *et al.* reported that the slope is positive at lower temperatures and negative at higher temperatures,[2] and Harvey observed that the γ-p curve has a minimum when temperature is low.[4] On the other hand, Jennings obtained the linear γ-p which bears a positive but very small slope.[5] The slopes obtained by these investigators are definitely small compared with those given in Table 1. Taking into consideration that they used pendant drop cells made of stainless steel with which water and organic liquids were in contact, it seems likely that the discrepancy among them can be ascribed to contamination by surface-active impurities, because it is found that the slope of γ-p curve is diminished by the adsorption of surface-active substances.[15]

TABLE 1. THE CONSTANTS OF THE Eq. 1 RESULTING IN THE BEST FIT TO THE EXPERIMENTAL DATA

	a/mN m^{-1}	b/mN m^{-1} MPa^{-1}
Octane	50.89	0.0287
Hexane	49.94	0.0259
Carbon tetrachloride	42.68	0.0188
Benzene	33.42	0.0138

According to the thermodynamics, the variation of interfacial tension with pressure at constant temperature is shown to be given by the equation

$$(\partial\gamma/\partial p)_{T,\sigma} = (\partial V/\partial\sigma)_{T,p} \qquad (2)$$

where V is the volume of the organic liquid–water system and σ the interfacial area.[16] The right-hand side of the above equation expresses the volume change ΔV accompanied by the interface formation. Applying this equation to the present data we see ΔV being positive, as shown in Table 1 as *b*.

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