

results in the disappearance of the pattern of the lead iodide while the PbO pattern remains. The lead iodide acts as a lubricant and thereby protects the PbO from distortion. This lubricating

action of the lead iodide arises from the weak forces existing between layers of iodide ions in the lead iodide crystals.

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Reproducible Contact Angles on Reproducible Metal Surfaces. III. Contact Angles of Saturated Aqueous Solutions of Different Organic Liquids on Silver and Gold

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Recent communications from this Laboratory have presented the results obtained in studies of water-air contact angles on silver and gold,¹ and of organic liquid-water interfacial contact angles on these same solids.² For each of these systems explanations were suggested for the "hysteresis" of the contact angles. The system solid-saturated aqueous organic liquid solution-air reported upon in this paper is even more complex than the two types of systems previously discussed, and though angles can be reproduced readily by controlled procedures, the factors which may contribute to the "hysteresis" of these contact angles are more numerous and more complex than those encountered in the other systems.

The liquids used in this investigation were "conductivity" water, isoamyl alcohol, normal butyl acetate, benzene, α -bromonaphthalene and heptane. The organic liquids were of the same high degree of purity as those previously used. The procedure for the formation and measurement of contact angles and the method for preparing reproducible surfaces of silver and gold have been described in a previous paper.¹

Three different groups of solution contact angles were measured. Angles formed by solution drops on initially fresh and clean surfaces of silver and gold comprised the first group, angles formed by solution drops on solids which had stood in air saturated with water and organic liquid vapors comprised the second, and angles formed by air bubbles on solids in saturated aqueous organic liquid solutions comprised the third group. The contact angles reported for both drop and bubble systems are the angles measured through the aqueous solution phase.

When a drop of saturated aqueous organic liquid

solution was placed upon a fresh and clean solid surface, in a cell with air saturated with water vapor alone, the angle measured immediately after formation of the drop was not reproducible. Initial air adsorption upon the metal surface was so rapid that exact duplicates could not be obtained for these initial angles. When the solution drop was left stationary on the solid for a short period of time and was then caused to advance by adding solution to increase the volume of the drop, the value of the contact angle of the advanced drop was not the same as that of the original drop. This change in the contact angle appeared to be much greater than would have been caused by further adsorption of air by the solid during the short period of time that the solution drop was allowed to stand on the solid, since after the initial rapid air adsorption the rate of air adsorption appears to decrease.¹ It was concluded that organic liquid must have evaporated from the solution drop into the air of the closed cell and subsequently have been adsorbed by the solid and that this adsorbed organic liquid caused part of the change.

Reproducible contact angles of solution drops on silver and gold surfaces could be obtained when these metal surfaces were exposed for sufficient periods of time to air saturated with the vapors of the given aqueous organic liquid solution. Values obtained for angles measured in air saturated with the vapors of the given solutions are shown in Table I. The advancing angles of Table I are the angles measured immediately after the drops were formed upon the surfaces which had been allowed to stand in contact with the vapors. The receding angles were obtained by immediately withdrawing the solution-drop once it was formed. On solids exposed to the vapors for a few seconds only, the receding angles were smaller than the

(1) Bartell and Cardwell, *THIS JOURNAL*, **64**, 494 (1942).

(2) Bartell and Cardwell, *ibid.*, **64**, 1530 (1942).

TABLE I
CONTACT ANGLES
SOLID-SOLUTION DROP-AIR SATURATED WITH WATER VAPOR AND ORGANIC LIQUID VAPOR

Satd. aqueous soln. of org. liq.	Time metal surfaces were in contact with the vapors	Angle on silver		Angle on gold	
		Advancing	Receding	Advancing	Receding
Isoamyl alcohol	Few seconds	36	7	25	5
	12 hours	36.5	37	25	23
	18 hours			25	25
<i>n</i> -Butyl acetate	Few seconds	61	15.5	50	0
	12 hours	64.5	41	51	29
	18 hours			51	35.5
	6 days	64.5	64		
	7 days			51	51
Benzene	Few seconds	72	25	61.5	0
	12 hours	86	45	63	16.5
	18 hours			72.5	25
	6 days	90	90		
	7 days			83.5	83
α -Bromonaphthalene	Few seconds	71.5	14	61	0
	12 hours			80	7
	18 hours	95	69		
	6 days	96	90	94.5	76
	7 days				
Heptane	Few seconds	91	74	85.5	9
	12 hours	103.5	103		
	18 hours			101	71
	7 days			101	101

advancing angles. This was probably the result of a partial removal of an incomplete adsorbed film by the solution-drop. Solids on which there was maximum adsorption of the organic liquid vapors gave advancing and receding angles which were equal or nearly equal when the drop was receded immediately. Drops allowed to stand on the solids even for short periods of time before being receded gave receding angles somewhat smaller than those of Table I, while drops allowed to stand for long periods of time gave receding angles approaching zero, which indicates that the adsorbed films of the organic liquids on the solids were gradually being removed by the solution-drops. It is of interest to note that the values of the contact angles given by solution-drops on adsorbed organic liquid films increase progressively with the hydrophobic nature of the organic liquid.

Contact angles formed by air-bubbles on surfaces immersed in saturated aqueous organic liquid solutions are given in Table II. The solution receding contact angles reported in this table were those formed as soon as the air-bubbles were advanced. The magnitude of the angles formed when the air-bubbles were withdrawn, solution advancing, depended upon the length of time the air-bubbles were left on the metal surfaces. The

longer the air-bubbles were allowed to stand on the solids before being withdrawn, the larger were the solution advancing angles. The solution advancing angles reported in Table II were obtained with air-bubbles which had stood on the metal surfaces for one minute before being withdrawn.

TABLE II
CONTACT ANGLES OF SOLID-SOLUTION-AIR BUBBLE

Satd. aqueous soln. of org. liq.	Angles on silver		Angles on gold	
	Advancing	Receding	Advancing	Receding
Isoamyl alcohol	47	22	43	21
<i>n</i> -Butyl acetate	58	36	48	33
Benzene	65	33	61	28
α -Bromonaphthalene	73	47.5	65	40
Heptane	74	37	66	34.5

Individual angle measurements for all angles reported showed a maximum variation of $\pm 1^\circ$ and in many cases the variation was less than $\pm 0.5^\circ$.

Discussion of Results

In the water drop and air bubble systems previously studied,¹ drop and bubble measurements were identical, within the limits of experimental error, when corresponding states were reproduced. In the solid-liquid-liquid systems previously reported² corresponding water drop and organic

liquid drop measurements were also identical, within the limits of experimental error. The contact angle values obtained for solution drops and air bubbles in the present study were not identical.

In the solid-solution-air systems the air adsorption factor, operative also in solid-water-air systems, has an effect; and at the same time the organic liquid adsorption factor, operative also in solid-liquid-liquid systems, has *two* effects. Organic liquid appears to be adsorbed on the solid surface both from saturated air and from saturated solution. The solid appears to adsorb a more complete layer from saturated air than can exist in equilibrium under a saturated solution, however, and the solution accordingly tends to remove both adsorbed air and adsorbed organic liquid. Water adsorption appears to be a negligible factor in any of the three systems. With such varied processes of adsorption and such different rates of adsorption and desorption as the measurements indicate, exactly corresponding states for drop and bubble would be very difficult, if not impossible, to achieve. Corresponding states were not achieved in the present study and the measurements on drop and bubble were, therefore, not identical.

Factors capable of causing hysteresis of contact angles were numerous and were effective to different degrees for each change of system. It was possible to obtain advancing and receding angles of the same value, however, and the method of obtaining such angles was similar to that used with the two previously described less complex systems. On solids left for long periods of time in atmospheres saturated with organic liquid, solution drops gave advancing and receding angles of the same value when the solution was immediately receded after being advanced.

It has been realized from the beginning of work on contact angles in this Laboratory that the sur-

face tension of identical solid surfaces does not always remain strictly constant when the solid is used in different systems. For some systems it probably is so nearly constant, or changes in the tension are so nearly identical, that combinations of equations effected by cancelling surface tension values of solid can give valuable information. The work reported in all three of the papers of this series re-emphasizes, however, that conclusions drawn from all such equations and from similar equations for solid-liquid-liquid systems must be subjected to careful analysis before their validity can be considered to be established.

Summary

Measurements have been made of the contact angles of drops of saturated aqueous organic liquid solutions on silver and gold in air and of air bubbles on silver and gold in saturated aqueous organic liquid solutions.

These measurements indicate that the metal surfaces adsorb air and adsorb also organic liquid both from air and from aqueous solution. A drop of solution caused to advance by stages over a fresh metal surface gives a different angle each time it is advanced because of evaporation of organic liquid into the air and subsequent adsorption of the vapor on the exposed metal.

Because of these complex adsorption conditions identical surface states for drop and bubble systems were not achieved, and, consequently, identical angles for the two systems were not obtained.

Identical advancing and receding angles were obtained for drops caused to recede immediately after they had been advanced on metal surfaces which had previously stood in the given aqueous solution vapors for sufficient time to attain adsorption equilibrium.