Studies on the Equilibrium between the Dilute Solution and Solute Vapour. II.(1)

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Part III. Factors Affecting the Condensation Coefficient (α) of Solute Vapour.

(9) *Relations between α and some physical properties of solvents* (L). No direct parallelism between α of iodine and some physical constants of L, surface tension σ, internal pressure, solubility, thermal conductivity (rapid vanishing of the heat of adsorption at the liquid surface was supposed to prevent re-evaporation of a solute molecule and to result in the increase of α) and the diffusion coefficient of iodine is not observed.

The potential difference measured by Frumkin(*) for aqueous solutions (or the estimated values from his data) is given in Table 7 and 8. This is governed by the orientation of water or adsorbed molecules and the distribution of ions near the surface. α of iodine seems to be entirely independent of its sign and magnitude. Though α of methanol (dipole moment$=1.68\times10^{-18}$ e.s.u.) is given below, the result of an analysis of a minute amount of it is not exact enough to decide whether the observed effects are true or not.

L	H_2O	$MgSO_4$ 1 mol. aqueous solution	i-$C_4H_9CO_2H$ 0.11 mol. aqueous solution
Surface potential difference (mv.)	—	+3	+300
(α at 15°C.) 10^4	6.2	7	8

(10) *Addition of electrolytes.*

Table 7. α of I_2 for Aqueous Solutions of Electrolytes. (See Fig. 8.)

Electrolyte	$MgSO_4$	KNO_3		H_2SO_4		
Conc. mol./l.	1	1		0.5	0.05	0.005
t°C.	25	25	12	22	21.7	20
α/(α for H_2O)	0.58	0.92	1.0	0.60	0.80	0.94
Ratio of solubility of I_2	0.47	0.872			1.01	
Surface potential in mv.	+3	—ca. 10		—7		
$\Delta\sigma$ dyne/cm.	+2.49	0.816		0.234		

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(1) I. Uhara, this Bulletin, **18** (1943), 412.

* See (9) in the preceding paper, *loc. cit.*

Ions are repelled from the liquid surface by the image force or large interaction with water. According to S. OKA⁽²⁾, the distribution of ions near the surface of an aqueous solution (0.05 mol./l.) of 1–1 type electrolyte is as follows:

Distance from surface (A)	0	0.5	1	2	5	20
Conc./conc. of bulk solution	0.0	0.0	0.05	0.26	0.71	0.99

The layer of pure water at the surface of a salt solution is concluded to be 3.3–4.2 A thick (monomolecular) from the increase of σ.⁽³⁾ Therefore, mere collision of an iodine molecule with a surface does not lead to the chemical reaction with ions in the solution. As the negative adsorption of ions takes place very rapidly, the obtained α is that for normal surface. In the aqueous solution of electrolyte and non-electrolyte, due to the electric field around ions, the component of a higher dielectric constant (water) is pulled preferentially into the field and the one of a lower dielectric constant (non-electrolyte) is forced out.⁽⁴⁾ The same repulsion may act on S molecules at the surface, decreasing α. Ions with many charges have large effect at equal distance, but as they exist deep in the liquid, the influence on α is not simply predicted.

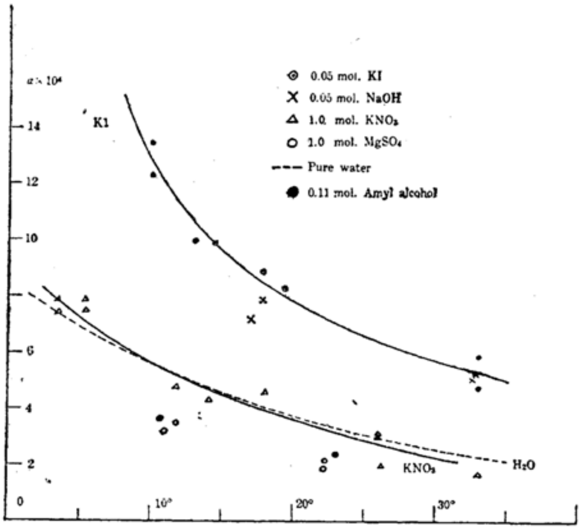

Fig. 8. α of Iodine on aqueous solution.

(11) *The case where chemical reaction takes place between the solute and the solvent.*

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(2) *Proc. Physi.-Math. Soc. Japan,* **14**(1932), 656.

(3) Langmuir, *J. Am. Chem. Soc.,* **39**(1917), 1897.

(4) Theory of salting-out effect by Debye, *Z. physik. Chem.,* **130**(1927), 56.

Table 8. α for Aqueous Solutions of Electrolytes Which React with S. $S = I_2$.

Electrolytes	NaCl(5)	HCl			KI (Fig. 8)			NaOH(6)		KOH
Conc. mol./l.	1	1	0.05	0.001	0.05			1	0.05	0.01
t°C.	20	17.2	18.2	18.2	25	15	10	20	20	16.3
α/(α for H_2O)	1.50	1.13	1.28	0.98	2.25	2.10	2.09	1.55	1.91	3.01
Ratio of solubility of I_2	1.70	2.76	1.09	1.00	19.3					
Surface potential (mv.)	−1	−23			−2			+0		+

	$S = HCl$		$S = NH_3$	
L	H_2O	0.05 N NaOH aq.	H_2O	0.5 N HCl aq.
t°C.	28.4	29	16	15
$\alpha \times 10^4$	1.89	1.67	48	49.5 (by alkalimetry)
α(/α for H_2O)		0.88		1.03

When the solution contains the electrolytes which can combine with iodine, perhaps iodine molecules vibrating in an adsorbed state at the surface have a chance to combine with them before re-evaporation, as ions exist only in the interior of the liquid. As the counter influence of ionic charge becomes effective with the concentration of electrolyte, more concentrated solutions do not necessarily show higher values of α. The absorption velocity of ammonia by water and acid is the highest value obtained, probably due to its ability to combine with water molecules at the surface (immersion in liquid is not necessary in these cases).

Small value of hydrogen chloride compared with equally high solubility in water (750 c.c. of ammonia, 451 c.c. of hydrogen chloride in 1 c.c. of water at 18°C. is explained as follows: the hydrogen chloride molecule itself shows no large affinity (Van der Waals' a is small) to water and it is only after the dissolution and ionization into $H_3O^+ + Cl^-$ that its high affinity to water is observed. The action of alkali is also for H_3O^+ and not for hydrogen chloride, hence no accerelating action is observed, as α is related to the phenomena before the dissolution. Ionization, however, shows some analogous effect to that of chemical reaction on α, and α of hydrogen chloride for water is considerably larger than those for various non-ionizing L (Table 1.). It depends on the difference in mechanism that the effect of reactable substances in solution on α is far less than in the case of ordinary absorption under bubbling or stirring (§ 13).

Next, the eqilibrium of I_3^- in 0.05 N potassium iodide aqueous solution (25°C) is discussed. $I^- + I_2 = I_3^- + 13.2$ kcal., $(I^-)(I_2) = (I_3^-)\ 0.00136$. The solution dissolves 25.77×10^{-3} mol./l. I_2 and the composition of this mixture is $(I^-)\ 25.65 \times 10^{-3}$, $(I_2)\ 1.42 \times 10^{-3}$, $(I_3^-)\ 24.35 \times 10^{-3}$ mol./l. α of iodine for 0.05 N potassium iodide aqueous solution and water are 7.0×10^{-4} and

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(5) Formation of ClI_2^- is proved from partition coefficient determination. Rây and Sarkar, *J. Chem. Soc.*, **121** (1922), 1449.

(6) For the analysis of I_2, the contact with organic substances must be avoided.

3.11×10^{-4}, and this difference is attributed to the above-mentioned reaction (the repulsion effect is negligible owing to the low concentration). As about half of I^- is left uncombined in the mixture and can catch iodine molecules at the surface, we may assume that α equals 4.8×10^{-4} for this mixture. For the equilibrium of the vapour and the solution, we can write, assuming β_1 and W of iodine are the same as in pure water,

$$\alpha p\, 10^3/RT = (\beta_1 C \sqrt{M/M'}\, e^{-W/RT})_{I_2} + (\beta_1 C \sqrt{M/M'}\, e^{-W/RT})_{I_3^-}$$

$$8.0 \times 10^{-9} = 5.56 \times 10^{-9} + 1.12 \times 10^{-11} \qquad \therefore \quad \beta_1 \text{ of } I_3^- = 220\,,$$

from $$\beta_1 = \beta_2 \left\{1 + 2\frac{W}{RT} + \frac{1}{2}\left(\frac{W}{RT}\right)^2\right\}, \qquad \beta_2 = 0.76. \quad \text{(See § 6.)}$$

(12) *Influence of surface active substances.*

Table 9. α of I_2 for Aqueous Solutions of Surface Active Substances.

	C_2H_5OH		$C_5H_{11}OH$		*sec*-$C_8H_{17}OH$	$C_9H_{19}CO_2H$	$C_{17}H_{35}CO_2Na$
1/(mol.fraction)	3	500	500		10^4	$>10^5$	15000 (new solution)
t°C.	33.3	23.3	23.0	10.7	22.1	33.0	24.0
$\frac{\alpha}{\alpha \text{ for } H_2O \text{ at } t°C.}$	1.39	1.07	0.72	0.67	0.45	0.73	0.25
$\frac{\alpha \text{ for pure org. subst.}}{\alpha \text{ on } H_2O \text{ at } 20°C.}$	1.19		1.7				
Surface potential (mv.)	+370		+250		+ca. 50	+70	−30

Rough parallelism is seen between (α for water)/α and following quantity: (quantity at the surface) × (length of alkyl radical) $\propto \left(-\frac{d\sigma}{dC}\right) \times$ (Conc.) × (the number of C in alkyl). That the mere existence of alkyl at the surface cannot be the cause of the decrease of α is apparent from higher α of pure hydrocarbons and higher alcohols or the aqueous solution of ethanol. A higher alcohol molecule at the water surface lies flat like a rod, with one side exposed in the air (§ 8). It may be supposed that iodine molecules colliding with the part are adsorbed less firmly than those colliding with smooth water surface, therefore such a diminution of effective area for dissolution results in the decrease of α. Considerable depression of α (not due to reducing impurities as were ascertained by the blank test) shows the existence of these solutes in a considerable amount at the surface in spite of the short time (under 0.01 sec.) that the liquid from the point of thin glass tube contacts with the vapour.

For *sec*-octyl alcohol solution, concentration = 3 molecules in $(100\,A)^3$. α is 45% of water, and then if assumed that about half of the surface of water is covered by these molecules (about 50 A^2 per molecule when it lies) 100 molecules per $(100\,A)^2$ are necessary, which is the quantity contained in the solution of 3000 A thick. As there is almost no concentration gradient in the solution, it is unable to bring this amount to the surface by diffusion in 1/200 sec., and σ of newly formed surface of the aqueous solution of surface active substances requires time 0.01–1.0 sec, sometimes over a few minutes till it shows a constant value, indicating the slowness of diffusion. According to the measurement of σ by the vibrating-jet method, the soap solution(7) of the same concentration used in our experiments shows the same value as water (the surface is about 0.01 sec. old), while the static method gives a value which is only 47% of that of water. This descrepancy may be explained by the following assumption: S is concentrated near the glass wall then flows down as in Fig. 9(a), stream lines being kept undisturbed (as the liquid in direct contact with the wall does not move, this adsorption must be multi-molecular)(8). The suspension of powdered glass in water increased its stability on adding minute quantity of amyl alcohol, presumably favouring the foregoing assumption. In the dynamical method of σ measurement, stream lines are disturbed and the stirring of a solution takes place. (Fig. 9 b, c).

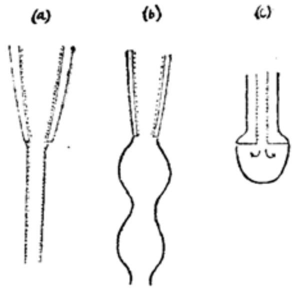

Fig. 9.

(13) *Relation between α and ordinary absorption velocity (V) of gas or vapour.* When acetone vapour of low pressure is sent on water surface stirred (170 r.p.m.) values 2.2–3.3 × 10^{-5} are obtained as α, while real value is far larger, 4.4 × 10^{-4}. In ordinary absorption, S accumulates near the liquid surface owing to slow diffusion in liquid, and re-evaporation takes place in consequence of partial pressure determined by Henry's law, hence V increases remarkably with solubility, while α, being governed by conditions of the first step of dissolution, is of the same order of magnitude for one solute, no parallelism with solubility observed. Condensation coefficient (α') calculated from the results of some bubbling methods convenient to measure initial velocity (V_0) of absorption is compared with α by the author's method.

	$V_0 \frac{\text{c.c./sq. cm.}}{\text{min.}}$	α'	α
HCl into H_2O	54.30(9)	0.91×10^{-4} (22°C.)	1.89×10^{-4} (28.4°C.)
NH_3 into H_2O	ca. 1800(10)	20×10^{-4}	48×10^{-4} (16°C.)

Though about half values of α are obtained in these cases due to large solubility and little re-evaporation, α' will be far less than α for less soluble gases, therefore α cannot be obtained by bubbling or stirring methods.

The effect of surface active impurity on absorption velocity of vapour. Here also, the difference between α and V is shown characteristically.

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(7) Rayleigh, *Proc. Roy. Soc.*, A, **47**(1890), 281.

(8) H. Akamatu, J. *Chem. Soc. Japan,* **17**(1942), 141, 161, 260, showed the existence of multi-molecular adsorption of lower fatty acid in benzene at the glass surface.

(9) Becker, *J. Ind. Eng. Chem.*, **16**(1924), 1223.

(10) Ledig and Weaver, *J. Am. Chem. Soc.*, **46**(1924), 650.

Table 10. Comparison between α and V on Aqueous Solution at Rest. $S = I_2$.

Impurity	Fat	$C_5H_{11}OH$	*sec*-$C_8H_{17}OH$	$C_{17}H_{35}CO_2Na$ (new solution)		
1/(mol. fraction)	monolayer	500	10^4	1.5×10^4	10^5	2×10^5
$\alpha/(\alpha$ for $H_2O)$	—	0.70	0.45	0.25		0.78
$V/(V$ for $H_2O)$	1.0	1.9	2.4		0.63	

It is quite natural that a fat layer has no effect on V, because the difusion velocity of iodine accumulated in the liquid near the surface is rate-determining. In an aqueous solution of a higher alcohol, the surface concentration is far higher than that of bulk solution (§ 8), and as this portion of the solution shows larger solubility than water for iodine, diffusion becomes faster by larger concentration gradient towards the interior. Effects on α and V are entirely reversed due to the difference in mechanism. Soap in solution is ionic and does not increase solubility of iodine, and moreover the space for iodine may be greatly diminished owing to remarkable adsorption and large molecular dimension.

V measured under stirring or flowing liquid is intermediate between two extreme cases above-mentioned.

Riou⁽¹¹⁾ and others stated that the velocity of absorption of carbon dioxide by flowing sodium carbonate solution is increased by the addition of substances which depress σ, but this does not coincide with our results for soap solution. In general, it may be concluded as follows:

(a) When liquid surface is renewed very quickly and the pressure of S is low (seldom met in practice), V is determined by α. A large molecule of strong surface activity depresses V.

(b) In most usual cases in which diffusion velocity at the surface is rate-determining, addition of a substance which increases solubility of a solute (with more solubility for S than water and it is better if it is surface active) is effective to increase V, e.g. methanol dissolves four times of carbon dioxide than water and addition of 2% methanol in sodium carbonate aqueous solution can increase V of carbon dioxide by 20%. Viscosity has no direct relation with V.⁽¹¹⁾

The effect of surface active impurity on evaporation of the solute. The evaporation velocity of iodine from aqueous solution is almost unaffected by addition of amyl alcohol, as the partial pressure of iodine is unchanged though its concentration is increased at the surface. To prevent evaporation of S, substances which can cover the surface without increasing solubility of S must be added.

(14) *The influence of T.* The existence of potential barrier at the interface of gas and liquid may be supposed from small values of α, which results in the increase of α with rising T, $(d\alpha/dT>0)$, and the same conclusion is also drawn out from a simple model of dissolution mechanism that the gap among liquid molecules at the surface is broadened with

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(11) *Compt. rend.*, **174**(1922), 1017, 1463; **184**(1927), 325; **186**(1928), 1543, 1727; Killeffer, *J. Ind. Eng. Chem.*, **29**(1937), 1293.

rising T. As a matter of fact (§ 4), however, a decreases considerably with T, and log a and $1/T$ are related linearly to data with comparatively high accuracy, hence

$$a = D\,e^{+A/RT} \tag{14}$$

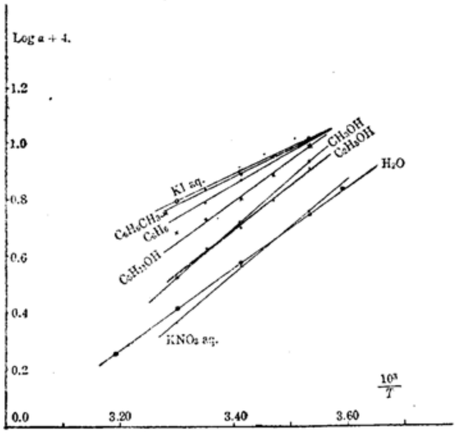

Fig. 10. The temperature dependence of α of iodine on various solvents.

Table 11. $S = I_2$. W = Heat of Solution of Vapour.

L	$A \frac{\text{kcal.}}{\text{mol.}}$	A/W	D
H_2O	6.54	0.68	4.86×10^{-9}
1N KNO_3 aq.	7.66	—	7.04×10^{-10}
0.05N KI aq.	4.31	—	4.68×10^{-7}
C_2H_5OH	7.11	0.54	2.48×10^{-9}
CH_3OH	8.02	0.62	5.26×10^{-10}
$C_5H_{11}OH$	6.61	—	7.36×10^{-9}
$C_6H_5CH_3$	4.48	0.48	3.68×10^{-7}

Summary.

(1) Various factors affecting condensation coefficient of solute vapour on the liquid surface of solvents (chiefly a of I_2) were studied.

(2) a has no parallelism with many physical quantities of solvents (surface tension, solubility etc.).

(3) Effects of addition of electrolytes, surface active non-electrolytes, reactable substances were discussed.

(4) a decreases with rising temperature.

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