

278. *The Distribution of the Lower Fatty Acids between Water and a Variety of Solvents.*

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The distribution of acetic acid and of propionic acid between water and a variety of relatively immiscible solvents has been examined experimentally at various concentrations and temperatures.

The increase in internal energy attending the dissociation of the double molecules, which is 14·5 kcal. in the vapour phase, is about 9 in typical un-ionising media such as benzene, *n*-hexane, and light petroleum, and about 6 in ionising solvents such as chloroform, chlorobenzene, and nitrobenzene.

The results for the two acids in the eight solvents used are consistent with the view that the force of attraction between the constituents of the dimers is principally if not entirely electrostatic.

WHEN a monobasic acid ionises to an extent, α , in water, and forms double molecules in a second solvent, *s*, with which the aqueous solution is in equilibrium, the total concentrations, C_w and C_s , in the water and in the second solvent are related to each other as follows :

$$C_s/[C_w(1 - \alpha)] = K_1 + 2K_1^2C_w(1 - \alpha)/K_2 \dots \dots \dots (1)$$

where K_1 and K_2 are the equilibrium constants governing, respectively, the transfer of un-ionised monomeric molecules from the aqueous layer to the other solvent [$\text{HA (water)} \rightleftharpoons \text{HA (solvent)}$], and the dissociation of the dimer in the non-aqueous layer [$(\text{HA})_2 \rightleftharpoons 2\text{HA}$]. In two earlier treatments of this distribution problem (Hendrixson, *Z. anorg. Chem.*, 1897, 13, 73; Moelwyn-Hughes, *J.*, 1940, 850), the factors 2 and α , respectively, were omitted.

Equation (1) satisfactorily accounts for the distribution of acetic acid between (*a*) water and (*b*) *n*-hexane, benzene, carbon tetrachloride, carbon disulphide, chlorobenzene, and nitrobenzene, and of propionic acid between (*a*) water and (*b*) light petroleum (b. p. 110—120°), carbon tetrachloride, benzene, chloroform, chlorobenzene, and nitrobenzene. The range of concentration used was such that the highest aqueous concentration was about *N*. The acids were purified by crystallisation, and the solvents by fractional distillation after appropriate treatment, *e.g.*, with mercuric sulphate in the case of carbon disulphide, dilute sodium hydroxide solution in the case of chlorobenzene, alkaline permanganate in the case of hexane, and phosphoric oxide in the case of nitrobenzene. The experimental method did not differ significantly from the conventional. Values of α were calculated from known ionisation constants (Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, 55, 652, 1379; Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1943). The units in which K_2 , the entropy *S*, and the heat content *H* are given in Tables I and II are, respectively, g.-mol. per l., cal. per g.-mol. °K., and kcal. per g.-mol. We accept 14·49 kcal. as the most reliable value of ΔH_2 for acetic acid in the vapour phase (Ritter and Simons, *J. Amer. Chem. Soc.*, 1945, 67, 757; cf. 14·57 found for acetic acid by Fenton and Garner, *J.*, 1930, 694, 14·03 \pm 0·20 found

for acetic acid by Johnson and Nash, *J. Amer. Chem. Soc.*, 1950, **72**, 547, and 14·125 given for formic acid by Coolidge, *ibid.*, 1928, **50**, 2166). Compared with this value, those of 16·4 for acetic acid (McDougall, *ibid.*, 1936, **58**, 2585) and of $18\cdot5 \pm 2$ for propionic acid (*idem, ibid.*, 1941, **63**, 3420) appear to be high. The equilibrium constants for the two gaseous dimerisations given

TABLE I.

Acetic acid.

Solvent.	Temp. (° K.)	10^3K_1 .		10^3K_2 .		ΔS°_1 .	ΔH_1 .	ΔS°_2 .	ΔH_2 .
		Obs.	Calc.	Obs.	Calc.				
None	308·10	—	—	0·072	—	—	—	—	—
$n\text{-C}_6\text{H}_{14}$	298·15	1·43	1·445	1·17	1·170	3·40	$4\cdot89 \pm 0\cdot25$	16·70	$8\cdot98 \pm 0\cdot54$
	308·15	1·89	1·892	1·925	1·926	—	—	—	—
	318·15	2·425	2·426	3·05	3·044	—	—	—	—
C_6H_6	298·15	8·9	8·75	7·68	7·67	3·91	$3\cdot97 \pm 0\cdot16$	17·79	$8\cdot19 \pm 0\cdot68^*$
	308·15	10·9	10·86	12·40	12·04	—	—	—	—
	318·15	13·2	13·34	18·27	18·31	—	—	—	—
CCl_4	298·15	3·55	3·549	2·07	2·066	2·17	$3\cdot99 \pm 0\cdot29$	13·07	$7\cdot56 \pm 0\cdot74$
	308·15	4·38	4·417	3·11	3·134	—	—	—	—
	318·15	5·42	5·421	4·60	4·605	—	—	—	—
CS_2	290·1	1·49	1·491	1·38	1·370	2·64	$4\cdot52 \pm 0\cdot23$	11·20	$7\cdot05 \pm 0\cdot43$
	300·1	1·95	1·930	2·02	2·054	—	—	—	—
	310·1	2·47	2·469	3·06	3·017	—	—	—	—
$\text{C}_6\text{H}_5\text{Cl}$	298·15	7·50	7·49	7·08	7·06	-0·55	$2\cdot74 \pm 0\cdot24$	7·00	$5\cdot02 \pm 0\cdot34$
	308·15	8·70	8·72	9·39	9·37	—	—	—	—
	318·15	10·03	10·04	12·06	12·10	—	—	—	—
$\text{C}_6\text{H}_5\text{NO}_2$	298·15	36·1	36·1	136	136	4·94	$3\cdot44 \pm 0\cdot11$	7·20	$5\cdot25 \pm 0\cdot42$
	308·15	43·7	43·7	180	182	—	—	—	—
	318·15	52·0	52·2	238	237	—	—	—	—

* Cf. 9·70 (*J.*, 1940, 850). A repetition of the distribution between benzene and water, carried out after communication of this paper, gave $8\cdot80 \pm 0\cdot2$.

TABLE II.

Propionic acid.

Solvent.	Temp. (° K.)	10^3K_1 .		10^3K_2 .		ΔS°_1 .	ΔH_1 .	ΔS°_2 .	ΔH_2 .
		Obs.	Calc.	Obs.	Calc.				
None	308·10	—	—	0·034	—	—	—	—	—
Light petroleum	293·2	7·03	7·02	7·41	9·29	6·692	$4\cdot855 \pm 0\cdot040$	17·62	$9\cdot37 \pm 0\cdot06$
	303·2	9·23	9·23	12·53	12·53	—	—	—	—
	313·2	11·90	11·91	20·56	20·56	—	—	—	—
	323·2	15·16	15·17	32·80	32·81	—	—	—	—
CCl_4	293·2	16·0	16·0	1·25	1·25	5·222	$3\cdot940 \pm 0\cdot20$	12·06	$7\cdot43 \pm 0\cdot25$
	303·2	20·1	20·0	1·93	1·91	—	—	—	—
	313·2	24·6	24·6	2·81	2·83	—	—	—	—
C_6H_6	293·2	42·8	42·9	6·17	5·96	7·16	$3\cdot935 \pm 0\cdot125$	16·25	$7\cdot75 \pm 0\cdot56$
	303·2	53·8	53·6	9·26	9·30	—	—	—	—
	313·2	65·8	65·9	13·7	13·94	—	—	—	—
	323·2	80·2	80·2	20·8	20·52	—	—	—	—
CHCl_3	293·2	162	162·5	29·8	29·7	5·49	$2\cdot67 \pm 0\cdot14$	15·72	$6\cdot66 \pm 0\cdot12$
	303·2	190	188·8	43·1	43·3	—	—	—	—
	313·2	218	217·7	61·6	61·5	—	—	—	—
	323·2	247	248·2	85·4	85·7	—	—	—	—
$\text{C}_6\text{H}_5\text{Cl}$	293·2	367	368·0	5·79	5·75	8·70	$3\cdot135 \pm 0\cdot16$	11·19	$6\cdot29 \pm 0\cdot21$
	303·2	441	438·3	8·56	8·19	—	—	—	—
	313·2	516	517·4	11·4	11·44	—	—	—	—
	323·2	607	606·4	15·7	15·64	—	—	—	—
$\text{C}_6\text{H}_5\text{NO}_2$	298·2	159	161·4	150	151·0	5·76	$2\cdot80 \pm 0\cdot21$	15·92	$5\cdot87 \pm 0\cdot57$
	323·2	234	232·7	317	324·4	—	—	—	—
	350·4	328	325·6	681	660·9	—	—	—	—

in Table III have been obtained from the published values after extrapolation and conversion of units. The dielectric constants D , and the characteristic reciprocal temperatures, $L = \frac{1}{D} \left(\frac{dD}{dT} \right)_p$, given in Table III, have been reproduced from Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd. edn., Oxford, 1947, p. 91, with the exception of the data for carbon

disulphide, for which L based on Landolt-Börnstein's "Tabellen" is found to be 8.99×10^{-4} degree $^{-1}$.

Because the aqueous solutions to which these results refer are saturated with the organic solvent, and the organic solvent is saturated with water, neither the heat of transfer, ΔH_1 , nor the heat of dissociation, ΔH_2 , refers to pure media. Nevertheless, a determination of ΔH_2 for

TABLE III.

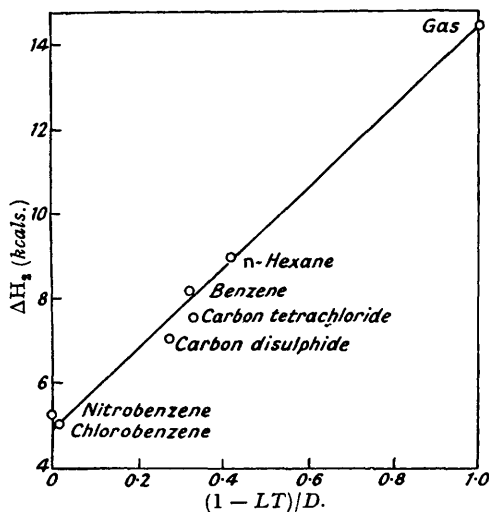
The dissociation of the double molecules of acetic acid and propionic acid in various media at 308.1° K.

Medium.	$10^3 K_2$.	K_2 relative for acetic acid.	$10^3 K_2$ for propionic acid.	$\frac{K_2 \text{ (acetic)}}{K_2 \text{ (propionic)}}$	D .	$(1 - LT)/D$
Vapour	0.072	1	0.034	2.1	—	—
$n\text{-C}_6\text{H}_{14}$	1.93	27	1.61	1.2	1.87	0.41
CCl_4	3.11	43	2.25	1.4	2.22	0.33
C_6H_6	12.4	172	11.4	1.1	2.25	0.32
CS_2	2.80	39	—	—	2.60	0.275
CHCl_3	—	—	51.5	—	4.31	-0.014
$\text{C}_6\text{H}_5\text{Cl}$	9.39	130	9.67	1.0	6.37	+0.014
$\text{C}_6\text{H}_5\text{NO}_2$	180	2,500	208	0.9	33.1	-0.020

benzoic acid in pure benzene by a vapour-pressure method (Wall and Rouse, *J. Amer. Chem. Soc.*, 1941, 63, 3002) gave a value 9.0 ± 0.4 , in substantial agreement with the value 8.7 found by distribution experiments (Hendrixson, *loc. cit.*). The presence of water in the organic layer does not, in this case, affect the heat of dimerisation.

It would be inappropriate on such incomplete evidence as we here present to discuss in detail the effect of the solvent on the hydrogen bridge (Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, 42, 1419)—a subject which has been extensively reviewed (Lasettre, *Chem. Reviews*, 1937,

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20, 259; Mansel Davies, *Ann. Reports*, 1946, 43, 5). Moreover, our data are only accurate enough to indicate the sign, but not the magnitude of $d(\Delta H_2)/dT$. The general trend of the heat and extent of dimerisation with the dielectric constant of the solvent, however, justifies brief comment.

If the dipole moment of a dissolved molecule is not affected by dissolution (see Onsager, *J. Amer. Chem. Soc.*, 1936, 58, 1486; Kirkwood, *J. Chem. Physics*, 1939, 7, 911), and if the force of attraction, though not necessarily that of repulsion, between the two molecules is electrostatic, then the increase in free energy ΔG_s , attending the dissociation of the dimer in solution, is given either by the expression :

$$\Delta G_s = \Delta G_g/D \dots \dots \dots (2)$$

or by the expression

$$\Delta G_s = (D + 2)\Delta G_g/3D \dots \dots \dots (2a)$$

