

[CONTRIBUTION FROM THE LABORATORIES OF THE MOUNT SINAI HOSPITAL]

DETERMINATION OF SOLUBILITY OF SPARINGLY SOLUBLE LIQUIDS IN WATERBY HARRY SOBOTKA AND JOS KAHN¹

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During a biochemical investigation, we found it necessary to ascertain the solubility in water of several simple aliphatic esters, primarily the ethyl esters of the saturated normal monocarbonic and dicarbonic acids. Except for a few of these esters, no data could be found in the reference books of physical and organic chemistry. We therefore proposed to determine the water solubility of a number of these substances.

The quantitative estimation of sparingly soluble liquids in their saturated aqueous solutions sometimes meets with obstacles caused by difficulties in the analytical determination of small amounts of these substances. More often, however, the difficulty arises with the separation of the saturated solution to be analyzed. Depending on the attempted method of separation, losses by evaporation, adsorption to filters or other difficulties of mechanical nature may hamper the effectual and correct separation of a saturated solution from the excess of undissolved substance. The proximity of specific gravity of solvent and solute limits the choice of methods in many instances; in other cases a substance with relatively low refractive index will escape detection by inspection.

Schuncke and Böttker² determined the mutual solubility in the system water-ether by mixing varying amounts of the two fluids and by observing the appearance of a second phase. Herz³ applied the same principle to the estimation of the water solubility of a few other liquids as chloroform, benzene, etc. An improved method was used by Klobbie.⁴ He added ponceau de xyline, a dye insoluble in ether and soluble in water, to dry ether and then added water. As soon as the ether was saturated with water the formation of water droplets changed the appearance of the hitherto dry ponceau particles.

We were unaware of Klobbie's method when we devised the following procedure to overcome the difficulties mentioned above. It offers a quick and simple method of ascertaining data on solubility with an accuracy, satisfactory for various purposes, of $\pm 0.001\%$ (*i. e.*, 0.01 cc. in one liter).

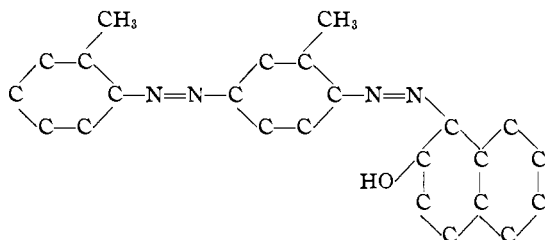
Principle and Description of Method.—A few cc. of purified ester was stained with a minute quantity of Sudan IV, a water-insoluble lipoid-

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² (a) Schuncke, *Z. physik. Chem.*, **14**, 331 (1894); (b) Böttker, *ibid.*, **22**, 505, 511 (1897).

³ Herz, *Ber.*, **31**, 2669 (1898).

⁴ Klobbie, *Z. physik. Chem.*, **24**, 615 (1897).



soluble dye. It was then added drop by drop from a micro-buret with a capillary tip to 100, 250, or 500 cc. of distilled water of constant temperature (usually 20°) in a narrow-mouthed stock bottle provided with a well-ground glass stopper. The bottle was thoroughly shaken after each addition of ester. While the added ester was dissolved, the Sudan dye contained in the ester was also wholly or partially dissolved, imparting a pink tinge to the aqueous solution. When Sudan had been added in more liberal quantities a part of it was precipitated and floated on the surface in the form of dark brown solid particles. When the water was saturated with ester, a second liquid phase formed, consisting of transparent droplets of ester. These readily dissolved the solid phase if such had been formed. The last reading of the buret before appearance of the droplets was used for the computation of the solubility.

The end-point of this titration was improved by the following modification. Instead of adding the Sudan IV to the ester, one to five mg. of it is put into the water. The ester is run into the water drop by drop. The dilute solution, shaken frequently, assumes a pink color. When saturation is reached, one additional drop will suffice to convert the floating jagged indicator particles into dark transparent droplets.

In the case of the more soluble esters, a slightly larger amount of Sudan must be added. With less soluble homologs, the accuracy can be enhanced by using larger volumes of water.

The influence of trifling amounts of Sudan is as negligible in regard to the solubility to be measured as that of indicators on the stoichiometric relations in ordinary acidimetric procedures.

Solubility of Ethyl Esters of Mono- and Dicarboxylic Acids.—This method was applied to the ethyl esters of the homologous series from propionic to capric acid and from malonic to sebacic acid. Most of these esters were supplied by the Eastman Kodak Laboratories, some were synthesized in our laboratory and all were purified by repeated distillation under reduced pressure. Their purity was checked refractometrically. The specific gravity had to be determined in the monocarboxylic series above ethyl caprylate and the refractive indices above ethyl valerate; the refractive indices of the propionate and butyrate were redetermined. Our refractive indices for the dicarboxylic esters tallied with those given by

Karvonen;⁵ the specific gravities of these esters were taken from this author.

The molecular refractions derived from our observations according to the Lorentz-Lorenz formula agreed throughout with the theoretical values calculated from Eisenlohr's atomic refractions.⁶ The theoretical value for ethyl propionate is 27.15, for laurate 68.70, for diethyl malonate 37.83 and for sebacate 70.16. The corresponding experimental figures (Tables I and II) are: 27.0, 68.8, 37.9 and 70.0.

TABLE I
SOLUBILITY OF ETHYL ESTERS OF SATURATED NORMAL MONOCARBONIC ACIDS IN WATER
AT 20°

Name	Formula	d_4^{20}	n_D^{20}	M_D	Gram dissolved in 100 cc. H ₂ O	Normality of satd. soln.	-Log ₁₀ of normality p_5
Propionate	CH ₃ CH ₂ COOEt	0.8889 ^a	1.3853 ^{a,b}	27.0	1.75 ^c	1.71	0.77
Butyrate	CH ₃ (CH ₂) ₂ COOEt	.8784 ^d	1.3931 ^d	31.6	0.510 ^c	0.044	1.36
Valerate	CH ₃ (CH ₂) ₃ COOEt	.8756 ^e	1.4016	36.2	.223 ^f	.0171	1.77
Caproate	CH ₃ (CH ₂) ₄ COOEt	.8728 ^e	1.4089	40.9	.063	.0044	2.36
Oenanthate	CH ₃ (CH ₂) ₅ COOEt	.8716 ^e	1.4137	45.4	.029	.00183	2.74
Caprylate	CH ₃ (CH ₂) ₆ COOEt	.8674	1.4197	50.0	.007	.00041	3.4
Pelargonate	CH ₃ (CH ₂) ₇ COOEt	.8647 ^g	1.4223	54.7	.003	.00016	3.8
Caprate	CH ₃ (CH ₂) ₈ COOEt	.8637	1.4269	59.5	(.0015)	(.00008)	(4.1)
Laurate	CH ₃ (CH ₂) ₁₀ COOEt	.8615	1.4323	68.8
Myristate	CH ₃ (CH ₂) ₁₂ COOEt	.8589	1.4381	78.6

^a Cf. Ref. 6. ^b Cf. Auwers and Eisenlohr, *Z. physik. Chem.*, **83**, 429 (1913); cf. also^(a) ^c Cf. Traube, *Ber.*, **17**, 2294, 2304 (1884). ^d Matthews and Faville, *J. Phys. Chem.*, **22**, 1 (1918). ^e Corrected from d_{20}^{20} in Lieben and Rossi, *Ann.*, **165**, 109 (1872-1873), and Lieben and Janecek, *Ann.*, **187**, 126 (1877). ^f Cf. W. D. Bancroft, *Phys. Rev.*, **3**, 114 (1895-1896). ^g Zincke and Franchimont, *Ann.*, **164**, 333 (1872).

TABLE II
SOLUBILITY OF DIETHYL ESTERS OF DICARBONIC ACIDS

Name	Formula	d_4^{20}	n_D^{20}	M_D	Grams dissolved in 100 cc. H ₂ O	Normality of satd. soln.	-Log ₁₀ of normality p_5
Malonate	COOEtCH ₂ COOEt	1.0550	1.4144	37.9	2.08	0.130	0.89
Succinate	COOEt(CH ₂) ₂ COOEt	1.0402	1.4200	42.4	1.92	.110	.96
Glutarate	COOEt(CH ₂) ₃ COOEt	1.0220	1.4242	46.9	0.882	.047	1.33
Adipate	COOEt(CH ₂) ₄ COOEt	1.0086	1.4278	51.6	.423	.0209	1.68
Pimelate	COOEt(CH ₂) ₅ COOEt	0.9945	1.4303	56.1	.199	.0092	2.04
Suberate	COOEt(CH ₂) ₆ COOEt	.9822	1.4334	60.9	.068	.00296	2.53
Azelate	COOEt(CH ₂) ₇ COOEt	.9729	1.4358	65.5	.025	.00102	2.99
Sebacate	COOEt(CH ₂) ₈ COOEt	.9646	1.4368	70.0	.008	.00031	3.5

The last column in both tables gives the negative logarithm of the concentration in saturated solution. These logarithms, when plotted against

⁵ Karvonen, *Ann. acad. sci. Fenn.*, [A] **10**, No. 5, 12 (1916).

⁶ Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1910).

molecular weights, would yield a straight line if there was a geometric decrease of solubility.

The graph for the dicarbonic esters shows an irregularity between malonate and succinate. Further on, it follows a regular course with a sharper decrease of solubilities above azelate.

The solubility of the monocarbonic esters shows a slightly sharper decrease than that of the dicarbonic ones. A zig-zag in this series is caused by the relatively higher solubility of the esters with an odd number of carbon atoms. This oscillation may be observed up to pelargonate while the figure for the very slightly soluble caprate does not harmonize, probably because of the limitations of accuracy in this range.

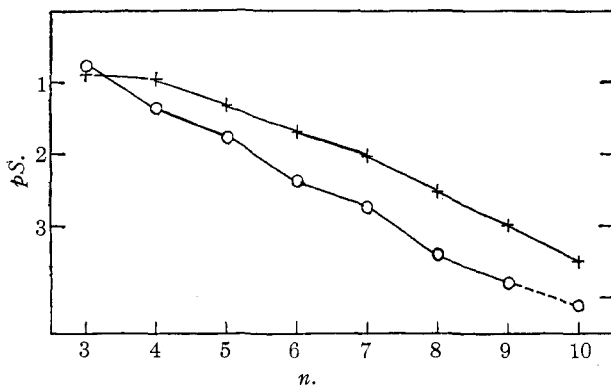


Fig. 1.—Solubility of ethyl esters of monocarbonic acids (O) and of dicarbonic acids (+) in water at 20°: n , number of carbon atoms; pS , $-\log_{10}$ of normality of saturated solution.

The solubility of the ethyl ester of a monocarbonic acid with n carbon atoms is between the solubilities of the diethyl esters of the dicarbonic acid with $(n + 1)$ and that with $(n + 2)$ carbon atoms.

Summary

1. A simple and inexpensive method is presented for the determination of the solubility in water of sparingly soluble liquids.
2. Complete data are given for the solubility at 20° of the ethyl esters in the monocarbonic series below capric (decanoic) acid and in the dicarbonic series below sebacic acid. The refractive indices of the monocarbonic esters were also determined.

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