[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PHILADELPHIA COLLEGE OF PHARMACY AND SCIENCE]

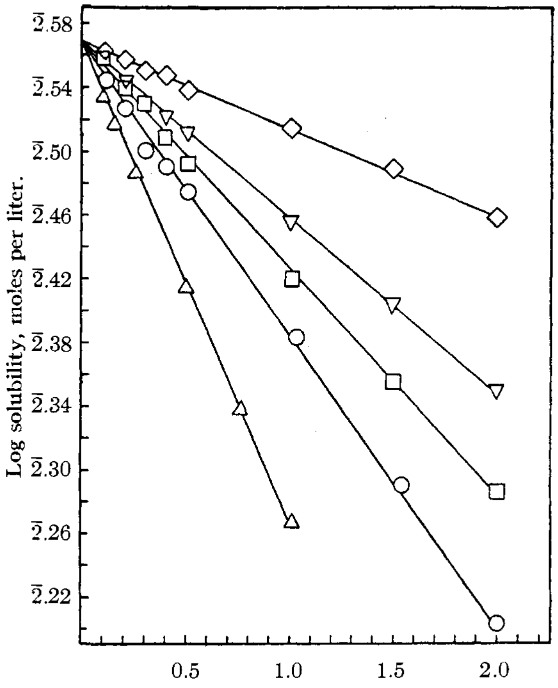
The Salting-out of Molecular Benzoic Acid in Aqueous Salt Solutions at 35°

BY GEORGE M. GOELLER AND ARTHUR OSOL[1]

The solubility of benzoic and other weak acids in aqueous salt solutions at 25° or below has been reported previously.[2] Where the experiments have been set up so as to minimize corrections for the ionized portion of the acid, or where the data have been corrected suitably, it has been found that for neutral electrolytes which decrease the solubility of the acid the following equation may be applied

$$\log S_0/S = kC \qquad (1)$$

where S_0 is the solubility of molecular acid in pure water, S is the corresponding solubility in the salt solution, C is the concentration of salt in moles per liter and k is the salting-out constant.



Concentration of electrolyte, moles per liter.

Fig. 1.—Solubility of molecular benzoic acid in salt solutions: ◇, KI; ▽, KBr; □, KCl; ○, LiCl; △, $BaCl_2$.

This equation is also frequently written in the form

$$\log f = kC \qquad (2)$$

where f is the activity coefficient of the molecular acid in the salt solution and is defined by the ratio S_0/S.

The purpose of this investigation is to determine the value of the salting-out constant for various salts with molecular benzoic acid at 35° and to compare the new data with corresponding values at lower temperatures.

Experimental

The experimental method was that of Chase and Kilpatrick and Osol and Kilpatrick.[2]

The benzoic acid was Merck Reagent Grade, having constant solubility upon repeated treatment of it with successive portions of water. Merck Reagent Grade salts, tested for absence of acidic or basic impurities, were used. Titrations were carried out in an atmosphere of nitrogen with carbonate-free sodium hydroxide, weight burets being employed.

A total solubility of 0.03873 mole per liter was found for benzoic acid in water at 35 ± 0.05°. This was corrected for the part present as ions by calculating the hydrogen ion concentration according to the mass law, using the value of K_c at the proper electrolyte concentration as given by Chase and Kilpatrick at 25°. The assumption that the values of K_c at 35° are not appreciably different is not unwarranted in view of findings reported by Riesch and Kilpatrick.[3] A molecular solubility of 0.03719 is thus obtained. In calculating the salting-out constants, however, the molecular solubility is taken to be 0.03690, this value being an average of the solubilities at zero ion concentration, calculated by the method of least squares, for all the salting-out experiments.

To minimize the correction for the part present as ions all solutions containing salt were buffered to 0.01 molar with respect to sodium benzoate by addition of sodium hydroxide. As the solubility of benzoic acid is increased by the addition of sodium benzoate a subtractive correction of 0.00022 mole per liter is applied to each result.

The data for all the salts are given in Table I and a graphical presentation of some of them in Fig. 1.

In calculating the concentrations of molecular acid in Table I, corrections for the ionized part of the acid were calculated from the law of mass action, using values of K_c as given by Riesch and Kilpatrick.[3]

Discussion

As the values of k, because of their logarithmic relationship to the ratios S_0/S, are susceptible

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[2] For references to these investigations see Chase and Kilpatrick, THIS JOURNAL, **53**, 2589 (1931), and Osol and Kilpatrick, *ibid.*, **55**, 4430 (1933).

[3] Riesch and Kilpatrick, *J. Phys. Chem.*, **39**, 891 (1935).

TABLE I

SOLUBILITY OF BENZOIC ACID IN SALT SOLUTIONS

Salt, moles per liter	Total acid, mole per liter	Molecular acid, mole per liter	Salting-out constant
	Lithium Chloride		
0.1139	0.03578	0.03502	0.199
.2068	.03426	.03369	.191
.3022	.03278	.03221	.195
.4016	.03151	.03094	.191
.5040	.03042	.02988	.182
1.0250	.02460	.02414	.180
1.5217	.01996	.01956	.181
2.0057	.01635	.01599	.181
	Sodium Chloride		
0.1	0.03595	0.03539	0.182
.2	.03435	.03377	.192
.3	.03324	.03267	.176
.4	.03179	.03122	.182
.5	.03057	.03003	.179
1.0	.02494	.02448	.178
1.5	.02020	.01980	.180
2.0	.01644	.01608	.180
	Sodium Bromide		
0.1	0.03594	0.03537	0.183
.2	.03494	.03436	.155
.3	.03351	.03303	.160
.4	.03245	.03187	.157
.5	.03115	.03061	.162
1.0	.02661	.02613	.150
1.5	.02278	.02236	.145
2.0	.01927	.01889	.146
	Potassium Chloride		
0.1	0.03672	0.03615	0.089
.2	.03527	.03468	.135
.3	.03450	.03392	.122
.4	.03281	.03223	.147
.5	.03173	.03117	.147
1.0	.02687	.02639	.146
1.5	.02313	.02271	.141
2.0	.01979	.01940	.140
	Potassium Bromide		
0.1	0.03663	0.03606	0.100
.2	.03560	.03501	.114
.3	.03468	.03409	.115
.4	.03381	.03322	.114
.5	.03288	.03231	.115
1.0	.02906	.02856	.111
1.5	.02576	.02524	.110
2.0	.02271	.02233	.109
	Sodium Iodide		
0.1044	0.03686	0.03628	0.071
.2051	.03604	.03544	.086
.3060	.03536	.03477	.084
.4002	.03477	.03417	.084
.5022	.03393	.03335	.087
1.0030	.03079	.03028	.086
1.5020	.02791	.02744	.086
2.0030	.02492	.02449	.089
	Potassium Iodide		
0.1	0.03711	0.03654	0.042
.2	.03674	.03614	.045
.3	.03624	.03564	.050
.4	.03596	.03535	.047
.5	.03527	.03469	.053
1.0	.03335	.03281	.051
1.5	.03139	.03089	.052
2.0	.02922	.02876	.054
	Barium Chloride		
0.05	0.03645	0.03588	0.244
.1	.03489	.03431	.316
.15	.03362	.03304	.320
.2	.03241	.03184	.320
.25	.03133	.03078	.314
.5	.02640	.02592	.306
.75	.02231	.02189	.302
1.0	.01896	.01858	.298

to large variation when the S_0/S ratio is close to unity, a better picture of the relative constancy of the former may be obtained from Fig. 1[4] or from a plot of the values of log f *versus* salt concentration. From graphs of the latter type we have calculated the average value of k for each salt used in our experiments and have compared it with corresponding data in the literature for benzoic acid at 25 and 18°. The comparison, recorded in Table II, indicates that there is no significant change in k over the temperature range 18 to 35°.

TABLE II

SALTING-OUT CONSTANTS FOR BENZOIC ACID AT 35, 25 AND 18°

Salt	35°	25°	18°
LiCl	0.183	0.188^a	0.192^b
NaCl	.179	.183^a	.177^b
NaBr	.147	.150^c	
KCl	.141	.138^d	.137^b
KBr	.110	.113^a (.108^c)	.070^b
NaI	.087	.094^c	
KI	.053	.054^a	.050^b
$BaCl_2$	.302	.318^a	.300^b

[a] From data of Kolthoff and Bosch, *J. Phys. Chem.*, **36,** 1685 (1932). [b] From data of Larsson, *Z. physik. Chem.*, **148A,** 148 (1930); *ibid.*, **153A,** 299 (1931). In view of the relative constancy of k for KBr at other temperatures it appears that Larsson's value for this salt is low. [c] Calculated from the results of Haeseler, Dissertation, Columbia University, 1929. [d] From data of Chase and Kilpatrick.[2]

Summary

The solubility of benzoic acid in aqueous salt solutions at 35° has been determined and from these data the molecular solubility and the salt-

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(4) Graphs for sodium chloride, sodium bromide, and sodium iodide were omitted in order to preserve legibility.

ing-out constant have been calculated for each concentration of salt studied.

The new values for the salting-out constant are compared with corresponding data at 25 and 18°.

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Additional Data on the *cis* and *trans* Isomers of Pentene-2

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The problem of the synthesis of the two stereoisomers of pentene-2 or of the separation of these from a mixture of the two has been attacked by various investigators with varying degrees of success. The problem has been under investigation in this Laboratory for some years and this report summarizes the results obtained in the synthesis of a pentene-2, which is largely the *cis* form, of one which is largely the *trans* form and for preparations which give mixtures of varying proportions of the two isomers.

The usual methods employed in the preparation of pentene-2 have been the dehydration of 3-pentanol and 2-pentanol and the removal of hydrogen bromide from 3-bromo- and 2-bromopentane.[2] The physical constants for the pentene obtained from the symmetrical alcohol and bromide by various investigators have been in remarkable agreement. The values found for the pentene from 2-pentanol or 2-bromopentane were in general slightly lower but showed greater variation. This may have been due to traces of pentene-1 which repeated fractionation failed to remove or to varying proportions of the two isomers of pentene-2.

After an unsuccessful attempt to separate the two isomers by fractionation or to bring about any isomerization into the other form Van Risseghem[3] concluded that the preparation from 3-pentanol was either the stable isomer or an equilibrium mixture of the two.

Since the physical constants for pentene-2 prepared from α-ethyl-β-bromobutyric acid were identical with those of the pentene obtained from 3-bromopentane, Lauer and Stodola[4] decided that the product in each case must represent the stable isomer. Since hydrogen bromide is an effective isomerizing agent and it has been shown[5] that the hydrogen bromide addition products of tiglic and angelic acids, α-methyl-β-bromobutyric acid, were in each case mixtures of the two stereoisomeric forms, it seems possible that the ethyl derivative would form an analogous mixture in which case the pentene-2 derived from this should be a mixture of the two geometrical isomers.

Applying the method used successfully in the synthesis of *cis*- and *trans*-butene-2[6,7] Lucas and Prater[8] prepared pentene-2 from the hydrogen iodide derivatives of the two α-methyl-β-ethylacrylic acids, $C_2H_5CH{=}C(CH_3)COOH$. The boiling points of the two products were identical but they differed considerably in density and refractive index (Table I). The *cis* form was assigned to the isomer with the higher values which are higher than those previously reported while the values for the *trans* form are practically identical with those obtained by other investigators.

Bourguel and co-workers[9] have reported the synthesis of *cis*-pentene-2 by reduction of pentyne-2 with colloidal palladium. Comparison of the Raman spectrum of this compound with that of pentene-2 from 3-pentanol[10] showed the latter to contain the characteristic lines of the former and in addition a number of new lines from which it was concluded that the preparation from pentyne-2 was the pure *cis* form and the other a mixture of *cis* and *trans*. The very characteristic line of all aliphatic unsaturated hydrocarbons found at about 1650 cm.$^{-1}$ was at 1658 cm.$^{-1}$ in the spectrum of the *cis* isomer, while in the other there was a line at 1674 cm.$^{-1}$ as well as at 1658 cm.$^{-1}$. The

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(1) Presented before the Organic Division at the Rochester meeting, Sept., 1937.

(2) For bibliography and data to 1929 see papers of Sherrill and co-workers, THIS JOURNAL, **51**, 3023, 3034 (1929).

(3) Van Risseghem, *Bull. soc. chim. belg.*, **28**, 53, 187, 288 (1914).

(4) Lauer and Stodola, THIS JOURNAL, **56**, 1216 (1934).

(5) Fittig and Pagenstrecker, *Ann.*, **195**, 108 (1879).

(6) Wislicenus, Talbot, Henze and Schmidt, *ibid.*, **313**, 207 (1900).

(7) Young, Dillon and Lucas, THIS JOURNAL, **51**, 2528 (1929).

(8) H. J. Lucas and A. N. Prater. Reported to the Organic Division of the American Chemical Society, San Francisco meeting, August, 1935. The authors are indebted to Professor Lucas for the data given in Table I. Private Communication, January, 1936.

(9) Bourguel, *Bull. soc. chim.*, **41**, 1476 (1927); **53**, 496 (1933).

(10) (a) Bourguel, Piaux and Grédy, *Compt. rend.*, **195**, 129 (1932); (b) Van Risseghem, Piaux and Grédy, *ibid.*, **196**, 938 (1933); (c) Grédy, *Bull. soc. chim.*, [5] **2**, 1029 (1935).