964. *Activity Coefficients of Non-electrolytes in Aqueous Solutions of Sugars.*

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Solubility and partition methods have been used to determine activity coefficients of quinol and of ethyl butyrate in aqueous solutions of various sugars. Both " salting-out " and " salting-in " effects have been observed, which follow the well-known Setchenow equation with numerical coefficients of the same order of magnitude as was found for electrolytes.

ALTHOUGH the phenomenon of " salting-out " has been extensively investigated during the past fifty years,[1] little attention has been paid to the effects of organic substances,

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[1] Rothmund, " Löslichkeit und Löslichkeitsbeeinflussung," Barth, Leipzig, 1907; Euler, *Z. phys. Chem.*, 1904, **49**, 303. Euler and Svanberg, *Z. Elektrochem.*, 1917, **23**, 192; Eyre, *Brit. Ass. Reports*, 1910, 425; 1912, 795; Randall and Failey, *Chem. Rev.*, 1927, **4**, 271, 285, 291; Scatchard. *ibid.*, **3**, 383; *Trans. Faraday Soc.*, 1927, **23**, 454; Gross, *Chem. Rev.*, 1937, **13**, 91; Albright, *J. Amer. Chem. Soc.*, 1937, **59**, 2098; Long and McDevit, *Chem. Rev.*, 1952, **51**, 119.

such as sugars, on the solubility of other organic compounds in aqueous solution. From the few examples available[2] it appears that sucrose, like salt, decreases the solubilities of esters in water. In the present work we examined this feature by following the solubilities of ethyl butyrate and of quinol in various sugar solutions.

Experimental.—*Ethyl butyrate.* Saturated solutions of ethyl butyrate in water and in sugar solutions of differing molality were prepared by shaking 50 ml. of solvent with 1 ml. of ester in glass-stoppered bottles immersed in a thermostat at 25° for periods up to 12 hr. Aliquot parts (3 ml.) were made up to 100 ml. with di-isopropyl ether and shaken at intervals for 2 hr.; then 5 ml. of the clear ether extract were removed for analysis, leaving behind the sugaring-out agent.

The ester was determined colorimetrically by a method due to Feigl[3] and Thompson,[4] based on the formation in alkaline solution of hydroxamic acids which form red complexes with ferric iron. Hydroxylamine reagent was prepared freshly before use by mixing equal volumes of methanol solutions of hydroxylamine hydrochloride (5%) and sodium hydroxide (12·5%); the precipitated sodium chloride was filtered off. A ferric perchlorate reagent was prepared by dissolving iron (0·4 g.) or hydrated ferric chloride (1·93 g.) in concentrated hydrochloric acid (5 ml.), adding 70% perchloric acid (5 ml.) and evaporating the solution, the residue being then dissolved in water and made up to 100 ml. To 10 ml. of this stock solution were added 70% perchloric acid (37·5 ml.) and ethanol (400 ml.), alternately in small amounts with cooling; this mixture was then made up to 500 ml. at room temperature.

The ethereal solution of the ester (5 ml.) was mixed with the hydroxylamine reagent (1·5 ml.) in small tubes with ground-glass stoppers. After 30 min. at 25°, ferric perchlorate reagent (12·5 ml.) was added and the whole shaken. After 10 min., the optical density at 520 mμ was read against a reagent control in 1 cm. closed silica cells, in a Hilger spectrophotometer. A calibration curve enabled ester concentrations to be calculated.

Quinol. Quinol was twice recrystallised from hot acetone. 50 ml. of a 0·05M-solution of quinol in di-isopropyl ether were shaken with 50 ml. of water or of the appropriate sugar solution in glass-stoppered bottles for 4—6 hr. in a thermostat at 25°, then left until the two layers had separated, after which 10 ml. portions of each layer were withdrawn and the quinol contents determined by titration with ceric sulphate with ferroin as indicator.

Results.—The solubility (s^0) of ethyl butyrate in water at 25° was found to be 1·76 g. l.$^{-1}$. Table 1 records the solubilities at varying molalities of sugars and other substances together

TABLE 1.

	Sucrose		Glucose		Fructose		Sorbitol	
m	$10s$	$\log_{10} f$	$10s$	$\log_{10} f$	$10s$	$\log_{10} f$	$10s$	$\log_{10} f$
0·25	1·54	0·058	1·65	0·028	1·66	0·025	—	—
0·50	1·40	0·099	1·47	0·078	1·49	0·072	1·46	0·081
1·00	1·06	0·220	1·24	0·152	1·29	0·135	1·19	0·170
2·00	0·68	0·413	0·80	0·342	0·90	0·291	0·80	0·342
k	0·206		0·167		0·146		0·163	

	Glycerol		Sodium chloride			Lactose		Maltose	
m	$10s$	$\log_{10} f$	$10s$	$\log_{10} f$	m	$10s$	$\log_{10} f$	$10s$	$\log_{10} f$
0·50	1·73	0·0095	1·40	0·100	0·125	1·70	0·015		
1·00	1·64	0·031	1·05	0·234	0·250	1·59	0·044		
2·00	1·59	0·044	0·63	0·446	0·375	—		1·55	0·055
4·00	1·33	0·122	0·21	0·923	0·500	1·30	0·132		
					0·75	—		1·21	0·163
					1·50	—		0·77	0·359
	0·032		0·234			0·270		0·240	

Glasstone and Pound[2] obtained the following k values for ethyl acetate: lactose, 0·25; sucrose, 0·216; glucose, 0·16; fructose, 0·132.

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[2] Glasstone and Pound, *J.*, 1925, **125**, 2660; Glasstone, Dimond, and Harris, *J.*, 1927, 2939; Philip, and Bramley, *J.*, 1915, **107**, 377; Sugden, *J.*, 1926, 175.

[3] Feigl, " Quantitative Analysis by Spot Tests," Elsevier, 3rd edn., 1946, p. 538.

[4] Thompson in Steyermark's " Quantitative Organic Microanalysis," Blakiston, N.Y., 1951, p. 244

with the corresponding values of log f = log s^0/s = km, where m is the sugar molality and k is Setchenow's salting-out coefficient.[5] Corresponding results for quinol are given in Table 2. Most of the results give a fairly good linear plot of log f against molality of sugar, for which the values of k have been calculated. The partition coefficient of quinol between di-isopropyl ether and water at 25° was found to be $C_{\mathrm{H_2O}}/C_{\mathrm{ether}}$ = 1·35.

Discussion.—The salting-out coefficients for ethyl butyrate vary over a wide range and some sugars, *viz.*, lactose and maltose, are even more effective than sodium chloride. The effect of some sugars on the solubility of ethyl acetate was studied by Glasstone and Pound [2] who expressed their results in terms of " hydration numbers." These data have been converted into activity coefficients and the salting-out coefficients derived therefrom (listed in Table 1) lie very close to the values obtained in the present work with ethyl butyrate.

TABLE 2.

	Cellobiose		Erythritol		Galactose		Glucose		Lactose		Maltose	
m	P	log f	P	log f	P	log f	P	log f	P	log f	P	log f
0·125	1·38	−0·007							1·39	−0·010		
0·25	1·41	−0·015	1·376	−0·007			1·34	0·005	1·42	−0·020		
0·375					1·37	−0·004					1·44	−0·026
0·50	1·45	−0·030	1·381	−0·009			1·32	0·012	1·48	−0·039		
0·75					1·38	−0·007					1·53	−0·051
1·0			1·403	−0·015			1·29	0·023				
1·5					1·41	−0·017					1·69	−0·095
2·0			1·447	−0·029			1·22	0·048				
k	−0·06		−0·013		−0·011		0·026		−0·076		−0·062	

	Mannitol		Me α-Glucoside		Rhamnose		Sorbitol		Sucrose	
m	P	log f	P	log f	P	log f	P	log f	P	log f
0·25	1·34	0·005	1·41	−0·021	1·39	−0·008				
0·50	1·32	0·010	1·47	−0·039	1·42	−0·018	1·33	0·009	1·34	0·014
0·75	1·29	0·020					1·31	0·013		
1·0			1·61	−0·079	1·48	−0·036	1·30	0·017	1·31	0·025
1·5									1·27	0·036
2·0			1·97	−0·167	1·59	−0·067	1·24	0·039	1·24	0·047
k	0·021		−0·084		−0·036		0·017		0·024	

Glycerol			Pentaerythritol			Sodium chloride		
m	P	log f	m	P	log f	m	P	log f
0·55	1·44	0·0186	0·075	1·39	−0·011	0·5	1·148	0·074
0·82	1·47	0·0287	0·15	1·42	−0·020	1·0	0·971	0·146
1·53	1·58	0·0605	0·30	1·46	−0·34	2·0	0·714	0·279
2·18	1·70	0·0916				4·0	0·386	0·547
4·15	2·09	0·1817						
k	0·048			−0·100			0·133	

Table 2 reveals the existence of " salting-in " effects of the same order of magnitude as the salting-out effects. Comparison with Table 1 shows that there is no correlation between the effects of given sugars on ethyl butyrate and on quinol. Lactose and maltose, which have the largest positive values of k with ethyl butyrate, have negative values with quinol. It is not yet possible to correlate these effects with the structures of the sugars and discussion must be deferred.

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[5] Setchenow, *Z. phys. Chem.*, 1889, **4**, 117.