

CCA-366

532.73.04

Original Scientific Paper

Saturated Ternary Systems. IV* Solubility Isotherms of Organic Compounds in Water-Ethanol Mixtures

H. Iveković and A. Gertner

Faculty of Pharmacy and Biochemistry, University of Zagreb,
Zagreb, Croatia, Yugoslavia

Received January 22, 1965

The constants in solubility isotherms were determined according to E. I. Ahumov¹ for the systems water-ethanol-organic substance, in which organic substances were: isobutyl bromide, benzaldehyde, bromotoluene, benzyl ethylether, propylbromide, *iso*-amylbromide, *iso*-amylether, *o*-xylene, isobutylalcohol, diethyl ketone, phenetole, *m*-xylene, chloroform, *p*-xylene, nitrobenzene, ethyl acetate, benzyl acetate, camphor, mesitylene, pinene, hexane, *p*-nitrotoluene, toluene, cyclohexane, ethyl bromide, *o*-toluidine, ethyl butyrate, ethyl propionate, methyl-aniline, benzene, xylene and bromobenzene.

In certain concentration ranges of these components the isotherms are represented by one or two straight lines.

INTRODUCTION

The equation for solubility isotherms according to E. I. Ahumov¹ is a special form of a general equation and the possibilities of its wider application have been demonstrated in the earlier papers^{2,3}. Since the author has tested their applicability on few systems only and there are few data to be found in the literature about such investigations so far, we have attempted to verify them on systems water-ethanol-organic substance.

The basic purpose of our work was to replace by one or two equations the not easily surveyed tables of experimental data for the single points of saturated ternary systems such as are regularly encountered in the literature. The usefulness of such equations for solubility isotherms cannot be doubted: by their application the concentrations of the third component can be easily determined when the concentrations of the other two are given. Also, within the limits set by the nature of the system itself, the ratio of two components can be chosen when only the concentration of the third component is known. The composition of a saturated ternary system can be determined for every concentration of two solvents in the whole range in which the equation is applicable. The importance of these relations for the laboratory and industrial practice is selfevident.

The second basic reason for the investigation of solubility isotherms is their contribution to the knowledge of the structure of binary and ternary systems and particularly of the solvation of their components.

* Port III.: A. Gertner, *Bull. sci. Conseil Acad. SFR Jugoslavie* 5 (1959) 20.

CALCULATIONS

By using literature data for 32 systems water-ethanol-organic compound, it was investigated whether the saturation concentrations of the three components can be determined by the equation

$$\log y = a + b \cdot \log(100 - x) \quad (1)$$

where y are moles of the dissolved organic substance in 100 moles of the ethanol-water mixture, x = moles of ethanol in 100 moles of the solvent mixture, a and b are constants characteristic for the stated system.

The equation (1) represents a slightly modified expression of the solubility equation according to E. L. Ahumov¹:

$$\log y' = \log y_1 + n \cdot \log(1 - x') \quad (2)$$

where y_1 should represent the solubility of the substance expressed as moles per mole of one of the solvents provided the substance is insoluble in the other solvent, x' = mole fraction of the other solvent, n is a constant specific for the investigated system.

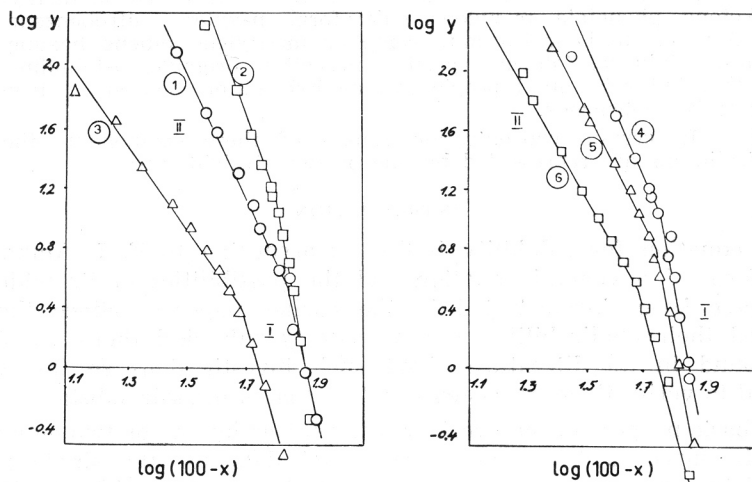


Fig. 1. Systems ethanol-water-*iso*-butyl bromide (No 1), -benzaldehyde (No 2), -bromotoluene (No 3).
Fig. 2. Systems ethanol-water-benzyl ethylether (No 4), -propyl bromide (No 5), -*iso*-amyl bromide (No 6).

The modification (1) of the equation (2) served the purpose of avoiding the location of isothermes in the left quadrants of the coordinate system.

Prior to the calculation of constants a and b for solubility isotherms, all the available experimental points compiled from the literature were plotted in diagrams represented in Fig. 1-12.

As can be seen from the figures, by the application of the equation (1) for 24 investigated systems two straight lines are obtained and for 8 systems a single straight line is obtained for the available range of data.

Some points of the experimental data obviously do not lie on straight lines and thus it was supposed that they include a greater experimental error. Besides, for the majority of systems deviations from straight lines

were found at extreme concentrations of one of the solvents. Consequently such points were not included in the calculation of constants a and b of the equation (1). These constants were determined by statistical methods in the usual way and the coordinates of the intersections were calculated from equations of the two straight lines.

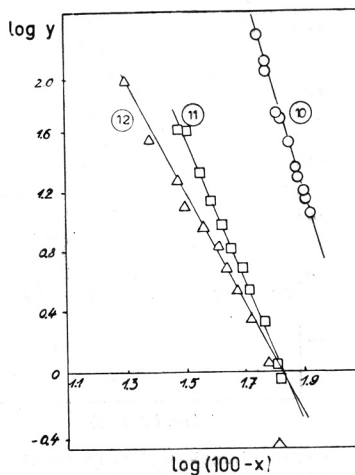
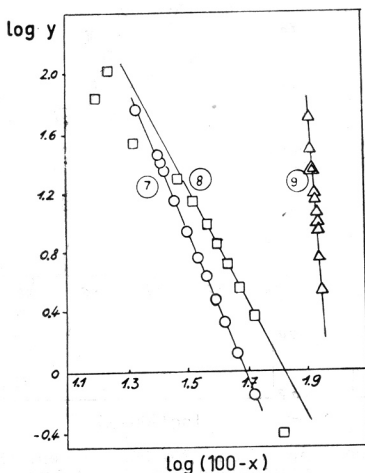


Fig. 3. Systems ethanol—water—*iso*-amyl ether (No 7), —*o*-xylene (No 8), —*iso*-butyl alcohol (No 9).

Fig. 4. Systems ethanol—water—diethyl ketone (No 10), —phenetole (No 11), —*m*-xylene (No 12).

In Table I the values of the constants a and b (headings 6 and 7) are presented as well as concentration range (% Mol ethanol) in which these parameters can be applied (heading 5). It is necessary to emphasize that

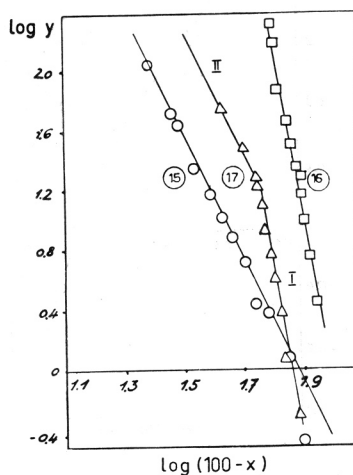
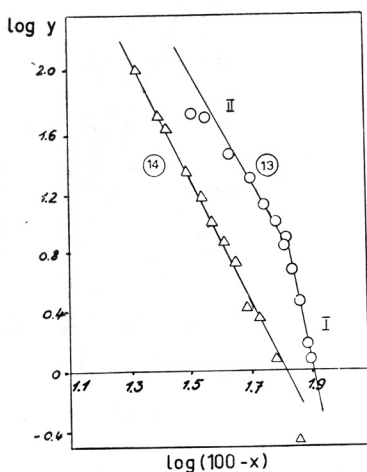


Fig. 5. Systems ethanol—water—chloroform (No 13), —*p*-xylene (No 14).

Fig. 6. Systems ethanol—water—nitrobenzene (No 15), —ethyl acetate (No 16), —benzyl acetate (No 17).

these concentration ranges are probably considerably wider for many systems. We could not determine these larger ranges since the corresponding experimental data could not be found in the literature (unfortunately only a limited

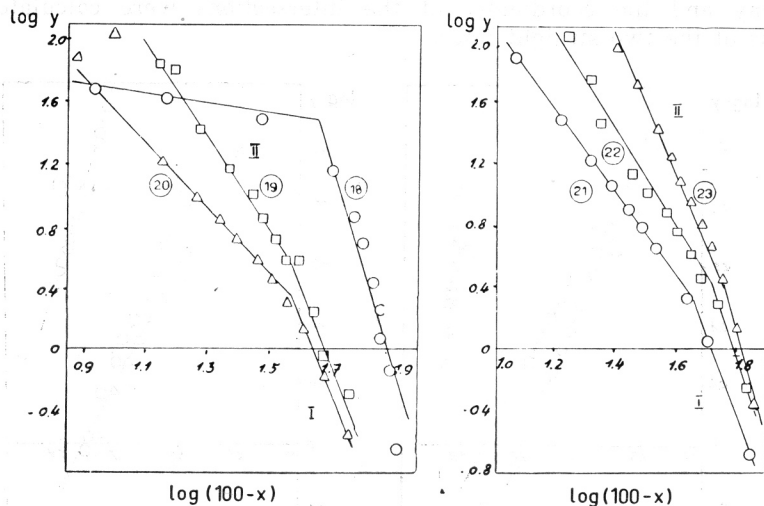


Fig. 7. Systems ethanol—water—camphor (No 18), —mesitylene (No 19), —pynene (No 20).
Fig. 8. Systems ethanol—water—hexane (No 21), —*p*-nitrotoluene (No 22), —toluene (No 23).

number of systems water-ethanol-organic substance have been examined in the whole range from 0 to 100% of these solvents). Consequently the

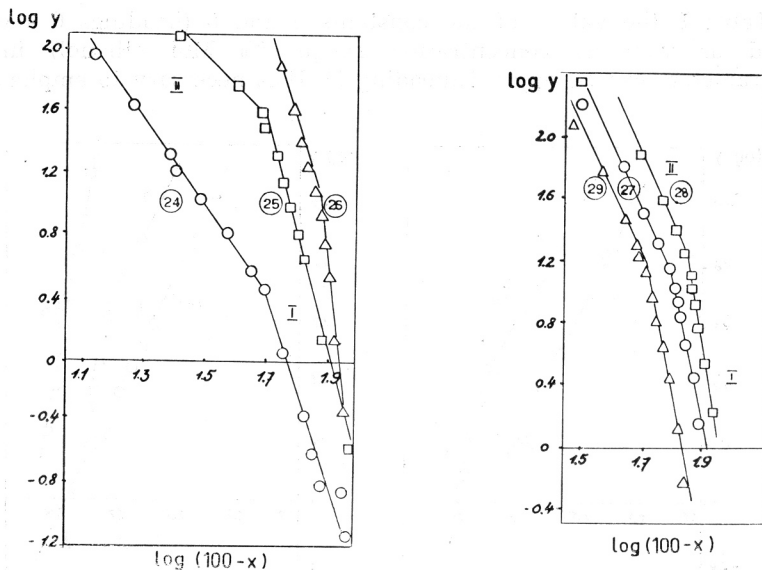


Fig. 9. Systems ethanol—water—cyclohexane (No 24), —ethyl bromide (No 25), —*o*-toluidine (No 26).

Fig. 10. Systems ethanol—water—ethyl butyrate (No 27), —ethyl propionate (No 28), —methyl aniline (No 29).

verification of equation (1) and the investigation of the solubility rules in these ranges is open to further studies.

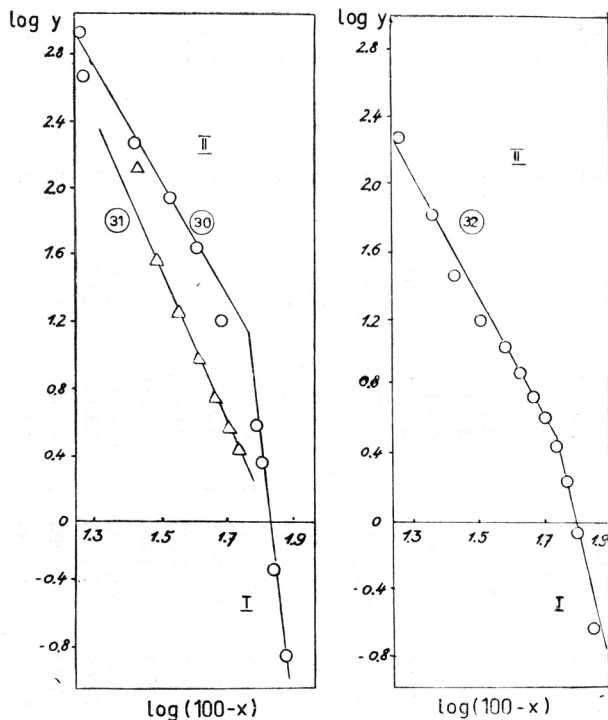


Fig. 11. Systems ethanol—water—benzene (No 30), —xylene (No 31)
Fig. 12. Systems ethanol—water—bromobenzene (No 32).

DISCUSSION

The molar concentrations of ethanol at the intersection of isotherms are equal to the highest concentration for which the isotherm I can be applied. For the majority (63%) of the investigated systems for which two isotherms (22 systems) were obtained, this concentration lies between 40—60 M % ethanol, i.e. the ratio of the moles of water to ethanol at the intersection is on the average 1 : 1. For all these systems (100 %) this concentration lies between 30 and 60 % M ethanol, which corresponds to the ratio of 1 M ethanol : 2 M water to 2 M ethanol : 1 M water.

The ratio of the vertical intercept a and the slope of the straight line b is for the isotherms I on the average $-1.84 (\pm 4 \%)$ and for the isotherms II on the average $-1.95 (\pm 6 \%)$.

Values of a obtained by calculation should refer according to E. I. Ahumov¹ to the solubility of the organic substance in 100 moles ethanol, whereas the constant b should represent the solvation number of the dissolved substance with regard to ethanol in the saturated state. We intend to deal with these equations in our further papers, and in particular to verify the regularities in the systems methanol-water-organic compounds and ethanol

TABLE I

No	Substance	t °C	Iso- therme	x	a	—b	—a/b	Dia- gram	References
1	Iso-Butyl bromide	0	I	27.80 — 45.24	14.8085	8.1469	1.82	1	4, 5, p. 136
		0	II	45.24 — 76.53	7.7037	4.0601	1.90		
2	Benzaldehyde	0	I	15.69 — 32.35	25.9573	13.6117	1.91	1	4, 5, p. 142
		0	II	32.35 — 59.13	10.7951	5.3220	2.03		
3	Bromotoluene	0	I	34.59 — 51.20	12.7232	7.3044	1.74	1	4, 5, p. 144
		0	II	51.20 — 80.65	5.3984	2.9661	1.82		
4	Benzyl ethylether	0	I	25.22 — 43.56	17.7029	9.4729	1.87	2	4, 5, p. 142
		0	II	43.56 — 59.14	8.4162	4.1709	2.02		
5	Propyl bromide	0	I	21.64 — 43.36	17.2328	9.3438	1.84	2	4, 5, p. 144
		0	II	43.36 — 74.84	7.3582	3.7112	1.98		
6	Iso-Amyl bromide	0	I	38.82 — 50.62	10.7754	6.0834	1.77	2	4, 5, p. 136
		0	II	50.62 — 79.71	6.9844	3.8450	1.82		
7	Iso-Amil ether	0	I	44.84 — 77.42	8.5058	4.9619	1.71	3	4, 5, p. 136
		0	II	77.42 — 100.00	6.5482	3.5696	1.83		
8	o-Xylene	0	I	46.95 — 70.70	6.5482	3.5696	1.83	3	4, 5, p. 145
		0	II	70.70 — 100.00	6.5482	3.5696	1.83		
9	Iso-Butanol	0	I	7.85 — 14.50	60.6207	30.5668	1.98	3	5, 5, p. 136
		0	II	14.50 — 100.00	60.6207	30.5668	1.98		
10	Diethyl ketone	0	I	21.04 — 46.18	14.0541	6.8455	2.05	4	4, 5, p. 131
		0	II	46.18 — 100.00	14.0541	6.8455	2.05		
11	Phenetole	0	I	32.89 — 68.27	9.2132	5.0519	1.82	4	4, 5, p. 142
		0	II	68.27 — 100.00	9.2132	5.0519	1.82		
12	m-Xylene	0	I	47.77 — 82.15	6.1681	3.3499	1.84	4	4, 5, p. 145
		0	II	82.15 — 100.00	6.1681	3.3499	1.84		
13	Chloroform	0	I	20.69 — 29.40	26.6623	13.9895	1.91	5	4, 5, p. 131
		0	II	29.40 — 54.00	7.4523	3.5975	2.07		
14	p-Xylene	0	I	44.06 — 77.88	7.5993	4.1301	1.84	5	4, 5, p. 145
		0	II	77.88 — 100.00	7.5993	4.1301	1.84		
15	Nitrobenzene	0	I	28.87 — 73.50	8.5330	4.5613	1.87	6	4, 5, p. 141
		0	II	73.50 — 100.00	8.5330	4.5613	1.87		
16	Ethyl acetate	0	I	5.86 — 32.84	23.0604	11.4864	2.01	6	4, 5, p. 132
		0	II	32.84 — 100.00	23.0604	11.4864	2.01		
17	Benzyl acetate	0	I	21.34 — 41.85	22.0262	11.7819	1.87	6	4, 5, p. 141
		0	II	41.85 — 67.12	8.6402	4.1956	2.06		
18	Camphor	25	I	19.18 — 50.55	12.7505	6.6806	1.91	7	8, 5, p. 679
		25	II	50.55 — 91.53	2.0183	0.3457	5.84		

19	Mesitylene	0	I II	39.97 — 66.16 66.16 — 86.23	7.2024 5.1829	4.2416 2.9211	1.70 1.77	7	4, 5, p. 136
20	Pinene	0	I II	39.92 — 63.62 63.62 — 92.46	6.8481 3.6538	4.1431 2.0966	1.65 1.74	7	4, 5, p. 144
21	Hexane	0	I II	29.53 — 58.80 58.80 — 88.50	8.1963 4.6137	4.7380 2.5753	1.71 1.79	8	4, 5, p. 147
22	<i>p</i> -Nitrotoluene	0	I II	31.41 — 46.40 46.40 — 79.64	10.2917 5.5624	5.7386 3.0036	1.79 1.85	8	4, 5, p. 144
23	Toluene	0	I II	24.75 — 41.76 41.76 — 74.49	14.1377 7.8168	7.7278 4.1471	1.83 1.88	8	4, 5, p. 144
24	Cyclohexane	25	I II	3.14 — 52.89 52.89 — 86.23	10.3013 4.9416	5.8215 2.6181	1.77 1.89	9	7, 5, p. 149
25	Ethyl bromide	0	I II	6.75 — 50.10 50.10 — 84.00	14.8946 4.6237	7.8265 1.7782	1.90 2.60	9	4, 5, p. 132
26	<i>o</i> -Toluidine	0	I II	9.53 — 34.73 34.73 — 45.10	32.9309 13.8714	17.0207 6.8645	1.93 2.02	9	4, 5, p. 144
27	Ethyl butyrate	0	I II	21.50 — 33.70 33.70 — 55.59	22.0873 8.9079	11.5563 4.3209	1.91 2.06	10	4, 5, p. 132
28	Ethyl propionate	0	I II	16.66 — 29.61 29.61 — 51.37	24.3902 9.3369	12.5561 4.4083	1.95 2.12	10	4, 5, p. 132
29	Methyl aniline	0	I II	19.16 — 42.19 42.19 — 67.54	17.3674 7.8384	9.1843 3.7762	1.89 2.08	10	4, 5, p. 142
30	Benzene	25	I II	14.45 — 38.03 38.03 — 82.09	26.5444 6.6660	14.1655 3.0739	1.87 2.17	11	6, 5, p. 139
31	Xylene	30	I	43.77 — 68.39	8.3042	4.4857	1.85	11	9, 5, p. 145
32	Bromobenzene	0	I II	24.35 — 43.81 43.81 — 81.82	14.9324 6.8543	8.2770 3.6600	1.80 1.87	12	4, 5, p. 144

(methanol)—water—inorganic salts as demonstrated in the present paper. On the basis of the obtained data we shall try to develop an idea about the structure of the examined saturated ternary systems.

REFERENCES

1. E. I. Ahumov, *Zhur. Obschchei Khim.* **9** (1939) 1207, 1220.
2. H. Iveković and B. Miličević, *Croat. Chem. Acta* **31** (1959) 91.
3. A. Gertner, *Bull. sci. Conseil Acad. SFR Jugoslavie* **5** (1959) 20.
4. W. D. Bonner, *J. Phys. Chem.* **14** (1910) 738.
5. A. Seidell, *Solubilities of Organic Compounds II*, Third Edition, D. van Nostrand, New York 1941.
6. J. Barbandy, *Compt. rend.* **182** (1926) 1279.
7. D. N. Tarassenkow and J. A. Paulsen, *Zhur. Obschchei Khim.* **7** (1937) 2143.
8. K. Scheringa, *Pharm. Weekblad* **59** (1922) 389.
9. W. R. Ormandy and E. C. Craven, *J. Inst. Petroleum Techn.* **7** (1921) 325, 422.

IZVOD

Zasićeni ternarni sistemi IV. Izoterme topivosti organskih tvari u smjesama voda—etanol

H. Iveković i A. Gertner

Određene su konstante u izotermama $\log y = a + b \cdot \log (100 - x)$, gdje je y broj molova organske tvari, a x broj molova etanola u 100 molova smjese etanola i vode. Izoterme su određene za slijedeće organske spojeve: *izo*-butilbromid, benzaldehid, bromtoluen, benziletilester, propilbromid, *izo*-amilbromid, *izo*-amilester, *o*-ksilen, *izo*-butanol, dietilketon, fenetol, *m*-ksilen, kloroform, *p*-psilen, nitrobenzen, etilacetat, benzilacetat, kamfor, mezitilen, pinen, heksan, *p*-nitrotoluen, toluen, cikloheksan, etilbromid, *o*-toluidin, etilbutirat, etilpropionat, metilanilin, benzen i bromobenzen.

ZAVOD ZA ANORGANSKU I FIZIKALNU KEMIJU
FARMACEUTSKO-BIOKEMIJSKI FAKULTET
ZAGREB

Primljeno 22. siječnja 1965.