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Saturated Ternary Systems. V.* Solubility Isotherms of Organic Compounds in Water-Methanol Mixtures

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Determined were the constants of solubility isotherms for the solutions of the following organic compounds in a mixture of methanol and water: benzene (20° C), bromobenzene (0°), hexane (0°), tetrachloromethane (0°), toluene (0°), ethylbromide (0°), chloroform (0°) and heptane (0°). The authors show that the solubility of the investigated organic compounds at the intersections of the isotherms changes according to the same law for the systems methanol-water and the systems ethanol-water. Lower concentrations of water diminish the solubility of the organic compounds in the mixture alcohol-water relatively more than higher concentrations. The inner angles under which two isotherms intersect vary in the systems organic compound — water — methanol between 165 and 175° and in the systems with ethanol between 169 and 175° in the majority of the systems investigated.

INTRODUCTION

In the present paper a report is given on the results of continued investigations into the law governing the concentrations of liquid ternary systems saturated with organic compounds and water. The third component (methanol) is perfectly mixible with both the mentioned components. The systems organic compound-water-methanol treated in the present paper are analogous to the systems organic compound-water-ethanol, treated in the preceding paper of the series¹. Therefore both these groups of systems will be discussed together. In this communication, as in the preceding one (IV), the applicability of a modified equation of E. I. Akhumov² has been investigated.

CALCULATIONS AND DISCUSSION

In the literature experimental data for 8 systems organic compound-water-methanol were found, the organic compounds being the following: benzene (20° C; curve 1, Fig. 1), bromobenzene (0° C; curve 2, Fig. 2), hexane (0° C; curve 3, Fig. 2), tetrachloromethane (0° C; curve 4, Fig. 2), toluene (25° C; curve 5, Fig. 3), ethylbromide (0° C; curve 6, Fig. 3), chloroform (0° C; curve 7, Fig. 3) and heptane (0° C; curve 8, Fig. 3).

Table I contains the calculated constants a and b of the isotherms, ranges of concentration of methanol in mole per cent (x) for which isotherms I and II are valid, ratios $-a/b$ as well as references from which the experimental data were taken.

* Part IV.: H. Iveković and A. Gertner, *Croat. Chem. Acta* 37 (1965) 99.

It ought to be mentioned that, for the systems given in the quoted literature data were found only for limited ranges of concentrations. Consequently, it is probable that many of these isotherms are valid also for wider ranges of

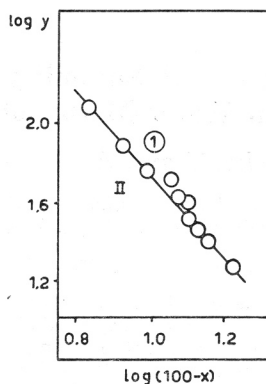


Fig. 1. Isotherm methanol-water-benzene (20°).

concentrations than given in Table I by the quantity x . As already mentioned¹, in calculating the constants a and b of equation

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

(y = number of moles of dissolved organic compound in 100 moles of a mixture of water and methanol; x = number of moles of methanol in this quantity of

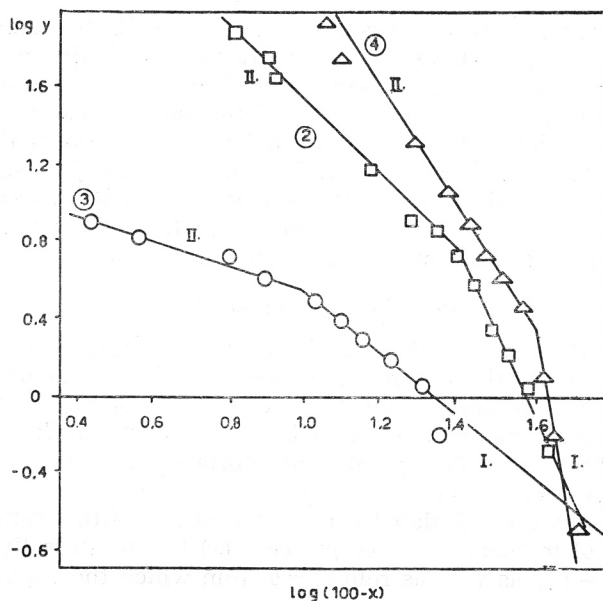


Fig. 2. Isotherms: methanol-water-organic compound; 2. bromobenzene (0°); 3. hexane (0°); 4. tetrachloromethane (0°).

TABLE I

No.	Substance	t° C	Iso-therm	x	a	$-b$	$-a/b$	Fig.	References
1	Benzene	20°	II	83.56—93.16	3.9263	2.1713	1.81	1	3; 4 p. 46
2	Bromobenzene	0°	I	54.50—72.32	6.0408	3.7754	1.60	2	5; 4 p. 48
		0°	II	72.32—93.50	3.6178	2.0953	1.73	2	
3	Hexane	0°	I	79.42—90.55	2.1606	1.6141	1.34	2	5; 4 p. 48
		0°	II	90.55—97.29	1.1856	0.6147	1.93	2	
4	Tetrachloro- methane	0°	I	37.63—63.33	11.3364	6.9146	1.64	2	5; 4 p. 45
		0°	II	63.33—88.97	4.7159	2.6824	1.76	2	
5	Toluene	25°	I	15.11—59.23	10.3967	6.1290	1.70	3	6; 4 p. 45
		25°	II	59.23—91.50	3.9563	2.1295	1.86	3	
6	Ethylbromide	0°	II	37.00—80.80	6.7180	3.6706	1.83	3	5; 4 p. 48
7	Chloroform	0°	I	13.21—50.62	14.4461	7.8383	1.84	3	5; 4 p. 45
		0°	II	50.62—66.32	6.2355	2.9901	2.09	3	
8	Heptane	0°	II	63.38—92.04	1.5786	1.3778	1.15	3	5

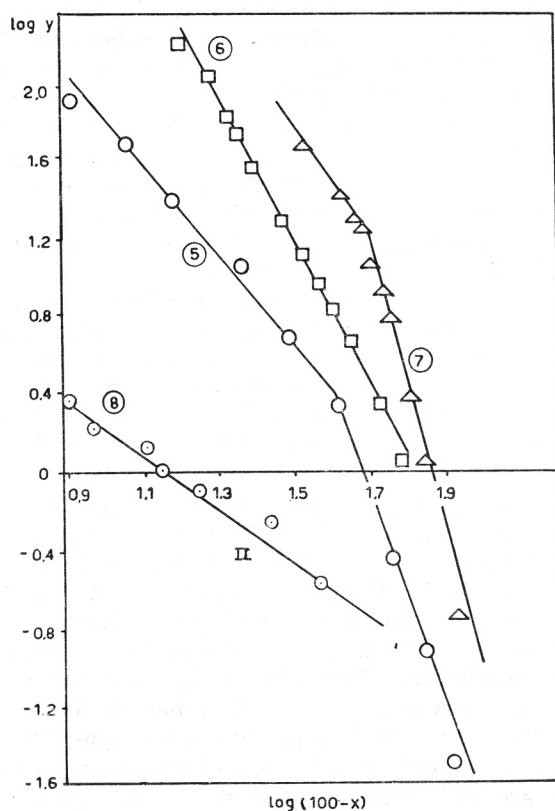


Fig. 3. Isotherms: methanol—water—organic compound; 5. toluene (25°); 6. ethylbromide (0°); 7. chloroform (0°); 8. heptane (0°).

mixture) those extreme data were not taken into consideration which had been shown by the graphic method to be off the isothermic straight lines.

In Figs. 1—3 the obtained data are plotted as $\log(100 - x)$ vs. $\log y$. With the exception of the systems water-methanol-benzene (for which data are available only for a very narrow range of concentrations 83.56—93.16 M - $\%$ of methanol), water-methanol-ethylbromide and water-methanol-heptane, the results in all the investigated systems thus plotted fall upon two intersecting straight lines.

The mole per cent of methanol in the mixture water-methanol range, at the intersection of isotherms I and II of the investigated systems (bromobenzene, hexane, tetrachloromethane, toluene, chloroform), is between 50.62 (chloroform) and 90.55 M - $\%$ (hexane). In the investigated systems organic compound-water-ethanol¹ this value was displaced towards smaller concentrations of ethanol (30—66 M - $\%$).

The molar ratio of alcohol and water at the intersection of the straight lines approaches for the majority of organic compounds ratios of small integers. Thus, for instance, in the systems with methanol this ratio amounts to approximately 1 : 1 (chloroform) and 3 : 2 (tetrachloromethane, toluene), and in the systems with ethanol 1 : 1 (bromotoluene, isoamylbromide, camphor, *p*-nitrotoluene, cyclohexane, ethylbromide), 1 : 2 (benzaldehyde, *o*-toluidine, ethylbutyrate), 2 : 3 (benzylacetate, toluene, methylaniline, bromobenzene, benzene), 2 : 1 (mesitylene, pinene) and 3 : 2 (hexane). Accordingly, these alcohol-water ratios are critical for the change in the trend of the solubility of the organic solutes, when the concentration of alcohol in the solvent mixture increases or decreases.

If the concentrations of alcohol at the intersection of the isotherms for the systems organic compound-water-methanol are compared with those in the systems organic compound-water-ethanol, it will be seen that the ratio of these concentrations for solutions with the same organic compound as solute varies within narrow limits. Thus, for instance, the ratio $x_{\text{methanol}}/x_{\text{ethanol}}$ at the intersection, with bromobenzene as solute amounts to 1.65, with hexane to 1.54, with chloroform to 1.72 and with toluene to 1.41 (only in these organic compounds data for both mixtures of solvents are available). The ratios of the concentrations of the organic compounds at the intersection are also almost equal and of the same magnitude as the concentration ratio of the solvents: the ratio $y_{\text{methanol}}/y_{\text{ethanol}}$ amounts for bromobenzene to 1.39, hexane to 1.35, for chloroform to 2.3 and for toluene to 1.68.

The values of the constants b_I and b_{II} *i. e.* the slopes of the straight lines constituting the isotherms, differ widely in the investigated systems. In the systems organic compound-water-methanol, b_I varies between -1.6 (hexane) and -7.8 (chloroform), and b_{II} between -0.6 (hexane) and -2.99 (chloroform); in the systems organic compound-water-ethanol values were found for b_I between -4.1 (pinene) and -17.0 (*o*-toluidine) and for b_{II} between -1.7 (ethylbromide) and -6.86 (*o*-toluidine). The ratio $b_I : b_{II}$ of the two isotherms of the same ternary system, however, varies within narrow limits. In the system organic compound-water-methanol it has the value 2.6—2.9 (average 2.7) in 4 of the 5 investigated systems, *i. e.* in 80% of the cases. In the systems with ethanol two groups are prominent: in one of them ratio b_I/b_{II} assumes the value of 2.0—2.8 (average 2.5) in 55% of the investigated systems, and in the other group 1.4—2.0 (average 1.8) in 28% of the total of 32 investigated systems.

The inner angles α (cf. Table II) under which isotherms I and II of the same system intersect, calculated by means of equations $\alpha = 180 - \varphi$ and $\operatorname{tg} \varphi = (b_2 - b_1) / (1 + b_2 \cdot b_1)$, vary in the systems organic compound-water-methanol between 165° and 170° (from these values hexane differs slightly with 154°). The same angles in the systems with ethanol vary between 169 and 175° (small differences from these values show ethylbromide with 158° and benzene with 163°; an exception shows only camphor with 118°). Accordingly, in the systems with the same alcohol these angles vary within very narrow limits. This fact suggests the assumption that at the critical point — intersection of isotherms I and II — the solubility of the organic compounds changes according to the same rule.

In the preceding communication IV we called attention to the ratio $-a/b$ of the same isotherm. The magnitude of this ratio varies for the system with the same alcohol but for different organic compounds within relatively small limits. In the systems organic compound-water-methanol we found that the average value of the ratio $-a/b$ for isotherms I amounts to 1.69 (the value 1.34 obtained with hexane was discarded), while in isotherms II it amounts to 1.86 (the value 1.15 obtained for heptane was discarded). In the systems with ethanol

TABLE II

Substance	α
<i>Systems Methanol—Water</i>	
Bromobenzene	170°
Hexane	154°
Tetrachloromethane	168°
Toluene	165°
Chloroform	169°
<i>Systems Ethanol—Water</i>	
<i>iso</i> -Butylbromide	174°
Benzaldehyde	174°
Bromotoluene	170°
Benzyl-ethyl-ether	173°
Propylbromide	172°
<i>iso</i> -Amylbromide	175°
Chloroform	170°
Benzylacetate	172°
Camphor	118°
Mesitylene	175°
Pinene	169°
Hexane	171°
<i>p</i> -Nitrotoluene	172°
Toluene	174°
Cyclohexane	169°
Ethylbromide	158°
<i>o</i> -Toluidine	175°
Ethylbutyrate	172°
Ethylpropionate	172°
Methylaniline	172°
Benzene	163°
Bromobenzene	172°

we obtained for isotherms I the value 1.85 and for isotherms II 1.98 (the value 5.84 for camphor was discarded).

Apart from the extremely great value for $-a/b = 5.84$ of isotherm II in camphor (see communication IV¹, Table I, No. 18) no essential difference could be noted between systems whose isotherms were given for higher temperatures (methanol-water: benzene 20° C, toluene 25°; ethanol-water: cyclohexane 25°, benzene 25°, xylene 30°) and those systems whose isotherms were determined at 0° C (all other systems).

The mentioned, small, differences in the magnitudes of the angles under which isotherms I and II intersect as well as the small differences among the ratios of constants $-a/b$ show that, a) in solutions of organic compounds investigated in a mixture of alcohol and water neither the chemical composition nor the size of the molecule of the solute nor the temperature (in the investigated ranges) plays an essential role in the change of the trend of solubility of organic compounds at the intersection of isotherms I and II; and b) the solubility of organic compounds in the mixtures methanol-water and ethanol-water is determined by the same basic law.

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IZVOD

Zasićeni ternarni sistemi. V. Izoterme topljivosti organskih spojeva u smjesama voda—metanol

H. Iveković i A. Gertner

Za smjese voda—metanol određene su konstante izoterme topljivosti slijedećih organskih spojeva: benzen (20° C), brombenzen (0°), heksan (0°), tetraklormetan (0°), toluen (0°), etilbromid (0°), kloroform (0°) i heptan (0°). Većina sistema može se u istraženom području koncentracija prikazati s dvije izoterme. Pokazano je da se topljivost ispitanih organskih spojeva u području sjecišta ovih izoterme mijenja po istoj osnovnoj zakonitosti kod smjesa voda—metanol kao i kod smjesa voda—etanol. Unutarnji kut pod kojim se sijeku izoterme varira kod najvećeg broja ispitanih slučajeva u uskim granicama: kod sistema s metanolom između 165 i 170°, a kod sistema s etanolom između 169—175°.

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