

CONDENSED PHASE EQUILIBRIUM IN THE SYSTEMS: WATER-NITROBENZENE-PHENOL AND WATER-NITROBENZENE-2,6-XYLENOL AT 20°C

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Solubility and liquid-liquid phase equilibrium data at 20°C are given for systems of interest in extraction. The systems measured consisted of water, nitrobenzene and as the third component either phenol or 2,6-xylenol. The experimental data are correlated in a mode suitable for systems of this type. A method is also described in detail for analytical determination of phenolic components using coulometric titration which is not common and has not been applied thus far for 2,6-xylenol.

In recent years the utilization of systems containing higher substituted phenols as well as phenol itself for extraction of alkali metals both for analytical and preparative purposes has received considerable attention (see *e.g.* cit.¹). In this connection arose the need of the study of phase liquid-liquid equilibria in systems containing water, organic solvent and a phenolic component. These equilibria for systems having nitrobenzene as the basic component of non-aqueous phase (the extraction efficiency of nitrobenzene is particularly favourable²) have not yet been described in the literature.

Since the systems in question are interesting also from the point of view of physical chemistry we proceeded to their investigation by selecting water-nitrobenzene-phenol and water-nitrobenzene-2,6-xylenol (in the following only xylenol for brevity) systems. These two systems may serve as models of the systems in which the phenolic component extracts well (the case of phenol), or poorly (the case of xylenol).

The phase diagrams were measured at 20°C and the atmospheric pressure. The attention was focused primarily on that range of concentration relevant to extraction. To measure the binodal curves, the method of analyzing equilibrium phases was chosen for both systems in the range where we were also interested in the determination of the direction of the tie lines. In a similar fashion were obtained also the solubility data for partial binary systems with liquid, respectively solid phases which have not been thus far known in the literature. These data were completed in the three-component region by additional, less accurately determined experimental

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data obtained by isothermal turbidity method. This method was employed in the region irrelevant to extraction.

A coulometric method, developed for the determination of phenol in aqueous solutions^{3,4}, was used in this work for the first time to determine xylenol. With respect to differences in behaviour of unsubstituted phenol and xylenol, the applicability of the method had to be verified in advance. Accordingly, this analytical method will be described in greater detail in Experimental part. The analytical method accepted for determination of nitrobenzene in water phase will also be discussed briefly since it is not common.

EXPERIMENTAL

Chemicals and Procedures

All chemicals used were of reagent grade purity. 2,6-Xylenol was a product of Loba-Chemie, Wien. The rest were products of Lachema, Brno. Sodium bromide and hydrochloric acid were used as purchased. Methanol was desiccated on a molecular sieve of the Nalsit 4A type and distilled at the atmospheric pressure before use. Nitrobenzene, phenol and xylenol were distilled *in vacuo* before use. The Fischer agent was provided by Lachema, Brno. Redistilled water was used.

All equilibrium measurements were carried out in a thermostat at $20 \pm 0.1^\circ\text{C}$. To determine the composition of the three-component conjugated solutions, sets of mixtures of phenolic component, nitrobenzene and water were prepared by weighing all components in such a quantity that the ratio of the organic components to water be approximately 1 : 1. After a vigorous shaking and establishing equilibrium between the water and organic phases and keeping a relatively small volume of vapour phase to check the error due to evaporation of individual components, samples of individual phases were taken for analysis. A centrifuge had to be used in some cases for better separation of both phases.

Nitrobenzene and phenolic component were determined analytically in the equilibrium water phase. In addition, the density of the water phase at the same temperature was determined using a pycnometer, enabling the molarity-to-weight percent conversion. Water in the organic phase was determined analytically. The content of undetermined components was calculated as a complement from the material balance on the basis of known analytical data and initial weight of the components.

To obtain the points on the binodal curves by the turbidity method, samples of nitrobenzene and phenolic component mixed in a suitable ratio were weighed and titrated at constant temperature by water until a turbidity was observed.

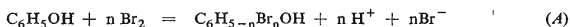
The composition of the binary mixtures saturated by solid phenolic component was determined by adding the surplus of the solid phase to the second, liquid component, long-term vigorous shaking at the constant temperature and by sampling and analyzing the saturated liquid phase. The establishment of equilibrium was verified by check experiments in which all solid phase was dissolved at an elevated temperature and the same point was reached by subsequent cooling to 20°C . The equilibrium composition of the solid phase was checked analytically in all runs. It has been confirmed that within experimental error the composition of the solid phase always corresponds to that of the pure phenolic component.

Analytical Methods

Determination of water. Water in the organic phase was determined by K. Fischer's method⁵ (for experimental set-up see cit.⁶). Weighed samples of the organic phase were injected by a syringe into the titration flask through an elastic stopper, after the titration of residual moisture. The titre of the Fischer agent was 2.35 mg H₂O per 1 ml. A solution of water in methanol⁷ was used for its standardization.

Determination of nitrobenzene. Nitrobenzene was determined in water phase at very low concentration, and in the presence of greater amount of the phenolic component by spectrophotometry. The wavelength of 530 nm was selected on the basis of orientational, unpublished spectrophotometric measurements under similar conditions⁸. At this wavelength the Lambert-Beer law was found to hold for dilute aqueous solutions of nitrobenzene with sufficient accuracy. An analysis of the model mixtures has shown that the method provides reproducible and correct results in the presence of the phenolic compound as well. The final diluted samples of the water phase were analyzed in the central laboratory of this University, on an Optica, Milano spectrophotometer at 350 nm in a measuring cell 1 cm thick. Redistilled water was in the reference cell. The concentrations were read-off from calibration curves. In the range of concentrations measured (the order of magnitude 10⁻³ molar) the calibration curves were always linear. The extinction coefficient of nitrobenzene under given conditions of measurement was 2.1 · 10² l mol⁻¹ · cm⁻¹. The resulting concentration data of the analyzed nitrobenzene solutions were converted from molarities to weight percent concentration units by means of the known values of the density of water phase.

Determination of the phenolic components. A coulometric titration of the phenolic compound based on the reaction



was selected for determination of phenol or xylenol. The chemical equilibrium and the kinetics of the reaction (A) is more favourable when the concentration of hydrogen ions is low. Decreasing concentration of hydrogen ions speeds up substitution of further hydrogen atoms and a polyhalogenated derivate forms.

The use of coulometric titration for direct determination of phenols by electrically generated bromine is limited by sufficient reaction rate. The titration agent generated at a constant rate must react before it may affect the indication electrodes. Excess free bromine not consumed by a slow reaction obscures the identification of the equivalence point in the solution. Francis, Hill and Johnston⁹ compared relative rates of substitution of aromatic rings by bromine as far as the third step and as a reference rate they took monobromination of aniline: $k_1 = 1$. The values of the constants¹⁰ for phenol are: $k_1 = 21$, $k_2 = 0.19$, $k_3 = 0.03$ and for 2,6-xylenol: $k_1 = 35$. These properties enable the coulometric titration to be employed in a strong acid solution, in which the end of the stoichiometric reaction leading to the monoderivative can be detected by biamperometric indication. The determination of phenol was carried out using a method described in paper³. Since the determination of 2,6-xylenol has not been investigated to date, it was verified on model solutions in the concentration range 2 · 10⁻⁵ to 4 · 10⁻⁴ mol/l with the total amount 60 to 1200 µg of xylenol. The titration itself was carried out in the solution containing 1–2 mol/l HCl and 0.1 mol/l NaBr, analogously to the titration of phenol. A modified potentiostat of our own construction was used as a source of generating current. The titration flask used has been described earlier¹¹. The titration current was 20, 10, 5 and 2 mA. The course of titration was followed by means of two polarized platinum electrodes, 10 cm² in surface area. The effect of polarization voltage on the shape of the titration curves

was examined in the range 100 to 400 mV. The curves were practically identical and we selected 200 mV as the optimum value with regard to concentration range of xylenol. An LP 60 polarograph, or an independent polarization unit was used as a source of voltage. The titration curves were recorded on an EZ 2 recorder with the time base 1 mm/s. A typical course of the titration is shown in Fig. 1. The shape of the curves corresponds to an irreversible reaction of xylenol with bromine. The increase of current past the equivalence point corresponds to the reversible redox pair: Bromine-bromide ion. The results of the model titrations were processed by the Dean-Dixon method. For the current intensity 2 mA and the number of experiments $n=5$, we found the mean equal 98.4% of the theoretical value, the standard deviation equal 0.90, the probable error equal 1.1 for 95% confidence level. Thus the result is $98.4 \pm 1.1\%$. For the current intensity 5 mA and $n=7$, the mean is 99.8%, the standard deviation 1.6, the probable error 1.4 and the result $99.8 \pm 1.4\%$. For 20 mA and $n=7$, the mean is 99.9%, the standard deviation 2.7, the probable error 2.4 and the result $99.9 \pm 2.4\%$. Further we tested on model solutions that under given experimental conditions nitrobenzene does not react with bromine. The values of the concentrations of phenolic compounds in equilibrium phases summarized in Tables are the averages of several analyses ($n=3$ to 5).

RESULTS AND DISCUSSION

In two-component systems the concentration of the component, in a phase in which that particular component was not analyzed for, was calculated as the remainder to 100 weight %.

For the three-component systems the missing data were calculated from derived relationships based on weight amounts of chemicals used, experimentally determined concentrations and material balances (subscript 3 for phenol replace by 4 for xylenol):

$$G^v = \frac{g_2 - w_2^0 \cdot 10^{-2}(G^v + G^0)}{1 - w_2^0 \cdot 10^{-2} - (10^{-3}/d^v)(c_1^v M_1 + c_3^v M_3)}, \quad (1)$$

$$g_1^0 = g_1 - G^v \cdot 10^{-3} M_1 c_1^v / d^v, \quad (2)$$

$$g_3^0 = g_3 - G^v \cdot 10^{-3} M_3 c_3^v / d^v. \quad (3)$$

The System Nitrobenzene-Water-Phenol

The results of equilibrium of solid phenol-nitrobenzene solution of phenol yielded following value of solubility of solid phenol: 80.13 weight% of phenol in nitrobenzene solution of the density 1.097 g/ml. Hence the saturated solution of phenol in nitrobenzene is 9.340 molar. The saturated solution of solid phenol in water contains according to the literature¹² 90.4 weight% of phenol, *i.e.* at the density 1.059 g/m the solution is 10.172 molar. The results of determination of solubility of the mixture of phenol and nitrobenzene in water are summarized in Table I. Table II gives the data of the composition of conjugated solutions together with the over-all composition of the mixture before separation, and the composition corresponding to the points on the binodal curve determined by the turbidity method.

TABLE I

Solubility of the Nitrobenzene-Phenol Mixtures in Water and Density of the Solutions Formed at 20°C

Concentration, mol/l		Density, d^v g/ml
nitrobenzene	phenol	
0.0155	0.0011	0.9982
0.0155	0.0022	0.9982
0.0155	0.0030	0.9982
0.0155	0.0040	0.9982
0.0154	0.0061	0.9982
0.0154	0.0080	0.9982
0.0154	0.0097	0.9978
0.0153	0.0221	0.9976
0.0153	0.0501	0.9987
0.0151	0.1018	0.9985
0.0146	0.1880	0.9991
0.0144	0.2345	0.9992
0.0142	0.2901	0.9994
0.0132	0.4220	0.9997
0.0116	0.5363	1.0002

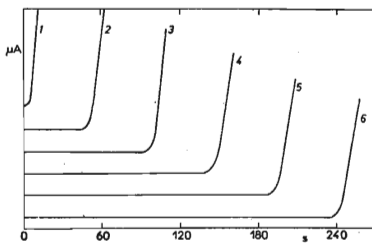


FIG. 1

Titration of Xylenol Solution by Bromine with Biamperometric Indication

Generating current 2 mA, polarization voltage 200 mV, volume of the solution 25 ml. Abscissa: time, s. Ordinate: indication current μA . Concentration of xylenol: 1 blank sample; 2 $2.2 \cdot 10^{-5}$; 3 $4.4 \cdot 10^{-5}$; 4 $6.6 \cdot 10^{-5}$; 5 $8.8 \cdot 10^{-5}$; 6 $1.1 \cdot 10^{-4}$ mol/l.

TABLE II
Concentration (weight %) of the Components in Conjugated Solutions at 20°C

Over-all composition		Organic phase		Water phase	
phenol	water	phenol	water	phenol	nitrobenzene
0.04	42.84	0.07	0.24	0.01	0.19
0.09	43.17	0.15	0.25	0.02	0.19
0.12	45.86	0.20	0.25	0.03	0.19
0.18	44.71	0.28	0.25	0.04	0.19
0.25	45.99	0.42	0.26	0.06	0.19
0.33	46.27	0.56	0.27	0.08	0.19
0.42	47.55	0.70	0.27	0.09	0.19
0.88	42.80	1.36	0.32	0.21	0.19
2.15	43.45	3.39	0.52	0.47	0.19
4.39	44.59	7.06	0.87	0.96	0.19
9.22	42.26	13.60	1.62	1.77	0.18
9.83	46.78	16.56	1.85	2.21	0.18
13.38	45.00	21.28	2.36	2.73	0.17
16.50	57.20	33.74	4.04	3.97	0.16
26.10	53.02	49.71	6.16	5.05	0.14
—	—	50.25 ^a	8.12	—	—
—	—	54.60 ^a	9.19	—	—
—	—	61.47 ^a	12.07	—	—
—	—	67.34 ^a	15.50	—	—
—	—	71.42 ^a	20.27	—	—
—	—	72.16 ^b	27.84	8.36 ^b	0.00
—	—	0.00	0.25 ^c	0.00	0.19

^a Determined by turbidity method. ^b Data from the literature.^{1,2} ^c Data from cit.⁶

TABLE III
Solubility of the Nitrobenzene-Xylenol Mixtures in Water and Density of the Solutions Formed at 20°C

Concentration, mol/l		Density, d^v g/ml	Concentration, mol/l		Density, d^v g/ml
nitrobenzene	xylenol		nitrobenzene	xylenol	
0.0140	0.0066	0.9990	0.0130	0.0108	0.9997
0.0137	0.0084	0.9991	0.0129	0.0124	0.9996
0.0135	0.0098	1.0006	0.0137	0.0156	0.9989

The summary results for the system studied with concentrations in weight% are plotted in triangular diagram in Fig. 2. The fact that the tie lines pass through the

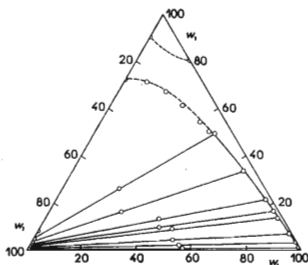


FIG. 2

Triangular Diagram of the System Nitrobenzene-Water-Phenol at 20°C (concentration in weight %)

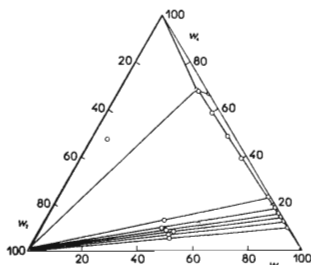


FIG. 3

Triangular Diagram of the System Nitrobenzene-Water-Xylenol at 20°C (concentration in weight %)

TABLE IV

Concentration (weight %) of the Components in Conjugated Solutions at 20°C

Over-all composition		Organic phase		Water phase	
xylenol	water	xylenol	water	xylenol	nitrobenzene
5.32	45.59	9.69	0.38	0.08	0.17
6.83	45.06	12.33	0.43	0.10	0.17
8.20	42.65	14.19	0.46	0.12	0.17
8.78	44.99	15.82	0.48	0.13	0.17
9.85	46.03	18.07	0.56	0.15	0.16
13.04	43.64	22.92	0.63	0.19	0.17
—	—	39.20 ^a	2.12 ^a	—	—
—	—	48.71 ^a	2.39 ^a	—	—
—	—	58.56 ^a	3.01 ^a	—	—
—	—	67.82 ^a	3.20 ^a	—	—
47.52 ^b	46.74 ^b	68.28 ^b	—	0.67 ^b	—
—	—	0.00	0.25 ^c	0.00	0.19

^a Determined by turbidity method. ^b A point belonging to the three-phase equilibrium region: organic phase, water phase and solid xylene. ^c Data from cit. ⁶.

points of original composition in the diagram confirms the correctness of material balances. A relatively wide single-phase region with low concentration of water is apparent from the diagram. The second, water-rich single-phase region forms a narrow strip near the apex of the triangle representing pure water. The two-phase region of equilibrium between solid phenol and the three-component liquid phase is well separated from a large area of interest in extraction, *i.e.* from the two-phase liquid-liquid area under the binodal curve. The course of the binodal curve is typical for systems where the solid component dissolves well in one of the components and has a limited solubility in the other component.

With respect to a relatively low solubility of phenol in the water phase, this diagram does not provide sufficient insight into the extraction efficiency of the system. Accordingly, another diagram plotting the equilibrium concentrations of phenol in both phases is presented in Fig. 4.

The System Nitrobenzene-Water-Xylenol

The results of equilibrium measurements in the system solid xylenol-water solution of xylenol and solid xylenol-nitrobenzene solution of xylenol provided following values of solubilities: 1.46 weigh% of xylenol in water solution of density 1.001 g/ml, *i.e.* the saturated water solution is 0.120 molar. 66.76 weight% of xylenol in nitrobenzene solution of density 1.077 g/ml, *i.e.* the saturated solution in nitrobenzene is 5.885 molar. The resulting solubilities of nitrobenzene and xylenol in water are shown in Table III. Table IV gives the data for the binodal curve and conjugated solutions in this system.

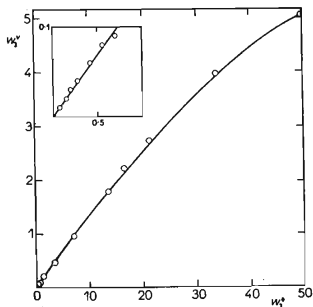


FIG. 4

Distribution of Phenol between Water and Nitrobenzene at 20°C

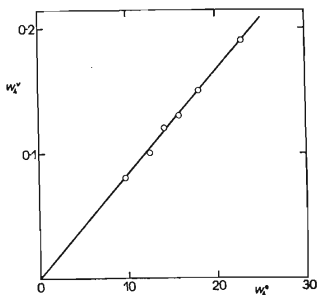


FIG. 5

Distribution of Xylenol between Water and Nitrobenzene at 20°C

The triangular diagram of this system is in Fig. 3 and it differs markedly from the preceding one. To begin with, a large three-phase area appears in which the system is invariant at constant temperature and pressure. In this region solid xylenol is at equilibrium with two liquid phases of constant composition. The single-phase area of mutual solubility for high concentrations of organic components has diminished in comparison with the previous system. Instead of one two-phase area of solid-liquid equilibrium as in the case of phenol, there are two such areas here. The larger of them represents the equilibrium of solid xylenol with the nitrobenzene-rich liquid phase. In the second, very narrow area close to the binary mixture water-xylenol solid xylenol is at equilibrium with the water-rich liquid phase. The two-phase liquid-liquid region of interest in extraction is here substantially smaller than that of the previous system. A plot of the equilibrium concentrations of xylenol in the water and organic phases is in Fig. 5.

Correlation of the Data

From Figs 4 and 5 it is apparent that at low concentration of phenolic compound the mutual dependence of the equilibrium concentrations is linear. In the case of xylenol this linearity persists for higher concentrations as well and thus the relation between the concentration of xylenol in the water and organic phases may be used

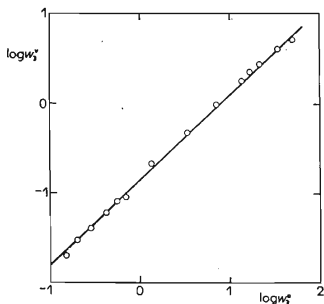


FIG. 6
Linear Correlation of Equilibrium Phenol Concentrations in Conjugated Phases

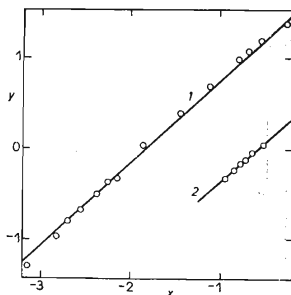


FIG. 7
Correlation of the Tie Lines
Abscissa: log of the ratio of concentration (weight %) of the phenolic component to nitrobenzene in the organic phase. Ordinate: log of the same ratio in the water phase.
Curve: 1 phenol; 2 xylenol.

conveniently in terms of weight percent. The dependence is described by Eq. (4). In the case of phenol the distribution curve is no longer linear at higher concentrations and may be described by Eq. (5) in the whole concentration range of analyzed phases.

$$w_4^y = 0.0083w_4^0, \quad (4)$$

$$w_3^y = 0.137(w_3^0)^{0.967}. \quad (5)$$

The data for phenol plotted in accordance with Eq. (5) in log-log scale are presented in Fig. 6.

Correlation of the tie lines for systems with two binary mixtures of limited mutual solubility may be carried out in some cases⁴ in terms of the ratio of weight percent of the distributed component to the weight percent of that perfectly miscible with the former. The dependence of this ratio in one phase on the equilibrium value of the same ratio in the other phase should be linear. For the systems examined, the equilibrium diagrams are in both cases more complicated due to the appearance of areas of solid-liquid equilibrium. Nevertheless, the same variables, *i.e.* the ratio of weight percent of the phenolic component to nitrobenzene, both in the organic and water phases may be used for correlation of the tie lines at least over low concentration range of the phenolic component, which is the range of interest for extraction equilibria. In both cases these dependences appear linear as a log-log plot, *i.e.*:

$$\log (w_3/w_1)_v = A + B \log (w_3/w_1)_0, \quad (6)$$

in the case of phenol, respectively w_4 instead of w_3 in the case of xylenol. The results for both systems are plotted in Fig. 7. The values of the constants A and B of Eq. (6) are 1.673 and 0.918 for phenol, for xylenol 0.520 and 0.872 respectively.

The course of dependences of the phenolic component especially Eq. (5) seems to indicate that, in contrast to xylenol, association of the monomers of phenol, eventually their interaction with other components occurs to a marked extent. This finding is fully consistent with the data from the literature about the behaviour of phenol in other solvents¹³, as well as with the results of spectrophotometric measurements in dilute solutions of phenol in nitrobenzene¹⁴.

The authors wish to thank Mr L. Jettmar for technical assistance.

LIST OF SYMBOLS

- c_i concentration of i -th component in a given phase [mol/l]
 d density [g/ml]
 g_i weight of i -th component (without subscript: total weight; subscripted: weight in a given phase) [g]

- G total weight of equilibrium phase
 M molecular weight
 w_i concentration of i -th component [weight %]

SUBSCRIPTS

- 1 nitrobenzene
2 water
3 phenol
4 2,6-xyleneol
o organic equilibrium phase
v water equilibrium phase

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