

PHASE EQUILIBRIA OF THE SYSTEM WATER-ETHANOL-DIVINYLBENZENE-ACRYLAMIDE

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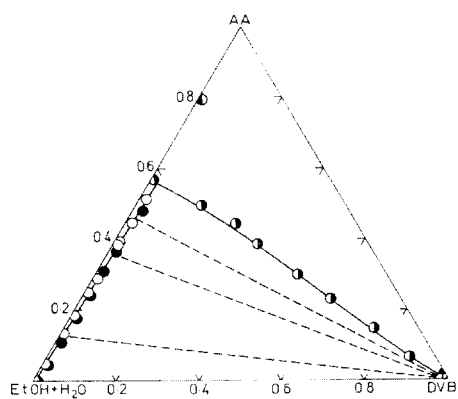
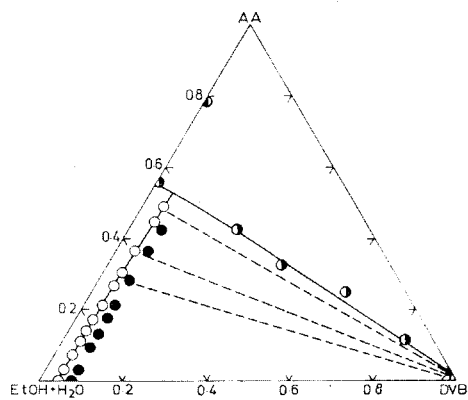
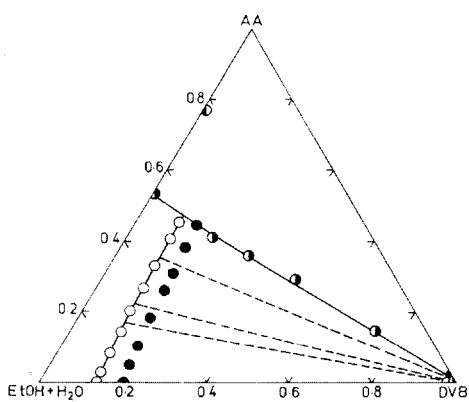
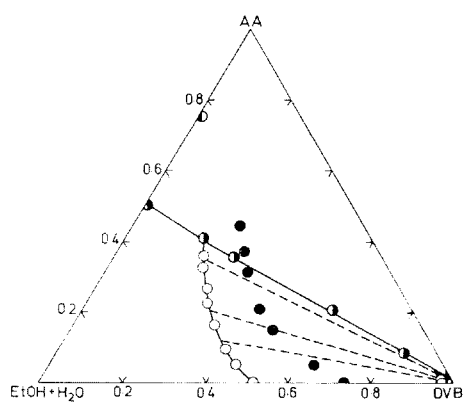
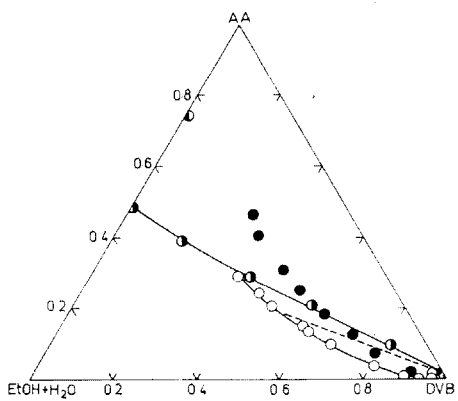
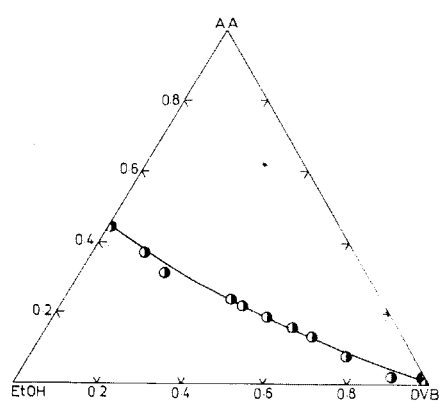
Phase equilibria of a four-component system water-ethanol-divinylbenzene-acrylamide (H_2O - $EtOH$ -DVB-AA) have been investigated in concentration regions with a water content lower than 50 vol.% and an ethanol content higher than this value. The equilibria were measured at 25°C and partly at 50°C. Two regions of a different effect of acrylamide on the solubility of divinylbenzene in ethanol-water mixtures were found. The solubility data were correlated by using the empirical Sečenov's equation.

Copolymers based on comonomers with a different chemical structure and consequently with quite different properties in many respects, which often leads to mutual immiscibility, are studied with an increasingly greater attention. The synthesis of such copolymers can have some special features, especially if it leads to the formation of products insoluble in the original medium. Acrylamide and divinylbenzene are a typical pair of comonomers having the above properties. The behaviour of acrylamide is that of a weak electrolyte; divinylbenzene is a typical representative of explicitly nonpolar monomers. It has been the objective of this paper to define regions of mutual miscibility of both comonomers in solutions of ethanol and water as a function of the water content, water being a very good solvent of acrylamide and a very poor solvent of divinylbenzene.

EXPERIMENTAL

Chemicals. Stabilized divinylbenzene (Dow Chemical Co., USA) was shaken with a 5% solution of sodium hydroxide, and after that with a 20% solution of sodium chloride. After separation of the aqueous phase it was dried with sodium sulphate, stabilized with a 1% phenothiazine and distilled *in vacuo* at 7–8 Torr and 65–66°C. The divinylbenzene thus obtained was analyzed on a gas chromatograph. The divinylbenzene used ($\rho_{25} = 0.91076 \text{ g/cm}^3$) contained: 51.98% of *m*-divinylbenzene, 13.56% of *p*-divinylbenzene, 32.5% of ethylvinylbenzene, 0.85% of diethylbenzene and 1.1% of higher-boiling admixtures. Acrylamide (Lachema, Brno) was a chemically pure compound, m.p. 83°C after Kofler.

Methods. The majority of data on solubility curves were determined by the method of volume measurements with a Rifai-Durandet's apparatus¹. Naturally, the method could not be used if the densities of both phases were very similar, so that even after staying for one hour no phase

*a**b**c**d**e**f*

separation took place, and the volume of the other phase formed could not be measured. In those concentration regions in which phase separation occurred difficultly the solubility data were determined by titration to the first turbidity. The same titration was also used to obtain solubility curves at 50°C, because the data had to be obtained as fast as possible in view of the danger of polymerization and concentration changes. The composition of conjugated phases was determined after measuring solubility curves. The nitrogen content in both conjugated phases was determined by Kjeldahl's method and recalculated to the acrylamide content. The solid compound-liquid equilibrium data were obtained on determining nitrogen in saturated acrylamide solutions in the mixture of remaining liquids (in the case that the equilibrium solid compound-liquid is adjacent to the homogeneous region of one liquid), and also by titration of a heterogeneous mixture solid acrylamide-divinylbenzene with solutions of ethanol and water.

RESULTS AND DISCUSSION

The data on the phase equilibria of the system under investigation are summarized in Fig. 1a–1f. For reasons of simplicity this four-component system was represented as a pseudoternary one. The perfect miscibility of water and ethanol was made use of and their solutions were used as a third component. The broken lines in triangular diagrams represent connecting straight lines of conjugated liquid phases at 25°C.

It can be seen from the above results that the magnitude of the region of unlimited miscibility and the course of the solubility curves are greatly dependent on the ethanol/water ratio in the system. The effect of an addition of acrylamide on the solubility of divinylbenzene in ethanol-water mixtures is very interesting, since here acrylamide exhibits two types of different influence on the liquid-liquid equilibrium. In concentration regions with 55–35 wt.% of water in the original ethanol-water mixture the presence of acrylamide raises the solubility of divinylbenzene. On the other hand, in those regions where the initial content is lower than 25 wt.% a small addition of acrylamide considerably reduces the solubility of divinylbenzene. Such behaviour of acrylamide cannot be explained in terms of the existing knowledge of its properties, and it will be the object of a further study.

It has been our objective to describe the whole concentration range by means of a single and comparatively simple correlation equation which could also be used in

FIG. 1

Equilibria of the System Water-Ethanol-Divinylbenzene-Acrylamide Having Different Water/Ethanol Ratios

○ Experimental points of the liquid-liquid equilibrium at 25°C; ● experimental points of the liquid-liquid equilibrium at 50°C; ◐ experimental points of the liquid-solid equilibrium at 25°C; ◑ experimental points of the liquid-solid equilibrium at 50°C. Fig. 1a shows the water content in a water-ethanol mixture 55.93% wt.; 1b 35.24% wt.; 1c 24.07% wt.; 1d 12.38% wt.; 1e 6.69% wt.; 1f 0.0% wt.

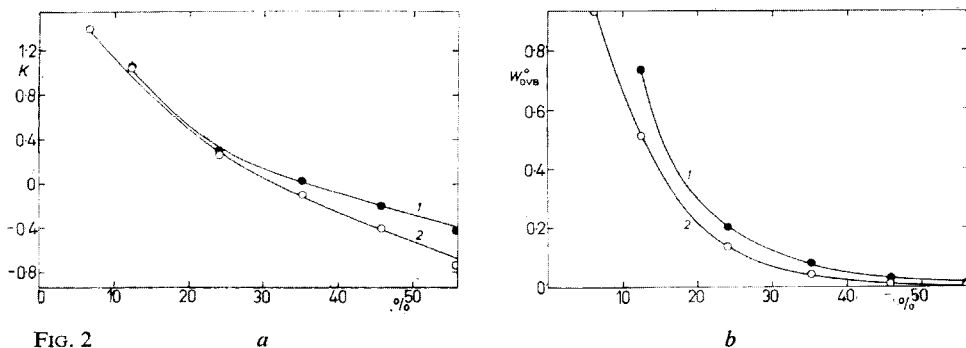


FIG. 2
 Dependence of the Constants of the Correlation Equation (1) on the Water Content (weight %) in Ethanol–Water Mixtures for Temperatures ○ 25°C and ● 50°C
 a constant K ; b constant W_{DVB}^0 .

practice. The empirical Sečenov's equation² was used in the form

$$\log(W_{DVB}^0/W_{DVB}) = K W_{AA}, \quad (1)$$

where W_{DVB}^0 is the mass fraction of divinylbenzene in the ethanol/water mixture at zero concentration of acrylamide, and consequently a constant of the equation depending on the water content in the ethanol/water mixture; W_{DVB} , W_{AA} are mass fractions of divinylbenzene and acrylamide respectively.

Fig. 2a, 2b shows the dependence of both constants of the above equation on the water content in water–ethanol mixtures. The constant K is positive in the concentration region in which acrylamide lowers the solubility of divinylbenzene; on the other hand, it assumes negative values in the region where the solubility of divinylbenzene increases with the content of acrylamide. Deviations between experimental data and values calculated according to the correlation equation show that the equation describes better the concentration region with K having positive values. It should be noted, however, that deviations in the other regions are also comparable with the error of the method (5% rel. at utmost). It can be stated, therefore, that the correlation equation is suitable for the description of the solubility curves of the system under investigation. It is possible now, by using the known dependences of the constants K and W_{DVB}^0 on the water content, to calculate the solubility curve for any ethanol–water system.

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