

LIQUID-LIQUID EQUILIBRIUM IN THE ISOBUTYL ACETATE-WATER SYSTEM

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The mutual solubility of components in the isobutyl acetate-water system was measured by the sealed tube method in the temperature interval of 20–150°C.

The knowledge of liquid-liquid equilibrium in the isobutyl acetate-water system is of practical importance for the development of esterification technology of isobutyl alcohol with acetic acid.

EXPERIMENTAL AND RESULTS

Substances used. Isobutyl acetate, a technical reagent, contained approximately 10% free alcohols (isobutyl alcohol and some n-butyl alcohol). Since these alcohols form azeotropes with the ester the product was refluxed with acetic anhydride (100 ml/1 l ester), then washed with saturated solution of K_2CO_3 and several times with water. Afterwards it was dried with anhydrous $MgSO_4$ and $CaCl_2$ (ref.¹). Finally it was distilled on a twenty-plate packed column. The purity of the isobutyl acetate obtained was checked by chromatography: It did not contain free acetic acid nor alcohols and the n-butyl acetate content was about 1.5%. The found values of physical constants of isobutyl acetate used were as follows: n.b.p. 117.5°C (ref.² 118.0, ref.³ 117.2–118.0), d_4^{20} 0.8715 (ref.² 0.8745), n_D^{20} 1.3902 (ref.² 1.39018). Distilled water with specific conductivity $\approx 4 \cdot 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was used.

Apparatus. Since the region of limited miscibility of other acetates lies above normal boiling points of the ester-water mixtures the liquid-liquid equilibrium of the isobutyl acetate-water system was determined by the sealed tube method. A modification of the equipment described in the literature⁴ was applied. An ampoule with solution of a given composition and a ferrite magnet (cadmium-plated roll with Teflon O-rings) was heated in a thermostatic glass tube provided with calibrated Anschütz thermometer with scale division of 0.2°C. The stirring of sample is ensured by a mechanism which lifts an external magnet (ring outside the tube) and this carries the ferrite stirrer inside the ampoule. The thermostating tube is connected into the circuit of a thermostat U 10 filled with triethylene glycol. During the measurement the temperature of the bath changes continuously and the appearance or disappearance of the second phase (turbidity) in ampoule is observed visually.

To decide whether and to what extent the ester hydrolysis plays part in measuring liquid-liquid equilibrium, the following preliminary experiments were carried out:

TABLE I
Liquid-Liquid Equilibrium in the Isobutyl Acetate-Water System

Isobutyl acetate mass %	Solution temperature, °C	Isobutyl acetate mass %	Solution temperature, °C
0.761	14.6 ^a	98.71	35.6
0.720	24.9 ^a	98.27	61.5
0.698	47.9	97.36	85.0
0.720	67.6	96.59	99.7
0.760	74.9	96.19	105.7
0.761	75.2	95.39	122.4
0.805	84.8	94.36	140.3
0.844	93.2		
0.968	111.5		
1.002	115.7		
1.206	147.1		

^a Lower solution temperature of isobutyl acetate in water.

A 1 : 1 isobutyl acetate and water mixture was refluxed under atmospheric pressure. After 20, 30, 60, and 120 minutes from the beginning samples (5 ml) were taken, diluted to 100 ml in volumetric flask, and an aliquot was titrated with 0.1M-NaOH ethanolic solution in nitrogen atmosphere using 0.1% neutral solution of thymol blue in 60% ethanol as indicator. It was found that, within the limits of experimental error, under these conditions a hydrolysis did not take place.

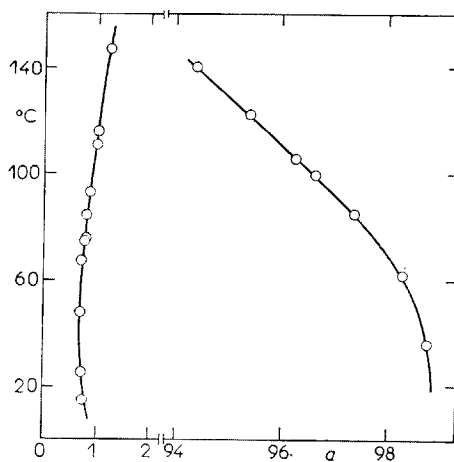


FIG. 1
Mutual Solubility of Components in the
Isobutyl Acetate-Water System
a Isobutyl acetate mass %.

The experimental data on liquid-liquid equilibrium are presented in Table I. The form of the mutual solubility partial curves (Fig. 1) is similar to those of other alkyl acetates, the regions of mutual solubility, in comparison with *e.g.* ethyl acetate, are comparatively very narrow especially on the water side. The mutual solubilities at 20°C read from the diagram are 0.74 mass % isobutyl acetate in the water phase and 98.83 mass % isobutyl acetate in the organic phase. The found value of the isobutyl acetate solubility in water at 20°C is in a reasonable agreement with the older literature data⁵ (at 20°C 0.67 g isobutyl acetate/100 g water and at 22°C 0.5 g isobutyl acetate/100 g water).

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