Liquid–Liquid Equilibria of Phenol, Acetic Acid, Oxalic Acid, and Glyoxylic Acid between Water and 1-Decanol and Tridecanol

Keith Scott,* Asghar Adhamy,† and Ian F. McConvey‡

Chemical and Process Engineering Department, Merz Court, University of Newcastle upon Tyne, U.K.,
ICI FCMO, Huddersfield, U.K., and Chemical Engineering Department, Teesside Polytechnic, U.K.

This paper reports experimental liquid–liquid phase equilibrium data of phenol and three carboxylic acids between water and 1-decanol and water and tridecanol, all at a temperature of 20 °C. Distribution coefficients for phenol between the organic solvents and water are typically greater than 15 and vary little with solute concentration over the range considered. For glyoxylic acid and acetic acid, values of the distribution coefficient are in excess of 18 and vary markedly with solute concentration. Distribution coefficients for oxalic acid between both solvents and water were less than 0.1.

Introduction

The production of organic chemicals at relatively low concentrations in aqueous solutions is typical of both electrochemical and biochemical syntheses. Recovery of these solute species can be achieved by solvent extraction or a combined process of extraction and membrane separation (1). In this latter process, termed emulsion membrane filtration (EMF), which in fact can involve the use of a secondary dispersion, the solvent phase should possess a number of key properties. These properties include a low solubility in water, a high partition coefficient for the solute, and a high boiling point relative to the solute. The solvent (organic) phase forming the emulsion was identified on the basis of these required properties, for the case of phenol as the solute, as coming from the homologous series of C_8–C_{13} alcohols. Thus, 1-decanol was selected on the basis of offering a compromise between a high partition coefficient for the solute and a low solubility in the aqueous phase. Tridecanol was selected on the basis of unreported experiments.

This paper describes experimental data of phase distribution coefficients of solutes phenol, oxalic acid, glyoxylic acid (HOCCOOH), and acetic acid in 1-decanol and tridecanol.

Experimental Section

The phase equilibrium data were determined in the apparatus shown in Figure 1 (2). This apparatus is a jacketed glass unit approximately 4 cm wide and 13 cm long, fitted with a variable speed stirrer. Water, at a known temperature, is circulated in the jacket from a thermostatic bath to give a constant temperature. All data are reported at a temperature of 20 ± 1 °C. Equilibrium data were determined by taking equal volumes (50 cm³) of the solute-laden aqueous phase and the solvent and stirring for 2 days to ensure equilibrium was established. The stirrer speed was controlled to give reasonable mixing without emulsion formation. After equilibrium was achieved the two phases were allowed to separate and decanted separately from the vessel.

The chemicals used, both solutes and solvents, were of Analar or of the purest grade available commercially and supplied by BDH or Aldrich Chemicals. Manufacturer
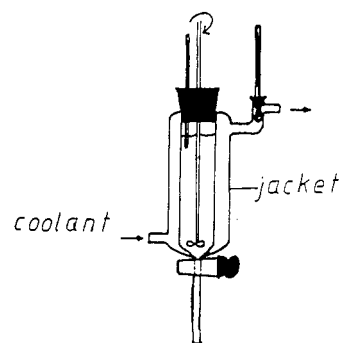
* To whom correspondence should be addressed at the University of Newcastle upon Tyne.
† Teesside Polytechnic.
‡ ICI FCMO.

Figure 1. Experimental apparatus for phase equilibrium studies.

reported purities were acetic acid, 99.8%; phenol, 99.5%; glyoxylic acid (hydrate), 98%; and decanol, 97%. One solvent, tridecanol ($C_{12}H_{25}CH_2OH$), was supplied by ICI C and P, and was of purity >99%. No further purification of chemicals was carried out. Aqueous solutions were made up with deionized water.

Distribution coefficients, K, were determined from the analysis of the aqueous phase before and after equilibrium. These values are expressed as

$$K = \frac{\text{concn/(g/L) in organic solvent}}{\text{concn/(g/L) in aqueous phase}}$$

Phenol concentrations in the range of 0.1–0.4 g/L were determined by UV spectroscopy. Carboxylic acid concentrations were determined by volumetric titration. All analyses were based on precalibration against known concentrations of solutions of the solutes. The accuracy of the measurements was typically within ±5%.

Phenol Equilibrium Data

A number of previous studies on the phase equilibria of phenol have been carried out (3–5). These works investigated 20 solvents for phenol extraction and concluded that ketones, esters, and alcohols had the highest distribution coefficients. Of the eight solvents which gave distribution coefficient K greater than 10, only 1-decanol (and 1-octanol) had sufficiently low solubilities in water. Overall it was concluded (5) that it is only feasible to use solvents (alcohols) in the C_6–C_{10} range. Alcohols higher than C_{10} had too low distribution coefficients for phenol between the solvent and water, and alcohols lower than C_6 were too soluble in water.
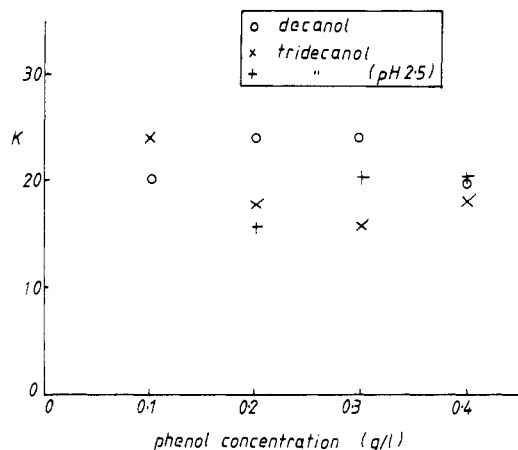
Figure 2. Distribution coefficients for phenol between decanol and water and tridecanol and water. Phenol concentrations are the initial values in the aqueous phase.

To minimize solvent losses in this work two solvents with solubilities <100 ppm in water were selected for study. These were 1-decanol and tridecanol, a mixture of isomeric branched-chain primary C_{13} aliphatic alcohols.

Distribution data of phenol are presented in Figure 2 as a function of phenol concentration. For both solvents, decanol and tridecanol, values of K are greater than 15 and show some dependence on phenol concentration, decreasing slightly from 0.1 to 0.4 g/L phenol. Values for decanol are slightly greater than those for tridecanol.

The effect of a more acidic pH in the aqueous phase, achieved by adding sulfuric acid, which represented conditions of the synthesis of phenol, has no significant affect on the distribution values.

Carboxylic Acids

There is a limited amount of equilibrium data on the carboxylic acids of interest in this work. The distribution coefficients for acetic acid in methyl isobutyl ketone (6) and tributyl phosphate (7) have been measured at 0.5–0.6 and 1.65–2.5, respectively. Distribution coefficients for oxalic acid in amyl acetate, amyl alcohol, aniline, and ether (8) and in butanol, ethyl acetate, and chloroform (9) are all much less than 1.0. In the case of oxalic acid, the addition of extractants to the inert solvents to promote extraction has been attempted. Two materials, triisooctylamine (10) and trioctylphosphine oxide (TOPO) (11), have been shown to be effective. In both cases the distribution obtained is almost linearly proportional to the concentration of extractant, which acts in a chemical reactive mode. One of these agents, TOPO, is also known to be a suitable extractant for acetic acid.

In view of the apparent lack of suitable solvents for carboxylic acids, phase equilibrium studies for oxalic acid, glyoxylic acid, and acetic acid were performed. This work was aimed at identifying suitable inert solvents for extraction, and not reactive agents, to keep operating costs to a minimum.

Oxalic Acid. A range of pure solvents were screened for the extraction of oxalic acid and included decanol, tridecanol, xylene, dodecane, carbon tetrachloride, octanol, styrene, pentanol, and hexane. None of these solvents were found suitable, distribution coefficients all being less than 0.1. These data together with published data confirmed that the extraction of oxalic acid with single solvents is not likely to be a practical proposition.

Acetic Acid. Distribution coefficients for acetic acid in decanol and tridecanol are given in Table I. The acetic acid concentration is the value in the aqueous phase prior to extraction.
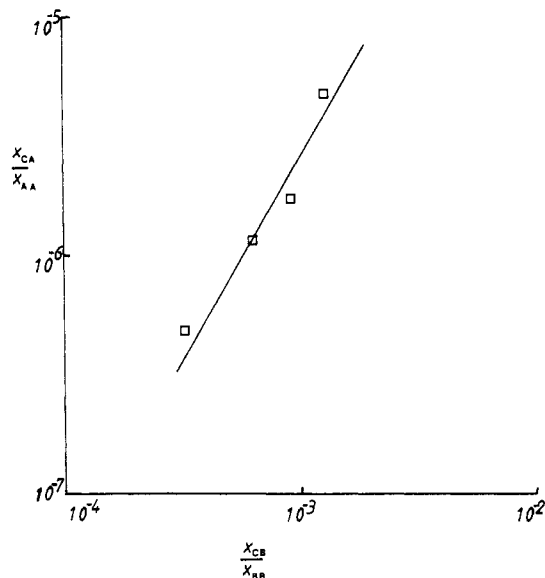

Figure 3. Correlation of the phase distribution of acetic acid between decanol and water according to Hand's rule.

Table I. Distribution Coefficient for Acetic Acid at 20 °C between Decanol or Tridecanol and Water

acetic acid concn (g/L)	0.1	0.2	0.3	0.4
K(decanol)	60	52.7	54	23.6
K(tridecanol)	54.1	29.3	32.3	18.6

Table II. Distribution Coefficient for Glyoxylic Acid at 20 °C between Tridecanol and Water

glyoxylic acid concn (g/L)	0.1	0.2	0.4
K	35.2	40.8	43.4

In this case high distribution coefficients, in the approximate range of 20–60, are obtained for acetic acid, with both decanol and tridecanol. In the case of the acetic acid/water/decanol system the data can be expressed with reasonable accuracy by Hand's phase equilibrium expression (see Figure 3)

$$X_{CA}/X_{AA} = k(X_{CB}/X_{BB})^r$$

where x is the mole fraction, A = water, C = acetic acid, and B = decanol. Values of k and r are 0.26 and 1.67, respectively.

Glyoxylic Acid. Experimental tests showed that solid glyoxylic acid was almost completely soluble in tridecanol. Phase distribution coefficients for the glyoxylic acid/water/tridecanol system are given in Table II and reflect the high "solubility" of tridecanol for glyoxylic acid. The glyoxylic acid concentration is that in the aqueous phase prior to extraction.

Conclusions

This work has shown the suitability of both decanol and tridecanol for the extraction of phenol, acetic acid, and glyoxylic acid from aqueous solutions. High phase distribution coefficients in excess of 18 were obtained, enabling a single-stage extraction of these solutes, based on an integrated membrane separation.

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