The Equilibrium Distribution of Wool-Grease Components and Contaminants between the Solvents Hexane and Aqueous Isopropanol

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ABSTRACT

A strategy has been developed that enables the equilibrium distribution of wool-grease components and contaminants to be specified in a form suitable for the design of a solvent extraction process. Experimentally determined equilibrium phase compositions for carefully selected model components were fitted by multi-variable least-squares regression to an empirical model to provide a convenient mathematical specification. The specification accounts for the dependency of distribution coefficient on concentration and also for the effects of component interactions.

NOMENCLATURE

a_i, equilibrium model parameter for component i; b_{ij}, binary interaction parameter for the effect of component j on i; x_i, concentration of component i in the hexane-rich phase; y_i, concentration of component i in the IPA-rich phase. Subscripts: 1 = cholesteryl stearate; 2 = cholesterol; 3 = stearic acid; and 4 = N7 detergent.

INTRODUCTION

The major consumers of wool-grease often specify quality limits for the content of free alcohols, free acids and detergent in the grease. Many workers (1-7) have shown that these components, being more polar than the bulk of the commercially desirable esters, may be preferentially extracted by a polar solvent from either the molten grease or a solution of the grease in a nonpolar solvent. However, no equilibrium data have been published in a suitable form for use in the design of multistage extraction equipment.

Useful separations of detergent, free acids and the insecticide diazinon from wool-grease have previously been obtained using hexane and aqueous isopropanol (60% v/v IPA) (8) as the nonpolar and polar solvents, respectively. These solvents have been further investigated using a strategy that enables the equilibrium distribution of wool-grease components and contaminants to be specified in a manner suitable for equipment design.

Application of this strategy to the system wool grease/hexane/aqueous IPA and statistical analysis and interpretation of the results are described in this paper.

EXPERIMENTAL

Strategy

The equilibrium distribution of all components of complex mixtures such as wool-grease, lubricating oils and glyceride oils is impossible to specify because of their very large number. One method of overcoming this problem has been to specify the miscibility boundary and tie-line equilibria by measuring a physical property of the phases in equilibrium such as viscosity gravity index (9) or iodine value (10). By this means, the effective number of components is reduced and the design problems are solved by standard graphical methods using triangular coordinates. However, Alders (11) has shown that this method is unsuitable for mixtures of components which have distribution interactions. Consequently, it could not be used for wool grease, the components of which were known to interact in hexane/aq-IPA systems.

In the approach adopted, the wool-grease was characterized in terms of groups of components of similar distribution coefficient, an approach analogous to the use of close-boiling fractions for the description of a complex mixture to be separated by distillation (12). Wool-grease had been earlier separated into a series of fractions by countercurrent solvent extraction using hexane and aqueous IPA (8). The fractions contained groups of components which distributed similarly under continuous extraction conditions. The principal components of the fractions were identified and then characteristic pure components were chosen to create a model wool-grease comprising a manageable number of components. The equilibrium distribution of the model components between the solvent phases was investigated over a range of concentrations corresponding to those likely to be encountered in solvent extraction applications. The experimentally determined phase compositions were fitted to an empirical model containing terms to account for binary interactions. The solution set, determined by multivariable least-squares regression, provides a convenient mathematical specification of the equilibrium distribution of the wool-grease components.

Model Grease

The selected model components must not only represent the characteristics of the wool-grease fractions but must also be amenable to accurate concentration measurement in both the hexane and IPA-rich phases. The most appropriate model compounds which satisfied these requirements were cholesteryl stearate, cholesterol, stearic acid and a refined detergent. High performance liquid chromatography (HPLC) methods were developed for the analysis of these components.

Commercial nonyl phenol ethoxylate detergents, such as TN450 (ICI), which are often found in wool-grease, contain a broad distribution of chain lengths (from 3 to 13 ethoxy units). Distribution between the solvents and, more importantly, the interaction effect of the detergent were found to be a function of chain length. Ideally, a single chain length should be used as representative of the detergent mixture. This was found impossible to obtain or synthesize with significant yield. Consequently, a refined detergent was obtained by multistage extraction of TN450. The product was fond to be concentrated in the chain length range 6-8 units, thus reducing the influence of different interaction effects. The component with 7 units in the chain (N7) was chosen as the reference component.

Determination of the Equilibrium Distribution of Model Wood-Grease

Reagents. Cholesteryl stearate, cholesterol and stearic acid

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were analytical grade supplied by Aldrich Chemical Company. The model detergent was the fraction rich in N7 prepared from TN450. All solvents were Analar grade unless otherwise stated.

Equilibration procedure. Equal volumes of hexane and aqueous IPA (60% v/v IPA) were equilibrated to yield a raffinate phase rich in hexane and an extract phase rich in IPA. All stock solutions and standards were prepared using these preequilibrated phases.

Thirty sets of equilibrations were concluded as follows. Cholesteryl stearate, cholesterol and stearic acid were added in the required amounts to a 250-mL separating funnel and the volume was brought up to 100 mL with raffinate solution. The chosen quantity of detergent was dissolved in 100 mL of extract solvent and added to the funnel. The funnel was agitated vigorously and immersed for 24 hr in a water bath which was thermostatically controlled at 25 C. Aliquots of both phases were withdrawn for analysis.

The component additions were selected so that their relative concentrations would be comparable to those produced in an extraction system processing a wool-grease containing 88% ester, 5% free alcohol, 5% free acid and 2% detergent. The maximal ester concentration was set at 30 g L^{-1} by solubility limitations.

For each equilibration, material balances were performed for all components as a check on the reliability of the calculated concentrations.

Analysis of Phases

A 5-mL aliquot of each hexane phase sample was evaporated to dryness under vacuum and the residue dissolved in 10 mL of 1:1 (v/v) dichloromethane/heptane containing hexanoic acid as the internal standard. A 50-mL aliquot of each IPA-phase sample was treated similarly. Standard solutions of the model components in raffinate and extract solvents were prepared for reference purposes and treated identically to the sample solutions.

Details of the analytical methods for all components are given in Table I.

The dichloromethane/heptane solutions were injected directly for the analysis of detergent. The nonyl phenol ethoxylate oligomers were resolved under the stated conditions to give chromatograms such as Figure 1. The ethoxylate chain lengths were assigned by comparison with short-chain standards of known median chain length.

For analysis of cholesteryl stearate and cholesterol, the dichloromethane/heptane solutions were redissolved in 10% v/v IPA in heptane.

Stearic acid was analyzed as the 4-nitrobenzyl ester prepared using di-isopropyl-o-4-benzyl-iso-urea under neutral conditions to avoid potential hydrolysis of the cholesteryl stearate (13).

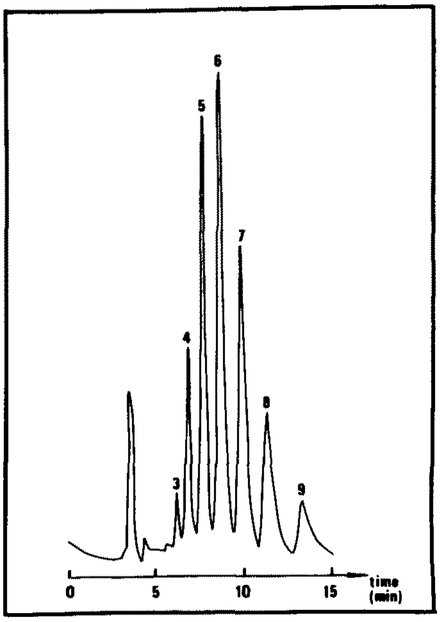

FIG. 1. Chromatogram for refined detergent in the IPA-rich phase. Ethoxylate chain lengths are labeled. Analysis conditions are given in Table I.

RESULTS AND DISCUSSION

Mathematical Specification of Phase Composition

Preliminary factorial experiments showed that the distri-

TABLE I

HPLC Analysis Conditions

	Component			
	Cholesterol stearates	Cholesterol	Stearic acid	Detergent
Injection volume (μL) Hexane	10	10	25	25
Injection volume (μL) IPA	100	100	25	10
Column specification				
Length (mm)	250	250	150	250
Inside diameter (mm)	4.60	4.60	4.60	4.60
Packing	Spherisorb, amine-bonded silica, 5 μm particle size	Spherisorb, amine-bonded silica, 5 μm particle size	Lichrosorb, SI-100 silica, 5 μ particle size	Lichrosorb, DIOL 5 μm particle size
Temperature (C)	ambient	ambient	ambient	ambient
Mobile phase				
Composition (% v/v)	IPA, 2; heptane, 98	IPA, 2; heptane, 98	Dichloromethane, 20; heptane, 79.75; IPA, 0.25	IPA, 10; heptane, 90
Flow rate (mL min^{-1})	1.0	1.0	2.0	0.5 → 2.0 under flow program
Detection mode	Refractive index	Refractive index	UV spectrophotometer, 265 nm	UV spectrophotometer, 210 nm

TABLE II

Parameters for Equilibrium Model

Parameter[a]	Cholesteryl stearate $i = 1$	Cholesterol $i = 2$	Stearic acid $i = 3$	Detergent N7 $i = 4$
a_i	4.90×10^{-2}	2.23×10^{-2}	2.95×10^{-1}	5.15
b_{i1}	-5.77×10^{-4}	2.58×10^{-4}	1.96×10^{-4}	6.72×10^{-2}
b_{i2}	-8.21×10^{-3}	4.37×10^{-3}	-5.98×10^{-2}	-4.66×10^{-1}
b_{i3}	-1.35×10^{-2}	4.54×10^{-3}	-7.71×10^{-2}	-3.92×10^{-2}
b_{i4}	9.73×10^{-2}	6.56×10^{-2}	1.87×10^{-1}	-7.26×10^{-1}

[a] a_i is dimensionless but b_{ij} has units $(g/L)^{-1}$.

bution coefficient of individual components was concentration-dependent and significantly affected by some binary interactions. Ternary or higher-order interactions did not occur. An empirical model containing terms to account for these observations was postulated. The following equation was written for each component, i.e., for $i = 1$ to 4:

$$y_i = a_i + \sum_{j=1}^{4} b_{ij} x_j \, x_i \qquad [\mathrm{I}]$$

Each component was considered independently and the experimentally determined phase compositions were substituted into the appropriate version of Equation I to yield 30 inexact equations in five unknown parameters, a_i and b_{ij}. The sum of the residual errors squared for the set of equations was minimized to obtain a least-squares solution for the set of parameters using matrix methods described by Graybill (14). These matrix methods facilitated computer solution using standard subroutines for matrix operations. The solution set is given in Table II.

The equilibrium model specified by these parameters provides a good fit to the experimental data within the range investigated. However, extrapolation is dangerous because the distribution curve specified by the model for a given component at fixed values of the other components is quadratic and will have a maximum lying outside the experimental range. The location of the maximum can be found by differentiating Equation I.

To illustrate the interactions predicted by the equilibrium model, the distribution curve for cholesteryl stearate has been plotted at specified cholesterol, stearic acid and detergent concentrations in Figure 2. Curves 1, 2 and 3 show that increasing the detergent concentration tends to increase the distribution of cholesteryl stearate in favor of the IPA-rich phase, viz., b_{14} is positive. A practical implication of this effect is that the loss of esters to the extract phase increases as the detergent concentration increases. Increasing the concentration of cholesterol or stearic acid has the opposite effect as shown by curves 1, 4, 5 and 6, viz., b_{12} and b_{13} are negative.

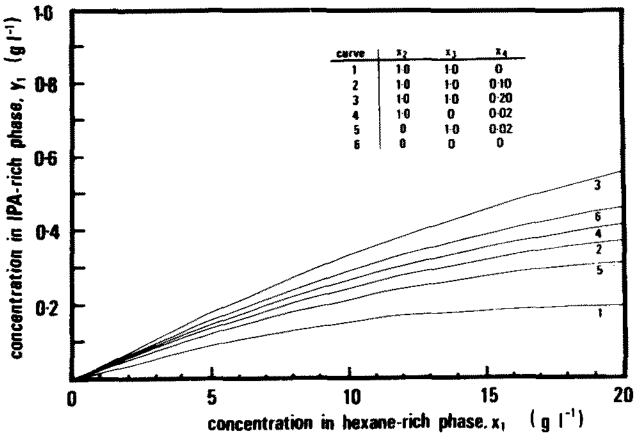

FIG. 2. The distribution of cholesteryl stearate between the hexane-rich and IPA-rich phases at 25 C.

Application of the Model

The equilibrium model specified by Equation I using the parameters given in Table II may be used in an appropriate multicomponent design method to predict the separation of components achieved by a given configuration of extraction stages. For each stage, material balance and equilibrium relationships may be written to create a set of highly nonlinear equations which must be solved to yield the component concentrations in the extract and raffinate phases. An iterative, matrix technique has been developed for this purpose and will be reported later with experimental tests of its predictions for the model wool-grease.

The predictions confirm the experimental observation that near-complete removal of detergent from wool-grease by countercurrent extraction using the selected solvents is relatively easily achieved, whereas the removal of free acids is far more difficult.

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