THE EFFECT OF SELECTED SOLVENTS ON THE RELATIVE VOLATILITY OF THE BINARY SYSTEM: 1-OCTENE - 2-HEXANONE WITH THE AIM OF SEPARATING THE AZEOTROPIC MIXTURE.

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Thesis for the degree Magister Engineering in Chemical Engineering

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Thesis accepted in the Faculty of Engineering of the Potchefstroom University for Christian Higher Education in partial fulfilment of the requirements for the degree Magister Engineering in Chemical Engineering.

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Potchefstroom

May 1994

ABSTRACT

The removal of oxygenates from olefins has tremendous industrial significance. This study dealt specifically with potential azeotropic and extractive distillation processes for the purification of higher alpha olefins.

An Othmer type vapour liquid equilibrium still was used to study the influence of selected solvents on the 1-octene / 2-hexanone system. These screening tests were performed under conditions of a fixed solvent concentration of 66% with the azeotropic ratio of 1-octene to 2-hexanone.

The resulting data was used to identify solvent properties and theoretical models which correlate well with actual performance. It is evident that specific available solvent properties and principles can indeed be successfully utilized to predict the effect of a solvent. Although many of these guidelines are not strictly quantitative, they agree well with theoretical understandings of solvent action and can save much time in future solvent searches.

The large difference in polarity between the two components appears to be the main factor on which the solvents discriminate. Differences in molar volume and complex forming ability are also meaningful. Related solvent properties are consequently important when selecting a solvent for similar systems. Effective solvents (such as dimethyl formamide and methanol) all have high values for properties (such as the dielectric constant and polar solubility parameter) which are associated with the strength of solvent solute interaction.

Binary vapour liquid equilibrium data was also measured for some solvents. The data was regressed and used to simulate actual distillation schemes. This verified that chosen solvents are indeed able to efficiently effect a high separation between the two components.

OPSOMMING

Die verwydering van oksigenate uit olefiene is van groot industriële belang. Hierdie studie handel spesifiek oor potensiële azeotropiese en ekstraktiewe distillasie prosesse vir die suiwering van hoër alfa olefiene.

'n Othmer tipe damp vloeistof ewewigsapparaat is gebruik om die effek van geselekteerde oplosmiddels op die 1-okteen / 2-heksanoon sisteem te ondersoek. Hierdie toetse is onder toestande van 'n konstante oplosmiddel konsentrasie van 66% met 'n azeotropiese verhouding van 1-okteen tot 2-heksanoon uitgevoer.

Die resultate is gebruik om oplosmiddel eienskappe en teoretiese modelle te identifiseer wat goed korreleer met die waargenome effekte. Dit is duidelik dat spesifieke beskikbare oplosmiddel eienskappe wel suksesvol gebruik kan word om die effek van 'n sekere oplosmiddel te voorspel. Alhoewel baie van die aanwysings nie streng kwantitatief is nie, is daar goeie ooreenstemming met teoretiese insigte rakende oplosmiddel aksie en baie tyd kan in toekomstige oplosmiddel soektogte bespaar word.

Die groot verskil in polariteit tussen die twee komponente blyk die hooffaktor te wees waarop die oplosmiddels diskrimineer. Verskille in molêre volume en die vermoë om komplekse te vorm is ook betekenisvol. Verwante oplosmiddel eienskappe is gevolglik belangrik by die identifisering van oplosmiddels vir soortgelyke sisteme. Effektiewe oplosmiddels (soos N,N-dimetiel formamied en metanol) besit almal hoë waardes vir eienskappe (soos die di-elektriese konstante en die polêre oplosbaarheidsparameter) wat met die sterkte van oplosmiddel opgeloste stof interaksies geassosieer word.

Binêre damp vloeistof ewewigsdata is ook gemeet vir sekere oplosmiddels. Regressies is op die data gedoen waarna werklike distillasie skemas gesimuleer is. Dit het bevestig dat gekose oplosmiddels inderdaad gebruik kan word om 'n effektiewe skeiding tussen die twee komponente te bewerkstellig.

PREFACE

This project was supervised by Professor R.C. Everson of the Potchefstroom University for Christian Higher Education and by H.R. Vorster, chief process engineer, Separation Technology, Sastech. The equipment, chemicals and financial support were provided by Sastech Process Development, Sasol Chemical Industries. The author expresses his sincere gratitude to Sastech for its invaluable assistance.

The author also wishes to thank the operational research section of the modelling group (Process Development) for their assistance regarding statistics.

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NOMENCLATURE

A	Coefficient which depends on the nature the solute and solvent functional groups (in the PDD equation).
B_a	Antoine constant.
B	Coefficient which depends only on the nature of the solvent functional group (PDD).
bp	Boiling point.
cc	Cubic centimetres (cm^3).
C	Coefficient which depends only on the solute functional group (PDD).
C_a	Antoine constant.
CAS	Chemical Abstract Service.
C_τ, C_α, C_β	Constants used in calculating τ, α, or ß by groups approach.
d	A term in the MOSCED model to account for differences in molecular size.
D	Coefficient which is independent of functional groups (PDD).
E	Maximum error of estimate (statistics). Energy of vaporization.
F	Coefficient which depends essentially only on the nature of the solvent functional group (PDD). Molal free energy at infinite dilution in the solvent.
fp	Freezing point.
G^E	Excess free energy of mixing.
H	Heat of vaporization.
k	Constant in the Weimer-Prausnitz equation.
K	K-value, defined as y_i/x_i. A constant in the Pierotti-Deal-Derr equation.
$\bar{L}$	Partial molar heat of solution of a component.
ln	Natural logarithm (base e).
log	Logarithm to the base 10.
mw	Molecular weight.

n	Sample size (statistics: number of items).
	Number of carbon atoms in a hydrocarbon component.
p°	Vapour pressure of pure component.
P	Pressure.
PDD	Refers to the Pierotti-Deal-Derr equation.
q	Induction parameter in MOSCED model.
r	Number of aromatic rings in a component hydrocarbon.
R	Gas constant (= 1.987 cal/gmol/deg K).
s	Standard deviation (statistics).
S	Selectivity.
t	Value for t-distribution (statistics).
	Temperature (°C)
T	Temperature (°Kelvin).
U	Energy of vaporization.
v,	
V	Molar volume (cc/gmol).
x	Average (statistics).
	Liquid-phase mole fraction.
y	Vapour-phase mole fraction.

GREEK SYMBOLS

α	Level of significance (statistics).
	Relative volatility (K_1/K_2).
	Polarizability.
	Coefficient of thermal expansion.
	Acidity parameter in the MOSCED model.
	First immiscible phase.
ß	Compressibility.
	Basicity parameter in the MOSCED model.
	Second immiscible phase.
γ	Activity coefficient.
δ	Solubility parameter
	(ie square root of the cohesive energy density).
τ	Polar cohesive energy.
	Polar solubility parameter.

	Polar parameter in MOSCED model $(cal/cm^3)^{1/2}$
Δ	Indicates the change in an argument.
λ	Solubility parameter.
	Nonpolar cohesive energy.
	Dispersion parameter in MOSCED $(cal/cm^3)^{1/2}$
	Thermal conductivity coefficient.
ϵ	Dielectric constant.
n	Viscosity coefficient.
κ_T	Isothermal compressibility.
κ_S	Adiabatic compressibility.
μ	Mean of a population (statistics).
	Dipole moment.
ξ	Hydrogen bonding asymmetry factor for MOSCED.
ϕ	(Liquid-phase) Volume fraction in solution.
ψ	Induction energy between polar and nonpolar components.
ω	Accentric factor.

SUBSCRIPTS

1	The value is for component number 1.
2	The value is for component number 2.
1,2	The value depends on both component 1 and 2.
c	Critical value.
d	The part due to dispersion forces.
h	The part due to hydrogen bonding.
i	The value is for a specific component i.
ij	The value is for component i, expressed relative to that for component j.
j	The value is for a specific component j.
p	The part due to polar interaction.
r	Reduced value.
s	Referring to the solvent.

SUPERSCRIPTS

—	Partial molal property.
E	Excess value.
L	Liquid phase.
M	The value is a partial molal one.
o	The value as for the pure component.
°	Degrees.
sat	Saturation value.
T	At constant temperature.
V	Vapour phase.
	The value is for vaporization.
	At constant molal volume.
*	Infinite dilution property of a component.

ABBREVIATIONS

ASEEK	Agent Seeker, the solvent evaluation program.
DAA	diacetone alcohol.
DIMA	N,N-dimethyl acetamide.
DMF	N,N-dimethyl formamide.
EXEA	2-ethoxy ethanol.
GC	Gas Chromatograph.
kerosol	A paraffinic solvent.
MBK	2-hexanone, methyl n-butyl ketone.
MIBK	methyl isobutyl ketone.
MOSCED	Modified Separation of Cohesive Energy Density.
MXEA	2-methoxyethanol.
NBP	Normal boiling point.
NMP	N-methyl pyrrolidinone.
NRTL	Non Random Two Liquid.
OCT1	1-octene, the C8 α-olefin.
RF	Response factor.
TX	Temperature and liquid mole fraction.
UNIFAC	UNIQUAC Functional Group Activity Coefficients.
UNIQUAC	Universal quasi-chemical.
XY	Liquid and vapour mole fractions.