

PROGRESS REPORT 2:

**MODELING SUPERCRITICAL ENTRAINMENT DISTILLATION:
VIRIAL EQUATION OF STATE / HENRY'S LAW.
EXTRAPOLATION TO THE HEPA SEPARATION PROBLEM.**

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1. Introduction

In this Progress Report 2, the present state of work will be described. Comparing to Progress Report 1, this work presents a new model to describe the occurring phase equilibrium of C16OH, C18 and CO2. This report should be seen as a brief summary of performed calculations. Only relevant equations will be presented. Comprehensive derivations will not be given. A rough prediction of the phase equilibrium in HEPA-supercritical fluidum systems will be made.

2. Modeling Phase Equilibria with the Virial EOS and Henry's Law

At the suggestion of prof. De Swaan Arons, the chosen test system C16OH, C18 and CO2 will be modeled using the virial equation of state. In his article [1], he described the solubility of solid heavy compounds in (supercritical) gases at high pressure. He derived that:

$$c_2 / c_{2id} = \exp \{ -2*B_{12}*\rho_1 \} \quad (1)$$

In (1) c_2 symbolyses the concentration of the considered heavy compound in the supercritical phase. c_{2id} symbolyses the same, but in this case the ideal gas law is considered as equation of state, causing Raoult's Law to be the equilibrium condition. The term c_2/c_{2id} is also known as the enhancement factor: the heavy compounds' solubility is enhanced by some factor, c_2/c_{2id} . B_{12} is the cross second virial coefficient of the supercritical fluidum (1) and the heavy compound (2). ρ symbolyses the density.

Like has been stated, c_{2id} can be calculated from Raoult's Law and the ideal gas law. For describing solubilities of solids, no supercritical fluidum can be dissolved in the heavy phase, so the mole fraction of the heavy compound in the heavy phase equals one. In that case, it can be derived that the concentration of the heavy compound in the supercritical phase equals:

$$c_{2id} = p_{2sat} * P_{OY2} / (R*T) \quad (2)$$

In (2) P_{OY2} is the Poynting correction which accounts for high pressures. R is the gasconstant, while T symbolyses temperature. p_{2sat} is the saturated vapour pressure of the heavy compound. (1) can be rewritten in terms of mole fraction, y , and the expression becomes:

$$y_2 = c_2 / \rho_1 \quad (3)$$

The poynting factor can be calculated from:

$$P_{OY2} = \exp\{ v_{2sat} * (p-p_{2sat}) / (R*T) \} \quad (4)$$

In (4) it has been assumed that the saturated molar volume of the heavy compound, v_{2sat} , is independent of pressure.

The above model can be used to calculate solubilities of heavy compounds in supercritical fluida. Only cross virial coefficient data and vapour pressure data are necessary to know. A suitable EOS must be chosen in order to calculate the supercritical fluidum's density.

The model must now be extended to a liquid heavy compound. In case liquids are used, the used supercritical fluidum will be dissolved in the liquid phase. In order to describe the supercritical phase, eq. (1)-(4) must be modified. That can be accomplished by multiplying eq. (2) by the mole fraction of the heavy compound in the liquid phase, x_2 , according to Raoult's Law:

$$c_{2id} = x_2 * p_{2sat} * P_{OY2} / (R*T) \quad (5)$$

Now, no mole fraction is calculated but the distribution coefficient of the heavy compound: y_2/x_2 . The mole fraction can not yet be calculated because the quantity of dissolved supercritical gas in the liquid phase, x_1 is not known. In that case x_2 is not known either, of course.

Therefore, a model must be developed to describe the liquid phase's fugacity.

At the suggestion of De Swaan Arons, the quantity of dissolved SCF will be estimated using Henry's Law. The equation which describes Henry's Law with high pressure, Poynting, correction is [2] :

$$\ln (y_1/x_1) = \ln (H_{12}) + v_{1\infty 2}^* (p-p_{2\text{sat}}) / (R^*T) \quad (6)$$

In (6) H_{12} is the Henry Coefficient of the supercritical solute 1 at infinite dilution in liquid 2. $v_{1\infty 2}^*$ is the molar volume of the supercritical solute at infinite dilution in liquid 2.

If the cross virial coefficient of the considered binary system and the vapour pressure of the heavy compound is known, the phase equilibrium can be estimated when the Henry Coefficient is known. These are the three most evident data which are required to simulate the phase equilibrium.

With help of corresponding states correlations all needed data can be estimated, using the critical properties of the considered components, except for Henry Coefficients and vapour pressure data.

The virial equation of state truncated after the second virial coefficient can only be used at densities smaller than half the critical density of the supercritical fluidum [2]. Because of this reason, the model can be made more accurately by adding the third virial coefficient. The only modification in the model occurs at eq. (1):

$$c_2 / c_{2id} = \exp \{ -2*B_{12}^*\rho_1 - 1.5*C_{112}^*\rho_1^*\rho_1 \} \quad (7)$$

The cross third virial coefficient can also be estimated from corresponding states correlations. The model can now be used up to 0.75 times the solvent's critical density.

2.1 Used Data and Data Sources for Computer Simulation

The above summarized model has been used in order to calculate the phase equilibrium of the ternary system C16OH, C18 and CO₂.

In corresponding states correlations presented in literature for the second and third virial coefficients, critical properties are needed as input parameters. The critical properties of CO₂ are known from literature [2]. For the heavy compounds, no data are available, because of their relatively low decomposition temperatures. For C16OH and C18 the critical properties have been estimated from Joback's estimation procedure. This procedure can for example be found in [2]. The critical properties are:

Table 1. Critical Data of Considered Compounds.

	CO2	C18	C160H
critical temperature [K]	304.1	748.0	767.1
critical pressure [bar]	73.8	12.0	14.1
critical molar volume [cm ³ /mol]	93.9	1043.5	950.5
critical compressib. factor [-]	0.274	0.195	0.210

From vapour pressure data the acentric factors can be calculated for the heavy compounds; for carbon dioxide the acentric factor has been given in [2]. Vapour pressure data for C160H can be found in [3] and [4]; for C18 in [3] and [5]. The acentric factors appeared to be respectively

$$0.239 \text{ (CO2)} \quad : \quad 0.790 \text{ (C18)} \quad : \quad 1.018 \text{ (C160H)}$$

The critical properties and acentric factors are essential in applying corresponding states correlations. They are pure compound properties and are assumed to be of sufficient accuracy.

Knowing the vapour pressure data for the heavy compounds it can be seen from eqs. (1)-(7) that the following quantities are not known:

$$v_{2sat}, v_{3sat}, v_{1inf2}, v_{1inf3}, B_{12}, B_{13}, C_{112}, C_{113}, \rho_1.$$

ρ_1 is calculated from the Peng Robinson EOS at certain temperature and pressure. The virial coefficients B_{12} (B_{13}) and C_{112} (C_{113}) can be calculated from corresponding states correlations. Because they are cross coefficients, mixing rules must be applied. Prausnitz [2] suggests:

$$T_{cij} = \{ \sqrt{T_{ci} T_{cj}} \} * (1 - k_{ij}) \quad (8)$$

$$v_{cij} = [\{ v_{ci}^{1/3} + v_{cj}^{1/3} \} * 0.5]^3 \quad (9)$$

$$k_{ij} = 1 - \{ \sqrt{v_{ci} v_{cj}} \} / v_{cij} \quad (10)$$

$$Z_{cij} = 0.5 * (Z_{ci} + Z_{cj}) \quad (11)$$

$$\omega_{ij} = 0.5 * (\omega_i + \omega_j) \quad (12)$$

$$p_{cij} = Z_{cij} * R * T_{cij} / v_{cij} \quad (13)$$

Knowing the critical properties of the mixture by using eqs. (8)-(13), the mixture is considered to be a pure substance and the virial coefficients can be calculated.

It was referred to by Prausnitz [2] that the following correlation will be a good estimation of the second virial coefficient:

$$B^*_{pc}/(R^*T_c) = B_0 + \omega * B_1 \quad (14)$$

$$B_0 = 0.083 - 0.422/Tr^{1.6} \quad (15)$$

$$B_1 = 0.139 - 0.172/Tr^{4.2} \quad (16)$$

Tr symbolyses the reduced temperature. By substituting the pure compound critical data and acentric factor, B11 and B22 are generated. By substituting the mixture's critical properties B12 can be generated. The second virial coefficient is only a function of temperature as can be seen from eqs. (14)-(16). Tsionopoulos [6] has also development a corresponding states correlation as function of temperature. Eqs. (14)-(16), however, are more recent and that is the reason why these relations are applied.

Corresponding states correlations for the third virial coefficient are harder to find, but Orbey and Vera [7] developed a correlation for this coefficient. This correlation can also be used with only the critical properties and acentric factor as known parameters and the correlation for C only depends on temperature. Using the same mixing rules as for the B coefficient, the binary C12 can be calculated as well as the pure compound coefficients C11 and C22. The correlation has the form:

$$C * \text{sqr} (pc/(R^*T_c)) = C_0 + \omega * C_1 \quad (17)$$

In (17) $C_0 = C_0(Tr)$ and $C_1 = C_1(Tr)$. In order to calculate the C112 coefficient, the following mathematical procedure must be applied:

$$C_{112} = \{C_{11} * C_{11} * C_{12}\}^{1/3} \quad (18)$$

With the above relations both virial coefficients can be calculated using only the critical properties and acentric factors.

In order to calculate the distribution coefficient for the binaries C18-CO2 and C16OH-CO2, only one quantity is not known, v_{2sat} (or v_{3sat} in case of the other binary). This is the molar volume of the saturated liquid compound. Prausnitz refers to the Hankinson-Brost-Thomson (HBT) technique.

It goes beyond the scope of this Progress Report 2 to present the equations in estimating the saturated molar volume, but it is important to know that these correlations are only a function of critical properties and acentric factors.

Now we can calculate the distribution coefficients applying the B truncated and C truncated virial EOS.

In order to calculate the distribution coefficient of carbon dioxide, eq. (6) is used. Therefore Henry Coefficients must be known. For these large hydrocarbons no explicit data were found in literature, but data for hexadecane, eicosane, 1-dodecanol and 1-tetradecanol were found [8], [9]. In [8] it appeared that plotting the logarithm of the Henry Coefficient versus absolute temperature would result in a straight line. This can be expressed as:

$$\ln [H_{12}] = a + b * T \quad (19)$$

Data for hexadecane (C16) and eicosane (C20) [8] were used in estimating the a and b parameters in (19) for C18 by using:

$$a(C18) = (a(C16) + a(C20))/2 \quad (20)$$

$$b(C18) = (b(C16) + b(C20))/2 \quad (21)$$

That is, the Henry Coefficient for C18 is linearly interpolated. The Henry Coefficient for C16OH can be estimated from 1-dodecanol and 1-tetradecanol data, which are reported as function of temperature [9]. The following assumptions have been made:

$$a(C16OH) = 2*a(C14OH) - a(C12OH) \quad (22)$$

$$b(C16OH) = 2*b(C14OH) - b(C12OH) \quad (23)$$

That is, the Henry Coefficient for C16OH is linearly extrapolated.

As can be seen in eq. (6), the only unknown quantity is v_{1inf2} (or v_{1inf3}). The molar volume of carbon dioxide at infinite dilution in liquid C18 or C16OH can also be estimated from the corresponding states correlation developed by Brelvi and O'Connell [10]. This correlation considers the compressibility of the liquid phase and the molar volumes at infinite dilution are found from the reduced density of the heavy hydrocarbons and the critical volume of carbon dioxide. These quantities fall in the category of critical properties and, thus, the molar volume of carbon dioxide at infinite dilution in or C18 or C16OH can be estimated.

In order to estimate the solubility of carbon dioxide in a liquid mixture of C18 and C16OH, the following mixing rule is assumed to be valid:

$$\ln(H1_{23}) = x2*\ln(H12) + x3*\ln(H13) \quad (24)$$

(24) was suggested by Prausnitz [2]. The fractions $x2$ and $x3$ should be seen as solute free mole fractions. Eq. (24) is valid when no interaction occurs between liquid compound 2 and 3.

The molar volume of CO2 at infinite dilution in a mixture can be estimated by averaging the density of the mixture by the same solute free fractions as in (24).

Now, the following important data are generated:

- distribution coefficients of C16OH and C18. (Virial EOS).
- distribution coefficient of CO2. (Henry's Law/Poynting).

When the equilibrium is desired to know for the binary system C18-CO2 or C16OH-CO2, no more data are required.

For example, if the binary C18-CO2 is considered:

Calculated distribution coefficient of C18 from the virial EOS:

$$(y/x)\{C18\} = KC18$$

Calculated distribution coefficient of CO₂ from Henry's Law:

$$(y/x)\{CO_2\} = KC_{CO_2}.$$

Knowing that $x\{C_{18}\} + x\{CO_2\} = 1$ and $y\{C_{18}\} + y\{CO_2\} = 1$, we have generated four equations with four variables unknown. Thus, the complete phase equilibrium can be calculated.

When the phase equilibrium of the ternary system C₁₆H-C₁₈-CO₂ is desired to know, it is necessary to know the ratio of C₁₆H versus C₁₈ that is present in the mixture. Then the mixing rules in Henry's Law can be applied and the following data are generated:

$$(y/x)\{C_{18}\} = KC_{18} ; (y/x)\{C_{16}H\} = KC_{16}H \text{ from the virial EOS.}$$

$$(y/x)\{CO_2\} = KC_{CO_2} \text{ from Henry's Law.}$$

$$x\{C_{18}\} / x\{C_{16}H\} = \text{RATIO from system specification.}$$

Knowing that $x\{C_{18}\} + x\{C_{16}H\} + x\{CO_2\} = 1$ and $y\{C_{18}\} + y\{C_{16}H\} + y\{CO_2\} = 1$, we have generated six equations with six variables unknown. Thus, the complete phase equilibrium can be calculated.

3. Discussion of Proposed Model

The model presented in section 2 is using the virial EOS, truncated after the second and/or third coefficient. The EOS can be applied at densities of carbon dioxide smaller than respectively half and three third carbon dioxide's critical density. In case of the latter this restriction means that at 70 degr. C the model can be applied at pressures up to about 122 bar. This is a great disadvantage.

The power of this method is that chemical interactions between the heavy compounds and carbon dioxide can be distinguished from the heavy compounds' volatility (B_{12} and p_{2sat}/p_{3sat} respectively). When other EOS would have been used, for example the in Progress Report 1 mentioned Peng Robinson EOS, these occurrences can not be seen separately. The chemical interaction and volatility are hidden in these types of EOS.

Another advantage in this model is that no iterations are needed, so calculation time is very small.

The model does not take into account interactions between the two heavy compounds. The solubility of both heavy compounds in the supercritical phase is assumed to be only a function of the driving forces: fraction in liquid of the heavy compound, volatility of the heavy compound and chemical interaction with the supercritical compound. The solubility in absolute sense is very small and therefore the solubility of both heavy compounds in the supercritical phase is assumed to be independent of their amount in the supercritical phase.

4. Comparing Model to Solubility Data Found in Literature

In literature two important publications were found that give solubility data of respectively C16OH in CO₂ [11] and the solubility of an equimolar mixture of C16OH/C18 in CO₂ [12].

Kramer [11] has published a lot of solubility data at different temperatures and pressures. He fitted his results by plotting the logarithm of the mole fraction of the heavy compound (C16OH) in the supercritical phase versus the reduced density of the supercritical solvent (CO₂). This relation could be expected from eq. (1). Using his correlation with calculated reduced density of carbon dioxide from the Peng Robinson EOS, Kramer predicts the mass fraction of C16OH in the supercritical phase to be 1.83E-3. It is important to know that this is an extrapolated value based on 19 data points. The inaccuracy of this value is assumed to be 5 % .

Brunner [12] reports that for an equimolar mixture of C16OH/C18 the solubility is: $y\{C18\} + y\{C16OH\} = 4E-3$ (mass fraction), while their ratio of distribution coefficients, $K\{C18\}/K\{C16OH\} = 2.5$. When is assumed that the transition of the heavy compounds towards the supercritical phase is small and thus the liquid phase compositions of both heavy compounds are equal, these data result in $y\{C16OH\} = 1.1E-3$ and $y\{C18\} = 2.9E-3$. Brunner did not report the accuracy of his experiments. Therefore it is assumed that the inaccuracy is also 5 % (Like in Kramer's experiments).

The in section 2 mentioned algorithm (C-truncated virial EOS) reproduces in case of pure C16OH the value of 8.40E-4 and in case of an equimolar mixture of C18/C16OH the values $y\{C18\}=1.84E-3$ and $y\{C16OH\}=4.51E-4$, thus $y\{C18\}+y\{C16OH\}=2.291E-3$.

As can be seen from the calculation results, the calculation estimates the mass fractions of the heavy compounds to be too small. That can be interpreted as follows. In case the B-truncated virial EOS is used, the B coefficient's influence is too rigorous: the B-truncated virial EOS exaggerates the solubility effect [1]. When the C coefficient is incorporated, the exaggerating effect of B is called back. At certain point (at reduced densities of carbon dioxide close to three third of its critical density) the C coefficient is calling back the B coefficient too much. In that case a fourth coefficient could be used in order to shorten the calling back effect of the C coefficient. This cannot be examined because no corresponding states correlations are available in literature yet for the fourth virial coefficient.

Because this effect could be expressed as some factor, a relation is desired for correcting the calculated solubilities. In the model it was assumed that the solubility of both heavy compounds is not influenced by their mutual presence: there was assumed that no interaction would take place between C16OH and C18. This assumption can be made plausible by considering that the solubility in the supercritical phase is very low and that the heavy compounds are to some extent similar in chemical structure (long hydrocarbon chain).

If this assumption is valid the correcting factor for solubility estimation of pure C16OH and for pure C18 would be sufficient for estimating the correcting factor in case of mixtures of both compounds. This implies that a linear expression is present for this correcting factor as function of the C16OH/C18 ratio.

The correction factor can bestly be incorporated in the model as a factor which the distribution coefficients are multiplied with, because the distribution coefficients depend only on temperature and pressure and not on composition.

The factor calculated from Kramer's datum and the calculation scheme appeared to be 2.3. The distribution coefficient of C16OH should be multiplied by this factor. From Brunner's experiments the factors appeared to be 2.4 (C16OH) and 1.6 (C18).

As can be seen from the correcting factor, Kramer's and Brunner's data can very well be correlated using the proposed model, corrected by the factor. The deviation in the two generated correcting factors appeared to be about 7 % . Kramer reported for his experiments an overall deviation of 3.4 %, but at higher temperatures this deviation becomes larger. Therefore the value of 5 % has been assumed. Because Brunner did not report the accuracy of his experiments, the same value of 5 % has been assumed. In that case the calculated correcting factors are in fair agreement with the reported data.

It can be concluded that the assumption of not taking into account the interaction between the two heavy compounds is valid and thus the distribution coefficients of the heavy compounds do not depend on composition (molar base). Because molar masses differ the distribution coefficients of the heavy compounds are a slight function of composition when the distribution coefficients are expressed in mass unit pro mass unit.

Because no data are known for the solubility of carbon dioxide in the liquid phase, it is assumed that the model of Henry's Law extended with the Poynting correction is describing reality with sufficient accuracy. The Henry Coefficients were, however, calculated based on experiments. Therefore, the Henry Coefficient data are assumed to be valid. The solubility of carbon dioxide is relatively large and thus the model is somewhat inaccurate because the model is valid for infinite dilutions of carbon dioxide in the liquid phase. Because neither Kramer nor Brunner reported solubilities of carbon dioxide in the liquid phase, it is impossible to say, at this moment, what the accuracy of the Henry/Poynting model will be. Therefore no correcting factor has been used in correcting the distribution coefficient of carbon dioxide. As can be seen from several text books considering thermodynamics, the solubility of a gaseous solute in a liquid solvent is estimated too high by Henry's Law. It can therefore be concluded that the mole fraction of the heavy compounds in the liquid phase would be higher than calculated and thus the solubility of the heavy compounds in the supercritical phase would be higher, because the heavy compounds' distribution coefficient remains the same. Another difficulty is present in case of carbon dioxide's distribution coefficient: it is dependent on composition of the liquid phase, because Henry Coefficients of CO₂ in either C18 or C16OH differ as well as the molar volume of CO₂ at infinite dilution in the liquid.

At this moment solubility experiments are done of the C18-CO2 system, so the found factor, 1.6 can be grounded. If this is the case, it can be assumed that the model is valid (at 120 bar/70 degr.C) with help of the correcting factors. At higher pressure the same calculations are to be made and correlated with Kramer's equation and Brunner's data. Then other correcting factors probably will be found.

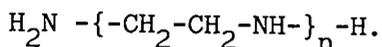
At this moment first concentration will be put on the environmental conditions of 70 degr C and 120 bar.

5. Modeling Phase Equilibria in HEPA Systems

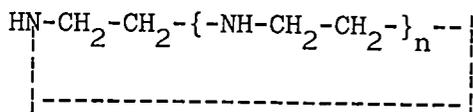
It was assumed in the beginning of this graduating assignment that the testmixture C16OH/C18 was representative for the HEPA separation problem. The supercritical solvent CO₂ had been chosen because of its wide applicance in SCE.

The validity of this representation of the test mixture should be interpreted as follows. The experimentally found number of equilibrium stages, or HETP, with the testmixture is the same as the number of equilibrium stages in case HEPA is considered. Therefore only phase behaviour should be estimated. Because HEPA consists of many components, some manner must be found in estimating the composition of HEPA. Vapour pressures of the HEPA components should be estimated as well as their critical properties. The largest problem in simulating the HEPA separation is the estimation of the solubility of the supercritical component in HEPA. No Henry Coefficients are known from literature. There are, however, solubility experiments done at this location by somebody else, and at this moment it is examined to what extend this experiments can be used in estimating Henry Coefficients.

HEPA is assumed to consist of six components. Delamine, the plant which produces HEPA, specifies HEPA to have linear and cyclic components (Appendix A). The linear components have molar masses in the range of 232.4-318.5 and the cyclic components 258.4-344.6. The linear components have the general chemical structure:



The cyclic components:



As can be concluded from the molar mass specification, n varies from 5 to 7. We have both cyclic and linear components, so their are six components.

The next problem is to estimate the composition of HEPA, when it consists of these six components. The Delamine brochure (Appendix A) gives specification of the nitrogen content of the ethylene amine considered. Ethylene amines with n=3 and higher are mixtures of the linear and cyclic component. For the components n=3..5 the nitrogen content is given. HEPA (n=5..7) is considered, for this nitrogen content analysis, to be the ethylene amine with n=6. It was searched for some relation of the composition depending on the value of n. A linear correlation was found with correlation coefficient 0.996:

$$\{\% \text{ linear}\} = 141.98 - 20.46*n \qquad (25)$$

Using (25) the composition of HEPA can be estimated. The composition of HEPA, expressed in mole fractions, would be, if the estimation procedure is assumed to be valid.

Table 2. Composition of HEPA (values in mole/mole)

n	% linear	% cyclic
5	13.23	20.11
6	6.41	26.93
7	0	33.33

The linear component with n=7 is assumed not to be present in the mixture, because eq. (25) estimates negative values.

The Delamine brochure (Appendix A) gives vapour pressure data of ethylene amines. It was already mentioned that ethylene amines with n>2 are mixtures of linear and cyclic components. In order to make a rough estimation of the vapour pressure of the linear components in HEPA, the vapour pressures of ethylene diamine and diethylene triamine are extrapolated to the ethylene amines with higher repeating unit (n). Antoine behaviour is assumed:

$$\ln P_{sat} = a - b / (T + c) \quad (26)$$

c is a constant and has in this approximation the value -273.15. Eq. (26) now becomes:

$$\ln P_{sat} = a - b/t \quad (27)$$

where t is the temperature in degr.C. From the data for ethylene diamine and diethylene triamine, it appeared that:

$$a_{n,lin} = 7.742 + 1.303 * n \quad (28)$$

$$b_{n,lin} = -230.4 + 517.2 * n \quad (29)$$

With eq. (27), (28), and (29) vapour pressures of all ethylene amines can be estimated, that is the linear component.

The Delamine brochure (Appendix A) also specifies the vapour pressures of the higher ethylene amines (n=3..5). Care must be taken here, because this vapour pressures are vapour pressures of the corresponding mixture! The Delamine plant produces ethylene amines of n=3..5 consisting of the mixtures of linear and cyclic components. At this moment therefore vapour pressure equations are known of the mixtures of ethylene amines (n=3..5), from the Delamine brochure (Appendix A), and of the linear ethylene amines (n=1..7), from eq. (27), (28) and (29).

In order to estimate the vapour pressure of the cyclic compounds some averaging, mixing rule like, formula must be invented. In equation (24), Henry Coefficients were averaged by logarithmic means. This was suggested by Prausnitz [2]. A Henry Coefficient is not really a vapour pressure representation, but it has also the unit of pressure and it is used as a substitution for vapour pressures. Therefore the same mixing rule is assumed to be valid:

$$\ln(P_{n,mix}^{sat}) = x_{n,lin} * \ln(P_{n,lin}^{sat}) + x_{n,cycl} * \ln(P_{n,cycl}^{sat}) \quad (30)$$

From Table 2, eqs. (27), (28), (29) and (30) the vapour pressures of the cyclic compounds can be estimated. Again, a linear expression appeared:

$$a_{n,cycl} = 11.85 + 0.717 * n \quad (31)$$

$$b_{n,cycl} = 775.2 + 537.0 * n \quad (32)$$

The correlation coefficients were respectively 0.995 and 0.991.

With eqs. (27), (28), and (29) the vapour pressures of the linear components can be estimated. With eqs. (27), (31) and (32) the vapour pressures of the cyclic components can be estimated.

At this moment an estimation has been made of the composition of HEPA and the vapour pressures of its components as function of temperature. The critical properties must be estimated with Joback's method [2]. It is now clear that only Henry Coefficients of the to be used supercritical solvent in the HEPA mixture are not known. In literature no systems were found consisting of similar molecules. It was mentioned before that solubility experiments of ethane in HEPA have been done. The possibility is examined to calculate the Henry Coefficients from these experiments. The acentric factor of the components must also be estimated.

The critical properties of the ethylene amines, calculatid by Joback's method [2] are given in Table 3.

Table 3. Critical Properties of Ethylene Amines. Linear and Cyclic Components with n=5..7

n	linear/cyclic	Tc [K]	pc [bar]	Vc [cc/mole]	Zc [-]
5	linear	996.6	24.7	793.5	0.237
5	cyclic	1142.5	35.4	767.5	0.286
6	linear	1069.6	20.8	940.5	0.220
6	cyclic	1251.8	31.8	892.5	0.273
7	linear	1182.5	17.8	1087.5	0.197
7	cyclic	1371.8	28.7	1017.5	0.256

The acentric factors of the components are calculated from:

$$\omega = (3/7) * \frac{Tb/Tc}{1-Tb/Tc} * \log (Pc/1.01325) \quad (33)$$

which is proposed by Prausnitz [2]. This relation is preferred because the vapour pressure relations calculated above can have a significant error. T_b is the normal boiling point of the considered component. It is estimated from Joback's method. P_c should be entered in [bar], the temperatures in [degr.K]. The acentric factors of the components are given in Table 4.

Table 4. Acentric Factors of Ethylene Amines. Linear and Cyclic Components with $n=5..7$.

n	linear	cyclic
5	1.066	0.842
6	1.450	0.961
7	1.378	1.073

With the above estimated properties of HEPA, that is its composition, the vapour pressure equations, the critical properties and the acentric factors, it is possible to calculate the distribution coefficients of the six HEPA components based on the C-truncated virial EOS. Knowing the composition of HEPA we add five more equations:

x_1/x_n , where $n=2..6$ (On gaseous solute free base).

By definition we know that $\sum x = 1$ and $\sum y = 1$, so there are $6+5+2 = 13$ equations, with 14 variables ($x_1..x_7$ and $y_1..y_7$) unknown. The missing equation is the Henry/Poynting relation reproducing the liquid phase behaviour. When the Henry constant is known, a simple Turbo Pascal program can calculate these 14 equations, while a solver like EUREKA can easily solve the produced set to result in the 14 desired values of the mole fractions.

At this moment calculations are done. Vapour pressures are estimated very low by eqs. (27)-(33). At for instance 75 degr. C vapour pressures of the cyclic compounds are in order of $E-10$ [Pa]. It was expected that vapour pressures are low, because solubility data are in order of $E-3$ mass fraction at 270 [bar]. Unless this high pressure, the solubility is in same order of magnitude as the octadecane/hexadecanol/carbon dioxide system at 120 [bar]. It is difficult, however, to predict the accuracy of the model, because at 270 [bar], the ethane's reduced density is about 2-3 times the border value 0.75 (while using C-truncated virial EOS).

In literature it was searched for a corresponding states correlation for to generate vapour pressure data, specifically for polar compounds. Nath [13] has proposed an equation that should very well describe vapour pressures of polar high boiling compounds even at low temperatures. This was suggested by Walas [14]. The difference between the Nath equation and the method described by eqs. (27)-(33) is extremely high: orders of $E7$ are more regular than exception. This suggests that eqs. (27)-(33) does not predict the vapour pressures very well and should be handled with great care.

Nath's equation predicts vapour pressures at about 70 degr.C, of about order E-1 [Pa]. The cyclic compounds' vapour pressures were in analogy with eqs. (27)-(33) lower estimated by Nath. Nath's equation relates the reduced vapour pressure to the reduced temperature. In the equation three constants occur, that depend on the acentric factor.

6. Conclusions

It has been shown that with a relatively small amount of data phase equilibria can be predicted. These data are vapour pressures and Henry Coefficients. With help of corresponding states correlations all other necessary parameters can be estimated. In the text references have been given to publications that report the development of the relevant correlation. Correlations have been found for the second and third virial coefficients, the molar volume of a gaseous solute at infinite dilution in a liquid solvent and the density of the liquid compounds.

The proposed model does not require for large iterative schemes, so calculation time is very short. The model can only be applied to systems where the density of the supercritical fluidum is smaller the three third of its critical density. For the system octadecane/1-hexadecanol/carbon dioxide this means at an ultimate pressure of about 120 bars. The shortcoming of the model has been shown comparing the calculation result with experimental data.

The extrapolation to the separation problem of the HEPA mixture must be considered to be a rough prediction. The accuracy of the produced vapour pressure equations and assumption of HEPA's composition is doubted. Because no better description of HEPA is available, this proposed HEPA simulation may be a first step in solving this HEPA separation problem. It is clear that more data are required.

7. Post Scriptum: Meeting with Prof. Brunner

A visit has been brought to Siegen, Germany, where a conference was held about high pressure technology. Professor Brunner was also present there. Contact has been made and it appeared that the complete phase equilibrium had been measured of the equimolar C18/C16OH/CO2 system, including the solubility of carbon dioxide in the liquid phase. This note has been made, because in Progress Report 1, the correspondence made with Brunner has been described.

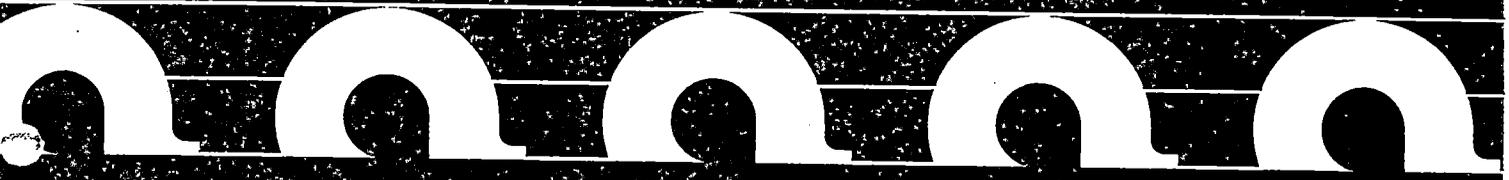
8. Literature

- [1] De Swaan Arons, J.; Coorens, H.; De Loos, Th.W.; Supercritical Extraction. Prediction of Capacity and Selectivity of Supercritical Solvents, Delft Progress Report, 12, 1988.
- [2] Prausnitz, J.M.; Reid, R.C.; Poling, B.E., The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York (1987).
- [3] Weast, R.C., et.al. (ed.), Handbook of Chemistry and Physics, 70th ed., CRC-Press, New York (1989-1990), pp. D121.
- [4] Smith et.al. (ed.), Thermodynamic Data for Pure Compounds. Physical Science Data 25, Part B: Halogenated Hydrocarbons and Alcohols, Elsevier (Amsterdam), 1986, pp. 508-509.
- [5] Vargaftik, N.B. (ed.), Handbook of Physical Properties of Liquids and Gases. Pure Substances and Mixtures, 2nd ed., Springer Verlag (Berlin), 1985, pp. 292-293.
- [6] Tsonopoulos, C., An Empirical Correlation of Second Virial Coefficients, J. AIChE, 20(2), 1974, pp. 263-272
- [7] Orbey, H.; Vera, J.H., Correlation for the Third Virial Coefficient Using T_c , p_c and ω as Parameters, J. AIChE, 29(1), 1983, pp. 107-113.
- [8] Chien-Ping Chai; Paulaitis, M.E., Gas Solubilities of CO₂ in Heavy Hydrocarbons, J. Chem. Eng. Data, 26(3), 1981, pp. 277-279.
- [9] Alessi, P. et.al., UNIFAC Model and the Gas Solubility, 3rd. Chemical Engineering Conference, Proc. Austrian-Ital.-Yugosl. Chem. Engineering Conference, Techn Univ. Graz, Austria.
- [10] Brelvi, S.W.; O'Connell, J.P., Corresponding States Correlations for Liquid Compressibility and Partial Molal Volumes of Gases at Infinite Dilution in Liquids, J. AIChE, 18(6), 1972, pp. 1239-1243.
- [11] Kramer, A., Thodos, G., Solubility of 1-Hexadecanol and Palmitic Acid in Supercritical Carbon Dioxide, J. Chem. Eng. Data, 33(3), 1988, pp. 230-234.
- [12] Brunner, G., Selectivity of Supercritical Compounds and Entrainers with Respect to Model Substances, Fluid Phase Equilib., 10, 1983, pp. 289-298.
- [13] Nath, J.; Das, S.S.; Yadava, M.L., On the Choice of Acentric Factor, Ind. Eng. Chem., Fundam. 15(3), 1976, pp.223-225.
- [14] Walas, S.M, Phase Equilibria in Chemical Engineering, Butterworth Publishers, Boston (1985).

Appendix A: The Delamine Brochure

At the following pages of this Appendix A, copies have been enclosed of the Delamine brochure, which specifies certain important quantities of HEPA and other ethylene amines. In Progress Report 2 the most evident data from this brochure are the nitrogen content of an ethylene amine (mixture) and the vapour pressure data.

del  mine



delamine

Introduction

Delamine produces and markets the complete range of Ethylene Amines. The company was established in 1976 and is owned by Akzo Zout Chemie Nederland bv (AZC – a division of Akzo) and Toyo Soda Manufacturing Company, Limited of Japan (Toyo Soda).

The co-operation of AZC and Toyo Soda in this company is logical and ideal because of complementary contributions. The process is based on the know-how and experience of Toyo Soda at a similar factory in Japan. The Delamine plant is situated in Delfzijl, near production units of AZC which produces two of the most important raw materials, namely Ethylenedichloride (EDC) and NaOH as well as steam, and provides services including maintenance. The arrangement has the dual advantage of permitting Delamine to be managed and operated as an independent entity, while enabling the company to enjoy economies of scale.

AZC and the Toyo Soda organisations sell the Ethylene Amines on behalf of Delamine, thus enabling Delamine to serve markets in Europe, North and South America, as well as a number of African and Asian countries. The products have an outstanding, constant quality, a high purity, and a high fraction content in the case of the higher Ethylene Amines. Moreover, Delamine can supply all kinds of mixtures, tailor-made to meet the requirements of its customers.

Ethylene Amines from Delamine

The Delamine range of Ethylene Amines consists of:

Ethylenediamine	(EDA)
Diethylenetriamine	(DETA)
Triethylenetetramine	(TETA)
Tetraethylenepentamine	(TEPA)
Pentaethylenehexamine	(PEHA)
Higher ethylene polyamines	(HEPA)
Piperazine	(PIP)
N-Aminoethylpiperazine	(AEP)

The ethylene amines are hygroscopic, water soluble products. They are strong organic bases with an ammoniacal odour. Their viscosity is fairly low, apart from HEPA which is somewhat viscous at ambient temperature.

Piperazine however, comes as white flakes. It is also supplied as a 65% aqueous solution, and as the Hexahydrate on special request. Special products designed to fulfill specific requirements of customers are provided also.

Structure of Ethylene Amines

The reaction of Ethylenedichloride (EDC) and Ammonia leads to the formation of a mixture of many chemical compounds, which are all characterized by the recurring $-CH_2-CH_2-N<$, ethylene amino group.

By advanced analysis techniques it can be shown that the reaction product contains compounds possessing a linear, branched, cyclic structure or combinations thereof.

By means of distillation the lower boiling Ethylene Amines – EDA, DETA, PIP and AEP – can be obtained in a chemically pure form (99-100% by wt).

The compounds – EDA, DETA – having a linear structure, can be well separated from their counterparts – PIP, AEP – which contain a cyclic structure. With the higher boiling products such a separation by distillation is not feasible.

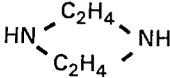
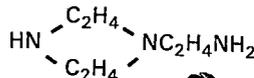
In the TETA product not only the linear and branched TETA isomers are present, but also the cyclic counterparts. Together these compounds constitute the TETA fraction. Since we do not have chemically pure TETA, it is more appropriate to use the term TETA fraction content in the TETA product than eg purity. In a similar way the next higher boiling products TEPA, PEHA are also mixtures which mainly consist of the TEPA and PEHA fractions respectively.

The HEPA product from Delamine contains the PEHA and the higher ethylene amine fractions. It is the only non-distilled product which, by subsequent purification, is made sediment free and low in chloride content.

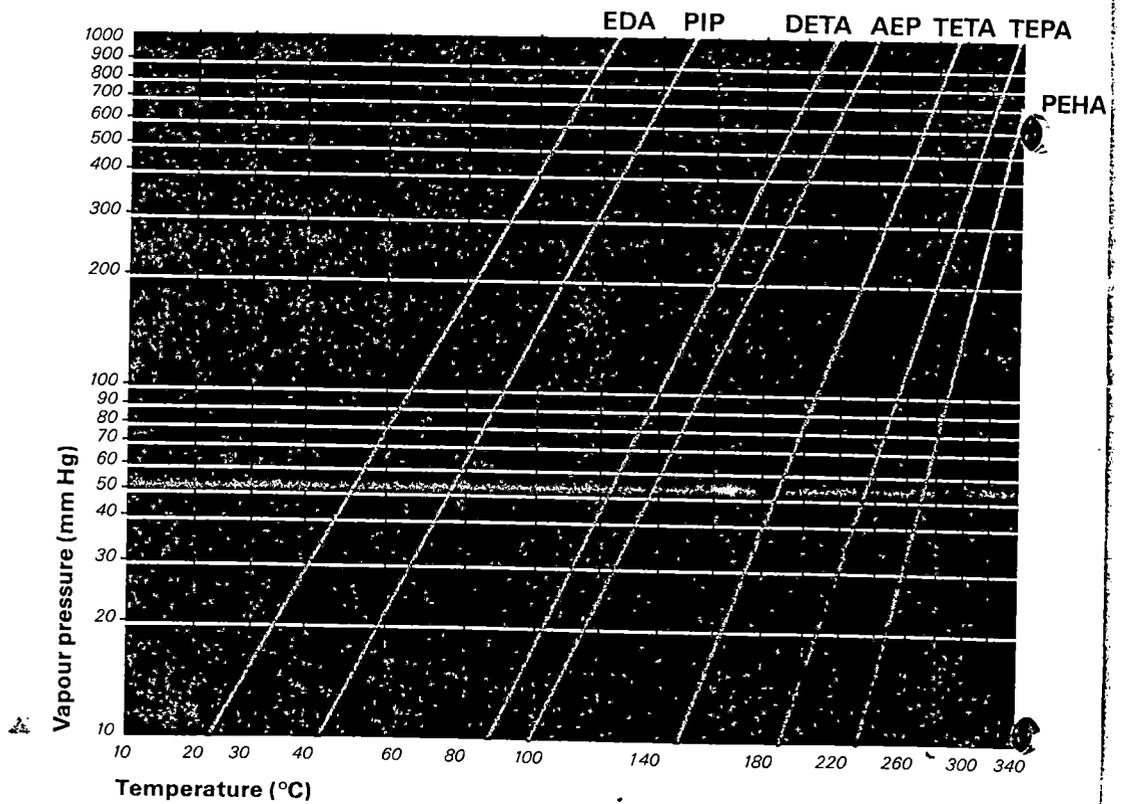
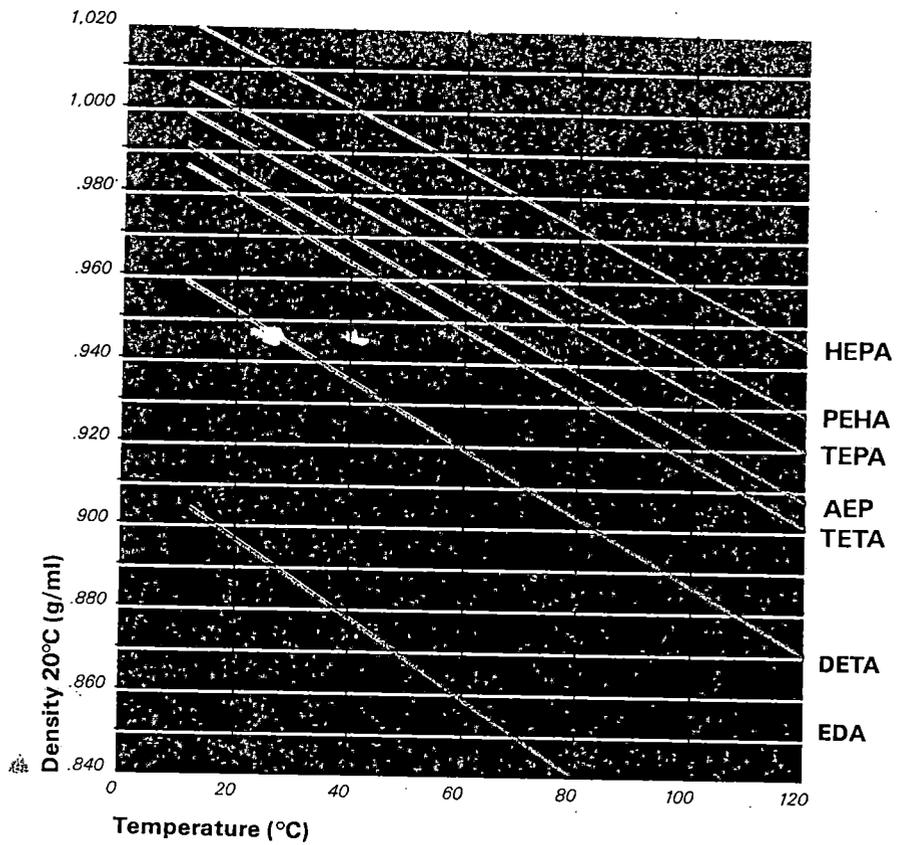
The higher boiling ethylene amine products – TETA, TEPA, PEHA, HEPA – are mixtures, the composition of which can not be rigorously standardized. Consequently physical properties given below have to be regarded as typical of Delamine's products.

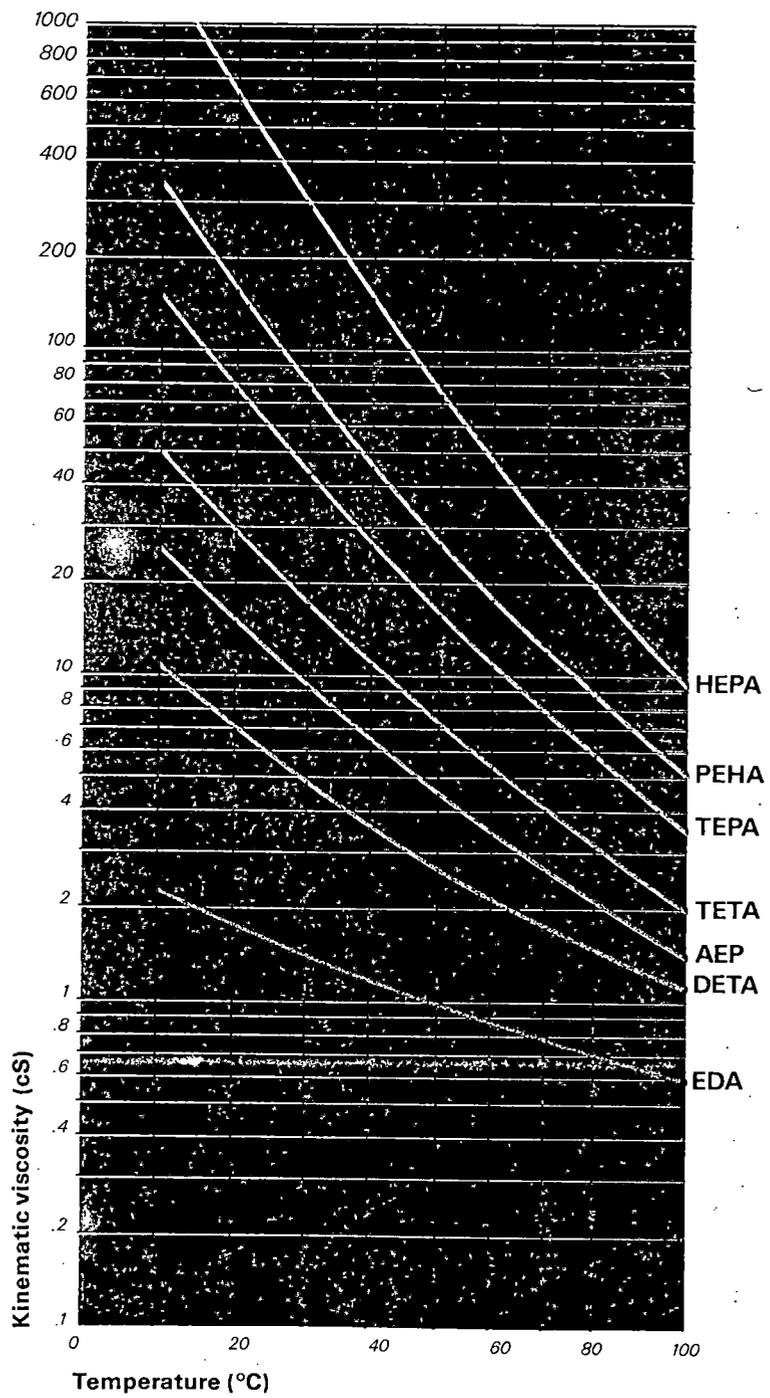
Physical properties

Sales specification

Formula	$H_2NC_2H_4NH_2$	$H_2N(C_2H_4NH)_2H$		
Name	Ethylene diamine	Diethylene triamine	Piperazine	N-Aminoethyl piperazine
CAS, ECIIN nr.	107-15-3	111-40-0	110-85-0	140-31-8
Relative molecular mass	60.1	103.2	86.1	129.2
Relative density 20/20°C	0.898	0.952	0.876*	0.986
Boiling point °C: 0.13 mBar 3.3 mBar	117 19	207 86	148	222 100
Vapour pressure 20°C mBar	13.3	0.3	2.8	0.08
Freezing point °C	10.8	-39	110	-18
Refractive index n _D ²⁰	1.4570	1.4832		1.5005
Kinematic viscosity 20°C cS	1.8	7.3		15
Total N content wt%	46.62	40.74	32.53	32.53
Total base number mg KOH/g	1867	1632	1303	1303
124 °C 4				
Appearance	Clear and free of suspended matter		White flake	Clear
Colour APHA	max. 15	max. 30		max. 50
Relative density 20/20°C	0.897 0.910	0.950 0.955		0.983 0.989
Distillation range °C: P P	min. 115.0 max. 119.0	min 195.0 max. 215.0		min. 210.0 max. 230.0
Purity wt %	min. 99.0	min. 98.5	min. 99.0	min. 98.0

Figures





Transport information

Transport

In bulk by road tanker, tank container (except PIP) or in drums.

Packing

In untreated steel drums. EDA however, with a polyethylene inner drum; PIP with a plastic inner bag. PIP also in fibre drums (30 kg) with a plastic inner bag.

Regulations

The transport regulations for the road and rail modes (ADR/RID), the sea mode (IMDG) and the air mode (ICAO/IATA) conform to the UN classification. However, ADR/RID have their own numbering system.

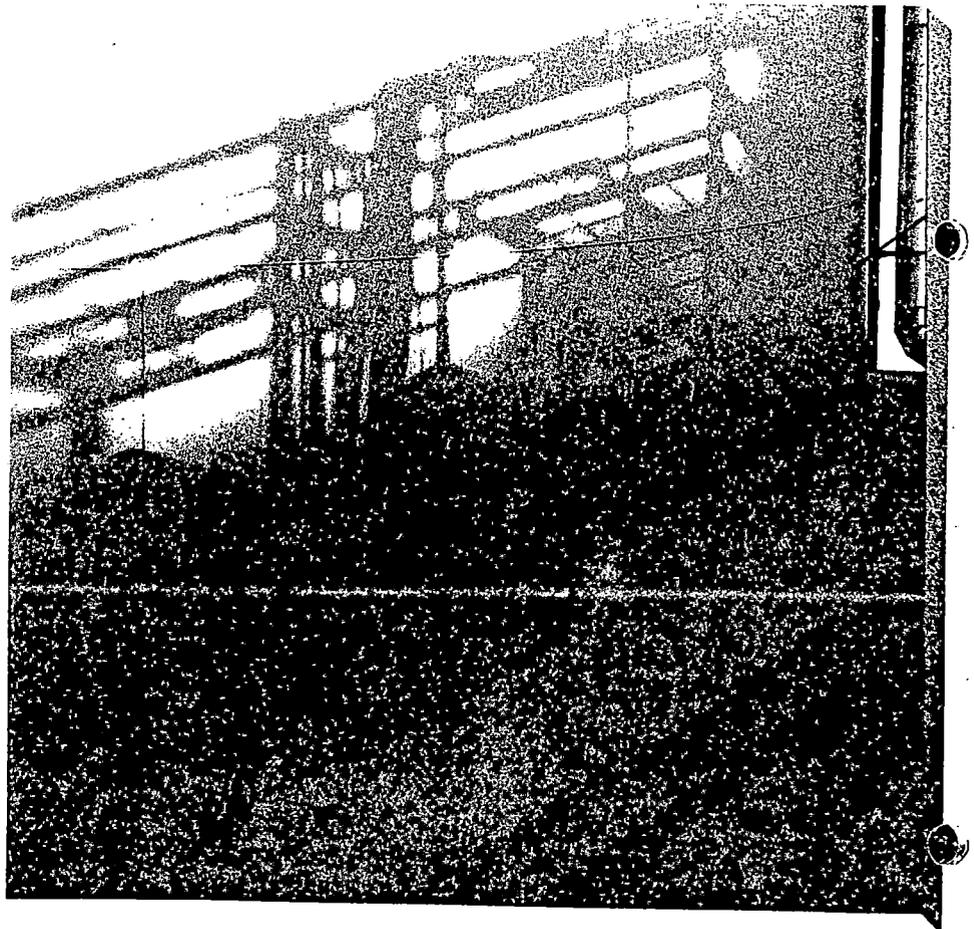
	EDA	DETA	PIP	AEP
Net drum weight (kg)	170	195	80 and 30	200
UN danger classification: Identification no Class Danger symbol Packing group	1604 8(+3) 'Corrosive' 'Flammable liquid' II	2079 8 'Corrosive' II	2579 8 'Corrosive' III	2815 8 'Corrosive' III
ADR/RID item no	8,53 b	8,53 b	8,52 c	8,53 c
EEC number	612-006-006	612-058-00-X	612-057-00-4	-
Special Risks R	10,21/2/3, 34, 43	21/2, 34, 43	21/2, 34, 43	21/2, 34, 43
Safety Advices S	9, 26, 36/7/9	26, 36/7/9	26, 36/7/9	26, 36/7/9
	DETA	DETA	DETA	DETA
Net drum weight (kg)	200	205	205	200
UN danger classification: Identification no Class Danger symbol Packing group	2259 8 'Corrosive' II	2320 8 'Corrosive' III	2735 8 'Corrosive' III	2735 8 'Corrosive' III
ADR/RID item no	8,53 b	8,53 c	8,53 c	8,53 c
EEC number	612-059-00-5	612-060-00-0	612-064-00-2	612-065-00-8
Special risks R	21/2, 34, 43	21/2, 34, 43	21/2, 34, 43	21/2, 34, 43
Safety Advices S	26, 36/7/9	26, 36/7/9	26, 36/7/9	26, 36/7/9

Handling and storage

Ethylene amines have a tendency to discolour when exposed to air and light for a prolonged period. Storage vessels should therefore be equipped with nitrogen blanketing, and light should be intercepted if colour is important.

Stainless steel, carbon steel, Teflon[®] and special type aluminium are suitable materials for the handling and storage of ethylene amines. Carbon steel is unsuitable for prolonged storage, should the colour be important. Copper, nickel and cobalt are readily attacked by ethylene amines so that ethylene amines should never be allowed to come into contact with these materials.

Ethylenediamine has a high freezing point (10.8°C). Consequently the outside tanks and piping will require heating and insulation to prevent freezing in the winter.



Fire hazards

Health & Safety

Generally, ethylene amines have a high flash point, so that fire hazards are comparatively small at normal temperatures. In case of fire, water and powder are suitable extinguishers.

Ethylene amines are fairly strong bases. Therefore if the product comes into contact with the eyes, the eyes must be flushed immediately with plenty of water for at least 10 minutes and a doctor should be consulted immediately after flushing.

Ethylene amines differ in acute toxicity. All of these materials can cause serious skin burns and should be handled with care.

Direct contact with liquids, flakes or vapours should be avoided. The use of protective clothing, rubber gloves and safety glasses is necessary.

Repeated exposure to ethylene amine vapours presents a definite health hazard. Consequently areas where ethylene amines may come into contact with the air, should be well ventilated.

Flash point °C (COC)	43	102	88	93
Autoignition temperature °C	385	395		300
Explosion limits in air vol%: Upper Lower	16.6 2.7	8 1.8	6.5	6.5 1.6
Threshold limit value mg/m ³ (CGIH) 1984	10	1	n.e.	n.e.
Acute oral toxicity LD ₅₀ rats mg/kg	760	1080	1900	2140
Flash point °C (COC)	143	170	206	> 200
Autoignition temperature °C	335	321	> 300	> 300
Explosion limits in air vol%: Upper Lower	7.2 0.7	9.2 0.4		
Acute oral toxicity, LD ₅₀ rats mg/kg	4340	3990	2500	
n.e. not established				



The information in this brochure is, to the best of our knowledge, true and correct and is given without warranty, express or implied.
August 1985.

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International & Intermediates Group,**

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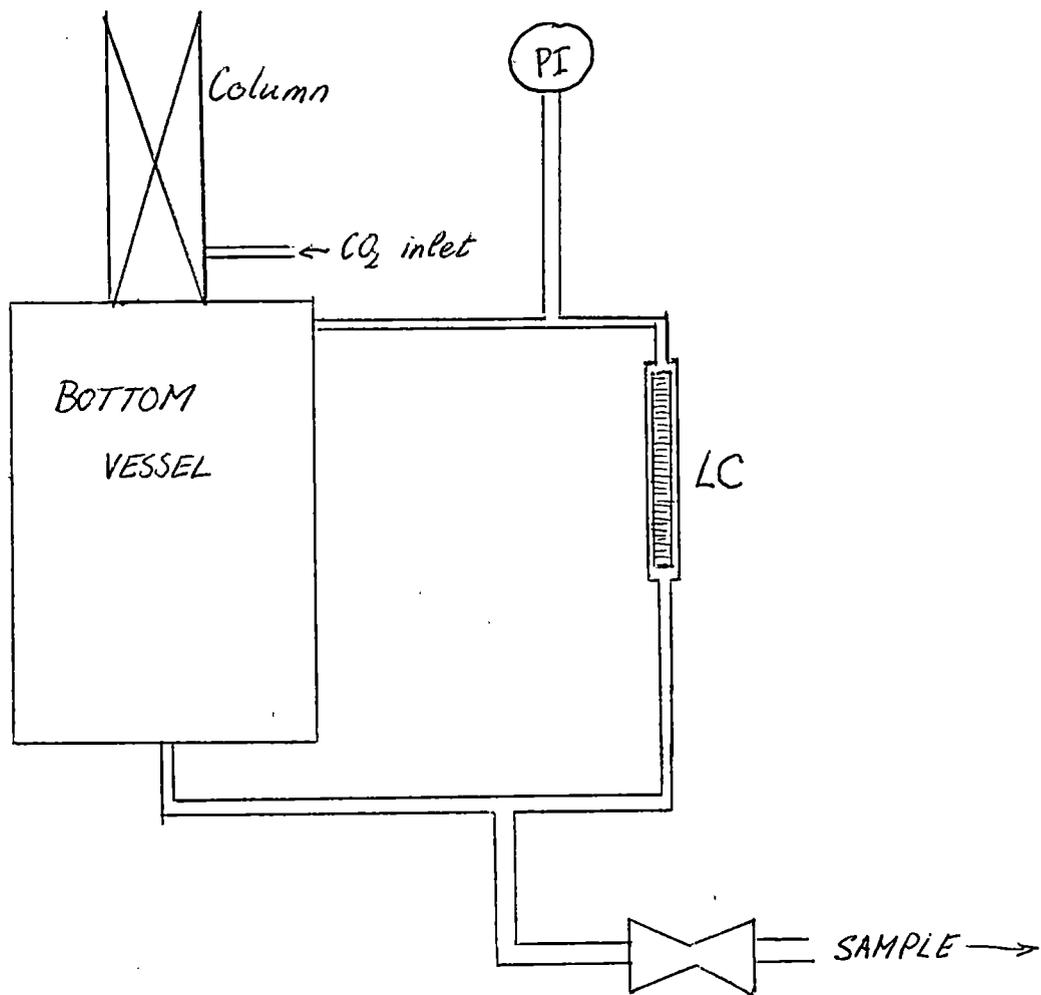


Figure B1: LEVEL CONTROL OF BOTTOM VESSEL
SEE TEXT FOR ELUCIDATION

Appendix B: Present Experimental State

In this Appendix B a short review will be given of experimental problems and reasons why no experimental data haven been produced yet.

As already mentioned in Progress Report 1, problems with pumps occurred. Gauging the two pumps has required a lot of time, because both pumps gave specific problems. The supercritical fluidum pump had to be gauged with 120 bars at the pressing side. Because of this reason problems occurred with circulation. At certain adjustments of the pump no circulation was reached. At last the gauge line had been produced (Progress Report 1). The liquid feed pump gave problems because of freezing of the to be pumped liquid. Both octadecane and 1-hexadecanol have melting points of above atmospheric temperatures. The pump head broke because of freezing of liquid. This required a lot of time. Now the pumps have been gauged.

Solubility experiments have started in the column for the system octadecane/carbon dioxide. Top product was generated, but no bottom product appeared, and thus it is not certain whether the measured solubilities are to be reproduced, because it could be possible that the outgoing carbon dioxide flow was not saturated with octadecane. The problem appeared to be some kind of flooding in the layer below the package. The inlet-point of carbon dioxide was changed, and now no flooding occurs.

At this moment problems occur at the level control of the bottom product. The communicating vessels, which the level control (LC) is based on, are somehow no communicating vessels. A strange thing happens. At some time, t , after starting the liquid feed pump, the level becomes higher in the LC. The product is added from above in the LC. Samples were taken and at certain time, t_t , the liquid pump was stopped. Then the LC runs completely out of liquid bottom product. The LC is drawn in figure B1.

As can be seen, the adding of product in the LC from above can only occur when the bottom vessel is full. Then the liquid product "overflows" into the LC. When liquid is tapped off, the LC-level still becomes higher. That can occur when liquid accumulated in the pressure indicator pipe flows downwards, while the bottom vessel is emptied. Then, after tapping off, the bottom vessel is empty while the LC is full. Logically, the liquid flows from the LC downwards to the bottom vessel until the communicating vessels have been installed. The above described occurrence can only take place when somewhere, somehow locally pressure is lost, so carbon dioxide will somewhat be flashed. Then the LC-bottom vessel = communicating vessels system is disturbed. It has been decided to remove the LC and replace it for a large autoclave/vessel in order to achieve sufficient buffer for liquid bottom product to accumulate. Then the system gets sufficient time to get into steady state.

At the moment I am writing this we have reached this point. When the other autoclave will be installed, I think that solubility data of octadecane in carbon dioxide, will not give any problems. But I have said that before. . .