

RESEARCH ON WORKING FLUIDS FOR REFRIGERATION, AIR-CONDITIONING, AND HEAT PUMP SYSTEMS

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INTRODUCTION

Research on the working fluids for refrigeration and air-conditioning and heat pump systems has been conducted at the Institute of Refrigeration (IKW) at the University of Hannover, Germany, for more than 15 years. This research is mainly concerned with the interaction between refrigerants and lubricants in those systems and only to a minor extent with refrigerants, because the IKW is working in the field of applied research. The investigation on properties of pure refrigerants and refrigerant blends is the domain of scientists in the field of thermodynamics at various universities, e.g. the University of Las Palmas de Gran Canaria (ULPGC). Up to the late seventies, the research has been carried out mainly with chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) like R12, R22, and R502 in the mixture with mineral oils. At that time, two facts were the starting point for refrigerant oil research at the IKW in Hannover:

Energy Conservation

The oil crisis in 1974 had initiated in the industrialized countries research for energy conservation, namely for domestic heating systems by the development of heat pumps. Those heat pumps had to compete with conventional heating systems with lower initial costs. In order to compensate for the higher capital costs of heat pumps in an adequate time, energetic improvements in comparison to conventional heat pump systems had to be achieved. For this reason, research at the University of Hannover was started in order to apply the Lorenz cycle with gliding temperatures for energy saving using zeotropic binary refrigerant mixtures [1]. The knowledge of the behaviour of those refrigerant mixtures like R12/R114 and R22/R114 in combination with lubricants were not known until that time when only some minor investigations on oil/refrigerant had been done on blends of R22 and R12 outside their azeotropic point. Further on, the higher working temperatures in heat pumps as compared to refrigeration systems asked for more thermal stability of the lubricants and required for that purpose special developments of synthetic oils [2].

Also the gradual shortage of mineral oils with adequate low temperature behaviour, namely more of the paraffinic than the naphthenic type, had led to the development of synthetic lubricants like alkylbenzenes (AB), polyalphaolefins (PAO) and polyglycols (PG) during that period. The behaviour of these new synthetic oils together with the conventional refrigerants and especially together with their mixtures, was mostly unknown at that time, when the research of oil/refrigerant systems at the University of Hannover started. This research led to two Ph.D. theses by Schroeder [3] and Hesse [4] dealing mainly with this problem in order to find a way for predicting oil/refrigerant properties by using thermodynamic relations, instead of what up to that time was only possible by empirical equations.

Environmental Effects

Ozone Depletion

Another impact on the oil/refrigerant research was the theory of ozone depletion by Molina and Rowland [5] issued in the same year of the oil crisis 1974 but acknowledged in the scientific and political world only in 1987 when the "Montreal Protocol on Substances that Deplete the Ozone Layer of the Earth" was signed. This agreement led to a new direction in the refrigerant oil research. Instead of chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) new hydrofluorocarbon (HFC) refrigerants as listed in table 1 without chlorine together with new lubricants of the polyglycol- or ester-type had to be applied in refrigeration and air-conditioning systems. The enforcement of the Montreal Protocol during the follow-up conferences in London 1990 and in Copenhagen 1992 accelerated the research towards ozone benign working fluids and led to a further Ph.D. thesis by Arnemann [6], who did experimental investigation with polyglycol/R134a systems as well as theoretical work in order to predict the behaviour of pure and mixed refrigerants with new lubricants theoretically. In parallel, measurements on those fluids were done extensively and published by Burke and Kruse [7, 8, 9].

With R134a a suitable alternative for the CFC R12 was found. So far there is no pure fluid from the HFC group known as a possible substitute for the HCFC R22 and the CFC R502. The presently most favoured alternatives are mixtures containing the HFCs R32, R125, R143a, and R134a [9]. To find a way to estimate the properties of binary and ternary refrigerant blends with oil will be the challenge in the future.

Refrigerant	No.	Chemical Formular	Molecular Mass [kg/kmol]	T _b [°C]	T _{cr} [°C]	P _{cr} [bar]
Chlordifluoromethane	R22	CHClF ₂	86,480	-40,8	96,0	49,7
Blend	R502	CHClF ₂ / CClF ₂ CF ₃	111,640	-45,4	82,2	40,7
	R22/R115 : 48.8/51.2					
Difluoromethane	R32	CH ₂ F ₂	52,020	-51,8	78,4	58,3
Pentafluoroethane	R125	CHF ₂ CF ₃	120,020	-48,1	66,3	36,3
Trifluoroethane	R143a	CH ₃ CF ₃	84,040	-47,8	73,1	37,9
Tetrafluoroethane	R134a	CH ₂ FCF ₃	102,030	-26,2	101,1	40,7
Propane	R290	C ₃ H ₈	44,094	-42,0	96,7	42,5
Ammonia	R717	NH ₃	17,030	-33,3	133,0	114,2

Table 1 -Properties of R12, R22, R502 and some of their possible alternatives

Global Warming, Greenhouse Effect

During the last years, another environmental problem, the global warming effect appeared on the horizon and influenced the development of refrigeration systems. This has led to the reappearance of old refrigerants like ammonia (NH₃), hydrocarbons (HCs), and now under development carbondioxide(CO₂), which require again lubricants under the aspect of modern, technologically well developed refrigeration and air-conditioning systems. Therefore, special lubricants for ammonia have been

detected in a research project at the IKW [10], which allow the application of ammonia in small refrigeration systems. These lubricants are now already on the market.

On the other hand, the market gain of hydrocarbons in refrigerators first in Germany and now in Europe has shown the importance of the interaction of lubricant and refrigerant. Especially concerning the lubrication behaviour of natural refrigerants together with new oils will further on be the challenge the lubricant/refrigerant research for technically well developed refrigeration and air-conditioning systems. Therefore, in the following, the general problems of the working fluids in refrigeration and air-conditioning systems will be described first and the results of the research on those working fluids at the IKW in Hannover will be briefly discussed later.

LUBRICANTS IN REFRIGERATION SYSTEMS

In contrast to the refrigerant, the lubricant, which is termed refrigeration oil, is needed only in the compressor of the refrigeration system. There, its primary job is to lubricate the bearings and other gliding areas inside the compressor. Besides, it provides for better sealing between the piston and the cylinder or heat transport out of the compressor. The migration of oil from the compressor into the refrigerant cycle can be reduced by an oil separator but not completely prevented. Driven by the refrigerant flow, the oil has to pass the cycle as balast and return to the compressor.

On its way through the refrigeration cycle, the lubricant must to withstand great fluctuations in temperature. The primary requirement for a refrigeration oil is a high thermal and chemical stability. Both, carbonization, chemical reactions with the refrigerant or other system materials at high temperatures as well as flocculations at low temperatures can reduce the life span of a refrigeration system dramatically.

For the so-called CFC and HCFC refrigerants, mineral oils, semi-synthetic and fully synthetic lubricants proved to be useful. Mineral oils are classified as paraffins, naphthenes, aromatics, and olefins. The available synthetic lubricants were mainly products on the basis of alkyl benzenes (AB) and polyalphaolefins (PAO). Only in rare cases, silicone or silicate oil or polyglycol lubricants (PG) were used.

The conversion of refrigeration systems from CFC to HFC refrigerants was accompanied by the conversion of the refrigeration system to new lubricants, as the previously used ones are not sufficiently miscible with the new refrigerants [7]. By the separation of lubricant and liquid refrigerant, which is termed miscibility gap of the oil/refrigerant system, the performance of the refrigeration setup can be influenced considerably.

Oil and Refrigerant in the Refrigeration System

An insufficient miscibility of lubricant and refrigerant can cause problems as is exemplified in the diagram of a refrigeration system in figure 1. On the right, in the scheme of a refrigerator system, there is the "oil cycle" consisting of the compressor and the oil separator. As mentioned before, a small fraction of the lubricant migrates into the refrigerant cycle and has to be transported back from there to the compressor in order to supply it with the necessary lubricant quantity.

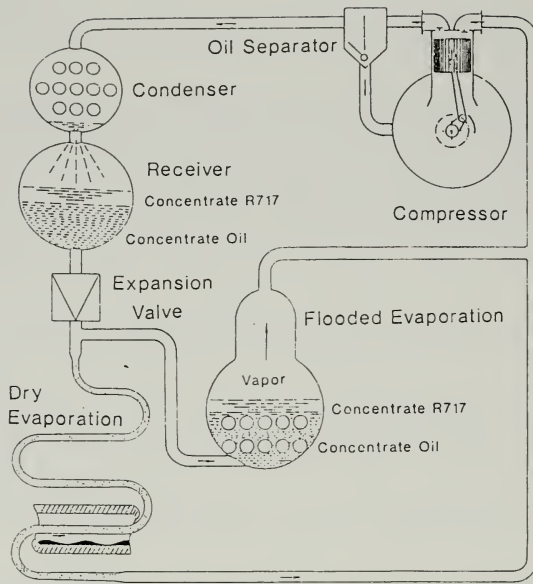


Figure 1 - Oil transport in a refrigerant cycle [8]

A good miscibility of oil and refrigerant has an advantageous effect on the oil-return from the refrigerant cycle to the compressor. Especially at low temperatures as they exist in the evaporator of a refrigeration system, in comparison to the pure oil the liquid viscosity of the oil/refrigerant mixture decreases considerably with an increasing refrigerant fraction. The flowability of the mixture grows correspondingly so that the lubricant, which is flowable because of its refrigerant fraction, can be transported by the refrigerant gas flow. In this condition, the oil can be returned to the compressor without any additional construction devices.

In the compressor, where the highest temperatures exist, a sufficient viscosity of the lubricant has to be guaranteed in order to ensure its lubrication. A good miscibility of oil and refrigerant results in a reduction of the lubricant's viscosity caused by the dissolved refrigerant. This fact has to be taken into consideration for the design of the compressor and the selection of the refrigeration oil.

In case of immiscibility with the refrigerant, oil separation may appear in the oil sump of the compressor and in apparatuses such as condenser, receiver or evaporator. Especially the evaporator may become an oil trap because of the increasing fluid viscosity with decreasing temperature. To realize a dry evaporation in the case of immiscibility, the pure oil has to be very low viscous in order to allow its transportation by the circulating refrigerant. Otherwise, the oil will remain in the evaporator. The oil-covered heat exchanger tubes will diminish the heat transfer and cause a pressure drop. In such refrigeration systems normally the principle of the flooded evaporation is applied. In a flooded evaporator, liquid refrigerant is always present. In the case of a miscibility gap, two liquid phases occur as shown in figure 1. If the oil has a lower density than the refrigerant--which is the case for CFC and HFC refrigerants in the relevant temperature range--, its evaporation is additionally hampered by the oil-rich liquid phase floating on top. These are unfavourable conditions.

The flooded evaporation is commonly used in large R22 and ammonia systems, where the oils are not miscible with ammonia or are only partly miscible with R22 [11]. The return of the separated oil is facilitated in that way that in the case of ammonia the density is lower than the density of oil. By constructive devices or by draining the evaporator's sump during maintenance works, the refrigeration oil is removed from the evaporator and refilled to the compressor. In the case of R22 the floating oil on top of the refrigerant liquid surface is sucked from there by special oil return lines to the compressor.

Such a procedure is only possible for high capacity refrigeration systems with costly oil separating systems, which are constantly maintained by trained personnel. For low capacity systems this procedure is not economical. In these systems well soluble oil-refrigerant systems are applied to enable a dry evaporation. To find an oil that provides both solubility with the refrigerant at low temperatures and sufficient viscosity at high temperatures even in the mixture with the refrigerant is very important for most applications in refrigeration.

THE MISCIBILITY GAP

Depending on temperature and pressure, not all liquids are fully miscible in each other. The separation of a system into two separate liquid phases as shown in figure 2, is called a miscibility gap. In the case of an oil/refrigerant mixture, there are two liquid phases, a more oil-containing liquid α and a more refrigerant-containing liquid β . They are divided by a phase boundary. The separation is caused by the different densities of the two liquid phases. Above the liquids is a vapour phase, which for oil/refrigerant mixtures in regard to the tremendous differences of oil and refrigerant in vapour pressure consists nearly of pure refrigerant so that its amount of oil can be neglected.

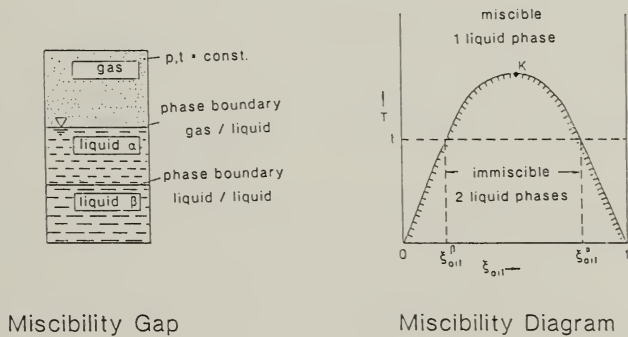


Figure 2 - Miscibility gap and miscibility diagram

In the right diagram of figure 2, the miscibility curve of the mixture is plotted as a function of temperature and mass fraction oil. The miscibility curve separates the scope of complete homogeneous solubility from the scope of the solubility gap, in which two liquids appear. The side of the miscibility curve, where the immiscibility starts here, is marked by a hatching.

Figure 3 shows a total of five possible versions of miscibility curves. The curves of type A to D have been determined both in past studies [12] and in the here presented results. Type E, a completely encompassed miscibility gap, for example occurs in the nicotine-water system.

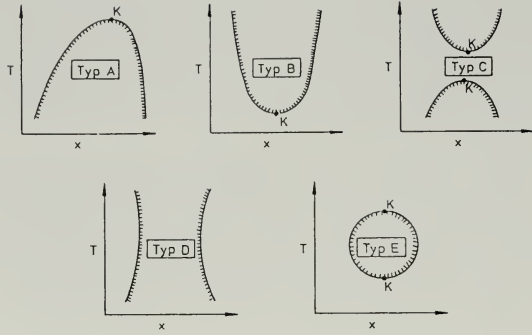


Figure 3 - Different forms of miscibility curves

Results of Experimental Investigations on Miscibility

Investigations made by Hesse [4] of the refrigerant mixture of R22 and R114 with an alkyl benzene (A1) of the viscosity class ISO 32, whose results are reflected in figure 4, led to a considerable decrease of the separation temperature of binary refrigerant blends in contrast to the pure substances. The investigated, binary refrigerant blends possess a clearly more favourable miscibility with this oil in comparison to their pure components.

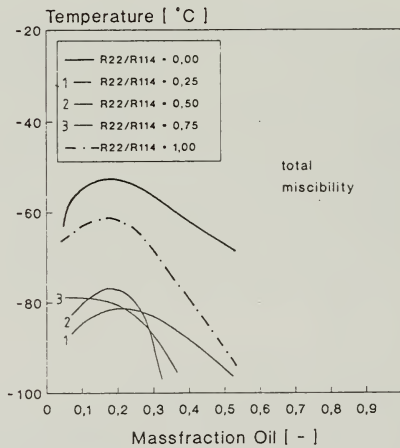


Figure 4 - Miscibility of R22 and R114 with the alkyl benzene lubricant A1

In a subsequent research project [7], the miscibility of the refrigerants R23, R134a and R152a as well as those of the binary blends R23/R152a and R134a/R152a with various oils were experimentally examined. Like R13, R23 is a low temperature refrigerant, whose normal boiling point is at -82.1°C and whose critical temperature at 25.6°C is quite low [13].

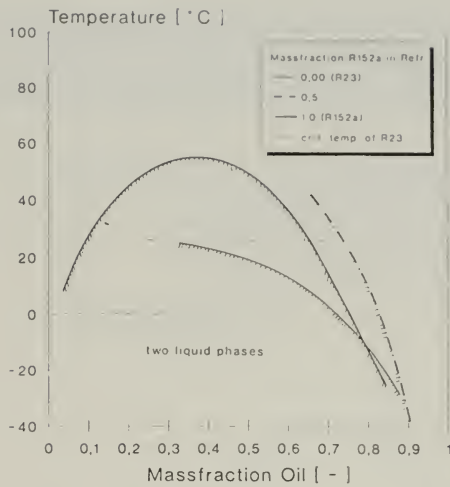


Figure 5 - Miscibility of R23 and R152a with an alkyl benzene lubricant A2

In contrast to the system R22/R114, the refrigerant blend R23/R152a shows another oil behaviour. Investigations of the solubility of this system with an alkyl benzene refrigeration oil A2 of viscosity ISO 46 of led to exactly the opposite effect as can be seen in figure 5. It shows the miscibility curve of the pure refrigerants as well as of a blend consisting in equal fractions of R23 and R152a with this oil. While R23 is only soluble with A2 for oil-rich compositions, R152a also has soluble compositions on the oil-poor side. With the refrigerant blend, the oil A2 shows an even more unfavourable solubility behaviour than the pure refrigerants.

While the examples of R22/R114 and R23/R152a show these unexpected results, the miscibility curves of most systems composed of oil and a refrigerant blend run inbetween those of the systems containing pure refrigerants and oil.

Within an ongoing research project of the European Community [14] at the IKW, the behaviour of the earlier mentioned refrigerants R32, R125, and R134a is investigated with a new but already commercially available lubricant (E8). This is a polyolester-type lubricant of the viscosity ISO 32, which is used in compressors for supermarket refrigeration.

The HFC R32 has the main disadvantage to be flammable, R125 of these three refrigerants has the highest contribution to the greenhouse warming effect, caused by its high direct greenhouse warming potential (GWP) and its high energy consumption as a refrigerant. As shown in table 1, R134a with a normal boiling point of -26.2°C is not suitable for a typical R22 or R502 application with evaporation temperatures down to -40°C .

Besides the pure refrigerants, the oil miscibility of a ternary refrigerant blend with mass fractions of 30% R32, 30% R125, and 40% R134a was determined by experiments.

The solubility behaviour of the three oil/pure refrigerant mixtures and the oil/refrigerant blend mixture is shown in figure 6. The investigations were carried out in the temperature range between -80°C and $+80^{\circ}\text{C}$. The system E8/R32 forms a miscibility gap at temperatures below -18°C and above $+70^{\circ}\text{C}$. The oil E8 proved completely soluble with R125 for low temperatures down to -80°C . Only for temperatures above $+65^{\circ}\text{C}$, that is near the critical

temperature of R125, separations of the liquid could be observed. The separation temperatures of the third binary mixture E8/R134a are below -70°C and thereby far below the application temperature of the refrigerant R134a. As with R134a, no miscibility gaps were identified for the ternary refrigerant blend with the oil E8 at high temperatures. For low temperatures these appear below -65°C .

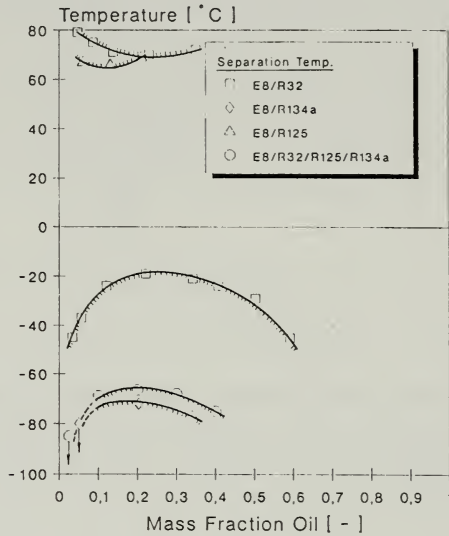


Figure 6 - Miscibility of R32, R125 and R134a with an ester-type lubricant E8

Since refrigerant blends, such as R32/R125/R134a are looked at as R502 substitutes for the application in a supermarket refrigeration system with evaporation temperatures of about -40°C , an oil/refrigerant mixture with this blend is sufficiently miscible.

Besides those HFC blends as substitutes for R502 and R22 in low temperature refrigeration, ammonia is an alternative refrigerant for R22, which contributes neither to the depletion of the ozone layer nor to the global warming of the atmosphere. Ammonia is energetically and volumetrically favourable as it has among other properties a large specific heat of vaporization and a high volumetric refrigerating capacity. Due to its favourable energetic behaviour, the indirect contribution to the greenhouse warming effect is kept at a minimum. Moreover, ammonia is inexpensive and available in sufficient quantities.

The nonferrous metals normally used in refrigerating systems, e.g. copper and brass are as well as the majority of the jointing materials are not compatible with ammonia. Further disadvantages are the flammability and the toxicity of ammonia. Ammonia is classified as a gas which is not easily inflammable and whose explosion hazard in air is relatively small. The smell of ammonia is regarded as very disagreeable. Even smallest volumetric amounts in the air are being perceived by human beings.

In spite of its local danger potential, the refrigerant ammonia has proved its reliability in large industrial plants for decades. It is used there in absorption as well as in compression refrigeration cycles. The commonly used oils in ammonia refrigeration systems, e.g. mineral oils or polyalphaolefines, are miscible with ammonia only on a very limited basis, as shown in

figure 7 [11] with a logarithmic abscissa. Only in compositions with oil mass fractions far below 1% or above 99%, these working fluids shown here are completely soluble. For concentrations inbetween these critical values, this mixture has a miscibility gap and therefore does not meet the requirements, which are necessary for a dry evaporation.

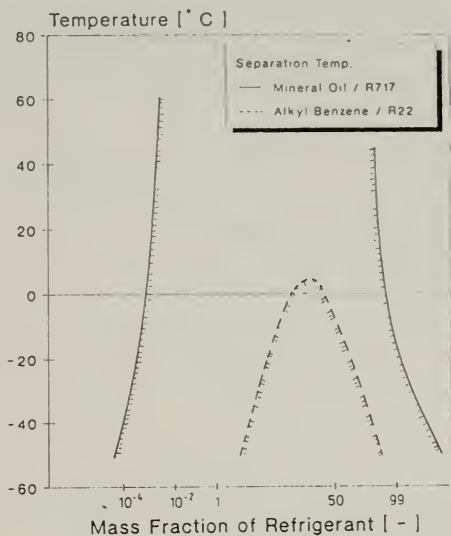


Figure 7 - Miscibility of a mineral oil with ammonia

This was one reason why ammonia could not be used economically in refrigeration systems of smaller capacity in the past and was exactly the starting point, where a research project [10] at the IKW was initiated, which comprised investigations of the miscibility of lubricants with ammonia. The basic idea was that similar to the polar R12-substitute R134a, the polar refrigerant ammonia could likewise be soluble with the new, polar, synthetic lubricants.

A total of five lubricants, one ester oil and four polyglycol oils, with regard to their miscibility with ammonia were investigated within this research project. The polyglycols P3, P4, and P5 are base oils, P6 is an added version of the oil P3. Some data of these oils are contained in table 2. Besides the kinematic viscosity, the pour point, and the principal solubility with water and mineral oil, the information to what fractions they are composed of ethylene oxide (EO) and of propylene oxide (PO) is additionally given for the polyglycols.

Table 2 -Investigated oils

Sign	Type of Oil (EO : PO)	ν [$10^{-6} \frac{m^2}{s}$] 40 / 100°C	Pour Point [°C]	Solubility in	
				Water	Min. Oil
E3	Polyol Ester	25 / 5	-54	no	?
P4	PG (0:1)	50 / 9	-45	no	yes
P3, P6	PG (1:1)	70 / 14	-50	yes	no
P5	PG (4:1)	55 / 11	0	yes	no

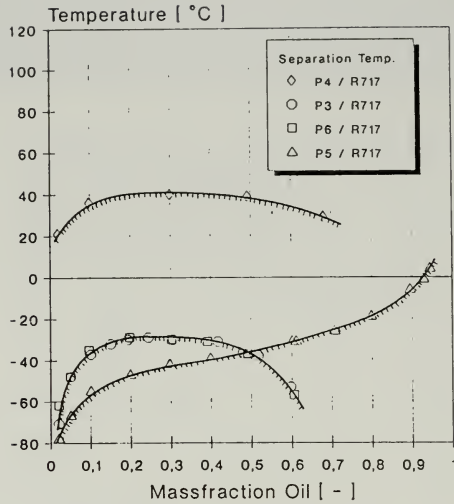


Figure 8 - Miscibility of polyglycols with ammonia

The results of the miscibility investigations with polyalkylene glycols are plotted in figure 8. Within the investigated temperature range between -80°C and $+90^{\circ}\text{C}$, none of the investigated oil/ammonia systems was completely miscible. The oil P4 consisting of pure propylene glycol, already showed separation at temperatures between $+20^{\circ}\text{C}$ and $+40^{\circ}\text{C}$. This oil, therefore, does not constitute an improvement in comparison to conventional refrigeration oils.

The solubility limit of the systems consisting of oil P3 or P6 --both composed of equal fractions of ethylene and propylene oxid-- and ammonia is shifted to clearly lower temperatures! For compositions with less than 5% oil as they can exist in the evaporator of a refrigeration system, the separation temperatures are clearly below -40°C . In refrigeration systems with evaporation temperatures between -40°C and -50°C the miscibility of this oil could, therefore, be sufficient for the necessary viscosity reduction in the evaporator and thereby enable the automatic oil return to the compressor. The additives of the oil P6 did not have any impact on the miscibility in this case.

For the mixture oil P5/ammonia, the miscibility curve is rather atypical. The mixture ratio EO to PO of this lubricant is 4 to 1. For refrigerant-rich compositions, this mixture showed the lowest separation temperatures. With a growing oil mass fraction, however, the separation temperature also increased continuously. Compositions with oil mass fractions of more than 95% already showed miscibility gaps for temperatures above 0°C . This could particularly cause problems for the oil transport through the suction line to the compressor in small capacity refrigeration systems due to the high viscosity of the oil-rich liquid phase.

The investigations with the polyol ester E3 revealed on the one hand insolubility with ammonia in the investigated temperature range and on the other hand chemical reactions. Therefore ester-type lubricants are not suitable for applications with ammonia.

Theoretical Investigations on the Miscibility of Oil/Refrigerant Systems

The calculation on the miscibility of oil/refrigerant systems at the Institute of Refrigeration in Hannover was started by Hesse [4]. For the mixture of oil A2/R22 as shown in figure 4. Using a Lee-Kesler-Ploecker equation of state for the vapour phase and the UNIQUAC equation for the liquid phase and binary interaction parameters, which were fitted to the results of the vapour pressure measurement, the miscibility line was estimated as presented in Figure 9. The shape of the curve was very similar to that of the experimentally determined miscibility curve. Unfortunately, the separation temperatures of the calculated curve show deviations up to 30 Kelvin.

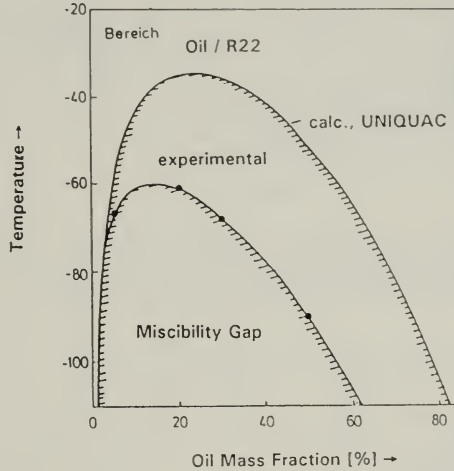


Figure 9 - Comparison of the measured miscibility gap and the results calculated by using the UNIQUAC model

The theoretical work was continued by Arnemann [6]. In addition to UNIQUAC, he included the equations of Flory-Huggins, of Wilson and the equation of Redlich-Kwong-Soave (RKS) for the calculation of the liquids in his investigations. The vapour phase was always calculated using the RKS equation of state. In the first step, the empirical equations were fitted to the vapour pressure data for the oil/refrigerant mixture. The results of the calculation are illustrated in figure 10, where the separation temperatures are shown as a function of refrigerant mass fraction. The results are similar to those of Hesse with similar shapes of the curves but a significant deviation in separation temperature. Although the binary interaction parameters of the Flory-Huggins equation were adapted as a linear and quadratic function of the temperature, the results calculated by UNIQUAC, using constant interaction parameters, are closer to the experimental data.

In the second step of this work, the calculations were fitted to the results of some miscibility measurements. As presented in figure 11, the deviation between the calculated and the experimental results decreased drastically and correspond very well for low refrigerant mass fractions. Like in the first step, using the UNIQUAC equation results in the best data.

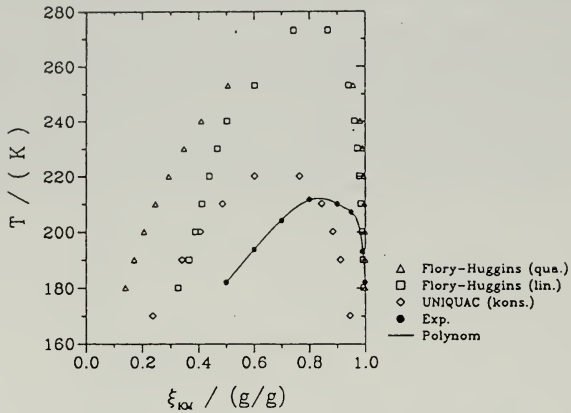


Figure 10 - Calculation on miscibility of alkyl benzene A1 with R22 using parameters fitted to the vapour pressure measurements

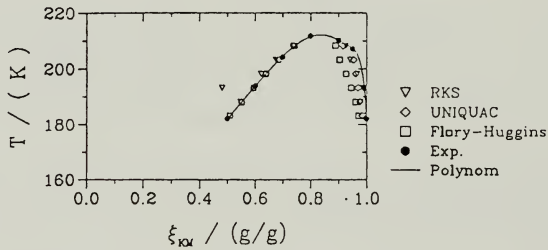


Figure 11 - Miscibility of alkyl benzene A1 with R22 using parameters fitted to the miscibility measurements

The results of the estimation on miscibility for mixtures of a polyglycol-type lubricant with R134a illustrated in the figures 12 and 13 showed the same tendencies as seen before. For this mixture, the immiscibility starts at the side above the curve for high temperatures. Only with the UNIQUAC equation, it was possible to predict liquid separation using parameters that are fitted to the vapour pressure, yield in high deviation to the measurements. Adapted to the results of some miscibility measurements, it was possible to estimate separation temperatures with a Flory-Huggins and RKS equation as well. For the lower mass fraction of refrigerant, the prediction of the RKS differs rather strong from other equations.

When comparing the binary interaction parameters for both oil/refrigerant systems, no physical relation could be found between the fits on the results of the vapour pressure measurements and miscibility measurements. Finding satisfactory possibilities in order to predict the miscibility behaviour of oil/refrigerant system will be one challenge of the future.

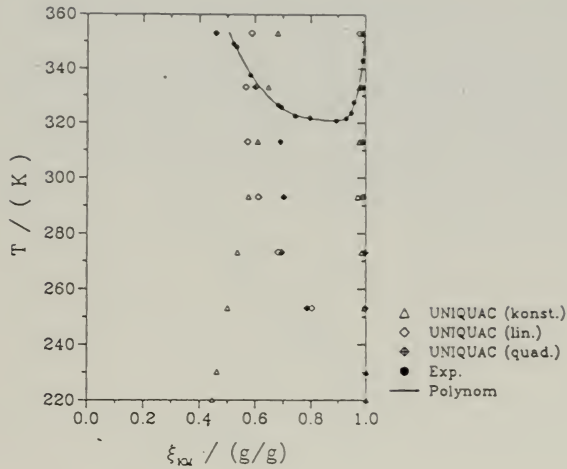


Figure 12 - Calculation on the miscibility of a polyglycol with R134a using parameters fitted to the vapour pressure measurements

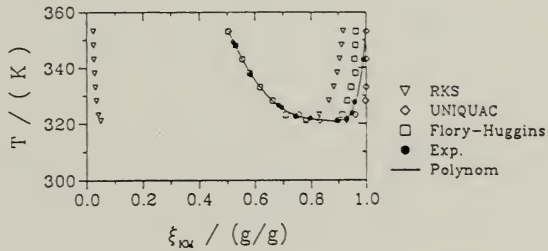


Figure 13 - Calculation on miscibility of a polyglycol with R134a using parameters fitted to the miscibility measurements

VAPOUR PRESSURE OF OIL/REFRIGERANT SYSTEMS

Results of Vapour Pressure Measurements

With increasing mass fraction of oil, the vapour pressure of the oil/refrigerant systems decreases as shown in figure 14, where the vapour pressure of the ternary blend R32/R125/R134a in the mixture with the ester-type oil E8 is shown as a function of temperature with the mass fraction of oil as a parameter. This kind of diagram is for example helpful to estimate the solved refrigerant in the oil in a crankcase of the compressor. For a given suction pressure and oil temperature the composition of the oil refrigerant mixture can be determined.

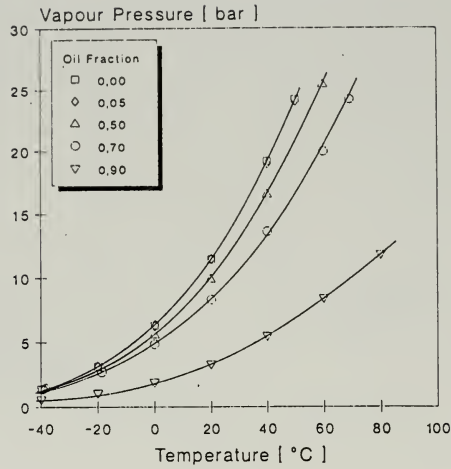


Figure 14 - Vapour pressure of the ternary refrigerant blend R32/R125/R134a (30/30/40) with the ester-type oil E8

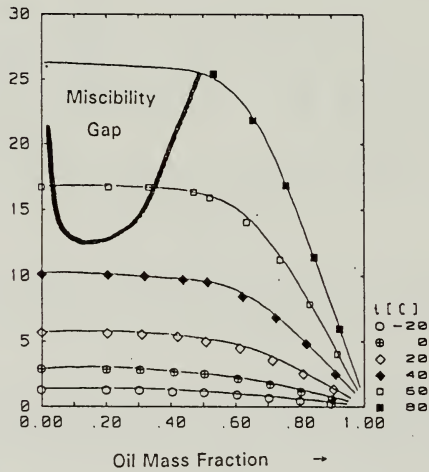


Figure 15 - Vapour pressure of a polyglycol/R134a system

In figure 15, the vapour pressure of six isotherms of the polyglycol/R134a system is shown as a function of mass fraction oil. In addition, the miscibility curve is included in this diagram. For oil mass fractions lower than 40%, the decrease in vapour pressure in comparison to the pure refrigerant is very small. With a higher oil mass fraction, the vapour pressure of the system drops drastically down to the pressure of the pure oil, which is negligibly low in comparison to the refrigerant.

Calculation of the vapour pressure of oil refrigerant systems

For the calculation of the vapour pressure simple, empirical polynoma equations were adapted to the results of the measurements by Schröder [3]. First improvements were done by Hesse [4] by the application of the Lee-Kesler-Plöcker, Wilson and UNIQUAC equation for the activity coefficients of the liquid. Using temperature dependent parameters, the average deviation in comparison to the results of measurements was about 5%. These results could be confirmed by Arnemann [6], who also included the Flory-Huggins equation and the RKS equation of state for the liquid.

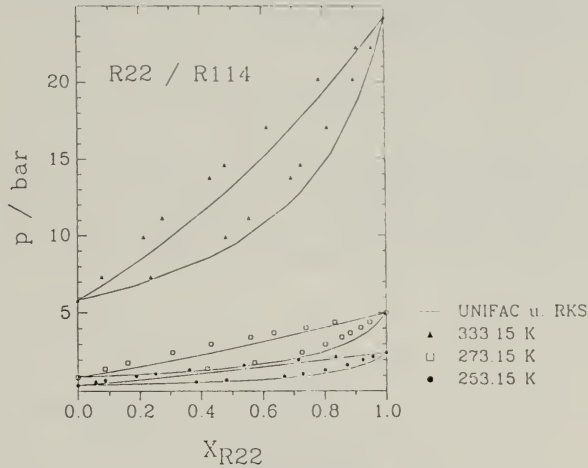


Figure 16 - Calculation on vapour pressure of the R22/R114 blend using the UNIFAC equation

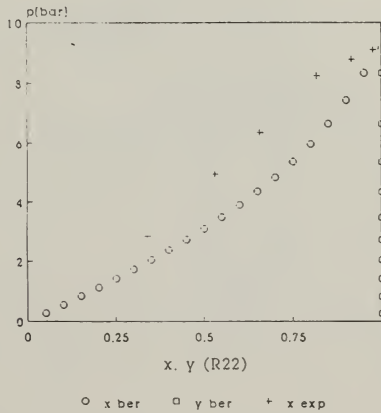


Figure 17 - Calculation on the vapour pressure of the mixture R22/A1 using the PSRK equation of state

Arnemann further on extended the prediction of the vapour pressure of oil/refrigerant systems using the UNIFAC equation. The results for the refrigerant blend R22/R114 are illustrated in figure 16, where the dew and boiling curves are given for three temperatures. The calculated pressures in tendency are too small and show high deviations in comparison to the results of the measurements. The average deviation for a temperature of 0°C is about 13%. For oil/refrigerant systems, the deviation increased to values from 30 to 60%. Further investigations at the IKW with an improved equation, a so-called Predictive Soave-Redlich-Kwong equation [15] confirmed the results of Arnemann. As an example, the vapour liquid data of the A1/R22 mixture at a temperature of 20°C are illustrated in figure 17. The estimation of the behaviour of HFCs was not possible because of the missing group parameters for the fluorine containing components.

VISCOSITY

The liquid dynamic viscosity is determined at the IKW by using a specially designed falling ball viscometer of the Höppler type as illustrated in Figure 18. Driven by gravity, a ball glides and/or rolls in an inclined glass tube filled with the test fluid. The dynamic viscosity of the fluid is a function of the falling time the ball needs for a given distance, the differences in the density of the ball and the fluid and an apparatus constant [8].

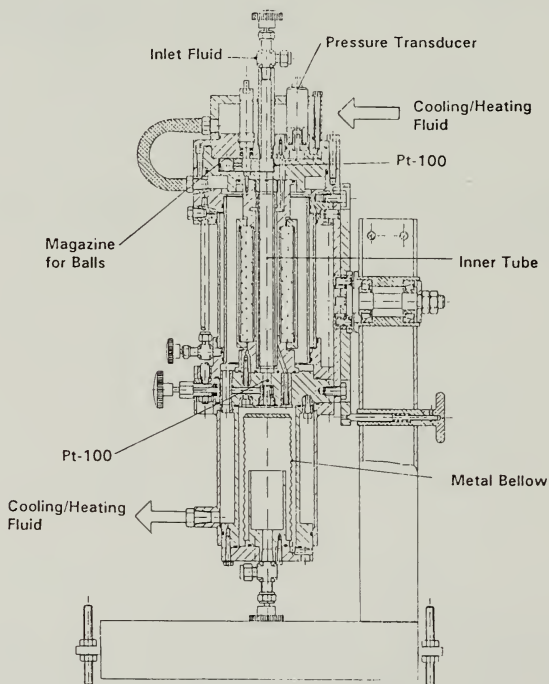


Figure 18 - Falling ball viscosimeter

Results of Viscosity Measurements

In figure 19 the dynamic viscosity of ammonia in the mixture with the polyglycol P3 for different concentrations is shown as a function of temperature. Besides some isobaric lines the miscibility curve is enclosed in this diagram. With respect to increasing ammonia fractions, the viscosity of the mixtures due to the mutual solubility of both fluids decreases drastically.

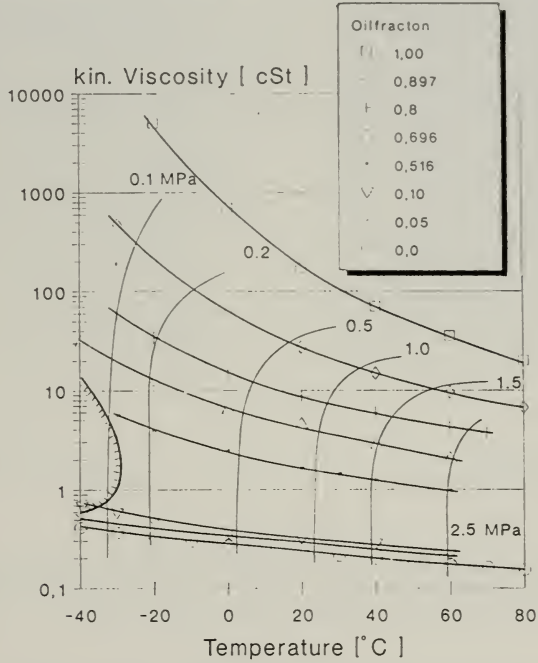
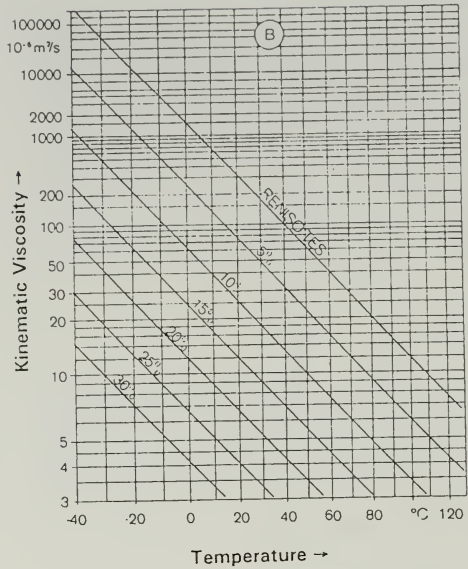


Figure 19 - Kinematic viscosity of oil P3 in the mixture with ammonia depending on temperature and pressure

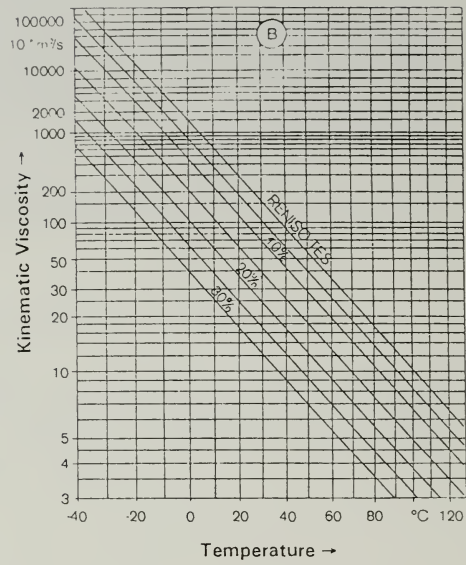
Pure oil at the temperature of 80°C has a viscosity of 20 cSt. The viscosity of a mixture containing 10% ammonia at the same temperature is about 7 cSt, extrapolated for 20% ammonia around 3 cSt and for 30% less than 2 cSt. On the other hand, the viscosity is sufficiently low for pure oil concentrations at low temperature. These are good conditions for an oil return driven by the refrigerant flow out of the evaporator into the compressor.

In contrast to ammonia and the new HFC-fluids, hydrocarbons show a high solubility with mineral oils, even higher than the former CFC refrigerants. As presented in figure 20, the reduction of viscosity with increasing mass fraction of propane is drastically higher than with increasing mass fraction of R12. The question is, if this reduces the oil viscosity to such a degree that it is necessary to increase the viscosity class when changing from the CFC R12 to a hydrocarbon refrigerant.

In figure 21 the kinematic viscosity also for the isobaric curves of propane and R12 is presented as the function of temperature. Concerning the higher vapour pressure of propane, the maxima of the isobaric lines are slightly higher than for R12 in the mixture with the same oil. With increasing pressure the deviation of both systems decreases.



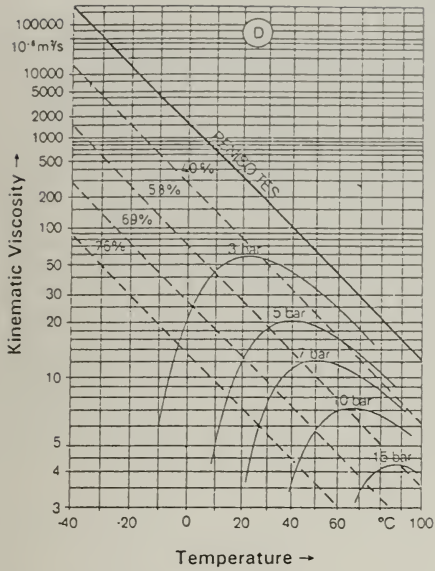
Mineral Oil / Propane



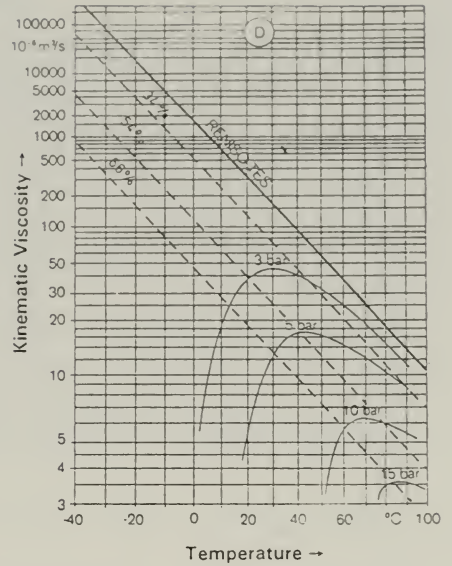
Mineral Oil / R12

Figure 20 - Viscosity Behaviour of a Mineral Oil/Propane and Mineral Oil/R12 System With Increasing Refrigerant Mass Fraction [16]

Beside the isobaric curves, the viscosity lines for different mole fractions of a refrigerant are included in this diagram. In contrast to the usually shown dependency on the mass fraction, the reduction of viscosity for given mole fractions of the refrigerant seems to be nearly the same for both systems. As is known from the thermodynamics, the vapour pressure of the mixture is related to the mole fraction of the components and not to their mass fraction. Comparable liquid viscosities of both systems are possible if the hydrocarbon and the CFC refrigerants have a similar vapour pressure. Then the difference in the liquid viscosity of both oil/refrigerant systems in the compressor crankcase can be expected to be very low.



Mineral Oil / Propane



Mineral Oil / R12

Figure 21 - Viscosity-Pressure-Temperature Diagram of a Mineral Oil/Propane and a Mineral Oil/R12 System With the Refrigerant Mole Fraction as Parameter [16]

Calculation of viscosities

For the calculation of the liquid viscosity, various simple approximations are known, where the viscosity of a mixture can be calculated as a function of its composition by mass, mole or volume fraction. Arnemann [6] found out that the equations of Lederer [17], Wilson [18] and Lees [19] showed the best results for the oil/refrigerant systems investigated. Beside the dependence on the mixtures' composition these equations include a binary interaction parameter that has to be fitted to the results of viscosity measurements. Arnemann showed that this interaction parameter depends both on temperature and composition.

As the above mentioned equations are only suitable for pure binary refrigerant/oil systems, Schroeder [3] and Hesse [4] tried to extend these equations to multicomponent oil/refrigerant systems. Their investigations resulted in high deviations from the experimental data. The estimation of the viscosity of an oil/refrigerant blend mixture could be improved in a way that instead of the pure components the viscosity each of the oil/refrigerant mixtures was used for the calculation.

SUMMARY

More than 15 years' work has been done at the Institute of Refrigeration of the University of Hannover in the research of working fluids for refrigeration, air-conditioning and heat pump systems. This research mainly included the determination of thermophysical properties of oil/refrigerant mixtures, both experimental and theoretical. With regard to the CFC and HCFC phase-out, alternatives are and will be introduced into the market. These alternatives include both HFCs and natural fluids, such as hydrocarbons, ammonia, or carbon dioxide. Beside pure components for the substitution of R12, for many applications the future alternatives for R22 and R502 are considered to be refrigerant blends belonging to the HFC group. The thermophysical properties of these blends and their mixture with a refrigeration oil are mostly unknown and have to be determined by experiments in the near future. The experimental measurements of properties, such as miscibility, density, vapour pressure, or viscosity are very time consuming and, therefore, cost extensive. The scientific tasks in the near future will be to improve the theoretical calculations in a way that the properties of oil/refrigerant systems can be estimated over a wide range of temperature, pressure, and composition, based on the properties of the pure components and the results of a few mixture measurements. This work is on a good way for the establishment of equations to calculate the vapour pressure and the liquid viscosity of oil/refrigerant systems. For the estimation on miscibility of oil/refrigerant systems some additional work and further investigations are necessary to yield satisfactory results.

LITERATURE

- [1] H. Kruse: Energy Saving by Using Suitable Refrigerants for Heat Pumps in Europe. ASHRAE Meeting Chicago, International Day, February 1977
- [2] H. Kruse, M. Schroeder: Fundamentals of Lubrication in Refrigeration Systems and Heat Pumps. ASHRAE Annual Meeting Kansas City, USA, 1984
- [3] M. Schroeder: Beitrag zur Bestimmung thermophysikalischer Eigenschaften von Mischungen synthetischer Kältemaschinenöle mit Ein- und Zweistoffkältemitteln. Forschungsbericht Nr. 19 des Deutschen Kälte- und Klimatechnischen Vereins, Stuttgart 1986.
- [4] U. Hesse: Experimentelle und theoretische Untersuchungen der Eigenschaften binärer und ternärer Öl-Kältemittelgemische. Forschungsbericht Nr. 29 des Deutschen Kälte- und Klimatechnischen Vereins, Stuttgart 1989.
- [5] F.S. Rowland, M.J. Molina: Chlorofluoromethans in the Environment. Reviews of Geophysics and Space Physics 1 (1974), pp. 1-35.
- [6] M. Arnemann: Methoden zur Bestimmung thermophysikalischer Eigenschaften von Öl-Kältemittel-Gemischen. Dissertation, Universität Hannover 1993.
- [7] H. Kruse, M. Burke: Untersuchungen zum Ölverhalten der Kältemittelgemische R23/R152a und R134a/R152a. Forschungsbericht Nr. 35 des Deutschen Kälte- und Klimatechnischen Vereins, Stuttgart 1992.
- [8] M. Burke, H. Kruse: Solubility and Viscosity of New Oil/Ammonia Systems. International Conference on Energy Efficiency in Refrigeration and Global Warming Impact, University of Ghent, Belgium, 1993.
- [9] M. Burke, S. Carré, H. Kruse: Oil Behaviour of the HFCs R32, R125, R134a and One of Their Mixtures. IIR International Conference "CFCs - The Day After", Padova, Italy, 1994.
- [10] H. Kruse, M. Burke: Untersuchungen von Schmierstoffen auf Löslichkeit und Anlagenverhalten mit Ammoniak. Abschlußbericht zum AIF-Forschungsvorhaben Nr. 161D, Hannover 1993.
- [11] J.G. Romijn: An Oil-Free Refrigerant Plant. 17th International Congress of Refrigeration, Vienna 1987.
- [12] H.P. Jaeger: Empirische Methode zur Vorausberechnung thermodynamischer Eigenschaften von Öl-Kältemittelgemischen. Dissertation, Universität Braunschweig 1972.
- [13] ASHRAE Handbook Fundamentals, American Society of Refrigeration and Air-Conditioning Engineers, Inc., Atlanta 1993.
- [14] EC-Joule II Project: Replacement of CFCs in Refrigeration Equipment by Environmentally Benign Alternatives. JOU11-CT92-0060.
- [15] T. Holderbaum: Vorausberechnung von Dampf-Flüssig-Gleichgewichten mit einer Gruppenzustandsgleichung. Fortschrittsbericht der VDI-Reihe 3 Nr. 243, VDI-Verlag Düsseldorf 1991.
- [16] Fuchs Mineralölwerke GmbH, Technische Mitteilungen Nr. 143 und Nr. 145.
- [17] E.L. L. Lerner: Viscosity of Binary Mixtures. Nature 139 (1937), pp. 27-28.
- [18] O.G. Wilson: Chart Method of Predicting Viscosity of Lubricating Oil Blends. Nat. Petrol News 21 (1929) 21, pp. 87-92.
- [19] C.H. Lees: On the Viscosities of Mixtures of Liquids and of Solutions. Phil. Mag. 1 (1901) 1, pp. 128-147.