

Composition Shift due to the Different Solubility in the Lubricant Oil for Multicomponent Mixtures

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ABSTRACT

The composition shifts of multicomponent mixtures used in low temperature Joule-Thomson refrigerators due to the different solubility in lubricant oils are studied in this paper. A compound of squalane with a high-boiling point temperature is treated as a kind of mineral oil. The Peng-Robinson (PR) equation of state (EOS) is selected to predict the solubilities, in which a group contribution model is used to predict the interact coefficients. The Gas-Liquid equilibria for the squalane and multicomponent mixtures is studied to determine the influence of the solubility on the composition shift. The results show that the dissolution in oil will greatly decrease the concentrations of those components with high-boiling point temperatures. The composition variation can reach about -74% for the highest-boiling component, and about 160% for the lowest-boiling component. Influences of the composition shifts on the thermodynamic performances is also studied.

INTRODUCTION

The mixed-gases Joule-Thomson refrigerator (MJTR) has many distinct advantages compared with other cryocoolers. One of the most obvious merits is that the commercial oil-lubricated single-stage compressor can be utilized to drive the low temperature MJTR. Commercial compressor can reduce the cost, achieve high reliability and can be easily built in industry scale because of several decades of commercialized applications in the commercial and domestic refrigeration fields. The disadvantage of utilizing an oil-lubricated compressor is the oil contamination in the refrigerant stream. An oil separation and removing unit is necessary in the compressor unit for a real MJTR system to ensure that no extra amount of oil is transferred to the low temperature section to avoid a failure. The typical oil separation and removing unit is already a commercialized unit in the room-temperature refrigeration application fields. One of those commonly used is controlled by a buoy-floater valve which works in a similar way as the water box of a toilet. That is, a certain amount of oil is pre-charged in the oil separator to ensure that it can work properly. Therefore, there are two amounts of oil distributed in the refrigeration system; one in the compressor, especially the low pressure part, the other in the oil separator.

For a typical MJTR, the mixtures used consist of from 4 to 7 components, which have different boiling temperatures which range from cryogenic to ambient temperatures. Different gases have different gas

vapor-liquid equilibrium behavior with the lubricating oil in the compressor and the oil separator. That is, different substances have different solubilities in the lubricant oil for the multicomponent mixed-refrigerant Joule-Thomson refrigerators. This is an important factor that causes the circulating composition shift from the initial charge.

The change of the mixture composition consequentially leads to a variation of the thermodynamic properties of the refrigerant. In turn, this will influence the performance of the refrigerator. This is a critical problem in the design of multicomponent mixtures J-T refrigeration systems. The authors have already measured the compositions shift in a typical mixed-gases Joule-Thomson refrigeration system.¹⁻³ However, there are few reports on the investigation of the composition shift for multicomponent cryogenic mixtures caused by the solubility of oil lubricants. In this paper, an attempt is made to investigate this variation of the mixture compositions caused by the differential solubility in the oil.

NOMENCLATURE

f	fugacity, kPa, MPa	T_f	normal freezing point temperature, K
i	component number	v_c	critical volume, cm ³ /mol
j	component number	x	liquid molar fraction
K	K-value	y	vapor molar fraction
M_w	molecular weight, kg/kmol	<i>Greek</i>	
n	mole flow rate, mol/s	γ	activity coefficient
p	pressure, MPa, kPa	ϕ	fugacity coefficient
p_c	critical pressure, 10 ⁻¹ MPa	ω	eccentric factor
R	molar ratio of residual mixture to the initial mixture	Subscripts and superscripts	
R_j	concentration shift of component j	0	in a standard state
R_{oil}	molar percentage of the oil in the blend of oil and refrigerants	i, j	component number
T	temperature, K	ini	initial
T_b	normal boiling point temperature, K	L	Liquid
T_c	critical point temperature, K	r	residual refrigerant
		V	Vapor

THE MJTR CYCLE AND THE LUBRICANT OILS DISTRIBUTION

Figure 1 shows a typical mixed-refrigerant Joule-Thomson cycle and the schematic diagram of one typical commercial oil separator controlled by a float valve. The typical refrigeration system consists of a compressor unit, a recuperative unit, a J-T valve and an evaporator. In most commercial refrigeration applications, the lubricant oil is selected based on the refrigerant used in the refrigeration system. For CFC, HCFC and hydrocarbon (HC) refrigerants, mineral oil can be used because of good lubrication and miscibility. However, the new generation of replacement HFC refrigerants show low solubility in the mineral oil. Therefore, synthetic oils are used to replace mineral oils for HFCs systems. The two types of compressors, both with the mineral oil and the synthetic oil, can be used in the low temperature mixed-refrigerants Joule-Thomson refrigeration system.

Mineral oils have been used for decades with chlorinated refrigerants (CFCs) because they form highly miscible combinations. The mineral oils are generally a blend of linear and branched alkanes (paraffins), cyclic alkanes (naphthenes) and aromatic compounds containing linear and branched alkanes. The mixtures are formulated to have the desired viscosity-temperature relationship. Synthetic lubricants have higher solubility with HFCs than mineral oils. There are three main synthetic oil types used in commercial refrigeration systems, which are polyalkylene glycol (PAG) lubricants, polyol ester (POE) lubricants, and the typical structure of alkyl benzenes (AB) lubricants. The

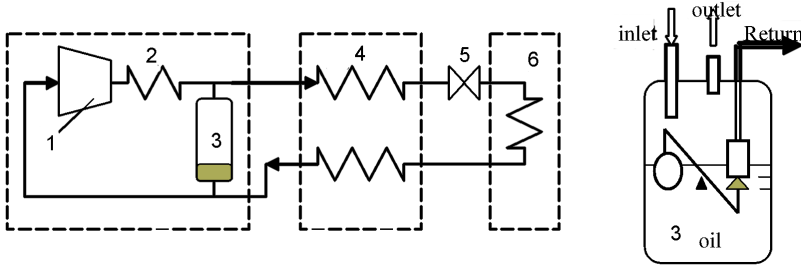


Figure 1. Schematic diagram of a typical MJTR cycle and the oil separator 1 compressor, 2 after cooler, 3 oil separator, 4 recuperative heat exchanger, 5 J-T valve, 6 evaporator

mineral oil and those synthetic oils are selected to provide the required lubrication of the compressors with different refrigerants.⁴

In fact, actual lubricant oils are mixtures of various compounds with very high boiling points. The detail compositions for both the mineral oil and the synthetic oil are very complicated and usually not available. Therefore, no vapor pressure data and critical parameters data are available for these lubricants oils. It is very difficult to predict the thermodynamic performance of the blend of the oil and refrigerants. In order to solve this problem, several authors have proposed different methods. When cubic equations of state are used to fit solubility data of refrigerant /lubricant mixtures, it is necessary to know their critical properties. For these purposes Teodorescu et al.⁵ have predicted the critical properties of PAG and POE oils with group contribution methods when experimental data are not available. Elvassore et al.⁶ has developed a group contribution method suitable for the prediction of the parameters of pure compounds for the perturbed hard sphere chain equation of state.

To simplify the calculation, squalane was selected as a mineral oil. The basic physical properties such as critical parameters of squalane and other pure gases usually used for MJTRs are shown in Table 1.⁷

THERMODYNAMIC METHODS

The solubility of the gas mixture in oil lubricant is typical gas-liquid equilibrium (GLE) or vapor-liquid equilibrium (VLE) behavior. This gas (vapor)-liquid equilibrium behavior can be predicted with many thermodynamic models.

When the liquid phase of a non-ideal multicomponent mixture is in equilibrium with its vapor phase at temperature T and pressure p , the fugacity of each component i in both phases must be the same, this can be expressed as:^{8,9}

$$f_i^V = f_i^L \quad (1)$$

$$f_i^V = \phi_i y_i p \quad (2)$$

$$f_i^L = \gamma_i x_i f_i^0 \quad (3)$$

Table 1. Basic properties of some high molecular compounds and pure gases⁷

No.	Formula	Name	Mw	T_f /K	T_b /K	T_c /K	p_c /bar	v_c m ³ /mol	ω
1	iC ₃₀ H ₆₂	squalane	422.8	235.2	720.0	863.0	8.68	1640	1.056
2	N ₂	Nitrogen	28.01	63.3	77.4	126.2	33.94	89.5	0.040
3	CH ₄	Methane	16.04	90.7	111.7	190.6	46.0	99.0	0.008
4	C ₂ H ₆	Ethane	30.07	89.9	184.5	305.4	48.84	148.0	0.098
5	C ₃ H ₈	Propane	44.09	85.5	231.1	369.8	42.46	203.0	0.152
6	iC ₄ H ₁₀	Isobutane	58.12	113.6	261.3	408.1	36.48	263.0	0.176
7	iC ₅ H ₁₂	Isopentane	72.15	113.3	301.0	460.4	33.84	306.0	0.227

From the above three equations, the equilibrium condition of a multicomponent mixture can be derived as:

$$\phi_i y_i p = \gamma_i x_i f_i^0 \quad (4)$$

Equation (4) can be used to predict most V-L-E behaviors at normal and low pressures. For gas-liquid equilibrium (G-L-E) and most high pressure V-L-E, Eqs. (3) and (4) can be rewritten as:

$$f_i^L = \phi_i x_i p \quad (5)$$

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \quad (6)$$

There are many thermodynamic methods developed to solve Eqs. (4) and (6). In this paper, a commercial software, ProII⁷, is used to calculate the properties and phase equilibria of the oil and refrigerants, in which PR equation of state are used to conduct the calculation. A group contribution method¹⁰ is used to estimate the binary interact coefficients of gases and squalane, which can be expressed as:

$$k_{ij}(T) = \frac{-\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \cdot \left(\frac{298.15}{T}\right)^{\left(\frac{b_{kl}}{A_{kl}} - 1\right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j}\right)^2}{2 \frac{\sqrt{a_i(T)a_j(T)}}{b_i b_j}} \quad (7)$$

where a and b are parameters in the PR equation of state, N_g is the number of function-contribution group.¹⁰

The measured VLE data¹¹ of three binary systems of $\text{CH}_4 + \text{C}_2\text{H}_6$, $\text{C}_2\text{H}_6 + n\text{C}_7\text{H}_{16}$ and $\text{C}_3\text{H}_8 + n\text{C}_{10}\text{H}_{22}$ is used to verify the methods described above. The results are shown in Figure 2. From Figure 2, it can be found that the predicted results agree well with the reference data.

PREDICTION RESULTS AND ANALYSES

With the simple cubic PR equation of state, the solubilities of different gases in squalane is calculated. The vapor-liquid equilibria of the multicomponent mixture with squalane is studied in detail. The interest is put on the composition shift due to the different solubility. In order to describe the problem clearly, some definitions is expressed as follows:

$$R = \frac{n_r}{n_{ini}} \times 100\% \quad (8)$$

$$R_j = \frac{y_j^r - y_j^{ini}}{y_j^{ini}} \times 100\% \quad (9)$$

$$R_{oil} = \frac{n_{oil}}{n_{oil} + n_{ini}} \times 100\% \quad (10)$$

Equation (8) is the mole ratio of residual gas mixture to the initial gas. Equation (9) indicates the relative mole concentration shift of component j . Equation (10) is the mole percentage of the oil (squalane in this paper) of the oil/refrigerants mixture.

Several multicomponent mixtures with different specifications are selected to determine the composition shift due to the different solubility in squalane (Table 2). Mix 1 in Table 2 has an average concentration for each component, Mix 2 has an increased mole fraction of low boiling point component, Mix 3 is a mixture with an increased composition of middle boiling point component, and Mix 4 has an increased concentration of the high boiling component, while Mix 5 is an optimized mixture for 120 K refrigeration.

Influence of the Oil Amount

Mix 1 in Table 2 is selected to study the influence of the squalane mole fraction in the blend of squalane and the refrigerant mixture. The prediction results show that the influence of the oil amount are illustrated in Figure 3. The calculation condition is: $T=300\text{ K}$, $p=0.1013\text{ MPa}$.

From Fig. 3, it can be found that with an increased concentration of squalane, the mole ratio of the residual gas mixture decreases while the composition shift of those components increases. This indicates that in a MJTR refrigeration system with a fixed amount of lubricant oil, when the amount of mixture

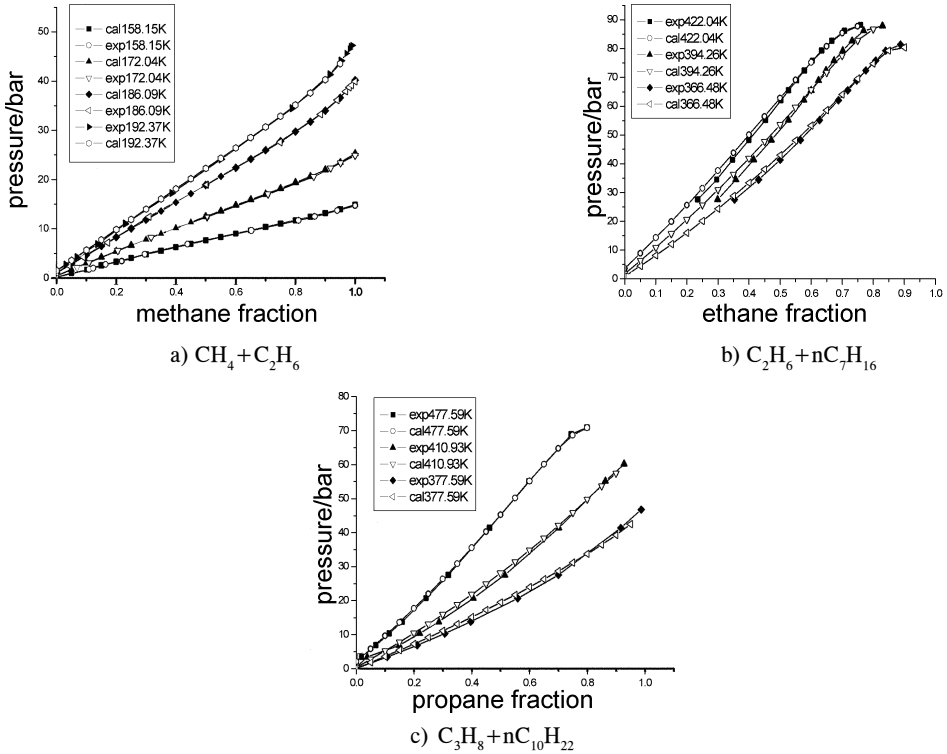


Figure 2. Comparison of predicted data and the reference data

charged is larger, the composition shift due to the solubility with the oil will decrease. This is obviously helpful to achieve better performance. In a typical MJTR system with an extra mixture store tank, the mole ratio of the oil to the refrigerant is about 0.2, that is $R_{oil}=20\%$. In the following part of this paper $R_{oil}=20\%$ is used in the predictions. The typical oil distribution in a MJTR refrigeration system (referring to Fig. 1) can be illustrated in Fig. 4.

Influence of the Temperatures and Pressures

In addition, the influences of temperature and pressure on the solubility of multicomponent mixtures with oil are also predicted. The calculation condition is: $R_{oil}=20\%$. Figure 5 shows the prediction results of Mix 1 with squalane at different temperatures. The influence of the pressure at 360 K on the composition shift of Mix 1 with squalane is shown in Fig. 6. From Figs. 5 and 6, the solubility will decrease when the temperature increases or the pressure decreases. Furthermore, it can be shown that it is much more sensitive for the variation caused by the change of pressure than that of the temperature within the typical MJTR system operation conditions.

Table 2. Specifications of multi-component mixtures

Components	Mixtures compositions /mol %				
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
N ₂	16.7	65	5	5	27
CH ₄	16.7	20	15	10	38
C ₂ H ₆	16.7	7	55	15	8.7
C ₃ H ₈	16.7	5	15	15	8.7
iC ₄ H ₁₀	16.7	2	7	25	8.8
iC ₅ H ₁₂	16.7	1	3	30	8.8

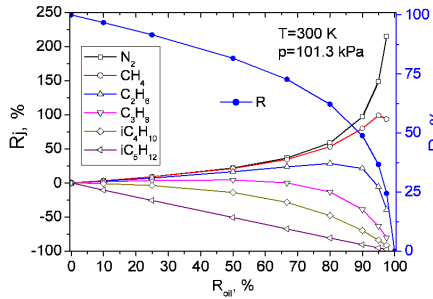


Figure 3. Influence of the amount of oil on the composition shift for Mix 1

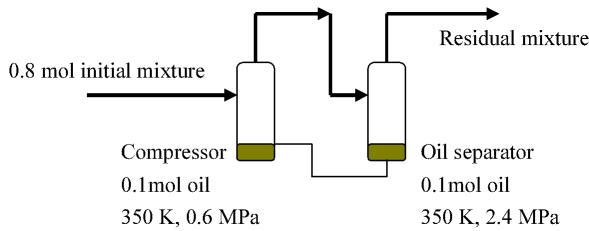


Figure 4. The schematic diagram of the oil distribution in a MJTR system

Compositions Shifts for Mixtures with Different Initial Concentrations

The five mixtures with the same components but different compositions, listed in Table 3, are studied to know their solubilities with squalane. The calculation condition is the same as that shown in Fig. 4. That is, the initial mixture first passes through the compressor then passes through the oil separator. The prediction results for those five mixtures are shown in Fig. 7.

From the results shown in Fig. 7, the mixture with different initial composition shows a different composition variation. In detail, the mixture with increased mole fraction of high boiling component shows a larger composition shift. The component with the highest boiling point, isopentane in this paper, shows the largest concentration variation. From Fig. 7, more than 30% to 60% of isopentane can be dissolved in squalane. From the results illustrated above, the composition of the component with a high boiling point in the mixture always decreases. On the contrary, the concentration of the low boiling point component increases due to low solubility in the oil. For these components with a middle boiling points, the concentrations have a relatively slight variation.

Influences of Compositions Shifts on the Thermodynamic Performance

In order to know the thermodynamic performance difference between the initial and the residual mixtures, five other multicomponent mixtures with different compositions are selected to determine the

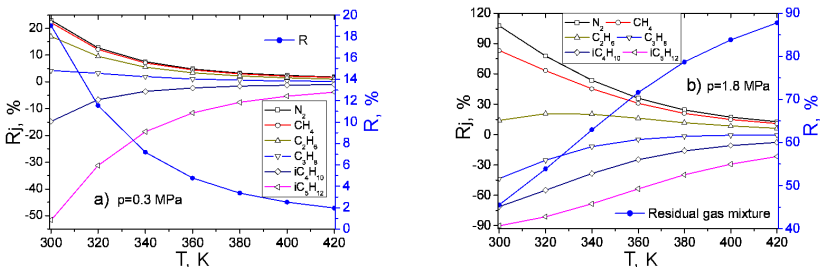


Figure 5. The influences of temperatures on the composition shift (Mix 1)

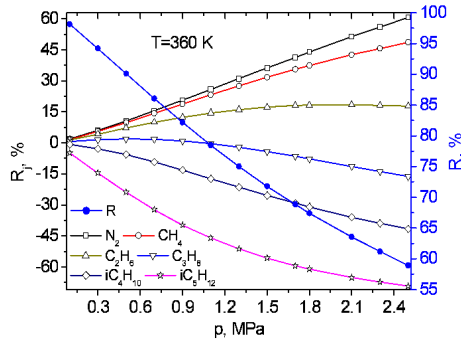


Figure 6. The influences of pressures on the composition shift (Mix 1)

performance variation. These five mixtures, listed in Table 3 and numbered from Mix 6 to Mix 10, are mixtures used for studying their refrigeration performances in different cycle configurations.¹² The mixtures from Mix 6 to 10 are mixtures with the same components (nitrogen, methane, ethane, propane, isobutane) and different compositions. Nitrogen and methane are in the low-boiling component group, ethane is a middle-boiling component, while propane and isobutane are high-boiling components. Mix 6 contains a relatively reduced fraction of high-boiling point components (propane and i-butane). Mix 7 contains a relatively increased fraction of high-boiling point components. Mix 8 contains a relatively reduced fraction of middle-boiling components. Mix 9 is a mixture with a relatively increased fraction of middle-boiling components. Mix 10 is a mixture with optimized composition for the single-stage cycle shown in Figure 1.

The calculation conditions for the thermodynamic performances are as follows: the ambient temperature is $T_0=300$ K, a high operating pressure is 1.8 MPa and 0.3 MPa for the low operating pressure, a minimum temperature difference in the heat exchanger is assumed as 0.2 K, and the refrigeration temperature is $T=120$ K. No pressure drop in the circuit is considered. The oil distribution in the refrigeration system is shown in Figure 4. The temperatures of the compressor and the oil separator are both 360 K.

From Table 3, it can be found that for most mixtures, the composition shift lead to a degradation of the performance. Only for those mixtures with a relatively increased concentration of high-boiling components may increase the performance.

SUMMARY

The composition shift for multicomponent mixtures due to the different solubility in the lubricant oil is a critical problem in the design of low temperature Joule-Thomson refrigeration system. In this paper, squalane was selected as a kind of mineral oil. The PR equation of state was selected to predict the V (G)-L-E behaviors with a group contribution model to predict the interact coefficients.

Some conclusions can be made from this study and are as follows:

1. The concentrations of high boiling components always decrease while the compositions of those with low-boiling point temperatures increase. The concentrations of middle-boiling point components vary

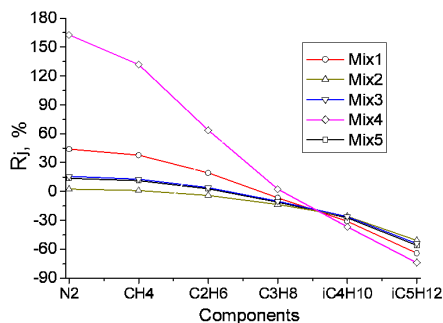


Figure 7. Composition shifts of five mixtures with same components but different initial composition

Table 3. Performance difference due the composition shift

Components	Mixtures compositions /mol %									
	Mix 6		Mix 7		Mix 8		Mix 9		Mix 10	
	initial*	residual	initial*	residual	initial*	residual	initial*	residual	initial*	residual
N ₂	60	60.75	10	11.90	30	32.39	10	10.59	22.78	24.51
CH ₄	25	25.10	15	17.5	35	37.31	15	15.71	32.38	34.4
C ₂ H ₆	10	9.73	15	16.43	2	2.04	55	55.41	6.8	6.93
C ₃ H ₈	3	2.75	25	24.52	5	4.71	15	14.06	20.9	19.68
iC ₄ H ₁₀	2	1.67	35	29.65	28	23.55	5	4.23	17.2	14.48
CEF ^a	6.33	6.11	9.93	13.83	24.43	18.69	8.92	9.945	38.81	20.34

^a CEF is the Carnot efficiency of the cycle, which is expressed as: $CEF = COP \times (T_0/T-1) \times 100\%$.

* Mixture compositions from reference¹²

slightly. The maximum decrease of concentration for the highest boiling point component can reach about -74%, while the maximum increase of the lowest boiling point component can reach about 160%.

2. The solubility will increase when the temperature decreases or pressure increases. Furthermore, the variation of solubility is much more sensitive for the change of the pressure than that of the temperature within the typical MJTR system operation conditions.
3. For a MJTR system with a fixed oil quantity, increasing the molar quantity of the mixture will decrease the degree of composition shift.
4. The composition shifts for most mixtures will degrade their thermodynamic performances, especially for those with optimized compositions. It suggests that when preparing a mixture it may be better to increase the fraction of those components with high-boiling points.

The results obtained in this paper can also provide a good reference for future design of such MJTR systems and can prevent a great performance degrading due to the large composition shift caused by the different solubility in oils.

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