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MUTUAL SOLUBILITY OF REFRIGERANTS AND POLYOL ESTERS

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ABSTRACT

The phase separation behavior of tetraesters of pentaerythritol in refrigerants was studied by analysis of $^1\text{H-NMR}$ spectra and three dimensional solubility parameters.

The proton signals of HFC134a shifted to a lower magnetic field with an increase in temperature, indicating that the hydrogen bonding was strengthened at high temperatures, which was definitely opposite to the characteristics of esters. This unique property of HFC134a could be the reason that HFC134a has its upper phase separation at high temperatures.

The three dimensional solubility parameters of alternative refrigerants and esters were determined and compared to conventional refrigerants. It was suggested that the polar parameter, δ_p , plays a key role in the understanding of the lower phase separation temperatures.

INTRODUCTION

HFC134a, HFC125, HFC143a, HFC32, and their mixtures are used as alternatives to conventional refrigerants because they do not contain chlorine atoms in their molecules and therefore should not appreciably affect the ozone layer. When we apply these refrigerants, one problem is that they are less miscible with synthetic refrigeration oils, such as esters, polyalkylene glycols, and so on. It is characteristic of these refrigerants that both lower and upper phase separation temperatures exist. In particular, when esters are applied, the lower phase separation temperatures have been often discussed in order to allow the compressors of refrigerators and air conditioners to operate satisfactorily. In this paper, the upper and lower phase separation temperatures of alternative refrigerants and esters are discussed by means of $^1\text{H-NMR}$ analysis and three dimensional solubility parameters^{1,3}).

EXPERIMENTAL

1. Materials (esters)

The esters used in $^1\text{H-NMR}$ and solubility parameter analysis were *n*-butyl (H4L), *n*-nonyl (H9L), and *i*-nonyl (H9B) tetraesters of pentaerythritol. These esters were used as models because the chain length effect (H4L and H9L) and linear/branched effect (H9L and H9B) of the alkyl groups can be observed from those esters. Shorter and branched alkyl chains show better miscibility with HFC134a compared to longer and linear chains. The general properties are given in Table 1.

2. $^1\text{H-NMR}$ measurement of refrigerant-containing samples

$^1\text{H-NMR}$ spectra were measured with JEOL GX-400. A special tube 5 mm in diameter manufactured by Nippon Seimitsu Kagaku Co. was used as an inner tube for high pressure measurements of the refrigerants' spectra. After the tube was degassed, the lower part of the tube was cooled with dry ice/ethanol or liquid nitrogen, followed by incorporation of a refrigerant. While the lower part of the tube was cooled, the top of the glass tube was sealed with burners. The sealed 5 mm tube was then inserted into an outer tube 10 mm in diameter which contained the reference solution. Spectra were obtained with the external reference of TMS in CDCl_3 for the measurements at or below room temperature and with TSP (sodium trimethylsilylpropionate) in D_2O for those at higher temperatures.

3. Solubility tests of the esters in various solvents

One ml of esters and 4 ml of solvents were taken in glass tubes with stoppers and placed in a bath at 25°C. The tubes were shaken vigorously and inspected visually to determine whether or not the esters were soluble in the solvents.

RESULTS AND DISCUSSION

1. Hydrogen bonding analysis by $^1\text{H-NMR}$

Fig. 1 shows the temperature dependence of the change in $\alpha\text{-CH}_2$ and methyl proton chemical shifts of neat H4L. As shown in Fig. 1, the proton signals shifted to a higher magnetic field with an increase in temperature; the hydrogen bonding effect was weakened. The same tendency was observed for other protons of H4L and also for all the protons of H9L and H9B. Since the hydrogen bonding is broken at high temperatures due to the increase in mobility of the molecules, the shielding by the electron cloud around the proton decreases with an increase in temperature, resulting in a higher magnetic field shift.

Fig. 2 shows the effect of temperature on the change in the proton chemical shift of HFC134a. Interestingly, the proton signals shifted to a lower magnetic field linearly with increasing temperature. This means that hydrogen bonding is strengthened at higher temperatures. This is the reverse of the phenomenon expected from the usual liquids including esters. It might be possible that the effect observed is due to the increased pressure in the tube or the change in the molar volume of HFC134a; however, the interesting point is the same phenomenon was observed below the boiling point of HFC134a (-26.3°C), as shown in the figure.

Therefore, the existence of the upper phase separation temperature is considered to be contributed to by the fact that HFC134a and esters have opposite temperature dependence of hydrogen bonding.

Fig. 3 shows the effect of temperature on the change in the proton chemical shift in mixed systems of HFC134a with H4L and H9B. It was found that the proton signals of esters are affected largely in their chemical shift and temperature dependence when dissolved in HFC134a, from which it is considered that the environment in HFC134a is very special.

2. Estimation of three dimensional solubility parameters

The total solubility parameters, δ , are defined by Eq. (1)²:

$$\delta = (\Delta E/V)^{1/2} = \{(\Delta H_{\text{vap}} - P\Delta V) / V\}^{1/2} \quad (1)$$

where ΔE is the change in the internal energy of vaporization; ΔV is the difference between the molar volume in liquid at 25°C and vapor; and ΔH_{vap} is the molar latent heat of vaporization at 25°C . The total solubility parameters of refrigerants which are shown in Table 1 were obtained according to Eq. (1)¹.

$$\delta = (\delta d^2 + \delta p^2 + \delta h^2)^{1/2} \quad (2)$$

The three dimensional solubility parameters are defined by Eq. (2), where δd , δp , and δh are the dispersion parameter, polar parameter, and hydrogen bonding parameter, respectively. The δd values cannot be determined experimentally. Possible approaches are to adopt the concept of homomorph³) or empirical calculation of group contribution³). The δd of HFC134a was estimated empirically before⁴). The δp is calculated by Beerbower's equation, Eq. (3)⁵:

$$\delta p = 18.3 \mu / V^{1/2} \quad (3)$$

where μ is the dipole moment in debye units and V is the molar volume at 25°C . The δh is calculated by substituting the above determined δ , δd , and δp values in Eq. (2).

The three dimensional solubility parameters of HFC134a, HFC143a, HFC125, and HFC32 were calculated according to the above method. The parameters used for the series of calculations were summarized in Table 2.

Three dimensional parameters of esters (H4L, H9L, and H9B) were determined by using the solubility envelopes. Fig. 4 shows the results of solubility tests of the esters in various solvents having known three dimensional solubility parameters. Each liquid used in the tests has been represented as a point on a three dimensional plot with δd , δp , and δh axes. Fig. 4 shows that the solubility region was different among the three esters, and furthermore that H4L, which showed the highest solubility in HFC134a, had a wider solubility region, which means it was soluble in the solvents having large δp and δh values. The solubility region, which is characteristic of a chemical substance, is represented by an ellipsoid defined by Eq. (4).

$$(\delta d - \delta d_0)^2 / a + (\delta p - \delta p_0)^2 / b + (\delta h - \delta h_0)^2 / c = 1 \quad (4)$$

The coordinate (δd_0 , δp_0 , δh_0) is the center of the ellipsoid, which corresponds to the three dimensional parameters of the esters³). The total solubility parameter, δ , was calculated using Eq. (2). The parameters for the esters are summarized in Table 2.

3. Discussion of miscibility using the three dimensional solubility parameters

Fig. 5 shows a comparison of the three dimensional parameters of esters (H4L, H9L, and H9B), conventional ref oils (an alkylbenzene and hydrocarbons), conventional refrigerants, and alternative refrigerants.

The order of δp was H4L (2.5), H9B (1.6) and H9L (1.4); the order of δh was H4L (2.5), H9B (1.8), and H9L (1.6). The higher the δp and δh of the esters, the better the miscibility with HFC134a. This is well understood by Fig. 5 because HFC134a has very high δp (3.6) and δh (4.6). The low miscibility of hydrocarbons such as mineral base stocks and alkylbenzenes with HFC134a are also well explained by Fig. 5 because their solubility parameters are far from that of HFC134a, especially in their δp and δh .

It is characteristic that HFCs such as HFC152a, HFC143a, and HFC134a have very high polarity parameters, δp , with values far from those of esters. On the other hand, conventional refrigerants (CFCs) have low δp and δh values. HCFCs such as HCFC22 and HCFC142b were about at the middle of CFCs and HFCs. The interesting point was that HFC125 had a relatively low δp value compared to other HFCs, in fact, slightly lower than HCFC22. Ordinary pentaerythritol tetraesters which are commercialized now will have almost the same solubility parameters as those of H9B and H9L. It is well understood from those parameters that esters have good miscibility with CFCs, HCFCs, and HFC125 and less miscibility with HFC143a and HFC134a.

Fig. 6 takes the lower phase separation temperature of a VG32 ref oil (pentaerythritol tetraester using branched acids) with refrigerants as the X axis and the δp of the refrigerants as the Y axis. When we focus on C2 HFCs (HFC152a, HFC143a, HFC134a, and HFC125), the δp value was well correlated with the lower phase separation temperature. The higher the δp was, the higher was the phase separation temperature; this means that when the δp of a refrigerant is far from that of an ester, it shows less miscibility. This tendency was also found for C1 refrigerants. It is well understood from Fig. 6 that the reason why HFC32 has a high phase separation temperature, which means it has less miscibility with the ester, is because of its very high δp (5.0) compared to conventional refrigerants such as HCFC22 ($\delta p=3.0$) and CFC 12 ($\delta p=1.0$). Therefore, it was suggested from this study that δp is the key to understanding or speculating about the lower phase separation temperature.

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Table 1 Properties of model esters

		H4L	H9L	H9B
Viscosity, mm ² /s	40 °C	15.50	32.20	125.0
	100 °C	3.387	6.105	11.95
Viscosity index		84	140	82
Molecular weight		416.5	697.1	697.1
Total acid number, mgKOH / g		0.51	0.03	0.46
Pour point, °C		-40	7.5	-25
Water content, ppm		40	26	37
(a)Upper phase separation temperature, °C		>95	Insoluble	>95
(a)Lower phase separation temperature, °C		<-70		-32

(a) Concentration: ester / R134a = 0.10

Table 2 Three dimensional solubility parameters of esters and refrigerants

	H4L	H9L	H9B	HFC 134a	HFC 143a	HFC 125	HFC 32
Total solubility param. δ , (cal/cm ³) ^{1/2}	7.8	7.6	7.4	6.8	5.7	5.3	7.5
Dispersion param. δ_d , (cal/cm ³) ^{1/2}	7.0	7.3	7.0	3.5	(a)	(a)	(a)
Polar param. δ_p , (cal/cm ³) ^{1/2}	2.5	1.4	1.6	3.6	4.5	2.8	5.0
Hydrogen bonding param. δ_h , (cal/cm ³) ^{1/2}	2.5	1.6	1.8	4.6	(a)	(a)	(a)
ΔH_{vap} , J mol ⁻¹				18,224	14,088	13,496	14,184
Molar volume $V_g \times 10^{-3}$, m ³ mol ⁻¹				3.18	1.53	1.34	1.11
Molar volume $V_l \times 10^{-5}$, m ³ mol ⁻¹				8.46	9.02	10.1	5.22
Saturated vapor pres. $P \times 10^6$, J m ⁻³				0.6664	1.261	1.385	1.689
Dipole moment, debye				1.80	2.340	1.563	1.978

(a) Not yet determined

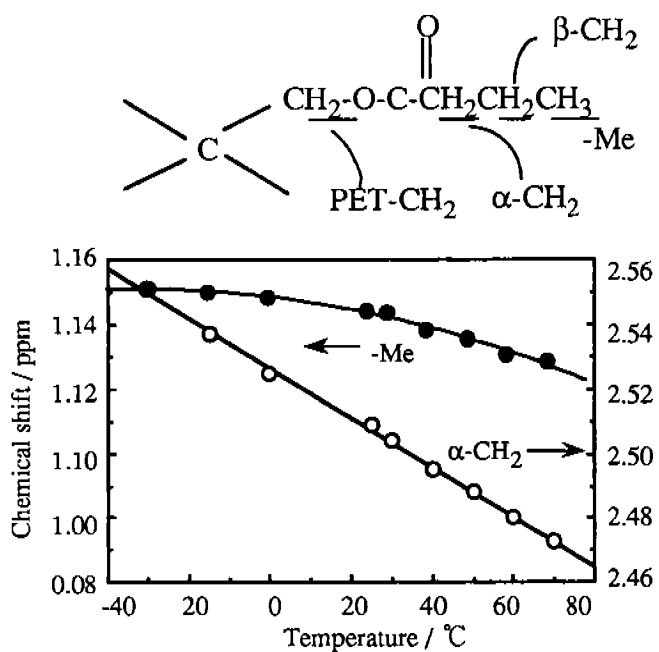


Figure 1 Temperature dependence of change in proton chemical shifts of H4L (neat)

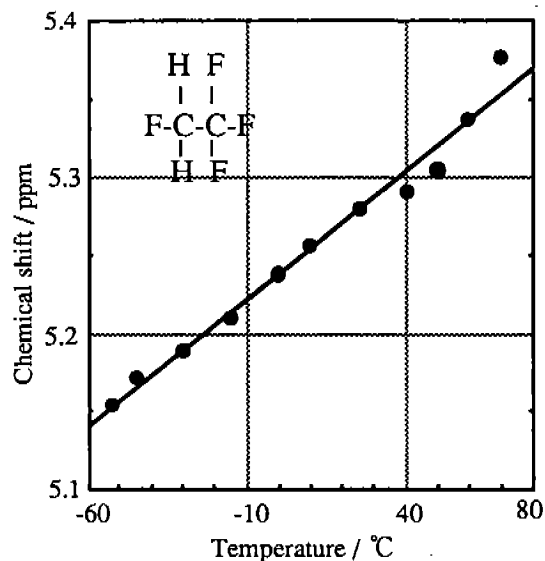


Figure 2 Temperature dependence of proton chemical shift of HFC134a

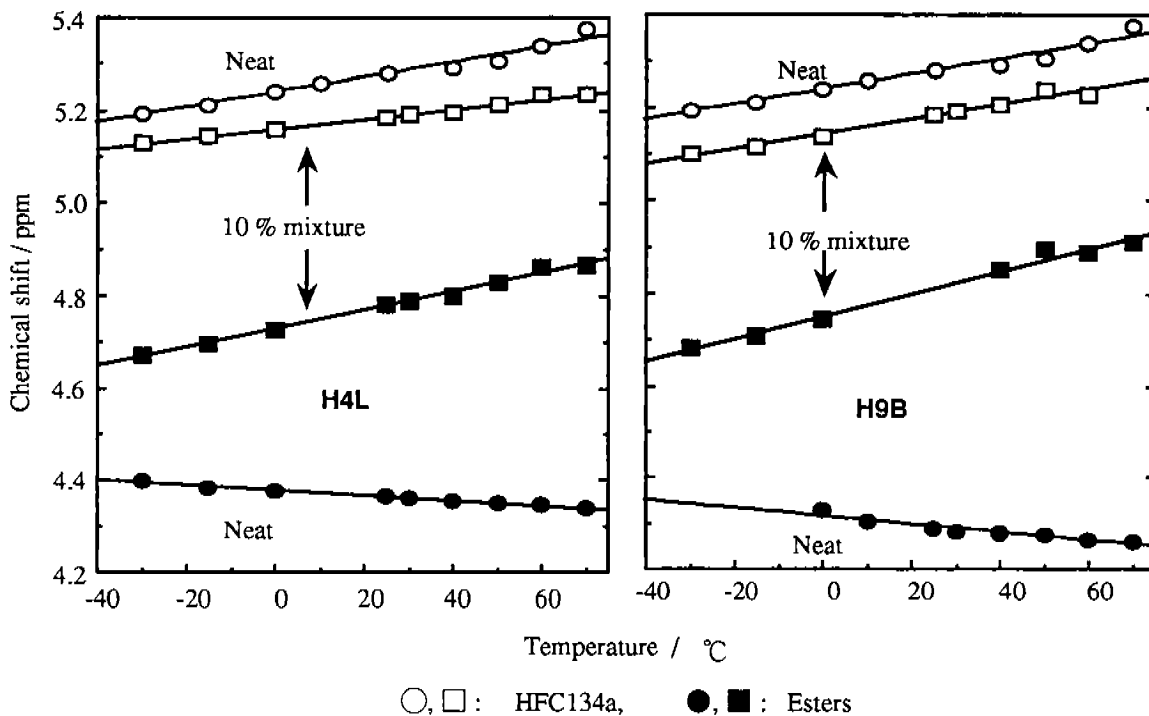


Figure 3 Temperature dependence of proton chemical shifts in mixed systems of HFC134a and esters

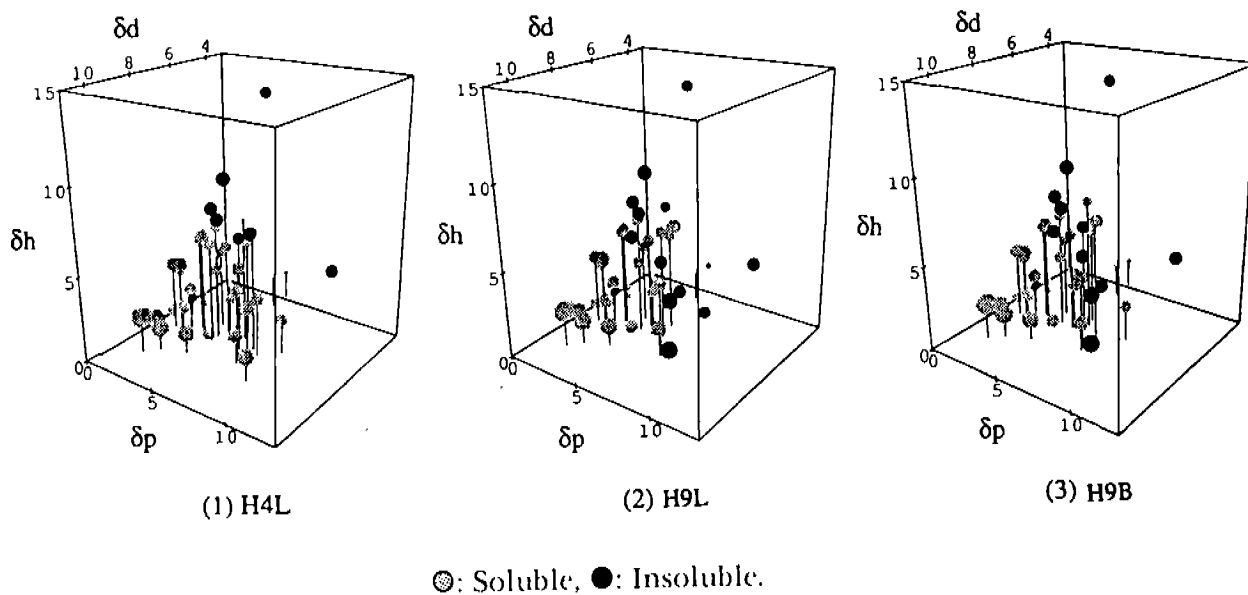


Figure 4 Solubility region of esters in various solvents

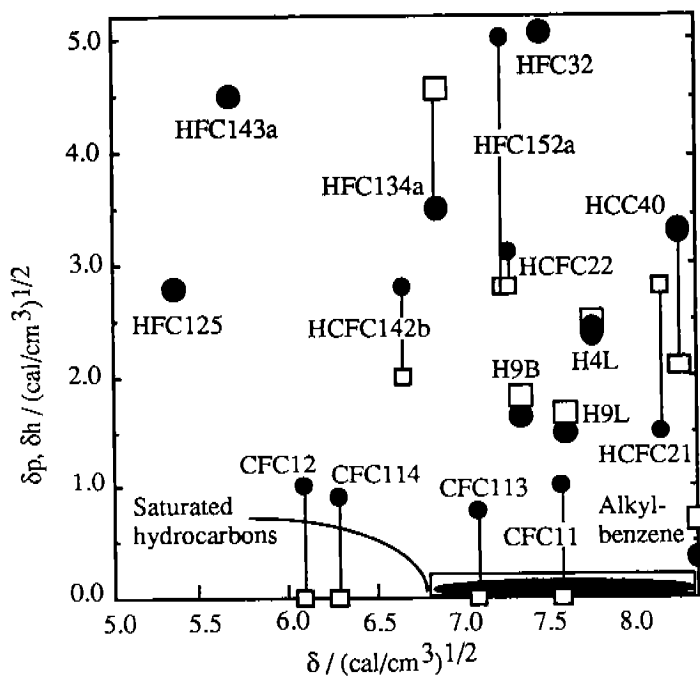


Figure 5 Comparison of three dimensional solubility parameters of esters, hydrocarbons, conventional refrigerants, and alternative refrigerants ●: δ_p □: δ_h

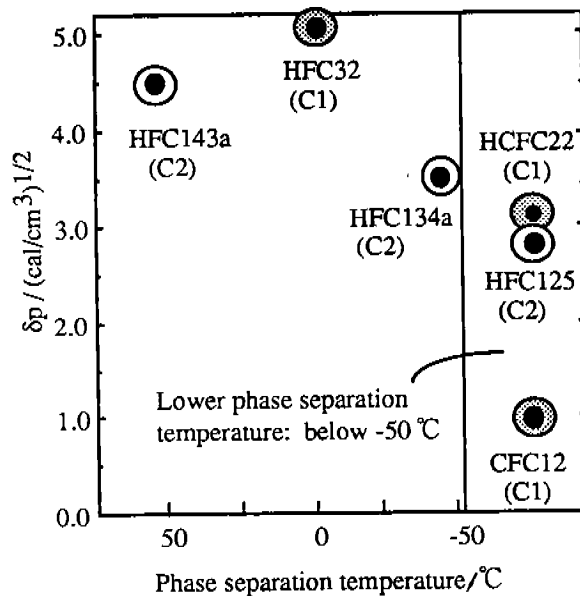


Figure 6 Polar parameters δ_p and lower phase separation temperature of a VG32 ref oil (pentaerythritol tetraester) with refrigerants