Solubility of HFC-134a Refrigerant in Glycol-Type Compounds: Effects of Glycol Structure

Spyros I. Tseregounis and Maynard J. Riley
Fuels and Lubricants Dept., General Motors Research and Development Center, Warren, MI 48090

Environmental concerns have dictated the replacement of CFC-12 refrigerant with HFC-134a in automotive air-conditioning (A/C) systems. Since polyglycols are synthetic compounds compatible with HFC-134a and considered as lubricants for the A/C compressor, interactions of HFC-134a with glycol-type compounds and thermodynamic properties of the solutions are important in designing an A/C system. In this work, the solubility of HFC-134a in four glycol-type compounds was measured at −5 to 80°C and 90 to 960 kPa. HFC-134a had the greatest solubility in tetraethylene glycol dimethyl ether. HFC-134a was less soluble in hexylene glycol and tetraethylene glycol and least soluble in triethylene glycol. Mixtures of HFC-134a with TRIG or TGDE showed phase separation. Solubility data were used to calculate the activity coefficient of HFC-134a in glycol solutions. An equation of the form, $\ln\gamma_r = (1 - x_r)[A + Bx_r]$, *was found to correlate* γ_r *to the mole fraction of HFC-134a in the solution where A and B are constants which may depend on the temperature. Based on a model assuming a specific interaction between molecules and using the activity of HFC-134a, a higher degree of interaction is expected between HFC-134a and tetraethylene glycol dimethyl ether molecules than between the molecules of HFC-134a and other glycols. In general, glycols with free -OH groups may have less affinity for HFC-134a. Solubility is discussed in terms of its parameters and chemical structure of the glycols, as well as the effect of temperature on the solubility, the activity coefficient, and the thermodynamic properties of the HFC-134a/glycol solutions.*

Introduction

CFC-12 (dichlorodifluoromethane) has been the refrigerant of choice in automotive air conditioning (A/C) systems. However, it has recently been determined that CFC-12 causes harm to the stratospheric ozone layer (Molina and Rowland, 1974; Embler et al., 1986); therefore, its use is restricted and eventually will be banned. An alternative refrigerant to CFC-12, which, however, is harmless to the stratospheric ozone, is HFC-134a (1,1,1,2 tetrafluoroethane, CF_3CH_2F) (McLinden and Didion, 1987). HFC-134a will replace CFC-12 in mobile A/C systems, and its use in production has already been commenced.

Replacing CFC-12 with HFC-134a in automotive A/C systems is not a simple operation, since the mineral (naphthenic) oils traditionally used to lubricate the compressors are not miscible with the HFC-134a refrigerant. In A/C systems that utilize positive displacement-type compressors, the lubricant is mixed with the refrigerant and both circulate through the refrigeration loop. Good solubility of the refrigerant with the lubricant is necessary for the compressor to be lubricated properly. For that reason, attention has focused on synthetic, polyalkylene glycol-type fluids for use as compressor lubricants, since they have good miscibility and solubility with HFC-134a.

The properties of the refrigerant/oil mixture, the so-called "working fluid," are important in designing an efficient and durable A/C system. Although transport and thermodynamic properties of a variety of refrigerant/oil mixtures have been reported in the literature, data for HFC-134a are generally not

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Correspondence concerning this article should be addressed to S. I. Tseregounis.
M. J. Riley is presently with Diversey Corporation, Wyandotte, MI.

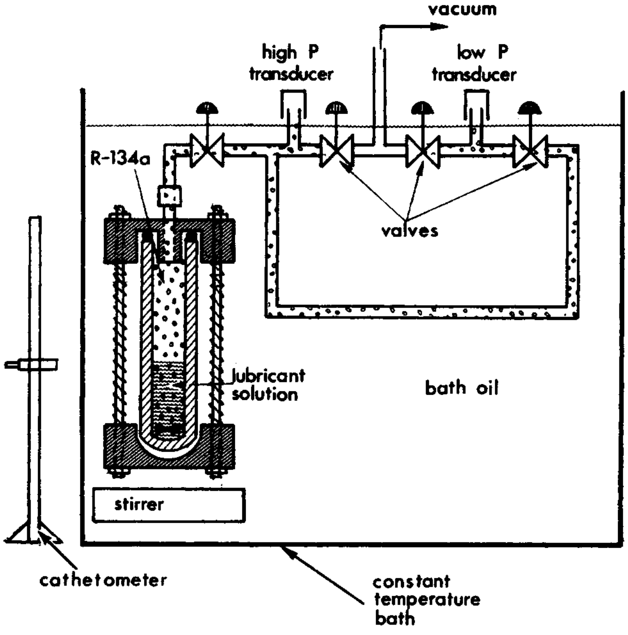

Figure 1. Solubility apparatus.

available. Solubility of HFC-134a in the compressor lubricant is a critical property of the mixture, since it determines the relative composition of the "working fluid" and therefore its physical characteristics as well as its thermodynamic properties. In addition, the structure and chemical nature of the glycol-type compound are important in determining the solubility of the refrigerant in the glycol and hence the properties of the solution.

In this report, the solubility of HFC-134a in a number of model glycol compounds was measured. The solubility data were used to determine the activity and the activity coefficient of HFC-134a in the refrigerant/glycol solutions. The effects of glycol structure on the solubility of HFC-134a and the properties of the solutions are discussed.

Experimental Details

The experimental apparatus used to determine the solubility of HFC-134a is shown in Figure 1. The solubility vessel was a pyrex tube (19.2 cm long, 1.9 cm OD, 0.3175 cm in wall thickness) sandwiched between two steel plates. With this arrangement, the system was able to tolerate continuous variations in pressure (100 to 1,800 kPa) and temperature (0 to 80°C) without breakage of the glass tube. A cathetometer was used to monitor the level of the liquid phase (and thus the volume of both the liquid and vapor phases in the tube). A stirrer was used to stir the solution and thus attain equilibrium quickly.

Two transducers were used in the solubility apparatus: one of low pressure range [0 to 100 psi (0 to 690 kPa)] and one of high pressure range [0 to 300 psi (0 to 2,100 kPa)]. To avoid damaging the low-pressure transducer at high-pressure levels, two valves were used to isolate this transducer from the system when data at higher pressures were acquired (Figure 1). When the low-pressure transducer was thus isolated, corrections for the amount of refrigerant trapped between the two valves and for changes in the system volume were made.

The solubility vessel was charged with the glycol compound and then with the HFC-134a refrigerant. By weighing the solubility vessel assembly before and after each charging, the exact amount of glycol and HFC-134a in the system was determined. The solubility of HFC-134a was measured as mass fraction of the refrigerant in the liquid phase and it was converted to mole fraction of HFC-134a, x_r, in the HFC-134a/glycol solution. For the calibration of the system and calculation of HFC-134a solubility, the following major assumptions were made:

- A Redlich-Kwong, cubic-type equation of state was assumed for HFC-134a (DuPont de Nemours Co., 1979):

$$P=\frac{RT}{v-\beta}-\frac{\alpha}{v(v+\beta)T^{1/2}} \tag{1}$$

- The vapor phase above the solution was assumed to be pure HFC-134a (due to the negligible vapor pressure of the glycol-type compounds studied).

The volume of the apparatus was determined by pressurizing the system with either Argon or HFC-134a and using either the ideal gas law or Eq. 1, respectively. The two methods agreed to within 5%. Other uncertainty limits determined for our experiments were: temperature, ±0.5°C; pressure, ±0.2%; glycol or refrigerant mass, ±0.01 g. The experimental procedure was tested by measuring the solubility of CFC-22 ($CHClF_2$) in TGDE. Our measurements agreed with literature values (Albright et al., 1960; Mastrangelo, 1959b) to within 2%.

To understand the effect of glycol structure on the solubility of HFC-134a, four glycol-type model compounds were used. These compounds are listed in Table 1. One is hexylene glycol (HEXG), a branched glycol. Two of them are linear ethylene oxide polyglycols, triethylene glycol (TRIG), and tetraethylene glycol (TETG). The last is tetraethylene glycol dimethyl ether

Table 1. Glycol-Type Model Compounds Used in the Solubility Studies

Compound	Formula	Mol. Wt.	Supplier
Hexylene Glycol (HEXG)	$CH_3C(OH)HCH_2C(OH)(CH_3)_2$	118.2	Union Carbide
Triethylene Glycol (TRIG)	$H(OCH_2CH_2)_3OH$	150.2	Union Carbide
Tetraethylene Glycol (TETG)	$H(OCH_2CH_2)_4OH$	194.2	Aldrich Chemicals
Tetraethylene Glycol Dimethyl Ether (TGDE)	$CH_3(OCH_2CH_2)_4OCH_3$	222.3	Aldrich Chemicals

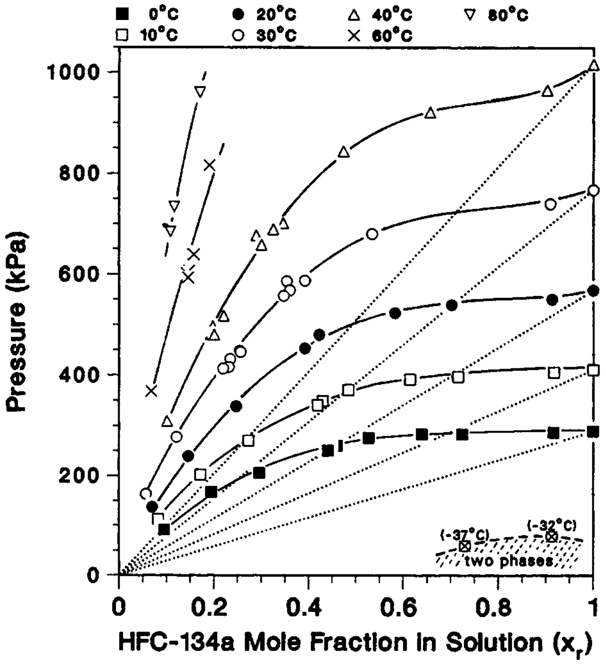

Figure 2. Solubility of HFC-134a in HEXG as function of temperature and pressure.

(TGDE), which is derived from TETG by replacing the end hydroxides by methoxy groups (capped).

Results and Analysis

Solubility and miscibility

The experimental solubility data for HFC-134a in the four compounds and the calculated values of the activity and the logarithm of the activity coefficient of HFC-134a in each solution are listed in the Supplement. Selected solubility data from the Supplement are shown in Figures 2, 3, 4, and 5 for HEXG, TRIG, TETG, and TGDE, respectively. The data indicate that the solubility and miscibility of HFC-134a vary in the compounds studied. TGDE shows very high affinity with HFC-134a; for example, the mole fraction of HFC-134a in TGDE at a specific temperature and pressure is higher (negative deviation) than that predicted for an ideal solution obeying

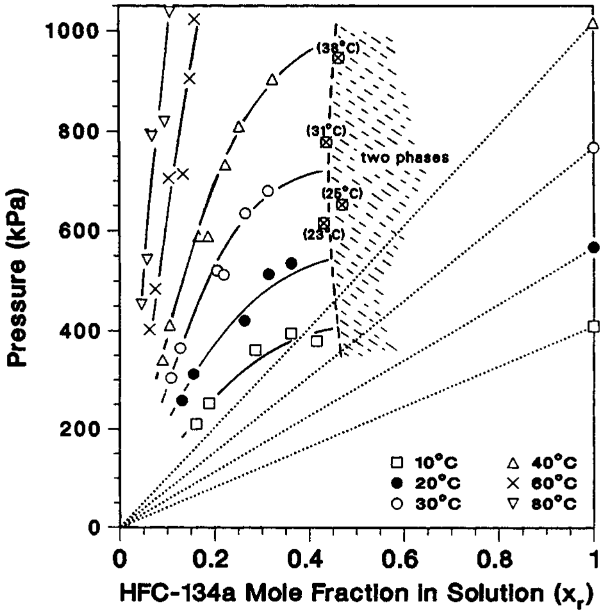

Figure 3. Solubility of HFC-134a in TRIG as function of temperature and pressure.

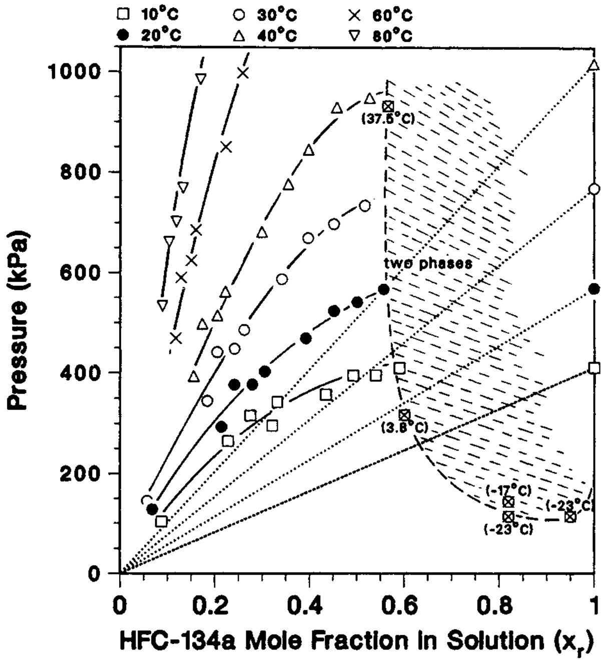

Figure 4. Solubility of HFC-134a in TETG as function of temperature and pressure.

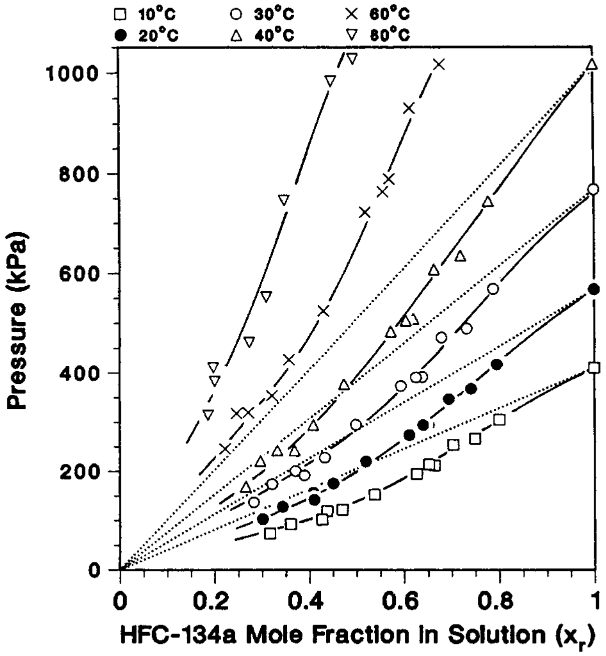

Figure 5. Solubility of HFC-134a in TGDE as function of temperature and pressure.

Raoult's law. HEXG shows less solubility for HFC-134a than TGDE. The mole fraction of HFC-134a in this glycol is lower (positive deviation) than that predicted for an ideal solution. TRIG and TETG show even less affinity with HFC-134a than HEXG.

Miscibility data are also shown in Figures 2, 3, and 4 to highlight the areas in the P-x_r diagrams where phase separation of the HFC-134a/glycol solution occurs. Miscilibity data outside the temperature and pressure ranges studied in this work were determined by sealed tube stability tests (Harrison Specification TM-217, 1987). Under the conditions studied in this work, TGDE is completely miscible with HFC-134a. The sealed tube miscibility data indicate that for the HFC-134a/HEXG system there is a UCST of about −30°C. Above this temperature, HFC-134a is completely miscible in HEXG. TRIG and TETG show only partial miscibility in HFC-134a. For both glycols, there is indication of the existence of LCST of the order of −20°C for TETG and lower than −40°C for TRIG. In addition, there is a maximum amount of HFC-134a that can dissolve in either TETG or TRIG at a specified temperature and any increase in pressure results in the appearance of two phases, as shown by the miscibility data. For the temperature range in this study (0 to 80°C), the maximum amount of HFC-134a that can dissolve in TRIG and TETG is approximately 0.45 to 0.55 and 0.55 to 0.6 mole fraction, respectively.

Activity coefficient

In Figures 6, 7, 8, and 9, the values of the logarithm of the activity coefficient of HFC-134a in HEXG, TRIG, TETG, and TGDE have been plotted, respectively. The activity coefficient was calculated by:

$$\gamma_r = \frac{f^l}{x_r f_o^s} = \frac{a_r}{x_r} \tag{2}$$

The detailed procedure for evaluating the activity coefficient, γ_r, from rigorous thermodynamic relations can be found in the literature (Reid et al., 1987; Walas, 1985).

The activity coefficient in a solution is a function of the composition and the temperature of the solution. Various semiempirical and empirical equation forms have been suggested in the literature (some of them based on group contributions) to correlate γ_r with the composition and temperature (Reid et al., 1987; Walas, 1985). In a binary solution (the case in this work), only the activity coefficient of HFC-134a in the solution (since the vapor phase is assumed to be pure refrigerant) is needed to fully describe the system and extract its thermodynamic properties (such as heat of mixing and free energy). The simplest form of an equation that may be used to fit the experimental data and correlate the activity coefficient with mole fraction and temperature is given by (Reid et al., 1987):

$$\ln\gamma_r = (1 - x_r)[A + Bx_r] \tag{3}$$

where A and B are constants that may depend on the temperature.

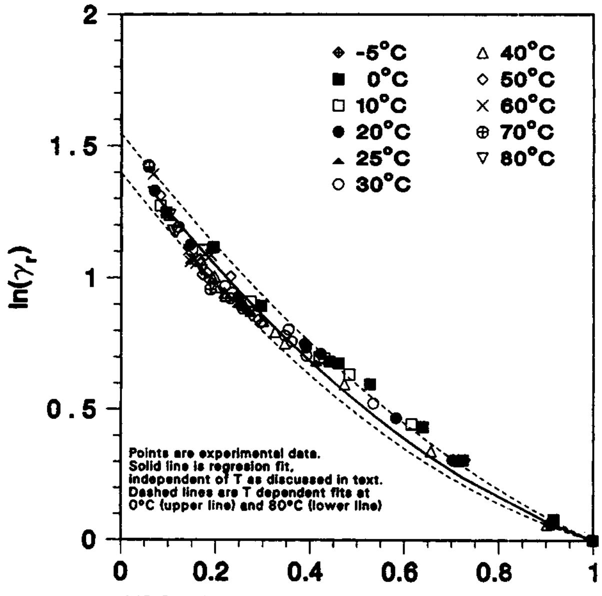

Figure 6. Activity coefficient of HFC-134a in HEXG as function of mole fraction at different temperatures.

The experimental data for $\ln\gamma_r$ shown in Figures 6 through 9 were used to evaluate the constants A and B for the different glycols used in this study. The numerical values are listed in Table 2. The data for TRIG and TETG (Figures 7 and 8, respectively) indicate that the activity coefficient is independent of temperature (the experimental variability of the results is higher than any temperature dependence). In this case, the solution behaves as an athermal solution where A and B are constants independent of T. In the case of HEXG, a small temperature dependence of γ_r may be seen in the results. Calculated, temperature-dependent A and B constants for HEXG

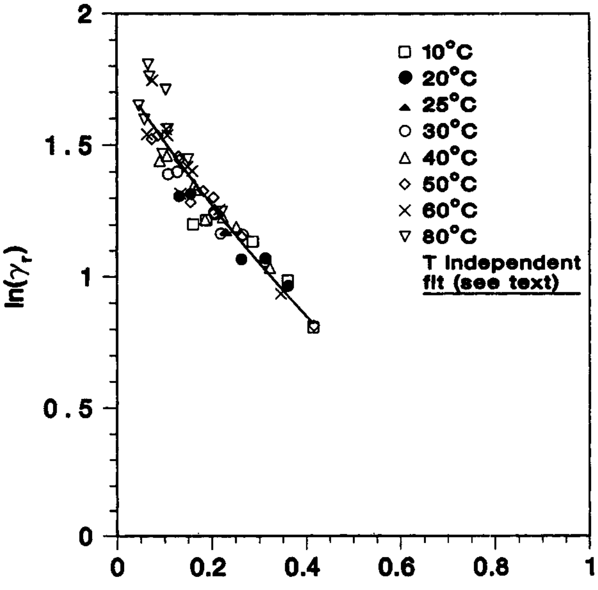

Figure 7. Activity coefficient of HFC-134a in TRIG as function of mole fraction at different temperatures.

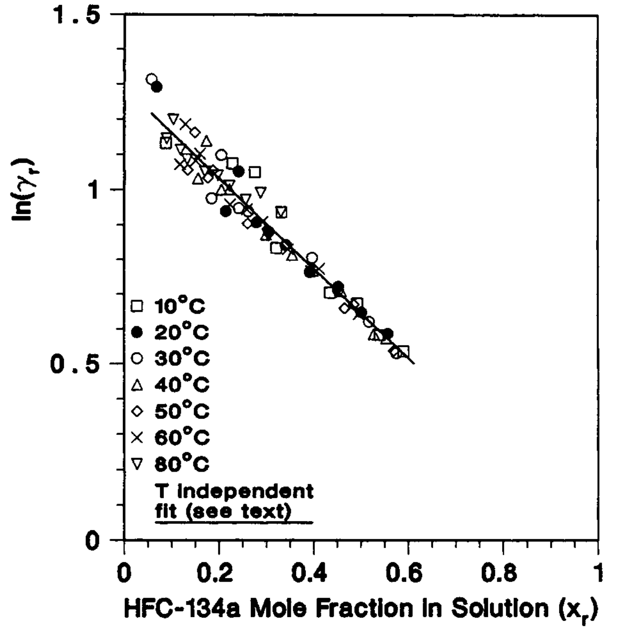

Figure 8. Activity coefficient of HFC-134a in TETG as function of mole fraction at different temperatures.

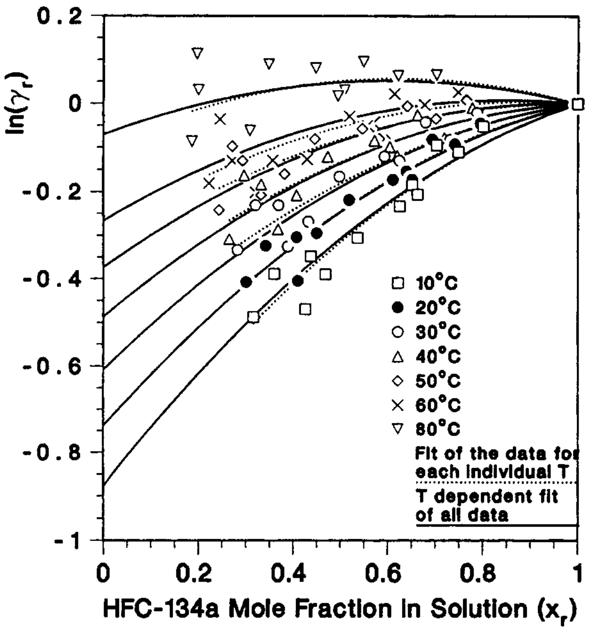

Figure 9. Activity coefficient of HFC-134a in TGDE as function of mole fraction at different temperatures.

are given in the Appendix. Since the temperature dependence is very small (variations in γ_r due to temperature are about of the same order as variations due to experimental uncertainties in the results), a temperature independent fit of the experimental data for HEXG was considered and the values of the temperature independent A and B constants are also shown in Table 2.

The picture is different with TGDE, the glycol with the highest affinity for HFC-134a. In this case, a clear temperature dependence of $\ln\gamma_r$ is present as indicated in Figure 9, where a fit of the experimental data values of the activity coefficient corresponding to a specific constant temperature is shown with dotted lines. It is obvious that a strong temperature dependence of γ_r is present. A fit of all the data based on Eq. 3 results in calculated values of the activity coefficient shown with solid lines in Figure 9. The values of the constants A and B are given in Table 2. Equation 3 with the values of A, B from Table 2 can be used to predict $\ln\gamma_r$ as a function of temperature and mole fraction. These values are expected to apply in the ranges in Table 2: they may not be applicable for dilute solutions.

Table 2. Fit of Experimental Values of ln γ_r on the Mole Fraction and Temperature as Suggested by the Regression Equation

$$\ln\gamma_r = (1 - x_r)[A + Bx_r]$$

Glycol	Constant Values		Experimental Data Range*		Notes
	A	B	Temp.	Mole Fraction	
HEXG	$0.887 + 180/T$	$-1.377 + 181/T$	0-80°C	0.05 − 1.0	Temp. dependent values (Appendix)
HEXG	1.473	−0.832	0-80°C	0.05 − 1.0	Temp. independent values
TRIG	1.769	−0.879	10-80°C	0.05 − ≅0.5**	Temp. independent
TETG	1.29 ± 0.05	0	10-80°C	0.05 − ≅0.6**	Temp. independent; linear dependence on mole fraction
TGDE	$3.187 - 1{,}150/T$	$-0.417 + 266/T$	10-80°C	≅0.2 − 0.8	Temp. dependent

*Regression equations are valid for pressures below the vapor pressure of HFC-134a at the corresponding temperature. The vapor pressure P_v (in kPa) of HFC-134a at temperature T (in K) is given by DuPont de Nemours Co. (1979):

$$\log P_v = 9.5838 - 1{,}314.4/T - 0.9074 \times \log T - 0.000365 \times T$$

**Upper value for x_r may depend on temperature. Value shown here is only approximate and represents the highest amount of HFC-134a that can be dissolved in the glycol before the appearance of a second liquid phase.

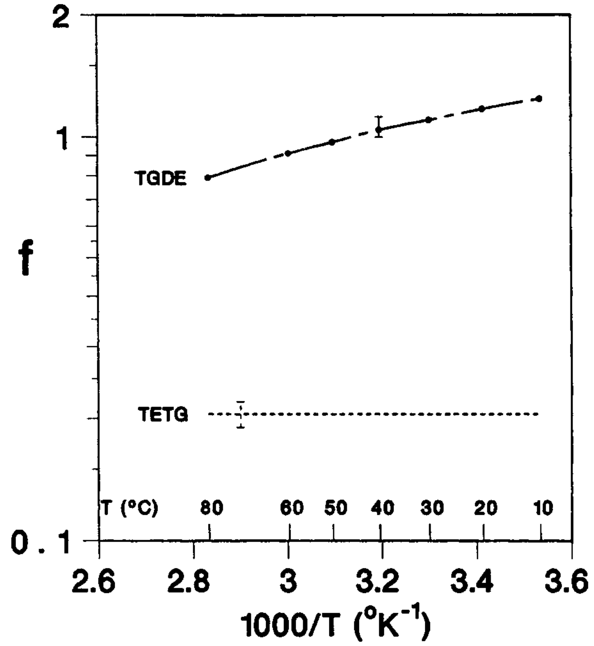

Figure 10. Functionality of solvent, *f*, for the HFC-134a/TETG and HFC-134a/TGDE solutions as function of temperature.

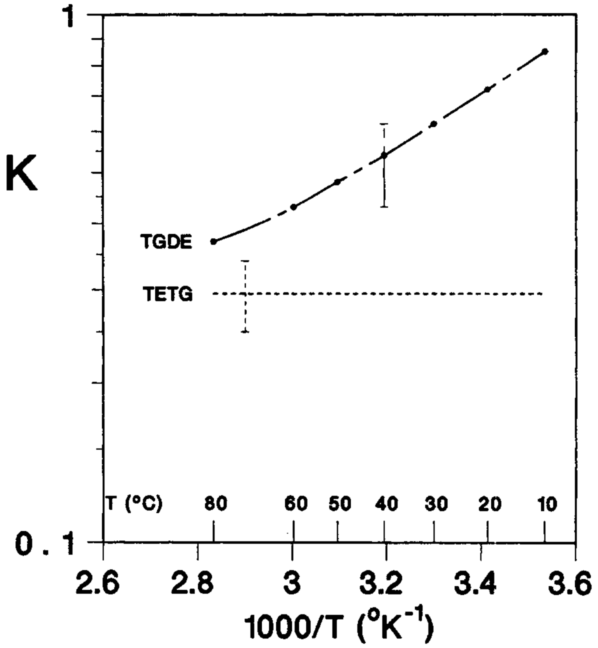

Figure 11. Equilibrium constant, *K*, for the HFC-134a/TETG and HFC-134a/TGDE solutions as function of temperature.

HFC-134a/glycol interactions

The solubility data for a number of chlorofluorocarbons in nonvolatile polar organic solvents have been modeled assuming a specific interaction per molecule (Mastrangelo, 1959A; Albright et al., 1962). The specific interaction is probably a form of hydrogen bonding, although a number of other interactions (steric hindrances or interactions among polar groups) may also occur. The relevant theory that has been proposed by Mastrangelo (1959a) assumes that the dissolution takes place through the formation of a complex, $R\cdots S$, according to:

$$R + S = R\cdots S \tag{4}$$

where R and S are the molecules of the refrigerant and the solvent, respectively.

Mastrangelo's model was developed based on the observation that when the experimental data for γ_r are plotted as a function of the activity a_r, a linear relation is observed for small values of the activity ($a_r < 0.5$), while a downward curve is observed for larger values of a_r. In this case, application of standard methods of statistical thermodynamics led Mastrangelo (1959a) to the derivation of the following relationship connecting γ_r with a_r (the activity of HFC-134a):

$$\gamma_r = K_1 + K_2 a_r + (1 - K_1 - K_2) a_r^2 \tag{5}$$

$$K_1 = \frac{1}{f(1+K)} \text{ and } K_2 = 1 + \frac{K-1}{f(1+K)} \tag{6}$$

The data (in Supplement) indicate that a second-order dependence of γ_r on a_r (as described in Eq. 6) is true for TETG and TGDE, but not so for HEXG (deviation at low a_r values) and TRIG (data uncertainties and deviations at low a_r values). Based on Eq. 6, the values of f and K for TETG and TGDE can be calculated and the values are plotted in Figures 10 and 11, respectively. The uncertainty in these values based in the uncertainty of our experimental data are also shown by the error bars in Figures 10 and 11.

For TGDE, a value of solvent functionality, f, of the order of 1 is observed. The value of f decreases with increasing temperature. In comparison, the value of f for TETG is of the order of 0.2, independent of temperature. The uncertainty of our experimental data overshadows any small T dependence that may exist (within the T range studied in this work). The value of the equilibrium constant, K, for reaction 4 for the HFC-134a/TGDE system lies in the interval 0.4–0.9 and increases with temperature. The value of K for the HFC-134a/TETG system is about 0.3 and is independent of temperature.

The γ_r vs. a_r plots for HEXG and TRIG do not show sufficient linear behavior at low a_r values to justify an analysis of the interaction of the glycol molecules with HFC-134a based on Mastrangelo's model. For HEXG and for mole fractions higher than about 0.4, Mastrangelo's model can be used to predict values of 0.17–0.22 and 0.15–0.26 for f and K, respectively, similar to those obtained for TETG.

Table 3 shows values of f and K constants for the HFC-134a/TGDE solution as determined in this work and for other refrigerant/TGDE solutions taken from the literature. Compared to its isomer (HFC-134), HFC-134a shows smaller f and K values, indicating a lesser degree of interaction with TGDE. Compared to chlorinated solvents, the values of f are smaller for HFC-134a implying that there are less active sites per molecule (possibly due to the higher activity of the Cl containing chemicals). Compared to the HCFC-124a/TGDE system, the HFC-134a/TGDE solution shows lower f values but higher K values, probably indicating that steric hindrances interfere with

Table 3. Equilibrium Constants for Use in Mastrangelo's Model (Eqs. 5 and 6) for Solutions of Tetraethylene Glycol Dimethyl Ether with Various Refrigerants

Temp. (°C)	K_1	K_2	f^*	K^*	Reference
HFC-134a (CF_3CH_2F)-Tetraethylene Glycol Dimethyl Ether					
10	0.44	0.93	1.24	0.85	This work
20	0.50	0.86	1.17	0.72	
30	0.56	0.79	1.10	0.62	
40	0.63	0.72	1.04	0.54	
50	0.70	0.64	0.97	0.48	
60	0.77	0.56	0.91	0.43	
80	0.93	0.41	0.79	0.37	
HCFC-21 ($CHCl_2F$)-Tetraethylene Glycol Dimethyl Ether					
37.8	0.178	0.968	3.08	0.825	Albright et al. (1962)
65.6	0.24	0.91	2.56	0.625	
HCFC-22 ($CHClF_2$)-Tetraethylene Glycol Dimethyl Ether					
37.8	0.235	0.85	3.13	0.359	Albright et al. (1962)
65.6	0.339	0.744	2.37	0.247	
HFC-134 (CHF_2CHF_2)-Tetraethylene Glycol Dimethyl Ether					
28.6	0.213	1.057	2	1.27	Mastrangelo (1959b)
56	0.285	0.925	2	0.74	
86	0.364	0.811	2	0.48	
HCFC-124a (CHF_2CClF_2)-Tetraethylene Glycol Dimethyl Ether					
35	0.374	0.682	2	0.149	Mastrangelo (1959b)
54.4	0.444	0.594	2	0.086	
73.9	0.505	0.508	2	0.026	

*$f = 1/(2K_1 + K_2 - 1)$ and $K = (K_1 + K_2 - 1)/K_1$.

the formation of the $R \cdots S$ complex (Eq. 4) in the case of the chlorinated refrigerant.

Solubility parameters

It is interesting to look at the solubility of HFC-134a in terms of the solubility parameter. The solubility parameter, δ, is a basic property of all liquids and is defined as the square root of the cohesive energy density (or the energy of vaporization per unit volume). The concept of the solubility parameter is useful in regular solution theory, but for nonregular solutions it is convenient to define an empirically determined total solubility parameter, δ_t, which is a vector sum of all the interaction modes between molecules. The total solubility parameter is given by:

$$\delta_t = [\delta_d^2 + \delta_p^2 + \delta_h^2]^{1/2} \tag{7}$$

Solubility parameters can be used to predict the affinity and mutual solubilities of molecules based on the concept in which mutually soluble substances have comparable solubility parameters. The solubility parameters of a substance can be calculated from group contributions or determined semiempirically by comparing with solvents of known solubility parameters. There are many literature references that describe how to obtain and use solubility parameters. The solubility parameters (of HFC-134a and the glycols used in this study) and the methods of their determination are shown in Table 4. For direct comparison of the solubility parameters between the glycols and HFC-134a, Figure 12 was constructed as a triangular plot of the "dispersive," "polar," and "hydrogen bond" character of each compound expressed as the fractions $d_d/(d_d + d_p + d_h)$, $d_p/(d_d + d_p + d_h)$, and $d_h/(d_d + d_p + d_h)$, respectively. Figure 13 compares the total solubility parameter of HFC-134a with those of the glycols.

Figures 12 and 13 demonstrate that TGDE, the compound

Table 4. Solubility Parameters of the Glycols Used and Method of their Determination

Compound	Solubility Parameters ($MPa^{1/2}$)				Notes
	d_d	d_p	d_h	d_t	
HFC-134a	15.6	10.3	5.1	19.3	*
HEXG	12.5	11.4	16.8	23.1	**
	15.8	8.4	17.8	25.2	*** or †
	16.6	5.5	17.8	24.9	‡
	12.6	11.4	17.1	24.1	*
TRIG	15	12.2	21.8	29.1	**
	16	12.5	18.6	27.5	***
	16	10.4	18.6	27.5	†
	17.4	6.7	14.7	23.7	‡
	13.2	12	23.2	29.2	*
TETG	17.4	8.2	12.7	23.1	‡
	12.9	11	18.2	24.9	*
TGDE	17.4	7.8	8.2	20.8	‡
	13.2	7.8	7.3	17	*

*Estimated based on group contributions as described by Hoy (1975).

**Values from Barton (1983); determined according to the method described by Hoy (1975).

***Values from Barton (1983); Adopted from Hansen and Beerbower (1971).

†Values from Barton (1983); Adopted from Beerbower and Dickey (1969).

‡Semiempirically determined at DuPont using Hansen's method as described by Barton (1975); the method is based on the concept of a d_d-d_p-d_h "solubility volume" and uses solvents with known solubility parameters in determining the solubility parameters of the compound. The uncertainty is about ±2 $MPa^{1/2}$.

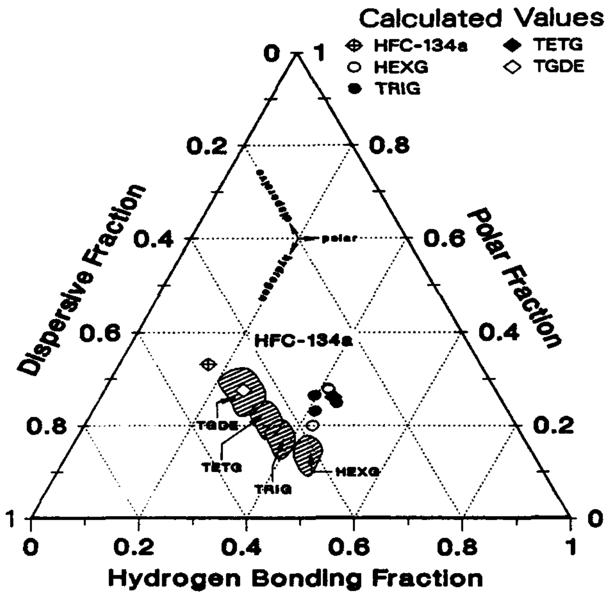

Figure 12. Polar, dispersive and hydrogen bonding character of HFC-134a and the glycol compounds.

Shaded areas represent semiempirically determined values (see Table 4 for details).

with the highest solubility for HFC-134a, has solubility parameters closer to those of the refrigerant than the other three glycols. The calculated values of the total solubility parameter (see Table 4) rank the polyglycols in exactly the same order as they dissolve in HFC-134a (TGDE > HEXG > TETG > TRIG). This is not the case for the values obtained from the semiempirical calculation or taken from the literature. Uncertainties in the values of the parameters and small differences in the solubility of HFC-134a in the other three glycols may contribute to these small discrepancies.

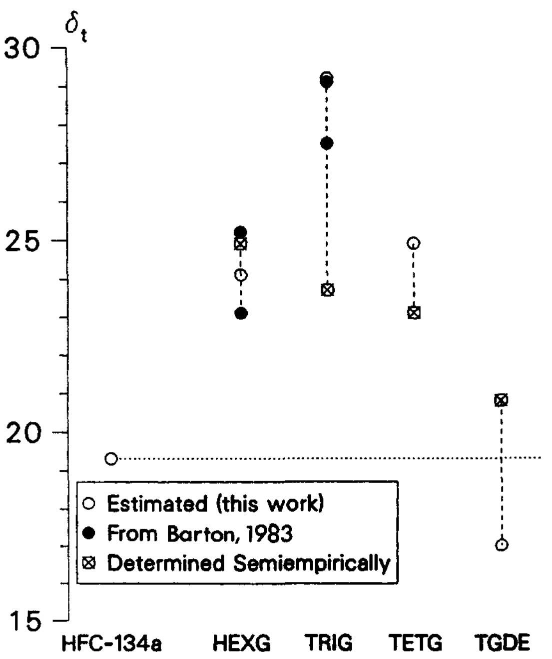

Figure 13. Comparison of the total solubility parameter, δ_t, of the glycol compounds with that of HFC-134a.

It is estimated that compounds with total solubility parameter within about 2 MPa$^{1/2}$ of that of HFC-134a will readily dissolve the refrigerant and possibly show a negative deviation from Raoult's law (TGDE). On the other hand, glycols with solubility parameters differing by more than 2 MPa$^{1/2}$ from those of HFC-134a will show low tendencies to dissolve the refrigerant and possibly positive deviations from Raoult's law (HEXG, TETG, TRIG). Figure 12 shows that the low hydrogen bonding fraction of HFC-134a, its moderate potential to form dispersive-type bonds, and its high polar character are major characteristics of this HFC. Therefore, compounds with low hydrogen bonding potential (such as capped end groups) and high polarity (straight, nonsymmetric molecules) may have high affinity with HFC-134a.

Thermodynamic properties

The thermodynamic properties of the HFC-134a/glycol solutions can be determined from the activity coefficient of the refrigerant. The excess properties and activity coefficient of the glycol in the solution may be obtained from rigorous thermodynamic relations and the expression for γ_r (Eq. 3). If the constants in Eq. 3, A and B, are written as

$$A = a_1 + a_2/T \text{ and } B = b_1 + b_2/T, \tag{8}$$

then the analytical expressions for the thermodynamic properties of the solution are given by:

$$g^e = -RT(1-x_r)\left[\left(\frac{a_2}{T}+\frac{b_2}{T}+a_1+b_1\right)\ln(1-x_r)+\left(\frac{b_2}{T}+b_1\right)x_r\right]$$

$$h^e_m = -R(1-x_r)[(a_2+b_2)\ln(1-x_r)+b_2x_r]$$

$$s^e = \left(\frac{1}{T}\right)(h^e_m - g^e) = R(1-x_r)[(a_1+b_1)\ln(1-x_r)+b_1x_r]$$

$$\ln\gamma_o = -\left(\frac{a_2}{T}+\frac{b_2}{T}+a_1+b_1\right)[x_r+\ln(1-x_r)] - \left(\frac{b_2}{T}+b_1\right)x_r^2 \tag{9}$$

Substituting numerical values for the constants in the above equations, the thermodynamic properties of the R-134a/glycol mixtures can be calculated. For the HEXG mixtures, the heat of mixing can be calculated for the case in which a temperature dependence of the activity coefficient is assumed yielding a maximum value for h^e_m of 250 to 300 cal/mol at about $x_r = 0.7$. Assuming no temperature dependence for γ_r (Table 2) the heat of mixing of the HEXG solution is of course zero. Therefore, using the solubility data acquired in this study an accurate determination of h^e_m cannot be made in the temperature range 0 to 80°C. The heat of mixing is estimated to be of the order of 200 cal/mol, but a more precise evaluation will require a direct determination of h^e_m.

Similarly, for the HFC-134a/TRIG and HFC-134a/TETG mixtures, the data indicate that the even less obvious temperature dependence of the activity coefficient justifies the assumption that these mixtures behave as athermal solutions in the temperature range investigated in this study. For the HFC-134a/TGDE solutions, the temperature dependence of the activity coefficient can be used to estimate the excess thermo-

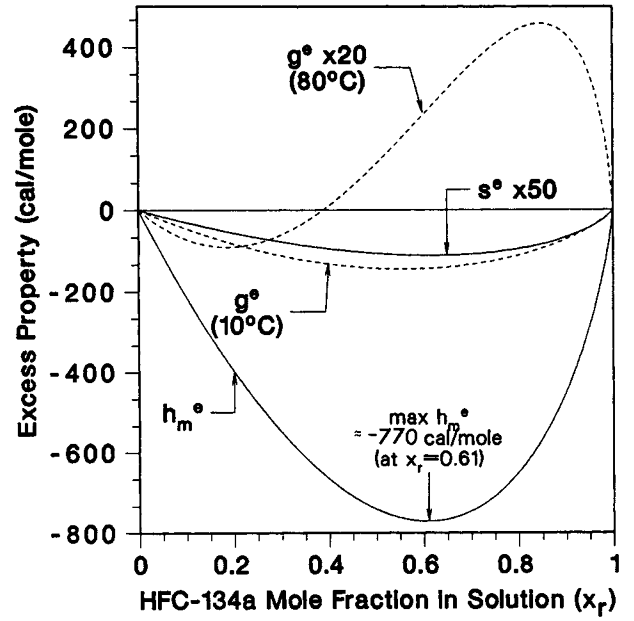

Figure 14. Calculated excess thermodynamic properties of the HFC-134a/TGDE mixture.

dynamic properties of the solution (Figure 14) and the activity coefficient of TGDE in the solution (Eq. 9). The heat of mixing for the TGDE mixture at the temperature range of interest in this study shows a maximum of about −770 cal/mol (exothermic) at $x_r = 0.61$.

Other polyglycols

Figure 15 depicts the solubility of HFC-134a in a number of propylene oxide polyglycols with either free end -OH groups or with capped (-OR) end alkyl groups. The capped compounds were synthesized using commercially available polypropylene oxides of the desirable molecular weight. Two major observations can be made based on the data in Figure 15. First, eliminating the free -OH groups from the polyglycols increases their affinity with HFC-134a (possibly by reducing the degree of interaction {hydrogen bonding} between the polyglycol molecules). Second, an increase in the molecular weight of the polyglycol results in an increase in the HFC-134a mole fraction in the solution. Both of these observations agree qualitatively with the results for the four glycol compounds used in this study, emphasizing the effect of eliminating the end -OH groups and increasing the number of the etheric (-O-) linkages in the solubility of HFC-134a.

Future work and use of the data to determine UNIFAC parameters

The data in this work could be utilized to obtain UNIFAC parameters for HFC-134a. Although Eq. 3 is adequate in describing the experimental results and UNIFAC calculations were beyond the scope of this study, possible use of the data for UNIFAC calculations will be described to explain complex systems involving fluorocarbons and glycols.

A possible UNIFAC development is outlined in Table 5 for the mixture of HEXG with HFC-134a. The experimental data for the activity coefficient (Supplement) could be compared to UNIFAC activity coefficients calculated from the parameters in Table 5. By optimizing an objective function (Skjold-Jorgensen et al., 1979) the values of the unknown group interaction parameters a_{56}, a_{17}, a_{57}, a_{67}, a_{65}, a_{71}, a_{75}, and a_{76} could be estimated for the HFC-134a/HEXG system. The group interaction parameters could be accurately predicted from the experimental data by comparing the UNIFAC activity coefficients with the experimental values and minimizing the objective functions for all the four refrigerant/glycol systems simultaneously. Thus, investigators with access to UNIFAC

Table 5. UNIFAC Parameters for the HFC-134a/HEXG system*[*]

Molecule	H	HEXG	CH_3-CH(OH)-CH_2-C(OH)-$(CH_3)_2$
Molecule	R	HFC-134a	CF_3-CH_2F

Molecule	Group	Group No.	Subgroup No.	j	R_j	Q_j	ν_j^H	ν_j^R
H	CH_3	1	1	1	0.9011	0.848	3	0
	CH_2	1	2	2	0.6744	0.540	1	0
	CH	1	3	3	0.4469	0.228	1	0
	C	1	4	4	0.2195	0.0	1	0
	OH	5	15	5	1.0	1.2	2	0
R	CF_3	40	74	6	1.406	1.38	0	1
	CH_2F	...	...	7	1.07**	1.0**	0	1

Group interaction parameters, a_{ij}

		j						
		1	2	3	4	5	6	7
	1	0	0	0	0	986.5	−2.859	a_{17}
	2	0	0	0	0	986.5	−2.859	a_{17}
	3	0	0	0	0	986.5	−2.859	a_{17}
i	4	0	0	0	0	986.5	−2.859	a_{17}
	5	156.4	156.4	156.4	156.4	0	a_{56}	a_{57}
	6	147.3	147.3	147.3	147.3	a_{65}	0	a_{67}
	7	a_{71}	a_{71}	a_{71}	a_{71}	a_{75}	a_{76}	0

*UNIFAC parameters were taken from Skjold-Jorgensen et al. (1979) and Gmehling et al. (1982) unless otherwise indicated.

**The group volume (R_7) and group surface area (Q_7) for the CH_2F group were calculated from Van der Waals parameters according to Bondi (1968).

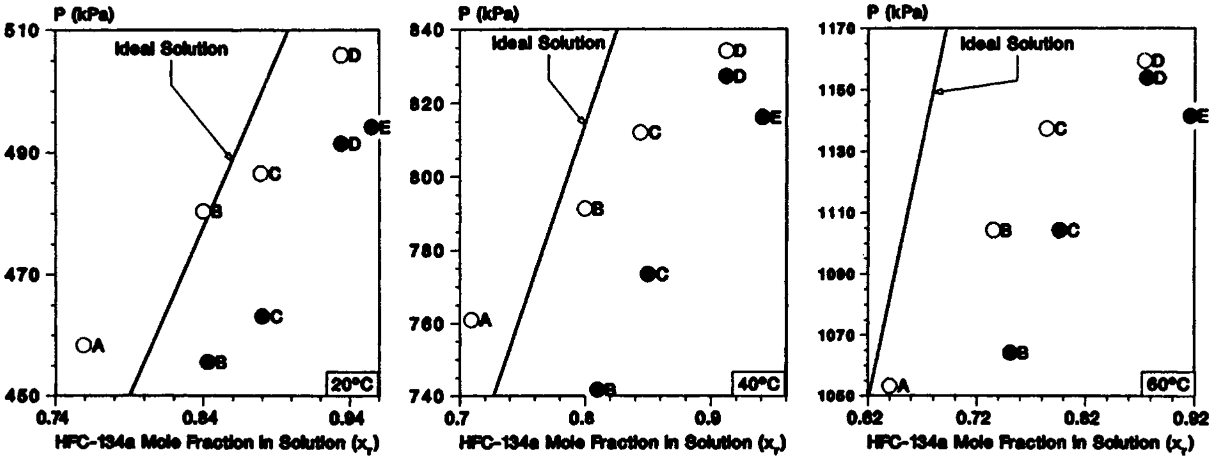

Figure 15. Solubility of HFC-134a in some propylene oxide polyglycols of different molecular weights (*A* = 425, *B* = 725, *C* = 1,000, *D* = 2,000, *E* = 3,000) and terminating in either free end hydroxyl groups (open circles) or alkyl end groups (dark circles).

computer codes could utilize the parameters in Table 5 and the experimental data to estimate group interaction parameters for the CF_3 and CH_2F groups to supplement existing tables.

Conclusions

The following conclusions can be drawn:

- TGDE showed high solubility for HFC-134a with negative deviations of the pressure vs. mole fraction data from Raoult's law. HFC-134a had lower solubilities in the other three glycols (HEXG, TRIG, TETG) with positive deviations from Raoult's law.
- Eliminating the free -OH groups from glycol compounds increases the solubility of HFC-134a.
- Increasing the number of the etheric links (-O-) in glycol compounds increases their affinity for HFC-134a.
- TRIG and TETG both showed low affinity with HFC-134a and phase separation. Phase separation occurs at 0.45–0.55 mol fraction for TRIG and 0.55–0.6 mol fraction for TETG, respectively. Both glycols formed athermal solutions with HFC-134a in the temperature range of 10–80°C and at pressures below the saturation pressure of the refrigerant.
- A small temperature dependence of HFC-134a/HEXG solution was observed, but was difficult to quantify due to data scatter.
- A strong temperature dependence of the activity coefficient for the HFC-134a/TGDE solution was observed. The temperature dependence for this solution indicates an exothermic process with a heat of mixing of the order of -770 cal/mol at a 0.61 HFC-134a mol fraction.
- Solubility parameters can be used to determine compounds with high affinity of HFC-134a. Specifically, compounds with solubility parameters within about 2 $MPa^{1/2}$ of that of HFC-134a may be readily soluble in the refrigerant.

Acknowledgment

Sue Beabout and Sue Halliday of Harrison measured the miscibility of the glycols in HFC-134a and determined the UCST and LCST. Shirley Schwartz of the Fuels and Lubricants Department furnished information concerning the solubility parameters, and Lori Vandenberg of Harrison calculated the solubility parameters for the glycols based on group contribution methods. David Bateman from DuPont provided the solubility parameters for HFC-134a. Hal Jackson from DuPont evaluated the solubility parameters for the glycols based on the semiempirical method with solvent envelopes. Zack Gardlund of the Polymers Department synthesized and supplied the polypropylene oxide glycols described in Figure 15.

Notation

A, a_1, b_2, B = constants, K
a_r = activity of HFC-134a in the solution
a_{ij} = UNIFAC group interaction parameters between groups *i* and *j*, K
CFC = chlorofluorocarbon ($C_xF_zCl_w$)
f = solvent functionality (number of active sites per molecule)
f^1 = fugacity of HFC-134a in the solution
f_o^1 = corrected standard state fugacity of HFC-134a in the *P* and *T* of the solution
g^e = excess free energy of the solution, cal/mol
h_m^e = heat of mixing, cal/mol
h_r^e = excess molal enthalpy of HFC-134a in the solution, cal/mol
HCFC = hydrochlorofluorocarbon ($C_xH_yF_zCl_w$)
HEXG = hexylene glycol
HFC = hydrofluorocarbon ($C_xH_yF_z$)
K = equilibrium constant for the association reaction (Eq. 4) expressed in terms of activities
K_1, K_2 = constants
LCST = lower critical solution temperature
n, n_r, n_o = number of moles in the solution: total, of HFC-134a, and of glycol, respectively
P = pressure, kPa
P_c = critical pressure of HFC-134a, 3,940.6 kPa
P_v = vapor pressure of HFC-134a at $x_r = 1$
Q_j = UNIFAC group surface area parameter for *j*
R = ideal gas constant, 81.5 $cm^3 \cdot kPa \cdot g^{-1} \cdot K^{-1}$
R_j = UNIFAC group volume parameter for *j*
s^e = excess entropy of the solution, $cal \cdot mol^{-1} \cdot K^{-1}$
T = temperature, K
T_c = critical temperature of HFC-134a, 373.7 K
TETG = tetraethylene glycol
TGDE = tetraethylene glycol dimethyl ether
TRIG = triethylene glycol
UCST = upper critical solution temperature
v = specific volume, cm^3/g
x_r = mole fraction of HFC-134a in the liquid phase

Greek letters

α = $0.42748(R^2T_c^{2.5})/P_c = 1.95\times10^6$ kPa·K$^{0.5}$·cm^6/g^2 (Redlich-Kwong constant)
β = $0.08664\ RT_c/P_c = 0.67$ cm^3/g (Redlich-Kwong constant)
γ_o = activity coefficient of the glycol in the solution
γ_r = activity coefficient of HFC-134a in the solution
δ_t, δ_p, δ_d, δ_h = solubility parameters: total, polar, dispersion, and hydrogen bonding, respectively, MPa$^{1/2}$
ν_i^M = number of type i groups in molecule, M

Literature Cited

Albright, L. F., T. C. Doody, P. C. Buclez, and C. R. Pluche, "Solubility of Refrigerants 11, 21, and 22 in Organic Solvents Containing an Oxygen Atom," *ASHRAE Trans.*, **66**, 423 (1960).

Albright, L. F., P. T. Shannon, F. Terrier, and P. L. Chueh, "Solubility of Chlorofluoromethanes in Nonvolatile Polar Organic Solvents," *AIChE J.*, **8**(5), 668 (1962).

Barton, A. F. M., *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL (1983).

Barton, A. F. M., "Solubility Parameters," *Chem. Rev.*, **75**(6), 731 (1975).

Beerbower, A., and J. R. Dickey, "Advanced Methods for Predicting Elastomer/Fluid Interactions," *Amer. Soc. Lubric. Eng. Trans.*, **12**, 1 (1969).

Bondi, A., *Physical Properties of Molecular Crystals, Liquids and Gases*, Wiley, New York (1968).

E.I. DuPont de Nemours Co., *Thermodynamic Properties of Freon-134a*, Freon Products Div., Wilmington, DE (1979).

Embler, L. R., P. L. Layman, W. Lepkowski, and P. S. Zurer, "The Changing Atmosphere," *Chem. & Eng. News*, **64**(47), 14 (1986).

Gmehling, J., P. Rasmussen, and A. Fredenslund, "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension: 2," *Ind. Eng. Chem. Process. Des. Dev.*, **21**(1), 118 (1982).

Hansen, C. M., and A. Beerbower, "Solubility Parameters," *Kirk-Othmer Encyclopedia of Chemical Technology*, Suppl. Vol., 2nd ed., A. Standen, ed., Interscience, New York, 889 (1971).

Harrison Radiator Div., General Motors Corp., "Sealed Glass Test Tube Refrigerant Stability Tests," Specification No. TM-217 (May 15, 1987).

Hoy, K. L., *Tables of Solubility Parameters*, 3rd ed., Union Carbide Corp., Chemicals and Plastics Res. and Dev. Dept., South Charleston, WV (1975).

Mastrangelo, S. V. R., "Equation of Solubility of Nonelectrolytes which Possess a Specific Interaction," *J. of Phys. Chemistry*, **63**, 608 (1959a).

Mastrangelo, S. V. R., "Solubility of some Chlorofluorohydrocarbons in Tetraethylene Glycol Dimethyl Ether," *ASHRAE J.*, **1**(10), 64 (1959b).

McLinden, M. O., and D. A. Didion, "Quest for Alternatives—A Molecular Approach Demonstrates Tradeoffs and Limitations are Inevitable in Seeking Refrigerants," *ASHRAE J.*, **29**(12), 32 (1987).

Molina, M. J., and F. S. Rowland, "Stratospheric Sink for Chlorofluoro-Methanes: Chlorine Atom-Catalyzed Destruction of Ozone," *Nat.*, **249**, 810 (1974).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).

Skjold-Jorgensen, S., B. Kolbe, J. Gmehling, and P. Rasmussen, "Vapor-Liquid Equilibria by UNIFAC Group Contribution: Revision and Extension," *Ind. Eng. Chem. Process. Des. Dev.*, **18**(4), 714 (1979).

Walas, S. M., *Phase Equilibrium in Chemical Engineering*, Butterworth Publishers, Boston (1985).

Appendix: Evaluation of Constants for $\ln\gamma_r$ in HFC-134a/HEXG Solutions

By combining Eqs. 3 and 8 we get:

$$\ln\gamma_r = (1 - x_r)\left[\frac{a_2}{T} + \frac{b_2}{T}x_r + a_1 + b_1 x_r\right] \tag{A1}$$

It is possible to fit the experimental data for the activity coefficient using Eq. A1 and thus to evaluate the constants. Due to scatter in the data, however, and the small temperature dependence of the activity coefficient, there may exist a number of diverse values of the constants in Eq. A1 which will result in a reasonable fit of the experimental data. In other words, it is statistically difficult to determine the best values of a_1, a_2, b_1, and b_2 by direct regression of the experimental data. A better way is to first determine the values of two of the constants, a_2 and b_2, by an independent method, and then evaluate a_1 and b_1 from a linear regression fit of Eq. A1 to the activity coefficient data.

In determining the values of a_2 and b_2 the thermodynamic expressions for the excess molal enthalpy of HFC-134a in the solution are used according to a procedure outlined by Albright et al. (1962). The thermodynamic relations that relate the excess molal enthalpy, h_r^e, the heat of mixing, h_m^e, and the activity coefficient, γ_r can be found in the literature (see, for example, Walas, 1985) and are summarized by Albright et al. (1962):

$$h_r^e = \left[\frac{\partial(nh_m^e)}{\partial n_r}\right]_{T,P,n_o} = \frac{(1-x_r)^2}{n_o}\left[\frac{\partial(nh_m^e)}{\partial x_r}\right]_{T,P,n_o} \tag{A2}$$

and

$$h_r^e = R\left[\frac{\partial\ln\gamma_r}{\partial(1/T)}\right]_{P,x_r} \tag{A3}$$

Since the total pressure is low (much lower than the critical pressure), the effect of pressure in Eq. A3 is very small (about an order of magnitude less than the effect of temperature) and can be neglected. In that case, the derivative of $\ln\gamma_r$ with respect to $1/T$ in Eq. A3 needs to be evaluated only at constant mole fraction.

Equations A1 and A3 show that the excess molal enthalpy of HFC-134a in the solution has a second-order dependence on the mole fraction according to:

$$h_r^e = R\left[\frac{\partial\ln\gamma_r}{\partial(1/T)}\right]_{P,x_r} = R(1-x_r)(a_2 + b_2 x_r) \tag{A4}$$

This is similar to the dependence suggested by Albright et al. (1962) for chlorodifluoromethane/tetraethylene glycol dimethyl ether solutions. Plotting $\ln\gamma_r$ as a function of $1/T$ at constant mole fraction, the slope of the curve provides the derivative term in Eq. A4. If the slope is then plotted as a function of x_r, the constants a_2 and b_2 can be determined.

The above procedure requires interpolation of the raw data (Supplement) to obtain the activity coefficient of HFC-134a at different temperatures and the same mole fraction. The best line through the P vs. x_r data points (Figure 2) was determined, and the pressure of HFC-134a vapor above the solution was estimated at a specified mole fraction for different temperatures. From the values of P, $\ln\gamma_r$ was calculated, and from that the slope of each $\ln\gamma_r$ vs. $1/T$ curve at constant mole fraction was obtained. A quadratic fit of the values of this slope as function of x_r yielded the values of the constants a_2 and b_2, 180 and 181 K, respectively.

The values of a_2 and b_2 were substituted in Eq. A1, and numerical values for the constants a_1 and b_1 were determined by fitting the experimental values of $\ln\gamma_r$ (Supplement) with the best regression line defined by Eq. A1. The values of a_1 and b_1 thus determined were 0.887 and -1.377, respectively. The agreement between the experimental values of $\ln\gamma_r$ and those predicted by Eq. A1 was very good (index of determination, $R^2 = 0.949$).

Manuscript received Apr. 12, 1993, and revision received July 21, 1993.

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