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Isothermal Vapor–Liquid Equilibria of Mixtures Containing Organic Compounds. 7. Excess Gibbs Energies of Chloroalkane + Oxaalkane Mixtures at 298.15 K[†]

Luciano Lepori and Enrico Matteoli

Istituto di Chimica Quantistica ed Energetica Molecolare, CNR, Via Risorgimento 35, 56126 Pisa, Italy

Maria Rosaria Tiné*

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

Vapor–liquid equilibria for a chloroalkane (1,2-dichloroethane or 1,1,1-trichloroethane) + a linear mono- or diether (diethyl ether, dipropyl ether, methyl butyl ether, 1,2-dimethoxyethane) or an acetal (diethoxymethane), were determined at 298.15 K by head-space gas chromatographic analysis of the vapor phase directly withdrawn from an equilibration apparatus. Excess Gibbs energies, activity coefficients at infinite dilution, and free energies of solvation were calculated for all the systems.

Introduction

As a continuation of our studies on the thermodynamic properties of binary mixtures containing oxaalkanes (*1–6*), we report in this work the results of vapor–liquid equilibrium (VLE) measurements, obtained by a head-space gas chromatographic technique, for binary mixtures of 1,2-dichloroethane + diethyl ether, + diethoxymethane, and + 1,2-dimethoxyethane and of 1,1,1-trichloroethane + diethyl ether, + dipropyl ether, + methyl butyl ether, + diethoxymethane, and + 1,2-dimethoxyethane. To the best of our knowledge, no VLE data for these mixtures have been reported in the literature.

Previously, we reported the excess Gibbs free energies for binary mixtures of linear ethers or acetals + tetrachloromethane (*4*), + dichloromethane, and + 1-chlorobutane (*5*). The purpose of this paper is to contribute to the study of the O–Cl interaction in organic mixtures, in particular, to point out the influence of the surroundings on the donor capacity of the oxygen atom and on the acceptor capacity of the chlorine atom, as well as the effect of the presence of two or more heteroatoms in the same molecule.

A detailed analysis in terms of DISQUAC (*7*), an extended quasichemical pseudolattice model, of the thermodynamic properties of mixing of the above indicated mixtures will be presented in a forthcoming paper.

Experimental Section

The head-space gas chromatographic (GC) analysis for measuring the vapor-phase mole fraction, y, as a function of the liquid-phase mole fraction, x, was employed. The apparatus is composed of an equilibration cell and a gas chromatograph (C. Erba 6000 Vega series), already described in detail elsewhere (*8*), and recently improved (*9*). The GC column was a 4 mm × 4 m stainless steel tube packed with different materials according to the various systems to be analyzed. Carbowax 20 M (C20M) on Chromosorb W 60–80, Porapak QS (PQS), Porapak N (PN), butanediol succinate (Lac 860), and Chromosorb 102 (C102) were employed in order to obtain a complete separation of the peaks.

All chemicals were products from Fluka or C. Erba of the best grade quality. They were used without further purification, and their purities, as checked by GC analysis, were 99.8 mass % for diethyl ether and 99.5 mass % for the other substances except methyl butyl ether, diethoxymethane, and 1,1,1-trichloroethane, which contained about 1% impurities. Thanks to the GC technique employed in determining the vapor composition, the amounts of impurities as large as those given above do not affect appreciably the goodness of the results.

All mixtures were prepared by weighing. The liquid mole fractions, x_i, after correction for buoyancy and for evaporation of constituents in the vapor space of the container, were evaluated to better than 0.0001. At least three vapor samples were analyzed for each given composition. All measurements were carried out at 298.15 K.

The values of vapor mole fraction, y_2, of the chloroalkane were obtained from

$$y_2 = 1/[1 + r_f/(A_2/A_1)] \qquad (1)$$

A_2/A_1 being the measured peak area ratio of the two components in the vapor phase and r_f the response factor of the chromatograph for the examined mixture. This latter is given by

$$r_f = (A_2{}^*/A_1{}^*)/(P_2{}^*/P_1{}^*) \qquad (2)$$

where $A_i{}^*$ is the measured peak area of vapor and $P_i{}^*$ the vapor pressure of the pure component i. The overall uncertainty in y_i, resulting mostly from the uncertainty in A_2/A_1, was generally less than 0.003. In the dilute regions, the y_i precision was better than 2% of the lowest y_i.

Data Treatment

The experimental A_2/A_1 values are related to the ratio of the experimental activity coefficients of the constituents, $(f_2/f_1)_{\text{exp}}$, according to

$$(f_2/f_1)_{\text{exp}} = (x_1/x_2)(A_2/A_1)(w_2/w_1)(P_1{}^*/P^*{}_2)(1/r_f) \qquad (3)$$

where, according to Scatchard and Ticknor (*10*),

$$w_i = \exp\left\{\frac{1}{RT}(B_{ii} - V_i{}^*)(P - P_i{}^*) + \frac{P}{RT}[d_{ij}\,y_j(1 - y_i) + d_{i3}\,y_3(1 - y_i)d_{j3}\,y_j\,y_3]\right\} \qquad (4)$$

P being the total pressure and

$$d_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (5)$$

Vapor-phase nonideality is calculated in terms of the second molar virial coefficients B_{ij} by taking into account the presence of air in the vapor phase assumed to be a three-component mixture, nitrogen being the third component (*8*). In Table I are

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[†] Part 1: Reference 8. This work is a contribution to the TOM (Thermodynamics of Organic Mixtures) Project (*7*).

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Table I. Vapor Pressure P_i^*, Liquid Molar Volume V_i^*, Second Molar Virial Coefficients B_{ii}, and Cross Molar Virial Coefficients B_{ij} at 298.15 K

compound	$10^{-3}P_i^*$/ Pa	$10^6 V_i^*$/ ($m^3\ mol^{-1}$)	$-10^3 B_{ii}$/ ($m^3\ mol^{-1}$)	$-10^3 B_{ij}^a$/ ($m^3\ mol^{-1}$)
1,2-dichloroethane	10.68[b]	79.46[b]	1.4[g]	
1,1,1-trichloroethane	8.64[c]	100.32[e]	1.5[g]	
diethyl ether	71.24[c]	104.72[f]	1.2[h]	1.0; 1.2
dipropyl ether	8.38[c]	137.68[f]	2.8[i]	1.4; 1.7
methyl butyl ether	18.51[c]	117.36[f]	1.9[i]	1.2; 1.4
diethoxymethane	8.97[c]	126.35[f]	2.8[i]	1.3; 1.5
1,2-dimethoxyethane	9.93[d]	104.54[f]	1.9[i]	1.0; 1.2
nitrogen			0.0[h]	0.1[j]

[a] Computed according to ref 10. The first quoted value refers to mixtures with 1,2-dichloroethane, the second one to mixtures with 1,1,1-trichloroethane. [b] Reference 12. [c] Reference 13. [d] Reference 14. [e] Unpublished result from our laboratory. [f] Reference 15. [g] Extrapolated from higher temperature data in ref 16. [h] Reference 16. [i] Estimated from B_{ii} values of related compounds in ref 16. [j] Reference 16. The same value applies for all mixtures of nitrogen (or oxygen) with listed substances.

collected the values of P_i^*, B_{ij}, and V_i^*, the molar volume of the pure liquids. Although most of the B_{ij} values used in the calculation are estimated and probably affected by large uncertainties, the w_i terms differ from 1 by less than 4% for all mixtures studied and partially compensate in the ratio w_2/w_1.

As a function representing the calculated activity coefficient ratio, $(f_2/f_1)_{\text{calc}}$, we have found convenient the Redlich–Kister equation with two parameters at most:

$$\ln (f_2/f_1)_{\text{calc}} = c_1(x_1 - x_2) - c_2(6x_1x_2 - 1) \qquad (6)$$

The coefficients c_m were obtained by a nonlinear least-squares procedure, similar to that described by Barker (*11*) for the treatment of P–x data. In our case, the objective function is

$$S = \sum_{k=1}^{n} [\ln (f_2/f_1)_{\text{exp}} - \ln (f_2/f_1)_{\text{calc}}]_k^2 \qquad (7)$$

the sum S extended over all n experimental points. The product $(P_1^*/P_2^*)(1/r_f) \equiv A_1^*/A_2^*$, appearing in eq 3, was treated as an adjustable parameter to be determined in the least-squares calculations. This is an important advantage of the present head-space GC technique for measuring VLE. In fact, neither the direct determination of the response factor r_f via calibration experiments nor the vapor pressures, P_i^*, are necessary for obtaining activity coefficients.

For the system diethyl ether + 1,2-dichloroethane, two different series of x–y measurements were carried out with different flow rates of the carrier gas. In this case, we used a least-squares method that was able to process data of different series altogether and to find a single set of c_m coefficients using two different r_f values.

Excess molar Gibbs energies, G^E, were calculated through the equation

$$G^E/RT = x_1x_2[c_1 + c_2(x_1 - x_2)] \qquad (8)$$

Results and Discussion

Table II. Experimental Vapor–Liquid Equilibrium Data, Liquid Mole Fraction x_2 and Vapor Mole Fraction y_2 for Binary Oxaalkane (1) + Chloroalkane (2) Mixtures at 298.15 K[a]

x_2	y_2	x_2	y_2	x_2	y_2
$(C_2H_5)_2O$ (1) + $C_2H_4Cl_2$ (2)[b]					
0.0448	0.0081	0.4545	0.1205	0.8064	0.3467
0.1323	0.0251	0.5107	0.1426	0.9053	0.5462
0.2334	0.0481	0.6196	0.2004	0.9721	0.8061
0.3385	0.0783	0.6917	0.2499		
0.0342	0.0061	0.5192	0.1429	0.8594	0.4539
0.1231	0.0237	0.6981	0.2503	0.9551	0.7170
$(CH_3OCH_2)_2$ (1) + $C_2H_4Cl_2$ (2)					
0.0380	0.0199	0.4135	0.3988	0.8188	0.8897
0.0839	0.0490	0.5290	0.5607	0.8954	0.9437
0.1942	0.1376	0.6297	0.6953	0.9668	0.9836
0.3188	0.2755	0.7109	0.7903		
$(C_2H_5O)_2CH_2$ (1) + $C_2H_4Cl_2$ (2)					
0.0808	0.0788	0.5068	0.5565	0.9082	0.9301
0.1863	0.1924	0.6293	0.6846	0.9546	0.9658
0.2748	0.2941	0.7310	0.7836		
0.3778	0.4133	0.8202	0.8595		
$(C_2H_5)_2O$ (1) + CH_3CCl_3 (2)					
0.0492	0.0053	0.4929	0.1115	0.8461	0.4365
0.1033	0.0123	0.5551	0.1422	0.9171	0.6007
0.2198	0.0311	0.6388	0.1940	0.9507	0.7273
0.3128	0.0509	0.7017	0.2389		
0.4105	0.0769	0.7758	0.3288		
$CH_3OC_4H_9$ (1) + CH_3CCl_3 (2)					
0.0484	0.0187	0.4355	0.2609	0.8195	0.7086
0.0966	0.0400	0.4889	0.3126	0.9072	0.8437
0.1722	0.0777	0.5815	0.4055	0.9544	0.9223
0.2593	0.1303	0.6626	0.4986		
0.3541	0.1879	0.7270	0.5789		
$(C_3H_7)_2O$ (1) + CH_3CCl_3 (2)					
0.0484	0.0455	0.3782	0.3784	0.7916	0.8055
0.1231	0.1165	0.4920	0.4986	0.8773	0.8896
0.2077	0.2014	0.5539	0.5615	0.9554	0.9612
0.2808	0.2762	0.6840	0.6978		
$(CH_3OCH_2)_2$ (1) + CH_3CCl_3 (2)					
0.0603	0.0416	0.4246	0.3778	0.8035	0.8102
0.1051	0.0755	0.5044	0.4617	0.8566	0.8709
0.1692	0.1275	0.5794	0.5506	0.9108	0.9197
0.2352	0.1846	0.6479	0.6270	0.9677	0.9738
0.3310	0.2812	0.7218	0.7175		
$(C_2H_5O)_2CH_2$ (1) + CH_3CCl_3 (2)					
0.0574	0.0447	0.4702	0.4471	0.8892	0.9076
0.1478	0.1218	0.5611	0.5513	0.9682	0.9777
0.2520	0.2171	0.6688	0.6738		
0.3628	0.3293	0.7836	0.8010		

[a] The y_2 values (which are consistent with P_i^* values in Table I) were obtained from eq 1 using the least-squares r_f values from Table III and experimental A_2/A_1 ratios. [b] The two sets of data were obtained under different chromatographic conditions (see text).

The experimental x–y quantities are collected in Table II. We preferred to report here the vapor mole fraction, y_2, from eq 1 instead of the more direct experimental quantity f_2/f_1 because of the wide use of y in practical applications. The c_m values are reported in Table III, together with the values of the response factor r_f obtained from the fitting (and from the P_i^* values in Table I) and the standard deviation s for the representation of $\ln (f_2/f_1)$. The s values did not exceed 0.03; the standard deviation of y_2, not reported in Table III, was usually less than 0.003. In the same table, the excess Gibbs energies for equimolar mixtures, G^E (x_1 = 0.5), as well as their standard deviations, are also reported. These latter values were calculated from the standard deviations of the c_1 coefficients and ranged from 2 to 8 J mol^{-1}. No more than two c_m coefficients were necessary for fitting data to the Redlich–Kister equation, which was found to be more appropriate than other equations such as Wilson or NRTL.

Figure 1 shows G^E for the mixtures examined. All systems exhibit negative deviations, with the exception of diethyl ether + 1,2-dichloroethane. The G^E curves are slightly asymmetrical with their extrema at $0.4 < x_1 < 0.6$. The behavior of the oxygen compounds in 1,1,1-trichloroethane is quite similar to that observed in tetrachloromethane (*4*). Mixtures involving dioxaalkanes (1,2-dimethoxyethane and diethoxymethane) have markedly lower G^E (x_1 = 0.5) than those containing diethyl ether.

Table III. Type of Gas Chromatographic (GC) Columns, Chromatographic Response Factor r_f, Coefficients c_m of Equation 6, Standard Deviations s for Representation of ln (f_2/f_1), and Excess Molar Gibbs Energy G^E at x_1 = 0.5 for Oxaalkane (1) + Chloroalkane (2) Binary Mixtures at 298.15 K

oxaalkane	GC column	r_f	c_1	c_2	s^a	$G^E(x_1=0.5)^b/(\mathrm{J\ mol^{-1}})$
1,2-dichloroethane +						
diethyl ether	C102	1.080^c 1.133	0.1971	−0.0807	0.020	122 ± 5
1,2-dimethoxyethane	C20M	0.960	−0.7604	−0.0401	0.020	−(471 ± 6)
diethoxymethane	C20M	0.918	−0.1877	−0.0665	0.006	−(116 ± 2)
1,1,1-trichloroethane +						
diethyl ether	PQS	2.352	−0.1625	−0.0583	0.021	−(101 ± 6)
methyl butyl ether	C20M	1.875	−0.2110	−0.0223	0.007	−(131 ± 2)
dipropyl ether	PN	1.669	−0.1089	0.0112	0.006	−(68 ± 2)
1,2-dimethoxyethane	Lac 860	2.093	−0.3025	0.0529	0.019	−(188 ± 5)
diethoxymethane	PN	2.157	−0.2956	0.0939	0.025	−(183 ± 8)

[a] $s = [\Sigma\{\ln (f_2/f_1)_{\mathrm{calc}} - \ln (f_2/f_1)_{\mathrm{exp}}\}^2/(n - p)]^{1/2}$, n being the number of experimental points and p the number of adjustable parameters. [b] Evaluated from eq 8. The quoted uncertainties are standard deviations and were calculated from the errors on c_1 coefficients. [c] The two r_f values of the quoted system are consistent with two different series of x–y data (see Table II) obtained under different chromatographic conditions. Both series of data are described by a single set of c_m parameters (see text).

Table IV. Activity Coefficients at Infinite Dilution f_i^∞ and Molar Gibbs Energies of Solvation ΔG_i°, Equation 9, of the Components of Binary Oxaalkane (1) + Chloroalkane (2) Mixtures at 298.15 K

component 1	component 2	f_1^∞	$-10^{-3}\Delta G_1^\circ/(\mathrm{J\ mol^{-1}})$	f_2^∞	$-10^{-3}\Delta G_2^\circ/(\mathrm{J\ mol^{-1}})$
diethyl ether	1,2-dichloroethane	1.32	14.39	1.12	18.82
diethoxymethane	1,2-dichloroethane	0.49	21.73	0.45	21.08
1,2-dimethoxyethane	1,2-dichloroethane	0.89	20.50	0.78	19.25
diethyl ether	1,1,1-trichloroethane	0.90	14.76	0.80	20.17
dipropyl ether	1,1,1-trichloroethane	0.83	18.30	0.79	19.92
methyl butyl ether	1,1,1-trichloroethane	0.89	20.09	0.91	19.18
diethoxymethane	1,1,1-trichloroethane	0.69	20.30	0.79	20.21
1,2-dimethoxyethane	1,1,1-trichloroethane	0.68	20.59	0.72	19.65

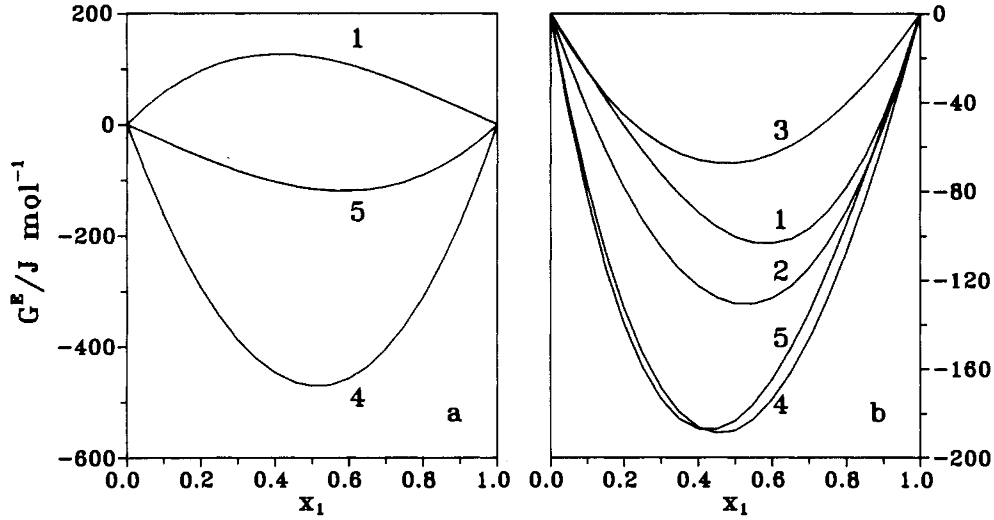

Figure 1. Excess molar Gibbs energies, G^E, at 298.15 K of oxaalkane (1) + chloroalkane (2) mixtures, against x_1, the mole fraction of the oxaalkane: (a) 1,2-dichloroethane and (b) 1,1,1-trichloroethane; (1) diethyl ether, (2) dipropyl ether, (3) methyl butyl ether, (4) 1,2-dimethoxyethane, and (5) diethoxymethane.

In Table IV are collected the values of the activity coefficients at infinite dilution f_i^∞ obtained from the c_m parameters (eq 6) as well as the molar Gibbs free energies of solvation, ΔG_i°, associated with the process component i(ideal gas, 1 mol dm^{-3}) → component i(solute obeying Henry's law, 1 mol dm^{-3}); these were obtained through the equation

$$\Delta G_i^\circ = RT \ln f_i^\infty + RT \ln (P_i^* V_j^* / RT) \qquad (9)$$

where V_j^* is the liquid molar volume of the solvent. The value for the standard process component (ideal gas, 101 325 Pa) → component(solute obeying Henry's law, at unit mole fraction) can be calculated as $RT \ln (f_i^\infty P_i^*/(101325\ \mathrm{Pa}))$. Pa)).

The linearity of a plot of ΔG_i° against the surface of the solute molecule shows that the observed ΔG_i° values can be reproduced by a simple scheme of group surface contributions (*5*) for both chlorinated solvents examined. The overall pattern of ΔG_i° for ethers here observed is consistent with that exhibited in tetrachloromethane, chloroform, dichloromethane, and 1-chlorobutane (*4*, *5*). The CH_2 contributions to ΔG_i° are similar (3 kJ mol^{-1}) in all solvents so far investigated, whereas the oxygen contribution in 1,2-dichloroethane (6 kJ mol^{-1}) is about twice as large as in 1,1,1-trichloroethane. Strong deviations from the additivity scheme are shown by dioxaalkanes.

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Glossary

A_i	peak area of component i in the vapor phase
A_i^*	peak area of vapor of pure component i
B_{ij}	molar second virial coefficient (i, j = 1, 2), m^3 mol^{-1}

c_m	coefficients of eq 6
f_i	activity coefficient of component i
f_i^∞	activity coefficient of component i at infinite dilution
G^E	excess molar Gibbs free energy, J mol^{-1}
ΔG_i°	Gibbs free energy of solvation of component i, J mol^{-1}
P_i^*	vapor pressure of pure liquid i, Pa
R	molar gas constant, 8.314 51 J mol^{-1} K^{-1}
r_1	response factor of gas chromatograph for a pair of component, eq 2
s	standard deviation of the fit
T	temperature, K
V_i^*	molar volume of pure liquid i, m^3 mol^{-1}
w_i	correction factor for component i, eq 4
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i

Subscript

i	component (i = 1, oxaalkane; i = 2, chloroalkane)

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Dipole Moments of Seven Refrigerants

Christopher W. Meyer* and Graham Morrison

Thermophysics Division, National Institute of Standards and Technology (Formerly National Bureau of Standards), Gaithersburg, Maryland 20899

Dielectric constant measurements have been performed on seven refrigerants in the gaseous state over the range 305–415 K in order to determine their dipole moments. Four of the refrigerants have temperature-independent moments: R123 (1,1-dichloro-2,2,2-trifluoroethane), μ = 1.356 ± 0.019 D; R141b (1,1-dichloro-1-fluoroethane), μ = 2.014 ± 0.018 D; R22 (chlorodifluoromethane), μ = 1.458 ± 0.003 D; and R32 (difluoromethane), μ = 1.978 ± 0.007 D. Two refrigerants have conformer-dependent moments, making their time-averaged moments temperature dependent: R114 (1,2-dichloro-1,1,2,2-tetrafluoroethane), with a moment ranging from 0.668 ± 0.001 D at 308 K to 0.699 ± 0.001 D at 410 K; and E134 (bis(difluoromethyl) ether), where the moment ranges from 1.739 ± 0.002 D at 309 K to 1.840 ± 0.001 D at 410 K. One refrigerant, R123a (1,2-dichloro-1,1,2-trifluoroethane), has a moment that in principle could be temperature-dependent but in fact is temperature-independent; its value is μ = 1.302 ± 0.007 D. Accurate determination of a molecule's temperature-dependent dipole moment requires an independent determination of its electronic polarizability; this determination has been made from index of refraction measurements. Where possible, the present results are compared with earlier determinations of dipole moments.

Introduction

This paper presents determinations of the dipole moments of seven molecules from dielectric constant measurements. The molecules are 1,1-dichloro-2,2,2-trifluoroethane (R123), 1,2-dichloro-1,1,2-trifluoroethane (R123a), 1,1-dichloro-1-fluoroethane (R141b), 1,2-dichloro-1,1,2,2-tetrafluoroethane (R114), chlorodifluoromethane (R22), difluoromethane (R32), and bis(difluoromethyl) ether (E134). Here, the names in parentheses are designations for halocarbons used by the refrigeration industry (*1*).

The current interest in these materials stems from the recent desire to know the thermophysical properties (the dipole moment has been used to interpret the value of equation of state parameters (*2*)) of alternative refrigerants. Two of the refrigerants (R32 and E134) have "zero" ozone depletion potential because they have no chlorine. R123, R123a, R141b, and R22 contain chlorine; however, they have shorter atmospheric lifetimes than the fully halogenated chlorofluorocarbons currently used as refrigerants (*3*). R114 is a fully halogenated chlorofluorocarbon that has been used as a blowing agent for foam packaging.

Of the seven refrigerants studied, four (R123, R141b, R22, and R32) have temperature-independent dipole moments. Three (R123a, R114, and E134) have temperature-dependent moments; we found, however, that the temperature dependence of R123a is too small to be determined. The temperature dependence results from the existence of nondegenerate internal-rotation conformers (*4*) that have different dipole moments.

Purity of Materials

The refrigerant R123 from Halocarbon Inc. (*5*) was 99.95 mol %, with the principle impurity water. R123a from Allied Signal Corp. (*5*) was 99.9 mol %, with the principle impurity R123. R141b from Pennwalt Co. (*5*) was 99.94 mol %, with the principle impurity $CF_3CH_2CF_2CH_3$. R22 from Racon, Inc. (*5*), was 99.9 mol %, with the principle impurity unknown. R32 from E. I. du Pont de Nemours & Co. (*5*) was 99.95 mol %, with the principle impurity unknown. R114 from Matheson Gas