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

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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

Products (*5*) was 99.9 mol %, with the principle impurity unknown. E134 from PCR Corp. (*5*) was 95 mol %, with the principle impurity CHF_2CH_2F. For E134 the purity was determined by gas chromatography (carrier gas/flow rate, He/(40 mL/min); column temperature, 50 °C; column, 60/80 carbopack, B/5% Fluorocol (10 ft, $^1/_8$-in. i.d.); and detector/current, TCD/100 mA). For the rest the purity listed is that claimed by the manufacturers. The refrigerants were additionally purified by freezing in liquid nitrogen, removing the volatile impurities with a mechanical pump, and thawing; this process was repeated several times.

Apparatus and Procedure

The dipole moments were determined from measurements of the dielectric constant ϵ of the refrigerants in the gaseous state at various temperatures and pressures. The measurements were performed with a capacitance cell such that $C = \epsilon C_0$, where C is the measured capacitance and C_0 is the capacitance under vacuum. The experimental arrangement has been described elsewhere (*6*). The resolution of the dielectric constant measurements was 3 ppm. The temperature T of the capacitance cell was controlled to within ±0.2 K and measured with a platinum-resistance thermometer having a specified accuracy of 10 mK. The pressure p was measured with a quartz pressure transducer having a range of 14 bar and a specified accuracy of ±0.07 mbar. The pressure values determined by the system were found to agree with those measured by a Bourdon tube gage to within ±0.1 mbar. The values of $\epsilon^* \equiv (\epsilon - 1)/(\epsilon + 2)$ as a function of temperature and pressure are listed in Table I.

The molar polarization P was determined as a function of temperature T. For the case of the molecules with temperature-independent dipole moments, the Debye equation was subsequently used to calculate the polarizability α and the dipole moment μ of the refrigerants from $P(T)$:

$$P = \frac{4}{3}\pi N_0\left[\alpha + \frac{\mu^2}{3kT}\right] = P_\alpha + P_\mu/T \qquad (1)$$

where N_0 is Avogadro's number and k is Boltzmann's constant. Equation 1 defines P_α and P_μ. For the molecules with temperature-dependent dipole moments, additional refractive index measurements were made to determine the electronic polarizability α_e from which estimations of P_α were made. Fluid density values necessary to obtain the electronic polarizability from refractive index measurements were furnished by Defibaugh and Morrison of NIST (*7*). The values of $\mu(T)$ were obtained from $P(T)$ and P_α through eq 1. Complete descriptions of all experimental and calculational procedures used have already been published (*6*).

Results

The values of the molar polarization as a function of temperature for the refrigerants with temperature-independent dipole moments are given in Table II. The uncertainties are 1 standard deviation in the least-squares fit to the capacitance data. Figure 1 shows $P-P_{calc}$ plotted vs $1/T$ for R123, where P_{calc} is the best fit line with slope 14871 ± 93 cm^3 K mol^{-1} and y intercept 21.9 ± 0.9 cm^3 mol^{-1}; the uncertainties are 1 standard deviation. The scatter is consistent with the uncertainties in the measurement of P. The slope and intercept yield $\mu = 1.356 \pm 0.019$ D and $P_\alpha = 21.9 \pm 0.9$ cm^3 mol^{-1}. We have found no previously reported measurement for R123.

Table III lists the values of the dipole moments determined for all the refrigerants with temperature-independent moments, along with the corresponding values of P_α. The fits of P to $1/T$ had scatter similar to that shown for R123. The values of $P_{\alpha e} \equiv 4\pi N_0\alpha_e/3$ as determined by the index of refraction measurements are also given in Table III.

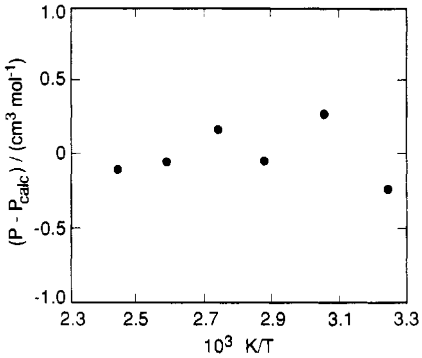

Figure 1. Deviation plot of $P-P_{calc}$ vs $1/T$ for refrigerant R123, where P is the molar polarization and P_{calc} is the best fit curve through the points ($P_{calc} = P_\alpha + P_\mu/T$, with P_α = 21.9 cm^3 mol^{-1}, and P_μ = 11200 cm^3 K mol^{-1}). The value of P_μ corresponds to a dipole moment of μ = 1.356 D.

Our result for the dipole moment of R141b is 2.014 ± 0.018 D. We have found no previous measurement of this moment with which to compare our value. Our result for R22 is 1.458 ± 0.003 D. Many previous measurements of this moment have been made. Kisliuk and Townes (*8*), Beeson et al. (*9*), and McLay and Mann (*10*) reported on Stark effect shift (spectroscopic) measurements; they obtained μ = 1.29 D, μ = 1.43 ± 0.02 D, and μ = 1.5 D, respectively. Dielectric constant measurements were performed by Smyth and McAlpine (*11*), Fuoss (*12*), and Sutter and Cole (*13*), who determined μ = 1.40 D, μ = 1.41 D, and μ = 1.48 ± 0.04 D, respectively. Our value is within the spread among these values and is in good agreement with those measurements for which uncertainties are provided. The dipole moment of R32 was measured by us to be μ = 1.978 ± 0.007 D, in excellent agreement with the Stark effect results of 1.96 ± 0.02 D by Lide (*14*) and of 1.9785 ± 0.0021 D by Kawaguchi and Tanaka (*15*).

Table IV lists the values of the molar polarization as a function of temperature for the refrigerants with temperature-dependent dipole moments, as well as the calculations of the effective dipole moments at these temperatures. Table V provides the results of the index of refraction and density measurements from which we determined $P_{\alpha e}$ and estimated P_α. For R114 an estimated value of $P_\alpha = 1.17P_{\alpha e}$ = 24.1 cm^3 mol^{-1} was used in the determination of the dipole moment. The value 1.17 for the ratio $P_\alpha/P_{\alpha e}$ is typical for that found in chlorofluorocarbons (see Table III in this paper and in ref 6).

Three previous determinations of the dipole moment of R114 have been made by using dielectric constant measurements. Boggs et al. (*16*), Magnuson (*17*), and Boggs and Deam (*18*) found μ = 0.46 D, μ = 0.533 ± 0.018 D, and μ = 0.56 D, respectively. However, all three groups evaluated the dipole moment by using the incorrect assumption that the moment of R114 was temperature-independent and determined its value without first estimating its polarizability. Their measurements of $P(T)$ agree well with ours; it is the different evaluation technique that is responsible for the discrepancy in the final result.

The temperature dependence of the moment of R114 is due to its multiple conformations. It can exist in either gauche (C_2) or trans (C_{2h}) conformations. The symmetrical trans conformer has no dipole moment and is more stable in the gas phase. As the temperature is increased, the population of the doubly degenerate gauche conformer, which has a nonzero moment, increases, resulting in an increasing dipole moment.

The measured dipole moment of R114 is related to the moments of the individual conformers by

$$\mu^2 = \frac{\mu_1^2 + \omega\mu_2^2 e^{-\Delta E/kT}}{1 + \omega e^{-\Delta E/kT}} \qquad (2)$$

Table I. Dielectric Constant as a Function of Temperature and Pressure

p/bar	$10^3\epsilon^*$	p/bar	$10^3\epsilon^*$	p/bar	$10^3\epsilon^*$	p/bar	$10^3\epsilon^*$	p/bar	$10^3\epsilon^*$	p/bar	$10^3\epsilon^*$
R123											
T = 307.6 K		T = 327.5 K		T = 348.0 K		T = 365.8 K		T = 387.0 K		T = 410.2 K	
0.0000	−0.001	0.0000	0.001	0.0000	−0.002	0.0000	0.001	0.0000	0.000	0.0000	0.000
0.2041	0.469	0.1965	0.407	0.2043	0.383	0.1976	0.345	0.2356	0.373	0.2491	0.361
0.4228	0.989	0.4176	0.875	0.4261	0.807	0.4208	0.731	0.3938	0.626	0.4262	0.619
0.5943	1.405	0.6051	1.280	0.5498	1.046	0.5981	1.045	0.5653	0.901	0.5436	0.793
0.7335	1.754	0.7759	1.654	0.7936	1.517	0.7333	1.288	0.8096	1.295	0.7661	1.122
0.4798	1.130	0.5900	1.250	0.5420	1.032	0.4891	0.858	0.6094	0.972	0.5182	0.756
0.4012	0.938	0.3491	0.734	0.4184	0.794	0.3313	0.576	0.4003	0.636	0.4078	0.593
0.2121	0.489	0.2093	0.439	0.2036	0.383	0.2019	0.350	0.2077	0.329	0.1905	0.275
0.0000	−0.004	0.0000	0.002	0.0000	−0.001	0.0000	−0.001	0.0000	−0.001	0.0000	0.001
R123a											
T = 308.2 K		T = 327.8 K		T = 349.4 K		T = 367.7 K		T = 387.0 K		T = 411.3 K	
0.0000	0.000	0.0000	0.001	0.0000	0.001	0.0000	0.000	0.0000	0.000	0.0000	0.000
0.2274	0.519	0.2500	0.517	0.2211	0.411	0.2259	0.389	0.2091	0.331	0.2036	0.296
0.4009	0.927	0.4100	0.853	0.4084	0.763	0.4053	0.700	0.3625	0.576	0.4433	0.645
0.5299	1.235	0.5814	1.218	0.5720	1.072	0.5917	1.026	0.5398	0.862	0.5716	0.835
0.7468	1.773	0.7208	1.518	0.7661	1.445	0.7468	1.299	0.7382	1.184	0.7483	1.094
0.5629	1.319	0.5671	1.188	0.5862	1.102	0.5402	0.936	0.5455	0.872	0.5698	0.832
0.4289	0.997	0.3921	0.814	0.3928	0.734	0.3987	0.689	0.3943	0.629	0.4209	0.611
0.2441	0.561	0.2035	0.420	0.2001	0.373	0.2048	0.353	0.2013	0.320	0.2133	0.309
0.0000	0.001	0.0000	0.000	0.0000	0.001	0.0000	0.002	0.0000	0.002	0.0000	0.001
R141b											
T = 308.6 K		T = 327.8 K		T = 348.3 K		T = 365.7 K		T = 387.1 K		T = 410.7 K	
0.0000	0.000	0.0000	0.000	0.0000	−0.001	0.0000	0.000	0.0000	0.000	0.0000	0.000
0.2160	0.869	0.2012	0.721	0.2405	0.772	0.2446	0.714	0.2163	0.574	0.1961	0.469
0.3950	1.604	0.3931	1.418	0.4162	1.334	0.4063	1.195	0.4327	1.154	0.4905	1.181
0.5792	2.379	0.5554	2.008	0.5807	1.867	0.5644	1.662	0.5424	1.446	0.5731	1.378
0.7227	2.991	0.7047	2.559	0.7159	2.310	0.7048	2.083	0.7242	1.940	0.6898	1.663
0.5881	2.410	0.4488	1.615	0.5511	1.778	0.4496	1.322	0.5592	1.497	0.5624	1.353
0.4166	1.687	0.3546	1.269	0.3313	1.066	0.3926	1.153	0.3976	1.062	0.3858	0.924
0.2103	0.841	0.2120	0.753	0.1858	0.595	0.2007	0.588	0.2035	0.543	0.2108	0.506
0.0000	−0.003	0.0000	−0.004	0.0000	0.001	0.0000	−0.002	0.0000	−0.001	0.0000	0.002
R114											
T = 308.4 K		T = 326.6 K		T = 348.5 K		T = 365.4 K		T = 388.5 K		T = 410.0 K	
0.0000	0.001	0.0000	0.000	0.0000	0.000	0.0000	0.000	0.0000	0.000	0.0000	0.000
0.5335	0.699	0.5194	0.634	0.5662	0.639	0.5068	0.539	0.5123	0.506	0.5205	0.481
1.0200	1.360	0.9818	1.211	0.9869	1.124	1.0340	1.108	0.9585	0.951	1.0364	0.964
1.5296	2.078	1.4206	1.769	1.4764	1.695	1.4806	1.596	1.4505	1.449	1.5483	1.448
1.8646	2.564	1.8763	2.370	1.8892	2.188	1.9297	2.101	1.8553	1.864	1.9435	1.824
1.5177	2.059	1.5057	1.886	1.4186	1.624	1.5145	1.635	1.5198	1.519	1.4554	1.358
1.0897	1.456	1.0828	1.342	1.0255	1.169	1.0755	1.154	1.0686	1.062	1.1153	1.037
0.5488	0.719	0.5686	0.696	0.5667	0.641	0.5224	0.556	0.5349	0.529	0.5129	0.474
0.0000	−0.001	0.0000	0.002	0.0000	0.001	0.0000	−0.001	0.0000	0.001	0.0000	0.001
R22											
T = 308.5 K		T = 326.3 K		T = 347.5 K		T = 366.3 K		T = 388.1 K		T = 407.9 K	
0.0000	0.000	0.0000	0.001	0.0000	0.001	0.0000	0.000	0.0000	0.000	0.0000	0.000
1.0195	2.265	1.0976	2.205	1.2856	2.311	1.2934	2.118	1.1051	1.633	0.9480	1.285
1.9897	4.487	2.2740	4.633	2.3197	4.215	2.0657	3.404	1.9921	2.965	2.1118	2.885
3.1060	7.120	3.0915	6.365	3.3114	6.074	2.9977	4.982	2.9906	4.479	3.1695	4.354
4.1292	9.625	3.9827	8.300	4.6432	8.647	4.1310	6.934	4.5388	6.873	4.2254	5.833
2.9123	6.652	3.0373	6.250	3.1693	5.803	2.9031	4.821	3.0478	4.569	3.0694	4.216
2.0929	4.720	2.0357	4.129	2.0671	3.740	2.0821	3.432	2.0616	3.070	1.7330	2.363
1.0615	2.357	1.4078	2.100	1.0930	1.968	1.0622	1.737	1.0173	1.507	0.9864	1.339
0.0000	0.000	0.0000	−0.002	0.0000	0.007	0.0000	0.001	0.0000	0.004	0.0000	0.002
R32											
T = 308.0 K		T = 326.4 K		T = 347.7 K		T = 366.2 K		T = 388.1 K		T = 410.7 K	
0.0000	0.001	0.0000	−0.001	0.0000	0.000	0.0000	0.000	0.0000	0.001	0.0000	0.000
1.1167	3.751	1.0879	3.280	1.1211	2.981	1.1257	2.712	0.9974	2.151	1.0190	1.972
1.9910	6.757	2.1763	6.614	1.9640	5.263	2.0466	4.956	2.0024	4.338	2.0668	4.015
3.0024	10.306	2.9899	9.155	3.0682	8.283	3.1254	7.617	3.3690	7.347	3.2755	6.397
4.3220	15.079	4.4685	13.866	4.1294	11.237	4.5976	11.309	4.2862	9.393	4.1114	8.057
2.9751	10.214	3.0657	9.391	3.0419	8.214	2.9274	7.123	2.9029	6.321	3.0584	5.969
1.9584	6.648	1.9928	6.047	2.0757	5.569	1.9909	4.817	1.9285	4.179	2.0341	3.953
1.0892	3.663	1.0698	3.225	1.0171	2.706	1.0439	2.511	0.9599	2.073	1.0639	2.061
0.0000	0.003	0.0000	0.009	0.0000	0.005	0.0000	−0.003	0.0000	0.005	0.0000	0.003
E134											
T = 309.2 K		T = 326.7 K		T = 347.1 K		T = 365.9 K		T = 386.8 K		T = 410.1 K	
0.0000	0.000	0.0000	0.000	0.0000	0.000	0.0000	0.001	0.0000	0.000	0.0000	0.000
0.5930	1.756	0.5578	1.513	0.4801	1.190	0.4512	1.027	0.5508	1.159	0.5072	0.975
0.9747	2.919	0.9992	2.738	1.0362	2.590	1.1278	2.598	0.9870	2.086	1.0274	1.987
1.4610	4.433	1.4272	3.949	1.4018	3.522	1.4954	3.458	1.4791	3.146	1.4824	2.883
1.8058	5.546	2.0122	5.647	1.8016	4.568	2.0224	4.718	1.8891	4.039	1.8246	3.561
1.4748	4.479	1.5272	4.242	1.4439	3.632	1.5385	3.564	1.4889	3.169	1.5157	2.947
1.0194	3.047	1.0582	2.904	1.0227	2.552	1.0579	2.432	0.9965	2.107	1.0400	2.012
0.5185	1.524	0.5616	1.526	0.5146	1.269	0.5106	1.167	0.5219	1.098	0.5230	1.006
0.0000	−0.005	0.0000	0.005	0.0000	0.005	0.0000	0.005	0.0000	0.002	0.0000	−0.002

Table II. Molar Polarization P for R123, R123a, R141b, R22, and R32 at Temperature T

T/K	P/(cm^3 mol^{-1})	T/K	P/(cm^3 mol^{-1})
	R123		
307.6	58.05 ± 0.10	365.8	52.66 ± 0.21
327.5	56.35 ± 0.20	387.0	50.76 ± 0.05
348.0	54.02 ± 0.13	410.2	49.08 ± 0.05
	R123a		
308.2	57.70 ± 0.15	367.7	52.42 ± 0.07
327.8	55.80 ± 0.05	387.0	50.87 ± 0.10
349.4	53.74 ± 0.07	411.3	49.34 ± 0.08
	R141b		
308.2	102.38 ± 0.27	365.7	88.53 ± 0.14
327.8	96.59 ± 0.32	387.2	85.45 ± 0.17
348.4	92.54 ± 0.18	410.7	81.51 ± 0.15
	R22		
308.5	56.00 ± 0.05	366.4	49.32 ± 0.02
326.2	53.64 ± 0.06	388.1	47.39 ± 0.04
347.5	51.30 ± 0.09	407.9	45.74 ± 0.04
	R32		
308.0	84.92 ± 0.05	366.3	72.80 ± 0.03
326.4	80.99 ± 0.05	388.1	69.30 ± 0.05
347.7	76.30 ± 0.04	410.8	65.82 ± 0.02

Table III. Temperature-Independent Dipole Moments

refrigerant	P_{α_e}/ (cm^3 mol^{-1})	P_α/ (cm^3 mol^{-1})	P_α/P_{α_e}	μ/D
R123	20.4	21.9 ± 0.9	1.07	1.356 ± 0.019
R123a	20.7	24.3 ± 0.3	1.17	1.302 ± 0.007
R141b	20.6	21.4 ± 1.2	1.04	2.014 ± 0.018
R22	11.2	14.0 ± 0.2	1.25	1.458 ± 0.003
R32	6.7	7.8 ± 0.5	1.16	1.978 ± 0.007

Table IV. Temperature-Dependent Dipole Moments: Dipole Moment as a Function of Temperature

T/K	P/(cm^3 mol^{-1})	μ/D
R114, P_α = 24.1 cm^3 mol^{-1} By Estimation		
308.4	32.91 ± 0.02	0.668 ± 0.001
326.6	32.71 ± 0.06	0.680 ± 0.001
348.5	32.40 ± 0.04	0.689 ± 0.001
365.4	32.04 ± 0.03	0.690 ± 0.001
388.6	31.72 ± 0.03	0.697 ± 0.001
410.0	31.35 ± 0.02	0.699 ± 0.001
E134, P_α = 14.9 cm^3 mol^{-1} By Estimation		
309.2	74.44 ± 0.12	1.739 ± 0.002
326.7	72.74 ± 0.04	1.761 ± 0.001
347.1	70.65 ± 0.15	1.783 ± 0.002
365.9	68.89 ± 0.08	1.801 ± 0.001
386.8	67.23 ± 0.02	1.823 ± 0.001
410.1	65.18 ± 0.02	1.840 ± 0.001

Table V. Results of Refractive Index Measurements

refrigerant	T/K	n_∞ (=0.990n)	$10^{-21}N$/ (molecules cm^{-3})	P_{α_e}/ (cm^{-3} mol^{-1})
R123	297.9	1.314	5.743	20.4
R123a[a]	303.2	1.313	5.647	20.7
R141b[a]	323.2	1.336	6.061	20.6
R114	297.6	1.280	5.118	20.6
R22	297.7	1.244	8.305	11.2
R32	297.7	1.183	10.601	6.7
E134[b]	302.8	1.230	6.908	12.7

[a] *Data from Chae et al. (20).* [b] *Data from J. Schmidt of NIST (21).*

where μ_1 and μ_2 are the dipole moments of the nondegenerate and degenerate conformers, respectively, and ΔE is the energy difference between the two conformers ($\Delta E = E_2 - E_1$). Here, $\omega = 2f_2/f_1$, where the factor 2 is due to the degeneracy. f_1 and f_2 are the vibrational and rotational partition functions of the nondegenerate and degenerate conformers, respectively (*4*). For the case of 1,2-dichloroethane it has been shown (*4*) that the value of ω varies from 1.90 at 300 K to 1.83 at 400 K.

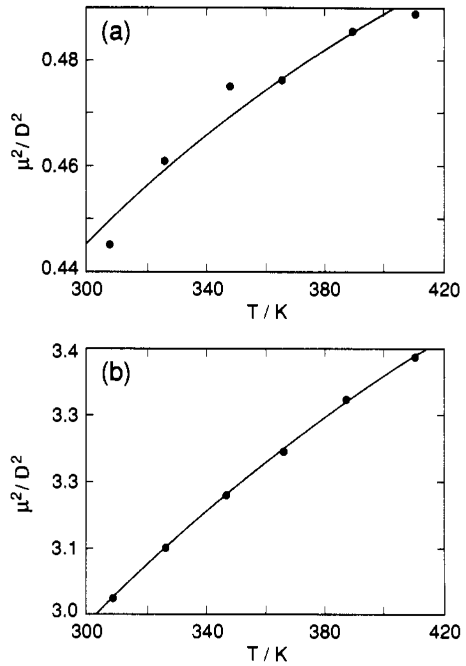

Figure 2. Square of the dipole moment of (a) R114 and (b) E134 as a function of temperature. The solid curves represent the best fit values using the functional form of eq 2 and assigning ω = 2.0 for R114 and ω = 1.0 for E134. For R114, μ_1 was assigned the value 0, and, for E134, μ_1 was a fitting parameter. For R114, the best fit parameter values are μ_2 = 0.96 D and ΔE = 1.9 kJ mol^{-1}. For E134, they are μ_1 = 1.20 D, μ_2 = 2.83 D, and ΔE = 2.98 kJ mol^{-1}.

We fit our measurements of $\mu(T)$ for R114 to the functional form of eq 2. Lacking data for the precise determination of ω we have used the approximation ω = 2.0. We found that use of this approximation adds only a small uncertainty (*6*). Figure 2a shows a plot of μ^2 against temperature for R114. The solid curve is a nonlinear least squares fit of the data to eq 2, while constraining the moment of the trans conformer μ_1 to be zero. The best fit values for the moment of the gauche conformer and the energy difference are μ_2 = 0.96 ± 0.03 D and ΔE = 1.9 ± 0.3 kJ mol^{-1}. This curve shows small but noticeable systematic deviations from the experimental results.

A measurement of ΔE for R114 has been made by using spectroscopic techniques. Kagarise (*19*), using infrared spectroscopic techniques, has measured the enthalpy difference between the trans and gauche conformers to be 2.09 ± 0.8 kJ mol^{-1}. This value agrees well with ours.

For E134 we estimated $P_\alpha = 1.17P_{\alpha e}$ = 14.9 cm^3 mol^{-1}. The values of μ versus temperature are listed in Table IV. We have found no previous dipole moment for this material. While the argument for temperature dependence in E134 is similar to that for R114, the situation is more complicated because E134 has nine separate conformers. Each methyl group in E134 has one conformer where the two fluorines are cis with respect to the other methyl and two where the two fluorines are gauche with respect to the other methyl. For the entire molecule there are four degenerate gauche–gauche conformers in the lowest energy state, four degenerate gauche–cis conformers in the middle energy state, and one cis–cis conformer in the highest energy state. As a first approximation one might estimate the energy of the highest energy state to be twice that of the middle energy state. Then, since the energy difference between conformer states is often 2.5–5.0 kJ mol^{-1} (this is the case for R114, as well as for (*6*) R134 and R143), the contribution of the highest energy term with respect to the lower energy terms in the partition function should be small (less than 3% at room temperature for 2.5 kJ mol^{-1}). By making this approximation one may relate the measured dipole moment to those of the two lowest energy conformers approximately by using eq 2 with $\omega = 1.0$ (since the degeneracy is the same in both states). In Figure 2b we plot μ^2 against T for E134 along with a best fit curve of the data to eq 2. The best fit parameters are $\mu_1 = 1.20 \pm 0.06$ D (gauche–gauche conformers), $\mu_2 = 2.83 \pm 0.04$ D (gauche–cis conformers), and $\Delta E = 2.98 \pm 0.2$ kJ mol^{-1}.

For R123a we initially estimated P_α and found $P_\alpha = 1.17 P_{\alpha e} = 24.2$ cm^3 mol^{-1}. We found that the dipole moment of R123a is $\mu = 1.302 \pm 0.007$ D and does not vary noticeably with temperature, although in principle it could because of the existence of nondegenerate conformers in its structure. Because of the constant value of the moment of R123a, we reevaluated the dipole moment using the method for temperature-independent moments and placed it in Table III.

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Diffusion Coefficient in Aqueous Polymer Solutions

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The diffusion coefficients for benzoic acid in a number of aqueous solutions of poly(vinyl alcohol) (3.0 and 6.0% polymer by weight) and poly(ethylene oxide) (0.75–3.5% polymer by weight) are reported. The diffusivity values are obtained by measuring the rate of mass transfer of benzoic acid from the surfaces of rotating disks. Data on solubility of benzoic acid in poly(ethylene oxide) are also reported. The diffusivities in the polymer solutions are found to be independent of shear rate and are lower than those in water.

Introduction

Studies on mass-transfer characteristics of highly viscous Newtonian and non-Newtonian polymeric fluids have assumed importance in recent years due to their application in several chemical and biochemical processes, like diffusion-controlled polymerization, fermentation processes, and the life processes of microorganisms, animals and plants, etc. The diffusion coefficient of the solute in the fluid is the prime factor which influences the rate of mass transfer in such systems. Fairly efficient predictive correlations are available for Newtonian fluids (*1*). But, apparently due to the very diverse nature of the polymeric solutions, until now, developing a totally predictive theory for diffusion in such systems appears to be a remote possibility. Therefore, it becomes essential to resort to experimental measurement of diffusivity in such systems. Considerable experimental information is available in the literature on the diffusivity of gases in non-Newtonian fluids (*2*). Such information on liquid and solid solutes is lacking.

Out of the various methods used by previous workers, the diffusion-cell, interferometric, membrane, polarographic, refractometric, and other stagnant-medium techniques are ineffective in showing the effect of shear rate, if any, on the molecular diffusivity in polymer solutions (*3*). Thus flow techniques like laminar jet (*4–7*), falling films and wetted walls (*8–10*), rotating cones, disks, and spheres (*11–21*), dispersion in flowing fluid stream (*22*), and dissolution during laminar flow along plates and through tubes (*3*, *23*, *24*) have been extensively used for the measurement of molecular diffusivity in polymer solutions. In many of these the experimental conditions were such that mass transfer occurred in a constant-velocity (or zero-shear) field (*4–10*). Consequently, the influence of shear rate on the molecular diffusivity could not be assessed from these studies. Remaining techniques (*11–24*), however, do indicate that the molecular diffusivities remain unaffected in a finite shear field.

Some of the flow techniques, which have been successfully used with gases, are unsuitable for solid solutes. The diffusivity of such solutes in polymer solutions has been determined either by laminar flow dissolution from inclined plates, rotating disks, and tubes or by laminar dispersion techniques. The rotating-disk technique offers several advantages over other techniques. It

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