Gas Chromatographic Measurements of Activity Coefficients at Infinite Dilution for Refrigerants with a Polyol Ester Oil as a Stationary Phase

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Activity coefficients at infinite dilution have been measured by gas chromatography for 14 refrigerants (R12, R22, R32, R124, R125, R134a, R142b, R143a, RE170, R236ea, R290, R600, R600a, and R236fa) as solutes, using a polyol ester oil (POE), EMKARATE by ICI, as a stationary phase (solvent). Instrumental analysis (NMR, IR) showed that the main components of the oil are pentaerithritol esters of carboxylic acids, and electrospray ionization spectrometry revealed an average molecular mass of the POE of 618 g·mol^{-1}. The measurements were performed within a temperature range of 244 K to 313 K, but a specific temperature range for each refrigerant was adopted depending on its retention data. The experimental findings are well-represented by the equation: $\ln \gamma_i^\infty = a_i - b_i/T$. Some refrigerants, i.e., R22, R124, R125, R236ea, and R236fa, show quite a considerable positive temperature dependence of their activity coefficients at infinite dilution, which can be attributed to hydrogen bonding with the POE, unlike other refrigerants that show a small, either positive or negative temperature dependence. To our knowledge, there are no data in the literature on activity coefficients at infinite dilution for refrigerant and oil (lubricant) systems, and details on the solubility of refrigerants in oils are also extremely scarce.

Introduction

Since the fundamental works of James and Martin (1952), Littlewood et al. (1955), and Pierrotti et al. (1956), gas chromatography has been widely applied to physicochemical measurements (Conder and Young, 1979), and, among other properties, activity coefficients at infinite dilution are probably the most frequently measured. A great advantage of the method is that a commercially available gas chromatograph (sometimes requiring minor modification) can be used as a basic instrument. In addition, a minute amount of the reagents, both solvents and solutes, are sufficient for the experiment and the solute need not have a high purity. Unfortunately, the method also has major limitations, the most important of which include the fact that a sufficiently large difference in the volatility of solvent and solute, a low saturated vapor pressure of the solvent, and its well-defined structure are conditions for accurate and reliable results. The limitation coming from the saturated pressure of the solvent can be disregarded for our systems because, within the temperature range of our experiments, the saturated pressure of the lubricant is below 1×10^{-5} Pa. The limitation coming from an ill-defined structure can be attenuated by interpreting the gas chromatography data in terms of relative, not absolute, quantity. What is essential is that, from gas chromatographic measurements, only one activity coefficient value (i.e. the value of the solute at infinite dilution) can be derived for a binary solute + solvent system. On the other hand, vapor−liquid equilibrium (VLE) data in the region of low solute concentrations in a system with a solvent of high molecular mass are very difficult to measure directly using a routine VLE setup.

The fluid-phase behavior of refrigerants and lubricants is an important property, for both modeling and engineering: the refrigerant's solubility in oil may produce a change of circulating composition in a circuit; the oil's volatility may influence the evaporation, condensation, and other parameters; and the refrigerant's solubility in oil strongly influences the viscosity in a compressor.

Unfortunately, papers (both experimental and theoretical) focusing on describing the phase behavior of refrigerants and lubricants have so far been scarce, and much of the experimental data are presented only in graphic form. Moreover, an analysis of the reported data shows that they mainly cover a concentration region rich in refrigerant, if the data are analyzed on a mole fraction basis.

Although the advantages of gas chromatography for measuring the fluid-phase behavior of systems with significant differences in saturated pressure are well-demonstrated, to our knowledge, that method was not explored for the refrigerants + lubricant systems.

As solutes, 14 technologically important refrigerants were studied.

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Theoretical Section

The procedure developed by James and Martin (1952), Littlewood et al. (1955), and Pierrotti et al. (1956) was applied with only minor modifications. The method adopted is similar to the one already described elsewhere (Stryjek and Luszczyk, 1978) and (Luszczyk and Stryjek, 1978), and in a series of contributions by Gmehling and co-workers (Gruber et al., 1998; only their most recent paper is quoted here); an important theoretical contribution on the simplification of the approach has recently been published (Orbey and Sandler, 1991).

Activity coefficients at infinite dilution were calculated from the following equation:

$$\gamma_i^{\infty} = RmT/jV_{\mathrm{r}}Mp_i^{\circ}\phi_i \tag{1}$$

where $R = 8.314\ 45$ is the universal gas constant (J·mol^{-1}·K^{-1}), T is the column temperature (K), m is the mass of solvent (stationary phase; g), M is the molecular mass of the solvent (g·mol^{-1}), V_{r} is the retention volume corrected to the column temperature (L), p_i° is the saturated pressure of the solute (kPa), ϕ_i is the fugacity coefficient at the saturated pressure, and j is the James−Martin coefficient which takes the pressure drop, p_{d}, through the chromatographic column, being defined

$$j = 1.5\frac{p_{\mathrm{d}}^{2} - 1}{p_{\mathrm{d}}^{3} - 1} \qquad p_{\mathrm{d}} = \frac{p_{\mathrm{inl}}}{p_{\mathrm{out}}} \tag{2}$$

where p_{inl} is the inlet pressure and p_{out} is the outlet pressure corrected according to the water vapor pressure, both in kilopascals.

The retention volume, V_{r} (L), was calculated from the equation

$$V_{\mathrm{r}} = F\,(t_{\mathrm{r}} - t_{\mathrm{o}})\left(\frac{p_{\mathrm{amb}} - p_{\mathrm{H_2O}}}{p_{\mathrm{amb}}}\right)\frac{T_{\mathrm{exp}}}{T_{\mathrm{amb}}} \times 10^{-3} \tag{3}$$

where t_{r} is the measured retention time extrapolated to the value corresponding to a sample size of nil (in fact, for most solutes the dependence of the retention time on the sample size was very small) and t_{o} is the gas hold-up retention time, both in minutes, F is the flow rate of the carrier gas (cm^3·min^{-1}), p_{amb} is the ambient pressure, $p_{\mathrm{H_2O}}$ is the saturated water pressure at ambient temperature, T_{exp} is the column temperature, and T_{amb} is the ambient temperature. The correction for the saturation of the carrier gas with water in the bubble flow meter, given by the second term on the right within parentheses, was based on the assumption of saturation.

The fugacity coefficient of the solute was calculated, in eq 1, with the Carnahan−Starling−De Santis (De Santis et al., 1976) equation of state using the coefficient values from the Huber et al. (1996) database, as recently described in detail elsewhere (Stryjek et al., 1998).

Experimental Section

Reagents. A list of the refrigerants and their structures is given in Table 1.

Polyol ester oil (POE) EMKARATE RL 32S, produced by ICI (batch no. F94/9728024), was used. Unfortunately, no information on the composition of the POE was available to us apart from a technical data sheet, because it is a blend of pentaerithritol esters of various carboxylic acids. NMR and IR spectrometric analysis confirmed its general chemical structure. Additional mass spectra, performed by the electrospray ionization (ESI) method using the Finnigan "Navigator" quadrupolar instrument at various nozzle potentials (9.10 × 10^4, 7.42 × 10^5, and 2.59 × 10^6 V), after recalibration with respect to dioctyl phthalate, enabled us to estimate an average molecular mass of the sample used as equating to 618 g·mol^{-1}, which was adopted for the subsequent calculation. Said value is close to the 610 (g·mol^{-1}) measured independently by Musso (1998). The average molecular mass value adopted here corresponds closely to the average structure $\mathrm{C(CH_2{-}CO_2{-}C_{\mathit{n}}H_{2\mathit{n}+1})_4}$ with $n \approx 6.6$.

Table 1. List of Refrigerants

refrigerant	structure	refrigerant	structure
R12	$\mathrm{CCl_2F_2}$	R143a	$\mathrm{CH_3{-}CF_3}$
R22	$\mathrm{CHClF_2}$	R290	$\mathrm{CH_3CH_2CH_3}$
R32	$\mathrm{CH_2F_2}$	R236ea	$\mathrm{CHF_2CHFCF_3}$
R124	$\mathrm{CHClFCF_3}$	R600	$\mathrm{CH_3CH_2CH_2CH_3}$
R125	$\mathrm{CHF_2CF_3}$	R600a	$\mathrm{(CH_3)_2CHCH_3}$
R134a	$\mathrm{CH_2FCF_3}$	R236fa	$\mathrm{CF_3CH_2CF_3}$
R142b	$\mathrm{CH_3CClF_2}$	RE170	$\mathrm{CH_3OCH_3}$

Apparatus. A gas chromatograph (HRGC 5300 Megaseries Carlo Erba) with a pneumatically operated sampling valve and an integrator was used. Subambient temperatures were obtained using Cryo 820 Fisons with liquid nitrogen as a cooling agent. We used helium as the carrier gas and a hot wire thermal conductivity detector. A precolumn before sampling valve was installed in the oven to avoid any temperature gradient along the GC column.

Temperature was controlled by the GC unit with the possibility of adjusting the required temperature to ±1 K; the exact temperature in the thermostatic cell was measured by the additional PT 100 (Ω) installed and was recorded by a data acquisition system (LABVIEW). We observed a stable temperature ± 0.1 K, and this is believed to correspond to the accuracy in the temperature measurements. Inlet and outlet carrier gas pressures were measured by a strain gauge with an accuracy of 1 kPa for the inlet pressure and 0.2 kPa for the outlet pressure.

The flow rate of the carrier gas was measured at ambient pressure by a standard bubble flow meter with an accuracy of ±0.5% of the reading.

Two copper columns (3 m long, 4 mm i.d.) were used, packed with Chromosorb W DMCS (80/100 mesh) coated with the POE as the stationary phase. The masses of the stationary phase were 2.016 g and 3.433 g, which correspond respectively to about 16% and 26% by mass in relation to the support.

Measurements were performed within a temperature range of 244 K to 313 K; however, a temperature range was selected for each solute to avoid very short and excessively long retention times leading to excessive errors.

Error Analysis. Since activity coefficient at infinite dilution is not a directly measured quantity, one of the crucial problems is the evaluation of the precision of the results and possible sources of systematic errors.

Here, the following assumptions were made that might contribute to systematic errors:

(a) The support is sufficiently loaded by the stationary phase, and results are not influenced by adsorption and diffusion phenomena (sufficient loading and the lack of adsorption are evident, while the results with various loads (16% and 26% by mass) are compared).

(b) The behavior of the carrier gas is ideal (helium at pressures ranging from 100 kPa to 200 kPa has a fugacity coefficient at a temperature ranging from 244 K to 313 K that is very close to 1).

Table 2. Activity Coefficient at Infinite Dilution of Refrigerants in POE

	T_{exp}/K	$V_{r,exp}$/L	$p_i°$/kPa	ϕ_i	$(\gamma_1^\infty)^*$	γ_1^∞	column[b]
R12	243.75	0.1297	102.71	0.9624	0.764	0.794	a
	244.35	0.1272	105.34	0.9617	0.764	0.794	a
	253.15	0.0925	150.40	0.9508	0.746	0.785	a
	254.25	0.0927	156.95	0.9493	0.742	0.782	a
	274.13	0.0918	317.54	0.9186	0.690	0.751	b
	292.25	0.0547	551.48	0.8847	0.710	0.802	b
R22	243.75	0.3910	167.94	0.9551	0.155	0.162	a
	244.35	0.3809	172.21	0.9543	0.156	0.163	a
	253.85	0.2545	251.72	0.9406	0.167	0.177	a
	254.25	0.2507	255.60	0.9400	0.168	0.179	a
	263.85	0.1726	363.29	0.9240	0.179	0.194	a
	264.35	0.1720	369.72	0.9231	0.179	0.193	a
	273.45	0.1148	502.61	0.9062	0.192	0.212	a
	274.13	0.2121	513.81	0.9048	0.185	0.204	b
	292.55	0.1099	895.70	0.8659	0.216	0.249	b
	313.55	0.0675	1552.58	0.8164	0.225	0.275	b
R32	243.75	0.0530	280.26	0.9487	0.685	0.722	a
	254.25	0.0396	422.88	0.9319	0.644	0.691	a
	274.13	0.0421	839.78	0.8930	0.569	0.637	b
	292.25	0.0264	1440.93	0.8510	0.558	0.655	b
R124	263.85	0.3638	112.87	0.9579	0.273	0.285	a
	264.35	0.3591	115.19	0.9573	0.274	0.287	a
	273.53	0.2334	164.89	0.9451	0.290	0.307	a
	274.13	0.3963	168.64	0.9443	0.301	0.319	b
	292.95	0.1984	323.99	0.9136	0.330	0.361	b
	313.55	0.1079	599.55	0.8728	0.362	0.415	b
R125	243.75	0.0640	233.89	0.9306	0.679	0.730	a
	253.85	0.0451	346.55	0.9101	0.684	0.752	a
	254.15	0.0452	350.44	0.9094	0.681	0.749	a
	274.13	0.0440	692.58	0.8617	0.660	0.766	b
	292.25	0.0253	1177.29	0.8126	0.716	0.881	b
R134a	243.75	0.1390	86.70	0.9693	0.845	0.871	a
	244.35	0.1357	89.18	0.9687	0.845	0.872	a
	253.85	0.0965	136.52	0.9574	0.812	0.848	a
	274.13	0.0890	302.78	0.9261	0.746	0.806	b
	292.25	0.0485	555.74	0.8904	0.794	0.892	b
R142b	263.85	0.1922	100.81	0.9641	0.579	0.601	a
	264.35	0.1914	102.86	0.9636	0.576	0.598	a
	273.57	0.1341	146.96	0.9531	0.561	0.589	a
	274.13	0.2377	150.05	0.9525	0.564	0.592	b
R142b	292.95	0.1294	287.15	0.9260	0.571	0.617	b
	313.55	0.0797	530.95	0.8900	0.554	0.622	b
R143a	243.75	0.0337	221.36	0.9376	1.363	1.454	a
	254.25	0.0260	329.42	0.9186	1.259	1.370	a
	274.13	0.0289	639.86	0.8758	1.088	1.242	b
	292.25	0.0190	1080.06	0.8307	1.035	1.246	b
R290	243.75	0.0766	171.56	0.9468	0.774	0.818	a
	244.35	0.0760	175.64	0.9459	0.767	0.811	a
	253.85	0.0582	250.57	0.9313	0.733	0.787	a
	254.25	0.0579	254.18	0.9306	0.734	0.788	a
	263.85	0.0450	353.41	0.9139	0.705	0.772	a
	264.35	0.0450	359.28	0.9130	0.702	0.769	a
	274.13	0.0622	489.34	0.8943	0.662	0.740	b
	292.25	0.0398	818.73	0.8561	0.651	0.760	b
R236ea	273.46	0.2939	79.22	0.9666	0.496	0.513	a
	292.85	0.2312	170.02	0.9425	0.538	0.571	b
	313.55	0.1195	341.06	0.9083	0.573	0.630	b
R600	273.46	0.1425	104.58	0.9601	0.773	0.805	a
	292.55	0.1420	203.72	0.9368	0.721	0.770	b
	313.55	0.0892	382.89	0.9045	0.685	0.758	b
R600a	263.85	0.1177	111.43	0.9567	0.856	0.894	a
	264.35	0.1158	113.57	0.9561	0.862	0.902	a
	273.40	0.0840	158.11	0.9448	0.835	0.884	a
	274.13	0.1522	162.22	0.9438	0.815	0.864	b
	292.55	0.0878	295.92	0.9160	0.816	0.890	b
	313.55	0.0588	535.64	0.8782	0.744	0.847	b
R236fa	273.05	0.1184	107.01	0.9568	0.872	0.911	a
	292.05	0.0610	220.68	0.9285	0.903	0.973	a
	292.65	0.1009	225.38	0.9275	0.920	0.991	b
	312.45	0.0339	428.67	0.8899	0.907	1.019	a
	313.55	0.0569	443.05	0.8876	0.934	1.052	b
RE170	243.75	0.3115	82.75	0.9737	0.395	0.405	a
	244.35	0.3257	85.03	0.9732	0.369	0.380	a
	253.85	0.2198	128.19	0.9639	0.379	0.394	a
	254.25	0.2177	130.32	0.9635	0.380	0.395	a
	263.85	0.1554	190.41	0.9523	0.379	0.398	a
	264.35	0.1552	194.05	0.9516	0.377	0.396	a
	274.13	0.1966	276.47	0.9384	0.370	0.394	b
	292.25	0.1115	497.02	0.9094	0.385	0.423	b

[a] $(\gamma_1^\infty)^*$ calculated with $\phi_i = 1$. [b] a and b columns with 2.016 g and 3.433 g of solvent, respectively.

(c) The stationary phase is not volatile (within the above-mentioned temperature range, the POE has a saturated pressure below 1×10^{-5} Pa at the highest temperature of our measurements, so it can be disregarded).

(d) The solute and carrier gas do not interact (the interactions between solute and carrier gas are usually disregarded as their contribution is also not so significant).

Within the same margin of error, we evaluated an uncertainty in the mass of the stationary phase as being within ±0.005 g. We assumed that all these contributions are no greater than ±1% of the activity coefficient values at infinite dilution.

The error contributions due to the uncertainties in inlet pressure, outlet pressure, and flow rate measurements, previously declared, were evaluated as corresponding to ±3% of the activity coefficient value.

Here, a further source of systematic error results from the reliability of the value adopted for the molecular mass of the stationary phase (POE), and, even assuming an uncertainty of ±10 g·mol^{-1} in the molecular mass, this leads to a maximum combined error in activity coefficients at infinite dilution no greater than ±5%. The authors are convinced that said value is definitely not underestimated.

Results and Discussion

The activity coefficients at infinite dilution were calculated from eqs 1 to 4, and the results are collected in Table 2.

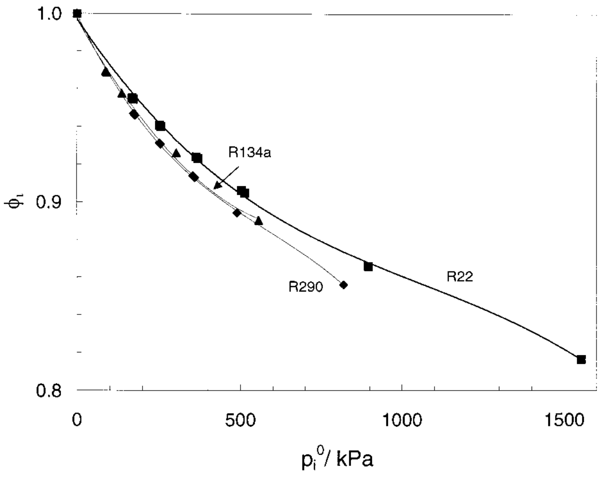

Figure 1. Course of fugacity coefficients for some refrigerants.

At low saturated pressure, eq 1 usually is simplified by setting $\phi_i = 1$. The activity coefficients at infinite dilution calculated with this assumption, $(\gamma_i^\infty)^*$, are included in Table 2 for comparison with γ_i^∞. For some refrigerants, by way of example, the ratio $(\gamma_i^\infty)^*/\gamma_i^\infty$, in fact equal to the actual value of ϕ_i, is also plotted in Figure 1. It is evident from the data that even at saturated pressures close to 100 kPa the difference between $(\gamma_i^\infty)^*$ and γ_i^∞ is

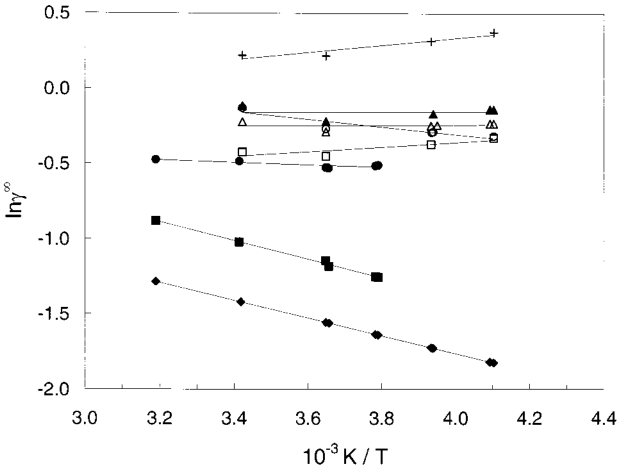

Figure 2. Activity coefficients at infinite dilution of methane and ethane fluoroderivatives: R12 (△), R22 (♦), R32 (□), R124 (■), R125 (○), R134a (▲), R142b (●), and R143a (+).

Table 3. Results of Fitting the Experimental Activity Coefficient at Infinite Dilution Data to Equation 4

refrigerant	a	$b \times 10^{-3}$	δ_{abs}
R12	−0.294 88	−13.50	0.012
R22	0.598 10	590.30	0.002
*R*32	−0.993 11	−159.11	0.013
R124	1.103 96	621.61	0.002
R125	0.693 54	249.45	0.016
R134a	−0.183 26	−7.66	0.018
R142b	−0.224 98	78.48	0.006
R143a	−0.628 39	−240.91	0.025
R290	−0.731 47	−125.86	0.009
R236ea	0.939 81	439.30	0.000
R600	−0.695 79	−129.69	0.005
R600a	−0.392 68	−73.97	0.009
R236fa	0.903 17	270.83	0.010
RE170	−0.579 21	89.13	0.007

still around a few percent, so clearly not negligible, and increases rapidly with increasing saturated pressures. It is clear that the values of the activity coefficient at infinite dilution thus derived will depend not only on the accuracy of the measurements but also on the model and saturated pressure data used for the calculation. To enable the reinterpretation of our results by readers adopting other models or assumptions, all the necessary information is contained in Table 2, as well as being reported in the text.

The experimental results from two chromatographic columns combined as one set were fitted to the equation

$$\ln \gamma_i^{\infty} = a_i - \frac{b_i}{T} \tag{4}$$

and findings are given in Table 3. The data representation for each refrigerant is good, as it is evident from Figures 2 and 3, where data for methane and ethane derivatives (Figure 2) and for C_{3+} and RE170—as a homomorph of propane (Figure 3)—are plotted. It could be also underlined that no systematic disruption of the results is coming from two columns; it confirms our assumption that the support in the two columns was loaded sufficiently by the solvent. Also, finding the overall absolute average deviation from the fit below 0.01 confirms our error analysis.

A few general comments can be drawn from observation of Figures 2 and 3 and an analysis of the values of the b_i coefficients of eq 4.

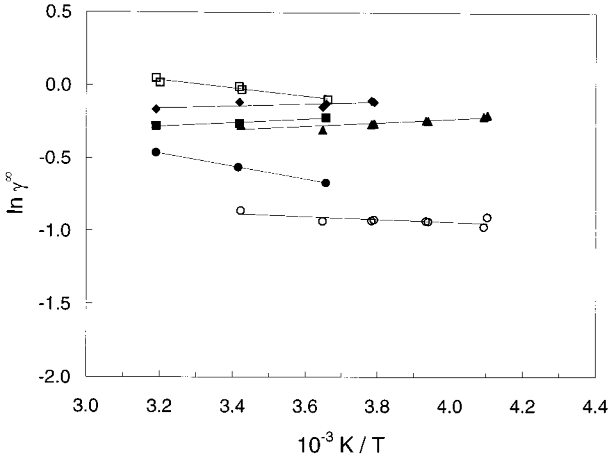

Figure 3. Activity coefficients at infinite dilution of C_{3+} and RE170: RE170 (○), R236ea (●), R290 (▲), R600 (■), R600a (♦), and R236fa (□).

The activity coefficients at infinite dilution of refrigerants R12, R32, R134a, R142b, R143a, R290, RE170, R600, and R600a with POE as the stationary phase show a small, either negative or positive, temperature dependence. Within this group, systems with R290, R600, and R600a show a very similar behavior and the slight difference may be attributed to the influence of differences in the size and shape of these hydrocarbons. The measured values result mostly from two opposite contributions to the actual activity coefficients, i.e., polar (POE) + nonpolar (hydrocarbon) being positive and size differences between low molecular mass hydrocarbons and high molecular mass POE being negative (a Flory−Huggins term). A systematically lower activity coefficient at infinite dilution for RE170 in POE result from polar + polar interaction, while the size and shape contributions are of magnitudes similar to those of the previous systems.

The results for R12, R32, R134a, R142b, and R143a are more complex to analyze; in addition to the above-mentioned interactions (all of them are polar, with a considerable differences in size with respect to POE), there are also strong repulsive forces between $-CF_3$, $-CF_2$ groups and the aliphatic chain of POE; in addition, information is currently lacking in the literature on the interactions of these groups with the ester group—thus observed values are resultant from all the interactions.

Qualitatively different behavior could be observed for the activity coefficient at infinite dilution values of the refrigerants R22, R124, R125, R236ea, and R236fa with POE. All of them increase with rising temperatures with clearly bigger temperature dependence values, and an analysis of the chemical structure of these refrigerants suggests that they have one or more active protons capable of H-bonding with the proton acceptor. In our opinion, said behavior is clearly due to the strong contribution of H-bonding (which decreases with rising temperatures) to the macroscopic property being measured. An interesting comparison emerges when the behaviors of two isomers, R236ea and R236fa, are considered. A much lower activity coefficient at infinite dilution of the former may result from the more active terminal proton in R236ea and, also, from the possible formation of two H-bondings by the R236ea molecule with two adjacent ester groups in the POE molecule; on the other hand, a potentially greater difficulty of R236fa in accessing the ester group may lower the strength of said bonding.

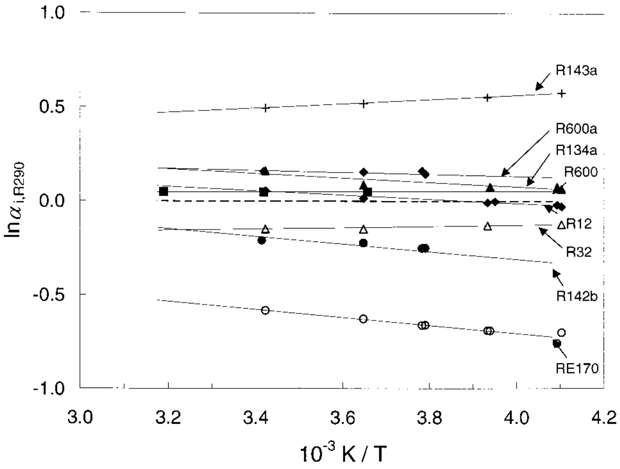

Figure 4. Relative activity coefficients at infinite dilution calculated with respect to R290 for non-H-bonding systems. Dotted line represents reference fluid.

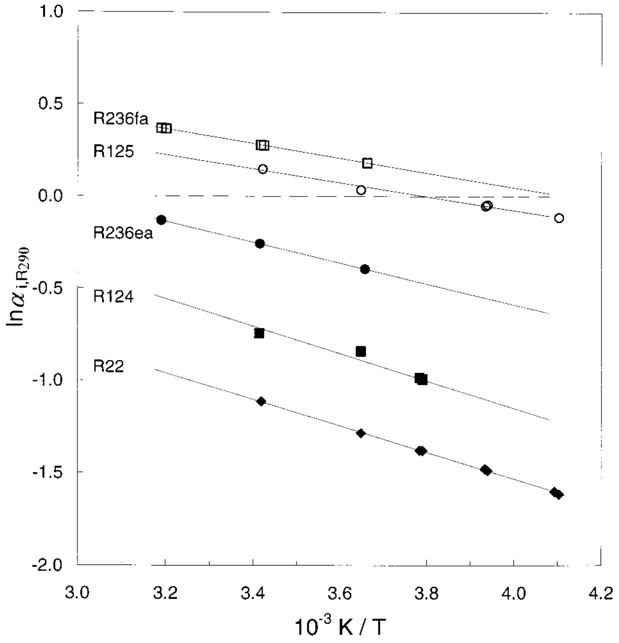

Figure 5. Relative activity coefficients at infinite dilution calculated with respect to R290 for H-bonding systems. Dotted line represents reference fluid.

To eliminate some sources of error in deriving activity coefficients at infinite dilution from the gas chromatography retention data, it is convenient to treat the data as relative, choosing one of the refrigerants as a reference. The advantage of said approach has been demonstrated elsewhere (Stryjek and Luszczyk, 1978) and (Luszczyk and Stryjek, 1978) and recently discussed in detail (Orbey and Sandler, 1991). In the present case, propane was selected as the reference refrigerant. The relative activity coefficients at infinite dilution, calculated using the following expression

$$\ln \alpha_{i,\mathrm{R290}} = \ln\left(\frac{\gamma_i^\infty}{\gamma_{\mathrm{R290}}^\infty}\right) \qquad (5)$$

are presented in Figures 4 and 5. Clearly, the refrigerants studied show two qualitatively different types of the $\alpha_{i,\mathrm{R290}}$ behavior: with a small, either negative or positive temperature dependence for R12, R32, R134a, R142b, R143a, R600, R600a, and RE170 (Figure 4) and with a more evident positive temperature dependence value for R22, R124, R125, R236ea, and R236fa (Figure 5). The former may be attributed to rather nonspecific intermolecular interactions between refrigerant and POE; for the latter, an important contribution also comes from the H-bonding, since all these refrigerants have proton donors in their molecule. This is consistent with reported VLE data on R22 + RE170 (Noles and Zollweg, 1992) and RE170 + R236fa (Bobbo et al., 1998), where a strong negative deviation from Raoult's law was attributed to H-bonding. Also, using NMR measurements, a strong H-bonding was reported between 1,*n*-pentadecafluoroheptane and typical donor acceptors (Alley and Scott, 1963).

Conclusions

Measuring activity coefficients at infinite dilution by gas chromatography can supply important information, contributing toward our understanding of the behavior of refrigerant + oil systems. From the analysis of the temperature dependence of the measured quantity, we were able to detect a specific intermolecular interaction that can be attributed to H-bonding. Said conclusion is consistent with the literature.

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