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Solubility of HFC32, HFC125, HFC152a, and HFC143a in Three Polyols

Satya S. Yelisetty and Donald P. Visco, Jr.*

Department of Chemical Engineering, Tennessee Technological University, Cookeville, Tennessee 38505

The solubility of a blowing agent in a polyol plays an important role in determining the overall quality of the polyurethane foam. For many years, concerns have been raised about the high ozone depleting potential (ODP) of traditionally used blowing agents such as chlorofluorocarbons and hydrochlorofluorocarbons. To this end, hydrofluorocarbons (HFCs) have been identified to be long-term replacements as the future blowing agents. In this study, we chose four HFCs, namely, HFC-125 (1,1,1,2,2-pentafluoroethane), HFC-152a (1,1-difluoroethane), HFC-143a (1,1,1-trifluoroethane), and HFC-32 (difluoromethane), and measured their solubilities in three polyols, namely, Pluracol 975, Pluracol 355, and Terol 352, using a degassed vapor pressure apparatus. Results indicate that there is a prominent effect of the structure of the blowing agent molecule and the functionality of the polyol on the solubility. HFC152a showed good solubility in Pluracol 975 and Pluracol 355, whereas all blowing agents showed limited solubility in Terol 352. In general, the least soluble blowing agent was HFC-143a. The experimental results have been correlated with the Sanchez−Lacombe equation of state, which was able to describe the polyol + blowing agent systems well.

Introduction

Polyurethane foams are one of today's most widely used plastic foams. Because polyurethane foams come in a wide range of flexibility, density, and stiffness, they are utilized in a variety of domestic and industrial applications.[1] Polyurethane foams are made by reacting a di-isocyanate molecule with a polyol in the presence of a blowing agent. A gas is produced in the liquid system, and it grows and is stabilized by added surfactants, with bubbles merging together to form cells.[2] Blowing agents are gaseous or liquid compounds that provide cellular structure to the foam, and a good blowing agent is considered to have considerable solubility in the polyol. Because of properties such as low combustibility, low diffusivity, and low toxicity, chlorofluorocarbons like CFC-11, CFC-12, and CFC-114 were the compounds traditionally used to make polyurethane foams. However, because of their ozone-depleting impact on the environment, the Montreal Protocol of 1987[3] called for total phase out of such compounds. Hydrochlorofluorocarbons were suggested as interim substitutes for CFCs,[4] but because of their nonzero ODP, these compounds are also to be completely phased out by 2030.

In addition to environmental concerns, the solubility of the blowing agent in the polyol is an important criterion in selecting a compound for blowing agent applications. The degree of foaming and cellular structure are all largely controlled by the solubility.[5]

To select proper blowing agent + polyol pairs, it is instructive to utilize thermodynamic models to predict relevant properties, such as solubility. In this way, information gleaned from modeling can be used to direct compound selection. To evaluate the available models, we need to assess them relative to experimental solubility data for systems of interest. Unfortunately, very limited experimental solubility data is available in the literature for blowing agent + polyol systems. To this end, we have chosen four HFC blowing agents and three representative polyols used in industry and have experimentally determined the solubility of each of these blowing agents in the three polyols. The blowing agents selected were HFC125 (1,1,1,2,2-pentafluoroethane), HFC152a (1,1-difluoroethane), HFC143a (1,1,1-trifluoroethane), and HFC32 (difluoromethane), whereas the polyols chosen were commercially available and were Pluracol 975, Pluracol 355, and Terol 352. Experiments were performed using a degassed vapor pressure apparatus on the basis of the principle of the pressure decay method[5−8] and were designed in house. The experimental results were correlated with the Sanchez−Lacombe[9] equation of state (SL EOS) partially on the basis of parametrizations that were previously performed by our group.[10] To the best of our knowledge, only Decaire et al.[5] have provided experimental work on one set of systems, namely, the solubility of the four blowing agents in Pluracol 975.

Experimental Section

Materials. Blowing agents studied in this work along with their relevant properties are listed in Table 1, whereas relevant properties of the polyols studied are summarized in Table 2. Honeywell provided the blowing agents used in this study, Pluracol 975 and Pluracol 355 were provided by BASF, and Terol 352 was supplied by Oxid.

Pluracol 975 is a polyether-based sucrose polyol. It is a light-colored, viscous fluid with a functionality of 4.3. Pluracol 355 is a clear, amine-based tetrol with a low equivalent weight and a functionality of 4.0. It has wide applications in flexible, semiflexible, and rigid foams. Terol 352 is an aromatic polyester polyol with a functionality of 2.0. Generally, Terol 352 is mixed with a polyether polyol for use in PUR (polyurethane) spray foam system.

The functionality, *f,* of a polyol (presented in Table 2) is a measure of the average number of hydroxyl groups per molecule of the polyol and can be calculated using eq 1

$$f = \frac{(\mathrm{OH})(\mathrm{MW})}{(56.1)(1000)} \tag{1}$$

where OH is the hydroxyl number of the polyol and MW is the molecular weight of the polyol.

Apparatus. The degassed vapor pressure apparatus used in this study is shown in Figure 1. The design is inspired by the

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* Corresponding author. E-mail: dvisco@tntech.edu.

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Table 1. Relevant Properties and SL EOS Parameters of Blowing Agents Studied in This Work[a]

compound	HFC125 1,1,1,2,2-pentafluoroethane	HFC152a 1,1-difluoroethane	HFC143a 1,1,1-trifluoroethane	HFC32 difluoromethane
molar mass/(g·mol^{-1})	120.03	66.06	84.05	52.02
molecular formula	CHF_2CF_3	CHF_2CH_3	CF_3CH_3	CH_2F_2
P^{Sat}(293.15 K)/MPa	1.11	0.52	1.11	1.38
T^{Sat}(0.1 MPa)/K	224.65	248.65	225.55	221.45
purity	99.50 %	99.90 %	99.90 %	99.90 %
P^*/MPa	378.04	495.66	384.27	630.09
T^*/K	309.12	356.06	325.55	336.55
ρ^*/(kg·m^{-3})	1971.36	1268.11	1448.59	1447.08

[a] All blowing agent data are provided by the manufacturer, Honeywell.

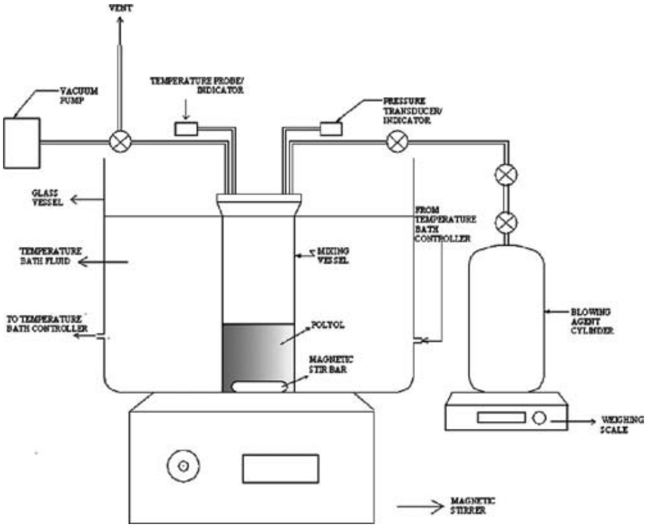

Figure 1. Degassed vapor pressure apparatus used to measure the solubility of the blowing agents in the polyols.

Table 2. Molar Mass, Density (ρ), Functionality (*f*), Viscosity (η), and SL EOS Parameters of Pluracol 975, Pluracol 355, and Terol 352

compound	Pluracol 975	Pluracol 355	Terol 352
molar mass/(g·mol^{-1})	600	500	325.7
ρ(298.15 K)/(kg·m^{-3})	1086.73	1006.97	1233
hydroxyl number/mg KOH per g polyol (functionality, *f*)	390 to 410 (4.3)	435 to 471 (4.0)	335 to 365 (2.0)
η(298.15 K)/(Pa·s)	4.5	2.7	3.0
P^*/MPa	397.07	397.51	577.17
T^*/K	565.81	650.30	745.26
ρ^*/(kg·m^{-3})	1178.55	1097.66	1285.69

apparatus used by Decaire et al.[5] The setup consists of four components: (1) mixing vessel, (2) blowing agent charging system, (3) vacuum application system, and (4) temperature bath. An 1108 series 342 mL oxygen bomb from Parr Instruments was redesigned to be used as the high-pressure mixing vessel. The lid of the oxygen bomb was modified to accommodate openings for the temperature probe, pressure transducer, blowing agent inlet line, and vacuum application line.

The vessel was kept inside an 18 L cylindrical glass container filled with about 8 L of ethylene glycol as the temperature bath fluid. Constant temperature was maintained using an Endocal RTE series refrigerated circulating bath. An Edwards E2M2 pump was used to apply vacuum to the vessel. Temperature inside the vessel was monitored using an RTD probe (part no. S603PD47Z36T) and controller system (part no. CT15021) from Minco. Pressure was monitored using MKS model 750 absolute single-ended pressure transducer (part no. 750B14TCD2GA) along with MKS model 660 single-channel power supply/digital readout (part no. 660B10). A super magnetic stirrer from Fauske & Associates LLC was used to maintain constant stirring inside the pressure vessel. The stirrer was specially designed to stir highly viscous fluids in thick containers. A 1.5 in. long, $^3/_8$ in. diameter cylindrical Neodymium magnet from K&J Magnetics was used as the stir bar. The magnet was coated with Teflon to reduce friction.

We calculated the amount of blowing agent sent in to the pressure vessel by measuring the blowing agent cylinder before and after sending the gas using a Sartorius GW6202 weighing scale with a resolution of 0.01 g.

Error Analysis. Because the solubility is not a directly measured quantity, various factors contribute to the precision of the solubility results. Uncertainty contribution from the weighing scale toward the mass of the blowing agent delivered to the mixing vessel was ± 0.014 g. Uncertainty in the pressure measurement was ± 1 % of reading. The uncertainty in each experimental run was propagated to get the uncertainty in each solubility result, and the maximum uncertainty was found to be ± 6 %.

Procedure. Solubility measurements by the pressure decay method were based on calculating the amount of blowing agent added to the mixing vessel, corrected for the amount of blowing agent vapor present in the overhead space and the supply lines of the vessel.

A known amount of polyol, approximately 100 g, was weighed in the mixing vessel containing the magnetic stir bar. The lid installed with the pressure transducer, temperature probe, vacuum supply line, and blowing agent supply line was then placed on the mixing vessel and tightly clamped using an outer leak-proof ring. Vacuum was applied for (10 to 12) h with constant stirring to degas the overhead space in the mixing vessel. Vacuum was applied until the pressure inside the vessel reached a minimum and was constant for about (4 to 5) h. We then added the blowing agent to the vessel by connecting the supply hose to the blowing agent cylinder. We calculated the amount of blowing agent added to the vessel by measuring the cylinder mass before and after delivering the blowing agent. As soon as the blowing agent was added, the pressure inside the vessel reached a maximum and gradually decreased as the blowing agent dissolved in the polyol. Pressure readings were taken after the system reached equilibrium, which was indicated by a constant pressure reading for at least 3 h. Each experimental run took about (50 to 60) h to equilibrate. Constant temperature and stirring at 70 to 80 rpm was maintained throughout the process. We determined the amount of blowing agent dissolved in the polyol by subtracting the amount of blowing agent present in the vapor phase from the total amount of blowing agent added to the vessel. This calculation included the application lines and the volume of the temperature probe and the stirring bar. Because NIST provided a precise equation of state for all of the blowing agents over a wide range of temperature and pressure, it was used to calculate the mass of blowing agent

Table 3. Mole Fraction (*x*) of HFC125, HFC152a, HFC143a, and HFC32 in Pluracol 975, Pluracol 355, and Terol 352 at 298.15 K

	Pluracol 975		Pluracol 355		Terol 352	
solute	*P*/MPa	*x*	*P*/MPa	*x*	*P*/MPa	*x*
HFC125	0.092	0.120	0.122	0.141	0.287	0.084
	0.148	0.165	0.250	0.318	0.367	0.111
	0.423	0.316	0.420	0.453	0.530	0.157
HFC152a	0.088	0.171	0.053	0.100	0.125	0.098
	0.159	0.287	0.109	0.203	0.204	0.171
	0.238	0.402	0.187	0.320	0.283	0.238
HFC143a	0.289	0.227	0.171	0.126	0.226	0.072
	0.428	0.303	0.310	0.208	0.353	0.102
	0.528	0.322	0.460	0.306	0.602	0.138
HFC32	0.108	0.200	0.162	0.176	0.172	0.157
	0.205	0.310	0.329	0.363	0.355	0.295
	0.276	0.371	0.391	0.413	0.474	0.337

present in the vapor phase on the basis of this volume. Once the mass of blowing agent dissolved in the polyol was determined, this was converted to a mole fraction using the molecular weight. The process was repeated with additional blowing agent to determine the solubility at higher pressure.

In the above calculations it is important to consider the polyol swelling as the polyol absorbs the blowing agent. As the polyol swelled, this reduced the volume of the vapor space available and, accordingly, affected the calculated solubility. To this end, we have utilized the SL EOS to account for this swelling following the procedure of Sato et al.[11]

Theoretical Section

The SL EOS[9] is used in this study to obtain the theoretical solubility of blowing agents in polyols. Equations of state provide a convenient way to obtain PVT relationships of polymer/gas systems. Pure component parameters for each component are obtained by fitting EOS predictions to experimental PVT data (for the polyols) and experimental VLE data (for the blowing agents). Corresponding mixing rules are used to predict the binary mixture (polyol + blowing agent) properties. For the polyol/blowing agent binary system, it is assumed that the polymer is nonvolatile such that the vapor phase contains only the blowing agent, and the liquid phase is a mixture of polyol + blowing agent.[11,12] At constant temperature and pressure, thermodynamic equilibrium is achieved when the chemical potential of the blowing agent (denoted BA in eq 2) in the vapor phase and the liquid phase are equal.

$$\mu_{\mathrm{BA}}^{V} = \mu_{\mathrm{BA}}^{L} \tag{2}$$

The SL EOS, which is often characterized as a lattice fluid theory, consists of a lattice in which each cell can accommodate a segment of a chain or a single molecule.[13] The SL EOS incorporates holes/vacant sites in the lattice to account for entropy change with temperature and volume.

The mathematical form of the EOS is given as

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] \tag{3}$$

where $\tilde{P} = (P)/(P^*)$ is the reduced pressure, $\tilde{\rho} = (\rho)/(\rho^*)$ is the reduced density, and $\tilde{T} = (T)/(T^*)$ is the reduced temperature of the system. The system parameters are P^*, T^*, and ρ^*, where P^* is the characteristic pressure, T^* is the characteristic temperature, and ρ^* is the characteristic bulk density, whereas, r is the characteristic fluid chain length, which is a function of the other three parameters.

For the four blowing agents and three polyols used in this work, we use pure component parameters based on parametrizations previously reported.[10] A more detailed description of the methodology employed in the parametrizations are contained in that work. However, the current parameter set used in this work is slightly different than that reported, so we provide this information in Tables 1 and 2 for completeness.

Very often, mixture predictions require binary interaction parameters to best correlate the data. For the binary systems in this work, the following combining rules are used to model the phase equilibrium properties[11,13]

$$P_{ij}^{*} = (1 - k_{ij})\left(P_i^{*} P_j^{*}\right)^{0.5} \tag{4}$$

$$P^{*} = \sum_i \sum_j \Phi_i \Phi_j P_{ij}^{*} \tag{5}$$

Here P_i^* and P_j^* are the pure component parameters, whereas k_{ij} is the binary interaction parameter. Φ_i is the segment fraction of component i. The predictive ability of the EOS is determined by the extent of deviation of k_{ij} from zero. Note that because the EOS is being used to determine polyol swelling, which in turn affects the vapor space volume available and, ultimately, the experimental measurement of solubility, optimization of k_{ij} to minimize the deviation between EOS-predicted solubility and experimental solubility is required. The objective function, OBJ, we use is as follows

$$\mathrm{OBJ} = \sum_{i=1}^{3}\left(\frac{x_{i,\mathrm{SLEOS}} - x_{i,\mathrm{EXPTL}}}{x_{i,\mathrm{EXPTL}}}\right)^2 \tag{6}$$

Results and Discussion

All solubility measurements were made at 298.15 K. The experimental solubility results for the four HFCs in the three polyols are tabulated in Table 3. For each polyol + blowing agent system, solubility measurements were taken at three equilibrium pressures. Of the systems examined in this work, only the blowing agents in Pluracol 975 have been previously experimentally studied, and our work compares favorably to those results.[5]

Solubility results for the four HFCs in the three polyols along with the correlations from the SL EOS are presented in Figures 2, 3, and 4, where the mole fraction of the blowing agent in the polyol is plotted against the pressure in MPa. The effect of swelling of the polyol was accounted for through the EOS. This swelling effect was almost always under 10 % in volume of the polyol for the systems and states examined, with the maximum change in solubility by including polyol swelling under 0.01 in mole fraction.

HFC152a was most soluble in all of the polyols, whereas HFC143a exhibited the poorest solubility in all of the polyols tested. The maximum solubility observed was HFC 152a in both Pluracol 355 and Pluracol 975, indicating its potential to produce polyurethane foam. In general, HFC32 was more soluble in the polyols than was HFC125, especially for both Pluracol 975 and Terol 352.

Hydrogen bonding plays an important role in determining the degree of solubility of the blowing agents in the polyols.[10,14] As all of the blowing agents studied in this work are polar in nature, they tend to form hydrogen bonds with the hydroxyl groups in the polyol when brought in contact with the polyol molecules. The degree of hydrogen bonding of a blowing agent molecule with a polyol molecule can be attributed to its structure. According to Takada et al.,[14] hydrogen bonding is higher for the blowing agents that have a $\mathrm{CHF_2}$ group in their structure. The fluorine atoms in the $\mathrm{CHF_2}$ group reduces the electron density of the adjacent hydrogen atom nearby, thereby

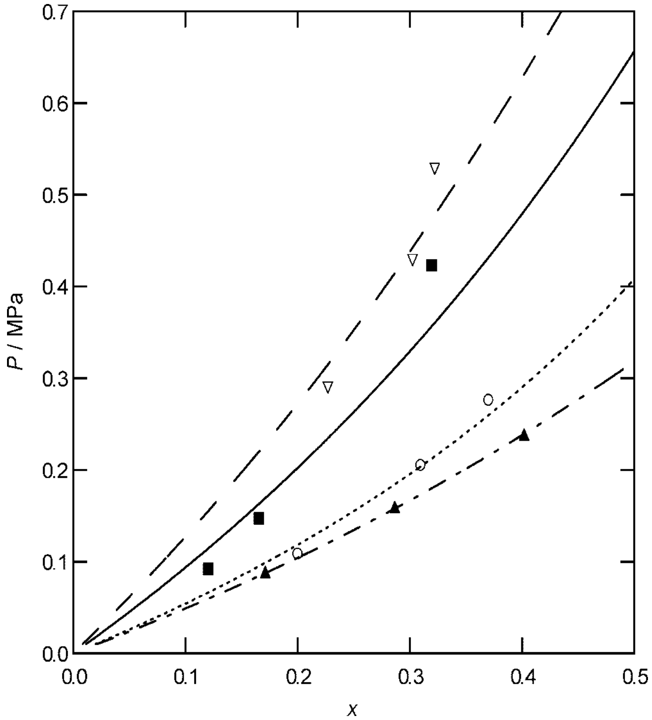

Figure 2. Experimental (symbol) and SL EOS (lines) calculated pressure versus mole fraction for (■, —), HFC125; (▲, •—•), HFC152a; (▽, — — —), HFC143a; and (○, •••), HFC32 in Pluracol 975 at 298.15 K.

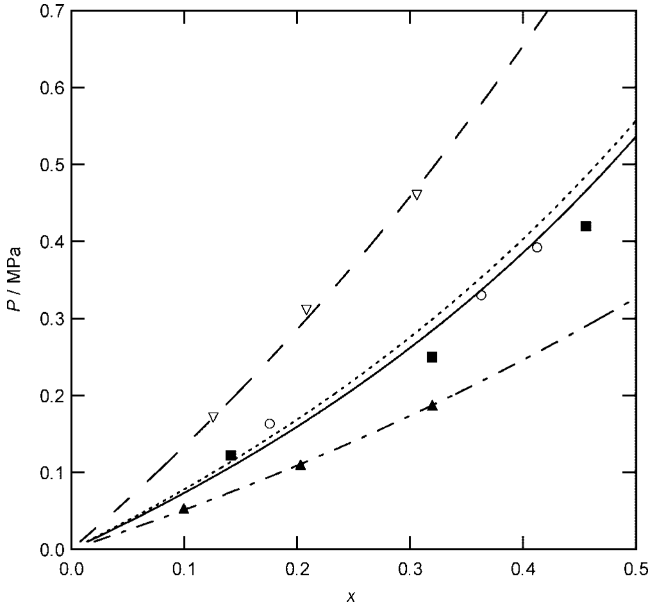

Figure 3. Experimental and SL EOS calculated pressure versus mole fraction for HFC125, HFC152a, HFC143a, and HFC32 in Pluracol 355 at 298.15 K. Symbols and lines same as those in Figure 2.

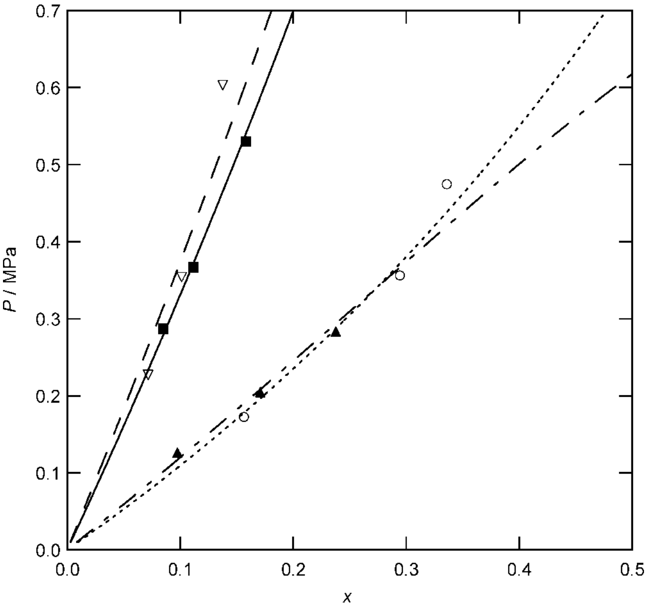

Figure 4. Experimental and SL EOS calculated pressure versus mole fraction for HFC125, HFC152a, HFC143a, and HFC32 in Terol 352 at 298.15 K. Symbols and lines same as those in Figure 2.

Table 4. SL EOS Binary Interaction Parameter, k_{ij}, for Polyol + Blowing Agent Systems at 298.15 K

	blowing agent	Pluracol 975	Pluracol 355	Terol 352
k_{ij}	HFC125	0.003	− 0.030	− 0.006
	HFC152a	0.030	0.015	0.026
	HFC143a	0.039	0.023	0.018
	HFC32	− 0.028	− 0.023	− 0.016

enhancing the hydrogen bonding between the hydroxyl group of the polyol and the hydrogen atoms of the blowing agent. Another factor that influences the hydrogen bonding between the blowing agent and the polyol molecule, thereby influencing the solubility, is the number of hydroxyl groups available in the polyol (functionality). The higher the functionality of the polyol, the more favorable the conditions for hydrogen bonding.

The presence of the CHF_2 group in the structure of HFC152a and the high functionality of both Pluracol polyols enhanced the hydrogen bonding between the HFC152a and Pluracol molecules, thereby increasing the solubility. Among the blowing agents used in this study, HFC125, HFC152a, and HFC32 have a CHF_2 group in their structure and, accordingly, showed better solubility in the polyols. The poor solubility of HFC143a can be attributed to the unfavorable conditions for hydrogen bond formation because of the lack of a CHF_2 group in the structure of the HFC143a molecule.

The theoretical solubility results indicate that SL EOS is able to correlate the solubility of blowing agents in polyols fairly well. The maximum value for the objective function, OBJ, was never greater than 10^{-2} for any of the 12 systems. Also, the fact that the binary interaction parameters for SL EOS presented in Table 4 did not deviate much from zero indicates that SL EOS can be used to predict the solubility of these types of systems in the absence of experimental data reasonably.

Conclusions

The solubility of four zero-ODP blowing agents in three commercially available polyols has been measured using a degassed vapor pressure apparatus. The theory that the presence of a CHF_2 group in blowing agent molecules increases its solubility in the polyol is supported by our results. Correlation of the experimental results with SL EOS shows that the model does a good job in describing the polyol + blowing agent systems.

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