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Excess Enthalpy, Excess Volume, Viscosity Deviation, and Speed of Sound Deviation for the Mixture Tetrahydrofuran + 2,2,2-Trifluoroethanol at (283.15, 298.15, and 313.15) K

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Excess enthalpies, densities, speeds of sound, and dynamic viscosities for the mixture tetrahydrofuran + 2,2,2-trifluoroethanol were measured at (283.15, 298.15, and 313.15) K. Excess volumes, deviations of the speed of sound, and deviations of the dynamic viscosity were calculated at the three temperatures. These properties with the excess enthalpies were graphically represented and fitted by Redlich−Kister equations.

Introduction

Given the relevance of the compound 2,2,2-trifluorethanol (TFE) in several fields,[1−7] it is desirable to obtain as much information as possible about it. In this sense, an important point is to know the thermochemical behavior of mixtures containing it. In fact, the thermodynamic properties of the mixtures (TFE + water), two components associated by hydrogen bonds, have been investigated in relation with the influence of the media on the selectivity in Diels−Alder reactions.[3,4] Thus, we started a study of mixtures of TFE with cyclic ethers that would also involve interesting specific interactions. Besides, the study of these mixtures is inscribed in an investigation of an extensive series of systems containing either associated or polar compounds, cyclic ethers[8,9] among them. That research line is just aimed to examine the interactions acting in those systems. Continuing a previous work in which the cyclic ether was tetrahydropyran[10] (THP), we report in this paper the excess molar enthalpy, density, speed of sound, and dynamic viscosity data for the binary mixture tetrahydrofuran (THF) + 2,2,2-trifluoroethanol (TFE) at atmospheric pressure and at (283.15, 298.15, and 313.15) K. Tetrahydrofuran is a compound used as solvent for many purposes. From the experimental data, excess volumes, deviations of the speed of sound, and deviations of the dynamic are calculated.

Experimental Section

Materials. The compounds used were tetrahydrofuran (purity, better than 99%) from Aldrich and 2,2,2-trifluoroethanol (purity, better than 99.8%) from Acros. The THF was dried with and stored over molecular sieves type 4 Å from Fluka. The purity of each compound was checked and confirmed by gas chromatography. Experimental densities, dynamic viscosities, and speeds of sound of the pure liquids are gathered and compared with available literature data in Table 1.

Table 1. Densities, ρ, Viscosities, η, and Speeds of Sound, u, of Pure Compounds at (283.15, 298.15, and 313.15) K: Comparison with Literature Data

		ρ/kg·m^{-3}		η/mPa·s		u/m·s^{-1}	
T/K		THF	TFE	THF	TFE	THF	TFE
283.15	expt	898.62	1408.10	0.5438	2.6935	1348.8	872.7
	lit.	895.3[a]	1408.21[b]				
298.15	expt	882.18	1382.56	0.4645	1.7548	1279.0	833.2
	lit.	882.5[a]	1382.31[b]	0.460[f]	1.769[f]	1277.8[c]	833.1[h]
		882.1[c]		0.4637[g]			
		881.97[d]					
		882.69[e]					
313.15	expt	865.95	1356.89	0.3992	1.2085	1204.8	793.3
	lit.	870.5[a]	1356.41[b]	0.3965[g]		1206.5[c]	
		865.3[c]					

[a] Reference 13. [b] Reference 14. [c] Reference 15. [d] Reference 16. [e] Reference 17. [f] Reference 18. [g] Reference 19. [h] Reference 20.

Table 2. Excess Enthalpies for the Mixture THF (1) + TFE (2) at (283.15, 298.15, and 313.15) K

	H^E/kJ·mol^{-1}		
x_1	T = 283.15 K	T = 298.15 K	T = 313.15 K
0.053	−0.383	−0.472	−0.474
0.107	−0.723	−0.939	−0.928
0.212	−1.235	−1.543	−1.570
0.316	−1.594	−1.883	−1.984
0.417	−1.735	−2.003	−2.144
0.517	−1.729	−1.956	−2.094
0.618	−1.569	−1.751	−1.869
0.717	−1.270	−1.427	−1.510
0.810	−0.904	−0.993	−1.063
0.908	−0.448	−0.489	−0.525
0.954	−0.213	−0.234	−0.257

Apparatus and Procedure. A Thermometrics flow calorimeter 2277 was used to measure the excess enthalpy. To introduce the liquids into the calorimeter, we used two Shimadzu LC-10ADVP HPLC pumps. These pumps were calibrated for each compound to determine the ratio between the real flow and the programmed flow. The uncertainty in the mole fractions of the mixtures, calculated from the uncertainty in the flow delivered by the pumps, is ±0.001. The calorimeter was checked by determining the excess enthalpy of the system 1,4-dioxane + tetracloromethane and comparing it with literature data.[11] The deviation lies within ±1%, so the uncertainty in H^E could be expected to be ±1%.

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Table 3. Densities and Excess Volumes for the Mixture THF (1) + TFE (2) at (283.15, 298.15 and 313.15) K

$T = 283.15$ K			$T = 298.15$ K			$T = 313.15$ K		
x_1	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	x_1	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}	x_1	ρ/kg·m^{-3}	10^6V^E/m^3·mol^{-1}
0.1087	1336.89	0.515	0.0362	1358.26	0.210	0.1024	1291.64	0.532
0.2084	1277.40	0.797	0.1041	1315.13	0.522	0.1991	1234.96	0.877
0.2990	1226.31	0.973	0.2053	1255.19	0.847	0.3032	1178.51	1.079
0.4038	1171.02	1.039	0.3031	1201.40	1.022	0.3554	1151.61	1.131
0.4953	1125.37	1.002	0.4018	1150.15	1.093	0.4972	1082.56	1.110
0.5967	1076.79	0.894	0.4986	1103.07	1.033	0.5960	1037.96	0.974
0.7048	1027.26	0.694	0.5989	1055.77	0.934	0.7191	983.05	0.742
0.8048	982.37	0.504	0.7019	1009.19	0.758	0.7922	952.13	0.544
0.8868	946.79	0.297	0.7978	967.32	0.541	0.8937	909.37	0.305
0.9657	913.10	0.094	0.8990	924.33	0.273			

Table 4. Speeds of Sound and Deviation of the Speed of Sound for the Mixture THF (1) + TFE (2) at (283.15, 298.15, and 313.15) K

$T = 283.15$ K			$T = 298.15$ K			$T = 313.15$ K		
x_1	u/m·s^{-1}	Δu/m·s^{-1}	x_1	u/m·s^{-1}	Δu/m·s^{-1}	x_1	u/m·s^{-1}	Δu/m·s^{-1}
0.1087	897.7	−26.7	0.1106	854.6	−27.9	0.1024	808.3	−27.1
0.2084	932.6	−39.8	0.2095	885	−41.6	0.1991	834.3	−40.9
0.2990	966.8	−48.2	0.3019	917.9	−49.9	0.3032	868.4	−50.7
0.4038	1010.1	−54.8	0.4065	959.4	−55.0	0.3554	886.4	−53.1
0.4953	1052.1	−56.4	0.5076	1003.3	−56.2	0.4972	942.6	−55.3
0.6013	1104.4	−54.6	0.6172	1055.8	−52.5	0.5960	985.9	−52.3
0.7048	1161.1	−48.1	0.7123	1104.9	−45.9	0.7191	1045.5	−43.7
0.7958	1213.8	−37.8	0.8205	1164.5	−34.5	0.7922	1082.8	−36.5
0.9058	1283.2	−20.7	0.9042	1216.3	−20.0	0.8937	1138.7	−22.3
0.9657	1324.1	−8.3						

Table 5. Dynamic Viscosities and Deviations of the Dynamic Viscosity for the Mixture THF (1) + TFE (2) at (283.15, 298.15, and 313.15) K

	η/mPa·s			$\Delta\eta$/mPa·s		
x_1	$T = 283.15$ K	$T = 298.15$ K	$T = 313.15$ K	$T = 283.15$ K	$T = 298.15$ K	$T = 313.15$ K
0.1022	2.1068	1.4670	1.0567	−0.3670	−0.1559	−0.0691
0.2018	1.5776	1.1691	0.8873	−0.6820	−0.3253	−0.1579
0.3033	1.2459	0.9632	0.7583	−0.7956	−0.4002	−0.2047
0.4037	1.0367	0.8286	0.6648	−0.7890	−0.4053	−0.2170
0.5014	0.8927	0.7228	0.5936	−0.7228	−0.3850	−0.2090
0.6036	0.7821	0.6432	0.5356	−0.6139	−0.3328	−0.1844
0.7004	0.7023	0.5841	0.4916	−0.4855	−0.2669	−0.1500
0.8532	0.6208	0.5222	0.4431	−0.2385	−0.1317	−0.0749
0.9033	0.5846	0.4959	0.4239	−0.1671	−0.0935	−0.0536

Density, ρ, and speed of sound, u, were determined with an improved Anton Paar densimeter and sound analyzer DSA 48 whose uncertaities are $\pm10^{-2}$ kg·m^{-3} for the density and 0.1 m·s^{-1} for the speed of sound. The densimeter was calibrated using dry air and milliQ quality water.

Finally, the kinematic viscosity, ν, was measured with a capillary Ubbelohde viscosimeter connected to an automatic Schott-Geräte AVS 440. The uncertainty is estimated to be $\pm10^{-4}$ mm^2·s^{-1}. At least four flow time measurements that did not differ more than 0.05% between them were performed for each composition and temperature, and the results were averaged. The temperature was kept constant within ±0.01 K. Densities required to calculate dynamic viscosity were estimated from the densities previously measured.

The mole fraction of the mixtures used for measure densities, speeds of sound, and viscosities was determined by mass using a Sartorius analytical balance with a precision of $\pm10^{-5}$ g. The precision of the mole fractions is estimated to be $\pm10^{-4}$.

Results and Discussion

We calculated excess volumes, deviations of the speed of sound, and deviations of the dynamic viscosity from densities, speeds of sound, and dynamic viscosities using the following equations:

$$V^E/\text{m}^3\cdot\text{mol}^{-1} = x_1M_1(\rho^{-1} - \rho_1^{-1}) + x_2M_2(\rho^{-1} - \rho_2^{-1}) \tag{1}$$

$$\Delta Y = Y - x_1Y_1 - x_2Y_2 \tag{2}$$

where V^E is the excess volume and ΔY is the deviation from the linear behavior of the property (Δu and $\Delta\eta$); x_i, ρ_i, M_i, and Y_i are respectively the mole fraction, the density, the molar mass, and the values of the property of the pure compounds; ρ and Y are density and the value of the property for the mixture. The excess enthalpies are shown in Table 2; the experimental densities and the excess volumes are given in Table 3; the speeds of sound and deviations of the speed of sound can be found in Table 4; and, finally, the dynamic viscosities and their deviations are included in Table 5. All the excess properties and the deviations of the properties are graphically represented in Figures 1−4 and fitted to Redlich−Kister equations.[12]

$$Y^E \text{ (or } \Delta Y) = x_1x_2\sum_{p=0}^{n} A_p(x_1 - x_2)^{p} \tag{3}$$

where A_p are adjustable parameters that were obtained by the least-squares method. These parameters and the standard deviations, σ, for the four properties at the three temperatures are gathered in Table 6. The expression used to calculate the standard deviation was

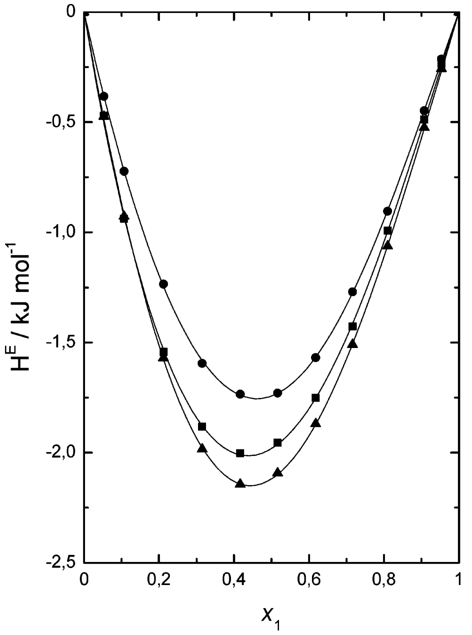

Figure 1. Excess enthalpies for the mixture THF (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

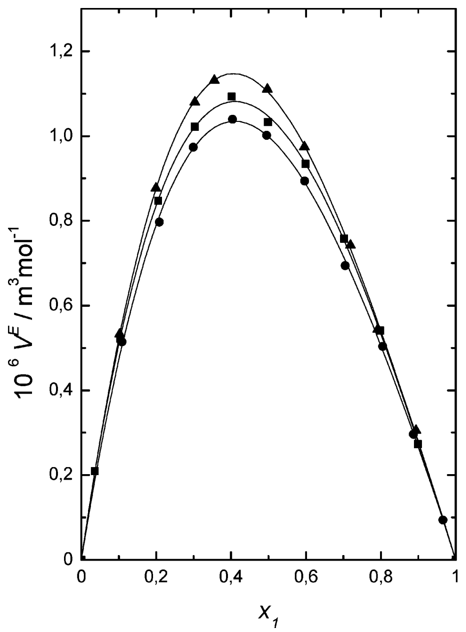

Figure 2. Excess volumes for the mixture THF (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

$$\sigma = \left[\frac{\sum_{m}(Y^{\mathrm{exp}} - Y^{\mathrm{cal}})^2}{m - n}\right]^{1/2} \tag{4}$$

where *n* is the number of parameters and *m* is the number of data fitted.

As can be observed, the excess molar enthalpies are negative over the whole composition range and they become more negative when temperature increases. The excess molar volumes are positive throughout and they become more positive when temperature rises. The deviations of speed of sound are always negative, and their values are scarcely influenced by temperature changes in the range considered. Finally, the deviations of the dynamic viscosity are also negative, and the higher the temperature, the less negative they become.

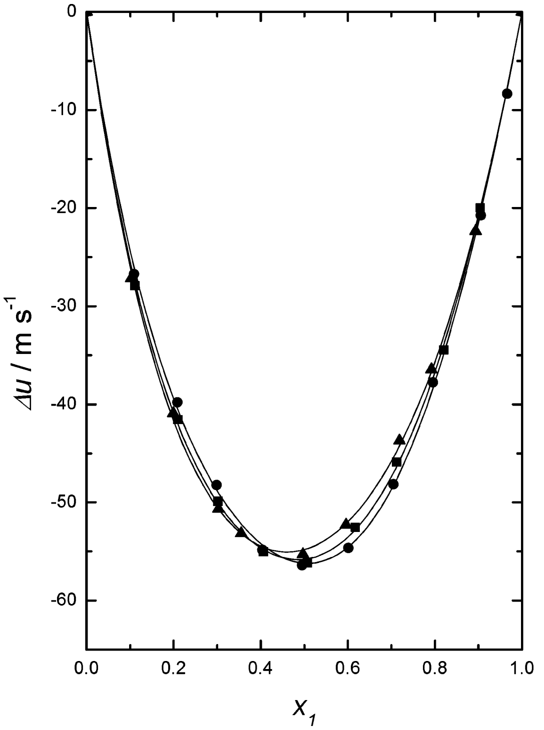

Figure 3. Deviations of the speed of sound for the mixture THF (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

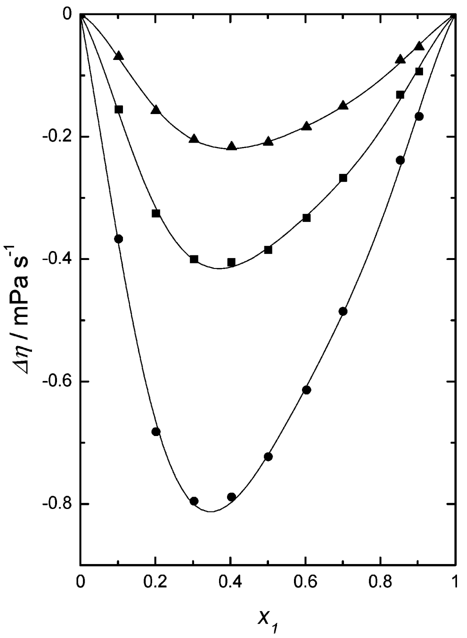

Figure 4. Deviations of the dynamic viscosity for the mixture THF (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

These results are very similar in their main features to those obtained for the mixture THP + TFE.[8] Therefore, they can be attributed to the same causes. Negative excess molar enthalpies point to the formation of hydrogen bonds between THF and TFE. However, these strong interactions do not completely determine the behavior of the remaining properties which show a sign opposite to that usually connected to negative excess enthalpies. Esteric effects, differences in molecular volume, or effects due to mixing entropies would explain the results observed for excess molar volumes and deviations of dynamic viscosity.

The absolute values of all properties except excess molar volume increase when THF instead of THP is mixed with

Table 6. Fitting Coefficients of the Redlich–Kister Equation for the Properties at the Temperatures (283.15, 298.15, and 313.15) K and Standard Deviations

	T/K	A_0	A_1	A_2	A_3	A_4	σ
10^6V^E/m^3·mol^{-1}	283.15	3.99	−1.56	0.16	0.2		0.008
	298.15	4.18	−1.54	0.26	−0.1		0.007
	313.15	4.41	−1.85	0.05	0.3		0.008
Δu/m·s^{-1}	283.15	−225	−6	−46	40		0.5
	298.15	−223	10	−54	33		0.4
	313.15	−219	25	−63	17		0.5
H^E/kJ·mol^{-1}	283.15	−6.97	1.23	0.81	0.2		0.014
	298.15	−7.93	2.08	0.15	0.5		0.007
	313.15	−8.48	2.16	0.78	−0.2		0.006
$\Delta\eta$/mPa·s	283.15	−2.88	2.0	−1.5	−0.9	2.2	0.003
	298.15	−1.53	0.88	−0.6	−0.7	1.4	0.007
	313.15	−0.83	0.39	−0.2	−0.4	0.7	0.011

TFE. The excess molar volume remains almost unchanged. These data indicate that probably more hydrogen bonds are formed in the case that TFE interacts with the smaller cyclic ether. At the same time, the esteric hindrances are also greater, as the excess volume does not undergo the foreseeable decrease that would accompany the more negative values of excess enthalpy. These esteric hindrances could be related to the smaller flexibility of the cycle of five carbon atoms of THF when compared with the cycle of six carbon atoms of THP. In any case, it is clear that the behavior of the mixtures cyclic ether + TFE is quite complex and makes difficult the correlation of the different properties.

Literature Cited

(1) Medrano, M.; Bourouis, M.; Coronas, A. Double-Lift Absorption-Refrigeration Cycles Driven by Low-Temperature Heat-Sources Using Organic Fluid Mixtures as Working Pairs. *Appl. Energy* **2001**, *68*, 173−185.

(2) Xu, S. M.; Liu, Y. L.; Zhang, L. S. Performance Research of Self-Regenerated Absorption Heat Transformer Cycle Using Tfe-Nmp as Working Fluids. *Int. J. Refrig.* **2001**, *24*, 510−518.

(3) Cativiela, C.; García, J. I.; Gil, J.; Martínez, R. M.; Mayoral, J. A.; Salvatella, L.; Urieta, J. S.; Mainar, A. M.; Abraham, M. H. Solvent effects on Diels−Alder reactions. The use of aqueous mixtures of fluorinated alcohols and the study of reactions of acrylonitrile. *J. Chem. Soc., Perkin Trans. 2* **1997**, 653−660.

(4) Cativiela, C.; García, J. I.; Mayoral, J. A.; Royo, A. J.; Salvatella. Fluorinated Alcohols as Solvents for Diels−Alder Reactions of Chiral Acrylates. *Tetrahedron: Asymmetry* **1993**, *4*, 1613−1618.

(5) Digiammarino, E. L.; Filippov, I.; Weber, J. D.; Bothner, B.; Kriwacki, R. W. Solution Structure of the p53 Regulatory Domain of the P19(ArF) Tumor-Suppressor Protein. *Biochemistry* **2001**, *40*, 2379−2386.

(6) Ohiso, I.; Tsunemi, M.; Zhao, B.; Nishi, N. Conformational Study of the Tandem Repeat Sequence in RNA-Polymerase-II by Circular-Dichroism Spectroscopy. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1139−1143.

(7) Keller, D.; Clausen, R.; Josefsen, K.; Led, J. J. Flexibility and Bioactivity of Insulin−An NMR Investigation of the Solution Structure and Folding of an Unusually Flexible Human Insulin Mutant with Increased Biological Activity. *Biochemistry* **2001**, *40*, 10732−10740.

(8) Gascón, I.; Pardo, J.; Santafé, J.; Domínguez, M.; Urieta, J. S. Experimental and Predicted Viscosities of the Binary System (*n*-Hexane + 1,3-Dioxolane) and for the Ternary System (*n*-Hexane + 1,3-Dioxolane + 1-Butanol) at 298.15 and 313.15 K. *Fluid Phase Equilib.* **2001**, *180*, 211−220. More references for mixtures containing cyclic ether can be found in this paper.

(9) Lafuente, C.; Cea, P.; Domínguez, M.; Royo, F. M.; Urieta, J. S. Excess Molar Enthalpies of Cyclic Ethers with Cyclohexane, Methylcyclohexane or Chlorocyclohexane. *J. Solution Chem.* **2001**, *30*, 795−805. More references for mixtures containing cyclic ether can be found in this paper.

(10) Pérez, E.; Mainar, A. M.; Santafé, J.; Urieta, J. S. Excess Enthalpy, Excess Volume, Viscosity Deviation and Speed of Sound Deviation for the Mixture Tetrahydropyran + 2,2,2-Trifluoroethanol at (283.15, 298.15, and 313.15 K). *J. Chem. Eng. Data* **2003**, *48*, 723−726.

(11) Marsh, K. N. *Recommended Reference Materials for the Realization of Physicochemical Properties*; Blackwell Scientific: Oxford, 1987.

(12) Redlich, O.; Kister, A. T. Thermodynamic of non electrolytic solutions. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(13) *TRC Thermodynamic Tables. Non-Hydrocarbons*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1985; p D-6170.

(14) Esteve, X.; Patil, K. R.; Fernández, J.; Coronas, A. Prediction of Density and Excess Volume for the Ternary Mixture (Water plus 2,2,2-Trifluoroethanol plus 2,5,8,11,14-Pentaoxapentadecane From Experimental Binary Values at Temperatures from 283.15 to 313.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 281−292.

(15) Rodríguez, S.; Lafuente, C.; Artigas, H.; Royo, F. M.; Urieta, J. S. Densities, Speeds of Sound, and Isentropic Compressibilities of a Cyclic Ether with Chlorocyclohexane, or Bromocyclohexane at the Temperatures 298.15 K and 313.15 K. *J. Chem. Thermodyn.* **1999**, *31*, 139−149.

(16) Kiyohara, O.; D'Arcy, P. J.; Benson, G. Thermal Expansivities of Water + Tetrahydrofuran Mixtures at 298.15 K. *Can. J. Chem.* **1978**, *56*, 2803−2807.

(17) Inglese, A.; Grolier, J. P. E.; Wilhelm, E. Excesss Volumes of Mixtures of Oxolane, Oxane, 1,3-Dioxolane, and 1,4-Dioxane with *n*-Alkanes at 198.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1983**, *28*, 124−127.

(18) Riddick, J. A.; Bunger, N. B.; Sakano, T. *Organic Solvents. Techniques of Chemistry, II*; Wiley-Interscience: New York, 1986.

(19) Rodríguez, S. Estudio de Propiedades Termodinámicas y de Transporte de Mezclas Líquidas Binarias Eteres + Halogenuros Cíclicos. Ph.D. Thesis, Area of Physical Chemistry, University of Zaragoza, Zaragoza, Spain, 1998.

(20) Sánchez, M. A.; Mainar, A. M.; Pardo, J. I.; López, M. C.; Urieta, J. S. Solubility of nonpolar gases in 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol at several temperatures and 101.33 kPa partial pressure of gas. *Can. J. Chem.* **2001**, *79*, 1460−1465.

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