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

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Excess enthalpies, densities, speeds of sound, and dynamic viscosities for the mixture tetrahydropyran + 2,2,2-trifluoroethanol were measured at the temperatures (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 those temperatures. These properties along with the excess enthalpies were fitted to Redlich−Kister equations.

Introduction

Knowledge of thermophysical properties of mixtures of organic liquids is essential for the right design of several types of relevant industrial equipment. Moreover, these data can also give us information about the intermolecular interactions in the mixture, information that is important from a theoretical point of view.

We report in this paper excess enthalpy, density, speed of sound, and dynamic viscosity measurements for the binary mixture tetrahydropyran (THP) + 2,2,2-trifluoroethanol (TFE). From them, excess volume, deviation of the speed of sound, and deviation of the dynamic viscosity were calculated. The measurements were carried out at atmospheric pressure and at three temperatures (283.15, 298.15, and 313.15 K).

Knowledge of the behavior of mixtures containing TFE is desirable because TFE is a compound widely used in several fields such as biochemistry,[1−3] organic chemistry,[4,5] and engineering[6,7] (for instance, as a component in absorption devices). As far as we know, there are no studies about the mixture here considered. Neither are there data reported about mixtures of TFE with other cyclic ethers although several authors[8−11] have studied the properties of the mixture of TFE with the polyether tetraethylene glycol dimethyl ether (TEGDME). Our aim is to obtain information about the effect of the trifluoromethyl group on the interaction between an alcoholic proton and a Lewis base.

Experimental Section

Materials. The compounds used were tetrahydropyran (purity, better than 99%) from Aldrich and trifluoroethanol (purity, better than 99.8%) from Acros. The THP was dried with molecular sieve type 4 Å from Fluka. The purity of both compounds was corroborated by gas chromatography. Measured densities, dynamic viscosities, and speeds of sound of the pure liquids are compared with available literature data in Table 1.

Apparatus and Procedure. A Thermometrics flow calorimeter 2277 was used to obtain the excess enthalpies.

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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		THP	TFE	THP	TFE	THP	TFE
283.15	expt	894.08	1407.89	1.0047	2.6931	1335.8	872.3
	lit		1408.21[a]				
298.15	expt	879.18	1382.44	0.8005	1.7546	1255.0	826.7
	lit	879.2[b]	1382.60[a]	0.764[c]	1.769[c]	1270.0[b]	833.1[f]
		877.2[c]		0.8008[e]			
		879.16[d]					
313.15	expt	864.37	1356.91	0.6494	1.2085	1199.8	791.7
	lit	863.8[b]	1356.41[a]	0.6513		1202.1[b]	

[a] Reference 9. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 19. [f] Reference 20.

Table 2. Excess Enthalpies for the Mixture THP (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
0.065	−0.428	−0.473	−0.478
0.127	−0.743	−0.855	−0.900
0.248	−1.184	−1.348	−1.457
0.360	−1.430	−1.608	−1.761
0.466	−1.513	−1.689	−1.856
0.570	−1.464	−1.620	−1.786
0.664	−1.269	−1.419	−1.564
0.755	−1.015	−1.120	−1.242
0.839	−0.701	−0.771	−0.851
0.921	−0.347	−0.380	−0.417
0.962	−0.155	−0.179	−0.195

The flow of the components was controlled through two Shimadzu LC-10ADVP HPLC pumps. Each pump was calibrated for its corresponding liquid to determine the ratio between the real flow and the programmed flow. The uncertainty in the mole fraction 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 + tetrachloromethane and comparing it with literature data.[12] The deviation lies within ±1%; then the uncertainty in H^E is expected to be of the same order.

10.1021/je025655p CCC: $25.00
Published on Web 04/22/2003

Table 3. Densities and Excess Volumes for the Mixture THP (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}	$10^6 \times V^E$/m^3·mol^{-1}	x_1	ρ/kg·m^{-3}	$10^6 \times V^E$/m^3·mol^{-1}	x_1	ρ/kg·m^{-3}	$10^6 \times V^E$/m^3·mol^{-1}
0.1039	1328.18	0.549	0.1023	1305.58	0.550	0.1028	1280.80	0.601
0.2071	1259.32	0.861	0.2029	1239.41	0.879	0.2000	1217.96	0.942
0.3073	1199.39	1.021	0.3203	1170.85	1.072	0.3049	1157.77	1.116
0.4127	1142.29	1.064	0.4120	1122.50	1.104	0.4108	1102.63	1.172
0.5017	1097.77	1.033	0.5192	1070.38	1.057	0.5040	1058.19	1.124
0.6011	1051.70	0.921	0.6171	1026.55	0.928	0.5961	1017.26	1.014
0.7183	1001.30	0.718	0.7342	977.81	0.703	0.6986	974.97	0.806
0.8206	960.36	0.485	0.7930	954.59	0.577	0.8321	923.77	0.472
0.8955	931.90	0.291	0.8967	915.73	0.305	0.8986	899.60	0.285

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

$T = 283.15$ K			$T = 298.15$ K			$T = 313.15$ K		
	u	Δu		u	Δu		u	Δu
x_1	m·s^{-1}	m·s^{-1}	x_1	m·s^{-1}	m·s^{-1}	x_1	m·s^{-1}	m·s^{-1}
0.1039	903.5	−17.0	0.1023	850.5	−20.0	0.0995	813.9	−18.4
0.2071	942.2	−26.1	0.2029	886.4	−27.2	0.2000	845.8	−27.5
0.3067	985.6	−28.9	0.3203	933.6	−30.3	0.3049	885.0	−31.1
0.4123	1034	−29.4	0.4120	972.6	−30.6	0.4111	927.4	−31.7
0.5017	1076.2	−28.7	0.5208	1021.0	−28.7	0.5040	967.4	−30.0
0.6011	1124.9	−26.0	0.6171	1065.4	−26.1	0.6032	1010.4	−27.5
0.7183	1184.3	−20.9	0.7342	1121.0	−21.2	0.7330	1070.3	−21.0
0.8206	1237.7	−14.9	0.7996	1152.3	−16.9	0.8321	1116.2	−15.1
0.8955	1278.1	−9.3	0.8967	1201.6	−9.1	0.8988	1149.4	−9.0

Density, ρ, and speed of sound, u, were measured with an improved Anton Paar densimeter and sound analyzer DSA 48 whose uncertainties were 10^{-5} g·cm^{-3} and 1 m·s^{-1}, respectively. The densimeter was calibrated using dry air and degassed miliQ quality water.

Finally, the kinematic viscosity, ν, was determined with a capillary Ubbelohde viscosimeter connected to an automatic Schott-Geräte AVS 440. At least four flow time measurements that did not differ by 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. The estimated uncertainty for the kinematic viscosity is $\pm 10^{-4}$ mm^2·s^{-1}. The composition of the mixtures used for measuring densities, speeds of sound, and viscosities was determined by mass using a Sartorius analytical balance with a precision of $\pm 10^{-5}$ g. The uncertainty of the mole fraction is estimated to be $\pm 10^{-4}$.

Results and Discussion

Excess volumes, deviations of the speed of sound, and deviations of the dynamic viscosity were calculated from densities, speeds of sound, and dynamic viscosities ($\eta = \nu\rho$) by using the following equations:

$$V^E/\mathrm{m}^3\cdot\mathrm{mol}^{-1} = x_1 M_1(\rho^{-1} - \rho_1{}^{-1}) + x_2 M_2(\rho^{-1} - \rho_2{}^{-1}) \quad (1)$$

$$\Delta Y = Y - x_1 Y_1 - x_2 Y_2 \quad (2)$$

where V^E is the excess volume and ΔY (Δu and $\Delta\eta$) is the deviation of the property from linear behavior; 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 compound i; ρ and Y are density and the value of the property for the mixture. Excess enthalpies are given in Table 2, whereas experimental densities and excess volumes are shown in Table 3. The speeds of sound and deviations of the speed of sound are included in Table 4, and the dynamic viscosities and their deviations can be found in Table 5. All the excess properties and the deviations of the properties were fitted to Redlich−Kister equations[13]

Table 5. Dynamic Viscosities and Deviations of the Dynamic Viscosity for the Mixture THP (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
0.0508	2.5212	1.6802	1.1711	−0.0861	−0.0260	−0.0090
0.1011	2.2653	1.5574	1.1118	−0.2570	−0.1007	−0.0401
0.2025	1.8338	1.3301	0.9911	−0.5174	−0.2313	−0.1042
0.3024	1.5462	1.1586	0.8910	−0.6363	−0.3075	−0.1484
0.4040	1.3481	1.0345	0.8127	−0.6628	−0.3346	−0.1699
0.5027	1.2201	0.9509	0.7570	−0.6243	−0.3241	−0.1704
0.6069	1.1231	0.8855	0.7128	−0.5452	−0.2900	−0.1563
0.7013	1.0639	0.8450	0.6832	−0.4451	−0.2405	−0.1331
0.8016	1.0264	0.8183	0.6642	−0.3133	−0.1716	−0.0962
0.9064	1.0104	0.8047	0.6543	−0.1523	−0.0850	−0.0474

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
$V^E \times 10^6$/m^3·mol^{-1}	283.15	4.12	−1.46	0.57	−0.5		0.002
	298.15	4.27	−1.59	0.54	−0.2		0.003
	313.15	4.51	−1.72	0.49	−0.7		0.005
Δu/m·s^{-1}	283.15	−114	37	−44	27		0.2
	298.15	−117	33	−62	63		0.3
	313.15	−121	42	−51	35		0.2
H^E/kJ·mol^{-1}	283.15	−6.03	0.66	0.31	0.9		0.008
	298.15	−6.73	0.93	0.25	0.9		0.004
	313.15	−7.42	0.95	0.64	0.6		0.008
$\Delta\eta$/mPa·s	283.15	−2.49	1.3	−1.1	−1.2	2.4	0.011
	298.15	−1.29	0.52	−0.3	−0.7	1.2	0.004
	313.15	−0.68	0.15	−0.02	−0.4	0.5	0.001

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

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

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

where n is the number of parameters and m is the number of data fitted. Both the experimental data and the fitting curves are represented in Figures 1−4.

As can be observed, the excess molar enthalpies and the deviations of the speed of sound are negative over the whole composition range and they become more negative as temperature increases. The excess molar volumes are positive over the whole composition range, and they become

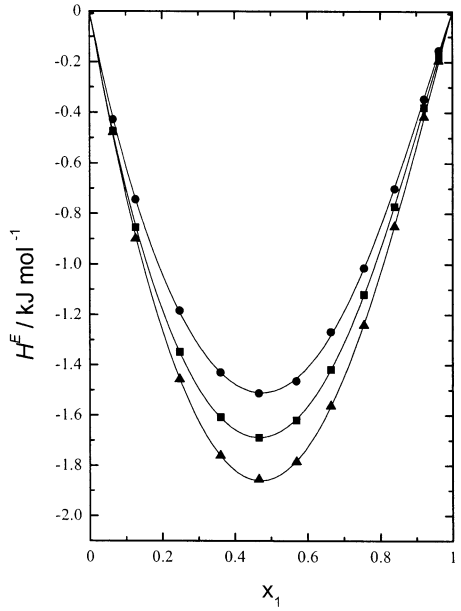

Figure 1. Excess enthalpies for the mixture THP (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

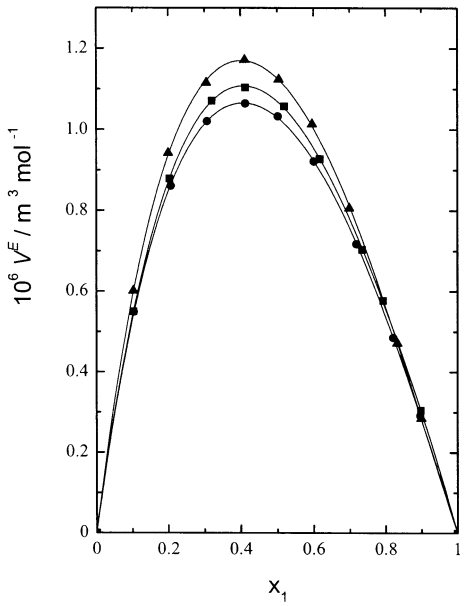

Figure 2. Excess volumes for the mixture THP (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

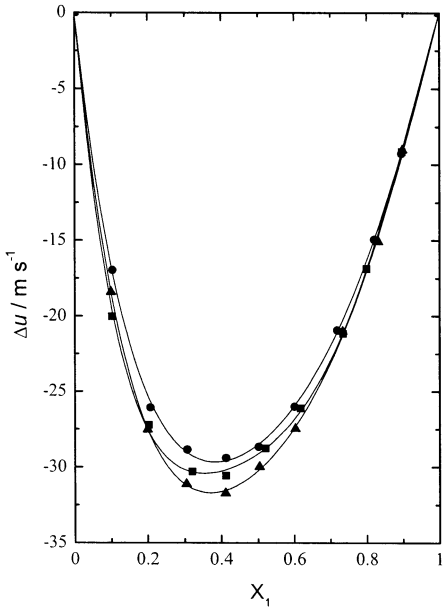

Figure 3. Deviations of the speed of sound for the mixture THP (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

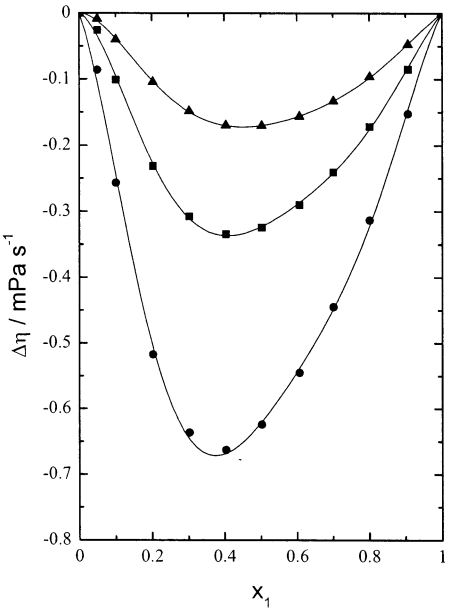

Figure 4. Deviations of the dynamic viscosity for the mixture THP (1) + TFE (2): ●, 283.15; ■, 298.15; ▲, 313.15 K.

more positive as temperature rises. Finally, deviations of dynamic viscosity are negative, and the higher the temperature, the less negative they become.

The very negative values of excess enthalpy point to the appearance of strong attractive interactions in the mixture. These interactions are probably hydrogen bonds between the oxygen atom of the ether and the alcoholic hydrogen atom of the fluoroalcohol. On the other hand, it has been verified[14] that two conformers exist for TFE. The prevailing conformer shows an intramolecular hydrogen bond between the alcoholic hydrogen and a fluorine atom, while the other does not. The addition of THP shifts the equilibrium, and this would affect the values of H^E.

Despite negative excess enthalpy values, quite positive excess volumes are observed. This effect could be a consequence of esteric effects (such as breaking of liquid order in THP in our system). The negative values of the deviations of the speed of sound follow the usual pattern when V^E is positive because they are in agreement with longer distances between molecules.

Finally, negative values of deviations of dynamic viscosity are related in many cases to positive values of excess enthalpy, but not in this system. Then the behavior of this property for the mixture THP + TFE is mainly controlled not by the strength of the interaction between components but by other effects such as differences in molecular volume of the components or mixing entropy.[15]

A comparison of the thermophysical properties of the mixture THP + TFE can be made with those corresponding to the mixture of TFE with TEGDME,[8−11] a compound that also contains ether groups. For the last system, excess enthalpies and excess volumes are negative, and deviations of the dynamic viscosity are positive. The values of excess enthalpies can be explained in the same way used for the mixture of TFE with the cyclic ether. In fact, the excess enthalpies are more negative for the polyether mixture.

This is in agreement with the existence of a greater number of oxygen atoms which are available for the formation of hydrogen bonds. The other properties of the mixture TFE + TEGDME follow the usual pattern when the excess enthalpies are negative, although it must be pointed out that the excess volume is slightly positive for the higher molar fractions of TEGDME at 283 K. It could be concluded that the presence of the THP introduces a major complexity in the mixture due surely to the cyclic character of the ether.

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Received for review December 11, 2002. Accepted March 30, 2003. The authors gratefully acknowledge the Diputación General de Aragón (DGA, Project PCB-0894) and the Ministerio de Educación y Cultura (CICYT-INFR IN96-0191) for financial support.

JE025655P