Densities, Speeds of Sound, and Refractive Indices of the Mixture Nonane + Triethylene Glycol Dimethyl Ether at 288.15 K, 293.15 K, 298.15 K, and 308.15 K

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Densities, speeds of sound, and refractive indices of the binary nonane + triethylene glycol dimethyl ether (2,5,8,11-tetraoxadodecane or triglyme or TODD) have been measured at the temperatures 288.15 K, 293.15 K, 298.15 K, and 308.15 K and atmospheric pressure, over the entire composition range. Using these data, excess molar volumes and increments in speed of sound and refractive index have been calculated. Excess quantities and increments have been fitted to a variable-degree polynomial equation. The correlation parameters together with the standard deviations between the experimental and calculated values were derived.

Introduction

Properties such as densities, speeds of sound, and refractive indices are useful to design engineering processes and are required to understand the interactions between the different molecules in liquid mixtures.

The thermodynamic behavior of liquid mixtures composed of a polyoxyethylene glycol dimethyl ether, also called glyme, and an *n*-alkane has been examined in detail in recent years.[1−5] The glymes or *n*(ethylene glycol) dimethyl ethers (*n*EGDME), which have the chemical structure $CH_3O(CH_2CH_2O)_nCH_3$, are particularly interesting, since they are electrochemically stable, analogous to the poly(ethylene oxide)s used in polymer−electrolyte batteries, and are employed as absorbent in the investigations of a new working fluid for use in absorption heat pumping systems.[6,7] Despite the similarities of their chains with the *n*-alkane chains, significant structural differences exist. First of all, the glyme molecules are polar, with their dipolar moment increasing with the length of the chain, whereas the *n*-alkanes are nonpolar. Second, glymes have less conformational flexibility than *n*-alkanes.

This paper reports new experimental data for the binary system nonane + triethylene glycol dimethyl ether. Speeds of sound, refractive indices, and their respective increments, Δu and Δn_D, together with the densities and excess molar volumes, V_m^E, for this mixture have been determined for the whole range of compositions at the temperatures 288.15 K, 293.15 K, 298.15 K, and 308.15 K and atmospheric pressure. Besides, the excess molar volumes to 298.15 K were compared with those determined by Tovar et al.[3]

Starting from the results obtained for the densities and the speeds of sound, the isentropic compressibilities could be determined by means of the Laplace equation $k_S = \rho^{-1}u^{-2}$.

Experimental Section

The alkane was supplied from Aldrich, while triethylene glycol dimethyl ether was provided by Fluka. The mole fraction purities of both components were better than 0.99.

The chemicals were dried using molecular sieves and degassed using ultrasounds. The general procedures of chemicals manipulation and technique applied in our laboratory have been described.[8]

The densities and speeds of sound of the pure liquids and binary mixtures were measured with a digital vibrating tube analyzer (Anton Paar DSA-48) with precisions of $\pm10^{-4}$ g·cm^{-3} and ±0.1 m·s^{-1}, respectively. This instrument incorporates a thermostat with a precision of ±0.1 K, which ensures the stability of temperature. For each temperature, the densimeter was calibrated using water of Millipore quality and atmospheric air in accordance with instructions, and no systematic errors were detected in the measurements.

The refractive indices of the mixtures and pure liquids were measured with a precision of $\pm10^{-5}$ by means of an ABBEMAT-HP Dr. Kernchen refractometer, using sodium D light (wavelength 589.3 nm). Instrument calibration was checked periodically by testing substances with known values of refractive index (water and atmospheric air). Temperature was controlled by a PolyScience controller bath model 9010 with a temperature stability of $\pm10^{-2}$ K.

Sample preparation was done by mass using a Mettler AE-240 balance with a precision of $\pm10^{-4}$ g, covering the whole composition range of the binary mixtures.

The uncertainty in the calculation of mole fractions, excess molar volumes, speed of sound increments, and refractive index increments was estimated as better than $\pm10^{-4}$, $\pm9 \times 10^{-3}$ cm^3·mol^{-1}, ±0.5 m·s^{-1}, and $\pm3 \times 10^{-4}$, respectively.

Values of measured properties, when available, were in accordance with those published in the open literature, as is shown in Table 1.

Results and Discussion

The densities, speeds of sound, and refractive indices measured at 288.15 K, 293.15 K, 298.15 K, and 308.15 K are given in Table 2. The derived excess molar volumes, increments in speed of sound, and refractive indexes were

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Table 1. Experimental Densities, ρ, Speed of Sound, u, and Refractive Indices, n_D, for Pure Liquids at the Temperatures 288.15 K, 293.15 K, 298.15 K, and 308.15 K

	ρ/(kg·m^{-3})		u/(m·s^{-1})		n_D	
T/K	exp	lit.	exp	lit.	exp	lit.
			Nonane			
288.15	721.6	721.79[3]	1247		1.408 01	
293.15	717.7	717.72[9]	1227		1.405 71	1.40542[10]
		717.63[10]				
298.15	713.9	714.09[3]	1206	1206.35[13]	1.403 22	1.40311[10]
		713.93[5]				1.4042[14]
		713.86[9]				
308.15	706.1	706.26[3]	1166		1.398 45	
		705.96[11]				
		706.42[12]				
			Triethylene Glycol Dimethyl Ether			
288.15	989.9	990.28[1]	1379		1.425 65	
		990.15[3]				
		990.27[15]				
293.15	985.3		1362		1.423 41	1.4233[17]
298.15	980.5	980.64[3]	1341		1.421 03	1.4239[6]
		980.82[15]				1.4209[17]
		980.01[16]				
308.15	971.0	971.15[3]	1303		1.416 70	
		971.26[15]				

determined using eqs 1, 2, and 3, respectively.

$$V_m^E = \sum_{i=1}^{2} x_i M_i (\rho^{-1} - \rho_i^{\circ -1}) \quad (1)$$

$$\Delta u = u - \sum_{i=1}^{2} x_i u_i^{\circ} \quad (2)$$

$$\Delta n_D = n_D - \sum_{i=1}^{2} x_i n_{Di}^{\circ} \quad (3)$$

In these equations, x_i is the mole fraction of component i and M_i is its molar weight. Also, ρ, u, and n_D are the densities, speeds of sound, and refractive indices of the mixture, respectively. The ρ_i°, u_i°, and n_{Di}° magnitudes are the properties of the pure components. The values of the excess properties are gathered in Table 2 too. A Redlich−Kister type equation[18] was used to correlate the excess molar volumes and the increments, by the method of least squares. This equation can be expressed as

$$\Delta Q = x_i x_j \sum_{p=0}^{M} A_p (x_i - x_j)^p \quad (4)$$

where ΔQ is the incremental property (V_m^E or Δu or Δn_D), x is the mole fraction, A_p represents the fitting parameters, and M is the degree of the polynomic expansion that was optimized by applying the F-test.[19] The correlation parameters, A_p, calculated using eq 4 are listed in Table 3, together with the root-mean-square deviations, σ. These deviations have been calculated by applying the following expression:

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \quad (5)$$

where property values and the number of experimental data points are represented by z and n_{DAT}, respectively.

Table 2. Densities, ρ, Speeds of Sound, u, Refractive Indices, n_D, Excess Molar Volumes, V_m^E, Speed of Sound Increments, Δu, and Refractive Index Increments, Δn_D, for the Nonane (1) + Triethylene Glycol Dimethyl Ether (2) System from 288.15 K to 308.15 K at Four Isotherms

x_1	ρ/(g·cm^{-3})	u/(m·s^{-1})	n_D	V_m^E/(cm^3·mol^{-1})	Δu/(m·s^{-1})	Δn_D
			T = 288.15 K			
0.9760	0.7275	1246	1.408 23	0.151	−4	−0.0002
0.8778	0.7521	1246	1.408 87	0.629	−17	−0.0013
0.7752	0.7785	1250	1.410 07	0.917	−26	−0.0019
0.6868	0.8018	1256	1.411 27	1.020	−32	−0.0023
0.5847	0.8288	1266	1.412 91	1.090	−36	−0.0024
0.5035	0.8506	1275	1.414 29	1.070	−37	−0.0025
0.3939	0.8802	1291	1.416 41	0.983	−36	−0.0023
0.2931	0.9077	1309	1.418 50	0.845	−31	−0.0020
0.1973	0.9341	1329	1.420 63	0.655	−24	−0.0015
0.0958	0.9627	1354	1.423 17	0.335	−13	−0.0008
0.0527	0.9749	1365	1.424 20	0.190	−8	−0.0005
			T = 293.15 K			
0.9568	0.7283	1226	1.405 92	0.270	−7	−0.0006
0.8636	0.7517	1227	1.406 73	0.684	−18	−0.0014
0.7801	0.7732	1231	1.407 69	0.906	−26	−0.0019
0.6854	0.7979	1237	1.409 03	1.055	−32	−0.0022
0.5799	0.8258	1247	1.410 79	1.110	−36	−0.0024
0.5288	0.8394	1254	1.411 69	1.116	−37	−0.0024
0.4946	0.8485	1258	1.412 33	1.112	−37	−0.0023
0.4375	0.8639	1266	1.413 39	1.068	−37	−0.0023
0.3905	0.8765	1274	1.414 35	1.041	−36	−0.0021
0.2952	0.9025	1291	1.416 30	0.892	−31	−0.0019
0.1955	0.9300	1311	1.418 64	0.680	−24	−0.0013
0.0962	0.9579	1335	1.420 92	0.367	−14	−0.0008
			T = 298.15 K			
0.9400	0.7285	1206	1.403 59	0.391	−9	−0.0007
0.8666	0.7469	1207	1.404 15	0.705	−18	−0.0014
0.9043	0.7374	1206	1.403 71	0.555	−14	−0.0012
0.7911	0.7662	1211	1.405 07	0.921	−24	−0.0019
0.6861	0.7934	1217	1.406 62	1.107	−32	−0.0022
0.5877	0.8193	1227	1.408 16	1.162	−35	−0.0024
0.4924	0.8447	1239	1.409 91	1.136	−36	−0.0024
0.3892	0.8724	1254	1.411 99	1.053	−35	−0.0021
0.2888	0.8997	1272	1.414 13	0.895	−30	−0.0018
0.1915	0.9266	1293	1.416 29	0.652	−23	−0.0013
0.1453	0.9394	1303	1.417 35	0.533	−18	−0.0011
0.0951	0.9534	1316	1.418 68	0.383	−13	−0.0007
0.0504	0.9662	1327	1.419 72	0.189	−7	−0.0004
			T = 308.15 K			
0.8794	0.7356	1167	1.399 23	0.679	−16	−0.0014
0.7755	0.7619	1172	1.400 53	0.994	−25	−0.0020
0.6829	0.7857	1179	1.401 91	1.159	−31	−0.0023
0.5882	0.8105	1189	1.403 50	1.203	−34	−0.0024
0.4900	0.8365	1201	1.405 33	1.179	−35	−0.0024
0.3910	0.8629	1216	1.407 31	1.096	−34	−0.0022
0.2938	0.8892	1234	1.409 42	0.934	−29	−0.0019
0.1963	0.9161	1254	1.411 73	0.667	−22	−0.0014
0.0966	0.9437	1278	1.414 19	0.380	−13	−0.0007

Table 3. Parameters A_p of Eq 4 and Standard Deviations, σ, for the Mixture Nonane + Triethylene Glycol Dimethyl Ether from 288.15 K to 308.15 K at Four Isotherms

	A_0	A_1	A_2	A_3	σ
		T = 288.15 K			
V_m^E/(cm^3·mol^{-1})	4.280	0.818	1.156	0.763	0.010
Δu/(m·s^{-1})	−149.0	2.65	−10.34	−10.96	0.12
$10^5 \Delta n_D$	−983	−131	−145		4
		T = 293.15 K			
V_m^E/(cm^3·mol^{-1})	4.437	0.648	1.140	0.759	0.005
Δu/(m·s^{-1})	−148.42	0.86	−14.79		0.13
$10^5 \Delta n_D$	−938	−211	−178		3
		T = 298.15 K			
V_m^E/(cm^3·mol^{-1})	4.578	0.922	1.146	0.644	0.010
Δu/(m·s^{-1})	−144.46	3.00	−10.81	−13.14	0.24
$10^5 \Delta n_D$	−93	−259	−205		6
		T = 308.15 K			
V_m^E/(cm^3·mol^{-1})	4.768	1.246	0.946		0.016
Δu/(m·s^{-1})	−140.24	0.36	−9.96	−9.30	0.10
$10^5 \Delta n_D$	−968	−161	−180	−230	1

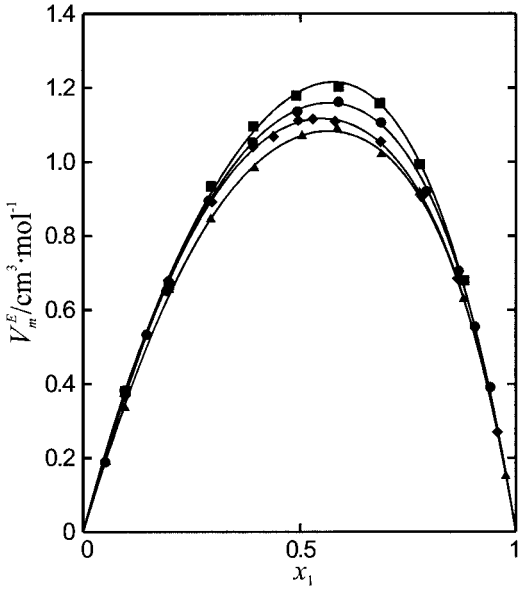

Figure 1. Variation of the excess molar volumes, V_m^E/(cm^3·mol^{-1}), with mole fraction for the mixture nonane (1) + triethylene glycol dimethyl ether (2) at the following temperatures: ▲, 288.15 K; ◆, 293.15 K; ●, 298.15 K; ■, 308.15 K. —, calculated from eq 4.

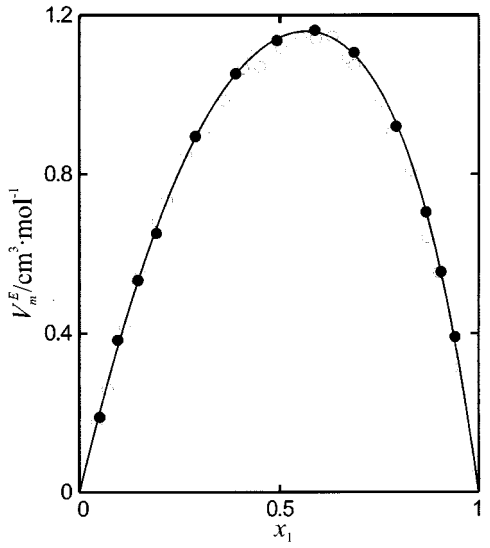

Figure 2. Excess molar volumes, V_m^E/(cm^3·mol^{-1}), against mole fraction at 298.15 K for nonane (1) + triethylene glycol dimethyl ether (2): ●, experimental values; ○, Tovar et al.;[3] —, calculated from eq 4.

Figure 1 represents the excess molar volumes, V_m^E, as a function of mole fraction of nonane at temperatures of 288.15 K, 293.15 K, 298.15 K, and 308.15 K. It is observed that this property is positive for all isotherms, reaches a maximum at the equimolar fraction, approximately, and increases as the temperature increases. Curves were calculated from eq 4 using the parameters given in Table 3. The experimental values of the excess molar volume to 298.15 K are compared with the results of Tovar et al.[3] in Figure 2. The deviations between our data correlated by the Redlich−Kister equation[18] (eq 4) and experimental values of Tovar et al.,[3] at the same mole fraction, enclose results falling within $\pm 3 \times 10^{-2}$ cm^3·mol^{-1}.

For all the studied temperatures, Figures 3 and 4 present, respectively, the values of Δu and Δn_D together with the Redlich−Kister fitting curves, which are practically symmetrical for both properties. Δu and Δn_D are negative for the whole range of concentrations and for all the considered temperatures. Δu becomes less negative when the temperature is increased. Δn_D does not show a clear tendency when the temperature is varied. The negative values of this property show, through the Maxwell equation ($\epsilon = n_D^2$), that the mixture has a permittivity at the Na D-line wavelength smaller than that in the ideal case. This behavior could be explained by considering that when the packing effect decreases ($V_m^E > 0$), the number of dipoles per unit volume diminishes and therefore n_D also becomes smaller, originating negative Δn_D. It would imply the influence of V_m^E in the polarization mechanisms at high frequency, just as seems to be reflected in the results obtained by the theoretical models for the prediction of n_D,[8] which improve when the real volume is considered ($V_m^E \neq 0$).

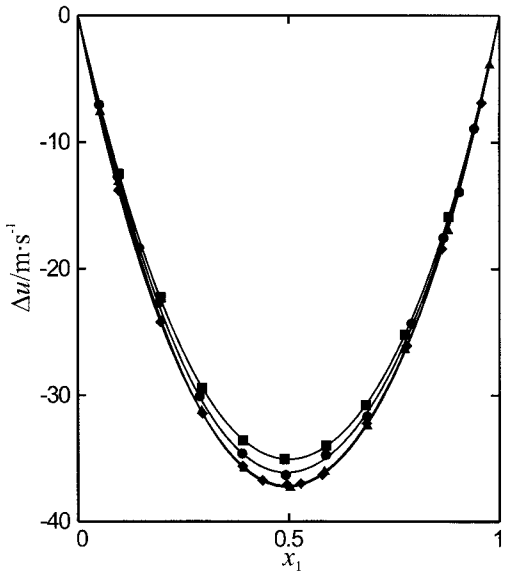

Figure 3. Curves of speed of sound increments, Δu/(m·s^{-1}), from eq 4 for nonane (1) + triethylene glycol dimethyl ether (2) at the following temperatures: ▲, 288.15 K; ◆, 293.15 K; ●, 298.15 K; ■, 308.15 K.

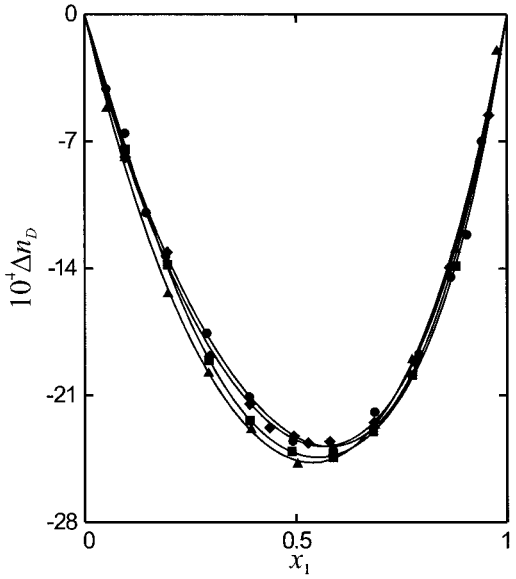

Figure 4. Refractive index increments, Δn_D, for nonane (1) + triethylene glycol dimethyl ether (2). Experimental values at the following temperatures: ▲, 288.15 K; ◆, 293.15 K; ●, 298.15 K; ■, 308.15 K. —, calculated from eq 4.

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Chemical Abstracts Service **Registry Numbers Supplied by the Authors:** triethylene glycol dimethyl ether, [112-49-2]; nonane, [111-84-2].

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