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Speeds of Sound, Densities, and Isentropic Compressibilities of the System Methanol + Tetraethylene Glycol Dimethyl Ether at the Temperatures from 293.15 K to 333.15 K

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Speed of sound, density, and isentropic compressibility have been measured over the entire composition range at atmospheric pressure for the system methanol + tetraethylene glycol dimethyl ether (2,5,8,11,14-pentaoxapentadecane) at five temperatures from 293.15 K to 333.15 K. The values of these magnitudes were fitted by a polynomial equation in mole fraction. The values of the densities and isentropic compressibilities have been used to calculate excess molar volumes and isentropic compressibility increments, respectively, for the mixing process. These results have been fitted to a variable-degree polynomial equation to obtain the correlation parameters together with the root-mean-square deviations between the experimental and calculated values.

Introduction

In recent years, research on working fluid systems for absorption technology has received considerable interest. The most important criteria to select a working pair are thermal and chemical stability and large solubility of the refrigerant in the absorbent, in accordance with the general characteristics of an absorption cycle. On the basis of the molecular behavior, a good solubility and thermal stability can be found with alcohols. The properties of the alcohols and their mixtures with other substances are related with the hydrogen bonding properties of the alcohols. These compounds have the activated hydrogen atom of their hydroxyl group available for interaction with a proton acceptor. Consequently, the suitable absorbent must be an electron donor that can form effective hydrogen bonds. Therefore, diverse authors[1,2] have suggested as a working fluid in absorption heat pumps and heat transformers the mixture of methanol as refrigerant with tetraethylene glycol dimethyl ether as absorbent. The second component belongs to the group of the polyalkyl ether glycols, which are also interesting because many of them have been used as transducer fill fluids in underwater Navy research.[3] These compounds have an acoustical match with seawater in terms of speed of sound, density, and specific acoustic impedance, so it avoids the loss of energy associated with the reflection of the sound wave.

As a part of research[4−8] concerning the thermophysical study on new working fluid pairs, we present here some useful data on speed of sound, density, and isentropic compressibility for the mixture of methanol with tetraethylene glycol dimethyl ether. These properties together with the excess molar volumes, V_m^E, and isentropic compressibility increments, $\Delta\kappa_S$, have been determined over the whole composition range at five temperatures ranging from 293.15 K to 333.15 K at atmospheric pressure. Also, we have compared the excess molar volumes with those determined at 293.15 K, 303.15 K, 313.15 K, and 323.15 K by Esteve et al.[5]

Experimental Section

The chemicals supplied by Aldrich and Fluka were acquired and kept in an argon (N-55) atmosphere, as soon as the bottles were opened. They were degassed ultrasonically and dried over molecular sieves type 0.4 nm for tetraethylene glycol dimethyl ether and type 0.3 nm for methanol (Aldrich Cat. No. 20860-4 or 20858-2, respectively), for several days before use to avoid moisturizing due to the hygroscopic behavior of both components. In accordance with the specifications of the supplier, their mass fraction purities were better than 0.999 for methanol and better than 0.99 for tetraethylene glycol dimethyl ether. Precautions such as cooling the components before sample preparation and minimizing empty space in vessels were taken in order to avoid evaporation during manipulation and possible errors in mole fraction calculations.

The speeds of sound and densities of pure components and their mixtures have been measured with an Anton Paar DSA-48 sound and density analyzer with precisions of $\pm 10^{-1}$ m·s^{-1} and $\pm 10^{-4}$ g·cm^{-3}, respectively. The sound velocity measuring cell consists of a cavity that is laterally bordered by a transmitter and a receiver of ultrasonic pulses. All other boundaries of the cavity are made of Teflon. The speed of sound is measured by determining the propagation velocity of the ultrasonic pulses in the sample that is 5007 μm long. The density of the mixtures and pure liquids was measured using a vibrating U-tube. This cell is made of glass (Duran 50) and inserted in a glass jacket with a gas of high thermal conductivity. The Anton-Paar DSA-48 incorporates a thermostat with a temperature stability of $\pm 10^{-1}$ K which ensures the stability for temperatures from 272.15 K to 348.15 K. Before the series of measurements corresponding to each studied temperature, the apparatus calibration was carried out periodically using atmospheric air and tridistilled water (Millipore quality) in accordance with the use instructions.

For each intermediate composition, the sample was prepared by mass using a Mettler AE-240 balance with a precision of $\pm 10^{-4}$ g. A digital controller bath with a temperature stability of $\pm 10^{-2}$ K was used to thermostat the samples at the measured temperatures for at least 20 min before experimental measurements.

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Table 1. Comparison of Speeds of Sound, u, Densities, ρ, and Isentropic Compressibilities, κ_S, with Literature Data for Pure Liquids at Temperatures from 293.15 K to 333.15 K

	$u/(\mathrm{m{\bullet}s^{-1}})$		$\rho/(\mathrm{g{\bullet}cm^{-3}})$		$\kappa_S/(\mathrm{TPa^{-1}})$	
T/K	exp	lit.	exp	lit.	exp	lit.
Methanol						
293.15	1120	1120[9]	0.7915	0.79115[5] 0.7917[9] 0.79119[12] 0.79104[13] 0.79129[14]	1007.2	1007[9]
303.15	1087	1086[10] 1080.8[11]	0.7822	0.78203[5] 0.7822[10] 0.78184[11] 0.78165[12] 0.78196[14] 0.7817[15]	1081.9	1081.7[11]
313.15	1052		0.7727	0.77247[5] 0.7726[14]	1168.7	
323.15	1024		0.7631	0.76283[5] 0.7637[14]	1249.6	
333.15	991		0.7531	0.7546[14]	1353.0	
Tetraethylene Glycol Dimethyl Ether						
293.15	1400		1.0109	1.01101[5] 1.01127[16] 1.01126[17]	504.7	
303.15	1362		1.0017	1.00185[5] 1.00211[18]	537.9	
313.15	1322		0.9925	0.99270[5,16] 0.99274[17]	576.3	
323.15	1289		0.9833	0.98323[5,16]	612.4	
333.15	1253		0.9741	0.97424[16]	653.4	

The uncertainties in the calculation of mole fractions, excess molar volumes, and isentropic compressibility increments were estimated as better than $\pm 10^{-4}$, $\pm 9 \times 10^{-3}$ $\mathrm{cm^3{\cdot}mol^{-1}}$, and ± 1 $\mathrm{T{\cdot}Pa^{-1}}$, respectively.

The experimental measurements of speeds of sound and densities determined at different temperatures, when available, were in accordance with those recommended and recently published values shown in Table 1.

Results and Discussion

The experimental results on mixing of the speed of sound, u, and density, ρ, together with the isentropic compressibility determined by means of the Laplace equation ($\kappa_S = \rho^{-1}{\cdot}u^{-2}$) are gathered in Table 2 at temperatures from 293.15 K to 333.15 K and atmospheric pressure. In this table, the excess molar volumes and isentropic compressibility increments have also been listed. These two properties were determined using eqs 1 and 2, respectively.

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

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{2} x_i \kappa_{Si}^{\circ} \tag{2}$$

In these equations, x_i is the mole fraction of component i and M_i is its molar mass. The ρ_i° and κ_{Si}° magnitudes are the properties of the pure components. The increments and excess molar volumes were correlated by means of the Redlich−Kister polynomial relationship:[19]

$$\Delta Q = x_i x_j \sum_{p=0}^{N} B_p (x_i - x_j)^p \tag{3}$$

Table 2. Speeds of Sound, u, Densities, ρ, Isentropic Compressibilities, κ_S, Excess Molar Volumes, V_m^E, and Isentropic Compressibility Increments, $\Delta\kappa_S$, for the System Methanol (1) + Tetraethylene Glycol Dimethyl Ether (2) at Temperatures from 293.15 K to 333.15 K

x_1	$u/\mathrm{m{\cdot}s^{-1}}$	$\rho/\mathrm{g{\cdot}cm^{-3}}$	$V_m^E/\mathrm{cm^3{\cdot}mol^{-1}}$	$\kappa_S/\mathrm{T{\cdot}Pa^{-1}}$	$\Delta\kappa_S/\mathrm{T{\cdot}Pa^{-1}}$
T = 293.15 K					
0.1193	1397	1.0066	−0.205	509.3	−55
0.2671	1390	1.0000	−0.498	517.8	−121
0.3054	1388	0.9979	−0.568	520.4	−138
0.4614	1374	0.9865	−0.763	536.6	−200
0.4996	1370	0.9828	−0.791	542.3	−214
0.5972	1355	0.9711	−0.841	561.1	−244
0.6971	1332	0.9542	−0.854	590.8	−264
0.8072	1292	0.9249	−0.771	647.9	−262
0.9022	1232	0.8811	−0.546	747.1	−211
0.9500	1187	0.8462	−0.346	838.3	−144
T = 303.15 K					
0.1277	1358	0.9969	−0.195	543.9	−64
0.2347	1354	0.9922	−0.409	550.1	−116
0.3185	1349	0.9876	−0.554	556.5	−155
0.4150	1341	0.9809	−0.691	566.6	−197
0.4992	1332	0.9733	−0.772	578.8	−231
0.5870	1320	0.9631	−0.844	596.3	−261
0.6986	1296	0.9446	−0.877	630.7	−287
0.8070	1256	0.9156	−0.789	692.5	−284
0.9070	1194	0.8686	−0.534	808.1	−223
0.9533	1149	0.8337	−0.324	908.6	−148
T = 313.15 K					
0.1189	1318	0.9881	−0.196	582.1	−65
0.2126	1315	0.9842	−0.407	587.7	−115
0.2842	1311	0.9806	−0.553	593.2	−152
0.4259	1301	0.9710	−0.760	608.4	−220
0.4904	1294	0.9652	−0.828	618.8	−248
0.5882	1280	0.9539	−0.901	639.6	−285
0.6937	1258	0.9364	−0.919	674.5	−313
0.8000	1222	0.9087	−0.834	737.1	−313
0.8989	1164	0.8642	−0.585	854.3	−255
0.9481	1119	0.8289	−0.372	963.2	−175
T = 323.15 K					
0.1451	1284	0.9778	−0.251	620.6	−84
0.2166	1281	0.9745	−0.374	625.5	−125
0.3046	1276	0.9699	−0.555	632.8	−174
0.4182	1268	0.9621	−0.734	646.4	−232
0.5082	1259	0.9539	−0.842	661.8	−274
0.5957	1246	0.9434	−0.915	682.6	−309
0.6955	1225	0.9265	−0.930	719.4	−336
0.8060	1187	0.8971	−0.841	790.8	−335
0.9039	1129	0.8516	−0.585	921.6	−267
0.9536	1082	0.8144	−0.347	1047.9	−172
T = 333.15 K					
0.1028	1250	0.9704	−0.199	659.1	−66
0.2461	1244	0.9640	−0.488	669.9	−156
0.3148	1241	0.9601	−0.608	676.6	−197
0.4233	1232	0.9523	−0.755	691.3	−258
0.5076	1224	0.9445	−0.855	706.8	−302
0.5915	1212	0.9345	−0.935	728.3	−339
0.6964	1190	0.9169	−0.971	769.6	−371
0.8034	1154	0.8886	−0.896	844.3	−371
0.9007	1099	0.8439	−0.627	981.9	−302
0.9516	1052	0.8064	−0.379	1119.4	−200

where ΔQ is the incremental property (V_m^E or $\Delta\kappa_S$), x is the mole fraction, B_p represents the fitting coefficients, and N is the degree of the polynomic expansion. A least-squares method was used to fit the data. The degree of the polynomials was optimized by applying the F-test.[20] The root-mean-square deviations, σ, between the calculated, z_{pred}, and the experimental, z_{exp}, values have been estimated by using

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\text{DAT}}} (z_{\text{exp}} - z_{\text{pred}})^2}{n_{\text{DAT}} - (N + 1)} \right)^{1/2} \tag{4}$$

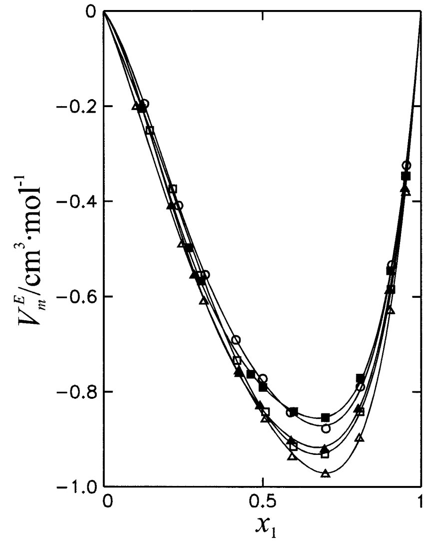

Figure 1. Variation of the excess molar volumes, V_m^E/cm^3·mol^{-1}, with mole fraction for the system methanol (1) + tetraethylene glycol dimethyl ether (2) at the following temperatures: ■, 293.15 K; ○, 303.15 K; ▲, 313.15 K; □, 323.15 K; △, 333.15 K. —, calculated from eq 3.

Table 3. Redlich−Kister Parameters and Root-Mean-Square Deviations, σ, at Temperatures from 293.15 K to 333.15 K at Five Isotherms

	B_0	B_1	B_2	B_3	B_4	σ
		T = 293.15 K				
V_m^E/cm^3·mol^{-1}	−3.158	−1.402	−1.291	−2.118		0.007
$\Delta\kappa_S$/T·Pa^{-1}	−860.3	−623.9	−387.3	−835.1	−878.5	3.6
		T = 303.15 K				
V_m^E/cm^3·mol^{-1}	−3.116	−1.780	−1.276	−1.779		0.006
$\Delta\kappa_S$/T·Pa^{-1}	−930.2	−689.6	−421.1	−875.8	−965.6	3.9
		T = 313.15 K				
V_m^E/cm^3·mol^{-1}	−3.356	−1.670	−1.240	−2.037		0.007
$\Delta\kappa_S$/T·Pa^{-1}	−1013.8	−747.7	−493.8	−979.5	−1005.7	4.3
		T = 323.15 K				
V_m^E/cm^3·mol^{-1}	−3.352	−2.078	−0.683	−1.480	−1.210	0.006
$\Delta\kappa_S$/T·Pa^{-1}	−1091.4	−822.5	−487.1	−988.0	−1170.9	4.1
		T = 333.15 K				
V_m^E/cm^3·mol^{-1}	−3.393	−2.065	−1.898	−1.576		0.007
$\Delta\kappa_S$/T·Pa^{-1}	−1200.1	−884.0	−561.8	−1210.5	−1242.8	5.4

where the denominator is the number of the degrees of freedom. This is the difference between the number of experimental data, n_{DAT}, and the number of adjustable coefficients, $N + 1$. The correlation parameters, B_p, obtained for the incremental properties in this study are summarized in Table 3, together with their corresponding root-mean-square deviations, σ.

Figure 1 shows, for the five studied isotherms, the experimental values of V_m^E plotted against the mole fraction of methanol. For this property, the curve obtained using eq 3 is asymmetric for each temperature.

The large negative values of V_m^E for all isotherms are minimum to compositions with high methanol content. This negative behavior of V_m^E could be mainly due to the intermolecular interactions between the oxygen atoms of the tetraethylene glycol dimethyl ether and the hydrogen atom of the hydroxyl group of methanol, as well as the packing effect. Tetraethylene glycol dimethyl ether could be accommodating alcohol molecules in its empty spaces, since it is more voluminous than the methanol. With respect to temperature dependence, it is found that the excess molar volume diminishes with the thermal agitation.

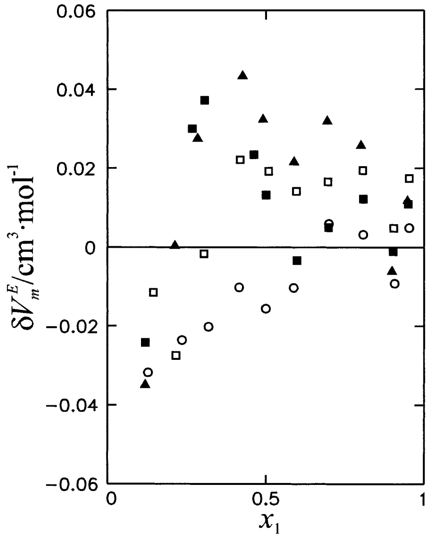

Figure 2. Deviations, δV_m^E/cm^3·mol^{-1}, for methanol (1) + tetraethylene glycol dimethyl ether (2) between our experimental excess molar volumes (zero line) and the correlated data (eq 3) corresponding to Esteve et al.[5] at the following temperatures: ■, 293.15 K; ○, 303.15 K; ▲, 313.15 K; □, 323.15 K.

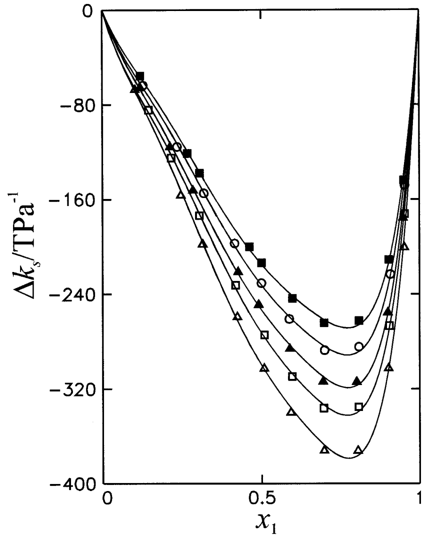

Figure 3. Curves of isentropic compressibility increments, $\Delta\kappa_S$/T·Pa^{-1}, from eq 3 for methanol (1) + tetraethylene glycol dimethyl ether (2) at the following temperatures: ■, 293.15 K; ○, 303.15 K; ▲, 313.15 K; □, 323.15 K; △, 333.15 K.

Table 4. Root-Mean-Square Deviations, σ, between Our Excess Molar Volumes and Those Correlated (Eq 3) by Esteve et al.[5] from 293.15 K to 323.15 K

T/K	σ(V_m^E/cm^3·mol^{-1})
293.15	0.018
303.15	0.015
313.15	0.025
323.15	0.016

A comparison at temperatures of 293.15 K, 303.15 K, 313.15 K, and 323.15 K between our experimental excess molar volumes and the correlated data by means of eq 3 found in the literature[5] is gathered in Table 4 in terms of root-mean-square deviations. Figure 2 represents the deviations between both groups of data for each temperature.

Finally, the results of $\Delta\kappa_S$ calculated for the five studied temperatures are represented in Figure 3. Its negative values represent asymmetry curves with a minimum to compositions with high alcohol content. On the other hand, it is observed that the absolute value of this magnitude increases as the thermal agitation grows.

Chemical Abstracts Service Registry Numbers Supplied by the Authors: tetraethylene glycol dimethyl ether, [143-24-8]; methanol, [67-56-1].

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