Thermodynamics of Mixtures Containing Alkoxyethanols. Part XXVI. Densities, Excess Molar Volumes, Speeds of Sound at (293.15, 298.15, and 303.15) K, and Isentropic or Isothermal Compressibilities at 298.15 K for 2-Methoxyethanol + Alkoxyethanol or 2-Propoxyethanol + Dibutylether Systems

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Densities, ρ, and speeds of sound, u, for the systems 2-methoxyethanol (2ME) + 2-ethoxyethanol (2EE), or + 2-butoxyethanol (2BE), or + 2-(2-methoxyethoxy)ethanol (22MEE) and for the 2-propoxyethanol (2PE) + dibutylether (DBE) mixture have been measured at (293.15, 298.15, and 303.15) K and atmospheric pressure using a vibrating-tube densimeter and sound analyzer (Anton Paar model DSA-5000). The ρ and u values were used to calculate excess molar volumes, V^E, at the mentioned temperatures, molar excess heat capacities at constant volume, C_V^E, at 298.15 K, and deviations from the ideal behavior at 298.15 K of the thermal expansion coefficient, $\Delta\alpha_P$, and of the isentropic and isothermal compressibilities, $\Delta\kappa_S$ and $\Delta\kappa_T$, respectively. In DBE systems, H^E(molar excess enthalpy) and V^E decrease with the size of the 2-alkoxyethanol. In 2ME + alkoxyethanol mixtures, these magnitudes increase with the size of the second compound, although their values depend on the number of etheric atoms of this component.

1. Introduction

Alkoxyethanols are a very interesting class of substances from a practical point of view, as oxygenated compounds are increasingly used as additives to gasoline due their octane-enhancing and pollution-reducing properties.[1,2] In addition, hydroxyethers are nonionic amphiphile molecules, very effective as surfactants with a large number of applications.[3,4] On the other hand, the investigation of mixtures involving alkoxyethanols makes possible the study of self-association via inter- and intramolecular hydrogen bonds related to the presence of the O and OH groups in the same molecule. In particular, the formation of the intramolecular H-bonds leads to enhanced dipole−dipole interactions in solutions containing alkoxyethanols and alkanes relative to those present in mixtures with homomorphic alkanols.[5]

As a continuation of previous works,[6–8] in this paper, ρ, u, and related quantities such as V^E, $\Delta\alpha_P$, $\Delta\kappa_S$, and $\Delta\kappa_T$ are reported for the systems 2-methoxyethanol (2ME) + 2-ethoxyethanol (2EE), + 2-butoxyethanol (2BE), or + 2-(2-methoxyethoxy)ethanol (22MEE) and for the 2-propoxyethanol (2PE) + dibutylether (DBE) mixture. V^E data at 298.15 K for the 2ME + 2EE, + 2BE, or + 22MEE mixtures are available in the literature.[9]

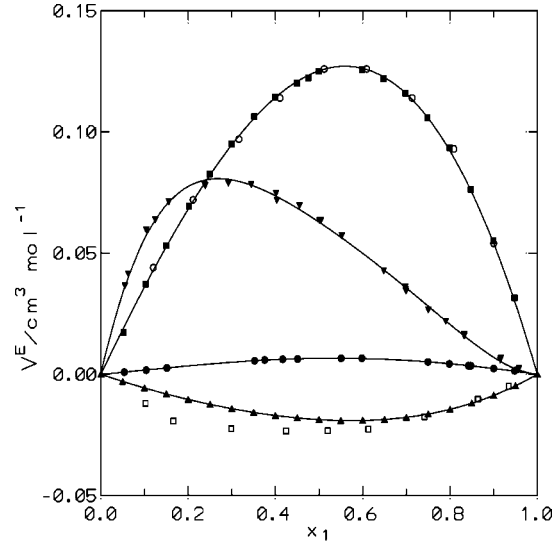

Figure 1. V^E at 298.15 K for 2-alkoxyethanol (1) + organic solvent (2) mixtures. Solid lines, calculations with eq 7 using the coefficients from Table 4. Points, experimental results (full symbols, this work; open symbols, ref 9): ●, 2ME (1) + 2EE (2); ■,○, 2ME (1) + 2BE (2); ▲,□, 2ME (1) + 22MEE; ▼, 2PE (1) + DBE (2).

2. Experimental Section

2.1. Materials. 2-Methoxyethanol, 2EE, and DBE (puriss p.a. ≥ 99.5 %), 2PE (puriss p.a. ≥ 99 %), 2BE, and 22MEE (purum. ≥ 98 %) were from Fluka and used without further purification. The ρ and u values at atmospheric pressure of the pure liquids are in good agreement with those from the literature (Table 1). The water contents were determined by the Karl Fischer method being 0.004, 0.010, 0006, 0.005, 0.01, and 0.006 mol % for 2ME, 2EE, 2PE, 2BE, 22MEE, and DBE, respectively.

2.2. Apparatus and Procedure. Binary mixtures were prepared by mass in small vessels of about 10 cm^3. Caution was taken to prevent evaporation, and the error in the final mole fraction is estimated to be less than ± 0.0001. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by I.U.P.A.C.[10]

The densities and speeds of sound of both pure liquids and the mixtures were measured using a vibrating-tube densimeter

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Table 1. Physical Properties of Pure Compounds 2-Methoxyethanol, 2-Ethoxyethanol, 2-Propoxyethanol, 2-Butoxyethanol, 2-(2-Methoxyethoxy)ethanol, and Dibutylether at Temperature T and Atmospheric Pressure[a]

property	T/K	2ME	2EE	2PE	2BE	22MEE	DBE
ρ/g·cm^{-3}	293.15	0.964656	0.929545	0.911515	0.900094	1.019810	0.768468
		0.96459[b]	0.92945[b]		0.900075[c]	1.02080[d]	0.76884[e]
	298.15	0.960088	0.925027	0.907151	0.895910	1.015408	0.764170
		0.96002[f]	0.92502[f]	0.907578[g]	0.89581[f]	1.01591[h]	0.76411[e]
	303.15	0.955471	0.920457	0.902736	0.891697	1.010908	0.759829
		0.9554[i]	0.920537[j]	0.903050[g]	0.8920[c]	1.01183[d]	0.76017[e]
u/m·s^{-1}	293.15	1359.23	1319.91	1316.61	1322.50	1432.37	1181.82
		1359.6[i]					
	298.15	1341.58	1301.73	1298.58	1304.94	1415.21	1161.19
		1341.9[i]	1302.51[g]	1299.57[g]	1305.84[g]	1415.5[k]	1161.1[k]
	303.15	1324.29	1284.15	1281.14	1288.02	1397.93	1142.07
		1324.5[i]					
$\alpha_P/10^{-3}$K^{-1}	298.15	0.9567	0.9825	0.9678	0.9374	0.8767	1.1307
		0.956[i]	0.9844[l]	1.003[g]	0.9377[c]	0.8493[m]	1.1335[e]
κ_S/TPa^{-1}	293.15	561.10	617.51	632.88	635.21	477.94	931.69
		560.86[i]					
	298.15	578.70	637.97	653.71	655.47	491.72	970.52
		578.4[i]	637.0[g]	652.4[g]	656[n]	490.0[m]	970.6[k]
	303.15	596.78	658.82	674.91	675.98	506.19	1009.02
		596.59[i]					
κ_T/TPa^{-1}	298.15	704.14	773.30	786.31	783.96	595.17	1204.03
		700.8[i]	783.6[g]	792[g]	765.1[g]	583.8[m]	1224[k]
C_P/J·mol^{-1}·$^{-1}$	298.15	172.43[o]	207.21[o]	241.78[p]	268.94[o]	262.12[o]	278.02[o]
C_V/J·mol^{-1}·K^{-1}	298.15	141.71	170.85	201.01	224.86	216.56	224.25

[a] ρ, density; u, speed of sound; α_P, isobaric thermal expansion coefficient; κ_S, adiabatic compressibility; κ_T, isothermal compressibility; C_V, isochoric heat capacity; and C_P, isobaric heat capacity. [b] Ref 11. [c] Ref 28. [d] Ref 29. [e] Ref 30. [f] Ref 31. [g] Ref 32. [h] Ref 33. [i] Ref 34. [j] Ref 35. [k] Ref 36. [l] Ref 37. [m] Ref 38. [n] Ref 39. [o] Ref 20. [p] Ref 21.

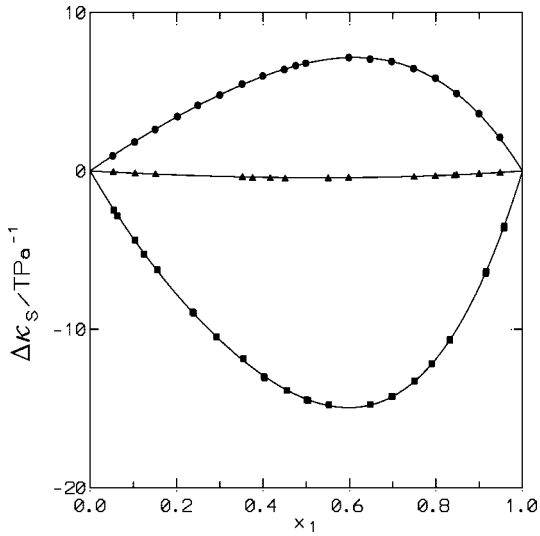

Figure 2. $\Delta\kappa_S$ at 298.15 K for 2-alkoxyethanol (1) + organic solvent (2) mixtures. Solid lines, calculations with eq 7 using the coefficients from Table 4. Points, experimental results (this work): ▲, 2ME (1) + 2EE (2); ●, 2ME (1) + 2BE (2); ■, 2PE (1) + DBE (2).

and a sound analyzer (Anton Paar model DSA-5000) automatically thermostatted within ± 0.01 K. The calibration of the apparatus was carried out with deionized double-distilled water, hexane, heptane, octane, isooctane, cyclohexane, and benzene, using ρ values from the literature.[11–13] The accuracy for the ρ and u measurements is ± 10^{-2} kg·m^{-3} and ± 0.1 m·s^{-1}, respectively, and the corresponding precisions are ± 10^{-3} kg·m^{-3} and ± 0.01 m·s^{-1}. The experimental technique was checked by determining V^E and u of the standard mixtures (cyclohexane + benzene) at the temperatures (293.15, 298.15, and 303.15) K and cyclohexane + hexane and 2-ethoxyethanol + heptane at 298.15 K. Our results agree well with published values.[14–19] The accuracy in V^E is believed to be less than ± (0.01$|V^E_{max}|$+0.005 cm^3·mol^{-1}), where $|V^E_{max}|$denotes the maximum experimental value of the excess molar volume with respect to the mole fraction. The accuracy of the deviations of u from the ideal behavior is estimated to be 0.3 m·s^{-1}.

3. Equations

The thermodynamic properties for which values are derived most directly from the experimental measurements are the density, ρ, the molar volume, V, the molar heat capacity at constant pressure, C_p, the coefficient of thermal expansion, $\alpha_P = -1/\rho(\partial\rho/\partial T)_P$, and the isentropic compressibility, κ_S. In this work, α_P values were obtained from a linear dependence of ρ with T. Assuming that the absorption of the acoustic wave is negligible, κ_s can be calculated using the Newton−Laplace equation

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

Values of the isothermal compressibility, κ_T, and of the isochoric heat capacity, C_V, can be obtained from the equations

$$\kappa_T = \kappa_S + \frac{TV\alpha_P^2}{C_P} \tag{2}$$

and

$$C_V = C_P - \frac{TV\alpha_P^2}{\kappa_T} = \frac{C_P\kappa_S}{\kappa_T} \tag{3}$$

For an ideal mixture at the same temperature and pressure as the system under study, the values M^{id} of the thermodynamic property, M, are determined using the equations[6,19]

$$M^{id} = x_1M_1 + x_2M_2 \quad (M = V; u; C_P) \tag{4}$$

and

Table 2. Densities, ρ, Molar Excess Volumes, V^E, and Deviations from the Ideal Behavior of the Speed of Sound, Δu, for 2-Methoxyethanol (1) + Alkoxyethanol (2) or 2-Propoxyethanol(1) + Dibutylether (2) Mixtures at Temperature T

x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	Δu / m·s^{-1}	x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	Δu / m·s^{-1}
			2-methoxyethanol (1) + 2-ethoxyethanol (2); T = 293.15 K				
0.1511	0.933958	0.0030	−1.409	0.7482	0.954326	0.0051	−2.301
0.2029	0.935531	0.0039	−1.744	0.7980	0.956272	0.0044	−1.985
0.3043	0.938709	0.0052	−2.300	0.7992	0.956321	0.0044	−2.023
0.3503	0.940193	0.0055	−2.461	0.8504	0.958373	0.0035	−1.624
0.5024	0.945313	0.0063	−2.823	0.8997	0.960393	0.0027	−1.196
0.5514	0.947031	0.0064	−2.876	0.9488	0.962456	0.0013	−0.646
0.6992	0.952448	0.0055	−2.515				
			2-methoxyethanol (1) + 2-ethoxyethanol (2); T = 298.15 K				
0.0536	0.926563	0.0009	−0.563	0.5507	0.942460	0.0066	−2.889
0.1039	0.928032	0.0017	−0.986	0.5981	0.944155	0.0066	−2.868
0.1510	0.929431	0.0027	−1.370	0.7494	0.949818	0.0051	−2.310
0.1517	0.929455	0.0026	−1.371	0.7987	0.951747	0.0043	−2.013
0.3523	0.935724	0.0056	−2.548	0.8423	0.953488	0.0035	−1.670
0.3757	0.936488	0.0059	−2.593	0.8475	0.953698	0.0035	−1.664
0.4166	0.937846	0.0062	−2.727	0.9002	0.955855	0.0024	−1.173
0.4509	0.939002	0.0063	−2.786	0.9483	0.957869	0.0014	−0.648
			2-methoxyethanol (1) + 2-ethoxyethanol (2); T = 303.15 K				
0.1537	0.924945	0.0018	−1.331	0.5505	0.937856	0.0070	−2.921
0.1543	0.924961	0.0019	−1.356	0.5979	0.939553	0.0067	−2.850
0.2017	0.926398	0.0029	−1.719	0.6504	0.941473	0.0060	−2.715
0.2495	0.927868	0.0042	−2.060	0.6979	0.943248	0.0054	−2.573
0.3013	0.929498	0.0051	−2.313	0.7488	0.945193	0.0048	−2.296
0.4020	0.932768	0.0066	−2.732	0.7998	0.947188	0.0039	−1.941
0.4505	0.934390	0.0071	−2.864	0.9001	0.951244	0.0021	−1.130
0.4985	0.936037	0.0071	−2.909				
			2-methoxyethanol (1) + 2-butoxyethanol (2); T = 293.15 K				
0.0524	0.902021	0.0211	−1.642	0.5492	0.926262	0.1237	−11.372
0.1023	0.903942	0.0402	−3.095	0.5987	0.929459	0.1237	−11.477
0.1513	0.905929	0.0562	−4.446	0.6489	0.932911	0.1202	−11.372
0.2009	0.908026	0.0721	−5.716	0.7291	0.938888	0.1086	−10.566
0.2491	0.910172	0.0850	−6.856	0.7487	0.940450	0.1047	−10.287
0.3006	0.912586	0.0964	−7.979	0.7996	0.944683	0.0917	−9.165
0.3411	0.914561	0.1058	−8.787	0.8491	0.949097	0.0753	−7.708
0.3986	0.917531	0.1144	−9.769	0.8992	0.953883	0.0551	−5.764
0.4484	0.920249	0.1210	−10.455	0.9495	0.959058	0.0296	−3.176
0.4994	0.923189	0.1255	−10.994				
			2-methoxyethanol (1) + 2-butoxyethanol (2); T = 298.15 K				
0.0522	0.897844	0.0173	−1.609	0.4987	0.918836	0.1250	−10.974
0.1029	0.899781	0.0373	−3.062	0.5985	0.925072	0.1257	−11.457
0.1500	0.901679	0.0531	−4.358	0.6476	0.928432	0.1222	−11.289
0.2019	0.903860	0.0693	−5.699	0.6975	0.932045	0.1160	−10.966
0.2489	0.905939	0.0826	−6.837	0.7481	0.935968	0.1059	−10.233
0.2999	0.908306	0.0951	−7.909	0.7988	0.940157	0.0935	−9.210
0.3514	0.910818	0.1064	−8.963	0.8476	0.944484	0.0762	−7.701
0.3994	0.913289	0.1143	−9.753	0.8993	0.949386	0.0550	−5.686
0.4490	0.915990	0.1201	−10.410	0.9478	0.954336	0.0315	−3.299
0.4755	0.917493	0.1223	−10.759				
			2-methoxyethanol (1) + 2-butoxyethanol (2); T = 303.15 K				
0.0483	0.893466	0.0172	−1.419	0.5031	0.914737	0.1258	−10.875
0.1002	0.895434	0.0372	−2.933	0.6119	0.921563	0.1262	−11.305
0.1519	0.897493	0.0554	−4.332	0.6471	0.923963	0.1245	−11.253
0.1997	0.899493	0.0704	−5.559	0.7275	0.929874	0.1122	−10.473
0.2393	0.901221	0.0820	−6.531	0.7491	0.931575	0.1071	−10.105
0.2476	0.901590	0.0843	−6.731	0.7969	0.935498	0.0951	−9.088
0.3501	0.906436	0.1078	−8.820	0.8463	0.939820	0.0790	−7.723
0.3985	0.908906	0.1168	−9.689	0.8986	0.944764	0.0565	−5.663
0.4499	0.911682	0.1231	−10.373	0.9475	0.949713	0.0321	−3.281
0.4966	0.914340	0.1266	−10.871				
			2-methoxyethanol (1) + 2-(2-methoxyethoxy)ethanol (2); T = 293.15 K				
0.1005	1.016018	−0.0054	1.873	0.5003	0.997850	−0.0172	5.960
0.1489	1.014091	−0.0073	2.640	0.5998	0.992362	−0.0170	5.909
0.1983	1.012062	−0.0096	3.395	0.6476	0.989566	−0.0168	5.712
0.2003	1.011979	−0.0097	3.429	0.6993	0.986398	−0.0159	5.324
0.2517	1.009775	−0.0111	4.074	0.7475	0.983311	−0.0142	4.840
0.2969	1.007770	−0.0125	4.595	0.7485	0.983242	−0.0142	4.866
0.2993	1.007666	−0.0127	4.650	0.7971	0.979992	−0.0128	4.211
0.3475	1.005453	−0.0147	5.141	0.8465	0.976527	−0.0103	3.451
0.3505	1.005311	−0.0145	5.129	0.8977	0.972767	−0.0075	2.471
0.3985	1.003011	−0.0153	5.504	0.9483	0.968858	−0.0038	1.333
0.4500	1.000453	−0.0162	5.807				

Table 2. Continued

x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	Δu / m·s^{-1}	x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	Δu / m·s^{-1}
2-methoxyethanol (1) + 2-(2-methoxyethoxy)ethanol (2); T = 298.15 K							
0.0523	1.013467	−0.0034	1.030	0.5455	0.990948	−0.0192	6.167
0.1027	1.011521	−0.0061	1.929	0.5989	0.987943	−0.0190	6.083
0.1523	1.009540	−0.0084	2.805	0.6471	0.985114	−0.0188	5.892
0.1974	1.007674	−0.0101	3.531	0.7005	0.981838	−0.0180	5.551
0.2507	1.005394	−0.0123	4.230	0.7490	0.978717	−0.0165	5.040
0.2940	1.003471	−0.0138	4.717	0.7983	0.975395	−0.0142	4.349
0.3472	1.001025	−0.0156	5.241	0.8460	0.972046	−0.0120	3.622
0.3976	0.998612	−0.0169	5.618	0.8832	0.969324	−0.0099	2.889
0.4502	0.995991	−0.0180	5.920	0.8956	0.968391	−0.0092	2.644
0.4981	0.993508	−0.0188	6.072	0.9483	0.964311	−0.0049	1.392
0.5000	0.993405	−0.0189	6.118				
2-methoxyethanol (1) + 2-(2-methoxyethoxy)ethanol (2); T = 303.15 K							
0.0536	1.008920	−0.0043	1.113	0.5028	0.988711	−0.0195	6.206
0.1018	1.007058	−0.0074	2.067	0.5499	0.986158	−0.0202	6.211
0.1500	1.005130	−0.0094	2.848	0.6000	0.983323	−0.0199	6.144
0.2011	1.003020	−0.0125	3.661	0.6482	0.980488	−0.0200	5.957
0.2499	1.000923	−0.0142	4.283	0.6941	0.977672	−0.0192	5.642
0.2515	1.000848	−0.0138	4.305	0.7485	0.974182	−0.0179	5.169
0.3010	0.998636	−0.0154	4.900	0.7979	0.970854	−0.0157	4.465
0.3527	0.996240	−0.0170	5.363	0.8989	0.963546	−0.0096	2.640
0.3986	0.994036	−0.0181	5.728	0.9476	0.959766	−0.0059	1.489
0.4493	0.991500	−0.0192	6.016				
2-propoxyethanol (1) + dibutylether (2); T = 293.15 K							
0.0625	0.774485	0.0301	−4.101	0.5990	0.840020	0.0373	−23.941
0.1231	0.780612	0.0477	−8.051	0.6019	0.840448	0.0375	−23.903
0.1827	0.786927	0.0560	−11.639	0.6498	0.847778	0.0309	−23.358
0.2394	0.793199	0.0608	−14.750	0.6536	0.848363	0.0301	−23.259
0.2492	0.794319	0.0601	−15.243	0.7431	0.862909	0.0186	−20.629
0.2944	0.799550	0.0623	−17.400	0.8304	0.878188	0.0109	−16.027
0.2949	0.799613	0.0611	−17.413	0.8329	0.878643	0.0097	−15.841
0.3486	0.806069	0.0601	−19.629	0.8750	0.886460	0.0053	−12.734
0.4023	0.812805	0.0581	−21.418	0.9173	0.894637	0.0013	−9.034
0.4544	0.819603	0.0531	−22.770	0.9567	0.902506	0.0000	−5.077
0.4567	0.819921	0.0517	−22.796	0.9568	0.902528	0.0011	−5.065
0.5556	0.833650	0.0410	−23.989				
2-propoxyethanol (1) + dibutylether (2); T = 298.15 K							
0.0551	0.769407	0.0366	−3.771	0.5521	0.828692	0.0572	−24.354
0.0626	0.770132	0.0414	−4.251	0.6483	0.843112	0.0427	−23.675
0.1039	0.774248	0.0596	−7.041	0.6976	0.850944	0.0360	−22.524
0.1246	0.776381	0.0638	−8.310	0.6984	0.851074	0.0349	−22.469
0.1556	0.779622	0.0712	−10.300	0.6993	0.851218	0.0343	−22.464
0.2367	0.788484	0.0785	−14.853	0.7502	0.859679	0.0266	−20.618
0.2393	0.788779	0.0779	−14.991	0.7902	0.866584	0.0219	−18.640
0.2922	0.794872	0.0788	−17.564	0.8325	0.874153	0.0165	−16.068
0.3545	0.802367	0.0783	−20.233	0.8325	0.874166	0.0158	−16.047
0.4014	0.808252	0.0747	−21.698	0.9152	0.889815	0.0059	−9.358
0.4031	0.808491	0.0718	−21.737	0.9163	0.890027	0.0066	−9.280
0.4550	0.815247	0.0696	−23.087	0.9571	0.898214	0.0019	−5.036
0.5006	0.821438	0.0635	−23.856	0.9581	0.898407	0.0025	−4.955
0.5043	0.821944	0.0636	−23.907				
2-propoxyethanol (1) + dibutylether (2); T = 303.15 K							
0.0645	0.765959	0.0462	−4.473	0.5997	0.831213	0.0612	−24.358
0.1249	0.772015	0.0724	−8.485	0.6542	0.839567	0.0505	−23.701
0.1826	0.778083	0.0884	−12.035	0.6988	0.846673	0.0432	−22.557
0.2383	0.784220	0.0941	−15.129	0.7434	0.854060	0.0361	−20.974
0.2383	0.784216	0.0951	−15.118	0.7899	0.862072	0.0269	−18.758
0.3481	0.797121	0.0937	−20.104	0.8319	0.869613	0.0188	−16.118
0.4032	0.804021	0.0898	−21.973	0.8764	0.877879	0.0150	−12.809
0.4542	0.810670	0.0832	−23.257	0.9168	0.885687	0.0084	−9.214
0.4567	0.810994	0.0850	−23.309	0.9168	0.885692	0.0083	−9.267
0.5058	0.817670	0.0778	−24.134	0.9553	0.893420	0.0038	−5.284
0.5547	0.824595	0.0694	−24.453	0.9575	0.893858	0.0045	−5.017
0.5548	0.824612	0.0684	−24.471				

$$M^{id} = \varphi_1 M_1 + \varphi_2 M_2 \quad (M = \alpha_P; \kappa_T) \tag{5}$$

$$\Delta M = M - M^{id} \tag{6}$$

where $\varphi_i = x_i V_i / V^{id}$ and M_i are the volume fraction and the M value of component i, respectively. For κ_S and C_V, the ideal values are calculated according to eqs 2 to 3. In this article, we have determined the deviations

The M_i values of pure compounds needed to calculate M^{id} are listed in Table 1. Most of them were determined in this work, as only C_{Pi} values were taken from the literature.[20,21]

4. Results

Table 2 lists values of densities, calculated V^E, and Δu vs x_1, the mole fraction of 2ME or 2PE. Table 3 contains derived quantities such as $\Delta\kappa_S$, $\Delta\alpha_P$, and C_V^E. The latter were calculated for mixtures involving two hydroxyethers as only for these systems C_P^E values (needed to determine C_P in eq 3) are available in the literature.[9] The data were fitted by unweighted least-squares polynomial regression to the equation

$$\Delta M = x_1(1-x_1)\sum_{i=0}^{k-1} A_i(2x_1-1)^i \qquad (7)$$

where M stands for the properties cited above. The number of coefficients k used in eq 7 for each mixture was determined by applying an F-test[22] at the 99.5 % confidence level. Table 4 lists the parameters A_i obtained in the regression, together with the standard deviations, σ, defined by

$$\sigma(\Delta M) = \left[\frac{1}{N-k}\sum(\Delta M_{\text{calcd}} - \Delta M_{\text{exptl}})^2\right]^{1/2} \qquad (8)$$

where N is the number of direct experimental values. Results on V^E and $\Delta\kappa_S$ are shown graphically in Figures 1 and 2. V^E data at 298.15 K are in agreement with those available in the literature[9] (Figure 1).

5. Discussion

Hereafter, we are referring to values of the excess properties at equimolar composition and 298.15 K. We note that in mixtures with 2ME, V^E (in $cm^3 \cdot mol^{-1}$) varies as follows: -0.0187 (22MEE) < 0.0066 (2EE) < 0.1252 (2BE). H^E varies similarly[9]: -13.4 (22MEE) < 39.4 (2EE) < 211 (2BE) $J \cdot mol^{-1}$. These results suggest that: (i) More interactions between unlike molecules are created upon mixing when the number of etheric atoms in the second compound is increased, and this effect predominates over the interactions between like molecules,

Table 3. Deviations from the Ideal Behavior at 298.15 K for κ_S, Adiabatic Compressibility, κ_T, Isothermal Compressibility, and α_P, Isobaric Thermal Expansion Coefficient and Excess Molar Heat Capacity at Constant Volume, C_V^E, for 2-Methoxyethanol (1) + Alkoxyethanol (2) or 2-Propoxyethanol (1) + Dibutylether (2) Mixtures

x_1	$\Delta\kappa_S$ / TPa^{-1}	$\Delta\kappa_T$ / TPa^{-1}	$\Delta\alpha_P$ / $10^{-6}\ K^{-1}$	C_V^E / $J \cdot mol^{-1} \cdot K^{-1}$	x_1	$\Delta\kappa_S$ / TPa^{-1}	$\Delta\kappa_T$ / TPa^{-1}	$\Delta\alpha_P$ / $10^{-6}\ K^{-1}$	C_V^E / $J \cdot mol^{-1} \cdot K^{-1}$
2-methoxyethanol (1) + 2-ethoxyethanol (2)									
0.0536	−0.04	−0.28	−1.1	0.04	0.5507	−0.43	0.01	0.6	−0.18
0.1039	−0.13	−0.42	−1.4	0.04	0.5981	−0.40	−0.03	0.4	−0.16
0.1510	−0.19	−0.41	−1.3	0.02	0.7494	−0.35	−0.26	−0.4	−0.09
0.1517	−0.19	−0.41	−1.3	0.02	0.7987	−0.30	−0.28	−0.6	−0.07
0.3523	−0.36	−0.01	0.4	−0.14	0.8423	−0.26	−0.29	−0.7	−0.05
0.3757	−0.41	−0.02	0.5	−0.16	0.8475	−0.22	−0.25	−0.7	−0.05
0.4166	−0.42	0.03	0.7	−0.17	0.9002	−0.16	−0.21	−0.6	−0.03
0.4509	−0.45	0.03	0.8	−0.18	0.9483	−0.09	−0.13	−0.4	−0.01
2-methoxyethanol (1) + 2-butoxyethanol (2)									
0.0522	0.95	0.33	−1.6	0.21	0.4987	6.80	5.78	1.5	0.56
0.1029	1.82	0.87	−2.1	0.34	0.5985	7.16	6.11	1.7	0.55
0.1500	2.61	1.52	−2.1	0.41	0.6476	7.06	6.02	1.7	0.53
0.2019	3.43	2.30	−1.6	0.46	0.6975	6.91	5.92	1.8	0.50
0.2489	4.14	3.03	−1.0	0.49	0.7481	6.46	5.58	1.9	0.44
0.2999	4.79	3.73	−0.3	0.50	0.7988	5.86	5.15	2.0	0.37
0.3514	5.48	4.46	0.4	0.52	0.8476	4.89	4.38	2.2	0.28
0.3994	5.99	4.99	0.9	0.53	0.8993	3.62	3.35	2.0	0.18
0.4490	6.40	5.40	1.2	0.54	0.9478	2.12	2.04	1.5	0.09
0.4755	6.65	5.64	1.4	0.55					
2-methoxyethanol (1) + 2-(2-methoxyethoxy)ethanol (2)									
0.0523	0.06	−0.51	−1.1	0.24	0.5455	−0.04	−2.59	−2.6	0.82
0.1027	0.12	−0.89	−1.8	0.42	0.5989	−0.09	−2.68	−2.9	0.80
0.1523	0.12	−1.24	−2.2	0.55	0.6471	−0.14	−2.75	−3.2	0.78
0.1974	0.11	−1.51	−2.4	0.64	0.7005	−0.21	−2.79	−3.5	0.74
0.2507	0.13	−1.73	−2.4	0.71	0.7490	−0.21	−2.71	−3.7	0.69
0.2940	0.14	−1.88	−2.4	0.76	0.7983	−0.19	−2.52	−3.8	0.62
0.3472	0.12	−2.05	−2.4	0.79	0.8460	−0.22	−2.28	−3.6	0.52
0.3976	0.11	−2.19	−2.4	0.81	0.8832	−0.19	−1.94	−3.3	0.43
0.4502	0.06	−2.33	−2.4	0.82	0.8956	−0.19	−1.82	−3.1	0.40
0.4981	0.03	−2.45	−2.5	0.82	0.9483	−0.10	−1.05	−1.9	0.22
0.5000	0.00	−2.48	−2.5	0.82					
2-propoxyethanol (1) + dibutylether (2)									
0.0551	−2.49		7.8		0.5521	−14.78		18.6	
0.0626	−2.84		8.7		0.6483	−14.76		15.6	
0.1039	−4.37		13.1		0.6976	−14.23		13.9	
0.1246	−5.25		14.9		0.6984	−14.27		13.8	
0.1556	−6.24		17.2		0.6993	−14.23		13.8	
0.2367	−8.91		21.0		0.7502	−13.25		12.0	
0.2393	−8.98		21.1		0.7902	−12.18		10.5	
0.2922	−10.48		22.2		0.8325	−10.65		8.8	
0.3545	−11.85		22.5		0.8325	−10.68		8.8	
0.4014	−12.98		22.1		0.9152	−6.46		5.0	
0.4031	−13.05		22.1		0.9163	−6.36		5.0	
0.4550	−13.87		21.2		0.9571	−3.61		2.8	
0.5006	−14.47		20.1		0.9581	−3.50		2.7	
0.5043	−14.50		20.0						

Table 4. Coefficients A_i and Standard Deviations, $\sigma(\Delta M)$ (Equation 8), for Representation of ΔM[a] at Temperature T for 2-Methoxyethanol (1) + Alkoxyethanol (2) or 2-Propoxyethanol (1) + Dibutylether (2) Mixtures by Equation 7

system[b]	T/K	property (ΔM)	A_0	A_1	A_2	A_3	A_4	$\sigma(\Delta M)$
2ME + 2EE	293.15	V^E	0.02544	0.0030				0.00008
		Δu	−11.29	−1.42	−1.0			0.02
	298.15	V^E	0.02637	0.0046	−0.0056			0.00007
		Δu	−11.48	−1.49	−0.51			0.018
		$\Delta\kappa_S$	−1.71	−0.24				0.018
		$\Delta\kappa_T$	0.16	−0.91	−5.72	3.4		0.018
		$\Delta\alpha_P$	3.06	−3.00	−22.18	13.3		0.02
		C_V^E	−0.735	0.07	1.27	−0.89		0.003
	303.15	V^E	0.02841		−0.0198	0.0141		0.00008
		Δu	−11.66	−1.35	0.61			0.018
2ME + 2BE	293.15	V^E	0.4961	0.102	0.037			0.0007
		Δu	−44.02	−18.07	−6.8			0.03
	298.15	V^E	0.5009	0.125				0.0008
		Δu	−43.91	−18.09	−6.4			0.04
		$\Delta\kappa_S$	27.18	12.43	4.3			0.03
		$\Delta\kappa_T$	23.06	11.07		10.0		0.03
		$\Delta\alpha_P$	5.68	6.7	−11.1	34.6		0.08
		C_V^E	2.216	0.28	1.00	−2.10		0.003
	303.15	V^E	0.5070	0.109	0.019	0.039		0.0005
		Δu	−43.54	−17.99	−6.0			0.05
2ME + 22MEE	293.15	V^E	−0.0682	−0.0159				0.0002
		Δu	23.776	4.01				0.017
	298.15	V^E	−0.0749	−0.0213	−0.0079			0.00019
		Δu	24.51	4.38				0.03
		$\Delta\kappa_S$		−1.88	−0.71			0.017
		$\Delta\kappa_T$	−9.88	−5.46	−7.6			0.03
		$\Delta\alpha_P$	−9.96	−5.55	−25.92	−4.9		0.03
		C_V^E	3.289	−0.146	1.76			0.003
	303.15	V^E	−0.0787	−0.0196	−0.024			0.0002
		Δu	24.70	4.32	1.58			0.019
2PE + DBE	293.15	V^E	0.1920	−0.204	0.087	−0.093		0.0008
		Δu	−94.25	−27.26	−2.8			0.05
	298.15	V^E	0.2511	−0.241	0.154	−0.154		0.0013
		Δu	−95.57	−27.26	−3.0			0.04
		$\Delta\kappa_S$	−57.62	−21.26	−10.7			0.05
		$\Delta\alpha_P$	80.44	−49.7	34.7			0.10
	303.15	V^E	0.3094	−0.303	0.152	−0.096		0.0009
		Δu	−96.20	−26.65	−3.4			0.04

[a] $\Delta M = V^E$, units: $cm^3 \cdot mol^{-1}$; $\Delta M = \Delta u$, units: $m \cdot s^{-1}$; $\Delta M = \Delta\kappa_S$ or $\Delta\kappa_T$, units: TPa^{-1}; $\Delta M = \Delta\alpha_P$, units: 10^{-6} K^{-1}; $\Delta M = C_V^E$, units: $J \cdot mol^{-1} \cdot K^{-1}$. [b] For symbols, see Table 1.

which is supported by the $\Delta\kappa_T$ variation (see Table 4). Note that H^E(2ME + 2BE) > H^E(2ME + 2-(2-butoxyethoxy)ethanol (22BEE))[9] = 110 $J \cdot mol^{-1}$and V^E(2BE) > V^E(22BEE)[9] = 0.0614 $cm^3 \cdot mol^{-1}$. (ii) In contrast, when passing from 2EE to 2BE, a larger number of interactions between 2ME molecules are broken by the longer 2-alkoxyethanol due to its more inert character (lower effective dipole moment[5]). The same trend is observed in 2ME + 22MEE, or + 22BEE systems: V^E(22MEE) < V^E(22BEE) and H^E(22MEE) < H^E(22BEE).

For mixtures with DBE, H^E and V^E decrease in the same sequence: V^E(2ME)[6] = 0.3125 > V^E(2EE)[6] = 0.2260 > V^E(2PE) = 0.0628 > V^E(2BE)[6] = −0.0544 $cm^3 \cdot mol^{-1}$ and H^E(2ME)[23] = 1196 > H^E(2EE)[23] = 1088 > H^E(2BE)[24] = 687 $J \cdot mol^{-1}$. This may be ascribed to the interactions between 2-alkoxyethanol molecules which become weaker in the same order, as is indicated by the relative variation of their effective dipole moments.[5,6] On the other hand, V^E is positive over the whole mole fraction range for the systems including 2ME, 2EE, or 2PE and is s-shaped for the 2BE solution.[6] In this case, V^E is positive at low concentration of 2BE.[6] The same occurs for 1-alkanol + fixed *n*-alkane mixtures when the chain length of the alcohol is increased.[25–27] Such variation has been typically ascribed to structural effects, namely, interstitial accommodation,[27] which are also present in the actual systems containing longer 2-alkoxyethanols.

6. Conclusions

Densities and speeds of sound of systems formed by 2ME and 2EE, or 2BE, or 22MEE and for the 2PE + DBE mixture have been measured at (293.15, 298.15, and 303.15) K and atmospheric pressure. The ρ and u values were used to calculate V^E at the same temperatures and C_V^E, $\Delta\alpha_P$, $\Delta\kappa_S$, and $\Delta\kappa_T$ at 298.15 K. In DBE systems, H^E and V^E decrease with the size of the 2-alkoxyethanol. In 2ME + alkoxyethanol mixtures, these magnitudes increase with the size of the second compound, although their values depend on the number of etheric atoms of this component.

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