Thermodynamics of Mixtures Containing Alkoxyethanols. XXIV. Densities, Excess Molar Volumes, and Speeds of Sound at (293.15, 298.15, and 303.15) K and Isothermal Compressibilities at 298.15 K for 2-(2-Alkoxyethoxy)ethanol + 1-Butanol Systems

Ismael Mozo, Isaías García de la Fuente, Juan Antonio González,* and José Carlos Cobos

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

Densities, ρ, and speeds of sound, u, of systems formed by 2-(2-methoxyethoxy)ethanol (22MEE), 2-(2-ethoxyethoxy)ethanol (22EEE), or 2-(2-butoxyethoxy)ethanol (22BEE) and 1-butanol (1-BuOH) 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 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.

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]

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 systems containing 2-(2-methoxyethoxy)ethanol (22MEE), 2-(2-ethoxyethoxy)ethanol (22EEE), or 2-(2-butoxyethoxy)ethanol (22BEE) and 1-butanol. Previously, we have provided data on the same magnitudes for the 2-alkoxyethanol[6] or 2-(2-alkoxyethoxy)ethanol[7] + dibutylether mixtures.

2. Experimental

2.1 Materials. 1-Butanol (puriss p.a. ≥ 99.5 %), 22MEE, 22EEE, and 22BEE (purum. ≥ 98 %) were from Fluka and were used without further purification. The ρ and u values 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 as (0.01, 0.02, 0.04, and 0.005) mol % for 22ME, 22EE, 22BE, and 1-butanol, 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.[8]

* Corresponding author. E-mail: jagl@termo.uva.es. Fax: +34-983-423136. Tel: +34-983-423757.

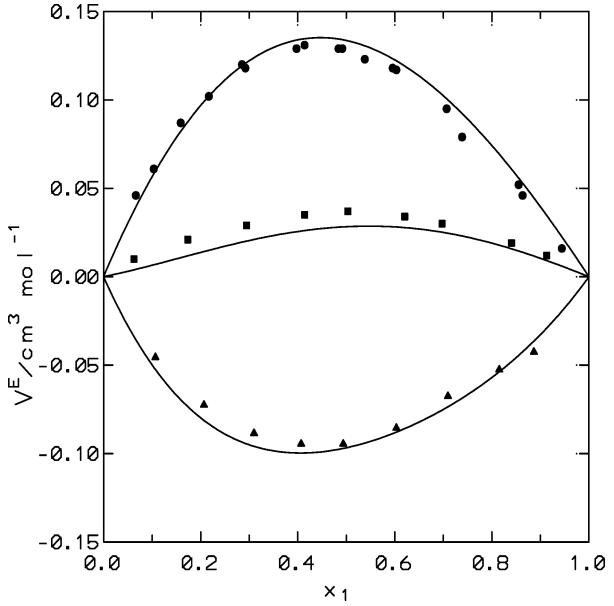

Figure 1. V^E at 298.15 K for $CH_3(CH_2)_{u-1}O(CH_2CH_2O)CH_2CH_2OH$ (1) + 1-butanol (2) mixtures. Solid lines, calculations with eq 7 using the coefficients from Table 4. Points, experimental results from the literature:[13] ●, $u = 1$; ■, $u = 2$; ▲, $u = 4$.

The densities and speeds of sound of both pure liquids and of the mixtures were measured using a vibrating-tube densimeter and a sound analyzer (Anton Paar model DSA-5000) automatically thermostated 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.[9−11] The accuracies for the ρ and u measurements are ± $1\cdot10^{-2}$ kg·m^{-3} and ± 0.1 m·s^{-1}, respectively, and the corresponding precisions are ± $1\cdot10^{-3}$ 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.[12−15] The accuracy in V^E is believed to be less than ±

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Table 1. Physical Properties of Pure Compounds 2-(2-Methoxyethoxy)ethanol (22MEE), 2-(2-Ethoxyethoxy)ethanol (22EE), 2-(2-Butoxyethoxy)ethanol (22BE), and 1-Butanol (1-BuOH) at Temperature T*

		22MEE		22EEE		22BEE		1-BuOH	
property	T/K	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
ρ/g·cm^3	293.15	1.019810	1.02080[a]	0.987876		0.952196	0.95688[b]	0.809644	0.80956[c]
	298.15	1.015408	1.0164[a]	0.983336	0.98429[b]	0.948103	0.94898[d]	0.805842	0.80575[c]
			1.01591[b]		0.9845[d]		0.9480[e]		0.80575[f]
	303.15	1.010908	1.01183[a]	0.978788		0.943743		0.801995	0.80180[f]
u/m·s^{-1}	293.15	1432.37		1392.35		1374.28		1256.74	1257[f]
	298.15	1415.21	1415.5[g]	1374.35	1385.2[g]	1356.97	1356.4[g]	1239.19	1240[f]
	303.15	1397.93		1356.60		1339.95		1222.70	1224[f]
$\alpha_P/10^{-3}$ K^{-1}	298.15	0.8767	0.8493[e]	0.9242	0.8462[h]	0.8918	0.8426[h]	0.9493	0.948[c]
κ_S/TPa^{-1}	293.15	477.94		522.16		556.06		782.01	782[f]
	298.15	491.72	490.0[e]	538.40	535.9[e]	572.80	571.7[e]	808.12	807[f]
	303.15	506.20		555.15		590.16		834.04	833[f]
κ_T/TPa^{-1}	298.15	595.17	583.8[e]	655.29	633.6[g]	687.14	672.8[e]	949.24	942[c]
C_V/J·mol^{-1}·K^{-1}	298.15	216.56		244.22		295.84		149.10	
C_P/J·mol^{-1}·K^{-1}	298.15		262.12[i]		297.24[i]		354.89[i]		175.14[j]

*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. [a] Ref 18. [b] Ref 19. [c] Ref 9. [d] Ref 20. [e] Ref 21. [f] Ref 22. [g] Ref 23. [h] Ref 24. [i] Ref 25. [j] Ref 26.

$(0.01|V^E_{max}| + 0.005$ 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 calculated using the equations[6,12]

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

and

$$M^{id} = \phi_1M_1 + \phi_2M_2 \quad (M = \alpha_P; \kappa_T) \tag{5}$$

where $\phi_i = x_iV_i/V^{id}$ 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 and 3. In this article, we have determined the deviations

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

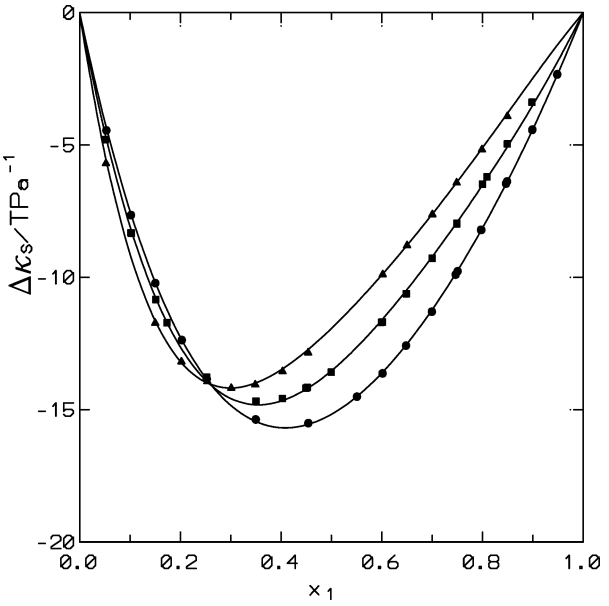

Figure 2. $\Delta\kappa_S$ at 298.15 K for $CH_3(CH_2)_{u-1}O(CH_2CH_2O)CH_2CH_2OH$ (1) + 1-butanol (2) mixtures. Solid lines, calculations with eq 7 using the coefficients from Table 4. Points, experimental results (this work): ●, u = 1; ■, u = 2; ▲, u = 4.

Obviously, $\Delta M = M^E$ (excess function) when M is an intensive function (V, C_V).

4. Results and Discussion

Table 2 lists values of densities, calculated V^E, and Δu vs x_1, the mole fraction of the hydroxyether. Table 3 contains derived quantities such as $\Delta\kappa_S$, $\Delta\alpha_P$, $\Delta\kappa_T$, and C_V^E using C_P^E values from the literature.[16] The data were fitted by unweighted least-squares polynomial regression to the equation

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

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[17] 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

Table 2. Densities, ρ, Molar Excess Volumes, V^E, and Deviations from the Ideal Behavior of the Speed of Sound, Δu, for 2-(2-Alkoxyethoxy)ethanol (1) + 1-Butanol (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}	x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	Δu / m·s^{-1}
2-(2-Methoxyethoxy)ethanol (1) + 1-Butanol (2); T = 293.15 K											
0.0535	0.823612	0.0312	−0.212	0.3990	0.905367	0.1258	−1.314	0.6526	0.957368	0.1081	−0.920
0.1527	0.848542	0.0744	−0.608	0.4007	0.905744	0.1245	−1.310	0.6961	0.965704	0.0979	−0.788
0.2000	0.860004	0.0883	−0.806	0.4522	0.916775	0.1267	−1.295	0.7503	0.975858	0.0869	−0.623
0.2003	0.860091	0.0875	−0.815	0.5012	0.927038	0.1261	−1.284	0.7973	0.984500	0.0736	−0.498
0.2518	0.872235	0.1027	−1.030	0.5527	0.937589	0.1221	−1.170	0.8492	0.993819	0.0583	−0.340
0.3009	0.883531	0.1149	−1.162	0.5978	0.946625	0.1163	−1.048	0.8978	1.002374	0.0404	−0.186
0.3032	0.884084	0.1120	−1.163	0.6019	0.947427	0.1167	−1.041	0.9470	1.010876	0.0199	−0.110
0.3546	0.895622	0.1210	−1.239								
2-(2-Methoxyethoxy)ethanol (1) + 1-Butanol (2); T = 298.15 K											
0.0530	0.819639	0.0318	−0.206	0.5507	0.932958	0.1279	−1.066	0.7977	0.980251	0.0751	−0.378
0.1019	0.832026	0.0587	−0.451	0.6013	0.943061	0.1215	−0.944	0.8465	0.988996	0.0593	−0.230
0.1502	0.843949	0.0800	−0.626	0.6480	0.952194	0.1135	−0.853	0.8486	0.989382	0.0586	−0.228
0.2028	0.856650	0.0971	−0.802	0.6994	0.962043	0.1017	−0.657	0.8987	0.998178	0.0405	−0.091
0.2523	0.868300	0.1105	−0.940	0.7465	0.970860	0.0902	−0.526	0.8990	0.998234	0.0401	−0.091
0.3497	0.890395	0.1302	−1.146	0.7505	0.971594	0.0894	−0.514	0.9481	1.006686	0.0199	−0.026
0.4540	0.912946	0.1371	−1.165	0.7968	0.980073	0.0765	−0.410	0.9483	1.006723	0.0200	−0.034
2-(2-Methoxyethoxy)ethanol (1) + 1-Butanol (2); T = 303.15 K											
0.0508	0.815157	0.0328	−0.213	0.3555	0.887558	0.1297	−0.928	0.6991	0.957619	0.1041	−0.496
0.1014	0.827941	0.0610	−0.428	0.4005	0.897361	0.1342	−0.932	0.7497	0.967071	0.0910	−0.387
0.1471	0.839220	0.0802	−0.575	0.4503	0.908007	0.1347	−0.906	0.7954	0.975414	0.0775	−0.254
0.2015	0.852303	0.1004	−0.733	0.4981	0.917960	0.1336	−0.871	0.8491	0.985035	0.0590	−0.153
0.2528	0.864365	0.1119	−0.809	0.5518	0.928933	0.1278	−0.783	0.8964	0.993318	0.0427	−0.091
0.3048	0.876239	0.1224	−0.890	0.5996	0.938439	0.1225	−0.680	0.9513	1.002746	0.0193	−0.018
0.3503	0.886405	0.1285	−0.901	0.6480	0.947877	0.1144	−0.579				
2-(2-Ethoxyethoxy)ethanol (1) + 1-Butanol (2); T = 293.15 K											
0.0519	0.823011	0.0025	1.855	0.4514	0.907402	0.0263	7.335	0.7015	0.947962	0.0242	5.824
0.1029	0.835520	0.0057	3.276	0.5492	0.924169	0.0273	7.120	0.7952	0.961375	0.0185	4.433
0.1999	0.857730	0.0127	5.370	0.5966	0.931866	0.0266	6.850	0.8477	0.968507	0.0148	3.473
0.2989	0.878535	0.0194	6.612	0.6500	0.940215	0.0255	6.390	0.8489	0.968677	0.0135	3.504
0.3513	0.888856	0.0224	7.001	0.7002	0.947765	0.0242	5.832	0.8966	0.974953	0.0097	2.466
0.4015	0.898337	0.0246	7.232	0.7009	0.947885	0.0235	5.831	0.9500	0.981736	0.0048	1.256
2-(2-Ethoxyethoxy)ethanol (1) + 1-Butanol (2); T = 298.15 K											
0.0512	0.818966	0.0030	1.841	0.4025	0.894359	0.0253	7.455	0.7001	0.943370	0.0250	5.922
0.1017	0.831315	0.0063	3.330	0.4490	0.902763	0.0277	7.511	0.7491	0.950466	0.0226	5.271
0.1026	0.831513	0.0069	3.333	0.4520	0.903287	0.0270	7.517	0.7491	0.950476	0.0224	5.298
0.1510	0.842801	0.0102	4.522	0.4995	0.911551	0.0288	7.488	0.8000	0.957603	0.0187	4.445
0.1733	0.847840	0.0120	4.980	0.5992	0.927958	0.0281	6.937	0.8086	0.958782	0.0180	4.284
0.2524	0.864926	0.0177	6.215	0.6015	0.928324	0.0284	6.965	0.8491	0.964231	0.0154	3.515
0.3500	0.884465	0.0227	7.187	0.6487	0.935658	0.0269	6.553	0.8982	0.970663	0.0107	2.484
2-(2-Ethoxyethoxy)ethanol (1) + 1-Butanol (2); T = 303.15 K											
0.0507	0.814940	0.0043	1.843	0.3035	0.871188	0.0252	6.763	0.5539	0.916330	0.0320	7.361
0.1007	0.827098	0.0089	3.306	0.3042	0.871343	0.0251	6.875	0.6000	0.923723	0.0311	7.043
0.1488	0.838296	0.0124	4.493	0.3492	0.880114	0.0283	7.204	0.6019	0.924030	0.0300	7.056
0.1539	0.839456	0.0122	4.629	0.4027	0.890141	0.0303	7.438	0.7506	0.946255	0.0227	5.309
0.1998	0.849635	0.0175	5.506	0.4543	0.899435	0.0315	7.602	0.8006	0.953229	0.0184	4.504
0.2025	0.850231	0.0167	5.523	0.5504	0.915759	0.0317	7.373	0.8496	0.959837	0.0140	3.552
0.2526	0.860864	0.0208	6.280	0.5525	0.916103	0.0317	7.330	0.9490	0.972571	0.0049	1.353
2-(2-Butoxyethoxy)ethanol (1) + 1-Butanol (2); T = 293.15 K											
0.1013	0.834791	−0.0513	8.440	0.3516	0.881978	−0.0985	17.395	0.6493	0.920670	−0.0836	14.602
0.1505	0.845543	−0.0666	11.347	0.4507	0.896487	−0.0996	17.744	0.7000	0.925984	−0.0754	12.490
0.2017	0.855876	−0.0800	13.674	0.5005	0.903110	−0.0979	17.407	0.7292	0.928912	−0.0684	11.562
0.2529	0.865450	−0.0909	15.455	0.5506	0.909377	−0.0958	16.764	0.7490	0.930843	−0.0650	10.916
0.3005	0.873704	−0.0952	16.577	0.6036	0.915608	−0.0902	15.716	0.8483	0.939967	−0.0448	7.132
2-(2-Butoxyethoxy)ethanol (1) + 1-Butanol (2); T = 298.15 K											
0.0521	0.819296	−0.0306	4.794	0.3487	0.877538	−0.0973	17.499	0.7003	0.921969	−0.0752	13.216
0.1500	0.841555	−0.0678	11.421	0.4028	0.885726	−0.0999	17.883	0.7486	0.926743	−0.0651	11.576
0.2022	0.852057	−0.0792	13.792	0.4536	0.892882	−0.0998	17.850	0.7986	0.931465	−0.0573	9.676
0.2535	0.861607	−0.0893	15.537	0.6017	0.911346	−0.0883	15.827	0.8491	0.935973	−0.0466	7.548
0.3010	0.869838	−0.0953	16.731	0.6501	0.916714	−0.0831	14.651				
2-(2-Butoxyethoxy)ethanol (1) + 1-Butanol (2); T = 303.15 K											
0.0462	0.813931	−0.0263	4.329	0.3513	0.873826	−0.0964	17.488	0.6992	0.917561	−0.0723	13.165
0.0516	0.815259	−0.0277	4.730	0.3997	0.881120	−0.0987	17.852	0.7074	0.918410	−0.0731	12.993
0.1015	0.827004	−0.0484	8.438	0.4513	0.888394	−0.0980	17.830	0.7476	0.922362	−0.0652	11.623
0.1522	0.837999	−0.0648	11.470	0.5047	0.895427	−0.0957	17.451	0.7976	0.927051	−0.0546	9.612
0.2002	0.847641	−0.0779	13.682	0.5520	0.901283	−0.0911	16.752	0.7988	0.927176	−0.0567	9.746
0.2536	0.857548	−0.0864	15.540	0.6546	0.912925	−0.0804	14.614	0.8959	0.935611	−0.0353	5.348
0.3008	0.865688	−0.0933	16.707								

Table 3. Deviations from the Ideal Behavior at 298.15 K for κ_S, Adiabatic Compressibility; α_P, Isobaric Thermal Expansion Coefficient; and κ_T, Isothermal Compressibility, for 2-(2-Alkoxyethoxy)ethanol (1) + 1-Butanol (2) Mixtures[a]

x_1	$\Delta\kappa_S$ / TPa^{-1}	$\Delta\alpha_P$ / 10^{-6}K^{-1}	$\Delta\kappa_T$ / TPa^{-1}	C_V^E / J·mol^{-1}·K^{-1}	x_1	$\Delta\kappa_S$ / TPa^{-1}	$\Delta\alpha_P$ / 10^{-6}K^{-1}	$\Delta\kappa_T$ / TPa^{-1}	C_V^E / J·mol^{-1}·K^{-1}
				2-(2-Methoxyethoxy)ethanol (1) + 1-Butanol (2)					
0.0530	−4.45	4.5	−3.08	−0.27	0.7465	−9.90	3.0	−9.45	−0.39
0.1019	−7.65	7.0	−5.56	−0.41	0.7505	−9.77	2.9	−9.33	−0.39
0.1502	−10.22	8.5	−7.78	−0.48	0.7968	−8.21	2.7	−7.80	−0.38
0.2028	−12.37	9.2	−9.85	−0.50	0.7977	−8.21	2.7	−7.79	−0.38
0.2523	−13.84	9.2	−11.43	−0.48	0.8465	−6.46	2.4	−6.08	−0.36
0.3497	−15.37	8.0	−13.48	−0.41	0.8486	−6.38	2.4	−5.99	−0.35
0.4540	−15.51	6.1	−14.25	−0.35	0.8987	−4.43	1.9	−4.11	−0.29
0.5507	−14.51	4.6	−13.69	−0.34	0.8990	−4.42	1.9	−4.09	−0.29
0.6013	−13.63	4.0	−12.97	−0.35	0.9481	−2.34	1.2	−2.13	−0.18
0.6480	−12.58	3.6	−12.02	−0.36	0.9483	−2.33	1.2	−2.12	−0.18
0.6994	−11.30	3.2	−10.81	−0.38					
				2-(2-Ethoxyethoxy)ethanol (1) + 1-Butanol (2)					
0.0512	−4.80	1.4	−3.97	−0.22	0.5992	−11.70	2.9	−10.57	−0.43
0.1017	−8.32	2.6	−6.93	−0.37	0.6015	−11.69	2.9	−10.57	−0.43
0.1026	−8.34	2.6	−6.94	−0.37	0.6487	−10.62	2.3	−9.73	−0.39
0.1510	−10.84	3.5	−9.07	−0.46	0.7001	−9.28	1.6	−8.64	−0.32
0.1733	−11.72	3.8	−9.83	−0.48	0.7491	−7.96	0.9	−7.54	−0.25
0.2524	−13.77	4.7	−11.65	−0.54	0.7491	−7.98	0.9	−7.56	−0.25
0.3500	−14.68	5.0	−12.60	−0.55	0.8000	−6.48	0.4	−6.26	−0.17
0.4025	−14.58	4.9	−12.63	−0.54	0.8086	−6.21	0.3	−6.02	−0.16
0.4490	−14.19	4.6	−12.38	−0.53	0.8491	−4.96	−0.1	−4.89	−0.10
0.4520	−14.16	4.6	−12.37	−0.53	0.8982	−3.39	−0.3	−3.43	−0.04
0.4995	−13.58	4.1	−11.97	−0.51					
				2-(2-Butoxyethoxy)ethanol (1) + 1-Butanol (2)					
0.0521	−5.66	0.8	−5.52	0.02	0.4536	−12.81	3.2	−13.71	0.78
0.1500	−11.69	2.2	−11.70	0.21	0.6017	−9.86	2.1	−10.99	0.87
0.2022	−13.15	2.7	−13.32	0.34	0.6501	−8.76	1.7	−9.91	0.87
0.2535	−13.90	3.1	−14.24	0.46	0.7003	−7.59	1.2	−8.74	0.86
0.3010	−14.15	3.3	−14.64	0.56	0.7486	−6.39	0.8	−7.50	0.84
0.3487	−14.02	3.4	−14.66	0.64	0.7986	−5.15	0.4	−6.18	0.78
0.4028	−13.52	3.4	−14.30	0.72	0.8491	−3.88	0.1	−4.76	0.69

[a] Also included is the molar excess isochoric heat capacity, C_V^E.

Table 4. Coefficients A_i and Standard Deviations, $\sigma(\Delta M)$ (Equation 8), for Representation of ΔM[a] at Temperature T for 2-(2-Alkoxyethoxy)ethanol (1) + 1-Butanol (2) Systems by Equation 7

system[b]	T/K	property (ΔM)	A_0	A_1	A_2	A_3	$\sigma(M)$
22MEE + 1-BuOH	293.15	V^E	0.5035	−0.086			0.0011
		Δu	−5.04	2.58	2.76	−2.1	0.016
	298.15	V^E	0.5346	−0.118			0.0010
		Δu	−4.54	2.24	2.51		0.015
		$\Delta\kappa_S$	−60.70	21.53	−8.5		0.04
		$\Delta\alpha_P$	21.59	−33.9	43.0		0.08
		$\Delta\kappa_T$	−56.47	10.50	5.3		0.03
		C_V^E	−1.352	0.287	−3.90	0.86	0.003
	303.15	V^E	0.531	−0.118	0.041		0.0010
		Δu	−3.418	2.39	1.04		0.012
22EEE + 1-BuOH	293.15	V^E	0.1087	0.0269	−0.037		0.0003
		Δu	29.14	−4.29	3.37	−2.3	0.018
	298.15	V^E	0.1132	0.0273	−0.03		0.0003
		Δu	29.87	−4.7	2.98	−1.7	0.019
		$\Delta\kappa_S$	−54.13	31.9	−15.9		0.10
		$\Delta\alpha_P$	16.54	−19.99	−6.5		0.03
		$\Delta\kappa_T$	−47.77	20.83	−13.66	5	0.02
		C_V^E	−2.025	1.07	−0.3	1.89	0.003
	303.15	V^E	0.1286	0.0076	−0.049		0.0004
		Δu	30.11	−4.08	3.2	−2.7	0.03
22BEE + 1-BuOH	293.15	V^E	−0.393	0.125	−0.085		0.0011
		Δu	70.0	−23.9			0.2
	298.15	V^E	−0.387	0.119	−0.113		0.0010
		Δu	69.91	−21.19	8.6		0.04
		$\Delta\kappa_S$	−47.72	36.7	−26.2	14.9	0.07
		$\Delta\alpha_P$	11.77	−12.17	−6.1		0.04
		$\Delta\kappa_T$	−51.75	33.3	−25.2	11.6	0.05
		C_V^E	3.286	1.41	0.51	2.60	0.005
	303.15	V^E	−0.3811	0.114	−0.099		0.0010
		Δu	69.88	−21.2	8.4		0.06

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

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

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[16] (Figure 1).

The observed V^E decrease with the size of the hydroxyether may be ascribed to the positive contribution to this excess function from the disruption of interactions between cellosolve molecules which also decrease in the same sequence, due to the weakening of the dipolar interactions between this type of molecules.[5,6] In addition, structural effects become more important when the difference in size between components increases.

5. Conclusions

Densities and speeds of sound of systems formed by 22MEE, 22EEE, or 22BEE and 1-butanol 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 $\Delta\alpha_P$, $\Delta\kappa_S$, and $\Delta\kappa_T$ at 298.15 K.

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