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Speeds of Sound and Isentropic Compressibilities of n-Alkoxyethanols and Polyethers with Propylamine at 298.15 K

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The speeds of sound (u) have been measured at 298.15 K and atmospheric pressure, as a function of composition for seven binary liquid mixtures of propylamine ($CH_3CH_2CH_2NH_2$, PA) + ethylene glycol monomethyl ether (2-methoxyethenol, $CH_3(OC_2H_4)OH$, EGMME); + diethylene glycol monomethyl ether [{2-(2-methoxyethoxy)ethanol}, $CH_3(OC_2H_4)_2OH$, Di-EGMME]; + triethylene glycol monomethyl ether [{2-(2-(2-methoxyethoxy)ethoxy) ethanol}, $CH_3(OC_2H_4)_3OH$, Tri-EGMME]; + diethylene glycol monoethyl ether [2-(2-ethoxyethoxy)ethanol, $C_2H_5(OC_2H_4)_2OH$, Di-EGMEE]; + diethylene glycol monobutyl ether [{2-(2-butoxyethoxy) ethanol}, $C_4H_9(OC_2H_4)_2OH$, Di-EGMBE]; + diethylene glycol diethyl ether [bis(2-ethoxyethyl)ether, $C_2H_5(OC_2H_4)_2OC_2H_5$, DEGDEE]; and + diethylene glycol dibutyl ether [bis(2-butoxyethyl) ether, $C_4H_9(OC_2H_4)_2OC_4H_9$; DEGDBE] using a Nusonic velocimeter based on the sing–around technique. These values have been combined with densities derived from excess molar volumes to obtain estimates of the molar isentropic compressibility $K_{S,m}$, and their excess values $K^E_{S,m}$. The $K^E_{S,m}$ values are shown to be negative for all mixtures over the entire composition range. The deviations u^D of the speeds of sound from the values calculated for ideal mixtures have been obtained for all estimated values of mole fraction x_1. The change of $K^E_{S,m}$ and u^D with composition and the number of $-OC_2H_4-$ units in the alkoxyethanol are discussed with a view to understand some of the molecular interactions present in alkoxyethanol – propylamine mixtures. Also, theoretical values of the molar isentropic compressibility of

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$K_{S,m}$ and of the speed of sound u^D have been calculated using the Prigogine-Flory-Patterson (PFP) theory with the van der Waals (vdW) potential energy model, and the results have been compared with experimental values.

KEY WORDS: alkoxyethanol; polyether; propylamine; speeds of sound.

1. INTRODUCTION

In previous papers [1,2] we have reported excess molar volumes of alkoxyethanols and polyethers with propylamine at 298.15 K. These results suggested that there exist specific interactions between an amine and an alkoxyethanol or polyether, and the results were influenced by intermolecular association of both the amine and alkoxyethanol molecules. Since the study of speeds of sound and isentropic compressibility in binary liquid mixtures are of considerable interest [3–6] in assessing the nature of molecular interactions and investigating the physicochemical behavior of liquid systems, we have performed measurements of the speed of sound for these mixtures in order to evaluate various thermodynamic properties and functions that give a better understanding of the molecular interactions existing between alkoxyethanols or polyethers and amines. Hence, we report here measured values of speeds of sound for mixtures containing propylamine and either ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol diethyl ether, or diethylene glycol dibutyl ether at 298.15 K. The isentropic compressibilities κ_S for all mixtures were estimated by combining the densities derived from excess molar volumes [1,2] and the speeds of sound. The molar volumes were multiplied by the isentropic compressibilities to obtain estimates of the product $K_{S,m}$. We have calculated the deviation of the speeds of sound u^D from those of ideal mixtures u^{id}, together with the excess molar quantities $K^E_{S,m}$. Also, the theoretical values of molar isentropic compressibility $K_{S,m}$ and speed of sound u have been estimated in the Prigogine-Flory-Patterson (PFP) theory applying the van der Waals (vdW) energy model.

2. EXPERIMENTAL

Ethylene glycol monomethyl ether was obtained from S.-D. Fine Chemicals, AR grade, and was dried and fractionally distilled [7]. The sources and purities of other liquids used have been described in our earlier papers [1,2,8]. All samples were kept in tightly sealed bottles to minimize the absorption of atmospheric moisture and CO_2, and dried over 0.4 nm molecular sieve to reduce water content. The purity of the liquids were checked by measuring and comparing the densities at 298.15 K with their corresponding literature values [7, 9–20] in Table I. Also given in Table I are our measured or literature values of those quantities which were required in the estimation of $K_{s,m}$, $K^E_{S,m}$, and u^D. The densities (ρ) of pure liquids were measured with a single–arm pycnometer that gave an uncertainty of $\pm 3 \times 10^{-2}\,kg\cdot m^{-3}$. Prior to measurements, all liquids were partially degassed under vacuum. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$.

The speeds of sound (u) in both the pure liquids and their mixtures were measured at 298.15 K using a Nusonic (Mapco, Model 6080 Concentration Analyzer) velocimeter based on the sing–around technique [21] with 4 MHz acoustic waves. The speeds of sound at 298.15 K are directly obtained from the average round trip period of the ultrasonic wave in a fixed path length between the piezoelectric transducer and reflector. The maximum error of the speed measured relative to water ($1496.687\,m\cdot s^{-1}$ at 298.15 K) [22] is estimated to be less than $0.2\,m\cdot s^{-1}$. Further details concerning this apparatus, experimental setup, and operational procedures have been given previously [23, 24]. A thermostated controlled, well stirred water bath whose temperature was controlled to ±0.01 K, was used for all measurements.

3. RESULTS AND DISCUSSION

Table II gives the experimental results for the speeds of sound at 298.15 K of all the binary mixtures at various mole fractions. Also listed there are deviations of the speeds of sound u^D from the values calculated for ideal mixtures u^{id}, the product $K_{S,m}$ of the molar volume and the isentropic compressibility, and their corresponding excess molar quantity $K^E_{S,m}$. The measured speeds of sound u were fitted with a polynomial of the type,

$$u = \sum_{i=0}^{n} a_i x_1^i \tag{1}$$

by the method of least squares with each point weighted equally. The values of coefficients a_i and the standard deviations σ are summarized in Table IIIa.

κ_S and $K_{S,m}$ were obtained from the equations,

$$\kappa_S = (\rho u^2)^{-1} = V(Mu^2)^{-1} \tag{2}$$

Table I. Experimental and Literature Values of Densities ρ^*; Isobaric Thermal Expansivities α_p^*; Molar Isobaric Heat Capacities $C_{p,m}^*$; Sound Speeds u^*; and the Product $K_{S,m}^*$ of the Molar Volume and Isentropic Compressibility of Pure Liquid Components at 298.15 K

	$\rho^* \times 10^{-3}$ (kg·m^{-3})			$C_{p,m}^*$	u^* (m·s^{-1})		$K_{\mathrm{S,m}}^*$(mm^3·mol^{-1}·MPa^{-1})
Components	Exptl.	Lit.	α_p^* (kK^{-1})	(J·K^{-1}·mol^{-1})	Exptl.	Lit.	
Propylamine	0.71225	0.7121 [7] 0.71244 [9]	1.378 [9]	161 [9]	1215.2	1215.4 [10]	78.906
Ethylene glycol monomethyl ether	0.96032	0.96024 [7] 0.9602 [11]	0.920^a	176.4 [12]	1343.3	1339.89 [11]	45.728
Diethylene glycol monomethyl ether	1.01643	1.0167 [7] 1.01591 [13]	0.849^b	271.1 [7]	1417.2	1415.98 [14]	57.903
Tri ethylene glycol monomethyl ether	1.04306	1.04310 [14]	0.828 [14]	358.0 [14]	1459.0	1457.80 [14]	70.900
Diethylene glycol monoethyl ether	0.98384	0.98387 [15] 0.983589 [16]	0.846 [16]	298.1 [16]	1377.3	1377.22 [16]	73.075
Diethylene glycol monobutyl ether	0.94798	0.94916 [15]	0.843 [16]	358.4 [16]	1358.9	1357.2 [16]	97.759
Diethylene glycol diethyl ether	0.90276	0.90281 [17] 0.9033 [18]	1.077^b	347.42^c	1241.9		129.066
Diethylene glycol dibutyl ether	0.87855	0.87830 [17] 0.87862 [19]	0.890^b	479.62^c	1270.1		175.355

[a] Derived from densities in Ref. 20.

[b] Calculated from our measured densities.

[c] Estimated using group additivity.

Table II. Sound Speeds u, Deviations u^D from Sound Speeds for Ideal Mixture u^{id}, Products $K_{S,m}$ of the Molar Volume and Isentropic Compressibility, and Corresponding Excess Quantities $K_{S,m}^E$ for Liquid Mixtures at 298.15 K

x_1	u ($\mathrm{m \cdot s^{-1}}$)	u^D ($\mathrm{m \cdot s^{-1}}$)	$K_{S,m}$ ($\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}}$)	$K_{S,m}^{\mathrm{E}}$ ($\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}}$)
Ethylene glycol monomethyl ether (1) + Propylamine (2)				
0.0036	1215.3	0.13	78.76	−0.04
0.0101	1216.4	1.29	78.39	−0.23
0.0272	1218.3	3.29	77.53	−0.60
0.0470	1221.7	6.73	76.40	−1.15
0.0831	1227.4	12.29	74.45	−2.05
0.1175	1232.5	17.00	72.69	−2.79
0.1521	1238.8	22.65	70.84	−3.61
0.1977	1247.0	29.58	68.51	−4.56
0.2378	1254.0	35.07	66.57	−5.27
0.2982	1265.6	43.68	63.70	−6.26
0.3629	1276.6	50.47	60.98	−6.93
0.4188	1285.8	55.14	58.82	−7.28
0.4740	1294.1	58.13	56.90	−7.39
0.5181	1299.6	58.73	55.56	−7.26
0.5862	1307.8	58.19	53.66	−6.87
0.6459	1314.6	56.03	52.15	−6.33
0.7102	1321.5	51.83	50.69	−5.55
0.7990	1329.7	41.92	48.94	−4.15
0.8253	1331.6	37.78	48.49	−3.66
0.8642	1334.2	30.82	47.85	−2.88
0.8918	1336.2	25.57	47.40	−2.33
0.9080	1338.0	22.91	47.10	−2.04
0.9316	1339.5	17.67	46.74	−1.53
0.9621	1341.5	10.46	46.27	−0.87
0.9824	1342.9	5.41	45.95	−0.44
0.9932	1343.4	2.37	45.80	−0.19
0.9989	1343.5	0.57	45.73	−0.04
Diethylene glycol monomethyl ether (1) + Propylamine (2)				
0.0055	1215.3	0.21	78.74	−0.10
0.0112	1217.0	2.00	78.37	−0.41
0.0240	1220.2	5.33	77.63	−0.98
0.0454	1225.5	10.62	76.47	−1.87
0.0749	1233.3	17.93	74.92	−3.03
0.0948	1238.6	22.61	73.94	−3.73
0.1292	1249.1	31.52	72.19	−4.97
0.1834	1264.6	43.27	69.81	−6.49
0.2523	1284.5	56.36	67.12	−7.99
0.3090	1301.5	66.20	65.10	−8.97

Table II. (*Continued*)

x_1	u ($\mathrm{m \cdot s^{-1}}$)	u^D ($\mathrm{m \cdot s^{-1}}$)	$K_{S,m}$ ($\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}}$)	$K^{\mathrm{E}}_{S,m}$ ($\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}}$)
0.3831	1320.8	74.16	63.01	−9.60
0.4484	1337.0	78.63	61.47	−9.79
0.5041	1349.4	79.80	60.41	−9.65
0.5603	1360.6	78.56	59.56	−9.25
0.6353	1373.2	72.86	58.77	−8.31
0.6792	1380.0	68.06	58.41	−7.62
0.7209	1385.9	62.33	58.15	−6.87
0.7775	1392.7	52.38	57.96	−5.68
0.8121	1397.5	46.40	57.81	−4.96
0.8725	1404.9	33.96	57.68	−3.56
0.9120	1408.8	24.18	57.70	−2.51
0.9332	1411.2	19.00	57.70	−1.96
0.9535	1413.1	13.48	57.75	−1.39
0.9852	1416.5	4.99	57.80	−0.50
0.9983	1417.1	0.56	57.89	−0.06
Triethylene glycol monomethyl ether (1) + Propylamine (2)				
0.0039	1216.1	0.98	78.74	−0.18
0.0134	1219.9	4.88	78.16	−0.80
0.0327	1226.9	11.75	77.12	−1.89
0.0519	1234.2	18.48	76.13	−2.93
0.0799	1245.4	28.16	74.73	−4.35
0.1080	1258.0	38.49	73.31	−5.77
0.1484	1274.9	50.99	71.59	−7.43
0.2102	1299.7	66.86	69.46	−9.38
0.2743	1324.5	80.10	67.69	−10.84
0.3410	1347.6	89.17	66.41	−11.70
0.3879	1361.8	92.48	65.85	−11.92
0.4351	1375.0	93.98	65.47	−11.91
0.5433	1398.7	88.51	65.48	−10.89
0.5904	1407.5	83.72	65.71	−10.18
0.6475	1416.0	75.11	66.23	−9.04
0.6873	1422.1	68.91	66.61	−8.22
0.7353	1429.5	61.09	67.07	−7.19
0.7806	1434.9	51.76	67.68	−6.05
0.8226	1441.1	44.00	68.14	−5.07
0.8873	1448.3	29.16	69.07	−3.32
0.9295	1452.6	18.75	69.72	−2.12
0.9565	1456.2	11.70	70.14	−1.30
0.9751	1457.0	6.96	70.46	−0.78
0.9898	1458.5	3.18	70.69	−0.35
0.9973	1458.7	0.67	70.86	−0.08

Table II. (*Continued*)

x_1	u $(\mathrm{m \cdot s^{-1}})$	u^D $(\mathrm{m \cdot s^{-1}})$	$K_{S,m}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$	$K^{\mathrm{E}}_{S,m}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$
	Diethylene glycol monoethyl ether (1) + Propylamine (2)			
0.0021	1215.3	0.13	78.87	−0.05
0.0048	1215.4	0.27	78.82	−0.10
0.0177	1218.7	3.68	78.24	−0.72
0.0374	1223.3	8.22	77.46	−1.55
0.0647	1230.5	14.92	76.36	−2.70
0.0909	1236.8	20.32	75.47	−3.62
0.1313	1247.7	29.10	74.08	−5.01
0.1669	1257.2	36.06	73.01	−6.06
0.2491	1278.4	49.35	70.97	−7.91
0.3135	1293.9	56.95	69.80	−8.86
0.3898	1310.7	62.75	68.83	−9.46
0.4519	1322.7	64.68	68.39	−9.54
0.4879	1329.1	64.83	68.25	−9.45
0.5348	1337.5	64.68	68.12	−9.26
0.5888	1344.5	61.29	68.30	−8.67
0.6314	1349.7	57.92	68.52	−8.11
0.6808	1355.5	53.40	68.84	−7.37
0.7314	1359.9	46.83	69.37	−6.40
0.7778	1363.7	40.23	69.90	−5.44
0.8381	1367.3	29.86	70.76	−4.00
0.8760	1370.0	23.52	71.26	−3.11
0.9121	1371.4	16.15	71.87	−2.14
0.9343	1373.1	12.37	72.15	−1.62
0.9624	1374.6	6.85	72.58	−0.90
0.9887	1375.9	1.49	72.99	−0.21
0.9971	1376.8	0.25	73.07	−0.04
	Diethylene glycol monobutyl ether (1) + Propylamine (2)			
0.0052	1215.5	0.25	78.97	−0.09
0.0133	1218.1	2.72	78.79	−0.50
0.0295	1223.0	7.21	78.49	−1.26
0.0505	1228.7	12.07	78.22	−2.09
0.0779	1236.9	18.73	77.84	−3.20
0.1487	1256.7	32.65	77.30	−5.50
0.2053	1272.3	42.04	77.11	−6.99
0.2645	1286.7	48.90	77.29	−8.09
0.3180	1298.6	53.30	77.70	−8.79
0.3780	1310.2	55.91	78.45	−9.21
0.4304	1319.4	56.88	79.28	−9.37
0.4767	1326.0	56.00	80.23	−9.26
0.5226	1331.6	54.02	81.32	−8.98

Table II. (*Continued*)

x_1	u $(\mathrm{m \cdot s^{-1}})$	u^D $(\mathrm{m \cdot s^{-1}})$	$K_{S,m}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$	$K^E_{S,m}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$
0.5715	1336.8	51.03	82.61	−8.53
0.6306	1342.1	46.31	84.32	−7.81
0.6855	1346.2	41.03	86.05	−6.97
0.7347	1349.4	35.79	87.68	−6.12
0.7728	1351.3	31.15	89.03	−5.36
0.8152	1353.3	25.87	90.56	−4.48
0.8700	1355.9	19.09	92.56	−3.31
0.9073	1356.7	13.52	94.05	−2.36
0.9289	1357.7	10.84	94.85	−1.88
0.9504	1358.3	7.79	95.69	−1.35
0.9663	1358.5	5.30	96.36	−0.92
0.9813	1358.7	2.96	96.98	−0.51
	Diethylene glycol diethyl ether (1) + Propyl amine (2)			
0.0035	1214.7	−0.33	79.13	0.04
0.0108	1214.5	−0.20	79.50	0.03
0.0250	1214.0	−0.14	80.24	0.03
0.0591	1214.1	0.93	81.89	−0.11
0.0865	1214.7	1.99	83.17	−0.25
0.1134	1215.2	2.69	84.46	−0.35
0.1662	1217.3	4.64	86.89	−0.64
0.2091	1218.8	5.59	88.93	−0.79
0.2738	1221.4	6.82	92.01	−1.00
0.3214	1223.8	7.91	94.23	−1.19
0.3658	1225.7	8.42	96.36	−1.29
0.3939	1227.0	8.77	97.70	−1.37
0.4846	1230.5	8.96	102.15	−1.46
0.5313	1232.3	8.95	104.45	−1.49
0.5713	1233.8	8.88	106.42	−1.50
0.6319	1235.6	8.25	109.50	−1.43
0.6754	1236.7	7.60	111.74	−1.34
0.7192	1238.1	7.23	113.95	−1.30
0.7754	1239.4	6.27	116.87	−1.15
0.8066	1240.1	5.72	118.50	−1.06
0.8729	1241.7	4.70	121.93	−0.90
0.9037	1242.1	3.90	123.58	−0.76
0.9238	1242.2	3.21	124.70	−0.63
0.9448	1242.3	2.50	125.86	−0.50
0.9638	1242.4	1.88	126.92	−0.37
0.9835	1242.5	1.23	128.01	−0.25
0.9916	1242.2	0.62	128.53	−0.13

Table II. (*Continued*)

x_1	u $(\mathrm{m \cdot s^{-1}})$	u^D $(\mathrm{m \cdot s^{-1}})$	$K_{S,m}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$	$K^{\mathrm{E}}_{S,m}$ $(\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}})$
	Diethylene glycol dibutyl ether (1) + Propyl amine (2)			
0.0033	1215.3	0.17	79.23	−0.02
0.0114	1215.5	0.51	80.03	−0.07
0.0330	1217.3	2.38	82.02	−0.33
0.0476	1218.4	3.32	83.39	−0.47
0.0724	1221.0	5.35	85.63	−0.78
0.0955	1222.8	6.34	87.82	−0.95
0.1390	1227.3	8.78	91.78	−1.37
0.1781	1231.7	10.93	95.29	−1.76
0.2413	1237.2	12.33	101.18	−2.10
0.3004	1242.0	13.04	106.72	−2.34
0.3569	1245.8	12.87	112.11	−2.41
0.4169	1249.5	12.39	117.86	−2.44
0.4689	1251.9	11.26	122.97	−2.31
0.5355	1255.2	10.17	129.44	−2.19
0.5925	1258.2	9.58	134.90	−2.14
0.6493	1260.8	8.74	140.39	−2.03
0.6979	1262.9	8.02	145.09	−1.92
0.7548	1264.7	6.66	150.72	−1.65
0.8153	1266.6	5.35	156.68	−1.37
0.8686	1268.2	4.25	161.93	−1.12
0.9000	1269.0	3.52	165.05	−0.95
0.9241	1269.5	2.87	167.47	−0.78
0.9526	1269.9	1.94	170.39	−0.54
0.9770	1270.1	1.03	172.92	−0.29
0.9910	1270.3	0.60	174.35	−0.17

$$K_{\mathrm{S,m}} = -(\partial V/\partial p)_{\mathrm{s}} = V\kappa_{\mathrm{S}} = \Sigma x_i M_i/(\rho u)^2 \qquad (3)$$

where ρ is the density, V is the molar volume, and x_i and M_i are the mole fraction and molar mass of component i in the mixture, respectively.

The excess molar quantities $K^{\mathrm{E}}_{\mathrm{S,m}}$ were calculated from:

$$K^{\mathrm{E}}_{\mathrm{S,m}} = K_{\mathrm{S,m}} - K^{\mathrm{id}}_{\mathrm{S,m}} \qquad (4)$$

where [25]

$$K^{\mathrm{id}}_{\mathrm{S,m}} = \Sigma x_i [K^*_{\mathrm{S,i}} - T A^*_{\mathrm{p,i}} \{(\Sigma x_i A^*_{\mathrm{p,i}} / \Sigma x_i C^*_{\mathrm{p,i}}) - (A^*_{\mathrm{p,i}}/C^*_{\mathrm{p,i}})\}] \qquad (5)$$

The densities of the mixtures at the appropriate mole fraction used in the speed of sound measurements, were obtained from the molar volumes of

Table IIIa. Fitting Coefficients a_i and Standard Deviations σ of Eq. (1) for u $(\mathrm{m\cdot s^{-1}})$ of Propylamine + Alkoxyalkanol or Polyether Binary Mixtures at 298.15 K

$F(x)$	a_0	a_1	a_2	a_3	a_4	σ
Ethylene glycol monomethyl ether (1) + Propylamine (2)						
u $(\mathrm{m\cdot s^{-1}})$	1214.65	138.40	198.61	−371.47	163.96	0.46
Diethylene glycol monomethyl ether (1) + Propylamine (2)						
u $(\mathrm{m\cdot s^{-1}})$	1213.92	245.83	267.82	−578.83	269.58	0.52
Tri ethylene glycol monomethyl ether (1) + Propylamine (2)						
u $(\mathrm{m\cdot s^{-1}})$	1213.03	427.40	24.75	−485.24	280.75	1.30
Diethylene glycol monoethyl ether (1) + Propylamine (2)						
u $(\mathrm{m\cdot s^{-1}})$	1214.35	240.63	162.97	−462.50	221.41	0.28
Diethylene glycol monobutyl ether (1) + Propylamine (2)						
u $(\mathrm{m\cdot s^{-1}})$	1213.69	310.32	−81.79	229.38	147.42	0.45
Diethylene glycol diethyl ether (1) + Propylamine (2)						
u $(\mathrm{m\cdot s^{-1}})$	1214.15	−0.70	143.64	−182.71	68.46	0.36
Diethylene glycol dibutyl ether (1) + Propylamine (2)						
u $(\mathrm{m\cdot s^{-1}})$	1213.89	109.51	−65.13	12.41		0.52

Table IIIb. Fitting Coefficients a_i and Standard Deviations σ of Eq. (8) for u^D $(\mathrm{m\cdot s^{-1}})$ and $K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$ of Propylamine + Alkoxyalkanol or Polyether Binary Mixtures at 298.15 K

$F(x)$	a_0	a_1	a_2	a_3	a_4	σ
Ethylene glycol monomethyl ether (1) + Propylamine (2)						
u^D $(\mathrm{m\cdot s^{-1}})$	234.45	46.35	−37.87	35.63	14.83	0.34
$K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$	−29.35	4.13	5.89	−4.18		0.03
Diethylene glycol monomethyl ether (1) + Propylamine (2)						
u^D $(\mathrm{m\cdot s^{-1}})$	318.26	−3.20	−53.91	40.58		0.44
$K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$	−38.59	10.01	1.71	−3.84		0.05
Triethylene glycol monomethyl ether (1) + Propylamine (2)						
u^D $(\mathrm{m\cdot s^{-1}})$	366.82	−115.48	−39.81	80.58		0.35
$K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$	−45.66	20.64	−0.82	−6.37		0.04
Diethylene glycol monoethyl ether (1) + Propylamine (2)						
u^D $(\mathrm{m\cdot s^{-1}})$	259.36	−28.16	−27.84	3.35	−32.82	0.35
$K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$	−37.63	9.99	0.51	0.52	3.97	0.04
Diethylene glycol monobutyl ether (1) + Propylamine (2)						
u^D $(\mathrm{m\cdot s^{-1}})$	220.39	−81.32	−14.22	36.54		0.32
$K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$	−36.53	11.74	0.39	−3.49		0.04
Diethylene glycol diethyl ether (1) + Propylamine (2)						
u^D $(\mathrm{m\cdot s^{-1}})$	36.06	−5.65	−2.47	27.56		0.24
$K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$	−5.87	−0.34	0.09	−4.71		0.04
Diethylene glycol dibutyl ether (1) + Propylamine (2)						
u^D $(\mathrm{m\cdot s^{-1}})$	43.95	−34.29	37.82	17.57	−26.30	0.22
$K_{S,m}^{\mathrm{E}}(\mathrm{mm^3\cdot mol^{-1}\cdot MPa^{-1}})$	−9.18	3.05	−3.02	−3.78		0.09

Table IV. Characteristic Parameters of Pure Components at 298.15 K

Component	κ_T (TPa^{-1})	$\tilde{V}$	$\tilde{T}$	$V^* \times 10^6$ (m^3·mol^{-1})	P^* (J · m^{-3})	T^* (K)	$\chi_{12} \times 10^{-6}$ (J · m^{-3})
Propylamine	1243	1.3204	0.0664	62.85	576	4490	
Ethylene glycol monomethyl ether	690	1.2311	0.0539	64.36	603	5532	−91.84
Diethylene glycol monomethyl ether	584	1.2159	0.0514	97.22	641	5801	−66.29
Triethylene glycol monomethyl ether	540	1.2113	0.0506	129.96	671	5892	−49.62
Diethylene glycol monoethyl ether	633	1.2153	0.0513	112.22	589	5812	−94.60
Diethylene glycol monobutyl ether	672	1.2146	0.0512	140.90	552	5823	−66.37
Diethylene glycol diethyl ether	897	1.2633	0.0588	142.25	571	5071	6.97
Diethylene glycol dibutyl ether	828	1.2247	0.0528	202.92	481	5647	5.04

pure components and excess molar volumes from the cubic-spline interpolation reported in Refs 1 and 2.

The deviations of the speeds of sound from their values in an ideal mixture were calculated from [11,16]

$$u^D = u - u^{\mathrm{id}} \tag{6}$$

where

$$u^{\mathrm{id}} = V_{\mathrm{m}}^{\mathrm{id}} / (K_{\mathrm{S,m}}^{\mathrm{id}} \cdot \Sigma x_i M_i)^{1/2} \tag{7}$$

The values of $K_{\mathrm{S,m}}^{\mathrm{E}}$, and u^D were fitted for each mixture by an equation of the type,

$$F(x) = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{8}$$

Values of the coefficients a_i and the standard deviations σ are summarized in Table IIIb. Experimental results for u, $K_{\mathrm{S,m}}^{\mathrm{E}}$, and u^{D} have been compared graphically in Figs 1 to 3 with those theoretically calculated from the PFP theory.

For all mixtures measured in the present study, $K_{\mathrm{S,m}}^{\mathrm{E}}$ is negative over the entire range of composition except with diethylene glycol diethyl ether and shows a minimum in the sequence: diethylene glycol diethyl

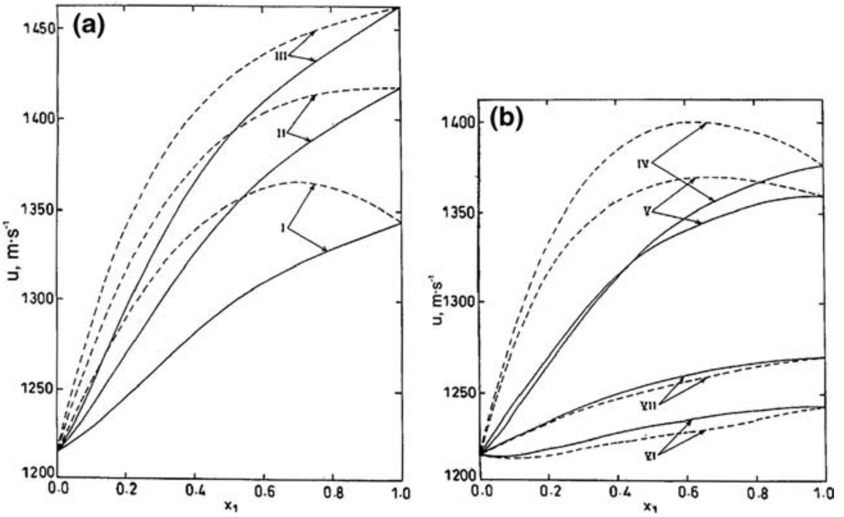

Fig. 1. Composition dependence of experimental —, and PFP theory – – –, values of speeds of sound u at 298.15 K for (a) $x_2CH_3CH_2CH_2NH_2 + x_1CH_3(OC_2H_4)OH$ (I); $+ x_1CH_3(OC_2H_4)_2OH$ (II); $+ x_1CH_3(OC_2H_4)_3OH$ (III); (b) $x_2CH_3CH_2CH_2NH_2 + x_1C_2H_5(OC_2H_4)_2OH$ (IV); $+ x_1\ C_4H_9(OC_2H_4)_2OH$ (V); $+ x_1C_2H_5(OC_2H_4)_2OC_2H_5$ (VI); $+ x_1C_4H_9(OC_2H_4)_2OC_4H_9$ (VII).

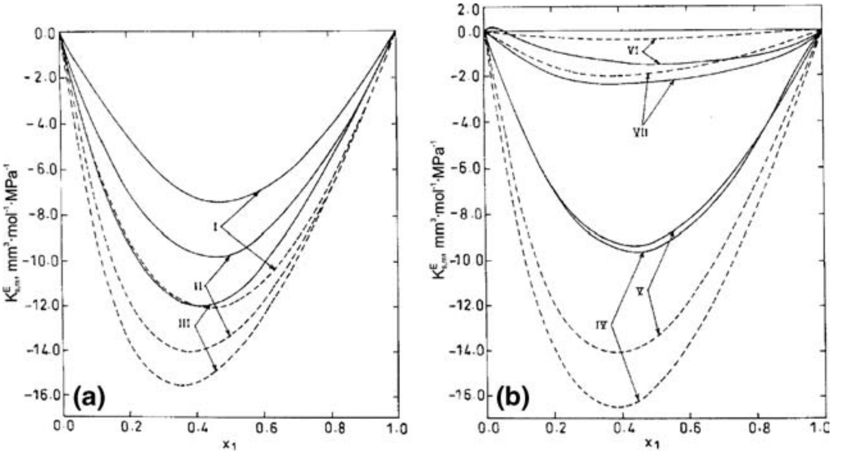

Fig. 2. Composition dependence of experimental —, and PFP theory – – –, values of excess molar isentropic compressibilities $K^E_{S,m}$ at 298.15 K for (a) $x_2CH_3CH_2CH_2NH_2 + x_1CH_3(OC_2H_4)OH$ (I); $+ x_1CH_3(OC_2H_4)_2OH$ (II); $+ x_1CH_3(OC_2H_4)_3OH$ (III); (b) $x_2CH_3CH_2CH_2NH_2 + x_1C_2H_5(OC_2H_4)_2OH$ (IV); $+ x_1C_4H_9(OC_2H_4)_2OH$ (V); $+ x_1C_2H_5(OC_2H_4)_2OC_2H_5$ (VI); $+ x_1C_4H_9(OC_2H_4)_2OC_4H_9$ (VII).

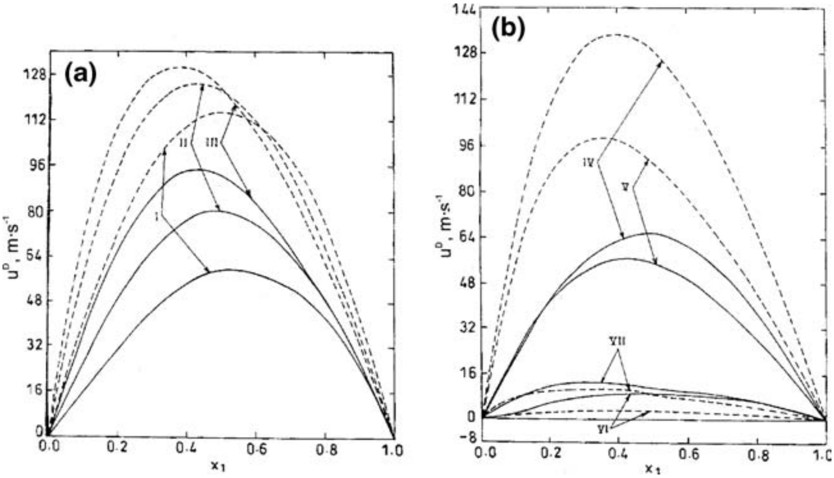

Fig. 3. Composition dependence of experimental —, and PFP theory – – –, deviation values of u^D of the speeds of sound from their ideal values at 298.15 K for (a) $x_2CH_3CH_2CH_2NH_2 + x_1CH_3(OC_2H_4)OH$ (I); $+ x_1CH_3(OC_2H_4)_2OH$ (II); $+ x_1CH_3(OC_2H_4)_3OH$ (III); (b) $x_2CH_3CH_2CH_2NH_2 + x_1C_2H_5(OC_2H_4)_2OH$ (IV); $+ x_1C_4H_9(OC_2H_4)_2OH$(V); $+ x_1C_2H_5(OC_2H_4)_2OC_2H_5$ (VI); $+ x_1C_4H_9(OC_2H_4)_2OC_4H_9$ (VII).

ether < diethylene glycol dibutyl ether < ethylene glycol monomethyl ether < diethylene glycol monobutyl ether < diethylene glycol monoethyl ether < diethylene glycol monomethyl ether < triethylene glycol monomethyl ether. The overall behavior of these mixtures is similar to that for u^D but gives an opposite sign. Also, the behavior of the excess molar volume [1, 2] seems to be consistent with a minimum value of $K^E_{S,m}$ and a maximum value of u^D with triethylene glycol monomethyl ether and diethylene glycol monoethyl ether with propylamine. A maximum value of u^D indicates that u is generally higher when the structure has high rigidity. For the same value of x_1, $K^E_{S,m}$ increases in a negative direction as the number of oxyethylene groups of the alkoxyethanol increases. Although $K^E_{S,m}$ is negative, that is, the mixture is less compressible than the corresponding ideal mixture, u^D is positive for all the mixtures, indicating that when the mixtures are created the free volume increases, and is higher in the mixtures containing triethylene glycol monomethyl ether and diethylene glycol dibutyl ether with propylamine. Again, the effect is that with an increase in the number of oxyethylene groups and with each substitution of a hydroxyl hydrogen for a butyl group in a mixture containing diethylene glycol monobutyl ether with propylamine, interstitial accommodation become less important, in that the molecules of the two components cannot accommodate easily. This additional rigidity is a good reason for the positive values of u^{D}. We have suggested earlier that the volumetric behavior of n-alkoxyethanols or polyethers + propylamine is the result of several opposing effects; the present results for $K_{\mathrm{S,m}}^{\mathrm{E}}$ and u^{D} support this suggestion.

4. THEORETICAL MODEL

The theoretical values of excess molar isentropic compressibilities $K_{\mathrm{S,m}}^{\mathrm{E}}$ and speed of sound u for both the liquid components and the liquid mixtures have been estimated using the van der Waals (vdW) potential energy model in the Prigogine-Flory-Patterson (PFP) theory. The relevant equations which were used for theoretical calculations of $K_{\mathrm{S,m}}$, $K_{\mathrm{S,m}}^{\mathrm{E}}$, and u^{D} are given elsewhere [26 – 30].

The derived parameters for the pure liquid components using the Flory theory [27, 31, 32] are presented in Table IV alongwith the contact interaction parameter χ_{12} for each liquid mixture obtained according to the PFP theory from the excess molar volumes at equimolar compositions.

Figures 1 and 2 compare the experimental and theoretical estimates of u and $K_{\mathrm{S,m}}^{\mathrm{E}}$ over the entire range of composition for the seven binary mixtures. The experimental and calculated values of u, $K_{\mathrm{S,m}}$, $K_{\mathrm{S,m}}^{\mathrm{E}}$, and u^{D} for all binary mixtures at $x_1 = 0.5$ are reported in Table V.

In order to perform a numerical comparison of the estimation capability of the vdW energy model in the PFP theory, we calculated the percentage standard deviation using the relation,

$$100\sigma = \left[\sum_{i=1}^{n} \{100(exptl. - theo.)/exptl.\}/(n-1) \right]^{1/2} \tag{9}$$

where n represents the number of experimental data. The values of σ are also included in Table V.

Figure 1 and Table V show that the calculated values of the speed of sound u and molar isentropic compressibilities $K_{\mathrm{S,m}}$ for the vdW energy model agree very well with the experimental values within 0.02 and 0.04, respectively, for the binary mixtures of diethylene glycol dibutyl ether + propylamine (VII), and within 0.1 and 0.3, respectively, for diethylene glycol diethyl ether + propylamine (VI). The theoretical values of u and $K_{\mathrm{S,m}}$ of alkoxyethanol + propylamine are in agreement within 0.3 to 1.0, respectively. Thus, the agreement between theoretical and experimental values of u and $K_{\mathrm{S,m}}$ for the binary mixtures containing alkoxyethanols + propylamine is not completely satisfactory.

Table V. Comparisons of the Experimental and Theoretical Estimates of the Speed of Sound (u), Molar Isentropic Compressibility ($K_{S,m}$), Excess Molar Isentropic Compressibility ($K^{E}_{S,m}$), and Deviation in Speed of Sound (u^D) of Binary Mixtures at Equimolar Composition, and Standard Percent Deviation (σ)

	u (m·s^{-1})			$K_{S,m}$ (mm^3·mol^{-1}·MPa^{-1})			$K^{E}_{S,m}$ (mm^3·mol^{-1}·MPa^{-1})				u^D (m·s^{-1})			
System	Exptl.	vdW	$10^2\sigma$	Exptl	vdW	$10^2\sigma$	Exptl.	vdW	$10^2\sigma$	$\Delta K_S{}^E{}_m$	Exptl.	vdW	$10^2\sigma$	Δu_D
Propylamine + Ethylene glycol monomethyl ether	1297.3	1353.1	0.4	56.103	51.571	0.8	−7.321	−11.853	9.3	4.532	58.51	114.31	13.7	−55.80
Diethylene glycol monomethyl ether	1348.3	1391.4	0.3	60.500	56.810	0.7	−9.645	−13.335	6.3	3.690	79.57	122.67	8.9	−43.10
Triethylene glycol monomethyl ether	1389.8	1421.4	0.3	65.387	62.512	0.5	−11.407	−14.282	4.5	2.875	91.65	123.25	6.0	−31.60
Diethylene glycol monomethyl ether	1331.4	1394.9	0.5	68.197	62.129	1.0	−9.422	−15.490	9.9	6.068	64.97	128.47	14.9	−63.50
Diethylene glycol monobutyl ether	1328.9	1364.2	0.3	80.775	76.648	0.6	−9.129	−13.225	7.1	4.126	55.07	90.37	9.9	−35.30
Diethylene glycol diethyl ether	1231.2	1224.8	0.01	102.886	103.964	0.3	−1.485	−0.407	8.9	−1.078	9.07	2.67	8.6	1.81
Diethylene glycol dibutyl ether	1253.9	1251.6	0.02	125.905	126.368	0.04	−2.341	−1.878	2.7	−0.463	11.19	8.89	2.8	7.92

Figures 2 and 3, and Table V show that the agreement between the calculated and experimental values of $K_{S,m}^{E}$, and u^{D} are quite good for mixtures containing diethylene glycol dibutyl ether + propylamine (VII), whereas for mixtures containing diethylene glycol diethyl ether or alkoxyethanols with propylamine, $K_{S,m}^{E}$ and u^{D} deviate considerably, $K_{S,m}^{E}$ by up to $6.068\,\text{mm}^3\cdot\text{mol}^{-1}\cdot\text{MPa}^{-1}$ and u^{D} up to $-63.50\,\text{m}\cdot\text{s}^{-1}$.

It can be concluded that for diethylene glycol dibutylether + propylamine (VII), the use of the vdW energy model is appropriate for the presentation of experimental results of u, $K_{S,m}$, $K_{S,m}^{E}$, and u^{D}.

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