Ultrasonic speeds and isentropic functions of 2-(2-alkoxyethoxy)ethanol + water at 298.15 K

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Abstract

Ultrasonic speeds were measured in 2-(2-ethoxyethoxy)ethanol + water and 2-(2-butoxy ethoxy)ethanol + water systems across their entire composition ranges, at the temperature 298.15 K, using a sing-around technique, at a frequency of 1.8 MHz. Measurements were also made of the densities of the two systems. From these measurements, values of the molar and excess molar volumes were obtained together with the values of $-(\partial V_m / \partial p)_{S,m}$ and the corresponding excess quantities. The various excess quantities were analysed using a segmented-composition model.

INTRODUCTION

In earlier papers, we have reported the results of our measurements, at the temperature 298.15 K, of some thermodynamic properties of the mixtures ethan-1,2-diol (EG) + water [1] and a 2-alkoxyethanol ($C_m E_1$) + water [2,3], whose organic component is a member of a specific family of non-ionic amphiphiles, the alkylpoly(ethylene glycol) monoethers. Their generic formula $C_m H_{2m+1}(OC_2H_4)_n OH$ is frequently and conveniently abbreviated to $C_m E_n$. We note that ethan-1,2-diol ($C_0 E_1$) is not an amphiphile in the accepted sense of that term. These investigations were concerned with the sensitivity to the alkyl chain length of the composition dependence of a variety of excess molar properties, together with the deviations u^D of the ultrasonic speeds from $u^{(id)}$, assumed to represent the value of the ultrasonic speed in an ideal mixture. With increasing alkyl chain length, the $C_m E_1$ + water mixtures exhibit radical changes in the mole-fraction derivatives of excess molar properties. Such abrupt changes

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in the composition dependence support the contention that C_4E_1 forms highly structured aggregates that warrant the use of terms such as "borderline surfactant". Unfortunately, higher homologs ($m > 4$) are only sparingly soluble in water.

The inclusion of one or more OC_2H_4 groups into an n-alkanol increases the hydrophilic strength and aqueous miscibility. While n-butanol (C_4E_0) has a miscibility gap at all temperatures within the aqueous liquid interval, 2-butoxyethanol (C_4E_1) is completely miscible with water up to its lower critical solution temperature of 49°C. Further, 2-(2-butoxyethoxy)ethanol (C_4E_2) is completely miscible with water up to 100°C.

In this paper, we report measured values of the ultrasonic speeds in the mixtures 2-(2-ethoxyethoxy)ethanol (C_2E_2) + water and 2-(2-butoxy-ethoxy)ethanol (C_4E_2) + water across the entire range of mole fractions. This property has not been reported previously. We have also measured the densities of the two mixtures over the whole composition range at the temperature 298.15 K.

The isentropic compressibility κ_S values were furnished by the recipro-cals of the products of the densities and the squared ultrasonic speeds. The density values were converted to molar volumes, V_m, which were combined with the ultrasonic speeds to furnish values of the quantities $-(\partial V_m/\partial p)_S$, which we have chosen to represent by the symbol $K_{S,m}$ and are equal to the products of the molar volume and the isentropic compressibility. We have calculated the excess molar quantities V_m^E and $K_{S,m}^E$ ($= -(\partial V_m/\partial p)_S^E$); also, we have calculated the values of the deviations u^D of the ultrasonic speeds from the quantities $u^{(id)}$, calculated by substituting the ideal properties in the relationship between $-(\partial V_m/\partial p)_S$ and u.

EXPERIMENTAL

2-(2-Ethoxyethoxy)ethanol (98–99 mass % pure) and 2-(2-butoxy-ethoxy)ethanol (more than 99 mass % pure), from Aldrich, were used without further purification. The chemicals were stored and protected against atmospheric moisture and carbon dioxide as far as possible.

All mixtures were prepared by mass, with a precision of 0.1 mg, using thoroughly degassed twice-distilled water. Corrections were made for buoy-ancy. The mole fractions are believed to be reliable to within 1×10^{-4}.

Densities were measured at 298.15 K using a Sodev densimeter type 03D, operating in a flow mode. The vibrating tube was thermostatted to within ± 0.002 K by means of a Setaram thermostat. The temperature was measured with a Hewlett–Packard quartz thermometer of type 2804 A. This was accurate to within ± 0.01 K, with a long-term stability of ± 0.002 K. Details of the calibration and operational procedures have been de-scribed in previous papers [3,4]. The measurements at 298.15 ± 0.01 K have an estimated reproducibility of $\pm 5 \times 10^{-3}$ kg m^3. The densities that were

TABLE 1

Densities, ρ^*, extensive properties, $A_{p,m}^* = -(\partial V/\partial T)_{p,m}$ (equal to the products of the molar volume V_m and the isobaric thermal expansivity $\alpha_{p,m}^*$), molar isobaric heat capacities, $C_{p,m}^*$, and ultrasonic speeds, u^*, for the component liquids at $T = 298.15$ K

	ρ^* (kg m^{-3})		$A_{p,m}^*$ (mm^3 K^{-1} mol^{-1})	
	Obs.	Lit.	Obs.	Lit.
Water		997.048 [5]		4.647 [5]
2-(2-Ethoxyethoxy)ethanol	983.589	983.87 [6]	115.4	
2-(2-Ethoxybutoxy)ethanol	948.016	949.16 [6]	144.2	
	$C_{p,m}^*$ (J K^{-1} mol^{-1})		u^* (m s^{-1})	
	Obs.	Lit.	Obs.	Lit.
Water		75.292 [7]		1496.687 [8]
2-(2-Ethoxyethoxy)ethanol	298.1	297.24 [6]	1377.22	
2-(2-Ethoxybutoxy)ethanol	358.4	354.89 [6]	1357.02	

obtained for the pure substances are given in Table 1, together with some values taken from the literature. Also given in Table 1 are literature values of those quantities which were required in the estimation of $-(\partial V_m/\partial p)_S$ and $-(\partial V_m/\partial p)_S^E$. Ultrasonic speeds in both the pure liquids and the binary mixtures were measured at 298.15 K by the sing-around principle [8], which involves the passing of repeated pulses of ultrasonic waves through the solution, with the arrival of one pulse triggering the next and the measurement of the frequency of this wave. The ultrasonic pulse repetition rate was obtained by means of a sonic solution monitor (Mapco Inc., Nusonics type 6105). This rate is related to the speed of sound in the liquid sample by a known explicit function of composition and temperature. The electronic processing circuit was coupled with a solution cell, a brass cylinder of length 8 cm, designed by E. Høgseth (Engineer, Department of Chemistry, University of Bergen, Norway). The cell was submerged in a thermostatted water bath, the temperature of which was measured using a Hewlett–Packard quartz thermometer of type 2804 A. All the measurements were carried out at 298.15 K. Water was used as a calibrant to determine the ultrasonic speed of the samples. Its ultrasonic speed was assumed to be 1496.687 m s^{-1} at 298.15 K [9]. Further details concerning this apparatus, its calibration and operating procedures have been described elsewhere [3,4]. The reproducibility of the speed of sound of the samples was estimated to be 0.05 m s^{-1}.

RESULTS

The set of densities for C_2E_2 + water and C_4E_2 + water mixtures are given in Table 2 at the temperature $T = 298.15$ K. The ultrasonic speeds are reported in Table 3, at $T = 298.15$ K.

TABLE 2

Densities of 2-(2-alkoxyethoxy)ethanol + water mixtures at $T = 298.15$ K

x	ρ (kg m^{-3})	x	ρ (kg m^{-3})	x	ρ (kg m^{-3})	x	ρ (kg m^{-3})
$x C_2H_5O(CH_2CH_2O)_2H + (1-x)H_2O$							
0	997.048	0.0244	1005.690	0.1432	1020.236	0.5800	995.466
0.0005	997.223	0.0251	1005.994	0.1463	1020.193	0.6509	992.759
0.0050	998.811	0.0280	1006.960	0.1781	1018.674	0.6533	992.640
0.0053	998.912	0.0281	1007.007	0.2214	1015.998	0.7078	990.874
0.0099	1000.567	0.0301	1007.608	0.2598	1013.375	0.7200	990.464
0.0150	1002.356	0.0327	1008.517	0.2954	1010.796	0.7782	988.729
0.0155	1002.561	0.0371	1009.927	0.3511	1007.243	0.7901	988.395
0.0163	1002.908	0.0425	1011.165	0.3675	1006.278	0.8491	986.914
0.0201	1004.230	0.0506	1013.444	0.3906	1004.878	0.8605	986.597
0.0224	1005.208	0.0699	1017.146	0.4382	1002.151	0.9300	984.985
0.0236	1005.493	0.0993	1019.973	0.5008	998.943	1	983.589
0.0239	1005.604	0.1373	1020.379	0.5708	995.869		
$x c_4H_9O(CH_2CH_2O)_2H + (1-x)H_2O$							
0	997.048	0.0077	998.378	0.1649	983.545	0.4532	963.950
0.0006	997.134	0.0080	998.422	0.1850	981.638	0.5000	961.771
0.0009	997.175	0.0097	998.720	0.1877	981.109	0.5753	958.781
0.0016	997.278	0.0110	998.933	0.1971	980.515	0.6385	956.664
0.0019	997.305	0.0141	999.399	0.2100	979.461	0.6755	955.630
0.0022	997.378	0.0170	999.686	0.2122	979.286	0.6980	955.044
0.0029	997.505	0.0232	999.653	0.2349	977.447	0.7106	954.624
0.0034	997.601	0.0330	998.742	0.2452	976.604	0.7269	954.228
0.0035	997.583	0.0352	998.542	0.2537	976.069	0.7596	953.316
0.0039	997.648	0.0383	998.161	0.2731	974.488	0.8083	952.016
0.0039	997.715	0.0434	997.520	0.2736	974.509	0.8347	951.440
0.0042	997.724	0.0482	996.892	0.2936	973.124	0.8364	951.388
0.0050	997.872	0.0560	995.927	0.3000	972.652	0.8672	950.674
0.0051	997.924	0.0653	994.749	0.3175	971.505	0.9137	949.724
0.0051	997.934	0.0789	992.897	0.3186	971.433	0.9269	949.482
0.0059	998.037	0.0967	990.569	0.3493	969.586	0.9387	949.222
0.0062	998.123	0.1023	989.320	0.3865	967.447	0.9492	949.035
0.0065	998.172	0.1118	988.659	0.4001	966.573	1	948.016
0.0072	988.287	0.1318	986.872	0.4255	965.312		

It has become customary to use, instead of the molar function of mixing $\Delta_{mix}Q_m$, the excess molar function Q_m^E defined by

$$Q_m^E = \Delta_{mix}Q_m - \Delta_{mix}Q_m^{id} \qquad (1)$$

so that "excess" means "excess over ideal" [10]. The excess molar quantities, Q_m^E, where Q_m represents respectively V_m^E and $K_{S,m}^E$ ($= -(\partial V_m/\partial p)_S^E$), were calculated from the general equation (eqn. (1)).

When Q_m represents the molar volumes, V_m, derived from the densities of the mixtures, their values in an ideal mixture, V_m^{id}, were calculated as the

TABLE 3

Ultrasonic speeds of 2-(2-alkoxyethoxy)ethanol + water mixtures at $T = 298.15$ K

x	u (m s^{-1})	x	u (m s^{-1})	x	u (m s^{-1})	x	u (m s^{-1})
$x C_2H_5O(CH_2CH_2O)_2H + (1-x)H_2O$							
0	1496.687	0.0280	1603.20	0.2598	1559.41	0.5800	1438.51
0.0053	1520.53	0.0419	1636.28	0.2954	1539.92	0.6509	1423.40
0.0099	1540.43	0.0699	1666.94	0.3511	1513.01	0.7200	1411.12
0.0150	1559.97	0.0993	1665.39	0.3675	1506.17	0.7901	1400.54
0.0155	1561.80	0.1432	1638.72	0.3906	1496.68	0.8605	1391.54
0.0201	1578.45	0.1781	1613.22	0.4382	1479.26	0.9300	1383.87
0.0239	1591.06	0.2214	1583.16	0.5008	1460.21	1	1377.22
$x C_4H_9O(CH_2CH_2O)_2H + (1-x)H_2O$							
0	1496.687	0.0236	1565.66	0.1761	1484.88	0.5999	1391.06
0.0025	1511.92	0.0250	1564.23	0.2100	1473.34	0.6669	1382.63
0.0052	1527.65	0.0299	1559.76	0.2498	1460.54	0.7000	1379.68
0.0076	1540.13	0.0422	1550.32	0.3000	1445.88	0.7498	1374.89
0.0104	1553.16	0.0547	1542.22	0.3500	1434.79	0.7848	1371.87
0.0128	1561.88	0.0713	1532.35	0.4001	1423.18	0.8243	1368.97
0.0150	1567.26	0.0906	1522.44	0.4498	1414.47	0.8715	1365.83
0.0172	1569.43	0.1201	1507.84	0.5000	1405.31	0.9308	1361.82
0.0207	1568.17	0.1494	1495.25	0.5500	1398.72	1	1357.02

mole-fraction weighted average of the molar properties of the pure components.

When Q_m represents the quantities $-(\partial V_m/\partial p)_S$, equal to the products of the molar volume V_m and the isentropic compressibility κ_S, as shown in eqn. (2)

$$-(\partial V_m/\partial p)_S = V_m \kappa_S = K_{S,m} \tag{2}$$

it is appropriate to comment upon our use of the quantity $-(\partial V_m/\partial p)_S^{id}$ that we symbolize $K_{S,m}^{id}$.

It is generally accepted that an ideal molar quantity Q_m^{id} can be defined, if the quantity $\Delta_{mix}Q_m^{id}$ can be obtained by differentiation of the basic equation

$$\Delta_{mix}G_m^{id} = RT[x \ln(x) + (1-x) \ln(1-x)] \tag{3}$$

with respect to temperature at constant pressure, or with respect to pressure at constant temperature. In that way, it is possible to define S_m^{id}, V_m^{id}, $C_{p,m}^{id}$, $A_{p,m}^{id} = (\partial V_m/\partial T)_p^{id}$ and $K_{T,m}^{id} = -(\partial V_m/\partial p)_T^{id}$, but not $K_{S,m}^{id} = -(\partial V_m/\partial p)_S^{id}$ or $C_{V,m}^{id} = (\partial U_m/\partial T)_V^{id}$.

To extend the list of ideal molar quantities, it is necessary to add the further assumption that the thermodynamic properties of an ideal mixture

are mutually related in the same manner as are those of real mixtures and pure substances. In the context of this extended definition

$$-\left(\partial V_{\mathrm{m}}/\partial p\right)_{\mathrm{S}}^{\mathrm{id}} = V_{\mathrm{m}}^{\mathrm{id}}\kappa_{\mathrm{S}}^{\mathrm{id}} = K_{\mathrm{S,m}}^{\mathrm{id}} = K_{\mathrm{T,m}}^{\mathrm{id}} - T\left(A_{\mathrm{p,m}}^{\mathrm{id}}\right)^2/C_{\mathrm{p,m}}^{\mathrm{id}} \tag{4}$$

whence

$$K_{\mathrm{S,m}}^{\mathrm{id}} = \sum_i x_i\left[K_{\mathrm{S},i}^* + T(A_{\mathrm{p},i}^*)^2/(C_{\mathrm{p},i}^*)\right] - T\left(\sum_i x_i A_{\mathrm{p},i}^*\right)^2/\left(\sum_i x_i C_{\mathrm{p},i}^*\right) \tag{5}$$

where $K_{\mathrm{S},i}^* = -(\partial V_i^*/\partial p)_{\mathrm{S}}$, the product of the molar volume V_i^* and the isentropic compressibility $\kappa_{\mathrm{S},i}^*$, $A_{\mathrm{p},i}^* = -(\partial V_i^*/\partial T)_{\mathrm{p}}$, the product of the molar volume V_i^* and the isobaric expansivity $\alpha_{\mathrm{p},i}^*$, and $C_{\mathrm{p},i}^* = (\partial H_i^*/\partial T)_{\mathrm{p}}$, the isobaric molar heat capacity, are properties of the pure liquid component i.

The corresponding excess quantity $-(\partial V_{\mathrm{m}}/\partial p)_{\mathrm{S}}^{\mathrm{E}}$ is obtained from the equation

$$-\left(\partial V_{\mathrm{m}}/\partial p\right)_{\mathrm{S}}^{\mathrm{E}} = -\left(\partial V_{\mathrm{m}}/\partial p\right)_{\mathrm{S}} + \left(\partial V_{\mathrm{m}}/\partial p\right)_{\mathrm{S}}^{\mathrm{id}} = K_{\mathrm{S,m}}^{\mathrm{E}} = K_{\mathrm{S,m}} - K_{\mathrm{S,m}}^{\mathrm{id}} \tag{6}$$

or

$$K_{\mathrm{S,m}}^{\mathrm{E}} = \left(V_{\mathrm{m}}^{\mathrm{E}} + V_{\mathrm{m}}^{\mathrm{id}}\right)\kappa_{\mathrm{S}} - V_{\mathrm{m}}^{\mathrm{id}}\kappa_{\mathrm{S}}^{\mathrm{id}} \tag{7}$$

The isentropic compressibility κ_{S} of a mixture is related to the speed of sound, u, by the following equation [11]:

$$\kappa_{\mathrm{S}} = 1/\left(M_{\mathrm{m}}u^2\right) = V_{\mathrm{m}}/\left(\rho u^2\right) \tag{8}$$

where $M_{\mathrm{m}} = \sum_i x_i M_i^*$ is the molar mass of the mixture and thus

$$K_{\mathrm{S,m}} = V_{\mathrm{m}}^2/\left(M_{\mathrm{m}}u^2\right) \tag{9}$$

As pointed out, the speed defined by this equation is, of course, a purely thermodynamic quantity [11]. When the dispersion is negligible (waves of low frequency and low amplitude), the experimental speed is equal to the speed defined by eqn. (8), and so may be regarded as an equilibrium property.

Several authors have rewritten the defining equation of u in terms of the ideal quantities; they defined a so-called "ideal" ultrasonic speed $u^{(\mathrm{id})}$ [12,13] which may be calculated from

$$u^{(\mathrm{id})} = V_{\mathrm{m}}^{\mathrm{id}}\left(M_{\mathrm{m}}K_{\mathrm{S,m}}^{\mathrm{id}}\right)^{-1/2} \tag{10}$$

This quantity has been described as being the ultrasonic speed in an ideal mixture. The deviations of the measured ultrasonic speeds from their "ideal" counterparts, u^{D} are calculated from the following equation [1,3]:

$$u^{\mathrm{D}} = u - u^{(\mathrm{id})} \tag{11}$$

TABLE 4

Excess molar volume V_m^E, the extensive property $K_{S,m} = [-(\partial V/\partial p)_{S,m}]$ and the corresponding excess quantity $K_{S,m}^E = [-(\partial V/\partial p)_{S,m}^E]$ and the deviations, u^D, from the ultrasonic speed $u^{(id)}$ for 2-(2-alkoxyethoxyethanol)+water mixtures at $T = 298.15$ K

x	V_m^E $(cm^3\ mol^{-1})$	$K_{S,m}$ $(mm^3\ MPa^{-1}\ mol^{-1})$	$K_{S,m}^E$ $(mm^3\ MPa^{-1}\ mol^{-1})$	u^D $(m\ s^{-1})$
$xC_2H_5O(CH_2CH_2O)_2H + (1-x)H_2O$				
0	0	8.0900	0	0
0.0053	−0.0448	8.0768	−0.4082	33.47
0.0099	−0.0858	8.0696	−0.7568	60.93
0.0150	−0.1332	8.0789	−1.1175	87.96
0.0155	−0.1379	8.0799	−1.1518	90.48
0.0201	−0.1835	8.0992	−1.4736	113.42
0.0239	−0.2214	8.1220	−1.7273	130.77
0.0280	−0.2618	8.1595	−1.9865	147.66
0.0419	−0.3976	8.3597	−2.7927	194.72
0.0699	−0.6458	9.0900	−4.0499	245.63
0.0993	−0.8491	10.2411	−4.9570	258.24
0.1432	−1.0542	12.3976	−5.8186	244.86
0.1781	−1.1524	14.3312	−6.2429	225.98
0.2214	−1.2263	16.9032	−6.5647	201.28
0.2598	−1.2563	19.2990	−6.7085	180.61
0.2954	−1.2586	21.5956	−6.7471	163.05
0.3511	−1.2439	25.3150	−6.6564	137.99
0.3675	−1.2335	26.4288	−6.6093	131.51
0.3906	−1.2147	28.0224	−6.5064	122.41
0.4382	−1.1591	31.3588	−6.2359	105.47
0.5008	−1.0677	35.8080	−5.7980	86.60
0.5800	−0.9323	41.6379	−5.0108	64.68
0.6509	−0.7915	46.8846	−4.2617	49.15
0.7200	−0.6492	52.0377	−3.4831	36.34
0.7901	−0.4914	57.2946	−2.6426	25.16
0.8605	−0.3331	62.5861	−1.7796	15.55
0.9300	−0.1642	67.8383	−0.8938	7.26
1	0	73.1209	0	0
$xC_4H_9O(CH_2CH_2O)_2H + (1-x)H_2O$				
0	0	8.0900	0	0
0.0025	−0.0276	8.0786	−0.2638	21.87
0.0052	−0.0602	8.0738	−0.5458	44.42
0.0076	−0.0887	8.0812	−0.7791	62.46
0.0104	−0.1232	8.1109	−1.0413	81.81
0.0128	−0.1511	8.1543	−1.2363	95.38
0.0150	−0.1751	8.2239	−1.3886	105.04
0.0172	−0.1974	8.3270	−1.5057	111.25
0.0207	−0.2296	8.5466	−1.6402	116.09
0.0236	−0.2509	8.7468	−1.7280	118.21
0.0250	−0.2619	8.8465	−1.7681	118.92
0.0299	−0.2978	9.1938	−1.9085	121.46
0.0422	−0.3723	10.0694	−2.2434	126.72
0.0547	−0.4374	10.9758	−2.5663	130.45

TABLE 4 (continued)

x	V_m^E (cm^3 mol^{-1})	$K_{S,m}$ (mm^3 MPa^{-1} mol^{-1})	$K_{S,m}^E$ (mm^3 MPa^{-1} mol^{-1})	u^D (m s^{-1})
0.0713	− 0.5094	12.2025	− 2.9500	132.64
0.0906	− 0.5767	13.6518	− 3.3500	133.12
0.1201	− 0.6807	15.9279	− 3.8675	129.56
0.1494	− 0.7739	18.2358	− 4.2990	124.25
0.1761	− 0.8327	20.4023	− 4.6090	118.51
0.2100	− 0.8964	23.1955	− 4.9307	111.04
0.2498	− 0.9497	26.5802	− 5.1749	101.37
0.3000	− 0.9835	30.9852	− 5.3100	89.09
0.3500	− 0.9968	35.3947	− 5.3915	79.33
0.4001	− 0.9779	40.0098	− 5.2533	68.43
0.4498	− 0.9447	44.5721	− 5.1134	60.04
0.5000	− 0.8931	49.3332	− 4.7995	50.96
0.5500	− 0.8321	54.0158	− 4.5393	44.29
0.5999	− 0.7661	58.8704	− 4.0853	36.45
0.6669	− 0.6774	65.3811	− 3.4731	27.68
0.7000	− 0.6316	68.5294	− 3.2270	24.54
0.7498	− 0.5433	73.3905	− 2.7429	19.45
0.7848	− 0.4667	76.8155	− 2.3821	16.21
0.8243	− 0.3889	80.6502	− 2.0061	13.06
0.8715	− 0.2906	85.2455	− 1.5457	9.62
0.9308	− 0.1684	91.0799	− 0.8963	5.23
1	0	98.0230	0	0

Some authors have referred to the quantity u^D as an "excess ultrasonic speed". It is preferable to limit the use of the term "excess" to the molar values of extensive properties. The quantity u^D should not be confused with $\Delta u(x)$, which is the departure of the ultrasonic speed from the mole-fraction weighted average of those of the pure components.

It proved to be impractical to make density and ultrasonic speed measurements on the same samples, allowing for the direct determination of the excess molar properties. In those cases, excess molar volumes, V_m^E, at the mole fractions of the ultrasonic speed measurements, were obtained by cubic spline interpolation. These values are reported in Table 4, together with the extensive property $K_{S,m} = [-(\partial V_m/\partial p)_S]$, the excess quantity, $K_{S,m}^E = [-(\partial V_m/\partial p)_S^E]$, and the deviations, u^D, of the ultrasonic speed calculated from eqns. (10) and (11).

Our values of V_m^E, $K_{S,m}^E$ and u^D are plotted against x in Figs. 1–3 respectively. Properties of the C_2E_2 + water system are seen to vary quite smoothly with increasing amphiphile concentration. By contrast, as is evident from Figs. 4–6, which cover the water-rich region, the properties of the C_4E_2 + water mixture exhibit abrupt changes of slope at $x_{C_4E_2} \approx 0.02$, as do the corresponding properties of C_4E_1 + water [1–3]. No such compo-

EXCESS MOLAR VOLUMES

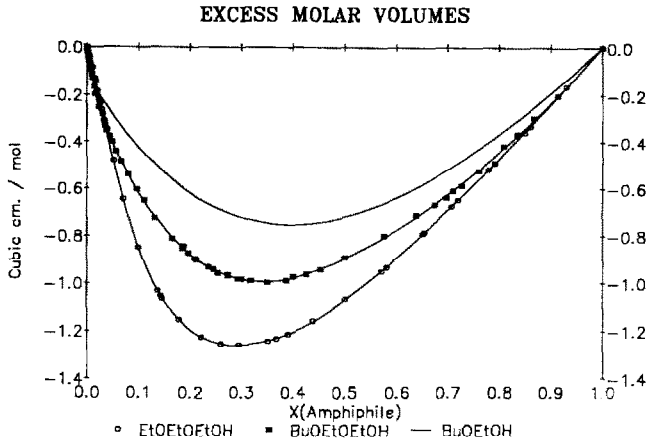Fig. 1. Excess molar volumes (cm^3 mol^{-1}) vs. mole fraction, at 25°C, of EtOEtOEtOH-(C$_2$E$_2$)+water (○), BuOEtOEtOH(C$_4$E$_2$)+water (■) and BuOEtOH(C$_4$E$_1$)+water (———). The markers represent the experimental values; the solid lines are optimised four-segment model values.

sition dependence of V_m^E, H_m^E and $C_{p,m}^E$ was observed for the binary mixtures of C$_4$E$_2$ or C$_4$E$_1$ with an organic solvent [14,15].

Various authors have suggested analytic procedures for fitting the excess molar thermodynamic properties of binary mixtures with functions of x [16–20]. These equations, whose coefficients are determined by least-squares optimisation and optimal number of terms by regression, give a reasonable fit to the excess-property curves of the C$_2$E$_2$ + water system; however, they are found to be quite unacceptable for the excess-property
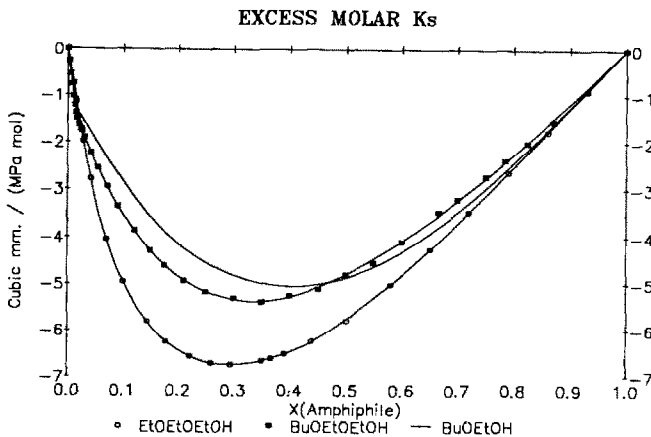
EXCESS MOLAR Ks

Fig. 2. Excess molar K_S (mm^3 MPa^{-1} mol^{-1}) vs. mole fraction, at 25°C, of EtOEtOEtOH-(C$_2$E$_2$)+water, BuOEtOEtOH(C$_4$E$_2$)+water and BuOEtOH(C$_4$E$_1$)+water. Symbols are the same as for Fig. 1.

DEVIATION IN U
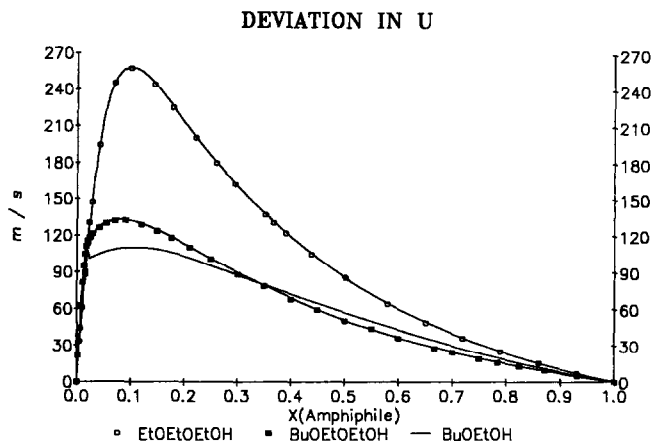

Fig. 3. Deviations of ultrasonic speeds (m s^{-1}) from their "ideal" values vs. mole fraction, at 25°C, in EtOEtOEtOH(C_2E_2)+water, BuOEtOEtOH(C_4E_2)+water and BuOEtOH-(C_4E_1)+water. Symbols are the same as for Fig. 1.

curves of C_4E_2 + water. It appears that these functions cannot accommodate the sharp changes of slope at $x_{C_4E_2} \approx 0.02$. Moreover, their coefficients are of little assistance in interpreting the results. It was obvious that some alternative analytic procedure was necessary for the C_4E_2 + water system and that the same procedure should be employed for the two mixtures.

We have chosen to use the four-segment composition model which assumes that the total composition range of any mixture of amphiphile + water can be partitioned into four reasonably discrete segments, each with its own characteristic composition dependence [21]. Since it was first
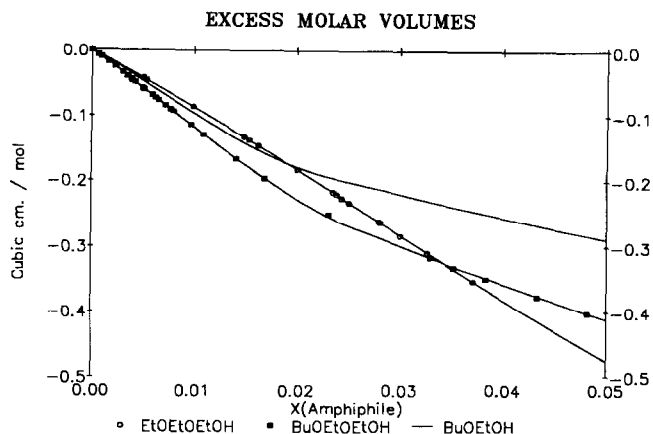
EXCESS MOLAR VOLUMES

Fig. 4. Excess molar volumes (cm^3 mol^{-1}) at low amphiphile mole fractions. Symbols are the same as for Fig. 1.
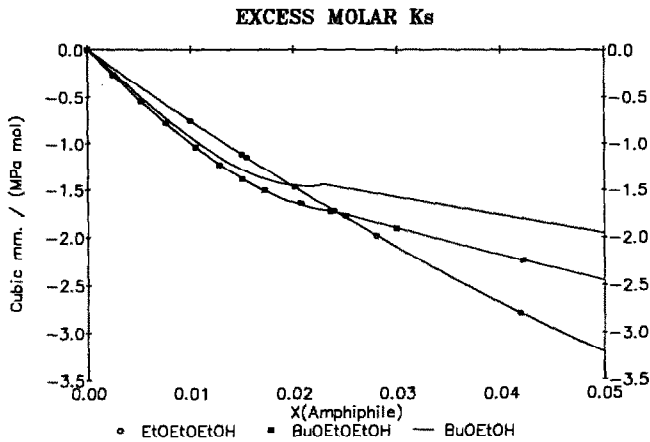
EXCESS MOLAR Ks

Fig. 5. Excess molar K_S (mm^3 MPa^{-1} mol^{-1}) at low amphiphile mole fractions. Symbols are the same as for Fig. 1.

introduced, several different versions of the sets of equations of the four-segment composition model have been proposed [2,3,22,23]. We have demonstrated that it is a relatively simple matter to devise a set of model equations, one for each composition segment, which collectively do an acceptable job of fitting excess-property curves [24]. Finding the "best" set of segment junction mole fractions, x_1, x_2 and x_3, is far less straightforward. Of several different approaches that have been tried, a "simplex" procedure appears to be the most satisfactory. This involves parameter optimisation at each of a substantial number of segment junction combinations. The optimum segment junction combination represents a local minimum of the standard deviation, within the space of x_1, x_2 and x_3. For a
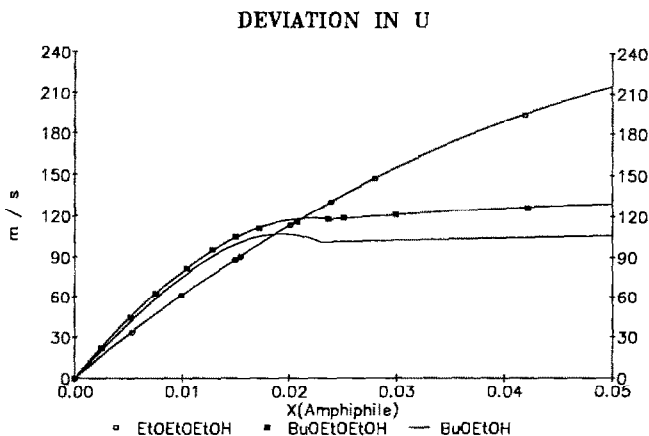
DEVIATION IN U

Fig. 6. Deviations of ultrasonic speeds (m s^{-1}) from their "ideal" values at low amphiphile mole fractions. Symbols are the same as for Fig. 1.

given data set and a specific model, several such local minima may well exist. By seeking out estimates of the "best" combinations of segment junction values for several different data sets for each system, it proved to be possible to arrive at a fairly well-defined representative set for each of the binary systems that we have studied.

The present model is based on the plausible assumption that mixtures of small amphiphile + water tend, to different extents, to mimic the patterns of molecular aggregation that are characteristic of mixtures of larger non-ionic surfactant + water. We have attempted to formulate the model equations, for the four composition segments, in such a way that their optimisable parameters can be assigned some kind of physical significance. It should be noted that the excess molar quantities are constrained to be continuous at each of the segment junctions, x_1, x_2 and x_3. The derivatives dQ_m^E/dx_A are required to be continuous at x_2 and x_3, but not at x_1.

The equations used in these analyses are reproduced in the Appendix. A rationale for their adoption follows.

Over the course of the water-rich mole-fraction range $0 \leq x \leq x_1$, several phenomena can be distinguished as far as x is increasing. At infinite dilution, the amphiphilic molecule is regarded as creating an aqueous cosphere, consisting of two parts created by the hydrophilic and hydrophobic hydration effects respectively. At modest amphiphile concentrations, solute–solute interactions begin to play a significant role. Two distinct types of interactions are considered to be important; those involving random contact between solute pairs and those resulting in the formation of amphiphile clusters. The ultimate results of increasing the amphiphile concentration will depend upon the relative strengths of the hydrophobic and hydrophilic groups. For a family of amphiphiles with a common hydrophilic head group, the hydrophobic character increases with the length of the non-polar hydrocarbon tail. If the hydrophobic group is sufficiently dominant, the water-rich segment terminates abruptly with either a phase separation or the formation of micelles. If the hydrophilic group is sufficiently dominant, the amphiphile and water will be miscible in all proportions. The water-rich segment, in this instance, appears to terminate at that concentration in which all of the water molecules are involved in solvation. In the present investigations, when rather small amphiphiles such as C_2E_2 are involved, there is a dominance of the hydrophilic effects. Some tendency towards labile cluster formation may exist.

There are substantial similarities between the profiles of the excess properties of the C_4E_2 + water and C_4E_1 + water systems. Both systems exhibit abrupt changes in the composition dependence of V_m^E, $K_{S,m}^E$ and u^D at an amphiphile mole fraction close to 0.02. Such abrupt changes are typical of detergent + water systems at their critical micelle concentrations. While we would not go so far to claim this as evidence that C_4E_1 and C_4E_2 are capable of forming stable micellar aggregates, it does appear to be

reasonable to suggest that they are capable of forming highly structured, albeit metastable, aggregates and that one may employ terms such as "borderline surfactant" and "pseudomicellar". The mole fraction value of 0.02 may thus be described as a critical micelle concentration analog. This value, at 25°C, is very close to that predicted by extrapolation of the experimental critical micelle concentrations of larger alkylpoly(ethylene glycol) monoethers.

The transition from the premicellar aggregates that make their appearance in the water-rich region to pseudolamellar aggregates, with increasing amphiphile concentration, over the composition range $x_1 \leq x \leq x_2$, is clearly a complex process that is likely to vary from one amphiphilic species to another. A more satisfactory name for this segment than "secondary", which we have employed previously, would appear to be "transitional". For the C_2E_2 + water system, in which the hydrophobic group is too weak to promote anything more than a modest tendency towards the formation of labile clusters, gradual depletion of the water content, above the concentration at which all water is involved in solvation, may be presumed to result in modifications to the scheme of aggregation in the direction of small labile and poorly defined pseudolamellar aggregates. On the contrary, in the C_4E_2 + water system, the two types of pseudomicellar and pseudolamellar aggregates might be presumed to possess reasonably well-defined size and shape.

The ability of certain amphiphiles to form some kind of lamellar aggregates in an aqueous environment is a phenomenon of considerable interest. In the binary systems, with which we are concerned, such aggregates occur in a single isotropic phase, in which amphiphile bilayers are separated by layers of water of a thickness of no more than a few molecules. This scheme of molecular aggregation has certain stoichiometric requirements that depend to some extent upon the size of the polar head group. We have chosen to call the composition range over which this type of aggregation exists, $x_2 \leq x \leq x_3$, the "pseudolamellar" segment.

The organic-rich segment ($x_3 \leq x \leq 1$) spans the composition range from the upper limit of the amphiphile mole fraction that is consistent with pseudolamellar aggregation to the pure amphiphile. The pure alkoxyethoxyethanols that we have studied are all liquids at 25°C. They are presumably quite highly structured with a significant level of contact between the polar head groups. The nature of the patterns of molecular aggregation that exist within this segment will depend upon the structure of the pure amphiphile. Such structural order, as exists in the pure amphiphile, is presumed to owe its origin to the molecules' abilities to adopt mutual orientations which take advantage of the stabilising effects of the attractions between polar head groups. Solute water molecules are expected to exhibit a preference for occupying sites adjacent to the polar groups of the amphiphiles. As the water concentration increases, aqueous

TABLE 5

Optimised four-segment model parameters for V_m^E and the excess quantity $K_{S,m}^E = [-(\partial V/\partial p)_{S,m}^E]$ of 2-(2-alkoxyethoxy)ethanol + water mixtures at $T = 298.15$ K

	C_2E_2	C_4E_2	C_2E_2	C_4E_2
x_1	0.075	0.0255	0.075	0.0255
x_2	0.255	0.205	0.255	0.205
x_3	0.480	0.403	0.480	0.403
	V_m^E (cm^3 mol^{-1})		$K_{S,m}^E$ (mm^3 MPa^{-1} mol^{-1})	
a_w	−8.321	−11.021	−79.03	−112.9
b_w	−51.16	−139.6	282.1	984.7
a_1	−9.09	−10.508	−56.29	−69.17
a_s	−3.268	−4.764	−19.13	−21.14
b_s	12.25	22.4	68.14	50.61
q_w	−0.912	−0.338	−4.8	−2.078
q_a	0.856	1.411	4.525	7.409
b_1	−4.17	−5.583	−22.52	−29.14
a_a	−2.403	−2.461	−12.7	−11.89
$10^2\sigma$	0.228	0.475	1.098	3.356

self-aggregation might, in some instances, be expected to give rise to the existence of some type of metastable inverted pseudomicellar aggregates which ultimately assume a pseudolamellar form.

DISCUSSION

The results of the four-segment model analyses are given in Table 5. It should be noted that the results for V_m^E of the C_2E_2 + water and C_4E_2 + water systems correspond to the original results and not to the interpolated values. The standard deviations indicate a fairly high quality of fit.

The composition dependences of the C_2E_2 + water system properties show no dramatic changes but appear as smoothed analogs of those of C_4E_2 + water. This leads one to suggest that there is a very modest degree of hydrophobic aggregation by the small amphiphile, resulting in highly labile clusters. The composition dependences of the properties of both mixtures look quite the same as those of the corresponding C_mE_1 + water system previously studied [3].

What is very nicely demonstrated here is that the ultrasonic speeds, in their composition dependence, reveal significant variations in the patterns of molecular aggregation. There is a very clear distinction between the results for C_2E_2 + water, on the one hand, and C_4E_2 + water, on the other.

While C_4E_2 may not satisfy all of the requirements for a truly micellar system, it is patently obvious that there exist some characteristic structural changes around $x \approx 0.02$, in the same way as we observed for C_4E_1 + water [2,3].

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APPENDIX: THE FOUR SEGMENT MODEL EQUATIONS

1. The water-rich segment, $0 \leq x \leq x_1$

$$Q^E = a_w x(1-y)^2 + b_w x^2(1-y) + a_1 xy^2$$

where

$$y = x/x_1$$

2. The transitional segment, $x_1 \leq x \leq x_2$

$$Q^E = Q^E_{p,mic}(1 - f_s) + Q^E_{p,lam} f_s$$

where

$$Q^E_{p,mic} = \left[a_1 x_1(1 - x) + a_s(x - x_1) + b_s(x - x_1)^2/(1 - x_1) \right]/(1 - x_1)$$

represents the composition dependence of the excess molar property of saturated solutions of the pseudomicellar aggregates and

$$Q^E_{p,lam} = q_w(1 - x) + q_A x + b_L x(1 - x)$$

represents the composition dependence of the excess molar property when there is a pseudolamellar scheme of molecular aggregation. The fractional transition from pseudomicellar to pseudolamellar aggregation is represented by

$$f_s = \tfrac{1}{2}\{\cos[(x - x_1)/(x_2 - x_1)] + 1\}$$

3. The pseudolamellar segment, $x_2 \leq x \leq x_3$

$$Q^E = Q^E_{p,lam}$$

4. The organic-rich segment, $x_3 \leq x \leq 1$

$$Q = q_w(1 - x)(2z - z^2) + q_A\left[z^2(1 + 2x_3) - z^3(1 + x_3) \right]$$
$$+ b_L(1 - x)\left[z(1 + x_3) - z^2 \right] + a_A(1 - x)(1 - z)^2$$

where

$$z = (1 - x)/(1 - x_3)$$