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Excess properties of mixtures of some *n*-alkoxyethanols with organic solvents. Part 7. V^E with toluene at 298.15 K

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Abstract

The excess molar volume at 298.15 K and atmospheric pressure for three (alkoxyethanol + toluene) mixtures have been determined over the whole mole fraction range from densities measured with a vibrating-tube densimeter. The alkoxyethanols were 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol. The three excess volumes curves have a maximum in the toluene rich region and those with 2-ethoxyethanol and 2-butoxyethanol are sigmoidal. The excess molar volumes increase as the alkyl chain length of the alkoxyethanol decreases.

Keywords: Alkoxyethanols; Excess molar volume; Toluene; Vibrating-tube densimeter

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1. Introduction

In the last few years we have studied excess functions of some alkoxyethanols with organic solvents at 298.15 K and atmospheric pressure. This is part of a more general programme in which we have studied mixtures containing oxygen (–O–) and hydroxyl (–OH) functional groups [1–5] with the aim of characterizing the molecular interactions of these groups. In Parts 1 [6, 11] and 2 [7, 12] of this series we studied the excess molar enthalpies, excess molar volumes and excess molar heat capacities of 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol and 2-(2-butoxyethoxy)ethanol with di-*n*-butyl ether. In

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Parts 3 [8,12] and 4 [9,12] we studied the same excess properties as before of the alkoxyethanols with butanol and 2-methoxyethanol, respectively. In Part 5 [10,13] we studied the excess enthalpies of 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol with some *n*-alkanes. Finally, in Part 6 [14] we studied the excess volumes of 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol and 2-(2-butoxyethoxy)ethanol with toluene. As a sequel, we report here measurements of the excess molar volumes of 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol with toluene at 298.15 K and atmospheric pressure.

2. Experimental

Toluene (Fluka, puriss p.a., > 99.5 mol%), 2-methoxyethanol (Fluka, puriss p.a., > 99.5 mol%), 2-ethoxyethanol (Fluka, puriss p.a. > 99.5 mol%), and 2-butoxyethanol (Fluka, purum, > 98 mol%) were used without further treatment. Prior to actual measurements, all liquids were partially degassed and dried with molecular sieves (Union Carbide 0.4 nm, from Fluka). The densities of the pure liquids at 298.15 K were in good agreement with literature values [11,12,15,16]. Mixtures were prepared by mass. Conversion to molar quantities was based on the relative mass table of 1985 issued by I.U.P.A.C. [17].

Measurements of density ρ were carried out with an Anton-Paar DMA 602 vibrating-tube densimeter [18,19] with a resolution of $5 \times 10^{-3}\,\mathrm{kg\,m^{-3}}$ achieved by determining the period of oscillation of the liquid in a U-tube. The period of the oscillator was measured with a Philips PM 6669 frequency meter. All the measuring operations and calculations were computer controlled. The temperature of the sample contained in the oscillator tube was kept constant with a Grant thermostatic bath. The temperature of the circulating water was continuously monitored at the position nearest to the densimeter with a calibrated quartz thermometer (Hewlett-Packard 2804 A) and was stable within 2 mK. Excess molar volumes were calculated from the densities.

The instrument was calibrated with doubly disitilled and degassed water [$\rho(298.15\,\mathrm{K}) = 99.7048\,\mathrm{kg\,m^{-3}}$] [20], cyclohexane [$\rho(298.15\,\mathrm{K}) = 773.896\,\mathrm{kg\,m^{-3}}$] [21], isooctane [$\rho(298.15\,\mathrm{K}) = 687.849\,\mathrm{kg\,m^{-3}}$] [21], and "vacuum". The experimental technique was checked by determining the excess molar volumes of the standard mixtures (cyclohexane + benzene) and (cyclohexane + *n*-hexane) at 298.15 K; our results agreed well with published values [20,22,23].

3. Results and discussion

The experimental values from our measurements of V^{E} as a function of x, the molar fraction of the alkoxyethanol, at 298.15 K and atmospheric pressure are given in Table 1.

Table 1
Experimental excess molar volume V^E at 298.15 K and atmospheric pressure

x	$V^E/(\mathrm{cm^3\,mol^{-1}})$	x	$V^E/(\mathrm{cm^3\,mol^{-1}})$
2-methoxyethanol(1) + toluene(2)			
0.0059	0.021	0.1940	0.196
0.0108	0.037	0.2479	0.199
0.0198	0.058	0.2981	0.197
0.0286	0.078	0.3529	0.190
0.0388	0.096	0.4044	0.180
0.0509	0.114	0.4510	0.167
0.0585	0.123	0.4893	0.154
0.0685	0.135	0.5471	0.134
0.0725	0.139	0.5898	0.120
0.0804	0.145	0.6474	0.097
0.0900	0.154	0.6957	0.081
0.0971	0.158	0.7508	0.062
0.1076	0.165	0.8077	0.042
0.1091	0.166	0.8262	0.037
0.1189	0.172	0.9023	0.016
0.1306	0.178	0.9484	0.007
0.1500	0.185		
2-ethoxyethanol(1) + toluene(2)			
0.0057	0.021	0.2063	0.162
0.0107	0.035	0.2498	0.158
0.0165	0.049	0.2924	0.149
0.0219	0.060	0.3507	0.133
0.0271	0.071	0.4006	0.117
0.0403	0.092	0.4444	0.103
0.0481	0.102	0.5094	0.077
0.0601	0.116	0.5376	0.069
0.0685	0.123	0.6020	0.047
0.0784	0.130	0.6582	0.030
0.0901	0.138	0.6997	0.015
0.0997	0.143	0.7573	0.003
0.1060	0.146	0.7898	−0.002
0.1201	0.152	0.8510	−0.009
0.1253	0.153	0.8899	−0.011
0.1400	0.156	0.9400	−0.009
0.1553	0.160		
2-butoxyethanol(1) + toluene(2)			
0.0051	0.017	0.1504	0.109
0.0106	0.032	0.1520	0.108
0.0154	0.041	0.1595	0.108
0.0194	0.049	0.1804	0.105
0.0299	0.067	0.1988	0.101
0.0301	0.069	0.2200	0.093
0.0419	0.084	0.2540	0.085

Table 1 *(continued)*

x	$V^E/(\mathrm{cm^3\,mol^{-1}})$	x	$V^E/(\mathrm{cm^3\,mol^{-1}})$
0.0511	0.091	0.2671	0.081
0.0605	0.097	0.2984	0.069
0.0704	0.104	0.3511	0.049
0.0726	0.106	0.4040	0.028
0.0797	0.109	0.4530	0.011
0.0917	0.112	0.5118	−0.009
0.1001	0.114	0.5497	−0.021
0.1032	0.114	0.5876	−0.030
0.1105	0.115	0.6599	−0.046
0.1110	0.115	0.7087	−0.051
0.1219	0.113	0.7504	−0.054
0.1299	0.113	0.8011	−0.052
0.1368	0.112	0.8550	−0.043
0.1378	0.110	0.8985	−0.035
0.1399	0.111	0.9372	−0.024

Each set of results was fitted with the equation

$$V^E/(\mathrm{cm^3\,mol^{-1}}) = x(1-x)\frac{\sum_{i=0}^{k} A_i(2x-1)^i}{1+B_1(2x-1)} \tag{1}$$

Values of the parameters A_i and B_1 and standard deviations s, determined using the Marquardt algorithm [24] with all points weighted equally, are listed in Table 2. A graphical representation of the experimental results together with the smoothing curves appears in Fig. 1, where not all the points have been represented for clarity of presentation. In Fig. 2 we represent our experimental results for molar fractions lower than 0.2. No literature results could be found for comparison.

The excess molar volume for the mixture of 2-methoxyethanol with toluene is positive over the whole molar fraction range. The excess molar volumes for the mixtures with 2-ethoxyethanol and 2-butoxyethanol are sigmoidal, with positive values at lower alkoxyethanol mole fractions and negative values for the alkoxyethanol rich region. For the same mole fraction, the excess molar volume decreases as the alkyl chain length of the alkoxyethanol increases. This behaviour is similar to that obtained

Table 2
Parameters A_i and B_1 and standard deviations s for least-squares representations of excess molar volumes at 298.15 K and atmospheric pressure, by Eq. (1)

Toluene	A_0	A_1	A_2	B_1	s
2-methoxyethanol	0.6036	−0.1257	−0.2792	0.8817	0.0007
2-ethoxyethanol	0.3305	−0.4332	−0.3098	0.8749	0.0009
2-butoxyethanol	−0.0222	−0.6574	−0.2072	0.8772	0.0015

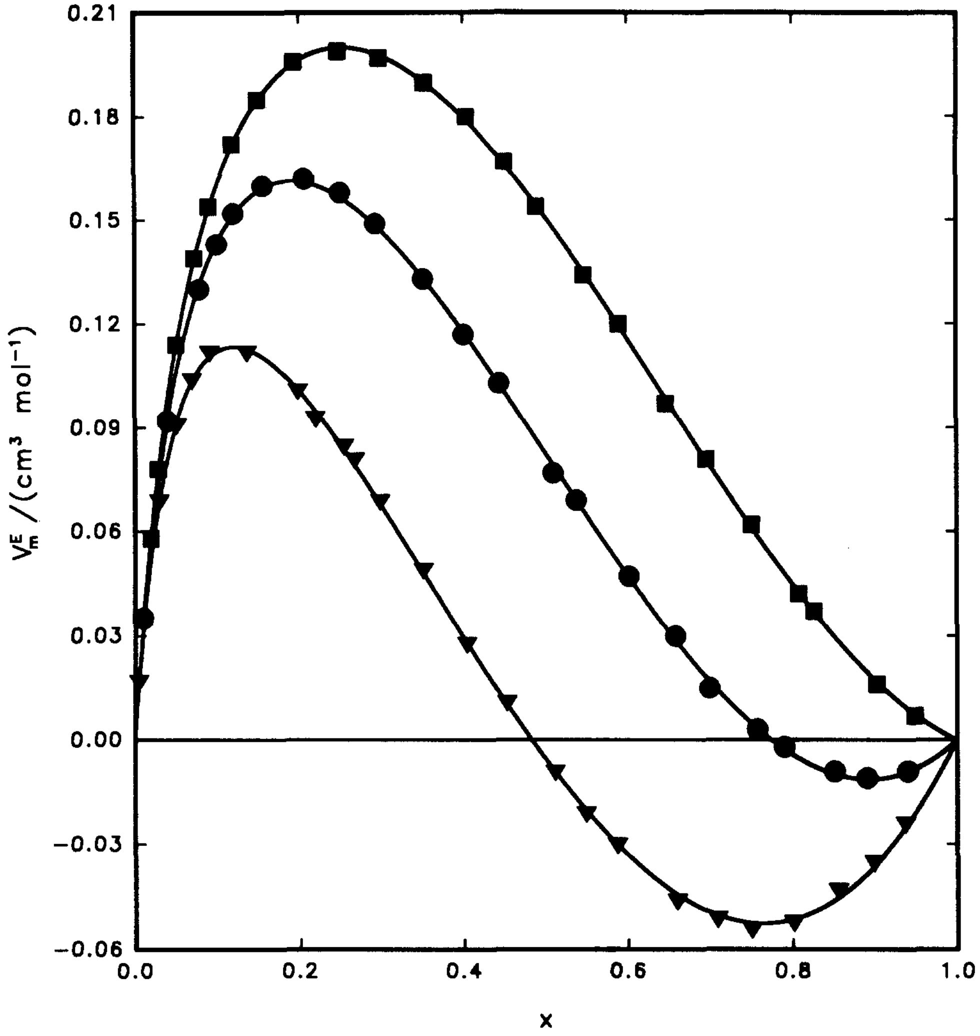

Fig. 1. Excess molar volume V^E against mole fraction x for *n*-alkoxyethanol + toluene at 298.15 K and atmospheric pressure: ■, 2-methoxyethanol; ●, 2-ethoxyethanol; ▼, 2-butoxyethanol. Solid lines represent the smoothing equation (1) with the parameters of Table 2.

by us with other alkoxyethanols of longer chain [14]. We show in Fig. 3 the smoothing curves corresponding to the V^E of the systems studied in this paper and those studied in ref. [14] for comparison.

The molecules of the alkoxyethanols are self-associated, like the alcohols. In fact, we observe similar characteristics in the mixtures formed with these liquids and toluene [25]: sigmoidal and asymmetric excess molar volumes skewed towards low alcohol

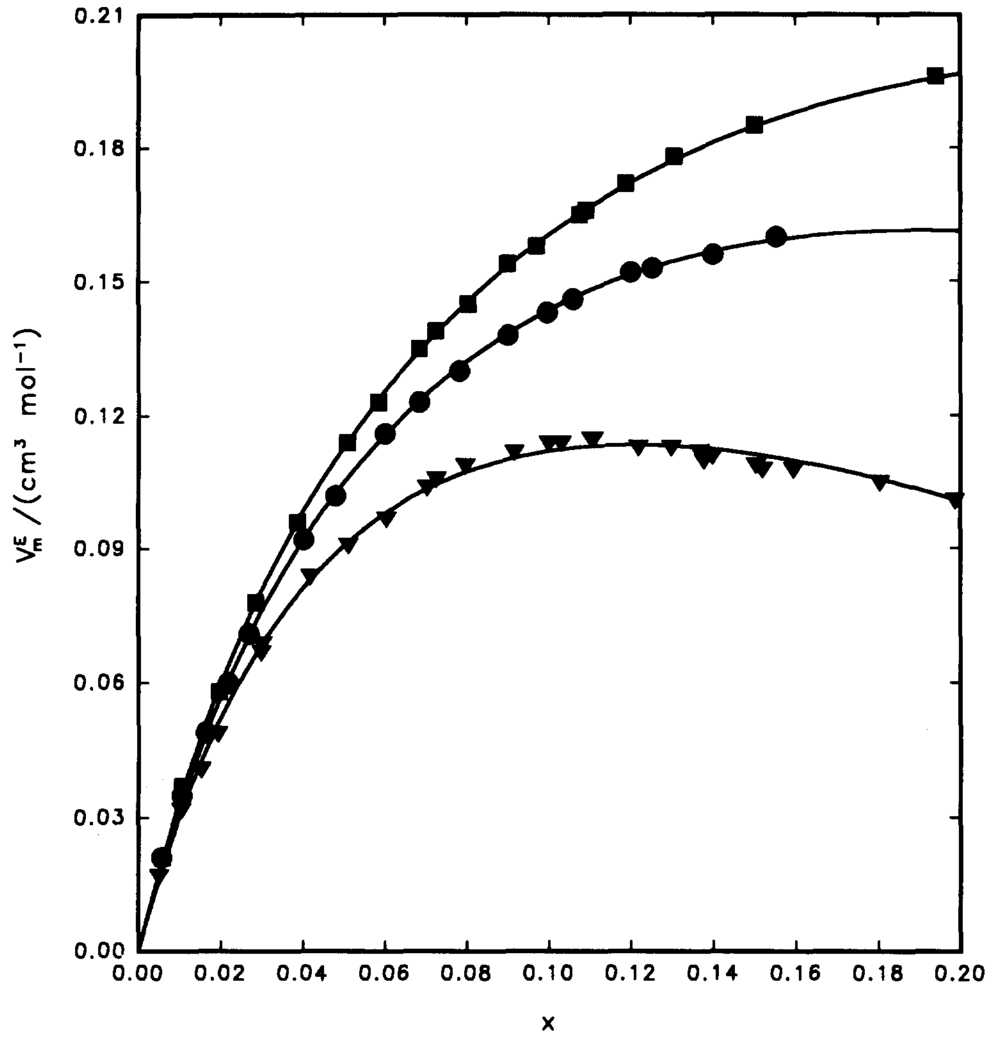

Fig. 2. Excess molar volume V^E against mole fraction $x < 0.2$ for *n*-alkoxyethanol + toluene at 298.15 K and atmospheric pressure: ■, 2-methoxyethanol; ●, 2-ethoxyethanol; ▼, 2-butoxyethanol. Solid lines represent the smoothing equation (1) with the parameters of Table 2.

mole fraction concentrations. Nevertheless, consideration must also be given to the possibility of intramolecular hydrogen bond formation in the alkoxyethanol molecules [26–28].

Using Eq. (1) and the parameters of Table 2, we have calculated the excess molar partial volumes at infinite dilution of the three alkoxyethanols in toluene. We obtained $V_1^{E,\infty} = 3.8\,\mathrm{cm^3\,mol^{-1}}$ for 2-methoxyethanol, $V_1^{E,\infty} = 3.6\,\mathrm{cm^3\,mol^{-1}}$ for 2-ethoxyethanol, and $V_1^{E,\infty} = 3.5\,\mathrm{cm^3\,mol^{-1}}$ for 2-butoxyethanol.

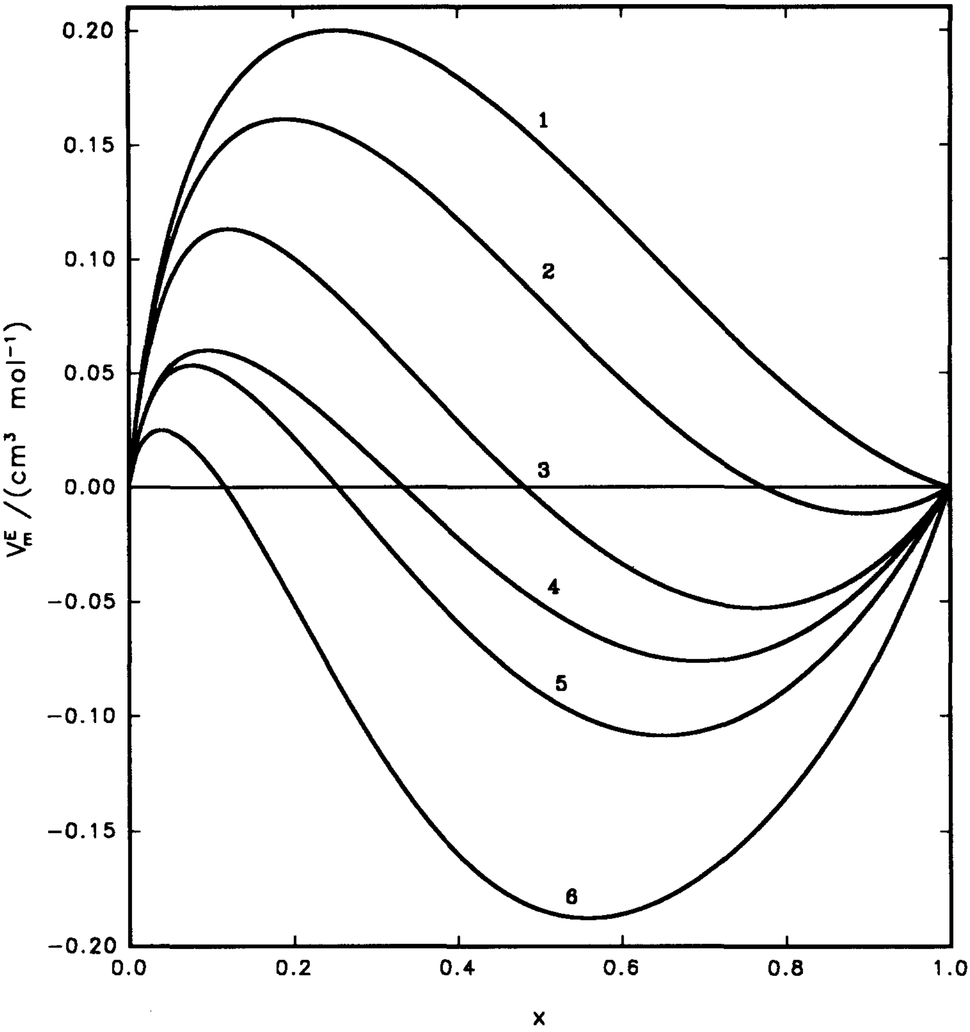

Fig. 3. Excess molar volume V^E agianst mole fraction x for n-alkoxyethanol + toluene at 298.15 K and atmospheric pressure: (1), 2-methoxyethanol; (2), 2-ethoxyethanol; (3), 2-butoxyethanol; (4), 2-(2-methoxyethoxy)ethanol [14]; (5), 2-(2-ethoxyethoxy)ethanol [14]; (6), 2-(2-butoxyethoxy)ethanol [14].

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