

Analysis and interpretation of excess molar properties of amphiphile + water systems

Part 3. Excess molar volumes of isopropoxyethanol + water and isobutoxyethanol + water

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Abstract

Excess molar volumes at 25°C, are reported for the systems isoPrOEtOH + water and isoBuOEtOH + water across their entire composition ranges. These data have been compared to those for their normal alkyl analogs in order to assess the effects of both α - and β -chain branching.

The results are discussed in terms of the relative abilities of the amphiphiles to form structured aggregates.

INTRODUCTION

In an earlier article [1], we described some significant differences between the excess molar volumes and excess molar enthalpies of the 1-propanol + water and 2-propanol + water systems. Excess molar volumes for the propoxyethanol + water [2] and butoxyethanol + water [3–5] systems are available in the literature.

We thought that it would be interesting to see if the same type of difference encountered in the excess molar volumes of the two isomeric propanol + water mixtures is also evident in the two isomeric 2-propoxyethanol + water systems. We also wished to establish whether a similar situation exists for the excess molar volumes of butoxyethanol + water and isobutoxyethanol + water.

The densities of isopropoxyethanol + water and isobutoxyethanol + water have been measured at 25°C. This article describes our findings and discusses their probable implications.

EXPERIMENTAL

Materials

Samples of isopropoxyethanol and isobutoxyethanol were obtained from Tokyo Kasei Chemical Corporation. The claimed purities were 99% and 98%

TABLE 1

Excess molar volumes of isopropoxyethanol + water at 25 °C ($\text{cm}^3 \text{mol}^{-1}$)

X_A	V^E	X_A	V^E	X_A	V^E
0.00000	0.0000	0.05456	-0.5393	0.3007	-1.2161
0.00585	-0.0544	0.05708	-0.5553	0.3262	-1.2311
0.00804	-0.0752	0.0575	-0.5588	0.3317	-1.2340
0.01190	-0.1127	0.0641	-0.6097	0.3735	-1.2388
0.01634	-0.1592	0.0720	-0.6628	0.3770	-1.2416
0.01680	-0.1628	0.0753	-0.6851	0.4474	-1.2107
0.01987	-0.1952	0.0848	-0.7361	0.5668	-1.0384
0.02268	-0.2237	0.0925	-0.7802	0.6164	-0.9243
0.02660	-0.2643	0.1040	-0.8348	0.6384	-0.8716
0.02865	-0.2876	0.1163	-0.8793	0.6670	-0.8302
0.03233	-0.3242	0.1358	-0.9493	0.6790	-0.7923
0.03523	-0.3535	0.1464	-0.9844	0.7334	-0.6913
0.03901	-0.3932	0.1766	-1.0521	0.7724	-0.6140
0.04171	-0.4168	0.1956	-1.0924	0.8088	-0.5223
0.04342	-0.4339	0.2257	-1.1487	0.8384	-0.4318
0.04678	-0.4667	0.2563	-1.1822	0.9056	-0.2447
0.04977	-0.4938	0.2673	-1.2057	0.9463	-0.1640
0.05217	-0.5146	0.2886	-1.2068	1.0000	0.0000

respectively. The materials were used directly from the manufacturers containers without further purification. The densities of the pure substances were found to be $0.89942 \text{ g cm}^{-3}$ for isopropoxyethanol and $0.88711 \text{ g cm}^{-3}$ for isobutoxyethanol.

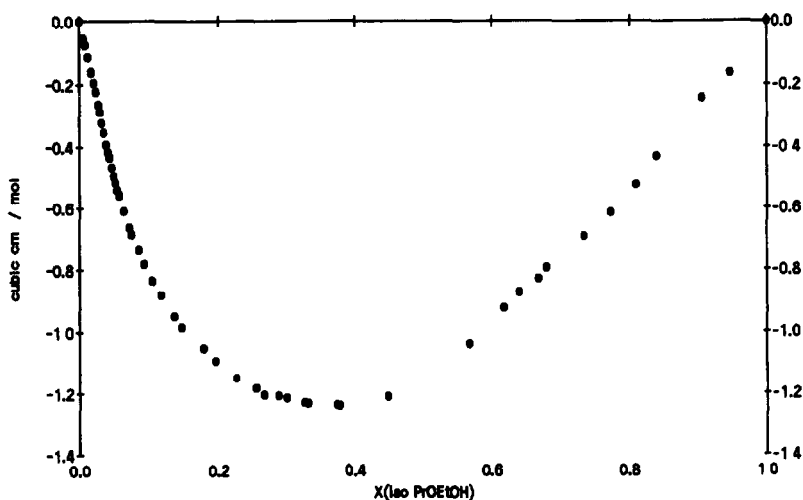


Fig. 1. Excess molar volumes of isopropoxyethanol + water at 25 °C ($\text{cm}^3 \text{mol}^{-1}$).

Aqueous mixtures were prepared by weight, using distilled–deionized water.

Densimetry

The densities of isopropoxyethanol + water and isobutoxyethanol + water mixtures were measured using a SODEV Model 03-D high precision flow densimeter [6]. The temperature was maintained at $25.00 \pm 0.02^\circ\text{C}$ by

TABLE 2

Excess molar volumes of isobutoxyethanol at 25°C ($\text{cm}^3 \text{mol}^{-1}$)

X_A	V^E	X_A	V^E	X_A	V^E
0.00000	0.0000	0.03366	-0.2446	0.1761	-0.6126
0.00038	-0.0035	0.0353	-0.2628	0.2260	-0.6909
0.00042	-0.0040	0.0368	-0.2762	0.2382	-0.6996
0.00056	-0.0053	0.0377	-0.2691	0.2424	-0.7075
0.00063	-0.0058	0.0379	-0.2781	0.2937	-0.7544
0.00073	-0.0071	0.0424	-0.2871	0.3396	-0.7775
0.00074	-0.0070	0.0425	-0.2860	0.4113	-0.7883
0.00096	-0.0092	0.0447	-0.2936	0.4256	-0.7935
0.00101	-0.0095	0.0466	-0.2987	0.4580	-0.7946
0.00118	-0.0114	0.0493	-0.3070	0.4586	-0.7794
0.00126	-0.0122	0.0515	-0.3211	0.4850	-0.7646
0.00275	-0.0279	0.0524	-0.3149	0.5126	-0.7544
0.00279	-0.0280	0.0569	-0.3236	0.5167	-0.7500
0.00286	-0.0290	0.0610	-0.3400	0.5565	-0.7127
0.00324	-0.0330	0.0649	-0.3532	0.5865	-0.6916
0.00327	-0.0332	0.0669	-0.3552	0.6955	-0.5480
0.00340	-0.0346	0.0669	-0.3561	0.7272	-0.5028
0.00354	-0.0361	0.0671	-0.3615	0.7421	-0.4866
0.00390	-0.0398	0.0703	-0.3681	0.7464	-0.4748
0.00397	-0.0405	0.0703	-0.3610	0.7754	-0.4255
0.00442	-0.0454	0.0740	-0.3784	0.7912	-0.4045
0.00467	-0.0480	0.0787	-0.3914	0.8000	-0.3708
0.00497	-0.0511	0.0824	-0.4014	0.8392	-0.3130
0.00533	-0.0553	0.0847	-0.4162	0.8478	-0.2807
0.00820	-0.0837	0.0922	-0.4313	0.8538	-0.2861
0.01002	-0.1080	0.1022	-0.4436	0.8946	-0.2012
0.01438	-0.1534	0.1107	-0.4664	0.8960	-0.2049
0.01920	-0.1962	0.1119	-0.4755	0.9154	-0.1716
0.01962	-0.1999	0.1210	-0.4984	0.9305	-0.1525
0.01968	-0.1868	0.1396	-0.5383	0.9386	-0.1236
0.01983	-0.1902	0.1417	-0.5374	0.9511	-0.0900
0.02465	-0.2254	0.1425	-0.5457	0.9792	-0.0361
0.02848	-0.2330	0.1484	-0.5560	0.9936	-0.0194
0.03060	-0.2552	0.1739	-0.6202	1.0000	0.0000

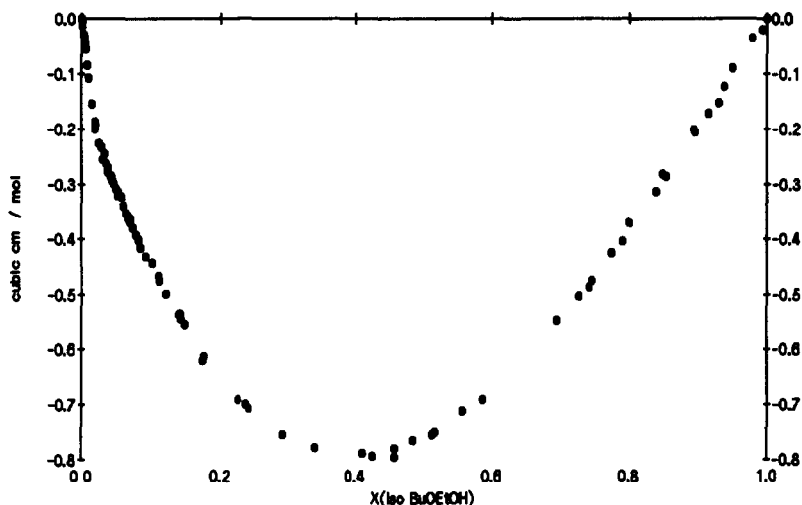


Fig. 2 Excess molar volumes of isobutoxyethanol + water at 25°C ($\text{cm}^3 \text{mol}^{-1}$)

means of a SODEV Model CT-L programmable circulating thermostat. The density values were converted to excess molar volumes.

RESULTS

The excess molar volumes of isopropoxyethanol + water mixtures are given in Table 1. The data are shown graphically in Fig. 1.

The excess molar volumes of isobutoxyethanol + water mixtures are given in Table 2. The data are shown graphically in Fig. 2.

DISCUSSION

Our interest is not so much with the individual excess molar property data sets as with the comparisons that can be made between them and those for other closely related systems. In ref. 1, a comparison was made between the excess molar volumes of 1-PrOH + water and 2-PrOH + water. Certain significant differences were found in that instance and it is obviously of some interest to see if such differences also exist between propoxyethanol + water and isopropoxyethanol + water. The relevant data are shown in Fig. 3. The curves shown are cubic splines fits to the original data. The 1-PrOH + water data are taken from ref. 7. The 2-PrOH + water data is from ref. 1 and the PrOEtOH + water data from ref. 2.

We have chosen to concentrate on the water-rich region of the data curves, as it is here that the differences between the four data sets show up most clearly. There are two major trends to be discerned. The excess molar volumes of the iso species are more negative than their normal counterparts.

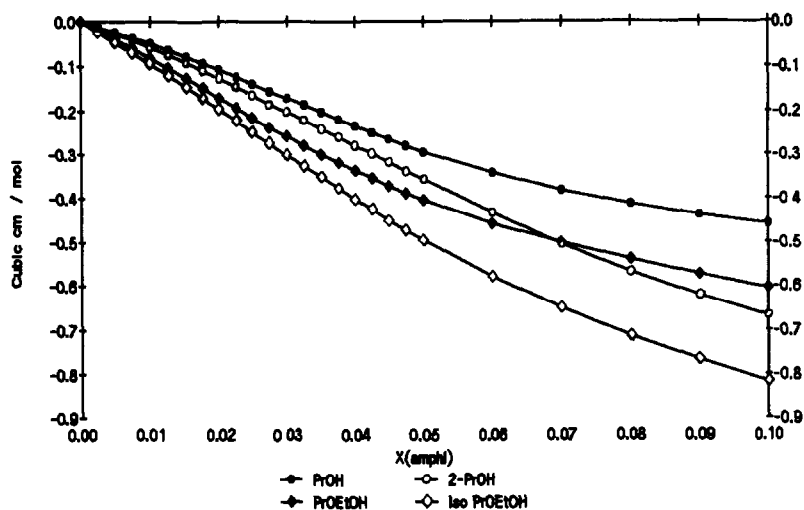


Fig. 3 Comparison of the excess molar volumes of 1-PrOH + water (●); 2-PrOH + water (○); PrOEtOH + water (◆); and isoPrOEtOH + water (◇) at 25 °C ($\text{cm}^3 \text{mol}^{-1}$)

Addition of an (OC_2H_4) group leads to a more negative set of excess molar volumes. In addition, the change in the slope (dV^E/dX_A) in the vicinity of $X_A = 0.06$ appears to be more pronounced for the normal isomers of each pair.

Both *n*-butanol and isobutanol have miscibility gaps which range from $X_A \approx 0.018$ to $X_A \approx 0.5$. As a consequence, we cannot provide a C_4 analog to Fig. 3. What we can do is generate a comparison of PrOEtOH + water, isoPrOEtOH + water and their C_4 analogs. This is shown in Fig. 4. The cubic-splines-interpolated curve for BuOEtOH + water is derived from a combination of the data of refs. 3–5. The most striking feature of this Fig. is the strong similarity between the data profiles of the two butoxyethanol + water data curves, which is in sharp contrast to the differences between the two propoxyethanol + water curves. Evidently, branching of the alkyl chain at the β carbon has significantly less impact upon the composition dependence of the excess thermodynamic properties than does branching at the α carbon.

We note, in addition the crossover of the PrOEtOH + water and BuOEtOH + water curves. At low amphiphile mole fractions, the BuOEtOH + water excess molar volumes are the more negative. Put in simple terms, the addition of a CH_2 group introduces a negative group contribution to V^E . At higher amphiphile mole fractions, the BuOEtOH + water excess molar volumes are distinctly less negative.

SUMMARY

There are a number of simple conclusions that one may draw from consideration of Figs. 3 and 4. These concern the effects of different types of

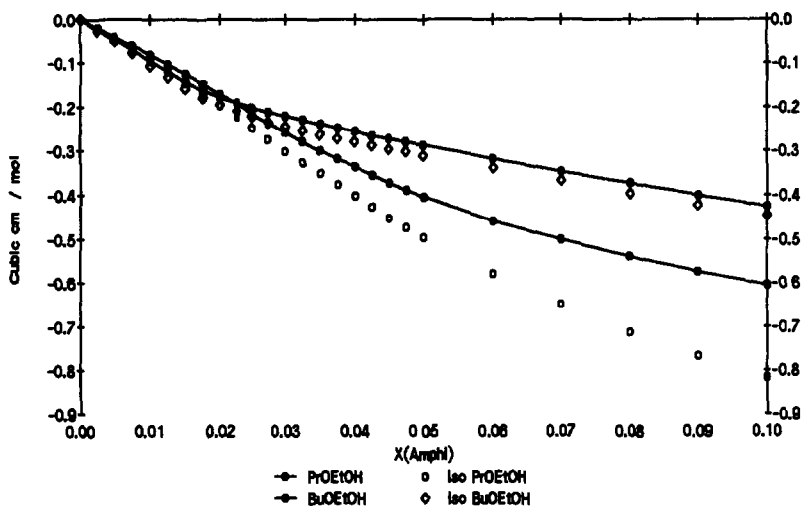


Fig 4 Comparison of the excess molar volumes of PrOEtOH + water (●), isoPrOEtOH + water (○); BuOEtOH + water (◆); and isoBuOEtOH + water (◇) at 25 °C ($\text{cm}^3 \text{mol}^{-1}$).

molecular structural modification of the amphiphile on the composition dependence of the thermodynamic properties of its aqueous mixtures.

There are three types of structural modification that may occur.

- (1) Extension of the alkyl chain for species with a common polar head group.
- (2) Enlargement of the polar head group, by the addition of an OC_2H_4 unit, for species with a common alkyl chain.
- (3) Branching of the alkyl chain among isomeric species.

For the amphiphiles with which we are concerned, there appear to be analogs of the critical micelle concentration (cmc). These occur at $X_A \approx 0.06$ for the C_3 species and at $X_A \approx 0.02$ for the C_4 species. These values are consistent with the formula for cmc values given by Digorgio for alkyl poly(ethylene glycol) monoether (C_mE_n) + water systems [8].

Below the cmc analogs, the excess molar volumes become progressively more negative with extension of the alkyl chain and addition of further OC_2H_4 groups. Branching of the alkyl chain also results in a decrease in the excess molar volumes.

Above the cmc analogs, extension of the alkyl chain leads to less negative excess molar volumes. Increasing the number of OC_2H_4 groups leads to more negative excess molar volumes. Branching of the alkyl chain at the α carbon, as in 2-PrOH and isoPrOEtOH, results in a substantial decrease in the excess molar volumes. Branching at the β carbon, as in isoBuOEtOH appears to have only a modest effect.

In a recent article [9], a rationale was given for identifying the composition range with greater amphiphile content than the cmc analog, as one in which there is a tendency for the amphiphilic species to form metastable

micelle-like aggregates. This is believed to account for the significant changes in the slope (dV^E/dX_A) in the vicinity of the cmc analogs. That those changes of slope are much less pronounced in the 2-propanol + water and isoPrOEtOH + water systems is taken as evidence that α branching is an impediment to ordered aggregation. No such impediment appears to result from β branching.

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