

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

## Part 2. Comparisons of the propanol isomers in their aqueous mixtures

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### Abstract

Measurements have been made at 25°C of the excess molar enthalpies of the 1-propanol + water system and of the densities of the 2-propanol + water system, across their entire respective composition ranges.

These data have been combined with others taken from the literature to provide a comparison between the excess molar properties of the two systems. Some fairly substantial differences are observed which indicate that, of the two isomers, 1-propanol is the more capable of forming structured aggregates.

### INTRODUCTION

In a number of previous articles (1–3), attention has been drawn to some of the interesting aspects of the composition dependence of the excess molar volumes of 1-propanol + water mixtures.

Of particular interest is the rather abrupt change in the slope  $dV^E/dX_A$ , where  $X_A$  is the mole fraction of amphiphile, at  $X_A = 0.06$ . This feature, at a somewhat lower mole fraction, had previously been noted in both the excess molar volumes and excess molar enthalpies of the 2-butoxyethanol + water system [4].

We were interested in ascertaining whether other thermodynamic features of the 1-propanol + water system resemble those of the 2-butoxyethanol + water system. We were also interested in comparing the excess molar properties of 1-propanol + water with those of 2-propanol + water.

We were unable to locate, in the literature, any adequate sets of excess molar enthalpies for the 1-propanol + water system at 25°C. Several sets of densities of 2-propanol + water mixtures at 25°C have been reported [5–7]. These data exhibit substantial mutual consistency for 2-propanol mole fractions up to 0.1. Beyond that point, they tend to be sparse and lack consistency.

We have measured the heats of mixing of 1-propanol and water across the entire range of compositions at relatively small mole fraction increments. We have also measured the densities of 2-propanol + water mixtures at 25 °C. It is evident that there are some significant differences between the excess properties of the two systems.

## EXPERIMENTAL

The 1-propanol used in this work was Baker Analysed Reagent Grade (99% +). The 2-propanol was Fisher HPLC grade. Both substances were taken directly from the manufacturers' containers and used without further purification. Mixtures were prepared by weight with distilled-deionized water.

### *Calorimetric*

The heats of mixing of 1-propanol + water were measured using a Parr solution calorimeter [8]. The procedures adopted have been described in ref. 4. Use was made of the heat capacity data of Benson et al. [9].

### *Densimetric*

The densities of 2-propanol + water mixtures at 25 °C were measured using a SODEV Model 03-D high-precision flow densimeter [10]. The temperature was maintained at  $25.00 \pm 0.02$  °C, by means of a SODEV Model CT-L programmable circulating thermostat.

The density of the 2-propanol sample was determined to be  $0.78069 \text{ g cm}^{-3}$ , which compares favorably with the literature values of 0.7807 [5] and 0.78062 [6]. Density values of the mixtures were converted to excess molar volumes.

## RESULTS

The excess molar enthalpy values for 1-propanol + water are given in Table 1. A plot of these data against the 1-propanol mole fraction is shown in Fig. 1.

The excess molar volumes of 2-propanol + water at 25 °C are given in Table 2. A plot of these data against the 2-propanol mole fraction is shown in Fig. 2.

## DISCUSSION

There is a striking difference between the profiles of the excess molar volumes for the two propanol + water mixtures, as is evident in Fig. 3. The data for the 1-propanol + water system were taken from ref. 11.

TABLE 1

Excess molar enthalpies of 1-propanol + water at 25 °C (J mol<sup>-1</sup>)

$X(1\text{-PrOH})$	$H^E$	$X(1\text{-PrOH})$	$H^E$	$X(1\text{-PrOH})$	$H^E$
0	0	0.0531	-385.89	0.5008	148.32
0.00134	-12.35	0.0534	-385.13	0.5062	149.45
0.00245	-23.97	0.0541	-385.56	0.5083	156.25
0.00393	-38.97	0.0549	-390.03	0.5159	159.78
0.00504	-50.64	0.056	-391.06	0.522	161.14
0.00614	-60	0.0561	-391.67	0.5264	174.31
0.00736	-73.3	0.0563	-391.5	0.5345	172.34
0.00854	-83.14	0.0575	-392.94	0.5474	183.2
0.01	-100.1	0.0583	-396.49	0.5537	188.73
0.0111	-109.45	0.0588	-395.97	0.5664	193.22
0.0122	-122.18	0.0589	-395.7	0.5733	196.38
0.0134	-130.27	0.0594	-395.51	0.5792	194.15
0.0145	-144.74	0.0598	-398.1	0.5864	202
0.0158	-152.98	0.061	-396.7	0.5864	202.63
0.0171	-164.33	0.0613	-398.44	0.5959	205.23
0.0181	-173.67	0.0623	-398.54	0.6023	207.8
0.0192	-183.5	0.0638	-399.71	0.6105	210.47
0.0204	-192.75	0.067	-401.8	0.6193	208.3
0.0215	-202.43	0.0778	-396.37	0.6255	212.62
0.0226	-216.23	0.0906	-385.18	0.6371	213.74
0.024	-223.14	0.1027	-371.8	0.6596	211.59
0.0251	-230.61	0.1147	-361.32	0.6726	215.94
0.026	-237.84	0.1209	-346.62	0.6769	216.01
0.0272	-252.76	0.1335	-328.52	0.6877	212.8
0.0285	-257.48	0.1434	-316.51	0.6964	212.85
0.0298	-273.41	0.1613	-289.8	0.7111	211.01
0.0305	-275.91	0.1713	-273.68	0.7297	201.83
0.0323	-284.53	0.1831	-252.46	0.7442	202.36
0.0326	-286.53	0.1959	236.52	0.7571	198.5
0.0343	-305.59	0.2064	-223.4	0.7709	186
0.03524	-302.15	0.2247	-194.77	0.7824	182.84
0.0361	-308.49	0.2446	-152.52	0.7964	170.01
0.0373	-319.15	0.2596	-133.39	0.8104	153.12
0.0391	-323.49	0.2877	-88.12	0.8251	147.65
0.0401	-329.12	0.3091	-57.57	0.8422	128.19
0.041	-335.8	0.31	-69.29	0.8558	114.94
0.0419	-345.99	0.3382	-25.24	0.8711	101.28
0.0432	-346.42	0.3687	15.5	0.8868	85.19
0.0443	-356.04	0.404	57.7	0.9033	65.85
0.0458	-358.44	0.4543	120.67	0.9249	46.43
0.047	-362.7	0.4759	134.2	0.9414	34.9
0.0483	-368.42	0.4784	131.62	0.9583	21.79
0.0493	-371.47	0.4835	139.75	0.9764	10
0.0502	-374.06	0.4887	143.89	1	0
0.0519	-378.09	0.4942	146.85		

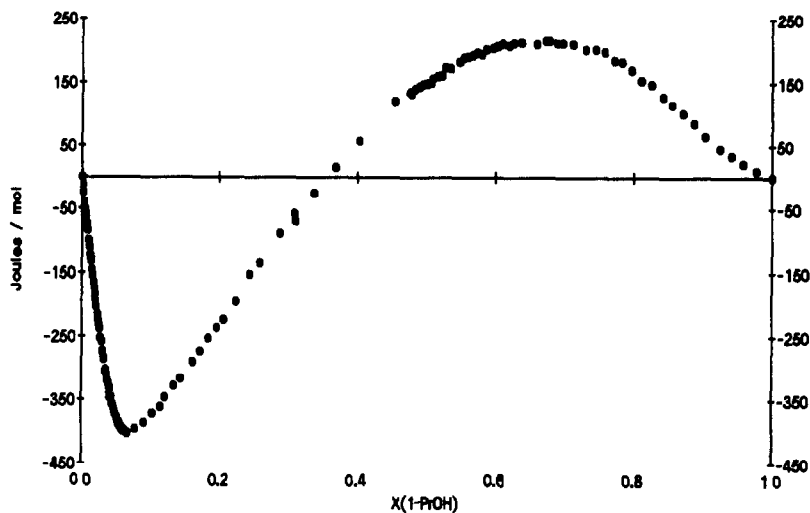


Fig. 1. Excess molar enthalpies of 1-propanol + water at 25°C ( $\text{J mol}^{-1}$ ).

The excess molar volume values shown in Fig. 3 were obtained by cubic splines interpolation of the original data sets. One notes that the rather abrupt change in slope for the 1-propanol + water mixtures at  $X(\text{PrOH}) = 0.06$ , is considerably diminished in the 2-propanol + water mixtures.

There are strong similarities between the excess molar enthalpies of the two systems, each having the same general S-shaped profile when plotted against mole fraction. There are, however, some interesting differences

TABLE 2

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

$X(2\text{-PrOH})$	$V^E$	$X(2\text{-PrOH})$	$V^E$	$X(2\text{-PrOH})$	$V^E$
0	0.0000	0.0841	-0.5902	0.6137	-0.8286
0.0015	-0.0082	0.0996	-0.6634	0.6695	-0.7521
0.0029	-0.0161	0.1138	-0.7234	0.7194	-0.6774
0.0071	-0.0396	0.163	-0.8379	0.7546	-0.6210
0.0115	-0.0664	0.1954	-0.8936	0.8012	-0.5287
0.0206	-0.1321	0.2468	-0.9508	0.8448	-0.4384
0.0273	-0.1829	0.3029	-0.9842	0.8799	-0.3510
0.035	-0.2416	0.3387	-0.9911	0.9101	-0.2806
0.0399	-0.2789	0.3906	-0.9925	0.9508	-0.1730
0.041	-0.2875	0.4263	-0.9818	0.9643	-0.1190
0.0542	-0.3825	0.4613	-0.9637	0.9808	-0.0669
0.0669	-0.4857	0.5351	-0.9113	1	0.0000
0.0803	-0.5755	0.5661	-0.8819		

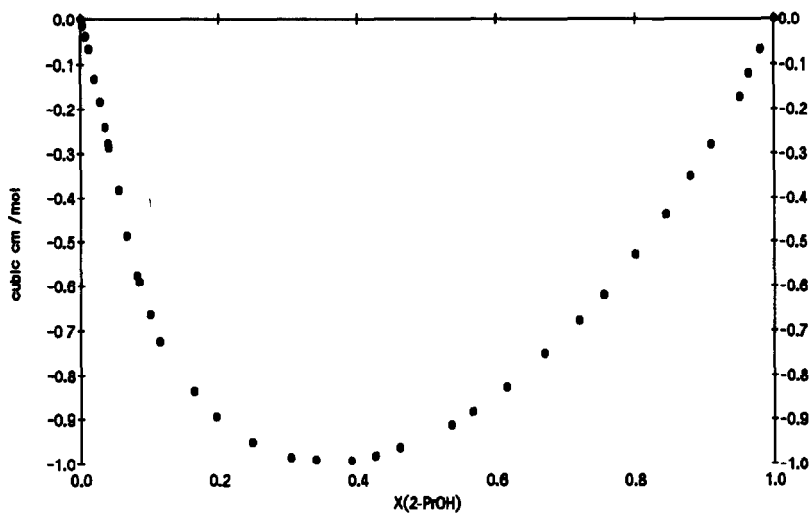


Fig. 2. Excess molar volumes of 2-propanol + water at 25°C ( $\text{cm}^3 \text{mol}^{-1}$ ).

between the two data sets at low amphiphile mole fractions. The two data sets are compared in Fig. 4. The 2-propanol + water data were taken from ref. 12. A few additional measurements for water-rich mixtures were made in this laboratory.

Here again, the sharpness of the change in slope is more pronounced in the 1-propanol + water system than in 2-propanol + water. Sharp changes in the nature of the composition dependence of the physical properties of

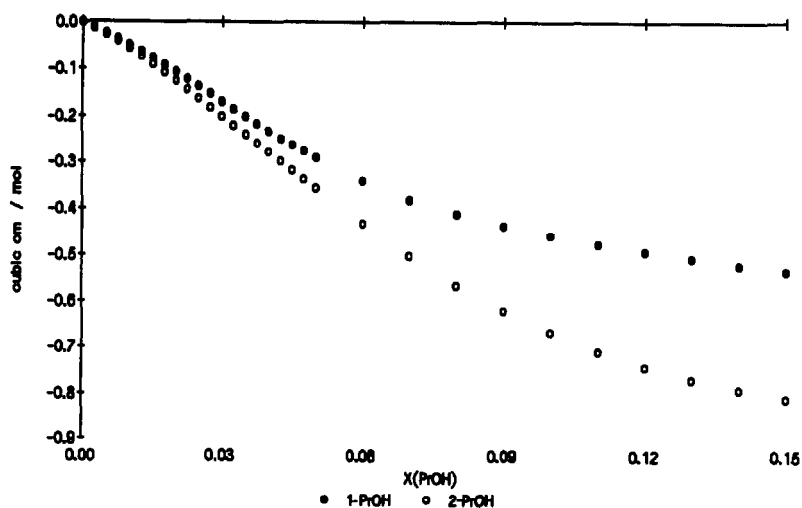


Fig. 3. Comparison of the excess molar volumes of water-rich mixtures of the propanol + water systems at 25°C ( $\text{cm}^3 \text{mol}^{-1}$ ).

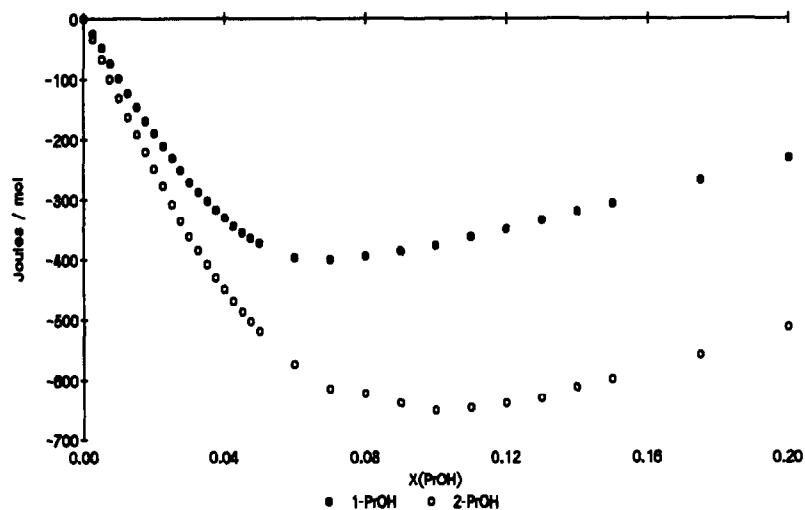


Fig. 4 Comparison of the excess molar enthalpies of water-rich mixtures of the propanol + water systems at 25 °C ( $\text{J mol}^{-1}$ )

binary systems are thought to result from, and therefore act as indicators of, a high concentration sensitivity of the pattern of molecular aggregation. One property that has been singled out as an indicator of the formation of micellar or metastable micelle-like aggregates is the apparent molar heat capacity. In Fig. 5, the excess apparent molar heat capacities of the two systems are shown. The 1-propanol + water values were calculated from the data of ref. 9; those for 2-propanol + water were taken from ref. 7.

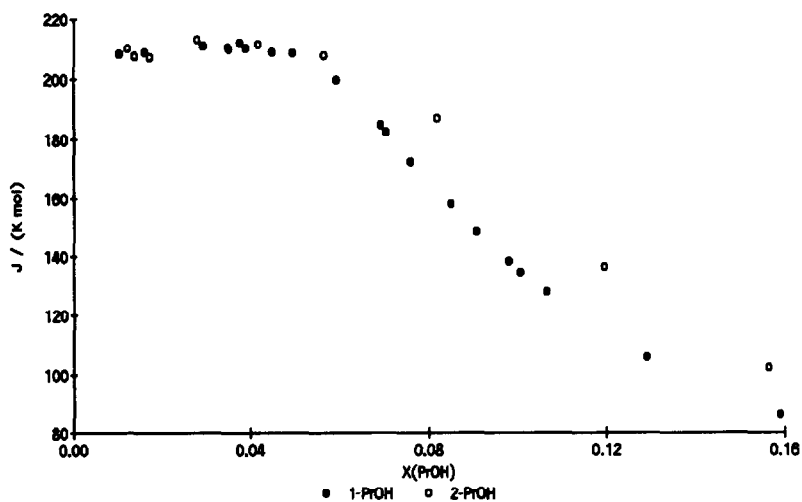


Fig. 5 Comparison of the excess apparent molar isobaric heat capacities of the propanol isomers in their water-rich aqueous mixtures at 25 °C ( $\text{J K}^{-1} \text{mol}^{-1}$ ).

A sharp break in the slope of the apparent excess molar heat capacities is characteristic of surfactant + water systems and has frequently been cited as evidence for the formation of micelle-like aggregates in the aqueous mixtures of smaller amphiphiles. The two systems appear to have virtually identical excess heat capacities in the propanol mole-fraction range 0–0.06. The change in slope above  $X_A = 0.06$  is seen to be greater in the 1-propanol + water system.

High composition sensitivity of thermodynamic properties is regarded as evidence of substantial variations in the nature of the molecular aggregation. In detergent + water systems, significant variations in the composition derivatives of thermodynamic properties occur at the critical micelle concentration. Figures 3–5 appear to indicate that such tendencies as the propanols have to form metastable micelle-like aggregates are more marked in the primary alkanol than in the secondary.

An empirical formula has been derived for the dependence of the critical micelle concentrations of *n*-alkyl poly(ethylene glycol) monoether on alkyl chain length [13]. Since the critical micelle concentrations (cmc) are independent of the number of  $\text{OC}_2\text{H}_4$  units in the polar head, one may extrapolate to the case of alkanols:

$$\log_{10}[\text{cmc}(n)] = 2 - n/2$$

where the [cmc] is the molality and *n* is the number of carbon atoms in the alkyl chain.

For *n* = 4, the cmc occurs at 1 M, which is equivalent to a mole fraction of the order of 0.018. This is very close to the sharp breaks in the apparent molar heat capacities of the butoxyethanol + water [14] and butoxyethoxyethanol + water [15] systems. For *n* = 3, if a cmc were to exist it would be at 3.0 M, a mole fraction of roughly 0.055.

#### SUMMARY

Both of the propanol isomers appear to qualify for the term “borderline surfactant”, by virtue of the fairly sharp changes in the mole fraction derivatives of their thermodynamic properties at concentrations which are cmc analogs. If this change in slope is taken to be indicative of significant changes in the pattern of molecular aggregation, the data indicate that the 1-propanol aggregates are more highly structured than those of 2-propanol. This may well be explained by the branching of the alkyl chain at the  $\alpha$ -carbon atom, in 2-propanol, constituting an impediment to ordered micelle-like aggregation.

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