

Excess molar enthalpies of 2-propanol + water at 25°C

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Abstract

Excess molar enthalpies have been measured for the system 2-propanol + water at 25°C. The values obtained have been compared with those reported in the literature.

Differences in the composition dependence of the excess molar enthalpies of the aqueous mixtures of 1- and 2-propanol are discussed and compared to the results obtained for other thermodynamic properties of those two systems.

Keywords: Enthalpies; Mixtures; Propanol; Water

1. Introduction

A few years ago, we published the results of some measurements of the heats of mixing of 1-propanol and water at 25°C [1]. As a part of our continuing interest in exploring the effects of alkyl chain branching upon the thermodynamic properties of amphiphile + water mixtures [2, 3], we have measured the heats of mixing of 2-propanol and water at 25°C. There have been a number of reported sets of measurements [4–6]. There is a displeasing inconsistency among those sets of values reported for 25°C. They are also all quite sparse in the water-rich region and therefore somewhat less informative than one would wish.

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2. Experimental

The 2-propanol used was spectroscopic grade, purchased from Aldrich Chemical Corporation. It was used from freshly opened containers without any attempts at further purification. The water was distilled and deionized. Mixtures were prepared by weight, their mole fractions being generally reliable to within 10^{-4} .

The heat of mixing measurements were made using a Parr solution calorimeter [7]. The operating procedures that we adopted have been described in an earlier publication [8]. The molar heat capacities, which were essential for the interpretation of the calorimetric output, were taken from Ref. [9].

3. Results

The results of our measurements are set out in Table 1. Our values have been plotted, together with those given in Refs. [4–6], in Fig. 1. It is interesting to note that our

Table 1
Excess molar enthalpies of 2-propanol + water at 25°C (in J mol⁻¹)

X_{PrOH}	H^E	X_{PrOH}	H^E	X_{PrOH}	H^E
0.00000	0.0	0.07630	-668.2	0.4249	-86.0
0.00488	-62.5	0.08024	-668.7	0.4256	-76.4
0.00938	-119.8	0.08534	-675.3	0.4358	-56.5
0.01191	-151.5	0.08719	-670.8	0.4380	-59.8
0.01407	-182.1	0.08880	-685.7	0.4543	-26.8
0.01648	-212.3	0.09750	-679.6	0.4724	4.1
0.01863	-236.7	0.09964	-679.6	0.5062	41.2
0.02073	-263.6	0.1110	-673.9	0.5129	51.5
0.02283	-290.1	0.1236	-659.7	0.5300	87.2
0.02683	-333.9	0.1651	-563.6	0.5322	91.9
0.02921	-364.8	0.1830	-532.7	0.5769	138.5
0.03163	-387.7	0.2159	-487.5	0.6224	194.6
0.03384	-410.5	0.2333	-452.5	0.6413	205.9
0.03603	-437.6	0.2564	-411.0	0.6583	214.0
0.03814	-451.6	0.2734	-380.5	0.6760	218.5
0.04029	-478.0	0.3010	-322.4	0.6980	237.8
0.04192	-493.3	0.3332	-260.6	0.7419	236.2
0.05533	-587.8	0.3417	-240.3	0.7678	225.6
0.05710	-596.2	0.3485	-228.2	0.7958	223.5
0.05908	-604.9	0.3559	-217.7	0.8230	211.4
0.06376	-621.4	0.3660	-200.8	0.8524	191.9
0.06580	-633.8	0.3696	-189.0	0.9199	117.3
0.06646	-641.6	0.3820	-162.6	0.9590	68.1
0.07239	-660.2	0.3872	-157.9	1.0000	0.0
0.07436	-658.6	0.3904	-141.3		
0.07579	-661.3	0.4229	-91.0		

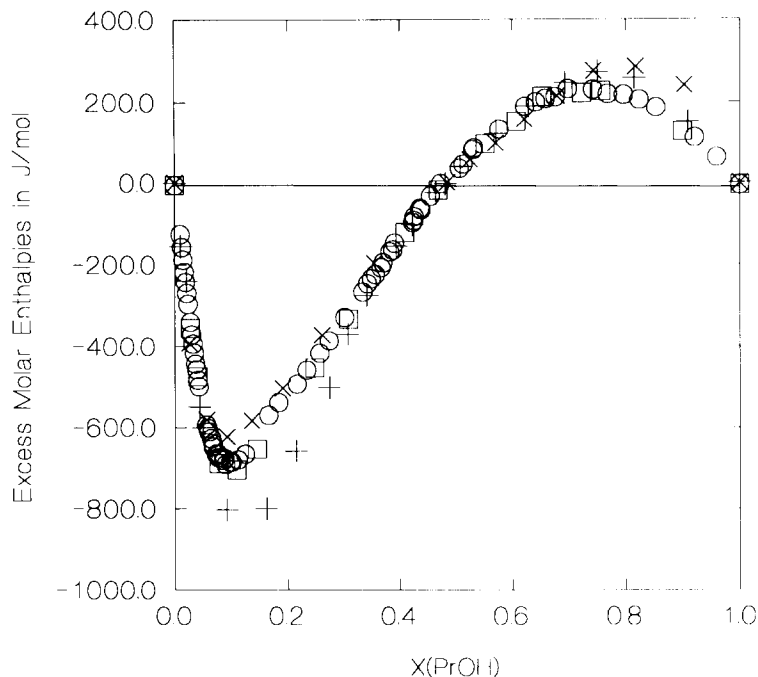


Fig. 1. Excess molar enthalpies of 2-propanol + water mixtures at 25°C in J mol^{-1} : \circ , this work; \square , Ref. [4]; $+$, Ref. [5]; \times , Ref. [6].

results are quite consistent with those given in Ref. [4], but they are substantially different from the more recent data of Refs. [5] and [6], which are also seen to be highly inconsistent with each other.

In Fig. 2, we compare our results for 2-PrOH + water with those published earlier for 1-PrOH + water [1]. There are a number of interesting features to Fig. 2. The mixing process is strongly exothermic at low propanol mole fractions for both systems. The partial (and apparent) excess molar enthalpy of 2-propanol at infinite aqueous dilution ($-13.3 \text{ kJ mol}^{-1}$) is substantially more exothermic than that of 1-propanol ($-10.1 \text{ kJ mol}^{-1}$). Of the two isomers, the 2-propanol value more closely follows the arithmetic sequence of the values for methanol (-7.3 kJ mol^{-1}) and ethanol ($-10.3 \text{ kJ mol}^{-1}$).

Both systems display endothermic mixing at the propanol-rich end. The partial excess molar enthalpy of water at infinite dilution in 2-propanol is estimated to be (1.7 kJ mol^{-1}) and appears to be substantially more endothermic than it is in 1-propanol (0.3 kJ mol^{-1}). The values for methanol and ethanol have been estimated to be -2.9 and -2.0 kJ mol^{-1} respectively.

Fig. 3 shows estimates of the derivative function dH^E/dX_A (where X_A is the alkanol mole fraction) for the two systems. These estimates were made by the implementation

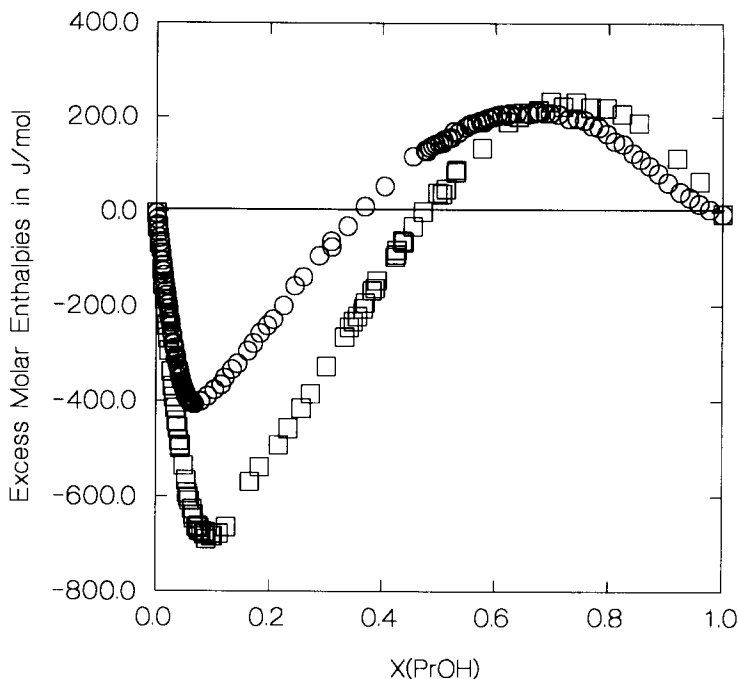


Fig. 2. Excess molar enthalpies of the aqueous mixtures of the propanol isomers in J mol^{-1} : \square , this work for 2-PrOH + water; \circ , the results for 1-PrOH.

of a modified cubic splines procedure. Both sets of data exhibit very sharp increases over the mole fraction range 0–0.1. Both curves then flatten out quite precipitously and stay reasonably constant before undergoing a fairly substantial and roughly linear descent. The two curves are strikingly different at the extreme alkanol-rich end. The dH^E/dX_A curve for 2-propanol is essentially linear above $X_A = 0.4$, all the way to the pure propanol. That for 1-propanol shows a totally different curvature above $X_A = 0.8$.

Fig. 4 shows the partial excess molar enthalpies of water at low alkanol mole fractions. As in Fig. 3, we see precipitous changes of slope at fairly low propanol mole fraction. What is evident from this figure is that the change occurs at a significantly lower alkanol mole fraction in the case of 1-propanol than in that of its isomer. The partial excess molar enthalpies of water in alkanol-rich mixtures show (Fig. 5) remarkably different composition dependences for the two systems.

4. Discussion

There are a number of features of the 2-propanol + water excess molar enthalpy data that seem to be worthy of comment. The excess apparent (and partial) molar

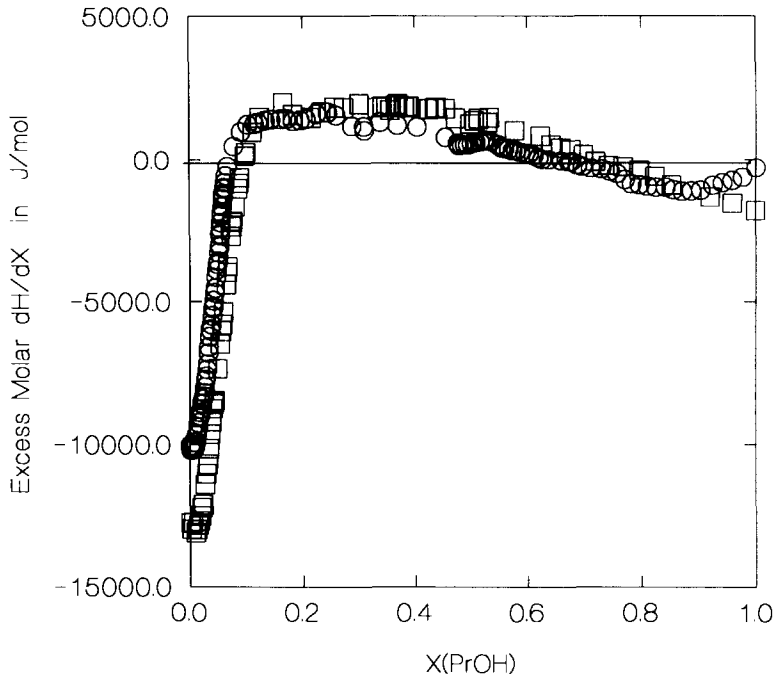


Fig. 3. Excess molar dH^E/dX_A for propanol + water mixtures. Units and symbols as for Fig. 2.

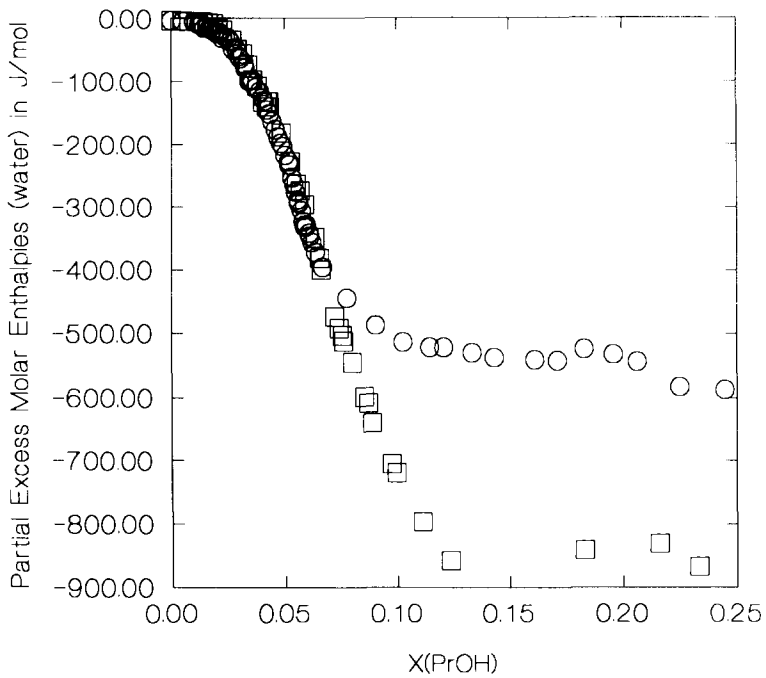


Fig. 4. Excess partial molar enthalpies of water in water-rich propanol + water mixtures. Units and symbols as for Fig. 2.

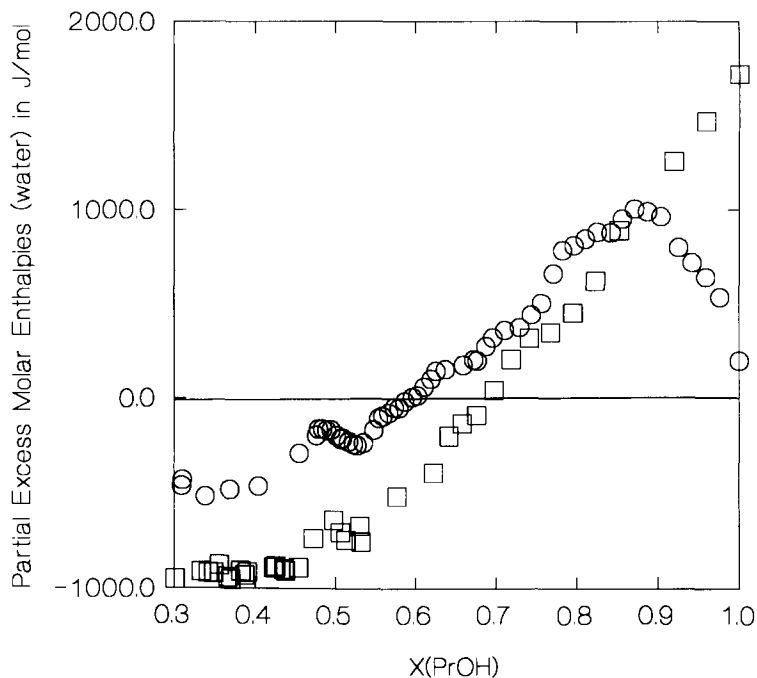


Fig. 5. Excess partial molar enthalpies of water in propanol-rich propanol + water mixtures. Units and symbols as for Fig. 2.

enthalpy of the 2-propanol at infinite aqueous dilution is the enthalpy change when one mole of the propanol molecules is transferred from their pure liquid environment to a totally aqueous environment. We might consider this process as being made up of two parts: vaporization and hydration. The enthalpies of vaporization at 25°C are given as 47.3 and 45.5 kJ mol⁻¹ for 1-PrOH and 2-PrOH respectively [10]. That would give rise to values for the molar enthalpies of hydration of -57.4 and -58.8 kJ mol⁻¹ respectively.

The sharp breaks in the slopes of the partial excess molar enthalpy of water curves indicate the onsets of some new type of alkanol aggregation at those concentrations. Plots of the partial excess molar volumes of water in the propanol + water systems are shown in Fig. 6. The volumetric data for 1-PrOH + water and 2-PrOH + water were taken from Refs. [11] and [12] respectively. There is seen to be a fairly sharp change of slope in the data for 1-PrOH + water at a mole fraction close to that of the pronounced change of slope in the partial excess enthalpy data. There is an obvious inflexion point in the 2-PrOH + water data but no precipitous change of slope. The partial excess molar isobaric heat capacities of water, for water-rich propanol + water mixtures, are shown in Fig. 7. The values for 1-PrOH + water were derived from the data of

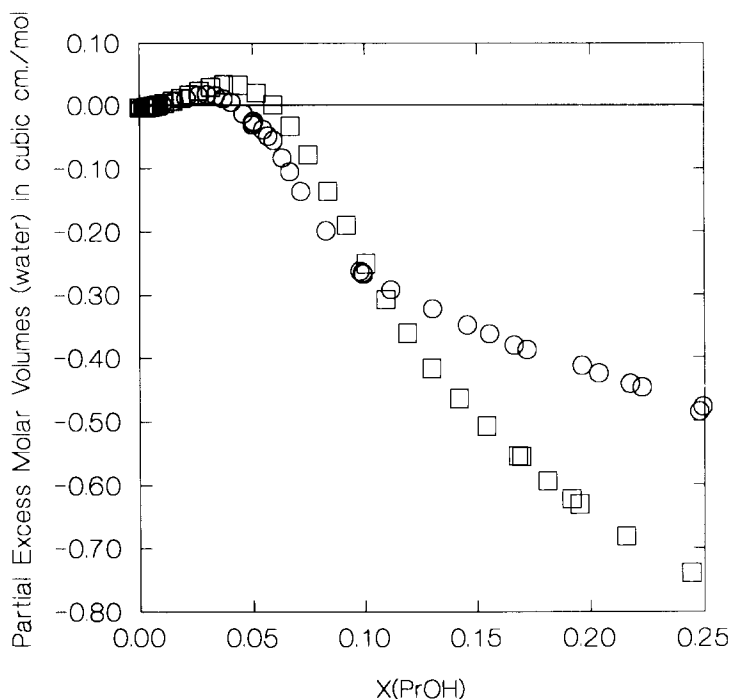


Fig. 6. Excess partial molar volumes of water in water-rich propanol + water mixtures. Units, $\text{cm}^3 \text{mol}^{-1}$, symbols as for Fig. 2.

Ref. [13]; those for 2-PrOH + water from Ref. [9]. Here, there are precipitous changes of slope below a propanol mole fraction of 0.05 for both systems. For the 1-PrOH + water system, there is a further sharp change of slope, just below a mole fraction of 0.1 and also one for the 2-PrOH + water system at a somewhat higher propanol mole fraction.

The partial excess molar isentropic compressibilities of water in the water-rich propanol + water systems are shown in Fig. 8. The values for 1-PrOH + water were taken from Ref. [14], those for 2-PrOH + water from Ref. [3]. Again, there are pronounced changes of slope at about the same compositions as for the other partial excess properties, with that for 1-propanol again occurring at the lower alkanol mole fraction.

The differences between the concentration dependence of the excess molar enthalpies of the two systems, at high propanol mole fraction, do not find analogs among the other properties but are presumed to be real. This is probably a reflection of differences between the nature of the patterns of aggregation of the two pure liquids.

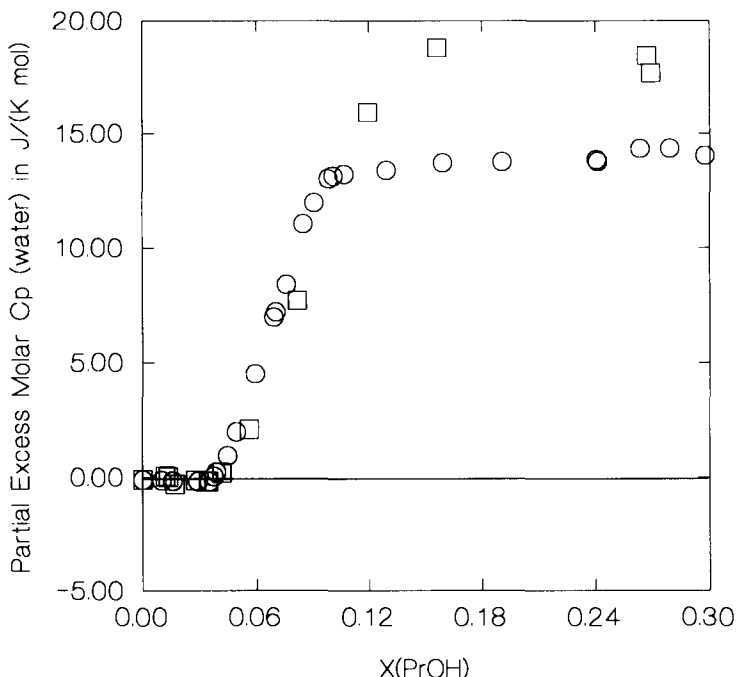


Fig. 7. Excess partial molar isobaric heat capacities of water in water-rich propanol + water mixtures. Units, $\text{J K}^{-1} \text{mol}^{-1}$, symbols as for Fig. 2.

5. Summary

Excess molar enthalpies have been measured for the 2-propanol + water system at 25°C . The results agree well with the much sparser data of Ref. [4]. They disagree significantly with the mutually inconsistent results of Refs. [5] and [6].

Like the 1-propanol + water system, sharp changes are observed in the composition dependence of the thermodynamic properties of 2-propanol + water at mole fractions between 0.05 and 0.1. These are very nicely shown in the partial excess molar enthalpies of the two systems. Similar abrupt changes of slope in plots of excess partial molar properties against mole fraction are found for volumes, heat capacities and isentropic compressibilities. Such abrupt changes are reminiscent of the changes in the thermodynamic property composition dependence that are found in the neighborhood of the critical micelle concentration of detergent + water systems. While thermodynamic studies cannot identify the nature of patterns of molecular aggregation, they do give clear indications of changes from one scheme to another.

An intriguing difference in the partial excess molar enthalpies of water in propanol-rich mixtures invites speculation about the possible differences in the structures of the two pure liquids and how they might incorporate solute water.

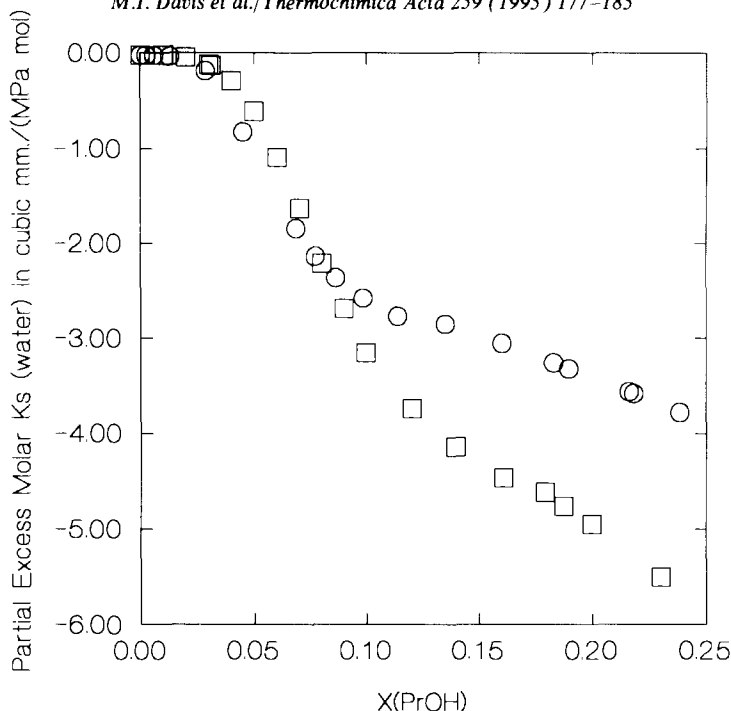


Fig. 8. Excess partial molar isentropic compressibilities of water in water-rich propanol + water mixtures. Units, $\text{mm}^3 \text{MPa}^{-1} \text{mol}^{-1}$, symbols as for Fig. 2.

Acknowledgements

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