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The Excess Enthalpies and Volumes of Mixing of Methanol with Octan-2-ol

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Abstract

The functions H^E and V^E have been measured at 303.15 K for the mixtures of methanol with (±), (+) and (−) octan-2-ol. As expected, it is found that the excess functions are identical for the optical isomers, within experimental error. The volume of mixing of the (+) and (−) isomers is also found to be equal to zero.

The present work is the last in a series of investigations on liquid mixtures, initiated over 30 years ago in this laboratory by *C.G. Boissonnas*. We wish to present the results for the system methanol + octan-2-ol, obtained with the modified equipment described previously [1].

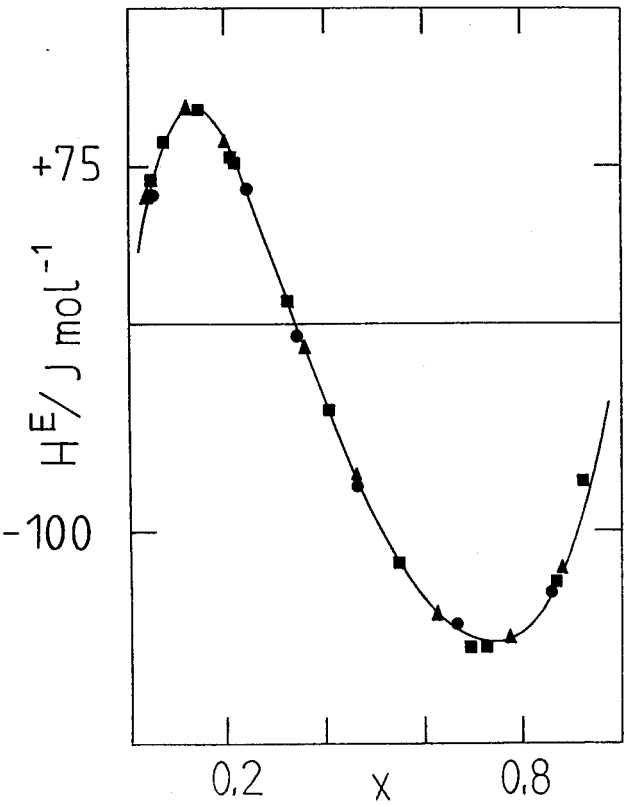

Fig. 1: Excess enthalpies of (±), (+) and (−) octan-2-ol with methanol at 30°C (●, ■ and ▲ respectively). Mole fraction × corresponds to octan-2-ol.

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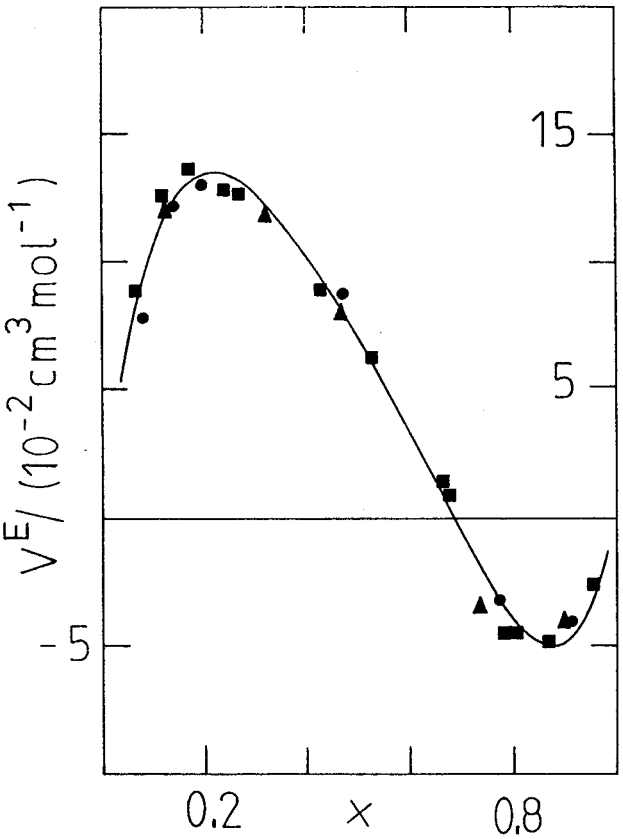

Fig. 2: Excess volumes of (±), (+) and (−) octan-2-ol with methanol at 30°C (●, ■ and ▲ respectively). Mole fraction × corresponds to octan-2-ol.

The results, shown in fig. 1 and 2, are interesting in view of the fact that V^E and H^E change sign as the mole fraction of octan-2-ol increases. This is in contrast with the work of *Benson* et al. [2] who showed that in the case of methanol + n-octanol, at 25°C, both excess functions were positive. The difference between the two types of isomers, normal octanol and octan-2-ol, appears in the region of smaller concentrations in methanol. As suggested by the data found in the litterature, the excess volumes V^E for the mixtures of n-alcohols are mostly positive [2, 3], and the enthalpies seem to be exclusively positive [4]. The present results, and in particular H^E, clearly show a positional effect of the −OH group in the two octanols.

As usual [1, 4], the experimental data shown in the figures were fitted to expressions of the type

$$H^E \text{ or } V^E = x(1-x)\sum_{n=0}^{3} A_n(1-2x)^n \qquad (1)$$

The corresponding values of the parameters A_n are given in table 1. Since the mixtures of methanol with (±), (+) and (−) octan-2-ol showed no differences between them, only the parameters for the overall fits are given.

As expected, it was also found that within experimental error V^E was equal to zero for the mixture of (+) and (−) octan-2-ol.

Table 1: Parameters A_n and standard deviations for the overall fits to eqn (1)

Function	V^E	H^E
t/°C	30	30
A_0	0.2811	− 381.5
A_1	0.6812	933.5
A_2	0.0439	536.2
A_3	0.6036	745.9
σ	0.006	4.1
Units	($cm^3\ mol^{-1}$)	($J\ mol^{-1}$)

Materials:

Methanol, (±), (+) and (−) octan-2-ol of "puriss" grade (> 99,5 %) were supplied by Fluka AG, Switzerland. Each liquid was dried over "Sikkon" for 24 hours, redistilled and outgassed prior to use.

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