

## Properties of Binary Mixtures of Alcohols Interpreted Using the Homomorph Concept

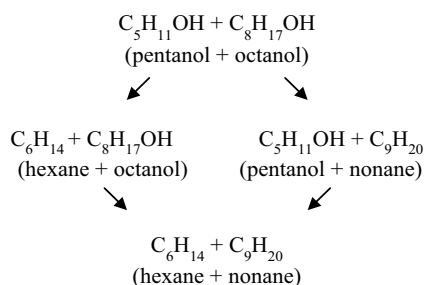
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Beside thermodynamic investigations, acoustic studies provide very useful information about the structure and intermolecular interactions in liquids. One of the most significant quantities which can be determined directly using speed of sound and density values, is the isentropic compressibility  $\kappa_S = (\rho c^2)^{-1}$ . Moreover, the isentropic compression,  $K_S = V\kappa_S$ , and its excess,  $K_S^E = K_S - K_S^{\text{id}}$ , make the knowledge of the properties of binary mixtures more complete. Detailed methods of the calculation of  $K_S^E$  can be found in the literature [1,2]. However, in the case of mixtures containing two associating components (e.g. alcohols), the molecular interactions are rather complex and the calculation and interpretation of the excess isentropic compressibility need a sophisticated mathematical procedure.

The homomorph concept [3-6] allows to determine the contributions of the processes taking place during the mixing of two alcohols to the excess isentropic compressibility. Generally, homomorphs of alcohols are compounds of similar molecular structure, but unable to associate by hydrogen bondings. In this work, alkanes were chosen as homomorphs of alcohols, *i.e.* compounds in that the hydroxyl group -OH of a particular alcohol is replaced by the methyl group -CH<sub>3</sub>. Thus, hexane is considered as the homomorph of pentanol and nonane as the homomorph of octanol. The usefulness of the homomorph concept was checked examining the pentanol + octanol system. The following diagram depicts the sequence of the mixtures studied:



The excess isentropic compression of the pentanol + octanol mixture and of the mixtures containing homomorphs are shown in Figs. 1 and 2.

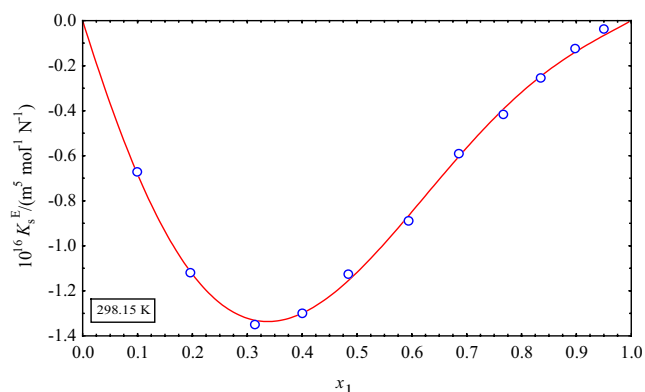


Fig. 1. Excess isentropic compression of the pentanol + octanol mixture; points - calculated from the speed of sound and density values [5]; lines - from a Redlich-Kister type polynomial

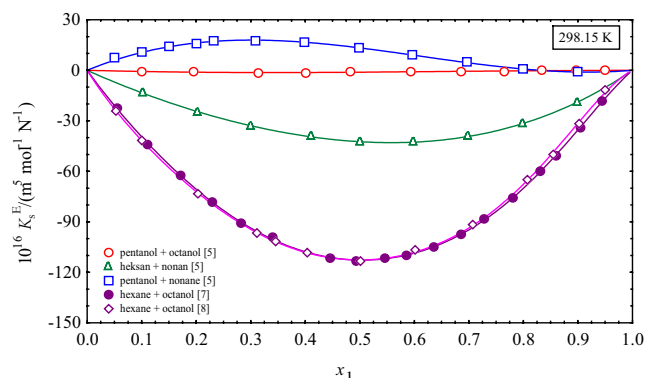


Fig. 2. Excess isentropic compression for the mixtures: pentanol + octanol, pentanol + nonane, hexane + nonane and hexane + octanol; points - calculated from the speed of sound and density values [5,7,8]; lines - from a Redlich-Kister type polynomial

It should be noticed that the  $K_S^E$  values of the pentanol + octanol mixture are significantly smaller than those of the mixtures containing homomorphs. In other words, the replacement of the alcohol by its homomorph causes significant changes in the  $K_S^E$  values.

A comparison of the excess isentropic compression of the binary alcohol mixture with those of the mixtures containing either one or two of the alcohol's homomorphs makes it possible to distinguish the contribution to  $K_S^E$  arising from the breaking of hydrogen bonds from that of hydrogen bond formations in the alcohol + alcohol system.

To obtain both contributions, the following procedure can be applied. According Brown and Fock [3], the excess of any molar quantity (like the excess isentropic compression) for the alcohol + alkane mixtures can be expressed as a sum of the term due to the breaking of hydrogen bonds of the alcohol during mixing with the alkane,  $X_{\text{chem}}^E$ , and that due to the mixing of the homomorph with the same solvent  $X_{\text{hom}}^E$ :

$$X^E(\text{alcohol} + \text{alkane}) = X_{\text{chem}}^E + X_{\text{hom}}^E$$

To separate the chemical contribution  $X_{\text{chem}}^E$  from the "homomorph" one, the  $X_{\text{hom}}^E$  term in latter formula should be rewritten as follows:

$$X_{\text{chem}}^E = X^E(\text{alcohol} + \text{alkane}) - X_{\text{hom}}^E$$

The subtraction of the two chemical contributions to the excess quantity,  $X_{\text{chem}}^E$ , (calculated for both the alcohol + alkane mixtures) from that of the alcohol + alcohol mixture results the contribution due to the formation of hydrogen bonds in the mixture. For the pentanol + octanol mixture, the procedure can be depicted by the following scheme:

$$X_x^E = X^E(\text{pentanol} + \text{octanol}) - X_{\text{chem}}^E(\text{pentanol} + \text{nonane}) - X_{\text{chem}}^E(\text{hexane} + \text{octanol})$$

The results of the subtraction for the excess of isentropic compression are shown in Fig. 3.

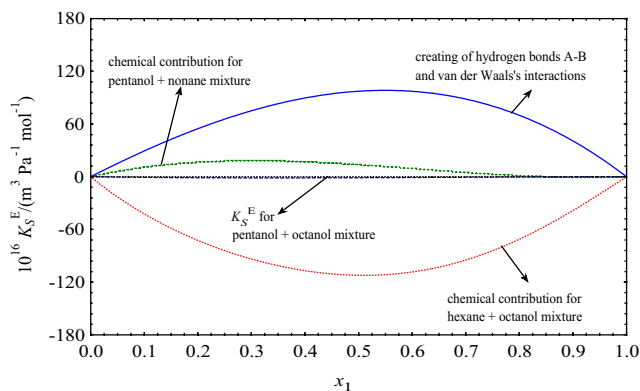


Fig 3. Contributions to the excess isentropic compression for the pentanol + octanol mixture obtained using the homomorph concept

The results obtained can be considered to be rather ambiguous. It is well known that the breaking of hydrogen bonds should increase the isentropic compression. Such increase is observed only for the pentanol + nonane mixture. Furthermore, despite the strengthening of the "net" of hydrogen bondings, the final effect of  $X_x^E$  due to creation the hydrogen bonds leads to large and positive values causing a significant increase in the isentropic compression.

It should be emphasized that for other thermodynamic molar quantities (for example, for the excess volumes and enthalpies) the application of the homomorph concept leads to results consistent

with our intuition [5]. It may be suggested a few reasons why the results obtained for the  $K_S^E$  are inconsistent with our general knowledge about the phenomena taking place during the mixing of two alcohols:

1) The excess isentropic compression is a very complex quantity; thus even for pure liquids, the interpretation of  $K_S^E$  is very difficult and consequently the results obtained for solutions are somewhat ambiguous.

2) The contribution due to the creation of hydrogen bonds calculated using the homomorph concept probably includes an additional term arising from the van der Waals' interactions.

Although the results obtained for excess isentropic compressibility are rather ambiguous, the presented method of determining the contributions to the excess quantities are undoubtedly still open to further improvements. Such an improvement can be most probably achieved by using ethers as homomorphs instead of alkanes [9].

Literature:

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