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HEAT CAPACITIES FOR BINARY MIXTURES OF (ALCOHOL + NON-POLAR LIQUID) AT 298.15 K

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The heat capacities for the binary mixtures of (n-$C_nH_{2n+1}OH$ + n-C_7H_{16}) for n=1-6, and (n-C_4H_9OH + C_6H_6) have been determined at 298.15 K. A sharp and high peak appears in the partial molar heat capacities of alcohol, $C_{p,1}$, in the heptane solution at a high dilution of alcohol. The values $C^{\infty}_{p,1}$ at the infinite dilution and $C^{*}_{p,1}$ at the pure state change linearly with n of alcohol. The results are related to the self-association of alcohol in the mixture.

The properties of the liquid mixtures containing alcohol as a component have been studied by various methods,[1,2] and those mixtures are classified as a strongly associated solution due to the hydrogen-bond of alcohol. In this paper, we report the results of the heat capacity measurements for the binary mixtures of (n-$C_nH_{2n+1}OH$ + heptane) for n=1-6, and (n-C_4H_9OH + benzene) at 298.15 K carried out by using a Picker flow calorimeter. The test and the operational procedures for this apparatus are detailed in the previous report.[3] The obtained values for volumetric heat capacities (C_p/V), i.e. the heat capacity divided by the volume of the mixture, were converted to the molar heat capacities $C_{p,m}$ by using the densities of the mixture. The molar excess heat capacities $C^E_{p,m}$ were calculated by the equation,

$$C^E_{p,m} = C_{p,m} - xC^{*}_{p,1} - (1-x)C^{*}_{p,2} \tag{1}$$

where the subscripts 1 and 2 represent alcohol and non-polar liquid, respectively, and $C^{*}_{p,i}$ represents the molar heat capacity for the pure component i. The partial molar heat capacities of alcohol $C_{p,1}$ were calculated from the coefficients for the equation fitted to the experimental points for $C^E_{p,m}$ by a least squares method. The partial molar heat capacities of alcohol at the infinite dilution, $C^{\infty}_{p,1}$ were determined from an extrapolation of the apparent molar heat capacities, $C_{p,\phi,1}$ by a least squares method.

The heat capacity of the associated solutions may be attributed essentially to the heat absorbed in the system to shift the distribution of species from a lower to a higher state in energy when the temperature is increased.[4] In this respect, the heat capacity reflects the thermal relaxation of the associated species in such a class of mixtures. The experimental results of $C_{p,1}$ for 1-butanol in both the heptane and the benzene mixtures are shown in Fig. 1. It is surprising that the value of $C_{p,1}$ is kept nearly constant from that in the pure state, $C^{*}_{p,1}$ to $x \simeq 0.1$

and it increases steeply to the peak at $x \simeq 0.008$. Since the curve of $C_{p,1}$ for the other alcohols in the heptane mixtures are very similar to that of 1-butanol, those are not shown in the figure. We believe this interesting phenomenon implies that the strongly polymerized alcohols are hardly dissociated by the addition of heptane to a considerably dilute concentration. This speculation is supported by the remarkable difference between the results of $C_{p,1}$ in the mixture of heptane and of benzene. Since alcohols are stabilized with benzene due to the OH•••π interactions the associated alcohols are easy to break in the mixture with benzene. Therefore, the value of $C_{p,1}$ begins to increase at a higher composition x with an addition of benzene, and the peak is much lower than in the heptane mixture.

The values $C^*_{p,1}$ and $C^\infty_{p,1}$ are plotted against the carbon number n of alcohol in Fig. 2. Those two values approach closer each other with smaller n, and become to be the same at n=1 within the experimental uncertainty. The strict linearities found in those plots confirms that the values $C^*_{p,1}$ and $C^\infty_{p,1}$ in heptane are divided into the contributions from the methylene and hydroxyl groups. Except for the mixtures with methanol and ethanol the sign of $C^E_{p,m}$ changes to negative below $x \simeq 0.003$. In those compositions most of the self-associated alcohols are dissociated into the monomeric ones so that $C^E_{p,m}$ becomes negative as has been also reported recently by Bhattacharyya et al.$^{5)}$

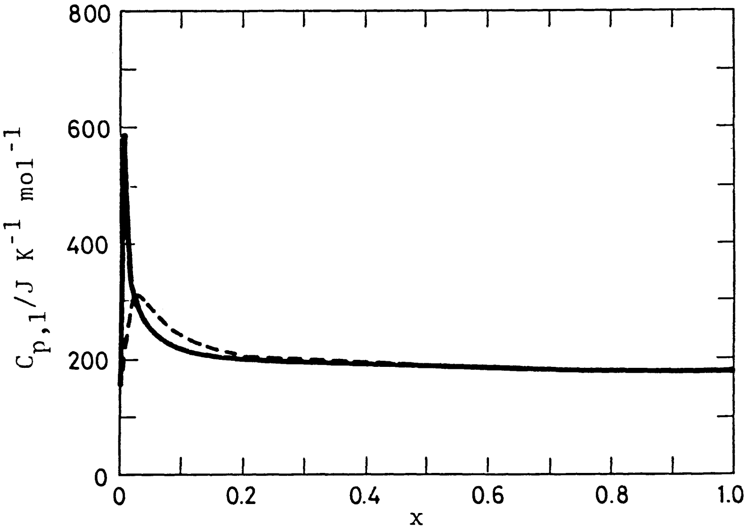

Fig. 1. Partial molar heat capacities of C_4H_9OH in $\{xC_4H_9OH + (1-x)\text{non-polar liquid}\}$ at 298.15 K. ——, in n-heptane. – – –, in benzene.

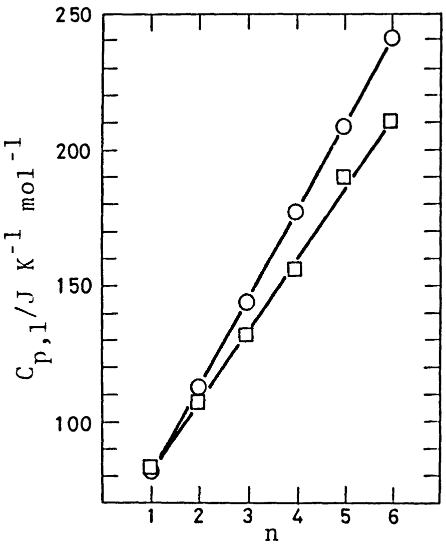

Fig. 2. Partial molar heat capacities of $C_nH_{2n+1}OH$ in the mixture of n-heptane at 298.15 K: □, at the infinite dilution; ○, at the pure state.

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