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THE SELF-ASSOCIATION OF ETHANOL IN NON-POLAR SOLVENTS

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ABSTRACT

The self-association of ethanol in solutions of n-hexane, cyclopentane, cyclohexane, carbon tetrachloride and benzene is studied on the basis of heat of dilution data published in the literature. The tetramer formation model fits the experimental data better than other self-association models. The corresponding self-association constants, $K_{1,4}$, and heats of reaction, $\Delta H^{\circ}_{1,4}$, are calculated. The solvent effect is studied using the solvent polarity factor, E_T, and the existence of a linear dependance of log $K_{1,4}$ on E_T values is shown.

1. INTRODUCTION

Organic molecules containing hydroxyl groups tend to self-associate. The degree of self-association depends on the nature of the molecules and of the medium where the self-association takes place. In the case of primary alcohols, various methods have been used to determine the structure of the alcohol associates and the corresponding stability constants. On the basis of heat of mixing and IR data Van Ness et al.[1] proposed a model of self-association consisting of monomers, dimers and linear polymers with 20 or more monomeric units. IR measurements performed by Fletcher and co-workers[2–4] offer another association model with monomer and tetramer, with no other species existing in amounts sufficient to affect the mass balance equation. Calorimetric measurements by Anderson et al.[5] as well as the works cited in their paper, strongly support the monomer–tetramer model. From the literature data[1–5] it can be concluded that the model consisting of two dominant species, monomer and tetramer, could be ascribed to the self-association process of primary alcohols.

According to available data, the role of the length of alkyl radicals of alcohol molecules on the self-association process is not definitely established. Fletcher[4] concludes that the order of alcohols' self-association is octanol > butanol > ethanol-d_1 > methanol, in contrast to Anderson's data[5] which does not show any general

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trend for the self-association of the alcohols proceeding from ethanol to octanol in isooctane. The measurements of the enthalpies of dilution of ethanol in non-polar solvents, carried out by Stokes and Burfitt[6] and Stokes and Adamson[7], do not contribute to the explanation of the self-association process of ethanol.

The aim of this paper is to determine the self-association constant of ethanol using the literature data on the enthalpies of dilution of ethanol in non-polar solvents [6, 7], and the data on excess volumes of ethanol in non-polar solvents[8], and to study the influence of the type of solvent upon the self-association equilibria.

2. EXPERIMENTAL

Experimental details of the data used in this work are given in the literature[6-8]. We are pleased to point out that we have dealt with experimental data of high precision and accuracy.

3. RESULTS AND DISCUSSION

The self-association equilibrium of an alcohol (P) has been considered by a general equation

$$nP \rightleftharpoons P_n \qquad (1)$$

and the equilibrium constant expression

$$K_{1,n} = \frac{[P_n]}{[P]^n} \qquad (2)$$

The brackets denote molar concentration and n is the number of monomeric units. In order to relate the equilibrium constant, given by eqn. (2), with the calorimetric measurements of the self-association process given by eqn. (1), the value Φ_L has been introduced[9]

$$\Phi_L = \frac{\Delta H^\circ_{1,n}}{n} - \frac{1}{n}\,[\Delta H^\circ_{1,n}]^{n-1}\left[\frac{1}{K_{1,n}}\right]^{1/n}\left[\frac{\Phi_L}{M^{n-1}}\right]^{1/n} \qquad (3)$$

Here, Φ_L is defined as the negative enthalpy of dilution of one mole of ethanol from a solution of a given molarity to infinite dilution[9], $\Delta H^\circ_{1,n}$ represents the standard enthalpy of the self-association process given by eqn. (1), while M denotes the molar concentration of ethanol. The precise data on the enthalpies of dilution of ethanol[6, 7] have enabled the extrapolation of Φ_L at infinite dilution with great accuracy. The data on densities of studied binary mixtures, needed for conversion of Φ_L values from mole fraction to mole l^{-1} concentration scale, were taken from volumetric properties of the same systems[8].

Equations (2) and (3) hold if one assumes that the measured heats of dilution (with negative sign) are only the consequence of the process represented by eqn. (1)

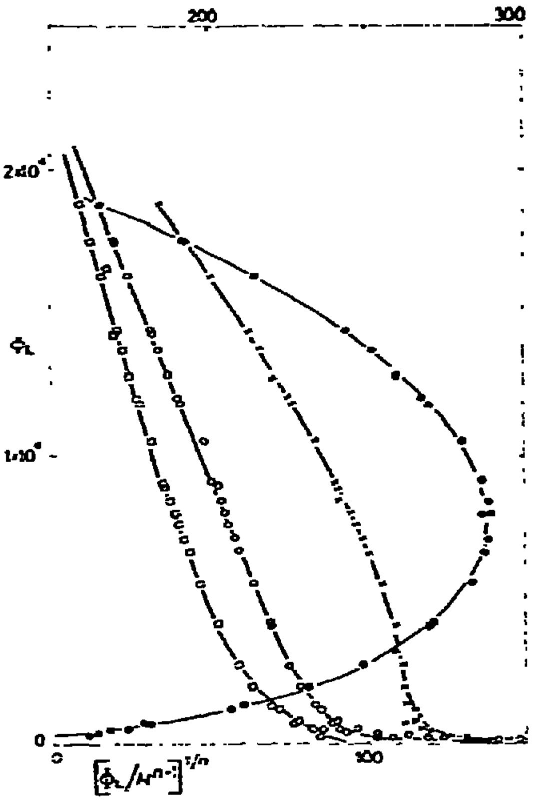

Fig. 1. Treatment of thermochemical data[6] of the ethanol–cyclohexane system at 298.15 K by eqn. (3). $n = 2$ (●), $n = 3$ (×), $n = 4$ (○), and $n = 5$ (□) Upper abscissa is valid for $n = 2$.

TABLE 1

SELF-ASSOCIATION CONSTANTS, OF ETHANOL IN VARIOUS SOLVENTS AT 298.15 K, STANDARD ENTHALPY OF THE SELF-ASSOCIATION, AND SOLVENT POLARITY FACTOR. ETHANOL CONCENTRATION RANGES FROM 0.028 TO 0.45 M.

Solvent	$K_{1,4}$ (l^3 mol^{-3})	$\Delta H^{\circ}_{1,4}$ (kJ mol^{-1})	E_T[a] (J mol^{-1})
n-Hexane	540 ± 1	91.07 ± 0.33	129.28
Cyclopentane	494 ± 2	90.02 ± 2.40	
Cyclohexane	612 ± 1	90.51 ± 1.55	130.21
Carbon tetrachloride	86 ± 3	70.29 ± 2.48	135.98
Benzene	3.2 ± 0.7	65.64 ± 0.33	144.35

[a] Taken from the literature[10] and recalculated to dimensions J mol^{-1}.

and that the activity coefficients of monomer and polymer are close to unity in very dilute solutions of alcohol.

The literature data[6–8] on the enthalpies of dilution of ethanol for different solvents have been treated by eqn. (3). They have been plotted as $\Phi_L = f(\Phi_L/M^{n-1})^{1/n}$

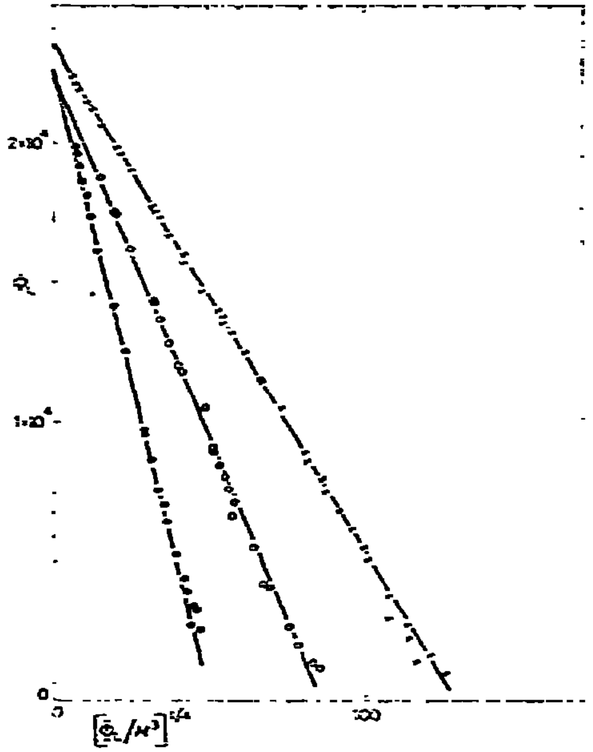

Fig. 2. The influence of temperature on the representation of data[6] on the ethanol–cyclohexane system by eqn. (3), for $n = 4$. 318.15 K (●), 298.15 K (○) and 283.15 K (×).

and the least squares method has been used to fit the data to a straight line. Figure 1 shows that $n = 4$ fits the data linearly better than other n values. However, Φ_L values, for very low concentrations of ethanol, do not follow the 1:4 model better than others, possibly due to the large experimental errors at high dilution and, perhaps also by the existence of another association model in that region.

The $K_{1,4}$ and $\Delta H^\circ_{1,4}$ values, calculated in this work by plotting data using eqn. (3), are listed in Table 1. The values of the regression coefficients, for the linear fit of the tetramer model, are within 0.9980 and 0.9998. In the case of benzene as the solvent, the value of the coefficient is 0.9244, which could be explained by the scattering and the insufficiency of the experimental points. However an interaction of ethanol with benzene probably has greater influence on the equilibrium considered than the interaction of ethanol with other solvents.

The self-association equilibria of alcohols are very temperature sensitive[2, 4, 5]. Using the literature data[6–8] we have calculated $K_{1,4}$ values for 273, 298 and 318 K for the ethanol–cyclohexane system, to be 2904, 612 and 77 respectively. Figure 2 shows Φ_L as a function of $(\Phi_L/M^{n-1})^{1/n}$, eqn. (3), for different temperatures. All three lines have the same intercept, within experimental error. This means that $\Delta H^\circ_{1,4}$ for the self-association of ethanol has the same value in the temperature region 283–318 K.

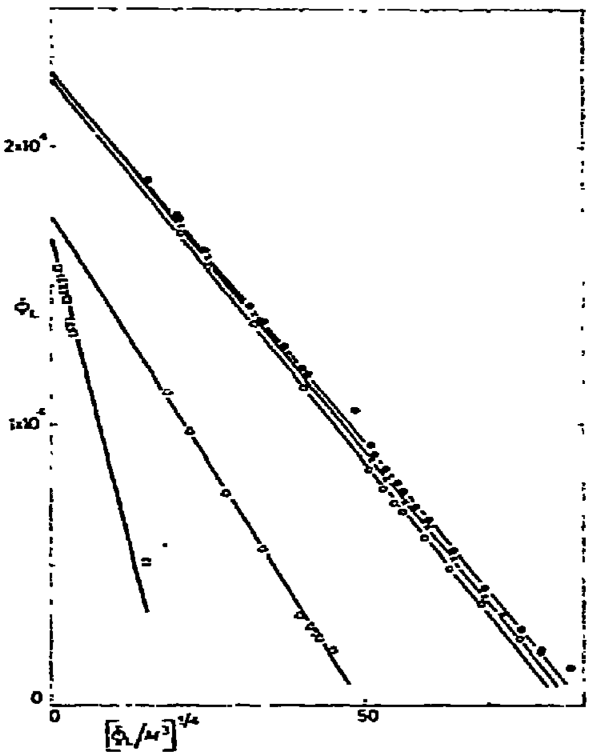

Fig. 3. The effect of solvent on the representation of data[6] on solutions of ethanol at 298.15 K, by eqn. (3). Cyclohexane (●), carbon tetrachloride (△), cyclopentane (○), benzene (□), and n-hexane (×).

The influence of the length of alkyl radicals of primary alcohols on the extent of their self-association is difficult to evaluate because of the rather scattered data on self-association constants available in the literature. This is a consequence of the different experimental techniques used by numerous authors. The different opinions of Fletcher[4] and Anderson et al.[5] on this matter have already been discussed. It is probable that such a correlation, if any, could be realized only with calorimetric data of very high precision.

The influence of solvent on the self-association of ethanol is more pronounced than that of lengthening of the alkyl chain. The literature data[6−8] on different ethanol–solvent systems have been treated by eqn. (3) and plotted graphically in Fig. 3. The self-association constants calculated vary by two orders of magnitude (Table 1). The nature of this influence can be described by a non-specific interaction in the case of the aliphatic hydrocarbons, or by a specific interaction of the various types in the case of interaction of alcohol with carbon tetrachloride and benzene. Fletcher[3] showed the existence of 1:1 complex of the isooctanol monomer with carbon tetrachloride. Although small, the formation of an alcohol solvate can considerably affect the self-association equilibria.

Due to the difficulties of determining the nature and extent of such side inter-

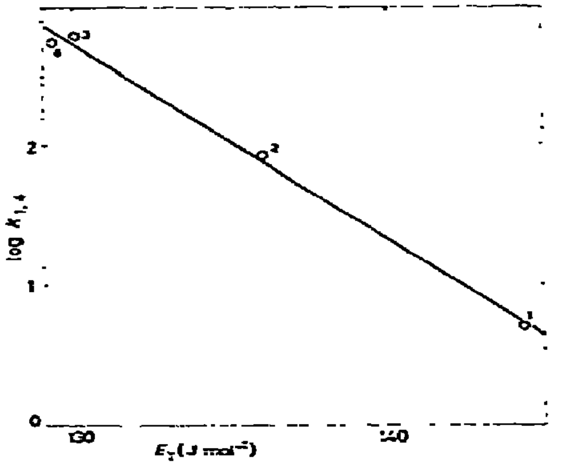

Fig. 4. Plot of the self-association constants of ethanol, determined in benzene (1), carbon tetrachloride (2), cyclohexane (3), and n-hexane (4), as a function of solvent polarity factor, E_T.

actions the solvent effect in the self-association equilibria can be considered in the light of the empirical polarity factor[10], E_T, of the solvent in which a reaction occurs. This factor is defined as a solvent polarity parameter based on the solvent dependent electronic $\pi \rightarrow \pi^*$ transition for N-phenolpyridinium betaines. Reinchard[10] showed the existence of the linearity between the logarithm of the reaction constant and the E_T values of solvents. Figure 4 illustrates that function for the systems we have considered in this work. Unfortunately, there is no E_T value for cyclopentane in the literature, but those which are available support the linearity between E_T values and the logarithms of the self-association constants we have determined.

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