

Furfuryl Alcohol. Part 2. Dielectric Behaviour of Furfuryl Alcohol and Carbon Tetrachloride Mixtures

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Self-association of furfuryl alcohol (FOH) in carbon tetrachloride solutions was previously studied by a near-infrared spectrometric method.¹ In an attempt to determine the structures of the associated FOH species, dielectric data are here analysed in terms of the Kirkwood-Fröhlich correlation parameter g , which is a measure of the short-range intermolecular forces that lead to specific dipole-dipole orientations.

Experimental. The samples were purified as in the preceding work.¹ The observed refractive indices were: furfuryl alcohol 1.4842 and carbon tetrachloride 1.4561 at 25 °C. The refractive indices were measured with an Abbe refractometer (Model G, Carl Zeiss, Jena) at the wavelength of the sodium D-line. The dielectric constants were measured by the heterodyne beat method at 2 MHz with a Dipolmeter DM 01 (Wissenschaftlich-Technische Werkstätten, Weilheim, West-Germany) and cells MFL 1/S and MFL 2/S. The values of dielectric constants were read from large-scale calibration curves. The densities were measured with an Ostwald-Sprengler pycnometer having a volume of 10.4733 cm³. The temperature was maintained at 25 °C within 0.1 °C. All weighings were corrected to vacuum.

Calculations and results. The dipole moment of FOH, $\mu_0 = 1.95$ D, was computed by the method of Hedestrand² from the measured values of dielectric constants ϵ and densities d of very dilute solutions. Both ϵ and d are within experimental error linear functions of X_1 , the mol fraction of FOH in CCl₄, for $X_1 < 0.04$. The estimated uncertainty in the dipole moment is ± 0.02 D.

The Kirkwood-Fröhlich parameters $g^{3,4}$ were calculated from the relations presented in Refs. 5 and 6 for the pure dipolar compound and for binary mixtures of polar liquid and nonpolar solvent. The results are given in Table 1. In general the g values for pure alcohols range from 2.5 to 3.1.^{5,6} When the alcohol concentration decreases ($X_1 \rightarrow 0.1$) g decreases to a minimum value, often considerably less than one. With further dilution, g increases towards unity. A value of g less than one indicates that a considerable amount of cyclic alcohol complexes are formed owing to an antiparallel alignment of near

Table 1. Values of the density, the dielectric constant and the correlation parameter at different mol fractions, X_1 , of FOH in CCl₄ at 25 °C. The uncertainty in the correlation parameter is about 2%.

X_1	d (g cm ⁻³)	ϵ	g
0.0000	1.5847	2.241	1.000
0.0395	1.5679	2.425	0.998
0.0620	1.5586	2.533	0.963
0.0851	1.5490	2.647	0.946
0.108	1.5396	2.788	0.976
0.165	1.5159	3.177	1.036
0.340	1.4409	4.934	1.268
0.489	1.3753	7.095	1.471
0.503	1.3693	7.319	1.485
0.660	1.2968	9.975	1.631
0.813	1.2230	13.00	1.765
1.000	1.1286	16.85	1.874

neighbour dipoles.³⁻⁷ Because the measured correlation parameter represents the overall average of the different sizes and structures of complexes formed, the reason for the somewhat low value 1.87 of pure FOH might be an equilibrium between open and cyclic associates, or more probably the association ratio is low owing to the steric hindrance against the formation of large multimers.⁵ The g values of FOH in dilute solutions give a minimum of 0.95 at $X_1 = 0.085$. The minimum g value of FOH remains closer to unity than that of most other alcohols studied.^{5,6,8} Accordingly, one can conclude that furfuryl alcohol has a relatively weak tendency to form cyclic dimers and/or trimers and open associates prevail.

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Received September 30, 1977.