

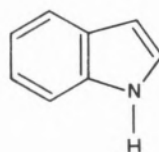


THE DIPOLE MOMENTS AND THE PARTIAL MOLAR VOLUMES OF INDOLE, INDENE AND INDAN IN CYCLOHEXANE SOLUTIONS

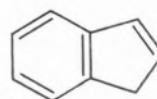
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Dipole moment measurements have increased their importance for the study of different kinds of physico-chemical problems [1]: determination of molecular structures, study of conformational equilibrium in chain polymers and other non-rigid molecules, study of the intermolecular interactions in liquid solutions, etc.

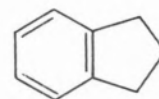
In the course of an investigation of the excited state dipole moment of indole [2, 3] we measured the electric dipole moments of indole I and two homomorph molecules: the indene II and the indan III.



I



II



III

For indole molecule we used GUGGENHEIM-SMITH [4, 5] and HALVERSTADT-KUMLER [6, 7] equations in order to estimate the dipole moment in dilute cyclohexane solution. The experimental results are presented in Table 1 where x_2 and w_2 are respectively the mole and weight fractions of the solute indole and ϵ_{12} , n_{12} and d_{12} are the permittivities, refractive indexes and densities of the solution at 25°C.

Table 1

Permittivities, refractive indexes and densities of solutions of indole in cyclohexane

x_2	w_2	ϵ_{12}	n_{12}	d_{12}
0.01000	0.01382	2.0559	1.4223	0.77596
0.00250	0.00348	2.0248	1.4209	0.77479
0.00050	0.00069	2.0159	1.4206	0.77407
0.00025	0.00035	2.0146	1.4205	0.77395
0.00015	0.00021	2.0144	1.4204	0.77392
0.00010	0.00014	2.0140	1.4204	0.77391
0.00003	0.00004	2.0138	1.4204	0.77388

From these results we obtain $\bar{V}_2 = 120 \text{ cm}^3 \text{ mol}^{-1}$ for the partial molar volume of indole at infinite dilution in cyclohexane (at 25°C), and $n_2^2 = 2,4759$ on the basis of the additivity of molar refraction. The indole dipole moment is $1.92 \pm 0.04 \text{ D}$ from Guggenheim-Smith equation and $1.94 \pm 0.04 \text{ D}$ from

Halverstadt-Kumler equation. These experimental values may be compared with 2.05 D [8] and 2.08 D [9] obtained in benzene solution, with 2.0 D and 2.1 D [10] obtained respectively in cyclohexane and *p*-xylene solutions, and with 1.83 D [9] calculated by the CNDO/2 method and 2.18 [11] calculated by the Pariser-Parr-Pople method.

For the estimation of the dipole moments of the indene and indan molecules we used a method of extrapolation based on the Onsager-Kirkwood-Frolich Theory [12]. The experimental values of refractive index we obtain for indene ($n_D=1.5675$) and for indan ($n_D=1.5332$) at 25°C lead us to estimate the permittivity at infinite frequency, $\epsilon_\infty = 1.05 n_D^2$, [13] for these two molecules. The experimental values of the static permittivity of the studied solutions are reported in Tables 2 and 3 as a function of the volume fraction (ϕ) of the solute.

Table 2

Static permittivities of solutions of indene in cyclohexane at 25°C

ϕ_2	ϵ_{12}
0.01496	2.0330
0.02992	2.0479
0.05984	2.0821
0.08976	2.1160
0.14960	2.1849
0.19879	2.2400
0.29919	2.3600

Table 3

Static permittivities of solutions of indan in cyclohexane at 25°C

ϕ_2	ϵ_{12}
0.01471	2.0238
0.02942	2.0338
0.05885	2.0533
0.08827	2.0737
0.14712	2.1141
0.18805	2.1422
0.29424	2.2178

The obtained dipole moments are 0.80 ± 0.02 D for indene and 0.49 ± 0.02 D for indan. The value for indene compare very well with the one reported by RAO [14] for CCl_4 , CS_2 and cyclohexane solutions (0.85 D) but it is somewhat different from the other values (0.67 and 0.44 D) reported in the literature [15]. The value for indan compare well with the ones reported in literature for cyclohexane solution [16] (0.55 D) and for benzene solution [17] (0.53 D). We have also obtained the values of partial molar volumes (\bar{V}_2^∞) of indene and indan at infinite dilution in cyclohexane solutions. In Tables 4 and 5 we report the results of density measurements for the studied solutions as a function of the molar fraction (x) of the solute.

Table 4

Densities of solutions of indene in cyclohexane at 25°C

x_2	d_{12}
0.2825	0.8334
0.1862	0.8117
0.1394	0.8027
0.0553	0.7826
0.0000	0.7739

Table 5

Densities of solutions of indan in cyclohexane at 25°C

x_2	d_{12}
0.2677	0.8243
0.1688	0.8056
0.1313	0.7992
0.0782	0.7885
0.0519	0.7830
0.0000	0.7739

From these results we obtained $\bar{V}_2^\infty = 121 \text{ cm}^3 \text{ mol}^{-1}$ for indene and $\bar{V}_2^\infty = 126 \text{ cm}^3 \text{ mol}^{-1}$ for indan, values which are similar to that obtained for indole. Indene and indan may thus be considered as good homomorphs of the indole molecule.

EXPERIMENTAL

Permittivity measurements have been performed in a dipolemeter type DMO1 of the Wissenschaftlich-Technische Werkstätten, G.m.b.H., Weilheim, with a measuring cell of the type DFL 1.

Refractive index measurement have been performed in a B-S dipping Refractometer from Bellingham & Stanley.

Density measurements have been performed in a digital densitometer model BMA 02 D from Anton Paark K. G., Austria.

All these measurements have been performed at $25 \pm 0.1^\circ\text{C}$.

Indole, indene and indan were BDH commercial reagents. Indole has been previously sublimated under reduced pressure. Indene and indan were previously distilled under nitrogen atmosphere and reduced pressure and the purity was confirmed by refractive index measurements.

Cyclohexane was a Merck UVASOL reagent and has been dried over molecular sieves.

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ABSTRACT

Static permittivities, refractive indexes and densities have been measured for dilute solutions of indole, indene and indan in cyclohexane solvent at 25°C. Dipole moments and partial molar volumes at solute infinite dilution have been obtained from experimental results.

RESUMO

Momentos dipolares e volumes parciais molares de indol, indeno e indano dissolvidos em ciclohexano.

Mediram-se as constantes dielétricas, os índices de refração e as densidades de soluções diluídas de indol, indeno e indano em ciclohexano a 25°C. A partir destes resultados experimentais obtiveram-se os momentos dipolares e os volumes parciais molares a diluição infinita dos solutos considerados em ciclohexano.