Intermolecular Interactions in Liquid Ethanol-Dioxane Mixtures

H. ILOUKHANI,* J. ARJOMANDI and A.A. RAFATI

Department of Chemistry, Faculty of Science, Bu-Ali-Sina University, Hamadan, Iran

The ^{1}H-NMR spectra of liquid mixtures, ethanol (EtOH)-dioxane (Dx), were recorded at 293.15 K within nearly the whole range of the mixed solvent compositions. From these data the values of the spectral parameter, $\Delta\delta$(EtOH-Dx) were found. The densities, volumes and viscosities of the mixed solvents were measured at 293.15 K. From all these new parent data, the values of molar volumes (V_{12}), viscosities (η_{12}) and their deviations from "ideality" were calculated. the scrutiny of all these structural parameters as functions of the mixture composition points to the formation of a "complex" (sub-unit) of the EtOH·2Dx and 2EtOH·3Dx types.

INTRODUCTION

Following our experimental study of thermodynamic properties of solutions in which specific interactions between unlike molecules can occur[1–3], we present here the internal structure of various liquid binary mixtures of ethanol (EtOH) and dioxane (Dx). ^{1}H-NMR spectra of liquid binary EtOH-Dx mixtures were recorded (at 293.15 K) within nearly the whole range of solvent compositions (*i.e.*, from 27.31 to 94.12 mol % of EtOH). The same graphical method as that used previously[4–6] has been applied for determination of the relative differences in the chemical shift values δ(EtOH-Dx) of the centre of the ^{1}H-NMR signals of —OH group of EtOH and the center of the ^{1}H-NMR signals of the dioxane molecules over a wide range of solvent composition. The two lone electron pairs at any oxygen atom as well as a strongly proton-donating hydrogen atom of the same —OH group create, however, a theoretical possibility of forming as much as three H-bonds by each individual alcohol molecule, EtOH, in its neat liquid. However, due to steric and other reasons it has been concluded that usually only two (in average) and no more H-bonds are involved[7]. Contrarily, the molecules of Dx are not self-associated in neat dioxane and may act solely as proton acceptors in their mixture with other solvents.[8, 9]

EXPERIMENTAL

Extra pure ethanol and dioxane (Merck) were used. Ethanol and dioxane were dried and purified by the known procedure[10]. The refractive index (n_D^{20}) of ethanol and dioxane had the values 1.36139 and 1.42238 respectively, in good agreement

with the literature data[11]. ^{1}H-NMR spectra were recorded on the spectrometer, of the type Jeol, Fx (90 MHz), at 293.15 K. The chemical shift for proton signals of EtOH and Dx was measured to an accuracy of about ±0.02 Hz with respect to an internal standard TMS (tetramethylsilane). Densities were measured at 293.15 K using a bicapillary pycnometer to an accuracy of 4 parts in 10^4. The viscosities were measured by means of a suspended level Ubbelohde viscometer. The time of efflux was measured with a stop watch to ±0.15. All solutions were prepared by weight.

RESULTS AND DISCUSSION

In the present paper, the chemical shift differences, δ(EtOH-Dx) (in Hz), were measured at 293.15 K, between the centre of the ^{1}H-NMR signals of —OH group of EtOH and the centre of the ^{1}H-NMR signals of the dioxane molecules over a wide range of solvent composition, i.e., from 27.31 to 94.12 mol % of EtOH. Subsequently, using the same method as previously[4-6], from these new spectral data the spectral parameters $\Delta\delta$(EtOH-Dx) have been evaluated. The maximal values of these parameters have been shown previously[4-6] to be located at the composition characterized by the strongest intermolecular interactions in which hydrogen bonds are involved. Values of the chemical shift differences (EtOH-Dx) measured over the whole range of concentrations are listed in Table-1. The changes of spectral parameter $\Delta\delta$(EtOH-Dx) shown in Fig. 1 exhibit maximum at ca. 40 mol % of EtOH. Thus, the conclusion can be drawn that at this composition the strongest hydrogen bond interactions are displayed, and that the most stable "complex" (sub-unit) is of the 2EtOH-Dx type. The deviations from "ideality" of densities $\Delta(d_{12})_{ideal}^{(x)}$, molar volumes $\Delta(v_{12})_{ideal}^{(x)}$ and viscosities $\Delta(\eta_{12})_{ideal}^{(x)}$ were evaluated by the following equations:
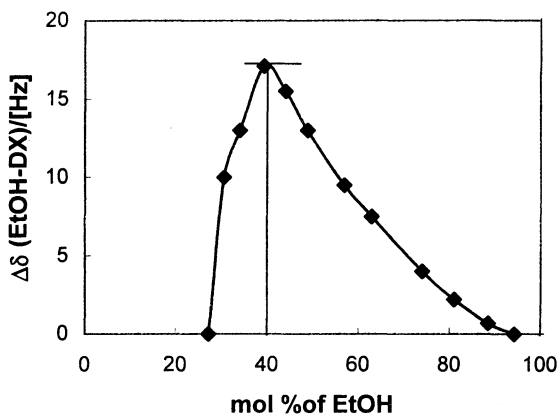

Fig. 1.   Changes in the function $\Delta\delta$(EtOH-Dx) = f(mol %) for the liquid ethanol-dioxane mixtures at 293.15 K

TABLE-1

RELATIVE ^{1}H-NMR CHEMICAL SHIFTS, δ(EtOH-Dx), MEASURED AT 293.15 K

mol % of EtOH	δ(EtOH-Dx) [Hz]
27.31	36.20
34.21	39.90
39.06	42.00
44.41	51.60
48.82	61.90
57.23	75.50
63.36	98.80
74.23	109.60
81.85	199.80
88.36	133.07
94.12	142.20

$$\Delta(d_{12})_{ideal}^{(x)} = d_{12} - \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{x_1 \cdot \dfrac{M_1}{d_1} + x_2 \cdot \dfrac{M_2}{d_2}} \qquad (1)$$

$$\Delta(v_{12})_{ideal}^{(x)} = v_{12} - (x_1 \cdot v_1 + x_2 \cdot M_2) \qquad (2)$$

where $v = M/d$.

$$\Delta(\eta_{12})_{ideal}^{(x)} = \eta_{12} - (\eta_1)^{x_1} - (\eta_2)^{x_2} \qquad (3)$$

The calculated values for the above quantities are listed in Table-2. The values of $\Delta(d_{12})_{ideal}^{(x)}$ and $\Delta(v_{12})_{ideal}^{(x)}$ exhibit the largest activation from "ideality" at the composition *ca.* 40 mol % of EtOH which suggests the formation a "complex" (sub-units) of the 2EtOH·3Dx type (Figs. 2 and 3). This confirms the conclusion drawn from ^{1}H-NMR spectral data. The value of $\Delta(\eta_{12})_{ideal}^{(x)}$ has a minimum at the composition *ca.* 33 mol % of EtOH (Fig. 4) which suggests the formation of
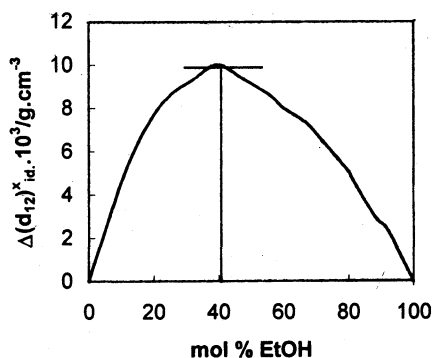

Fig. 2.   The changes of deviations from ideality of density as a composition for the liquid ethanol-dioxane mixtures.

"complex" (sub-units) of EtOH·2Dx type. The complexes (sub-units) of 2EtOH·3Dx and EtOH·2Dx types, forming internally H-bonded "flickering" internal structures of types (2EtOH·3Dx)$_n$ and (EtOH·2Dx) can enter convert with each other.
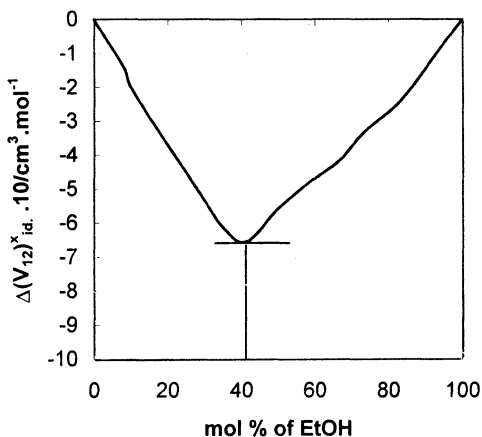

Fig. 3. Deviations from ideality of molar volume as a composition for ethanol-dioxane mixtures.

TABLE-2

DEVIATIONS FROM IDEALITY OF DENSITIES, MOLAR VOLUME AND VISCOSITY AS A FUNCTION OF COMPOSITION FOR THE LIQUID ETHANOL-DIOXANE MIXTURES AT 293.15 K

Mol % EtOH	$\Delta(d_{12})_{ideal}^{(x)} \times 10^3$ $(g\ cm^{-3})$	mol % EtOH	$\Delta(v_{12})_{ideal}^{(x)} \times 10$ $(cm^{-3}\ mol^{-1})$	mol % EtOH	$\Delta(\eta_{12})_{ideal}^{(x)} \times 10$ (cP)
11.13	5.03	8.09	−1.40	8.39	−3.21
19.36	7.52	10.26	−2.03	14.41	−5.03
25.52	8.66	20.03	−3.70	19.98	−6.21
32.01	9.31	28.65	−5.11	24.63	−7.21
39.62	10.02	35.05	−6.13	32.18	−8.14
47.74	9.36	41.32	−6.56	38.20	−7.96
55.51	8.63	50.36	−5.55	45.98	−7.44
60.06	8.00	59.47	−4.73	55.51	−6.88
66.66	7.36	66.74	−4.16	63.87	−6.11
72.11	6.45	73.21	−3.34	72.11	−5.32
79.98	5.07	81.18	−2.63	80.08	−4.06
81.23	4.70	87.03	−1.91	88.03	−3.04
88.31	2.96	92.39	−1.09	93.39	1.63
92.11	2.36	−	−	−	−
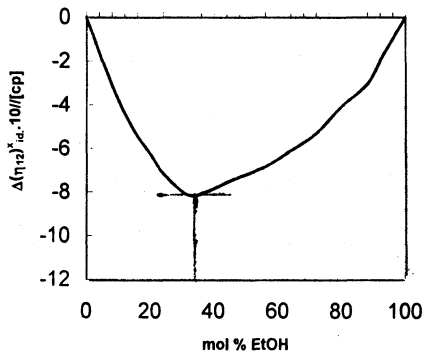
Fig. 4.   The course of deviations from ideality of viscosity for ethanol-dioxane systems.

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