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STUDIES ON INTERMOLECULAR INTERACTIONS
IN PYRIDINE-WATER LIQUID MIXTURES
BY MEANS OF ^1H -NMR SPECTRA AND ELECTRIC PERMITTIVITY VALUES

This paper continues my previous studies [1-4] on liquid binary mixtures. The ^1H -NMR spectra discussed herein were newly recorded for nine binary mixture of pyridine (Py) with water (H_2O) at 298.15 K, within the possibly full range of composition (i.e. from 2.42 to 66.79 mol% of Py). Subsequently, based on these spectral data, the relative differences in the chemical shift values were measured between the center of the H_2O protons signal and the center of multiplet derived from the five Py aromatic protons (i.e. $\delta(\text{Py} - \text{H}_2\text{O})$). Using the same method as described previously [1-4] from these new spectral data the values of the spectral parameter, $\Delta\delta(\text{Py} - \text{H}_2\text{O})$, were determined. Independently, the values of the temperature coefficients of electric permittivities, ϵ , viz. $\alpha = (1/\epsilon) \cdot [d\epsilon/d(1/T)]$, were calculated at 298.15 K within the full range of compositions of the studied binary mixtures. The analysis of the results thus obtained as well as the available literature reports would indicate the formation of some relatively most stable "complexes" (dihydrates), $\text{Py} \cdot 2\text{H}_2\text{O}$, in the liquid mixtures under investigation.

I have chosen the said binary mixtures for the present study, since molecules of water and pyridine due to the known structures of their molecules are apt to strong intermolecular interactions mainly by hydrogen bonding.

EXPERIMENTAL

Chemically pure pyridine (Fluka) was dried and purified according to the known procedure [5]. Redistilled water from a quartz

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glass distilling device was used. All the binary solutions studied, Py - H₂O, were prepared by weight. The ¹H-NMR spectra (at 298.15 K ± 1 K) were recorded on a Tesla spectrometer of the type BS 487 C (80 MHz). The chemical shift values for the proton signals of Py and H₂O in each binary mixture were measured with an accuracy of ±0.2 Hz, in respect to an external standard, HMDS (hexamethyldisiloxane).

RESULTS AND DISCUSSION

Using the same method as previously [1-4] new data of the spectral parameter, $\Delta\delta(\text{Py} - \text{H}_2\text{O})$, were determined. The location of a maximum in the graph plotted vs. the composition of the mixed solvent points at a particular composition where the strongest intermolecular interactions between the components are displayed. The parent, $\delta(\text{Py} - \text{H}_2\text{O})$ data as well as the respective $\Delta\delta(\text{Py} - \text{H}_2\text{O})$ values are shown in Tab. 1 and are visualized in Fig. 1 as a function of the mixture compositions.

Later on, using the literature, temperature-dependent, data of electric permittivities (ϵ_{12}) measured over the whole range of solvent compositions for the Py - H₂O mixtures [5-7], I have calculated the values of the temperature coefficients of ϵ (at 298.15 K), denoted α , viz. $\alpha = (1/\epsilon) \cdot [d\epsilon/d(1/T)]$. The maximum of this coefficient, in agreement with the results submitted by R a e t z s c h [8] and based on some thermodynamic reasoning, points at a "complex" with the strongest intermolecular interaction between the components. Changes of α as a function of the mixture compositions are visualized in Fig. 2.

In the previous papers [1-4] I have shown that there is a fairly good agreement in conclusions drawn from both the plots of the spectral $\Delta\delta$ parameter and of the α property. Before considering the significance of results obtained in this work, it is necessary to make a brief review of the literature opinions pertaining to mutual interactions between molecules of pyridine and water in their liquid mixtures. D u n s t o n, T h o l e and H u n t [9] had measured densities for the Py - H₂O mixtures, at 298 K, and plotted a curve showing a number of characteristic features which were attributed to the existence of several dif-

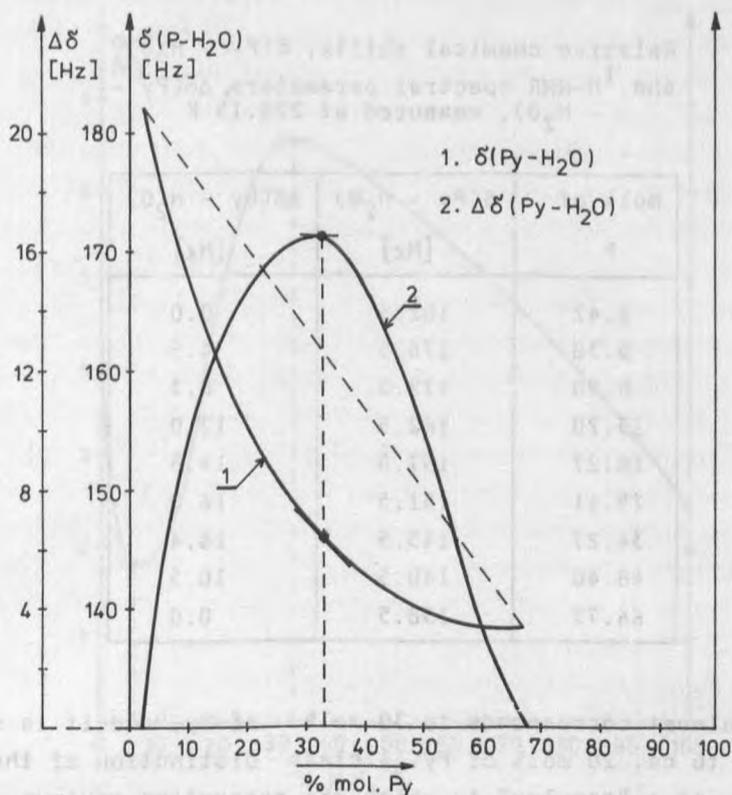


Fig. 1. Changes in the functions, $\delta(\text{Py} - \text{H}_2\text{O}) = f(\text{mol}\%)$ and $\Delta\delta(\text{Py} - \text{H}_2\text{O}) = f(\text{mol}\%)$, for the liquid pyridine-water mixtures, at 298.15 K

ferent hydrates in aqueous solutions of pyridine. H a r t l e y, T h o m a s and A p p l e b e y [10] have repeated the same density measurements, and their density show no other characteristic features but only one maximum at ca. 30 mol% of Py. Therefore, the existence of a sole dihydrate, $\text{Py} \cdot 2\text{H}_2\text{O}$, is suggested by them. Also, the density curve obtained by T r e w and S p e n c e r [11] shows only a single maximum, which corroborates the results in [10]. The mentioned above authors have also observed, by plotting the density curves at different temperatures, that the maxima are shifted towards lower pyridine concentrations with increasing the temperature. Thus, at 273 K the

Table 1

Relative chemical shifts, $\delta(\text{Py} - \text{H}_2\text{O})$, and ^1H -NMR spectral parameters, $\Delta\delta(\text{Py} - \text{H}_2\text{O})$, measured at 298.15 K

mol% of P	$\delta(\text{Py} - \text{H}_2\text{O})$ [Hz]	$\Delta\delta(\text{Py} - \text{H}_2\text{O})$ [Hz]
2.42	182.5	0.0
5.38	176.5	4.5
8.90	172.0	8.3
13.20	162.5	12.0
18.27	157.0	14.3
25.11	151.5	16.0
34.27	145.5	16.4
48.40	140.5	10.5
66.79	138.5	0.0

maximum almost corresponds to 30 mol% of Py, and it is shifted at 298 K to ca. 20 mol% of Py. A clear distinction of the composition of a "complex" to which the respective maximum was due was then made by plotting the deviations of the density values from the values calculated by the additive law of mixtures against the composition, since in this way the effect of the relative temperature coefficients of water and pyridine would be possibly eliminated. The results obtained by Trew and Spencer [11] point at the existence of a dihydrate $\text{Py} \cdot 2\text{H}_2\text{O}$. According to them, that conclusions is confirmed by the corresponding property-composition curves for refractive indices [12], volume contractions [13], vapour pressures [14], and viscosities [15], all of which are found to display a maximum at the composition equal to ca. 30 mol% of Py. Very interesting discussion concerning this problem was later on presented by Cini and Taddei [16]. They have analysed changes in densities and susceptibilities of the water-pyridine liquid mixtures over the full concentration range, at 299 K. They have interpreted their results as an evidence for the existence of "com-

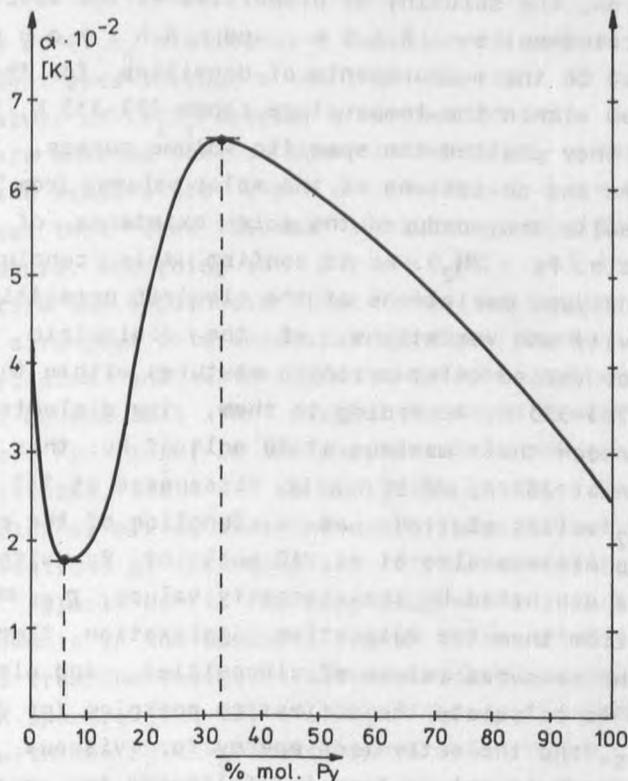


Fig. 2. Changes in the temperature coefficients of dielectric permittivity drawn as a function of composition for the liquid pyridine-water mixtures at 298.15 K

plexes" (dihydrates) of the type $\text{Py} \cdot 2\text{H}_2\text{O}$. They have also been very critical as to reliability of the results previously obtained by Hartley [10] and Trew [11]. In turn, Rizk and Shinouda [17] have denied the results obtained by Cini and Taddei [16] who postulated a possibility of formation of hydrogen bonds between molecules of pyridine in neat liquid Py. Rizk analyzed the Kirkwood parameter in pure pyridine, whereas Holmes et al. [18] excluded a possibility of the presence of short-range intermolecular forces in neat Py as well as its self-association there. Therefore, they have assumed that the conclusions drawn by Cini and Taddei [16] are not correct.

Further on, the scrutiny of properties of the water-pyridine mixtures carried out by Rizk and Shinouda [17, 19] was based on the measurements of densities for the Py - H₂O liquid system within the temperature range 283-333 K. From those parent data they plotted the specific volume curves, the molar volume curves and deviations of the molar volumes from "ideality". From the results they deduced the sole existence of a stable dihydrate, i.e. Py · 2H₂O. As to confirm this conclusion they have also analysed deviations of the electric permittivities ϵ_{12} from additivity and variations of the dielectric relaxation times (τ) for varied water-pyridine mixtures within the temperature range 283-333 K. According to them, the dielectric relaxation times reach their maximum at 30 mol% of Py; this maximum is clearly seen at 283 K, and it nearly disappears at 333 K. Similarly, the ϵ_{12} values plotted as a function of the composition reach a deep minimum also at ca. 30 mol% of Py quite identical behaviour is exhibited by the viscosity values, η_{12} , as well as by calculated from them the respective relaxation times. Rizk [17] used the measured values of viscosities and electric permittivities to calculate the activation energies for dipole relaxation, E_{ϵ} , and the activation energy for viscous flow, E_{η} . They obtained these values from the following two equations:

$$\tau = \frac{A}{T} \cdot \exp [E_{\epsilon}/R \cdot (T - T_0)]$$

$$\eta = B \cdot \exp [E_{\eta}/R \cdot (T - T_0)]$$

Both E_{ϵ} and E_{η} reach their maxima at 33 mol% of Py in the studied Py - H₂O mixtures. The modified Arrhenius equation given below also has been applied to calculate the values of V_f ("free volumes") for the studied binary mixtures, over the temperature range from 283 to 333 K.

$$(V_f)_{\eta} = V_f/V_i = (T - T_0) \cdot R/E_{\eta}$$

$$(V_f)_{\epsilon} = V_f/V_i = (T - T_0) \cdot R/E_{\epsilon}$$

where: V_f - "free volume", V_i - specific volume, $V_i = V_{12} = 1/d_{12}$.

Values of $(V_f)_\eta$ plotted as a function of composition of the mixed solvent pass through a minimum at ca. 35 mol% of Py, whereas values of $(V_f)_\tau$ display a minimum 32 mol% of Py. These minima are shifted towards lower contents of water with increasing the temperature. Cohen and Turmbull [20] have suggest that "free volumes" are proportional to the changes in temperature. According to Rizk [17] all these observations confirm the hypothesis that some particular composition where the strongest intermolecular hydrogen bond interactions between pyridine and water are displayed corresponds to ca. 33 mol% of Py and that the stable hydrogen-bonded "complex" (dihydrate), $\text{Py} \cdot 2\text{H}_2\text{O}$, is the only possible one complex in the studied mixtures. Adon et al. [21] measured variations of the entropies of mixing over the whole range of solvent compositions. Deviations of this function from additivity show a minimum at ca. 33 mol% of Py. The same suggestion can be drawn from IR measurements in the spectral region below 3400 cm^{-1} [22-24] as well as from the energetic measurements based on analysis of the $^1\text{H-NMR}$ spectra [22, 23, 25, 26]. The electrochemical studies carried with the $\text{Py} - \text{H}_2\text{O}$ mixtures by Singh, MacLeod and Parker [27] seem to be also worth mentioning. They have reported values of the limiting conductance for NaNO_3 , AgNO_3 , CuNO_3 and $\text{Cu}(\text{NO}_3)_2$ over the whole range of the compositions of the mixed solvent, $\text{Py} \cdot 2\text{H}_2\text{O}$, at 298 K. The limiting conductances, Λ_0 , exhibit for all the studied electrolytes, a minimum at ca. 33 mol% of Py. It means that this minimum is observed for the same composition region for which the previously mentioned authors have assumed the existence of the most stable internal structure of the mixed solvent. My own $^1\text{H-NMR}$ studies as well as the analysis of temperature coefficients of electric permittivities in the mixtures of $\text{Py} - \text{H}_2\text{O}$ enabled me as well to disclose the composition range characterized by the strongest hydrogen bonding between molecules of pyridine and water.

As I have mentioned earlier, determined in this work values of the $\Delta\delta(\text{Py} - \text{H}_2\text{O})$ spectral parameter and the α coefficient are good criteria for estimating the mutual interactions between

polar components of binary solvents. The $\Delta\delta(\text{Py} - \text{H}_2\text{O})$ values are visualized in Fig. 2 as a function of the mixture compositions. They show a distinct maximum at ca. 33 mol% of Py. As it was evidenced earlier [1-4] the maximum for this parameter points at the compositions where the strongest interactions between water and pyridine occur, and stable "complexes" (sub-units) $\text{Py} \cdot 2\text{H}_2\text{O}$ are formed. Also the α values reach maximum for the composition having ca. 33 mol% of Py (see Fig. 2). Further interesting results can be obtained by detailed analysis of the function $\alpha = f(\text{mol\% of Py})$. It indicates that on increasing addition of Py to water up to 6 mol% of Py, where a minimum is reached, causes a rapid drop in the α values. Further addition of pyridine to the studied mixtures causes an increase in α , which results in a maximum at ca. 33 mol% of Py. Therefore, it is possible to assume that small amounts of pyridine being added to neat water break its internal structure (composition region up to 6 mol% of Py), whereas further addition of pyridine, up to ca. 33 mol% of Py, makes the internal structure of the mixed solvent more and more stabilized by the hydrogen bonding bonds between molecules of its components. The same analysis made for the pyridine-rich composition region shows a permanent increase of values of the α coefficient down to ca. 33 mol% of Py. Therefore, it seems that molecules of water in the studied mixture, within the composition range between 100 to 33 mol% of Py, play a role of "structure-makers" in respect to molecules of Py in the neat solvent. On the basis of the present results and those found in the literature, it may be concluded that the most stable internal structure of the binary solvent under study occurs at ca. 33 mol% of Py, which corresponds to formation of the most stable "complex" (sub-units) of the $\text{Py} \cdot 2\text{H}_2\text{O}$ - type, mostly stabilized by the intermolecular hydrogen bonding.

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BADANIA ODDZIAŁYWAŃ MIĘDZYMOLEKULARNYCH
W MIESZANINACH PIRYDINY Z WODĄ METODĄ POMIARU ICH WIDM $^1\text{H-NMR}$
I PRZENIKALNOŚCI ELEKTRYCZNEJ

Zmierzono widma $^1\text{H-NMR}$ ciekłych mieszanin wody i pirydyny (Py) w temperaturze 298,15 K, w zakresie od 2,42 do 66,79 mol% Py. Z danych doświadczalnych wyznaczono przebiegi względnych przesunięć chemicznych, $\delta(\text{Py} - \text{H}_2\text{O})$, pomiędzy środkami sygnałów protonów pochodzących od wody i środkami sygnałów pochodzących od pięciu protonów molekuli pirydyny. Następnie wyznaczono wartości parametru spektralnego, $\Delta\delta(\text{Py} - \text{H}_2\text{O})$, w badanych mieszaninach.

Z temperaturowych zależności przenikalności elektrycznej wyznaczono dla badanych układów wartości temperaturowego współczynnika przenikalności elektrycznej α .

Otrzymane wyniki wskazują na tworzenie się względnie trwałych "kompleksów" o składzie $\text{Py} \cdot 2\text{H}_2\text{O}$ w ciekłych mieszaninach wody i pirydyny.