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Thermodynamics of the Isopropanol/*n*-Hexane and Isopropanol/*n*-Heptane Systems Part II. NMR Studies

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The nuclear magnetic resonance spectra of the systems isopropanol/*n*-hexane and isopropanol/*n*-heptane are recorded to deduce thermodynamic functions. A discussion of *Saroléa-Mathot*'s methods follows.

(Keywords: Alcohol/n-alkane, thermodynamics; Association constants, isopropanol/n-alkanes)

Zur Thermodynamik des Isopropanol/n-Hexan und Isopropanol/n-Heptan Systems, II. NMR-Untersuchungen

Für die im Titel genannten Systeme werden aus den NMR-Spektren thermodynamische Funktionen abgeleitet. Eine Diskussion der *Saroléa-Mathot*- Methode wird präsentiert.

Introduction

In Part I of this work we showed that for very low concentrations of alcohol there is an interval where only dimers exist, mainly of the cyclic type, though some linear species are also present.

Since also other alcoholic conglomerates were present and we gave amounts and intervals as well as formation mechanisms, we decided to continue this work by measuring NMR spectra, to deduce thermodynamic functions and activity coefficients and to compare these results with those we have found by vapour measurements (Part III). An easy way for the description of the systems was satisfactorily tested.

Experimental

Measurements were taken at 30 °C in a Hitachi-Perkin-Elmer 60 Megacycles instrument with tetramethylsilane as an internal standard. Chemicals were carefully dried and purified as explained in Part I[1] and mixtures were prepared by weight. Chemical shifts were measured by side band technique[2].

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Method

In the concentration interval where only dimers are present we were able to detect a single NMR band; we assume here that the isopropanol is highly diluted, $X_A \to 0$, and that this peak corresponds to the cyclic dimer (Part I). Here, the relation

$$\left[\frac{\mathrm{d}\,\delta}{\mathrm{d}x_A}\right]_{x_A \to 0} = 2\,K\,\Delta_D \tag{1}$$

holds true[2], with

δ	chemical shift
x_A	molar fraction of isopropanol
K	equilibrium constant for the association; in this work monomer → cyclic dimer; later as $K_{1,2}$
Δ_D	$\delta_D - \delta_M = f(\Delta_p)$
Δ_p	$\delta_1 - \delta_0$ (Table 2)
D	index for dimers
M	index for monomers
δ_0	δ^M extrapolated to $x_A \to 0$
δ_1	δ_M extrapolated to $x_A \to 1$

Data to calculate Δ_p are given Table 1, being $\Delta_p = 235.62$ Hz for the system with n-hexane and $\Delta_p = 239.75$ Hz for the system with n-heptane.

The δ_D as well as δ_1 signals are affected by other alcoholic conglomerates, and therefore the best way to know Δ_D is using our infrared spectra[3].

To evaluate the Δ_D value which is influenced by the predominant tetramers, we use our IR experiences in Part I, where the dimers signal amounted $\Delta\nu = 200\ \mathrm{cm}^{-1}$ before any evidence of tetramers was found. The tetramer signal amounted $\Delta\nu = 270\ \mathrm{cm}^{-1}$ evidently influenced by the dimers, since

$$\Delta\nu_{\mathrm{tetramers}} = 270\ \mathrm{cm}^{-1} \neq 2\Delta\nu_{\mathrm{dimers}} = 400\ \mathrm{cm}^{-1}$$

The tetramers' signal in absence of any other conglomerate, should then amount $\Delta\nu = 400\ \mathrm{cm}^{-1}$. The difference of $130\ \mathrm{cm}^{-1}$, about $\frac{1}{3}$ of the $400\ \mathrm{cm}^{-1}$, is to be attributed to the dimers. Half of this quantity is the tetramers' influence on the dimers obviously with the opposite sign.

Thus, referring to our NMR measurements the expression for Δ_D, the dimers signal in a mixture formed mainly by tetramers, amounts

$$\Delta_D = \frac{1}{2}\Delta_p + \frac{1}{2}\frac{1}{3}\Delta_p = \frac{1}{2}\Delta_p + \frac{1}{6}\Delta_p \tag{2}$$

The values for Δ_D are given in Table 2.

The slope

$$\left[\frac{\mathrm{d}\,\delta}{\mathrm{d}\,x_A}\right]_{x_A \to 0}$$

Table 1

Isopropanol/n-hexane system

Concentration mol fraction isopropanol	NMR frequency in Hz from *TMS*
1.0000	308.75
0.7299	300.50
0.6592	296.23
0.4492	288.90
0.2444	270.70
0.2019	265.61
0.1055	238.55
0.0528	200.42
0.0324	151.63
0.0220	129.37
0.0208	123.90
0.0203	123.00

Isopropanol/n-heptane system

Concentration mol fraction isopropanol	NMR frequency in Hz from *TMS*
1.0000	308.75
0.8990	307.64
0.6802	299.15
0.5934	295.07
0.4934	290.82
0.4373	285.68
0.3177	278.59
0.1992	263.81
0.1025	236.79
0.0794	222.78
0.0503	194.05
0.0370	161.82
0.0290	142.81

for the monomer was calculated graphically from the data of Table 1 obtaining 2441.1 for isopropanol/n-hexane and 2320.0 for isopropanol/n-heptane; substitution of Δ_D and

$$\left[\frac{\mathrm{d}\,\delta}{\mathrm{d}\,x_A}\right]_{x_A \to 0}$$

in Eq. (1) yields K; Table 2 shows K values calculated by this method and from infrared data; both yield coincident values and they also agree with values given by other authors for the formation of cyclic dimers of alcohol[4].

Table 2

	δ_1	δ_0	Δ_D	$\left[\frac{d\,\delta}{d\,x_A}\right]_{A\to 0}$	$[K_{1,2}]_{\mathrm{NMR}}$	$[K_{1,2}]_{\mathrm{IR}}$
Isopropanol/*n*-Hexane	308.75 Hz	73.13 Hz	157.08 Hz	2441.1	7.7	7.7
Isopropanol/*n*-Heptane	308.75 Hz	69.00 Hz	159.83 Hz	2320.0	7.2	6.8

Table 3

Isopropanol/*n*-Hexane System					Isopropanol/*n*-Heptane System		
x mol fraction Isopropanol	x_1 monomer	$\frac{N_1}{N}$	$K_{i-1,i}$	x mol fraction Isopropanol	x_1 monomer	$\frac{N_1}{N}$	$K_{i-1,i}$
0.001	0.000985	0.985	1527	0.001	0.000986	0.986	1521
0.002	0.001941	0.970	759.8	0.002	0.001945	0.972	768.8
0.005	0.00466	0.932	321.2	0.005	0.00468	0.936	319.9
0.007	0.00637	0.910	235.2	0.007	0.00641	0.915	233.8
0.10	0.00881	0.881	170.3	0.01	0.00887	0.887	169,1
0.02	0.01606	0.803	93,4	0.02	0.01624	0.812	118,2
0.03	0.02239	0.746	67.0	0.03	0.02269	0.756	66,1
0.04	0.02809	0.702	56,3	0.04	0.02852	0.713	52.7
0.05	0.0333	0.666	45.1	0.05	0.0338	0.676	44.4
0.06	0.0382	0.636	39.3	0.06	0.0388	0.646	38.7
0.07	0.0427	0.610	35.2	0.07	0.0435	0.621	34,5
0.08	0.0471	0.588	31,9	0.08	0.0480	0.600	31.3
0.09	0.0512	0.568	29.4	0.09	0.0523	0.589	28.8
0.1	0.0552	0.552	27.3	0.10	0.0564	0.564	26.7

Discussion

Saroléa-Mathot[5] proposes the thermodynamic description of a system, with two constants:

$K_{1,2}$ equilibrium constant for dimer from monomers and
$K_{i-1,i}$ equilibrium constant for i-mers from i—1 conglomerates.

$$x = \frac{x_1 + 2K_{1,2}x_1^2}{1 + K_{1,2}x^2} \tag{3}$$

$$\alpha = \frac{N_1}{N} = \frac{x_1}{x_1 + 2K_{1,2}x_1^2} \tag{4}$$

and for higher concentrations with other conglomerates being present

$$K_{i-1,i} = \left[1 - \left(\frac{\dfrac{K_{1,2}}{K_{i-1,i}}}{\dfrac{K_{1,2}}{K_{i-1,i}} + \dfrac{N}{N_1} - 1} \right)^{1/2} \right] x_1^{-1} \tag{5a}$$

x	analytical molar fraction of alcohol
x_1	molar fraction of the monomer according to *Saroléa-Mathot*[5]
N_1	number of monomer particles.
N	total number of particles

Introduction of Eq. (4) in Eq. (5a), allows to calculate an approximate value of $K_{i-1,i}$.

$K_{i-1,i}$ has two solutions depending on the analytical alcohol concentration x; the selection of the suitable one according to *Saroléa-Mathot*[5] is in short the one for which $\frac{K_{i-1,i}}{K_{1,2}} = 8 \pm 4$.

For our systems this means $31 < K_{i-1,i} < 93$ isopropanol/n-hexane and $29 < K_{i-1,i} < 87$ for isopropanol/n-heptane.

Table 3 shows $K_{i-1,i}$ values at different concentrations; around molar fraction $x = 0.04$ these $K_{i-1,i}$ values are similar to those measured by infrared corresponding to the concentration where infrared spectra show the formation of higher conglomerates. Furthermore, Table 3 shows similar values K_{2c3c} and K_{34} for both systems calculated by NMR and IR (compare with Part I). Fig. 1 shows $K_{i-1,i}$ vs. concentration. Obviously no straight lines are obtained forming another argument against a formation mechanism of conglomerates by sequential steps as was already shown in Part I.

An alternative method to find this suitable $K_{i-1,i}$ would be the graphic determination, by drawing tangents in Fig. 1 as shown.

For the following calculation we use $K_{1,2}$ as given in Table 2 and $K_{i-1,i} = 53.1$ for isopropanol/*n*-hexane and 47.6 for isopropanol/*n*-heptane as given by Fig. 1*a* and 1*b*.

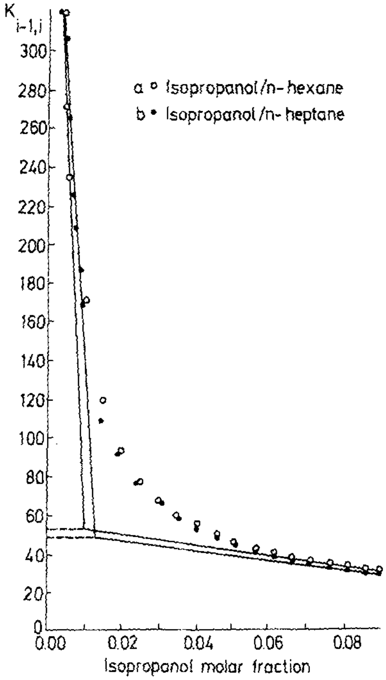

Fig. 1. Isopropanol/*n*-hexane and isopropanol/*n*-heptane systems; $K_{-1,i}$ vs. molar fraction of isopropanol

The monomer concentration x_1 at higher analytical concentrations is given directly by Eq. (5b).

$$x_1 = A + \sqrt[3]{-(A)^3 + B - C} \tag{5b}$$

$$A = \frac{x_A\left(K_{i-1,i} + \dfrac{K_{1,2}}{K_{i-1,i}}\right) + 2\left(1 - \dfrac{K_{1,2}}{K_{i-1,i}}\right)}{3\,(K_{i-1,i} - K_{1,2})}$$

$$B = \frac{\left[x_A\left(K_{i-1,i} + \dfrac{K_{1,2}}{K_{i-1,i}}\right) + 2\left(1 - \dfrac{K_{1,2}}{K_{i-1,i}}\right)\right]\left(2\,x_A + \dfrac{1}{K_{i-1,i}}\right)}{6\,(K_{i-1,i} - K_{1,2})^2}$$

$$C = \frac{x_A}{2\,K_{i-1,i}\,(K_{i-1,i} - K_{1,2})}$$

Table 4

Isopropanol/ n-Hexane	$(\ln K_{i-1,i} + \ln p)RT = -\Delta H = 3524 \pm 176$ cal/mol
	$(\ln K_{1,2} + 2\ln p)RT = -\Delta H = 3500 \pm 175$ cal/mol
Isopropanol/ n-Heptane	$(\ln K_{i-1,i} + \ln p)RT = -\Delta H = 3457 \pm 172$ cal/mol
	$(\ln K_{1,2} + 2\ln p)RT = -\Delta H = 3457 \pm 172$ cal/mol

Table 5

Isopropanol/n-hexane system

x mol fraction *Isopropanol*	x_1 *monomer*	$\frac{\Sigma x_i}{1\text{-}0.44\Sigma x_i}$	$\frac{1}{\Sigma i^\circ x_i}$	$\log f_A$	$\log f_B$
0.1	0.018	0.08	0.74	0.7875	0.0130
0.2	0.018	0.08	0.74	0.4832	0.0596
0.3	0.018	0.08	0.74	0.3711	0.1085
0.4	0.018	0.08	0.74	0.2328	0.1568
0.5	0.018	0.08	0.74	0.1396	0.2148
0.6	0.018	0.08	0.74	0.1226	0.2733
0.7	0.018	0.08	0.74	0.0921	0.3348
0.8	0.018	0.08	0.74	0.0000	0.4150
0.9	0.018	0.08	0.74	0.0000	0.4710
1.0	0.018	0.08	0.74	0.0000	0.6923

Isopropanol/n-heptane system

x	x_1	$\frac{\Sigma x_i}{1\text{-}0.44\Sigma x_i}$	$\frac{1}{\Sigma i^\circ x_i}$	$\log f_A$	$\log f_B$
0.1	0.020	0.083	0.75	0.7301	0.0100
0.2	0.020	0.083	0.75	0.5168	0.0561
0.3	0.020	0.083	0.75	0.2929	0.1055
0.4	0.020	0.083	0.75	0.1966	0.1575
0.5	0.020	0.083	0.75	0.1610	0.2123
0.6	0.020	0.083	0.75	0.1388	0.2705
0.7	0.020	0.083	0.75	0.0952	0.3421
0.8	0.020	0.083	0.75	0.0000	0.4000
0.9	0.020	0.083	0.75	0.0000	0.5102
1.0	0.020	0.083	0.75	0.0000	0.6923

Eq. (5b) expresses the only meaningful solution, since other x_1 solutions have no physical interest.

The values of x_1 calculated from Eq. (5b) are given in Table 5 and are not necessarily equivalent to the analytical molar fraction of the monomers at different concentrations.

Association Enthalpy. Calculating according to *Guggenheim*[6]

$$\frac{K_{i-1,i}}{K_{1,2}} = p = \frac{53.1}{7.7} = 6.9 = 2(z—1)$$

for the n-hexane system and $p = 6.6 = 2(z—1)$ for the n-heptane system the value of z, i.e. the number of molecules surrounding an individual conglomerate forming a higher polymer, can be evaluated.

For both systems we use $z = 4.6$; from

$$K_{1,2} = p^{-2} \exp \frac{—\Delta H}{RT} \tag{6}$$

or

$$K_{i-1,i} = p^{-1} \exp \frac{—\Delta H}{RT} \tag{7}$$

ΔH, the average association enthalpy per hydrogen bridge, might be calculated; values are given in Table 4 and show agreement with values calculated in Part I[1].

The Activity Coefficients. Prigogine et al.[7] suggest some formulae for the calculation of activity coefficients of systems defined by them as ideal.

In the special case of our systems where hydrogen bridges are present, *Saroléa-Mathot* suggests corrections to consider molecular interactions, orientations and in general effects which will affect the partition function.

The suggested final formulas to be tested are

$$\begin{gathered} f_A = \frac{N_1}{{}^\circ N_1} \left[\frac{\frac{z—2}{z} N_A + \frac{2}{z} \Sigma {}^\circ N_i}{x_A\left(N_B + \frac{z—2}{z} N_A + \frac{2}{z} \Sigma N_i\right)} \right]^{\frac{z}{2}} \\ f_B = \left[\frac{N_A + N_B}{N_B + \frac{z—2}{z} N_A + \frac{2}{z} \Sigma N_i} \right]^{\frac{z}{2}} \end{gathered} \tag{8a}$$

with sub index A for isopropanol
sub index B for n-paraffin
sub index i for conglomerate i

N_1 number of monomeric molecules of alcohol in mixture

$^{\circ}N_1$ number of monomeric molecules in pure isopropanol (we consider this only as a parameter since in Part I we could not demonstrate their existence)

N number of particles.

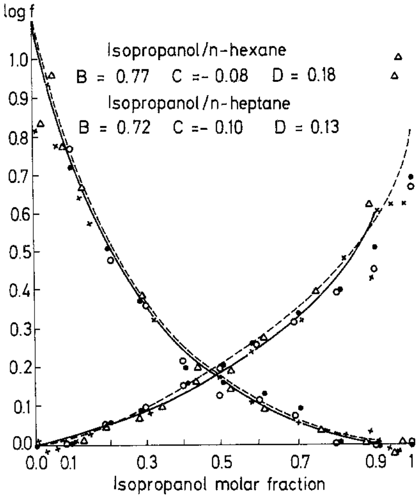

Fig. 2. Logarithm of activity coefficients of the system isopropanol/*n*-hexane and isopropanol/*n*-heptane vs. molar fraction of isopropanol at 30 °C. This method, ○ for isopropanol/*n*-hexane and ● for isopropanol/*n*-heptane. Vapour/liquid equilibrium, × for isopropanol/*n*-hexane and Δ for isopropanol/*n*-heptane. $\log f_A = (1-x)^2 [B-C+D+(4C-8D)x+12x^2]$ $\log f_B = x^2[B-3C+5D+(4C-16D)x+12x^2]$ ———— for isopropanol/*n*-hexane and — — — — — for isopropanol/*n*-heptane

For our systems Eq. (8a) become

$$f_A = \frac{x_1}{^{\circ}x_1}\left[\frac{0.56x_A + \dfrac{1}{\Sigma i^{\circ}x_i} - 0.56}{x_A\left(x_B + 0.56x_A + 0.44\dfrac{\Sigma x_i \cdot (x_B + 0.56x_A)}{(1-0.44\Sigma x_i)}\right)}\right]^{2.3} \tag{8b}$$

$$f_B = \left[\frac{x_A + x_B}{x_B + 0.56x_A + 0.44\dfrac{\Sigma x_i \cdot (x_B + 0.56x_A)}{(1-0.44\Sigma x_i)}}\right]^{2.3}$$

which immediately give the numerical values of the activity coefficients of each component; $K_{1,2} = 7.7$, $K_{i-1,i} = 53.1$ for the system isopropanol/n-hexane and $K_{1,2} = 7.2\, K_{i-1,i} = 47.6$ for the system isopropanol/n-heptane were the values used in this calculation.

Fig. 2 shows points for $\log f_A$ and $\log f_B$ as a function of the molar fraction of isopropanol calculated by this method, calculated from vapour/liquid equilibria (Part III) and the curve by the *Redlich* and *Kister* method[8] at 30 °C.

Eq. (8) expressed as function of p are

$$f_A = \frac{x_1}{{}^\circ x_1} \left[\frac{\frac{p-2}{p+2} x_A + \frac{1}{\Sigma i^\circ x_i} - \frac{p-2}{p+2}}{x_A \left(x_B + \frac{p-2}{p+2} x_A + \frac{4}{p+2} \frac{\Sigma x_i}{\left(1 - \frac{4}{p+2} \Sigma x_i\right)} (x_B + \frac{p-2}{p+2} x_A) \right)} \right]^{\frac{1}{2}\left(\frac{p}{2}+1\right)}$$

$$f_B = \left[\frac{x_A + x_B}{x_B + \frac{p-2}{p+2} x_A + \frac{4}{p+2} \frac{\Sigma x_i}{\left(1 - \frac{4}{p+2} \Sigma x_i\right)} \left(x_B + \frac{p-2}{p+2} x_A \right)} \right]^{\frac{1}{2}\left(\frac{p}{2}+1\right)}$$

with

${}^\circ x_1$	molar fraction of monomeric alcohol in the pure component
index A	alcohol
index B	solvent

which allow an additional test with the measured data of the systems methanol/carbon tetrachloride and ethanol/carbon tetrachloride at 20 °C given by *Niini*[9] using $p = 12$ and $K_{12c} = 4$ (molar fraction units) for the methanol system and $p = 6$ and $K_{12c} = 1.48$ (molar fraction units) for the ethanol one.

The Eq. (8) take the form: system methanol/carbon tetrachloride

$$f_A = \left[\frac{0.71 x_A + \frac{1}{\Sigma i x_i} - 0.71}{x_A \left(x_B + 0.71 x_A + 0.29 \frac{\Sigma x_i}{(1 - 0.29 \Sigma x_i)} (x_B + 0.71 x_A) \right)} \right]^{3.5} \qquad (9a)$$

$$f_B = \left[\frac{x_A + x_B}{x_B + 0.71 x_A + 0.29 \frac{\Sigma x_i}{(1 - 0.29 \Sigma x_i)} (x_B + 0.71 x_A)} \right]^{3.5} \qquad (9b)$$

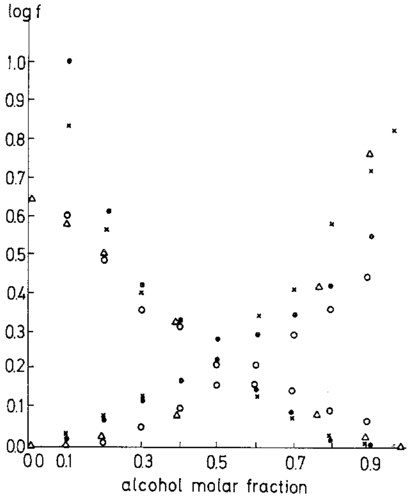

Fig. 3. Log of activity coefficients vs. molar fraction of alcohol at 20 °C. This method, ● for the system methanol/carbon tetrachloride and ○ for the system ethanol/carbon tetrachloride. Vapour/liquid equilibrium, × for the system methanol/carbon tetrachloride and Δ for the system ethanol/carbon tetrachloride

and system ethanol/carbon tetrachloride

$$f_A = \left[\frac{0.5x_A + \dfrac{1}{\Sigma i^\circ x_i} — 0.5}{x_A\left(x_B + 0.5x_A + 0.5\dfrac{\Sigma x_i}{(1—0.5\Sigma x_i)}(x_B + 0.5x_A)\right)}\right]^2 \tag{10}$$

$$f_B = \left[\frac{x_A + x_B}{x_B + 0.5x_A + 0.5\dfrac{\Sigma x_i}{(1—0.5\Sigma x_i)}(x_B + 0.5x_A)}\right]^2 \tag{11}$$

Fig. 3 shows $\log f$ vs. x for both systems. Calculation of $K_{1,3}$, $K_{1,4}$, $K_{1,5}$ and the frequency curve.

The NMR spectra are related to the conglomerates present in a solution by

$$\nu = \frac{\nu_1 x_1 + 2\nu_2 K_{1,2} x_1^2 + 3\nu_3 K_{1,3} x_1^3 \ldots}{x_1 + 2K_{1,2} x_1^2 + 3K_{1,3} x_1 \ldots} \tag{12}$$

$$x = x_1 + 2K_{1,2} x_1^2 + 3K_{1,3} x_1^3 \ldots \tag{13}$$

ν	OH frequency in Hz
ν_1	frequency of monomer in Hz
ν_i	frequency of polymer in Hz.

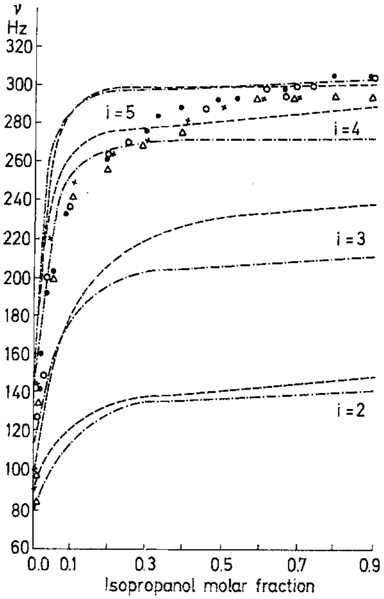

Fig. 4. NMR frequency of the system isopropanol/*n*-hexane and isopropanol/*n*-heptane vs. molar fraction of isopropanol. Experimental points ○ for isopropanol/*n*-hexane and ● for isopropanol/*n*-heptane.

$\nu = \frac{\nu_1 x_1 + i\nu_i K_{1i} x_1^i}{x_1 + i K_{1i} x_1^i}$, ——— for isopropanol/*n*-hexane and —.—.—.— for isopropanol/*n*-heptane

$\nu = \frac{\nu_1 x_1 + 2\nu_2 K_{12} x_2^2 + \ldots . 4\nu_4 K_{14} x_1^4}{x_1 + 2K_{12} x_1^2 + \ldots 4K_{14} x^4}$ for the region $x = 0.01–0.4$, × for ispropanol/*n*-hexane and Δ for isopropanol/*n*-heptane

$$\nu = \frac{\nu_1 x_1 + 2\nu_2 K_{12} x_1^2 + \ldots 5\nu_5 K_{15} x_1^5}{x_1 + 2K_{12} x_1^2 + \ldots 5K_{15} x_1^5}$$

for the region $x = 0.5–1.0$, × for the isopropanol/*n*-hexane and Δ for isopropanol/*n*-heptane

For numerical applications of Eqs. (12) and (13) the abreviated versions are used

$$\nu = \frac{\nu_1 x_1 + i\nu_i K_{1,i} x_1^i}{x_1 + i K_{1,i} x_1} \tag{14}$$

$$x = x_1 + i k_{1,i} x_i^i \cong \frac{x_1}{(1 - K_{1,2} x_1)^2} \tag{15}$$

The second Eq. (15) gives another possibility to evaluate x_1 for every x with $K_{1,2} = 7.7$ for the system with n-hexane and $K_{1,2} = 7.2$ for the system with n-heptane.

Introduction of these x_1 values in Eq. (14) and (15) allows to find tentative values for every couple ν_i, $K_{1,i}$, for instance ν_3, $K_{1,3}$; ν_4, $K_{1,4}$, so as to obtain the measured ν in the left side of Eq. (14).

The values obtained are:

Isopropanol/n-Hexane		Isopropanol/n-Heptane	
$\nu_2 = 204$ Hz	$K_{1,2} = 7.7$	$\nu_2 = 202$ Hz	$K_{1,2} = 7.2$
$\nu_3 = 234$ Hz	$K_{1,3} = 409$	$\nu_3 = 234$ Hz	$K_{1,3} = 322$
$\nu_4 = 284$ Hz	$K_{1,4} = 23869$	$\nu_4 = 278$ Hz	$K_{1,4} = 16559$
$\nu_5 = 300$ Hz	$K_{1,5} = 1316872$	$\nu_5 = 300$ Hz	$K_{1,5} = 1024025$

These ν_i values are substituted in Eq. (12) which should reproduce the measured ν values.

Furthermore, values for K_{23} and K_{34} can be calculated following *Hoffmann*[4] for instance $K_{1,2} \cdot K_{2,3} = K_{1,3}$ yielding accordingly $K_{23} = 53$, $K_{34} = 58$ for the system isopropanol/n-hexane and $K_{23} = 45$, $K_{34} = 58$ for the system isopropanol/n-heptane in molar fraction units, in good agreement with those calculated by infrared data.

Fig. 4 shows our NMR spectra and the calculated ν values. From this graph the preponderance of the tetramer conglomerate in the diluted concentration interval is evident as is known from Part I of this work[1]. In addition this finding also legitimates our way to calculate Eq. (2) where we considered only the tetrameric conglomerate as a starting assumption.

We feel most grateful to Prof. *Tohá* and Dr. *Henríquez* for kindly taking the NMR spectra for us.

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