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Thermodynamics of the Isopropanol/*n*-Hexane and Isopropanol/*n*-Heptane Systems. Part I. Infrared Studies

Sonia Martínez and **José Edwards***

Facultad de Ciencias, Universidad de Chile, Santiago, Chile

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The association equilibria for different conglomerates are calculated for the isopropanol/*n*-Hexane, isopropanol/*n*-Heptane systems from the infrared spectra.

(Keywords: Association constants; Isopropanol/n-heptane; Isopropanol/n-hexane)

Zur Thermodynamik des Isopropanol/n-Hexan und Isopropanol/n-Heptan Systems, I. Untersuchungen mittels IR-Spektroskopie

Es werden die Assoziationsgleichgewichte für verschiedene Konglomerate im Isopropanol/*n*-Hexan- bzw. -/*n*-Heptan-System aus den IR-Spektren abgeleitet.

Introduction

By measuring vapour pressures of the binary systems isopropanol/*n*-hexane and isopropanol/*n*-heptane, respectively (Part III), we became interested in the association mechanism of alcohol molecules. For this reason infrared and nmr (Part II) measurements were started[1].

Experimental

n-Hexane and *n*-heptane from Phillips Petroleum Co. and isopropanol from Merck were carefully purified and dried; the samples were prepared by weight.

IR spectra were taken with a Perkin-Elmer 621 instrument at a temperature of 30 ± 1 °C.

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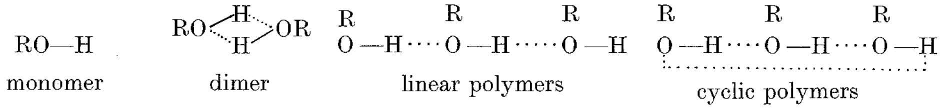
Method

The infrared spectra of isopropanol in *n*-hexane and *n*-heptane show for a specific composition of the mixture various absorption bands each characteristic for a definite alcohol polymeric conglomerate[2–6].

Accepting that these mixtures are ideally associated in the *Prigogine* sense[7] (Part II) the following hydrogen bonds should be considered at least



The assignment of one of the above types of bond to every characteristic spectral is the basis for the determination of the polymers predominant in a given mixture of known concentration[8–10]. For an extremely dilute solution only monomers are assumed to be present. *Lambert-Beer*'s Law

$$D = \varepsilon\, C l$$

becomes

$$D_1 = \varepsilon_1 C l \qquad (1)^{3,4,8-12}$$

D = optical density also called absorbance
ε = coefficient of molar extinction for $C \to 0$
C = concentration
l = cell length
sub index $_1$ = monomer.

We assume now that for a polymer i Eq. (1) becomes

$$D_i = \varepsilon_i C_i l \qquad (2)$$

Substitution of Eq. (2) in the expression for the analytical concentration of the mixture

$$C = C_1 + 2\,C_2 + 3\,C_3 \,\ldots\ldots\ldots + i\,C_i \qquad (3)$$

yields

with $l = 1$

$$C = \frac{D_1}{\varepsilon_1} + 2\frac{D_2}{\varepsilon_2} \,\ldots\ldots\ldots\ldots\ldots\ldots\, i\frac{D_i}{\varepsilon_i} \qquad (4a)$$

$$C = \frac{D_1}{\varepsilon_1} + 2\left[\frac{D_{2l}}{\varepsilon_{2l}} + \frac{D_{2c}}{\varepsilon_{2c}}\right] + \,\ldots\ldots\ldots\, i\left[\frac{D_{il}}{\varepsilon_{il}} + \frac{D_{ic}}{\varepsilon_{ic}}\right] \qquad (4b)$$

D_1, D_{2l}, D_{2c}, ... D_{il}, D_{ic} are read from the spectra at each analytical concentration C; Eq. (4) allows to know the ε values, by formation of the matrix from the set of spectra taken at these different concentrations. The chosen intervals were of 0.001 molar units. These ε values are plotted against concentration and extrapolated for $C_x \to 0$ yielding the definite values for substitution in Eq. (2) and thus allowing to know C_1, C_2 ...... C_i, i.e. the concentrations of the polymer species present at a given analytical concentration C.

The law of mass action is supposed to represent equilibria between monomer and polymer, or between polymer i, j and $i—j$, with $j + k = i$

$$K_i = \frac{C_i}{(C_1)^i} \tag{5a}$$

$$K_i = \frac{C_i}{(C_j)(C_{i-j})} \tag{5b}$$

Thus allowing to calculate the different equilibrium constants K_i.

The assumption made in Eq. (2) is checked by substitution of the values obtained in Eq. (4) in the expression for the standard deviation σ.

Our method gives better results than others[11–14] as demonstrated by our σ values 0.017 and 0.012 for each of the systems in the concentration interval where only monomers and dimers are expected and $\sigma = 0.059$ and 0.08 for higher concentrations.

The coefficients of linear regression are 0.93 for the n-hexane and 0.98 for the n-heptane mixtures.

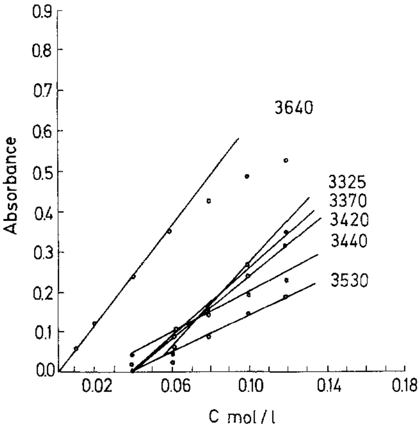


Fig. 1. Absorbance vs. concentration (mol/l) in the system isopropanol/n-hexane at 30 °C

Results and Discussion

The 3,640 cm^{-1} band is recognized as due to the absorption of monomeric alcohol molecules[8–12].

Fig. 1 shows the absorbance vs. concentration graphs for the principal bands for one of these systems; it is easy to recognize that monomeric alcohol is the predominant type present in the 0–0.06 mol/l region since at higher concentrations the slope of the straight line 3,640 cm^{-1} changes.

The procedure to assign a specific polymer conglomerate to each of the other absorption bands is to plot

$$P = \frac{\text{absorbance of polymer } i}{(\text{absorbance of monomer})^{i}}$$

for every measured concentration vs. concentration remembering that i has to be such an integer that the graph becomes a straight line; the plot of log P vs. log C gives horizontal lines, which made these tentative determinations of i easier.

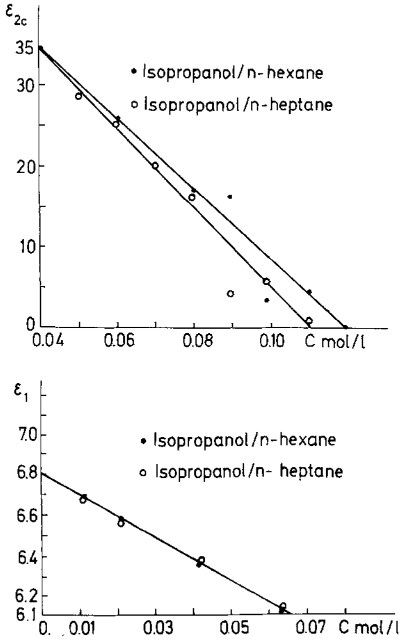


Fig. 2. Coefficient of molar extinction vs. concentration (mol/l) at 30 °C

Results are shown in Table 1.

From the spectra and Table 1 one can attempt to make a polymeric distribution for different intervals as shown in Table 2; no other polymers were detected.

Fig. 1, Table 1 or the measured spectra allow an immediate reading of the values C_i at which the values ε_i have to be extrapolated; these are $C = 0$ for the monomer and $C_i = 0.04$ mol/l for higher polymers. The ε values for higher conglomerates are shown in Table 1.

Table 1a. *Isopropanol/n-hexane system at 30 °C*

Concentration mol l^{-1}	0.00	0.01	0.02	0.04	0.06	0.08	0.10	0.12	0.17
D_{3640}		0.06702	0.13077	0.25181	0.36653	0.44370	0.50864	0.53760	0.57675
ε_1	6.79	6.7	6.56	6.33	6.05				
D_{3490}		0.001099	0.004364	0.01772	0.03662				
ε_{21}	35	32.7	32.4	28.8	26.6				
$\log D_{3490}/(D_{3640})^2$		—0.61	—0.59	—0.55	—0.57				
D_{3440}				0.048176	0.10237	0.16115	0.2076	0.23657	0.26760
ε_{2c}				35	26	17.5	0.7		
$\log D_{3440}/(D_{3640})^2$				—0.11	—0.11	—0.09	—0.10	—0.09	—0.10
D_{3420}				0.03385	0.09691	0.16997	0.28399	0.3010	
ε_{3c}				81	55	29.2	4.5		
$\log D_{3420}/(D_{3640})^3$				0.32	0.29	0.28	0.33	0.28	
D_{3530}				0.01029	0.04576	0.0995	0.15490	0.20761	
ε_{41}				257	186	111	40		
$\log D_{3530}/(D_{3640})^4$				0.40	0.40	0.40	0.36	0.40	
D_{3370}				0.01547	0.07185	0.1520	0.27572	0.35654	
ε_{4c}				246	149	42	10		
$\log D_{3370}/(D_{3640})^4$				0.58	0.60	0.61	0.61	0.63	
D_{3325}				0.008773	0.05552	0.15490	0.2581	0.36653	
ε_{5c}				308	196	140	84		
$\log D_{3325}/(D_{3640})^5$				0.93	0.92	0.91	0.86	0.91	

Table 1b. *Isopropanol/*

Concentration mol l^{-1}	0.00	0.01	0.015	0.02
D_{3640}	0.06661	0.09963	0.13077	0.25571
ε_1	6.79	6.68	6.56	6.34
D_{3490}	0.0008694	0.002117	0.003438	0.01322
ε_{21}	35	33	32.3	30.3
$\log D_{3490}/(D_{3640})^2$	—0.70	—0.67	—0.69	—0.69
D_{3450}				
ε_{2c}				
$\log D_{3450}/(D_{3640})^2$				
D_{3390}				
ε_{3c}				
$\log D_{3390}/(D_{3640})^3$				
D_{3530}				
ε_{41}				
$\log D_{3530}/(D_{3640})^4$				
D_{3370}				
ε_{4c}				
$\log D_{3370}/(D_{3640})^4$				
D_{3330}				
ε_{5c}				
$\log D_{3330}/(D_{3640})^5$				

Example for a calculation: Concentration of cyclic dimer in the system isopropanol/n-hexane.

Fig. 2 shows a plot of ε values vs. concentration in mol/l; extrapolation to $C_{2c} = 0.04$ yields $\varepsilon_{2c} = 35$; introduction of this value ε_{2c} in Eq. (2) gives a C_{2c} values for every analytical concentration (with every D value). Eq. (5a) allows to evaluate the K_{12c} value for each concentration. The concentration of the monomer was evaluated in the same way. The mean $\overline{K} = 1.0 \pm 0.1$ is taken.

The different K values are given in Table 3.

Since the law of mass action demands constant values of K for any analytical concentration we discard the existence of the reactions forming cyclic or linear tetramers from linear dimers, this is $K_{2l4c} = K_{2l4c} = 0$ because of the dispersion of the K data for different concentrations of the system.

This is also supported by forming the $K_{i-1,i}$ ratios

$$\frac{K_{13c}}{K_{12c}} = \frac{K_{12c}K_{2c3c}K_{3c4c}K_{4l4c}}{K_{13c}K_{2c3c}} = \,.....\, = q$$

yielding for $q/K_{12c} = p \simeq 7.1$ for both systems, only if no K_{2l4} values appear on the fractions.

n-heptane system of 30 °C

0.04	0.06	0.08	0.010	0.12	0.17
0.36653	0.44977	0.50364	0.52284	0.552840	0.55284
6.11					
0.02657					
26.0	20.8				
—0.70					
0.05060	0.10237	0.16749	0.20066	0.21112	0.23657
35	25.5	15	0.6		
—0.11	—0.11	—0.08	—0.11	—0.11	—0.11
0.02918	0.08618	0.17393	0.25181	0.28399	0.34679
81	52	22			
0.26	0.24	0.28	0.28	0.29	0.31
0.00966	0.04576	0.10791	0.18046	0.18709	0.21824
257	160	55			
0.41	0.40	0.42	0.43	0.40	0.36
0.01682	0.07572	0.16749	0.25571	0.26761	0.32231
246	143	47	5		
0.62	0.65	0.61	0.58	0.55	0.54
0.00966	0.06048	0.1366	0.26761	0.28391	0.38875
308	260	56			
0.94	0.96	0.88	0.87	0.87	0.97

An interesting coincidence is obtained by comparing this method to obtain K with *Hoffmann*'s method[4].

It is well kown that the K values for a specific final reaction do not give detailed information about the intermediate steps. Therefore it is possible to assume a certain machanism which just be convenient to calculate this constant for the total reaction; in this case the assumption will be made that polymers are formed starting from the monomer (even for concentrations where no monomer is present) and the K values be compared with our own method., i.e., those given in Table 3. Example:

Reaction: monomer → cyclic dimer → cyclic trimer → cyclic tetramer → cyclic pentamer

$$\text{Isopropanol}/n\text{-hexane}\ \overline{K}_{15c} = \sqrt[3]{K_{12c} \cdot K_{2c3c} \cdot K_{3c4c}\, K_{4c5c}} = 4.4$$

$$\left[\sqrt[4]{K_{15c}} = 4.5\right] \quad \text{Table 4}$$

These values for the description of the association are in good agreement with those measured by *Duboc*[12, 13], *Dunken* and *Fritzsche*[16], *Hoffmann*[4] and *Thiel*, *Becker* and *Pimentel*[15].

Table 2

Concentration mol l^{-1}	monomers	linear dimers	cyclic dimers	cyclic trimers	linear tetramers	cyclic tetramers	cyclic pentamers
0.01 -0.04	+	+	—	—	—	—	—
0.041-0.06	+	+	+	+	+	+	+
0.061-0.17	+	—	+	+	+	+	+

Table 3

System Isopropanol/*n*-Hexane			System Isopropanol/*n*-Heptane		
K_{ij}	$K^c_{ij} \pm 10\%$	$K^x_{ij} \pm 10\%$	K_{ij}	$K^c_{ij} \pm 10\%$	$K^x_{ij} \pm 10\%$
K_{12l}	0.34	2.4	K_{12l}	0.27	1.8
K_{12c}	1.0	7.7	K_{12c}	1.0	6.8
K_{2l2c}	2.8	2.8	K_{2l2c}	3.8	3.8
K_{2l3c}	21.5	161	K_{2l3c}	25.4	171
K_{2c3c}	7.4	55	K_{2c3c}	7.2	48
K_{23}	28	216	K_{23}	32	220
K_{2c4l}	21	157	K_{2c4l}	19	133
K_{2c4c}	38	285	K_{2c4c}	30	201
K_{24}	59	442	K_{24}	50	335
K_{13c}	7.5	416	K_{13c}	7.2	328
K_{3c4l}	2.7	20	K_{3c4l}	2.8	19
K_{3c4c}	4.7	35	K_{3c4c}	4.5	30
K_{34}	7.4	55	K_{34}	7.3	49
K_{35}	54	3,042	K_{35}	49	2,253
K_{14c}	37	15,614	K_{14c}	33	10,205
K_{14l}	20	8,715	K_{14l}	20	6,300
K_{14}	58	24,300	K_{14}	54	16,506
K_{4l4c}	1.6	1.6	K_{4l4c}	1.5	1.50
K_{4c4l}	0.6	0.6	K_{4c4l}	0.67	0.67
K_{4l5c}	18	137	K_{4l5c}	16	110
K_{4c5c}	11	85	K_{4c5c}	12	80
K_{45}	29	222	K_{45}	28	191
K_{15c}	415	1,292,202	K_{15c}	409	839,346

ij formation of conglomerate *j* from *i*, for instance; 34 formation of tetramers from trimers (total); 3*c*4*c* formation of cyclic tetramers from cyclic trimers; K^c association constant in mol/l concentration units; K^x association constant in molar fraction units.

Energy and Hydrogen Bridge. At concentrations higher than 0.04 mol/l several polymeric alcoholic conglomerates are present. The individual alcohol molecules are associated via hydrogen bonds. The enthalpy ΔH_i engaged in these hydrogen bonds for every conglomerate is proportional to the frequency difference (ν_m—ν_i) between the absorption band of the polymer and the monomer.

ΔH_i Enthalpy engaged in hydrogen bonds for a polymer $i = k(\nu_m - \nu_i)$ cal/mol

ν_m frequency of the monomer absorption band

ν_i frequency of the polymer i absorption band

k proportionality constant.

Introduction of this value ΔH_i in the law of mass action

Table 4a. *Isopropanol/n-hexane system at 30 °C*

Hydrogen Bond Type i	K_{ij}	$-\Delta H_i \pm 10\% \frac{\text{cal}}{\text{mol}}$	$-\Delta S_i \pm 10\% \frac{\text{cal}}{\text{mol}}$	$-\Delta G_i \pm 10\% \frac{\text{cal}}{\text{mol}}$
Linear tetramers		1 (3783)		
Linear dimers	K_{12l}	2 (2583)	16	543
Cyclic dimers	K_{12c}	2 (3443)	19	1235
Cyclic trimers	K_{13c}	3 (2525)	13	3633
Cyclic tetramers	K_{14c}	4 (2324)	12	5817
Cyclic pentamers	K_{15c}	5 (2169)	8	8477
$A_{2l} \rightarrow A_{2c}$	K_{2l2c}	1 (3012)	8	621
$A_{4l} \rightarrow A_{4c}$	K_{4l4c}	1 (3054)	9	306
$A_{2l} + A_1 \rightarrow A_{3c}$	K_{2l3c}	2 (3332)	12	3062
$A_{2c} + A_1 \rightarrow A_{3c}$	K_{2c3c}	2 (2982)	12	2417
$A_{3c} + A_1 \rightarrow A_{4c}$	K_{3c4c}	2 (2433)	8	2417
$A_{3c} + A_1 \rightarrow A_{4l}$	K_{3c4l}	2 (3154)	15	1807
$A_{4c} + A_1 \rightarrow A_{5c}$	K_{4c5c}	2 (2245)	6	2608
$A_{4l} + A_1 \rightarrow A_{5c}$	K_{4l5c}	2 (3054)	11	2966
$A_{2c} + A_{2c} \rightarrow A_{4l}$	K_{2c4l}	2 (3613)	10	4259
$A_{2c} + A_{2c} \rightarrow A_{4c}$	K_{2c4c}	2 (2882)	4	4619

Table 4b. *Isopropanol/n-heptane system at 30 °C*

Hydrogen Bond Type i	K_{ij}	$-\Delta H_i \pm 10\% \frac{\text{cal}}{\text{mol}}$	$-\Delta S_i \pm 10\% \frac{\text{cal}}{\text{mol}}$	$-\Delta G_i \pm 10\% \frac{\text{cal}}{\text{mol}}$
Linear tetramers		1 (3788)		
Linear dimers	K_{12l}	2 (2583)	16	361
Cyclic dimers	K_{12c}	2 (3271)	18	1158
Cyclic trimers	K_{13c}	3 (2869)	17	3491
Cyclic tetramers	K_{14c}	4 (2324)	13	5561
Cyclic pentamers	K_{15c}	5 (2135)	8	8217
$A_{2l} \rightarrow A_{2c}$	K_{2l2c}	1 (2921)	7	804
$A_{4l} \rightarrow A_{4c}$	K_{4l4c}	1 (3054)	9	244
$A_{2l} + A_1 \rightarrow A_{3c}$	K_{2l3c}	2 (3326)	12	3099
$A_{2c} + A_1 \rightarrow A_{3c}$	K_{2c3c}	2 (3068)	13	2340
$A_{3c} + A_1 \rightarrow A_{4c}$	K_{3c4c}	2 (3068)	13	2354
$A_{3c} + A_1 \rightarrow A_{4l}$	K_{3c4l}	2 (3326)	10	1777
$A_{4c} + A_1 \rightarrow A_{5c}$	K_{4c5c}	2 (2228)	6	2655
$A_{4l} + A_1 \rightarrow A_{5c}$	K_{4l5c}	2 (2959)	13	2833
$A_{2c} + A_{2c} \rightarrow A_{4l}$	K_{2c4l}	2 (3611)	10	4101
$A_{2c} + A_{2c} \rightarrow A_{4c}$	K_{2c4c}	2 (2795)	4	4349

$$\ln K_i = -\frac{\Delta H_i}{RT} + \frac{\Delta S}{R}$$

yields, for the formation of a polymer i from a monomer

$$\ln K_i = -k\frac{(\nu_m - \nu_i)}{RT} + \frac{\Delta S}{R} \tag{6a}$$

or

$$\ln K_j = -k\frac{\dfrac{(\nu_m - \nu_i)}{i} + \dfrac{(\nu_m - \nu_i)}{j}}{RT} + \frac{\Delta S}{R} \tag{6b}$$

if j formed from i.

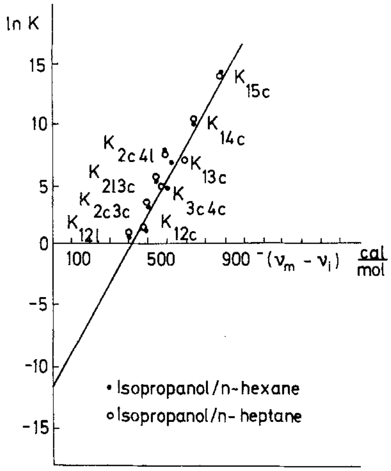


Fig. 3. Equilibrium constants for the different alcohol conglomerates vs. $(\nu_m - \nu_i)$ cal/mol at 30 °C

Equations (6a) and (6b) are straight lines in a plot of ln K vs. $\Delta\nu$ and therefore k and $\frac{\Delta S}{R}$ are evaluated graphically. The values obtained for both systems are $k = -12.04$ and $\frac{\Delta S}{R} = -11.5$ (Fig. 3).

It is now possible to obtain an average numerical value of ΔH_i, the enthalpy of one hydrogen bridge for every different polymeric species present, directly from Eq. (6a) and Eq. (6b). The K values of the left

Table 5. *ΔS and ΔH evaluated*

Compound	Refs.	K_{li}^{m}	$(\nu_m - \nu_i)\frac{\text{cal}}{\text{mol}}$	k
Methanol	9	$K_{12} = 3.2$	371.57	18.1
in CCl_4				
30 °C	13	$K_{14} = 244512.34$	857.48	
Ethanol	11, 13	$K_{12} = 1.4$	385.86	19.28
in CCl_4				
30 °C	11, 13	$K_{14} = 48262.98$	771.73	
n-Propanol	3, 13	$K_{14} = 12.89$	428.74	18.68
in CCl_4				
30 °C	13	$K_{14} = 57644.31$	857.48	
Isopropanol	13	$K_{12} = 11.39$	500.14	11.25
in CCl_4	11	$K_{13} = 243$		
30 °C	13	$K_{14} = 32778.13$	857.48	
n-Butanol	20	$K_{12} = 11.21$	428.74	13.25
in CCl_4				
30 °C	13	$K_{14} = 54253.27$	857.48	
t-Butanol	16, 22	$K_{12} = 5.5$	340.13	17.65
in CCl_4	16, 22	$K_{13} = 22.9$	383.0	
55 °C	16, 22	$K_{14} = 565140$	771.73	
t-Butanol	20, 22	$K_{12} = 6.0$	340.13	14.56
in CCl_4				
20 °C	20, 22	$K_{14} = 86014.35$	771.73	
t-Butanol in	20, 22	$K_{12} = 5.36$	340.13	12.05
cyclo Hexane	20, 22	$K_{14} = 24900$	771.73	
27 °C				
Phenol	11, 22	$K_{12} = 19.47$	338.73	19.17
in CCl_4	11, 22	$K_{13} = 1866.3$	771.73	
30 °C	11, 22	$K_{14} = 51879.88$	794.6	

side of these equations are those calculated in the former section. Table 4 shows values of the enthalpy for the hydrogen bridge calculated from the above formulas taking different types of conglomerates which are in accordance with the accepted values of approx. 3,000 cal/mol. As for the physical meaning of $\Delta S = -22.7$ cal/mol we come to discuss it later.

The method explained above has been applied to data taken by other authors. Table 5 lists literature systems and their authors, their calculated values as well as our calculations by this method with their measurements for thermodynamic functions.

by our method with literature data

$\frac{\Delta S}{R}$	$-\Delta H_i \pm 10\% \frac{\text{cal}}{\text{mol}}$	$-\Delta S \pm 10\% \frac{\text{cal}}{\text{mol}}$	$-\Delta H \frac{\text{cal}}{\text{mol}}$	$-\Delta S \frac{\text{cal}}{\text{mol}}$	Refs.
9	2 (3362)	20	2 (4600 ± 1200)	18 ± 8	9
	4 (3880)	27			
11	2 (3719)	24	2 (3600 ± 800)	20 ± 5	9
			2 (3400)	16.57	18
	4 (3820)	29	4 (2480)	20.36	18
9	2 (4004)	21.5	2 (5800)	—	19
	4 (4004)	31			
6	2 (2813)	14	1 (4000) gas	16	17
	4 (2358)	10.5	1 (2324)	11.48	17
7	2 (2840)	14	2 (3000)	15	21
	4 (2810)	16		15	
7	2 (3003)	15	2 (2400 ± 600)	11 ± 2.75	9
	3 (2253)	15			
	4 (3405)	16			
6	2 (2476)	13.5	2 (2400 ± 600)	11 ± 2.75	9
	2 (2809)	16			
5	2 (2049)	10			
	4 (2324)	11	4 (3850)	11	20
14	2 (3863)	26	1 (4350)	13.1	23
	3 (5111)	36			
	4 (3947)	31			

Discussion

The Cyclic Conglomerate

From *van't Hoff*'s equation and assuming $\Delta H_{ic(i+1)c} = \Delta H_{(i-1)cic}$ we obtain

$$\frac{K_{1(i+1)c}}{K_{1ic}} = \exp \frac{1}{R} \left(\Delta S_{1(i+1)c} - \Delta S_{1ic}\right) = q$$

Table 3 allows the calculation of $R \ln q = 7.8 \pm 2.5$ from the ratio of the K values; the graphic determination is shown in Fig. 4 by plotting the straight line

$$\Delta S_{ic} = —(\Delta S_{(i+1)c} — \Delta S_{ic})\,(i — 1) + \Delta S_1 \tag{7}$$

with data taken from Table 4 yielding the slope

$$R \ln q = 5.4 \text{ and } \Delta S_1 = 20.8\,\text{cal/mol},$$

as intercept with the ordinate, which compares well with our previous value of $\Delta S_1 = —22.4$ cal/mol as entropy difference between the pure and the dissolved isopropanol monomer at 30 °C; intersection with the abscissa axis leads to $5 < i_c < 6$, this is cyclic pentamers and hexamers are the most abundant conglomerates; besides $S_{5c6c} = 0$ no formation of cyclic hexamers from cyclic pentamers are possible; this assumption might also be checked by substitution of the values of Table 4 in *van't Hoff*'s equation, yielding in molar fraction units

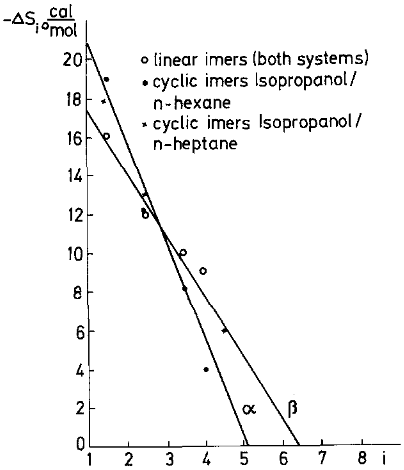


Fig. 4. $—\Delta S_i$ vs. i for the systems isopropanol/n-hexane and isopropanol/n-heptane; the curves for the cyclic i-mers and for the linear i-mers are represented

$$K_{4c5c} = 85.5 \quad K_{5c6c} = 2.5 \cdot 10^{-2} \quad K_{6c7c} = 2.5 \cdot 10^{-3}$$

Determination of the Entropy Function

We assume that the entropy of an alcohol conglomerate in the concentration interval of our interest is

$$S(i) = ai^2 + bi + c$$

$$= S(i_0) + S'(i_0)(i - i_0) + \frac{S''(i_0)}{2!}(i - i_0)^2 + R(i).$$

If we identify

$$S'(i) = 2ai + b = -(\Delta S_{(i+1)} - \Delta S_i)(i - 1) + \Delta S_1$$

a straight line and

$$S''(i) = 2a = -\Delta S_{(i+1)c} - \overline{\Delta} S_{ic} = 5.4$$

graphic determination of the slope in Fig. 4 we obtain the general expression for the entropy of a cyclic imer

$$S(ic) = -\frac{1}{2}[\Delta S_{(i+1)c} - \Delta S_{ic}]i^2 + [\Delta S_{(i+1)c} - \Delta S_{ic} + \Delta S_1]i + C \tag{8}$$

The value of C is given by the condition that for any cyclic polymer not present in the solution the entropy $S(ic) = 0$, this is

$$C = -\Delta S_1 = 20.8 \text{ cal/mol}$$

and Eq. (8) becomes

$$S(i_c) = -2.5\, i^2 + 25.8\, i + 20.8 \tag{9a}$$

as entropy of a cyclic isopropilic conglomerate present in our systems at 30 °C. If the slope of the line in Eq. (7) is taken as 7.8, Eq. (9a) changes to

$$S(ic) = -3.8\, i^2 + 28.5\, i + 20.8 \tag{9b}$$

which shows a 0.5% discrepancy for the monomer's entropy calculated by Eq. (9a).

The value for the entropy of monomeric isopropanol diluted in *n*-heptane or *n*-hexane at 30 °C is given by making $i = 1$ in Eq. (9a) and amounts $S_1 = 44.1$ cal/°mol showing a 2.5% difference with $S_1 = 43.04$ cal/°mol given by *Kelley*[24] for isopropanol at 25 °C.

Eq. (9) might also be expressed as a function of q or p which in certain cases will be easier for numerical calculations, leading to

$$S(ic) = -\frac{1}{2}(R \ln q)i^2 + (R \ln q + \Delta S_1)i + \Delta S_1$$

$$= -\frac{1}{2}(R \ln pK_{12c})i^2 + (R \ln pK_{12c} + \Delta S_1)i + \Delta S_1$$

The entropy $S(i_c)$ as a function of different i values is represented in Fig. 5 for these systems; $S(i_c)$ shows a maximum for $5 < i_c < 6$ which shows graphically that cyclic pentamers and hexamers are the most probable conglomerates for our mixture, as was pointed before. From the spectra we found the cyclic tetramer as the most probable conglomerate bur our IR measurements could only be taken in the 0-0.2 molar fraction interval.

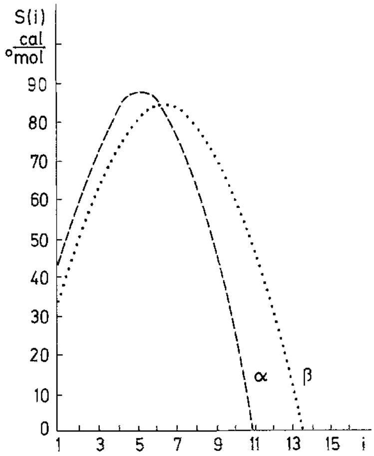


Fig. 5. $S(i)$ vs. i according to Eq. (9a) and (9c) for the systems isopropanol/n-hexane and isopropanol/n-heptane; α curve for the cyclic i-mers.; β for the linear i-mers

This interpretation is only valid for the cyclic type of association.

From Fig. 5 it is also clear that the highest existent cyclic conglomerate is $i = 11$, which is not far from the value given by *Biais* for the system triethylcarbinol/carbon tetrachloride[25].

The Linear Conglomerates

The value for the entropy of linear conglomerates might also be known in principle by the same method used to evaluate this function for the cyclic ones; taking the values of $\Delta S(i_l)$ for those reactions involving linear polymers from Table 4, a graph $-\Delta S(i_l)$ vs. i gives again a straight line as shown in Fig. 4, line β, and allows the determination of the slope 3.2 and the intersection of 17.8 cal/°mol with the ordinate. The final expression for the entropy of a linear aggregate is

$$S(i_l) = -1.6\, i^2 + 21\, i + 7.8 \qquad (9c)$$

and is represented in Fig. 4 for different i values.

The highest existent linear polymer appears to be $i_l = 14$ and the most abundant linear conglomerate the heptamers.

Huffmann[26] gave an equation to calculate the entropy of paraffins; our modification allowing the calculation of the entropy for different polymeric alcohols

$$(Si)_{298\,\mathrm{K}} = -4\,i^2 + 7.6\,(j+k)i + 19 - 4.4\,l \qquad (10)$$

i *i*mer
j carbon atoms in the linear chain
k OH atoms in the molecule
l carbon atoms in the lateral chain

is compared with measured values and those calculated by Eq. (10) in Table 5 for several systems.

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