Thermochimica Acta, 176 (1991) 305-320
Elsevier Science Publishers B.V., Amsterdam

STUDY OF THE ASSOCIATION OF DIFFERENT *n*-ALKANOLS IN *n*-ALKANES USING INFRARED SPECTROSCOPY *

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(Received 25 August 1989; in final form 1 June 1990)

ABSTRACT

The infrared (IR) spectra of *n*-alkanol–*n*-alkane systems at various concentrations are studied at different temperatures. By using the continuous chain association model, the association equilibrium constants are calculated. The $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values of association are also calculated and the molecular interactions discussed.

INTRODUCTION

The association of alcohol in alkane has been studied by using spectroscopic and thermodynamic methods, and some association models have been proposed [1-4].

In this paper, the dependence of the association of *n*-alcohol–*n*-alkane systems on the chain length of the molecules of *n*-alcohols and/or *n*-alkanes is studied by using infrared (IR) spectra. Some contradictions were found between these results and those of earlier studies. Sjöblom and Lilieström [5] proposed, from their experimental data on viscosity and dielectric constants, that long-chain alcohols tend to linear association whereas short-chain alcohols prefer cyclic association. However, Wilson et al. [6] concluded, from IR spectra, that the association of alcohols in alkanes is independent of the number of carbon atoms in both alcohols and alkanes.

EXPERIMENTAL

All commercial reagents, except *n*-hexane (AR) and *n*-hexadecanol ($\geqslant$ 98%), were further purified, by methods described earlier [7,8], and stored over 4-Å molecular sieves before use. The refractive index values, density

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* Paper presented at the International Conference on Chemical Thermodynamics and Calorimetry, Beijing, China, 25-28 August 1989.

TABLE 1

Refractive index values, density values and water content of the reagents used

Reagent	Refractive index		Density ($g\ cm^{-3}$) (25 °C)		Water content (p.p.m.)
	Experimental value	Literature value [9,10]	Experimental value	Literature value [10]	
n-Butyl alcohol	1.3973 (25 °C)	1.3971 (25 °C)	0.8056	0.8060	15.4
n-Hexyl alcohol	1.4157 (25 °C)	1.4161 (25 °C)	0.8157	0.8162	18.7
n-Octanol	1.4268 (25 °C)	1.4275 (25 °C)	0.8216	0.8221	25.2
n-Decanol	1.4348 (25 °C)	1.4345 (25 °C)	0.8263	0.8263	32.0
n-Hexane	1.3758 (20 °C)	1.3749 (20 °C)	0.65481	0.65481	29.3
n-Octane	1.3979 (20 °C)	1.3974 (20 °C)	0.69887	0.69849	
n-Decane	1.4096 (20 °C)	1.4102 (20 °C)	0.72651	0.72625	
n-Dodecane	1.4195 (20 °C)	1.4216 (20 °C)	0.74521	0.74516	
n-Hexadecane	1.4325 (25 °C)	1.4325 (25 °C)	0.77023	0.76996	11.4

values and water content of the purified reagents are listed in Table 1. It can be seen that the values of refractive index and density of the reagents are in good agreement with those given in the literature. A Microlab™ 600 (Beckman) IR spectrometer was used for this study. The width of the sample cell (l) was 0.52 mm.

The IR spectra of the following *n*-alkanol–*n*-alkane systems have been determined at various temperatures:

n-C_6H_{14}–n-C_4H_9OH, –n-$C_6H_{13}OH$, –n-$C_8H_{17}OH$, –n-$C_{10}H_{21}OH$, –n-$C_{12}H_{25}OH$, –n-$C_{16}H_{33}OH$;
n-C_8H_{18}–n-$C_6H_{13}OH$, –n-$C_{10}H_{21}OH$, –n-$C_{16}H_{33}OH$;
n-$C_8H_{17}OH$–n-C_8H_{18}, –n-$C_{10}H_{22}$, –n-$C_{12}H_{26}$, –n-$C_{16}H_{34}$;
n-$C_6H_{13}OH$–n-$C_{10}H_{22}$, –CCl_4.

The mole fraction of the free hydroxyl group (α) for each system at various concentrations of *n*-alkanol have been calculated from the equation

$$\alpha = \epsilon/\epsilon^{o} \tag{1}$$

where ϵ is the apparent molar absorption coefficient of the free hydroxyl group and is defined by

$$\epsilon = A_{max}/(lC_o) \tag{2}$$

where A_{max} is the maximum absorbance of free hydroxyl, C_o is the concentration of alcohol in alkane (mol l^{-1}), and l is the width of the sample cell. $\epsilon^{o} = A_{max}/(lC_1)$ is the molar absorption coefficient of alcohol of infinite dilution, and C_1 is the concentration of monomer.

In this paper, it is assumed that the absorption of free OH at the end of a linear polymer alcohol is at about 3645 cm^{-1} [6] and has the same molar

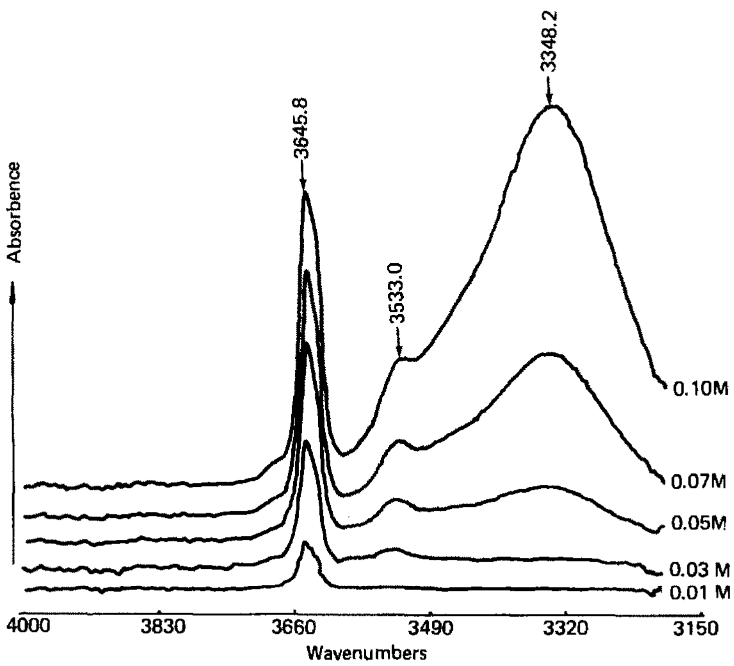

Fig. 1. IR spectra of *n*-hexanol in *n*-hexane of various concentrations at 21.5 ° C.

extinction coefficient as for the alcohol monomer. Figure 1 shows the IR absorption spectra of *n*-hexanol in *n*-hexane at 21.5 ° C.

RESULTS

The results of the IR spectra determinations are shown in Tables 2–11. In all these tables, C_0 is expressed in mol l^{-1} (or M), ϵ is in l mol^{-1} cm^{-1}, and T is in degrees Celsius.

DISCUSSION

From the experimental $\alpha - C_0$ data the association constants have been calculated according to the above-mentioned models. However, only those calculated from the continuous chain association model [2,3] are constant at various concentrations. In this model it is assumed that the associated chain-like complexes are formed by successive reactions of the type

$$(ROH)_i + ROH \rightleftharpoons (ROH)_{i+1}, \quad i = 1, 2, 3, 4\ldots \qquad (3)$$

and the association equilibrium constant for the above equilibrium reaction is independent of i.

TABLE 2

IR data for various *n*-alkanol–*n*-hexane systems at about 25 °C

System	T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
n-Butanol–*n*-hexane	23	0.0107	0.024	43.5	0.881	49.4	7.53
		0.0198	0.039	38.3	0.775		
		0.0308	0.056	35.0	0.709		
		0.0515	0.077	28.6	0.579		
		0.0989	0.115	22.3	0.451		
		0.1524	0.140	17.6	0.356		
		0.1978	0.148	14.4	0.291		
		0.4928	0.208	8.12	0.164		
n-Hexanol–*n*-hexane	27	0.0103	0.0254	47.4	0.898	52.8	6.46
		0.0157	0.0360	44.1	0.835		
		0.0344	0.0659	36.8	0.697		
		0.0505	0.0855	32.6	0.617		
		0.0753	0.114	29.0	0.549		
		0.1049	0.136	24.9	0.472		
		0.1485	0.161	20.8	0.394		
		0.2004	0.179	17.2	0.326		
n-Octanol–*n*-hexane	28	0.0123	0.031	48.7	0.856	56.9	7.19
		0.0208	0.048	44.9	0.789		
		0.0489	0.087	34.3	0.603		
		0.0673	0.108	30.8	0.541		
		0.0995	0.134	26.0	0.457		
		0.1494	0.164	21.2	0.373		
		0.2444	0.196	15.4	0.271		
n-Decanol–*n*-hexane	27	0.0158	0.0361	44.0	0.839	52.4	6.12
		0.0391	0.0742	36.5	0.696		
		0.0642	0.104	31.1	0.573		
		0.0699	0.109	30.1	0.574		
		0.0993	0.133	25.8	0.492		
		0.150	0.162	20.8	0.397		
		0.207	0.189	17.5	0.334		
n-Hexadecanol–*n*-hexane	25	0.0107	0.0253	45.5	0.892	51.1	6.15
		0.0162	0.0367	43.6	0.853		
		0.0211	0.0443	40.3	0.789		
		0.0315	0.0608	37.1	0.726		
		0.0509	0.0863	32.6	0.638		
		0.0689	0.106	29.3	0.573		
		0.1004	0.131	25.0	0.489		
		0.1513	0.159	20.3	0.397		
		0.2000	0.180	17.3	0.339		

TABLE 3

IR data for *n*-Hexanol–*n*-decane and *n*-hexanol–carbon tetrachloride at about 25 °C

System	T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
n-Hexanol–*n*-decane	27	0.0163	0.0358	42.1	0.854	49.4	5.17
		0.0233	0.0481	39.7	0.803		
		0.0302	0.0604	38.5	0.779		
		0.0500	0.0872	33.5	0.678		
		0.0703	0.111	30.3	0.613		
		0.0985	0.136	26.5	0.536		
		0.1453	0.166	22.0	0.44		
		0.1973	0.192	18.7	0.378		
		0.2927	0.223	14.7	0.297		
n-Hexanol–carbon tetrachloride	25	0.0203	0.0607	57.4	0.891	64.4	2.69
		0.0293	0.0867	57.0	0.885		
		0.0518	0.136	50.6	0.786		
		0.0677	0.168	47.6	0.739		
		0.0994	0.227	44.0	0.683		
		0.1963	0.347	34.0	0.528		
		0.3104	0.435	26.9	0.418		

Mecke and Kempter [11] derived a formula for calculation of the association constant K_c as follows:

$$K_c = \frac{1-\sqrt{\alpha}}{C_o\alpha} = \frac{1-\sqrt{\epsilon/\epsilon^o}}{C_o\sqrt{\epsilon/\epsilon^o}} \tag{4}$$

where K_c is the equilibrium constant expressed by molarity concentration of

TABLE 4

IR data for *n*-hexanol–*n*-dodecane, –*n*-hexadecane systems at 35 °C

System	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
n-Hexanol–*n*-dodecane	0.0667	0.111	31.6	0.705	44.8	3.35
	0.0981	0.146	28.2	0.629		
	0.1516	0.192	24.0	0.535		
	0.2203	0.234	20.1	0.449		
	0.2970	0.271	17.3	0.385		
	0.3901	0.300	14.6	0.325		
n-Hexanol–*n*-hexadecane	0.0292	0.0499	32.4	0.910	35.6	1.75
	0.0501	0.0801	30.3	0.851		
	0.0679	0.105	29.2	0.820		
	0.0977	0.138	26.8	0.753		
	0.0982	0.140	27.1	0.760		

TABLE 5

IR data for *n*-hexanol–*n*-octane system

T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
35	0.0495	0.0829	31.7	0.798	39.7	2.60
	0.0991	0.143	27.3	0.687		
	0.1461	0.183	23.8	0.599		
	0.1939	0.217	21.1	0.531		
45	0.0495	0.0831	31.8	0.854	37.2	1.65
	0.0991	0.151	28.8	0.773		
	0.1461	0.202	26.2	0.704		
	0.1939	0.240	23.4	0.628		
54	0.0991	0.152	29.0	0.787	36.8	1.44
	0.1461	0.204	26.4	0.717		
	0.1939	0.251	24.5	0.665		
63	0.0991	0.148	28.3	0.826	34.3	1.08
	0.1461	0.207	26.8	0.782		
	0.1939	0.253	24.7	0.721		

TABLE 6

IR data for *n*-decanol–*n*-octane system

T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
35	0.0695	0.115	31.3	0.633	49.5	4.55
	0.0999	0.149	28.2	0.569		
	0.1486	0.182	23.2	0.468		
	0.2087	0.206	18.7	0.378		
	0.3028	0.258	16.2	0.327		
45	0.0695	0.112	30.4	0.751	40.5	2.33
	0.0999	0.154	29.3	0.722		
	0.1486	0.195	24.9	0.615		
	0.2087	0.239	21.7	0.535		
	0.3028	0.300	18.8	0.463		
54	0.0695	0.114	31.0	0.834	37.2	1.61
	0.0999	0.149	28.3	0.761		
	0.1486	0.203	25.9	0.696		
	0.2087	0.250	22.7	0.610		
	0.3028	0.328	20.5	0.551		
68	0.0695	0.109	29.6	0.899	32.9	0.944
	0.0999	0.145	27.5	0.837		
	0.1486	0.204	25.9	0.789		
	0.2087	0.262	23.8	0.723		
	0.3028	0.351	22.9	0.698		

TABLE 7

IR data for *n*-hexadecanol–*n*-octane system

T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
35	0.0501	0.0837	31.6	0.776	40.8	3.00
	0.0666	0.105	29.8	0.731		
	0.1015	0.142	26.5	0.651		
	0.1525	0.182	22.6	0.554		
	0.2167	0.222	19.4	0.477		
45	0.0501	0.0807	30.5	0.858	35.6	1.57
	0.0666	0.104	29.6	0.833		
	0.1015	0.148	27.6	0.777		
	0.1525	0.201	24.9	0.701		
	0.2167	0.251	21.9	0.616		
54	0.0501	0.0785	29.4	0.901	32.7	1.02
	0.0666	0.100	28.6	0.873		
	0.1015	0.148	27.7	0.846		
	0.1525	0.208	25.8	0.790		
	0.2167	0.263	23.0	0.703		

TABLE 8

IR data for *n*-octanol–*n*-octane system

T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
35	0.0262	0.0615	45.2	0.807	56.0	4.24
	0.0502	0.105	40.3	0.719		
	0.0796	0.148	35.9	0.640		
	0.1075	0.178	31.9	0.570		
	0.1266	0.192	29.3	0.523		
	0.1666	0.213	24.7	0.441		
45	0.0262	0.0626	46.1	0.867	53.1	2.98
	0.0502	0.107	40.9	0.710		
	0.0796	0.154	37.4	0.704		
	0.1075	0.191	34.3	0.645		
	0.1266	0.213	32.4	0.610		
	0.1666	0.240	27.8	0.523		
57	0.0262	0.0628	46.2	0.878	52.6	2.76
	0.0502	0.107	41.0	0.780		
	0.0796	0.156	37.7	0.717		
	0.1075	0.194	34.8	0.662		
	0.1266	0.214	32.6	0.620		
	0.1666	0.248	28.7	0.545		

TABLE 9

IR data for *n*-octanol–*n*-decane system

T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
35	0.0866	0.162	35.9	0.550	65.3	5.42
	0.1372	0.208	29.2	0.447		
	0.1852	0.242	25.1	0.384		
	0.2125	0.250	22.7	0.347		
	0.2486	0.272	21.1	0.323		
45	0.0866	0.166	37.0	0.622	59.5	3.87
	0.1372	0.223	31.3	0.526		
	0.1862	0.259	26.8	0.451		
	0.2125	0.286	26.0	0.436		
	0.2486	0.291	22.6	0.380		
57	0.0866	0.169	37.7	0.735	51.3	2.29
	0.1372	0.233	32.7	0.638		
	0.1862	0.277	28.6	0.559		
	0.2125	0.317	28.7	0.560		
	0.2486	0.330	25.6	0.499		
65	0.0866	0.172	38.3	0.766	49.9	1.90
	0.1372	0.240	33.7	0.675		
	0.1862	0.297	30.7	0.615		
	0.2125	0.323	29.2	0.586		
	0.2486	0.353	27.3	0.549		

alcohol. K_c may also be calculated by the following equation from the slope and intercept of the line for ϵC_o vs. $\sqrt{\epsilon}$:

$$\epsilon C_o = \frac{\epsilon^o}{K_c} - \frac{\sqrt{\epsilon^o}}{K_c}\sqrt{\epsilon} \tag{5}$$

The resulting K_c values are listed in Tables 12–16.

The ΔH^o and ΔS^o values of reaction (3) can be calculated from the slope and the intercept of the line plotted for ln K_c vs. $1/T$:

$$\ln K_c = -\frac{\Delta H^o}{R} \times \frac{1}{T} + \frac{\Delta S^o}{R} \tag{6}$$

The resulting ΔH^o and ΔS^o values are listed in Tables 17 and 18.

Table 17 shows that in *n*-octane the negative values of ΔH^o, that is, the hydrogen bond enthalpies of various *n*-alkanols, increase with chain length of *n*-alkanol molecules. Table 18 shows that the negative values of ΔH^o and the hydrogen bond enthalpies of association of *n*-octanol in various *n*-alkanes decrease with increasing *n*-alkane molecule chain length. The dissociation of the system is related to the interaction between the hydroxyl group and the *n*-alkane molecule: the interaction force increases with the *n*-alkane chain length. Therefore, less enthalpy is necessary to break the hydrogen

TABLE 10

IR data for *n*-octanol–*n*-dodecane system

T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^o	K_c
35	0.0349	0.0805	44.4	0.770	57.7	4.44
	0.0630	0.128	39.2	0.680		
	0.0919	0.157	32.8	0.569		
	0.1174	0.186	30.5	0.529		
	0.1428	0.204	27.6	0.478		
	0.1890	0.239	24.4	0.423		
45	0.0349	0.0813	44.9	0.783	57.3	3.74
	0.0630	0.133	40.7	0.710		
	0.0919	0.173	36.2	0.632		
	0.1174	0.197	32.3	0.564		
	0.1428	0.224	30.2	0.526		
	0.1890	0.252	25.7	0.448		
57	0.0349	0.0815	45.0	0.835	53.9	2.72
	0.0630	0.133	40.8	0.757		
	0.0919	0.179	37.6	0.698		
	0.1174	0.214	35.2	0.654		
	0.1428	0.232	31.3	0.582		
	0.1890	0.277	28.2	0.524		
65	0.0349	0.0826	45.6	0.880	51.9	2.15
	0.0630	0.133	40.8	0.787		
	0.0919	0.180	37.8	0.729		
	0.1174	0.218	35.8	0.691		
	0.1428	0.247	33.3	0.643		
	0.1890	0.296	30.2	0.582		

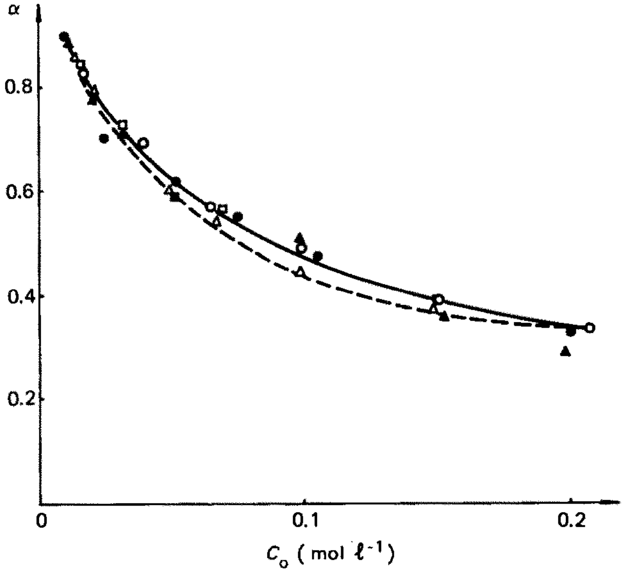

Fig. 2. *n*-Alkanol–*n*-hexane at about 25 °C. ▲, *n*-C_4H_9OH, 23 °C; ●, *n*-$C_6H_{13}OH$, 27 °C; △, *n*-$C_8H_{17}OH$, 28 °C; ○, *n*-$C_{12}H_{25}OH$, 27 °C; □, *n*-$C_{16}H_{33}OH$, 25 °C.

TABLE 11

IR data for *n*-octanol–*n*-hexadecane system

T (°C)	C_o (M)	A_{max}	ϵ	α	ϵ^0	K_c
35	0.0951	0.162	32.7	0.585	55.9	4.24
	0.1231	0.187	29.2	0.522		
	0.1439	0.206	27.6	0.494		
	0.1711	0.224	25.2	0.451		
	0.2070	0.246	22.9	0.410		
45	0.0951	0.174	35.3	0.593	59.5	4.01
	0.1231	0.207	32.3	0.543		
	0.1439	0.226	30.2	0.508		
	0.1711	0.244	27.5	0.462		
	0.2070	0.270	25.1	0.421		
57	0.0951	0.186	37.7	0.646	58.4	3.20
	0.1231	0.218	34.0	0.583		
	0.1439	0.245	32.8	0.562		
	0.1711	0.268	30.2	0.517		
	0.2070	0.294	27.4	0.469		
65	0.0951	0.190	38.4	0.730	52.6	2.04
	0.1231	0.231	36.2	0.687		
	0.1439	0.259	34.7	0.659		
	0.1711	0.290	32.7	0.620		
	0.2070	0.322	29.9	0.569		

TABLE 12

K_c of various *n*-alkanols in *n*-octane at different temperatures

T (°C)	System		
	n-C_8H_{18}– *n*-$C_6H_{13}OH$	*n*-C_8H_{18}– *n*-$C_{10}H_{21}OH$	*n*-C_8H_{18}– *n*-$C_{16}H_{33}OH$
35	2.60	4.55	3.00
45	1.65	2.33	1.57
54	1.44	1.61	1.02
68	1.08	0.944	–

TABLE 13

K_c of *n*-octanol in various *n*-alkanes at different temperatures

T(°C)	System			
	n-$C_8H_{17}OH$– *n*-C_8H_{18}	*n*-$C_8H_{17}OH$– *n*-$C_{10}H_{22}$	*n*-$C_8H_{17}OH$– *n*-$C_{12}H_{26}$	*n*-$C_8H_{17}OH$– *n*-$C_{16}H_{34}$
35	4.28	5.42	4.44	4.24
45	2.98	3.87	3.77	4.01
57	2.76	2.29	2.73	3.20
65	2.38	1.90	2.15	2.04

TABLE 14

K_c of various n-alkanols in n-hexane at about 25 °C

System	n-C_6H_{14}– n-C_4H_9OH	n-C_6H_{14}– n-$C_6H_{13}OH$	n-C_6H_{14}– n-$C_8H_{17}OH$	n-C_6H_{14}– n-$C_{10}H_{21}OH$	n-C_6H_{14}– n-$C_{16}H_{33}OH$
T (°C)	23	27	28	27	25
K_c	7.5	6.5	7.2	6.1	6.2
$K_{25°C}$ [a]	6.9	6.7	7.6	6.3	6.0

[a] $K_{25°C}$ are the association constants at 25 °C, calculated from K_c at other temperatures according to $\Delta K_c/\Delta T \doteq -0.2\ K^{-1}$ (assuming $\Delta H^o = 35$ kJ mol^{-1}).

TABLE 15

K_c of n-hexanol in various solvents at about 25 °C

	n-$C_6H_{13}OH$– n-C_6H_{14}	n-$C_6H_{13}OH$– n-C_8H_{18}	n-$C_6H_{13}OH$– n-$C_{10}H_{22}$	n-$C_6H_{13}OH$– CCl_4
T (°C)	27	27	27	25
K_c	6.5	3.5 [a]	5.2	2.7

[a] This value is obtained by extrapolation of the line for $\ln K_c$ vs. $1/T$.

TABLE 16

K_c of n-hexanol in various n-alkanes at 35 °C

	n-$C_6H_{13}OH$–n-C_8H_{18}	n-$C_6H_{13}OH$–n-$C_{12}H_{26}$	n-$C_6H_{13}OH$–n-$C_{16}H_{34}$
K_c	2.6	3.4	1.8

TABLE 17

ΔH^o and ΔS^o of association for various n-alkanols in n-C_8H_{18}

	n-$C_6H_{13}OH$– n-C_8H_{18}	n-$C_{10}H_{21}OH$– n-C_8H_{18}	n-$C_{16}H_{33}OH$– n-C_8H_{18}
ΔH^o (kJ mol^{-1})	−26.9	−41.4	−48.5
ΔS^o (J K^{-1} mol^{-1})	−79	−122	−148

TABLE 18

ΔH^o and ΔS^o of association for n-octanol in various n-alkanes

	n-Octanol– n-octane	n-Octanol– n-decane	n-Octane– n-dodecane	n-Octanol– n-hexadecane
ΔH^o (kJ mol^{-1})	−32.7	−31.4	−21.7	−11.0
ΔS^0 (J K^{-1} mol^{-1})	−90.9	−87.7	−57.5	−23.4

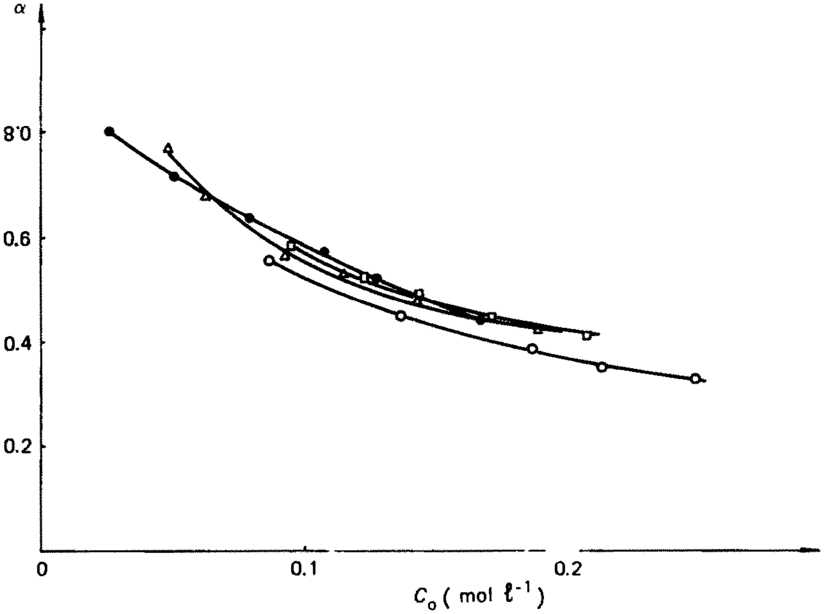

Fig. 3. *n*-Octanol–*n*-alkane at 35° C. ●, *n*-C_8H_{18}; ○, *n*-$C_{10}H_{22}$; △, *n*-$C_{12}H_{26}$, □, *n*-$C_{16}H_{34}$.

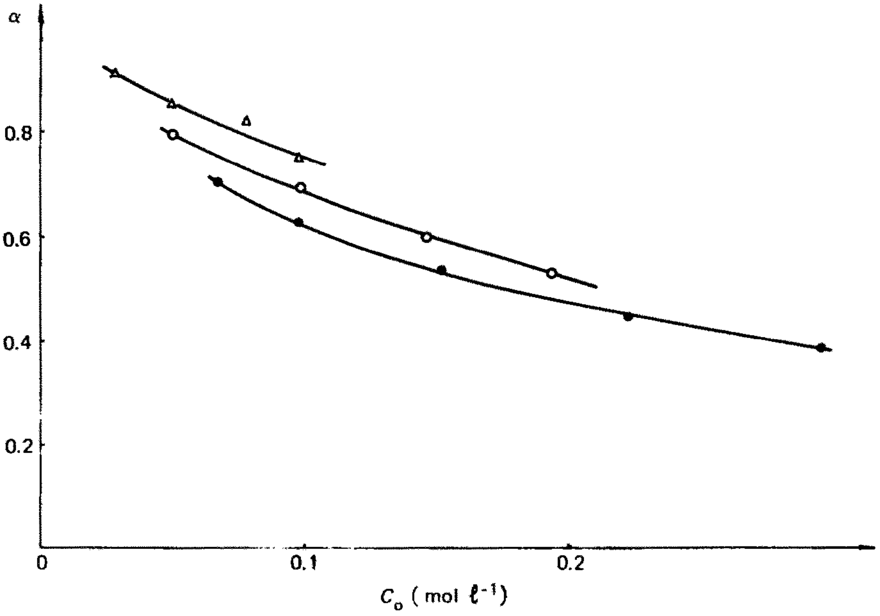

Fig. 4. *n*-$C_6H_{13}OH$–*n*-alkane at 35° C. ○, *n*-C_8H_{18}; ●, *n*-$C_{12}H_{26}$; △, *n*-$C_{16}H_{34}$.

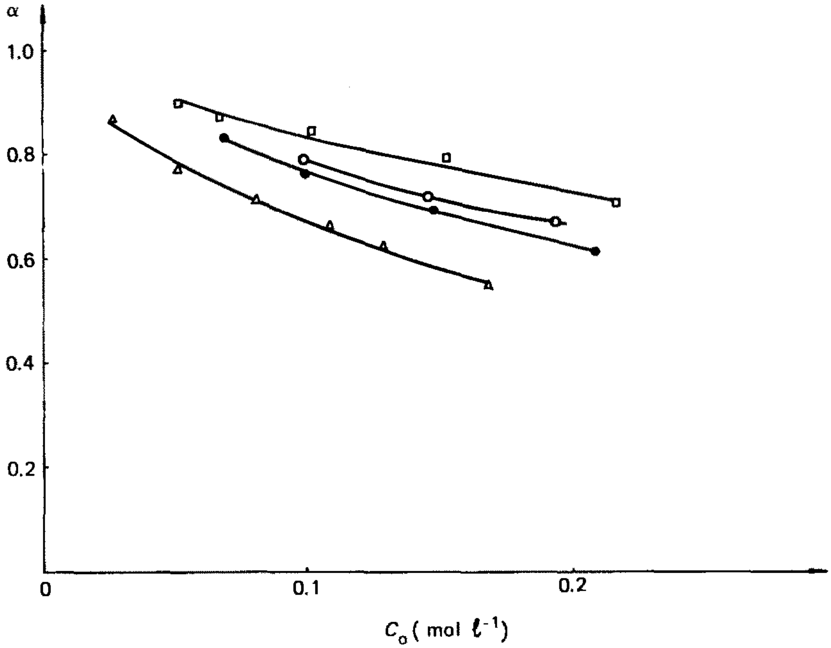

Fig. 5. *n*-Alkanol–*n*-octane at 54° C. ○, *n*-$C_6H_{13}OH$; ●, *n*-$C_{10}H_{21}OH$; □, *n*-$C_{16}H_{33}OH$; △, *n*-$C_8H_{17}OH$ (57° C).

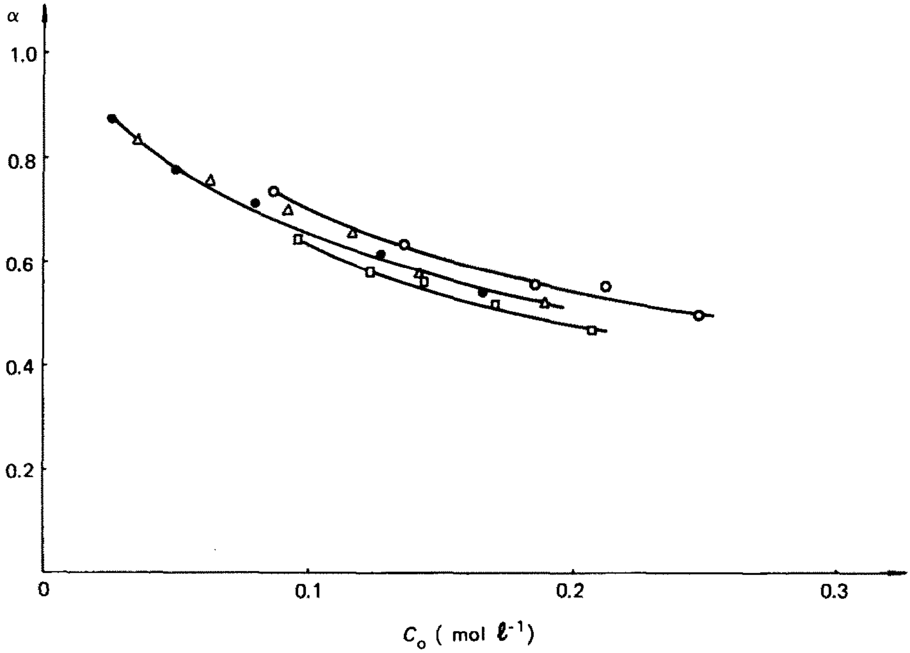

Fig. 6. *n*-Octanol–*n*-alkane at 57° C. ●, *n*-C_8H_{18}; ○, *n*-$C_{10}H_{22}$, △, *n*-$C_{12}H_{26}$; □, *n*-$C_{16}H_{34}$.

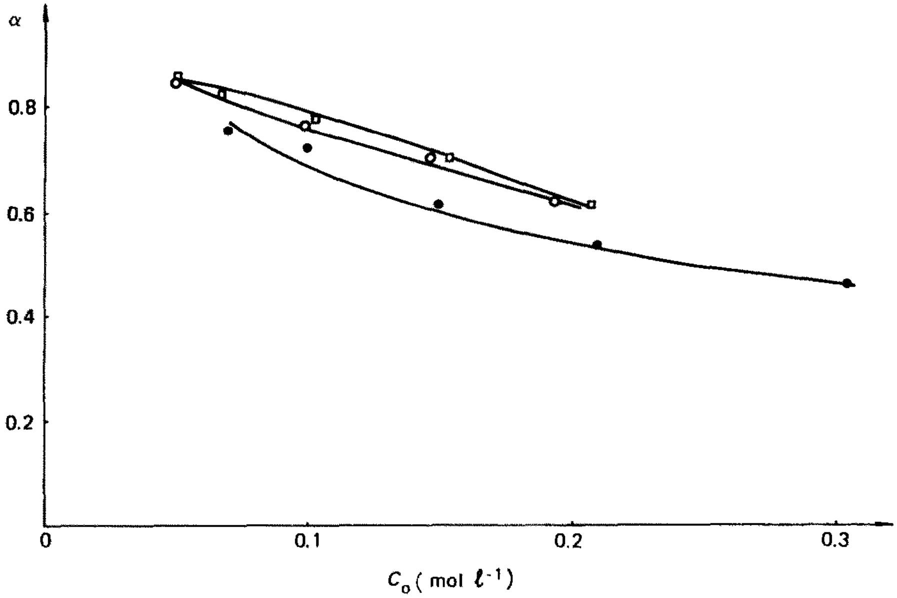

Fig. 7. *n*-Alkanol–*n*-octane at 45 °C. ○, *n*-$C_6H_{13}OH$; ●, *n*-$C_{10}H_{21}OH$; □, *n*-$C_{16}H_{33}OH$.

bond, explaining the trend of ΔH° values seen in Table 18. However, in Table 17, that is, for various *n*-alkanols in *n*-octane, the hydrogen bond enthalpies ΔH° depend mainly on the chain length of *n*-alkanol molecules.

The α–C_0 curves of various *n*-alkanols in *n*-hexane at about 25 °C are shown in Fig. 2, according to Table 2. It can be seen that α values of various *n*-alkanols in *n*-hexane are the same or very similar and therefore there are only slight differences in the K_c values for these systems (Table 14). Similar results are found for other systems studied at higher temperatures, as illustrated in Figs. 3–8 for α–C and in Tables 12–18 for K_c. If we were to plot all the α–C_0 curves on one figure, they would be concentrated in the upper part of the figure. That is to say, α, or the degree of association, and K_c are not greatly affected by the chain length of the *n*-alkanol and *n*-alkane molecules, whereas the hydrogen bond enthalpy ΔH° is affected by the chain length of both molecules. It is unreasonable to assume a different association mode for various *n*-alkanol–*n*-alkane systems as Sjöblom and Lilieström [5] did. Our results are similar to that of Wilson [6], who studied *n*-alkanol–*n*-alkane systems only at a concentration of 0.2 M.

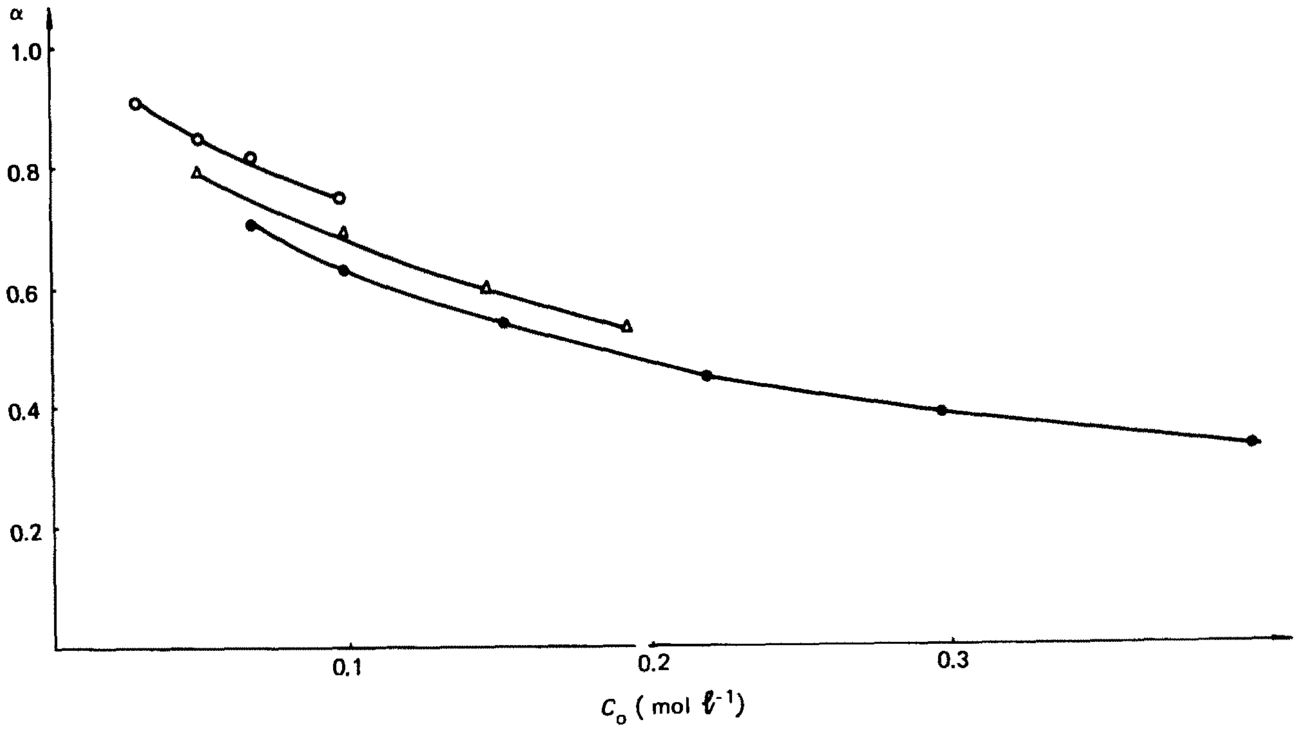

Fig. 8. *n*-Hexanol–*n*-alkane at 35° C. ○, *n*-$C_{16}H_{34}$; ●, *n*-$C_{12}H_{26}$; △, *n*-C_8H_{18}.

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