行政院國家科學委員會專題研究計畫　成果報告

以 IR 及 NMR 光譜研究氫鍵之溫度及溶劑效應

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CONTENTS

Abstract:

Two equations of linear type have been derived to analyze the IR data to determine the dimerization constant consistently. The first equation is to be used to fit the integrated absorbance of the monomer band to obtain the molar monomer absorptivity, ε_{m} , and dimerization constant,K; the second equation is to be used to fit the integrated absorbances of the dimmer bands to obtain the molar dimmer absorptivity, ε_{d} ,and dimerization constant ,K .Thus the same dimerization constant can be independently determined either from the monomer band or from the dimer band. The discrepancy between the two determined values provides an assessment of the consistency of determination. The monomer-dimer self-association of 2,2-dimethyl-3-ethyl-3-pentanol and 3-ethyl-2-methyl-3-pentanol in various solvents at different temperatures was chosen to demonstrate the utility of these two equations.

Keywords: Monomer-dimer self-association, Hindered alcohols, IR spectroscopy, van’t Hoff plot

中文摘要:

我們首先推導出適合于對自結合系統紅外線光譜數據處理的兩條線型公式. 一為處理單體吸收峯之用,以求取自結合常數及單體吸收峯係數.一為處理雙體吸收峯之用,以求取自結合常數雙體吸收峯係數.因此同一物理量自結合常數可由兩種數據獨立求出.所得值的接近度可為判定實驗做的好不好,數據可靠性的評估標準.2, 2-dimethyl-3-ethyl-3-pentanol 及 3-ethyl-2-methyl-3-pentanol 在不同的溶劑中,不同的溫度下的自結合系統作為此兩公式適用性的試金石.

關鍵詞: 單雙體自結合, 立體障礙醇, 紅外線光譜, 凡德霍夫作圖

Introduction

Association due to hydrogen bonding has drawn many attentions to chemists over a long period.[1-7] Various theoretical, and experimental means have been employed to investigate this problem. For the experimental part, nuclear magnetic resonance (NMR), infrared (IR), dielectric polarization and dispersion, neutron scattering, ultrasonic absorption, and Raman spectroscopy, etc. have been used.[1-5] Among various experimental methods, NMR and IR have been proven to be the most convenient and powerful.[1-4,7-8] We have been using NMR to study hydrogen-bonded association in several systems, including monomer-dimer self-association, $A+A \rightleftharpoons A_2$,[9-12] simultaneous existence of self-association and hetero-association, $A+A \rightleftharpoons A_2$ and $A+B \rightleftharpoons AB$, with $B+B \rightleftharpoons B_2$[13] or without $B+B \rightleftharpoons B_2$.[14,15] While in NMR spectra all signals related to hydrogen bond of different aggregates (monomer, dimer, trimer, etc.) coalesce, in IR the vibrational signals related to hydrogen bond of different aggregates appear separately due to longer IR time scale. Thus IR information provides more insight into the hydrogen bonding association. In this report we will restrict our attention to the system of monomer-dimer association, although it is quite a common occurrence to have hydrogen bonding association beyond dimer in an inert solvent. We do this because that association beyond dimer is subject to a lot of uncertainty in conjecturing what kind (dimer, trimer, etc.) and what configuration (chain or ring) of oligomers existing in the system,[16-22] which as a rule leads to erraneous results of determination. The mere monomer-dimer association can be achieved in the system of aliphatic alcohols with steric hinderance due to bulky sidechains in inert solvents.[23,24] In this report 2,2-dimethyl-3-ethyl-3-pentanol and 3-ethyl-2-methyl-3-pentanol in various solvents at different temperatures was used as an example to illustrate the usage of the newly derived equations.

Procedure to Treat the Data of the Absorbance of Monomer and Dimer Bands

In a self-associating system exhibiting monomer-dimer dynamic equilibrium

$$S_1 + S_1 \rightleftharpoons S_2 \qquad (1)$$

The mole fraction of monomer and dimer, f_m and f_d, respectively, are defined and derived to be

$$f_d = \frac{2[S_2]}{[S]_0} = \frac{(1+8K[S]_0)^{1/2} - 1}{(1+8K[S]_0)^{1/2} + 1} \qquad (2)$$

$$f_m = \frac{[S_1]}{[S]_0} = 1 - f_d = \frac{2}{(1+8K[S]_0)^{1/2} + 1} \qquad (3)$$

Where $[S_1]$, $[S_2]$ are the concentrations of monomer, dimer respectively and $[S]_0$ are their total concentration, K is the dimerization constant.

The observed integrated absorbance of the monomer band is given by

$$A_m = \int \varepsilon_m(\tilde{v})b[S_1]d\tilde{v} = (\int \varepsilon_m(\tilde{v})d\tilde{v})b[S]_0 f_m = \varepsilon_m b[S]_0 \frac{2}{(1+8K[S]_0)^{1/2}+1} \qquad (4)$$

where $\varepsilon_m (= \int \varepsilon_m(\tilde{v})d\tilde{v})$ is the molar absorptivity of the monomer band, and $\varepsilon(\tilde{\upsilon})$ is the molar absorptivity at wavelength $\tilde{\upsilon}$, b is the optical path of the cell. Equation(4) can be the transformed into a linear type of the form through some mathematical operations,

$$\frac{[S]_0}{A_m^2} = \frac{1}{(\varepsilon_m b)} \times \frac{1}{A_m} + \frac{2K}{(\varepsilon_m b)^2} \qquad (5)$$

Based on Eq. 5, a plot of $y = \frac{[S]_0}{A_m^2}$ vs. $x = \frac{1}{A_m}$ gives a straight line with a slope $p = \frac{1}{\varepsilon_m b}$ and an intercept $q = \frac{2K}{(\varepsilon_m b)^2}$. The molar absorptivity of the monomer band and the dimerization constant K thus can be obtained from the slope and intercept.

Following the line of deriving Eq. 4, the integrated absorbance of dimer band, A_d, can be obtained to be

$$A_d = \varepsilon_d b[S_2] = \varepsilon_d b[S]_0 \frac{f_d}{2} = \frac{\varepsilon_d b[S]_0}{2} \frac{(1+8K[A]_0)^{1/2}-1}{(1+8K[A]_0)^{1/2}+1} \qquad (6)$$

where ε_d is the molar absorptivity of dimer band. Again this is transformed to

$$\frac{2A_d}{[S]_0} = \varepsilon_d b - (\frac{\varepsilon_d b}{K})^{1/2} \frac{A_d^{1/2}}{[S]_0} \qquad (7)$$

Based on Eq. 7 a plot of $y = \frac{2A_d}{[S]_0}$ vs. $x = \frac{A_d^{1/2}}{[S]_0}$ gives a straight line with a slope $p = -(\frac{\varepsilon_d b}{K})^{1/2}$ and intercept q = ε_db. The molar absorptivity of the dimer band and the dimerization constant are then obtained from the slope and intercept. The central part of this report consists in Eqs. 5 and 7.

Experimental Section

The solute chemicals 2,2-dimethyl-3-ethyl-3-pentanol and 3-ethyl-2-methyl-3-pentanol and solvents were used without further purification. Concentration on molarity scale was used in plotting Eqs. (5) and (9), and reported in Table 1. All the spectra in the range of 3200 cm^{-1} – 3750 cm^{-1} were taken from an FTIR spectrometer

(Bio-Rad Spc. 3200) using CaF_2 windows of 1.0 mm optical length. The spectrometer was connected to a person computer implanted with a commercial software package PeakSolve (Galatic Industries Corp) which was used to resolve, curve-fit the overlapped bands and calculate the integrated absorbance of the monomer and dimer bands.

Results and Discussion

Typical results for this investigation are shown in Figs.1-5. Fig. 1 displays a collection of vibrational spectra of OH fundamental strechting in the range 3200 cm^{-1}–3750 cm^{-1}, for various concentrations of 2,2-dimethyl-3-ethyl-3-pentanol (DMEP) in CCl_4 at 298 K. Shown in Fig. 2 is a result from resolving and curve-fitting the overlapped spectra for 0.1167 M DEMP in CCl_4 at 298 K. The integrated absorbance of the monomer and dimer bands are respectively listed in Table 1 for each concentration of DMEP in CCl_4 at temperatures 283 K, 298 K, 313 K and 328 K. The concentration-dependent integrated absorbance of monomer band and dimer band at a given temperature were employed to obtain the absorptivities and dimerization constant via a linear plot based on Eq(5) and Eq(9) as shown in Fig. 3 and 4 respectively. The molar absorptivities of monomer and dimer band, and the dimerization constants respectively determined from monomer and dimer bands were listed in Table 2. It is seen that all the molar absorptivity of monomer band, ε_m, and that of dimer absorptivity, ε_d, decrease as temperature increases.

Once dimerization constants for different temperatures have been obtained, we use the van't hoff plot to calculate the standard enthalpy of dimerization, ΔH^o, and standard entropy of dimerization, ΔS^o, as shown in Fig. 5. Results of the study of other self-association systems have been summarized in Table3-6.

To my knowledge, only monomer bands were used to obtain the dimerization constant for most IR study of self-association. Liddle and Becker[25] used the limiting slope of a plot for apparent molar absorptivity, $\frac{A_m}{[S]_0}$ against concentration, $[S]_0$, i.e.,

$$\lim_{[S]_0 \to 0} \left(\frac{d\left(\frac{A_m}{[S]_0}\right)}{d[S]_0} \right) = -2K\varepsilon_m \tag{8}$$

Here, ε_m was obtained from extrapolating to infinite dilution. This approach may lead to erraneous results if the slope is steep. Another approach[8] is to fit the integrated absorbance of monomer band, A_m, as a function of initial concentration and dimerization constant,

$$A_m = \varepsilon_m \frac{\sqrt{1+8K[S]_0}-1}{4K_m} \tag{9}$$

using Levenberg-Marquardt nonlinear method. Both Eqs. 8 and 9 can be derived from Eq. 7. Luck[5] used a linear equation, which is also derivable from Eq. 5, to obtain the dimerization constant and molar absorptivities, ε_m, of the fundamental or overtone of the monomer band. In our notation, it reads

$$\frac{A_m}{[S]_0} = \varepsilon_m - \frac{2K}{\varepsilon_m} \times \frac{A_m^2}{[S]_0} \tag{10}$$

They have found ε_m to be temperature independent in overtone spectra, but temperature dependent in fundamental stretching.

Self-assessment

Our approach based on Eqs. 5 and 7 can supplant the methods based on either one of Eqs. 8, 9 and 10 in that, in addition to monomer band, the dimer band is also supplemented to determine the dimerization constant, with the obtainment of molar absorptivity of dimer band, ε_d, as a bonus. Another advantage is to determine K, ΔH^o, and ΔS^o indepently from monomer and dimer bands. The disparity between those obtained from monomer bands and their counterparts from dimer bands can be used to access the merit of determination.

We have derived two equations 5 and 7 to treat, respectively, the data of the concentration-dependent integrated absorbance of the monomer and dimer band of the IR spectra displayed by a monomer-dimer self-associating system. Equation 5 enables us to obtain at a given temperature the molar absorptivity of monomer band and dimerization constant; Eq. 7 the molar absorptivity of the dimer band and dimerization constant. Dimerization constants determined either form Eq. 5 or from Eq. 7 are expected to be equal since they are referred to the same entity. Thus their discrepancy can be use as a criterion for the merit of determination.

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Appendix

Part of the results of this project have been published in

1. Da-Yu Kao, "FTIR study of hydrogen bonding association of sterically hindered alcohols:2,2-dimethyl-3-ethyl-3-pentanol and 3-ethyl-2-methyl-3-pentanol" Ph. D dissertation,2004, Dept. of chemistry. Nation Chiao-Tung university.
2. J. S. Chen and D. Y. Kao. "New Method to Analyse IR Data of Monomer-Dimer Self-Association: 2,2-Dimethyl-3-ethyl -3-pentanol in Carbon Disfulfide as an Example," **Z. Phys . Chem.**, 218, 231-243(2004).
3. J. S. Chen, C. C. Wu and D. Y. Kao, "New Apporach to IR Study of Mnomer-Dimer Self-Association: 2,2-Dimethyl-3-Ethyl-3-Pentanol in Tetrachloroethylene as an Example," **Spectrochim. Acta. A.,** 60, 2287-2293(2004).
4. J. S. Chen and D. Y. Kao. "New Apporach to IR Study of Mnomer-Dimer Self-Association: 3-Ethyl-2-Methyl-3-Pentanol in Carbon Tetrachloride as an Example," **J. Chin. Chem. Soc.,** 51,881-888 (2004).

Table 1. The integrated absorbance of OH stretching bands from the monomer and dimer for different concentrations of 2,2-dimethyl-3-ethyl-3-pentanol in CCl_4 at different temperatures.

	283 K			298 K			313 K			328 K	
conc. mol L^{-1}	monomer absorbance	dimer absorbance	conc. mol L^{-1}	monomer absorbance	dimer absorbance	conc. mol L^{-1}	monomer absorbance	dimer absorbance	conc. mol L^{-1}	monomer absorbance	dimer absorbance
0.1190	14.54	4.41	0.1167	14.23	2.94	0.1747	20.27	4.19	0.1712	19.46	2.84
0.1371	16.56	5.61	0.1346	16.22	3.81	0.1923	22.57	4.98	0.1884	21.57	3.41
0.1596	18.78	7.23	0.1567	18.52	4.97	0.2089	24.05	5.81	0.2047	23.76	3.99
0.1789	20.42	8.72	0.1781	20.65	6.27	0.2314	26.45	6.99	0.2268	25.89	4.86
0.2015	22.86	10.75	0.1960	22.44	7.34	0.2514	28.88	8.12	0.2464	28.03	5.72
0.2221	24.75	12.61	0.2129	24.24	8.51	0.2715	30.80	9.18	0.2660	29.83	6.62
0.2413	26.63	14.55	0.2359	26.42	10.13	0.2878	32.21	10.19	0.2820	30.99	7.35
0.2613	28.71	16.67	0.2563	28.63	11.87	0.3092	34.02	11.59	0.3030	33.11	8.41
0.2844	30.11	19.17	0.2767	30.35	13.41	0.3277	34.94	12.87	0.3211	35.11	9.42
0.2971	31.44	20.55	0.2933	31.91	14.78	0.3441	37.15	13.98	0.3373	36.11	10.38

Table 2. Molar monomer absorptivities (ε_m) molar dimer absorptivities (ε_d), dimerization constants (K) for 2,2-dimethyl-3-ethyl-3-pentanol in CCl_4 at different temperatures, and the standard enthalpy (ΔH^o) and entropy (ΔS^o) of dimerization obtained from monomer band and dimer band.

Temp. (K)	From monomer band fit K (L mol^{-1})	 $_m$ (L cm^{-1} mol^{-1})	From dimer band fit K (L mol^{-1})	 $_d$ (L cm^{-1} mol^{-1})
283	0.753 ± 0.045	1412 ± 18	0.735 ± 0.049	5559 ± 185
298	0.519 ± 0.020	1351 ± 08	0.508 ± 0.030	5196 ± 185
313	0.347 ± 0.062	1302 ± 34	0.341 ± 0.020	4945 ± 148
328	0.234 ± 0.058	1239 ± 31	0.222 ± 0.020	4687 ± 239
H^o/kJ mol^{-1}	-19.57 ± 2.29		-19.83 ± 2.35	
S^o/J mol^{-1} K^{-1}	-71.38 ± 7.79		-72.44 ± 7.98	

Table 3. Molar monomer absorptivities (ε_m) molar dimer absorptivities (ε_d), dimerization constants (K) for 2,2-dimethyl-3-ethyl-3- pentanol in n-octane at different temperatures, and the standard enthalpy (ΔH^o) and entropy (ΔS^o) of dimerization obtained from monomer bands and dimer bands.

	From IR monomer fit		From IR dimer fit	
Temp./K	K (L mol^{-1})	ε_m (L cm^{-1} mol^{-1})	K (L mol^{-1})	ε_d (L cm^{-1} mol^{-1})
288	0.629 ± 0.028	1311 ± 21	0.651 ± 0.039	12152 ± 327
298	0.418 ± 0.008	1166 ± 7	0.438 ± 0.012	11715 ± 156
308	0.294 ± 0.010	1082 ± 8	0.273 ± 0.009	11319 ± 190
318	0.202 ± 0.007	1004 ± 6	0.186 ± 0.019	10851 ± 562
ΔH^o/kJ mol^{-1}	-28.61 ± 3.88		-31.81 ± 3.88	
ΔS^o/J mol^{-1} K^{-1}	-103.2 ± 13.0		-113.9 ± 13.1	

Table 4. Molar monomer absorptivities (ε_m), molar dimer absorptivities (ε_d), and dimerization constants (K) for 3-ethyl-2-methyl-3-pentanol in CCl_4 at different temperatures, and the standard enthalpy (ΔH^o) and entropy (ΔS^o) of dimerization obtained from monomer band and dimer band.

	From monomer band fit		From dimer band fit	
Temp. (K)	K (L mol^{-1})	ε_m (L cm^{-1} mol^{-1})	K (L mol^{-1})	ε_d (L cm^{-1} mol^{-1})
283	2.644 ± 0.143	1724 ± 32	2.515 ± 0.213	4789 ± 179
298	1.819 ± 0.193	1692 ± 52	1.603 ± 0.102	4270 ± 127
313	0.926 ± 0.069	1447 ± 20	0.884 ± 0.075	4072 ± 174
328	0.406 ± 0.094	1401 ± 35	0.430 ± 0.018	4013 ± 88
ΔH^o/kJ mol^{-1}	-31.13 ± 2.41		-29.57 ± 2.38	
ΔS^o/J mol^{-1} K^{-1}	-100.3 ± 7.76		-95.7 ± 7.60	

Table 5. Molar monomer absorptivities (ε_m) molar dimer absorptivities (ε_d), dimerization constants (K) for 3-ethyl-2,2-dimethyl-3-pentanol in carbon disulfide at different temperatures, and the standard enthalpy (ΔH^o) and entropy (ΔS^o) of dimerization obtained from monomer band and dimer band.

	From monomer fit		From dimer fit	
Temp. (K)	K (L mol^{-1})	ε_m (L cm^{-1} mol^{-1})	K (L mol^{-1})	ε_d (L cm^{-1} mol^{-1})
283	0.472 ± 0.043	1632 ± 21	0.493 ± 0.053	4734 ± 99
298	0.394 ± 0.015	1490 ± 113	0.420 ± 0.022	4593 ± 115
313	0.319 ± 0.026	1415 ± 14	0.355 ± 0.017	4508 ± 103
328	0.239 ± 0.030	1372 ± 17	0.264 ± 0.012	4476 ± 107
ΔH^o/kJ mol^{-1}	-11.12 ± 2.81		-10.05 ± 2.71	
ΔS^o/J mol^{-1} K^{-1}	-45.58 ± 9.35		-41.16 ± 9.02	

Table 6. Molar monomer absorptivities (ε_m), molar dimer absorptivities (ε_d), and dimerization constants (K) for 3-ethyl-2-methyl-3-pentanol in tetrachloroethylene at different temperatures, and the standard enthalpy (ΔH^o) and entropy (ΔS^o) of dimerization obtained from monomer and dimer bands.

	From fitting A_m		From fitting A_d	
Temp./K	K (L mol^{-1})	ε_m (L cm^{-1} mol^{-1})	K (L mol^{-1})	ε_d (L cm^{-1} mol^{-1})
283	0.836 ± 0.023	1407 ± 8	0.812 ± 0.036	11294 ± 259
298	0.489 ± 0.006	1342 ± 2	0.468 ± 0.014	11193 ± 178
313	0.341 ± 0.013	1316 ± 5	0.356 ± 0.014	10925 ± 235
328	0.195 ± 0.003	1287 ± 1	0.208 ± 0.010	10826 ± 288
ΔH^o/kJ mol^{-1}	–23.93 ± 2.20		–22.43 ± 2.22	
ΔS^o/J mol^{-1} K^{-1}	–86.02 ± 7.54		–80.99 ± 7.58	

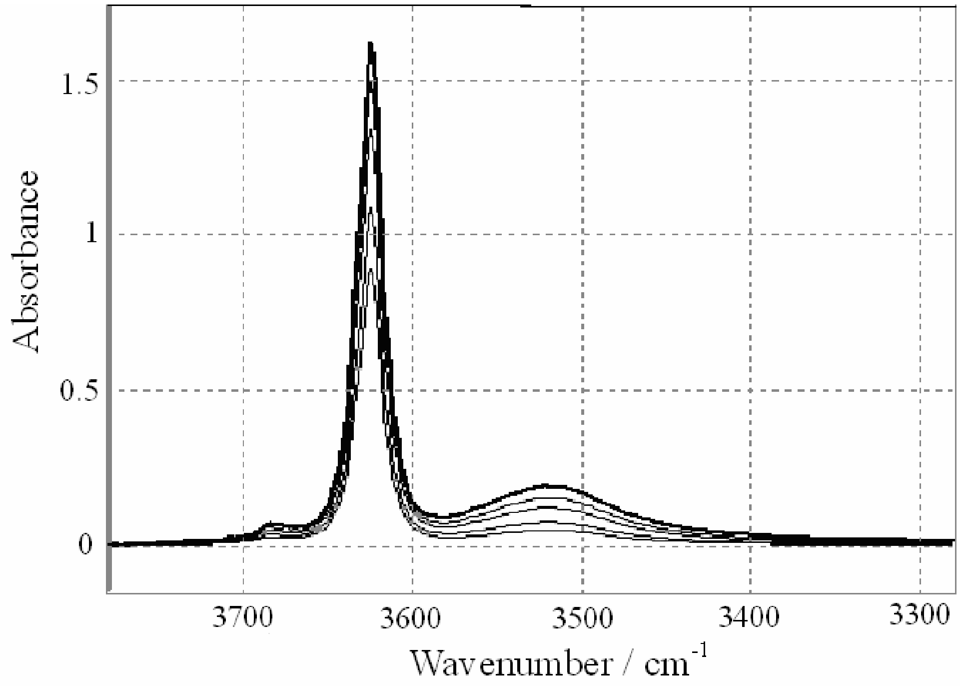

Figure 1. Spectra of the fundamental OH stretching bands for different concentrations of 2,2-dimethyl-3-ethyl-3-pentanol in CCl_4 at 298 K, from bottom to top: 0.1167 mol L^{-1}, 0.1567 mol L^{-1}, 0.2129 mol L^{-1}, 0.2563 mol L^{-1}, and 0.2933 mol L^{-1}.

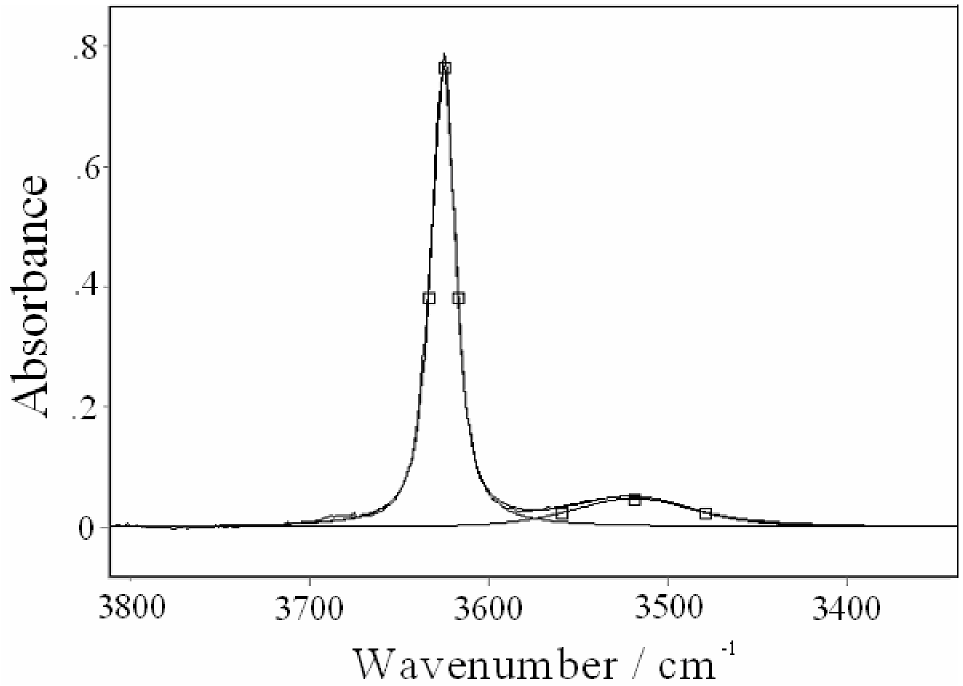

Figure 2. Curve fitting for 0.1167 mol L^{-1} 2,2-dimethyl-3-ethyl-3-pentanol in CCl_4 at 298 K.

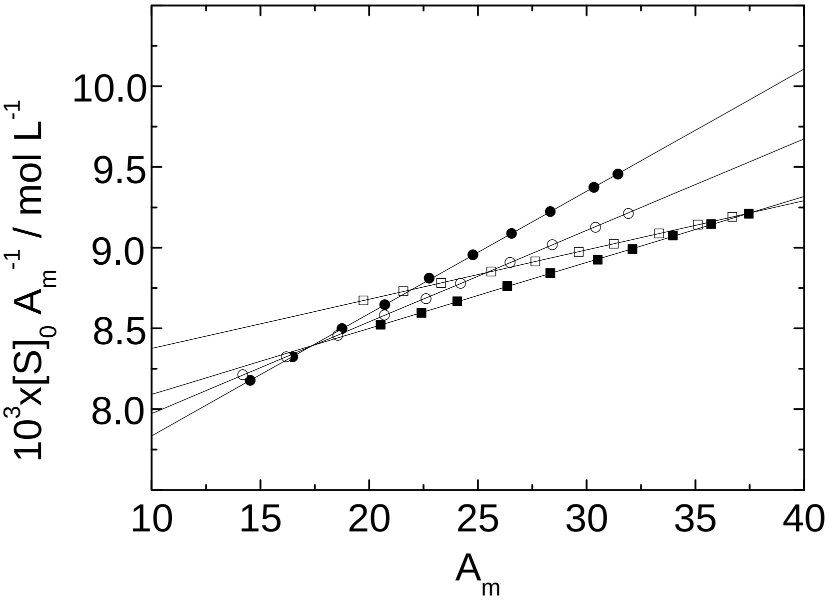

Figure 3. Linear plot based on Eq. (9) for different concentrations of 2,2-dimethyl-3-ethyl-3-pentanol in CCl_4 at different temperatures: (—●—) 283 K, (—○—) 298 K, (—■—) 313 K, (—□—) 328 K.

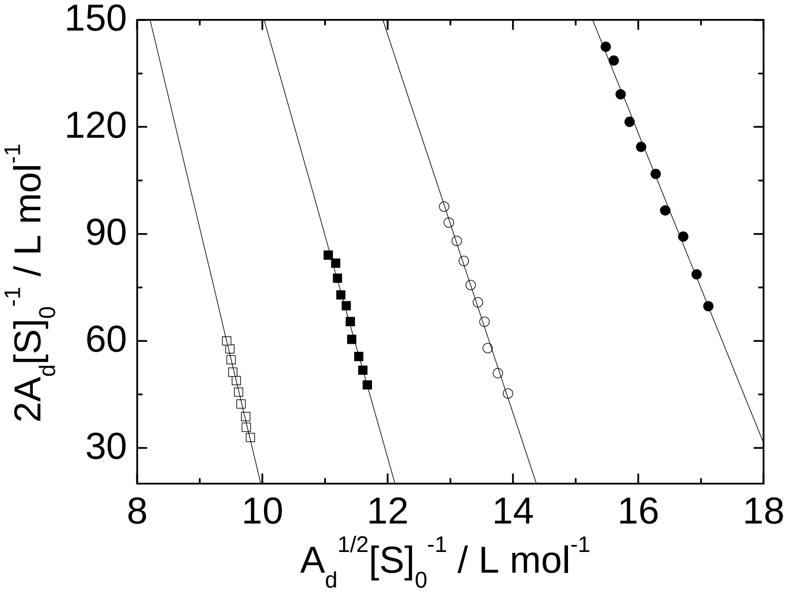

Figure 4. Linear plot based on Eq. (13) for different concentrations of 2,2-dimethyl-3-ethyl-3-pentanol in CCl_4 at different temperatures: (—●—) 283 K, (—○—) 298 K, (—■—) 313 K, (—□—) 328 K.

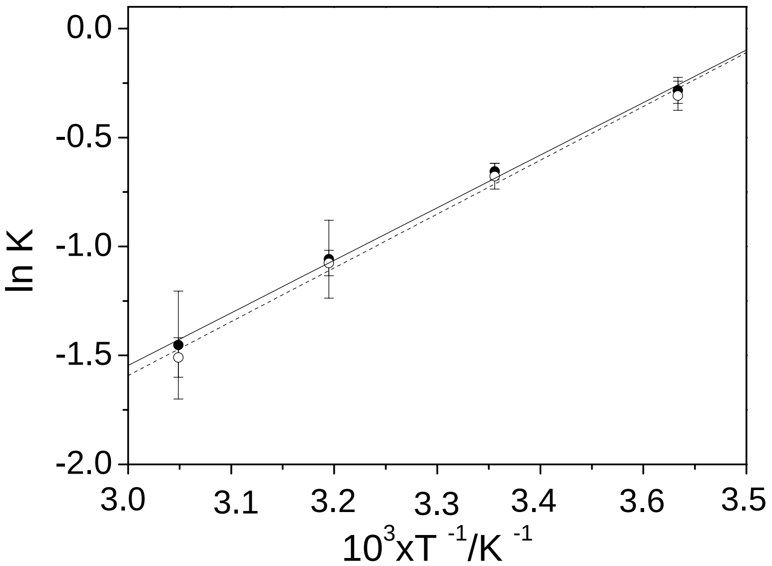

Figure 5. van't Hoff plot to obtain ΔH^o and ΔS^o for the dimerization of 2,2-dimethyl-3-ethyl-3-pentanol in CCl_4 from the dimerization constants obtained at different temperatures from the monomer band (—●—) and from the dimer band (···○···).