

New approach to IR study of monomer–dimer self-association: 2,2-dimethyl-3-ethyl-3-pentanol in tetrachloroethylene as an example

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Abstract

The dimerization of 2,2-dimethyl-3-ethyl-3-pentanol in tetrachloroethylene in the diluted region has been studied at four temperatures by IR spectroscopy. The aforementioned solute compound is chosen because self-association beyond dimerization is hampered by the steric hindrance generated by the bulky sidechains. The integrated absorbances of the monomer bands were treated based on Eq. (9) to obtain its molar absorptivity and dimerization constant. The same dimerization constant as well as the molar absorptivity of dimer band can be obtained based on Eq. (13) from the data treatment of the integrated absorbances of the dimer band. The disparity between two values of dimerization constant determined by two independent sources offers an opportunity to check the consistency of the determination. The standard enthalpy and entropy of dimerization have also been calculated by means of van't Hoff plot, respectively, from the data of temperature-dependent dimerization constants obtained from the monomer bands and dimer bands.

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1. Introduction

The concept of hydrogen bonding pioneered by Pauling and Huggins [1] plays an important role in interpreting the structure and function of the biological molecules, such as the helical or sheet of proteins [2,3], base-pairing of DNA [4], and enzyme kinetics [1]. Hydrogen bonding is also considered to be one of the major factors to render solutions deviant from normal behavior [5]. Since the advent of the establishment by Errera and Mollet [6] for the infrared (IR) spectral characteristics of hydrogen bonding in alcohols, IR spectroscopy has emerged as a major tool to investigate the problems of this sort. Other experimental methods for hydrogen bonding study include nuclear magnetic resonance (NMR), X-ray diffraction, neutron scattering, dielectric polarization, and ultrasonic absorption [1,7,8]. In IR spectra, it is common that several bands related to hydrogen bonding appear concomitantly. Each

band corresponds to the aggregate of a certain size and configuration. Therefore, the data treatment of the spectra should be based on the assumption as to what sizes and what configurations existing in the system [9–13]. The assumption is difficult to justify and, as a rule, leads to unreliable determination of the spectral and thermodynamic parameters. In order to circumvent this difficulty, association limited to dimerization is adopted in this study. It is understood that this limitation will not embrace most of the situations of self-association. However, it is still considered to be crucial in that dimerization is the starting point of any study of self-association. The mere Monomer–dimer self-association can be realized by alcohols with bulky sidechains in the vicinity of hydroxyl group [14–17]. The steric hindrance due to neighboring bulky sidechains would prevent molecules from further association. In this report, we choose dilute solution of 2,2-dimethyl-3-ethyl-3-pentanol in tetrachloroethylene as a model system to investigate monomer–dimer self-association, in view of the fact that the solute exhibits only monomer–dimer association in diluted solution [14,15,17], and that the solvent exhibits almost no absorption within the range 3300–3750 cm⁻¹

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under study so as not to interfere the absorption of the solute in this range. As can be seen below, Eq. (9) allows us to treat the integrated absorbances of the monomer band to obtain its molar absorptivity and dimerization constant. The dimerization constant, in addition to the molar absorptivity of the dimer band, can be also obtained from the data treatment of the integrated absorbances of the dimer band using Eq. (13). Hence, the same dimerization constant can be determined independently either from the data of monomer band or from those of dimer band. This offers an opportunity to check the consistency of the whole determination.

2. Equations for data treatment of the monomer and dimer bands

The dynamic equilibrium in a self-association system,



is restricted by a relation,

$$[A] + 2[A_2] = [A]_0 \quad (2)$$

and characterized by a temperature-dependent dimerization constant,

$$K = \frac{[A_2]}{[A]^2} \quad (3)$$

where $[A]$ and $[A_2]$ are the equilibrium concentrations of monomer, A , and that of dimer, A_2 , respectively; $[A]_0$ is the initial concentration of the self-associating species. A combination of Eqs. (2) and (3) allows us to solve for $[A]$ and $[A_2]$ in terms of $[A]_0$ and K to be

$$[A] = \frac{2[A]_0}{(1 + 8K[A]_0)^{1/2} + 1} \quad (4)$$

$$[A_2] = \frac{1}{2} \frac{(1 + 8K[A]_0)^{1/2} - 1}{(1 + 8K[A]_0)^{1/2} + 1} [A]_0 \quad (5)$$

Eqs. (4) and (5) have already been derived in the NMR study of monomer–dimer self-association [17–20].

According to Beer–Lambert's law, the absorbance at a particular wavenumber $\tilde{\nu}$ for a vibration taking place in monomer species is given by

$$A_m(\tilde{\nu}) = \varepsilon_m(\tilde{\nu})b[A] \quad (6)$$

where $\varepsilon_m(\tilde{\nu})$ is the molar absorptivity of the monomer band at $\tilde{\nu}$, b the optical path length of the cell. The integrated absorbance of the whole monomer band, A_m , then is obtained by an integration over the whole range of the wavenumber covered by this band. That is

$$A_m = \int \varepsilon_m(\tilde{\nu})b[A]d\tilde{\nu} \\ = \int \varepsilon_m(\tilde{\nu})d\tilde{\nu}b[A] = \frac{2[A]_0}{(1 + 8K[A]_0)^{1/2} + 1} \varepsilon_m b \quad (7)$$

In writing the last equation, Eq. (4) has been used, and $\varepsilon_m (= \int \varepsilon_m(\tilde{\nu})d\tilde{\nu})$ is the molar absorptivity of the monomer band. If we invert the fractions of the first and last terms of the above equation, then multiply them by $2\varepsilon_m b[A]_0$, we obtain

$$\frac{2\varepsilon_m b[A]_0}{A_m} = (1 + 8K[A]_0)^{1/2} + 1 \quad (8)$$

If we subtract unity from both sides of Eq. (8), then take squares, we finally arrive at

$$\frac{[A]_0}{(A_m)^2} = \frac{1}{(\varepsilon_m b)} \left(\frac{1}{A_m} \right) + \frac{2K}{(\varepsilon_m b)^2} \quad (9)$$

upon dividing by $4\varepsilon_m^2 b^2 [A]_0$. Eq. (9) allows us to fit the experimental data of $y = ([A]_0/A_m^2)$ vs. $x = A_m^{-1}$ to a straight line. ε_m and K then can be obtained from the slope, p , and intercept, q , of this regressed line by $\varepsilon_m = (1/pb)$ and $K = (q/2p^2)$, respectively.

Along the line of deriving Eq. (7), the integrated absorbance of the dimer band can be derived to be

$$A_d = \varepsilon_d b[A_2] = \frac{\varepsilon_d b[A]_0}{2} \frac{(1 + 8K[A]_0)^{1/2} - 1}{(1 + 8K[A]_0)^{1/2} + 1} \quad (10)$$

where $\varepsilon_d (= \int \varepsilon_d(\tilde{\nu})d\tilde{\nu})$ is the molar absorptivity of the dimer band. If we divide the first and last terms in Eq. (10) by $\varepsilon_d b[A]_0/2$ and use the fact that if $(a/b) = (c/d)$, then $(a + b/a - b) = (c + d/c - d)$, we obtain

$$\frac{\varepsilon_d b[A]_0 + 2A_d}{\varepsilon_d b[A]_0 - 2A_d} = (1 + 8K[A]_0)^{1/2} \quad (11)$$

The above equation can be further manipulated by taking squares followed by using the fact if $(a/b) = (c/d)$ then $(a - b/b) = (c - d/d)$ to yield

$$\frac{\varepsilon_d b A_d}{K} = (\varepsilon_d b[A]_0 - 2A_d)^2 \quad (12)$$

We then take square roots and divide by $[A]_0$ on both sides of Eq. (12) to transform it into a linear equation

$$\frac{2A_d}{[A]_0} = \varepsilon_d b - \left(\frac{\varepsilon_d b}{K} \right)^{1/2} \frac{(A_d)^{1/2}}{[A]_0} \quad (13)$$

This equation can be used to fit the experimental data of $y = (2A_d/[A]_0)$ versus $x = ((A_d)^{1/2}/[A]_0)$ to a straight line. From the slope, p , and intercept, q , of the regressed line, ε_d and K can be obtained by $\varepsilon_d = (q/b)$ and $K = (q/p^2)$, respectively.

3. Experimental section

The chemical 2,2-dimethyl-3-ethyl-3-pentanol (98%) and tetrachloroethylene (99.98%) were purchased from Aldrich, and Tedia, respectively, and used as received. The sample concentrations on molality scale were prepared with the help of microsyringes, vials, and an analytical balance. The concentrations on molality scale were then converted

into molarity scale based on the density of the solvent at various temperatures obtained from the published data (283 K: 1.63120, 293 K: 1.62260, 303 K: 1.60640, 393 K: 1.44865 g ml⁻¹) [21]. All subsequent calculation, plotting and tabulation were then carried out in terms of molarity scale when concentration is concerned. The spectra were recorded by an FTIR spectrometer (Bio-Rad Spc. 3200) with a CaF₂ cell window of 0.5 mm optical path length. The cell temperature was controlled by the circulating water, which was from a thermostat, flowing through the cell jacket. A thermal couple was inserted into the jacket to measure the temperature. The error of the temperature was estimated to be ± 1 K. A personal computer implanted with a commercial software package PeakSolve (Galatic Industries Corp.) was hooked to the spectrometer to perform the task of curve-fitting the overlapped spectra and of calculating the integrated absorbance of the resolved spectra. Other tasks of regression, plotting graphs were performed with the help of Mathematica software on another personal computer.

4. Results and discussion

In this system, the OH fundamental stretching vibration exhibits two absorption bands in the range 3300–3750 cm⁻¹. The sharp one at higher wavenumber corresponds to the OH stretching in the monomer. The broad one at lower wavenumber corresponds to that in the hydrogen-bonded dimer. A collection of the spectra within this region for different concentrations of 2,2-dimethyl-3-ethyl-3-pentanol in tetrachloroethylene at 298 K has been presented in Fig. 1. These two bands are not well separated. They were resolved and their integrated absorbance were calculated with the help of a software package PeakSolve. A typical result is presented in Fig. 2 for 0.1958 mol l⁻¹ 2,2-dimethyl-3-ethyl-3-pentanol in tetrachloroethylene at 298 K. The integrated absorbances of the resolved monomer

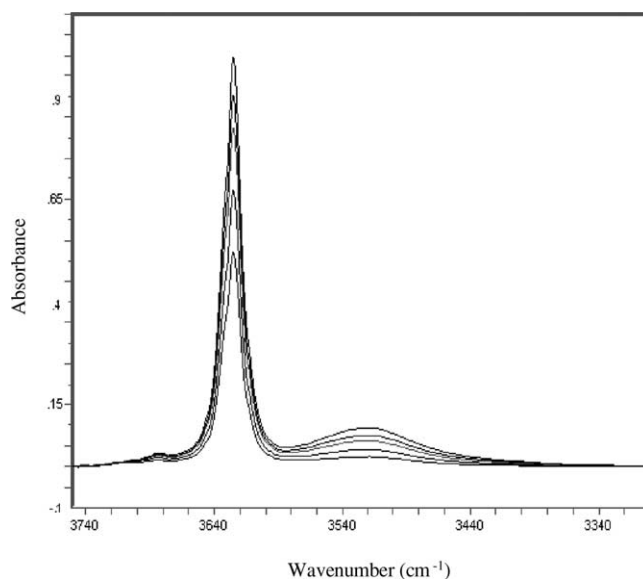


Fig. 1. A collection of the spectra of the fundamental OH stretching bands for different concentrations of 2,2-methyl-3-ethyl-3-pentanol in tetrachloro-ethylene at 298 K: from bottom to top 0.1621, 0.2100, 0.2610, 0.2917, and 0.3243 mol/l.

band, A_m , and that of dimer bands, A_d , for various concentrations at four different temperatures, 278, 288, 298, 308 K are listed in Table 1. The errors of A_m and A_d calculated from several times of fitting are estimated to be within $\pm 0.8\%$ and $\pm 0.5\%$, respectively.

From this table it is observed that at a given temperature both A_m and A_d increase with initial concentration, $[A]_0$, while the ratio A_d/A_m decreases. Furthermore, in Fig. 3, A_d/A_m^2 for each temperature keeps constant as $[A]_0$ varies. This is a clear implication of the occurrence of Monomer–dimer self-association. Once A_m and A_d for different concentrations of solute at a given temperature have been available. We are in a position to deduce ϵ_m and K from the slope and intercept of the linear plot of

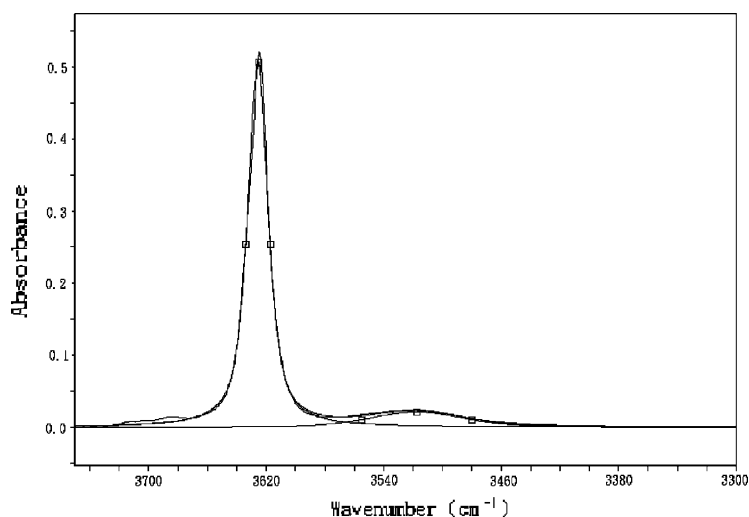


Fig. 2. Curve fit for 0.1958 mol/l 2,2-methyl-3-ethyl-3-pentanol in tetrachloro-ethylene at 298 K.

Table 1

The integrated absorbances of OH stretching bands from the monomer, A_m , and those of dimer, A_d , for different initial concentrations of 2,2-dimethyl-3-ethyl-3-pentanol in tetrachloroethylene at different temperatures

$[A]_0/\text{mol l}^{-1}$	A_m	A_d
278 K		
0.1649	12.65	5.52
0.1821	13.83	6.58
0.1980	14.82	7.61
0.2132	15.81	8.65
0.2293	16.84	9.81
0.2489	18.09	11.25
0.2624	18.87	12.31
0.2796	19.91	13.68
0.2954	20.84	15.02
0.3138	21.95	16.64
0.3300	22.84	18.04
288 K		
0.1638	12.31	3.89
0.1805	13.52	4.65
0.1973	14.64	5.45
0.2124	15.68	6.22
0.2285	16.69	7.09
0.2458	17.73	8.06
0.2604	18.71	8.92
0.2767	19.71	9.92
0.2941	20.75	11.04
0.3097	21.73	12.09
0.3333	23.22	13.71
298 K		
0.1621	11.96	2.67
0.1813	13.28	3.29
0.1958	14.26	3.79
0.2100	15.15	4.32
0.2265	16.30	4.96
0.2421	17.37	5.61
0.2610	18.68	6.42
0.2747	19.44	7.06
0.2917	20.44	7.85
0.3091	21.63	8.72
0.3243	22.60	9.50
308 K		
0.1615	11.86	1.54
0.1772	13.04	1.84
0.1937	14.10	2.17
0.2081	15.11	2.49
0.2244	16.28	2.88
0.2408	17.30	3.28
0.2568	18.47	3.71
0.2728	19.63	4.15
0.2888	20.44	4.62
0.3043	21.70	5.10
0.3203	22.73	5.61

$y = ([A]_0/(A_m^{\text{obs}})^2)$ versus $x = (1/A_m^{\text{obs}})$ based on Eq. (9), and to deduce ε_d and K from the slope and intercept of the linear plot of $y = (2A_d^{\text{obs}}/[A]_0)$ versus $x = ((A_d^{\text{obs}})^{1/2}/[A]_0)$ based on Eq. (13). Such plots at four temperatures for the monomer bands, and for the dimer bands are presented in Figs. 4 and 5, respectively. K from the monomer bands and dimer bands, ε_m , and ε_d at each temperature thus deter-

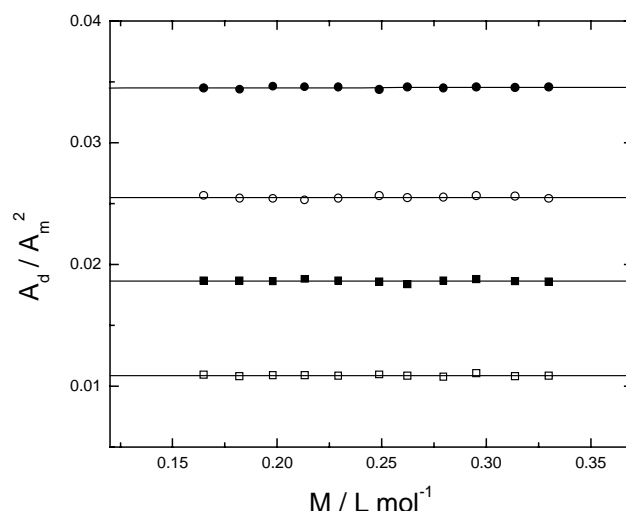


Fig. 3. Plot of A_d/A_m^2 vs. $[A]_0$ to demonstrate the validity of monomer–dimer self-association and the consistency of the parameter determination: (●) 278 K, (○) 288 K, (■) 298 K, (□) 308 K.

mined were collected in Table 2. The errors associated with ε_m , ε_d and K were calculated based on a standard method [22] with the assumption of equal variances for A_m or A_d .

It is seen that ε_m and ε_d decrease with increasing temperature. This phenomenon can not be simply explained by Boltzmann distribution. The molar absorptivity, ε (ε_m or ε_d), is proportional to the absorption coefficient, $\alpha(\omega)$, with a proportionality constant independent of temperature, T , [23]

$$\alpha(\omega) = \frac{2\pi}{3c\hbar n} \omega(1 - e^{-\hbar\omega/kT}) \times \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \vec{M}(0) \vec{M}(t) \rangle \quad (14)$$

where c is the speed of light, $\hbar = 2\pi/h$ with h being the Planck constant, n the refractive index of the medium, ω the angular velocity of the radiation absorbed, k the Boltzmann

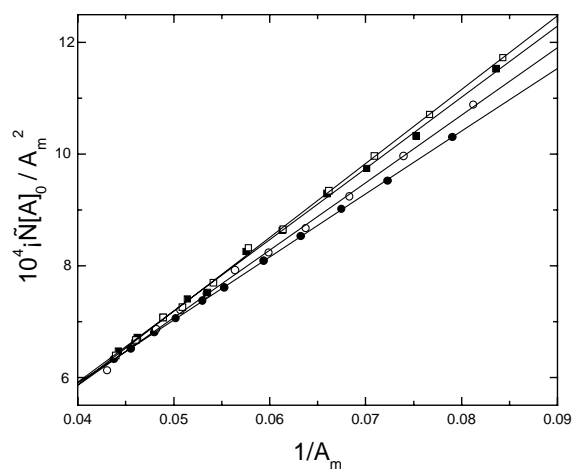


Fig. 4. Linear plot based on Eq. (9) for different concentrations of 2,2-methyl-3-ethyl-3-pentanol in tetrachloroethylene at different temperatures: (●) 278 K, (○) 288 K, (■) 298 K, (□) 308 K.

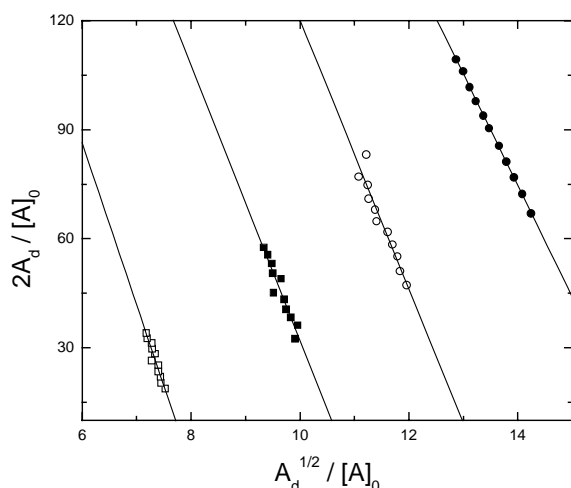


Fig. 5. Linear plot based on Eq. (13) for different concentrations of 2,2-methyl-3-ethyl-3-pentanol in tetrachloroethylene at different temperatures: (●) 278 K, (○) 288 K, (■) 298 K, (□) 308 K.

constant, and the integral represents the Fourier transform of the time correlation function of the dipole moment of the sample, $\langle M^{\rightarrow}(0) M^{\rightarrow}(t) \rangle$. The values of the factor $(1 - e^{-\hbar\omega/kT})$ calculated for $\omega (= 2\pi c\tilde{\nu})$ and temperature involved are fairly close to unity. Thus, it is understood that $\langle M^{\rightarrow}(0) M^{\rightarrow}(t) \rangle$ are mainly responsible for the variation of ε (ε_m or ε_d) with temperature. This may attribute to the temperature variation of the electrostatic field strength in the cavity where solute molecule (monomer or dimer) is seated, and to the strong, direct interaction between the solute and solvent molecules.

The dimerization constants at different temperatures allow us to obtain the standard enthalpy, ΔH° , and entropy, ΔS° , of dimerization through van't Hoff plot. For this system, the plots can be done either by the dimerization constants from A_m or by those from A_d . Both plots are juxtaposed in Fig. 6 for better visual comparison. The errors associated with ΔH° and ΔS° were calculated based on a standard method [22] with unequal variance for K listed in Table 2. In order to assess the goodness of our determination, we plot in Fig. 7 the original data of A_m against $[A]_0$ at each temperature juxtaposed with the respective theoretical

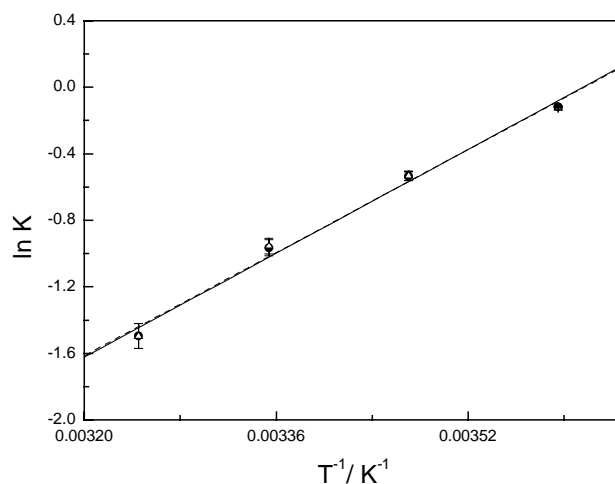


Fig. 6. van't Hoff plot to obtain ΔH° and ΔS° for the dimerization of 2,2-methyl-3-ethyl-3-pentanol in tetrachloroethylene from the data of dimerization constants obtained at different temperatures from the monomer band (●), and from the dimer band (Δ).

curves calculated by inserting the determined values of ε_m and K into Eq. (9). Similar plots for A_d against $[A]_0$ juxtaposed with the theoretical curves calculated by Eq. (13) were also shown in Fig. 8. A further assessment can be done by the comparison between the experimental values (A_d/A_m^2) and the calculated values of $(A_d/A_m^2) = (K\varepsilon_d/\varepsilon_m^2)$ for each temperature as shown in Fig. 3.

It is observed that the isotherms, i.e. the data points or the theoretical curve at a given temperature, in Figs. 5 and 8, are well separated for the dimer bands. However, this is not the case for monomer bands as shown in Figs. 4 and 7. Such a difference can be explained as follows. Since K decreases with temperature, $[A]$ would increase with temperature at a given initial concentration $[A]_0$. On the contrary, ε_m decreases with temperature as seen from Table 2. Thus two factors counteract against each other, leading to a clustering of the data points for different temperatures at a given initial concentration. But, in case of dimer band, the decrease of both ε_d and $[A_2]$ with temperature at a given $[A]_0$ effect A_d in a parallel way, resulting in a well-separated isotherms as shown in Figs. 5 and 8.

Table 2

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

	From monomer bands		From dimer bands	
	K (l mol^{-1})	ε_m ($\text{l cm}^{-1} \text{ mol}^{-1}$)	K (l mol^{-1})	ε_d ($\text{l cm}^{-1} \text{ mol}^{-1}$)
Temperature (K)				
278	0.544 ± 0.007	1773 ± 5	0.539 ± 0.007	10040 ± 60
288	0.361 ± 0.013	1670 ± 9	0.362 ± 0.005	9820 ± 60
298	0.235 ± 0.012	1580 ± 8	0.238 ± 0.003	9810 ± 60
308	0.141 ± 0.015	1535 ± 10	0.140 ± 0.003	9120 ± 120
ΔH° (kJ mol^{-1})	-31.07 ± 4.06		-30.71 ± 4.07	
ΔS° ($\text{J mol}^{-1} \text{ K}^{-1}$)	-116.6 ± 14.1		-115.4 ± 14.1	

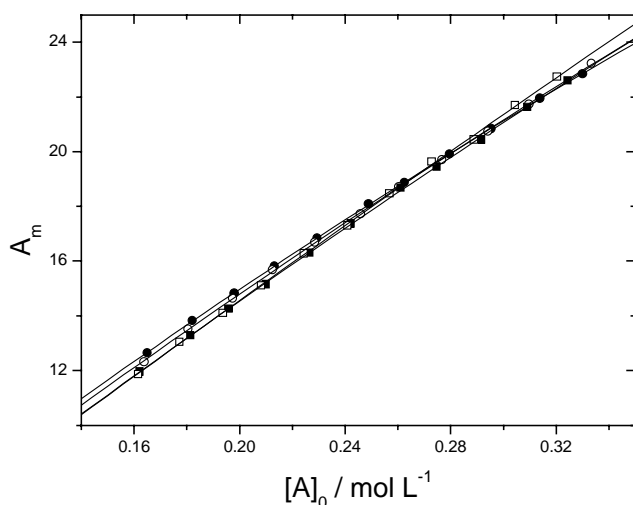


Fig. 7. Plot for comparing the theoretical curves calculated based on Eq. (9) with experimental data for A_m vs. $[A]_0$ of 2,2-methyl-3-ethyl-3-pentanol in tetrachloroethylene at different temperatures: (●) 278 K, (○) 288 K, (■) 298 K, (□) 308 K.

In IR study of the monomer–dimer self-association, to the best of our knowledge, only monomer band is employed to determine the spectral parameter ε_m and dimerization constant, K . For example, Liddle and Becker [24] obtained K from the limiting slope of a plot of apparent absorptivity, $A_m/[A]_0$, against $[A]_0$, via the equation

$$\lim_{[A]_0 \rightarrow 0} \left(\frac{d(A_m/[A]_0)}{d[A]_0} \right) = -2K\varepsilon_m \quad (15)$$

Here ε_m is obtained from another limiting slope

$$\lim_{[A]_0 \rightarrow 0} \frac{dA_m}{d[A]_0} = \varepsilon_m \quad (16)$$

The disadvantage of this determination is that, if either one of the limiting slopes is steep, considerable errors may ensue.

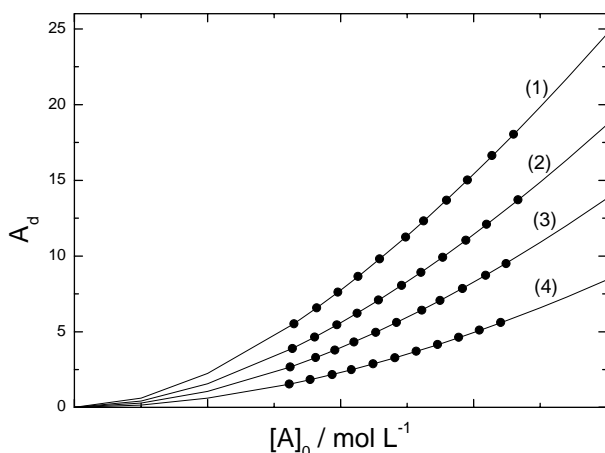


Fig. 8. Plot for comparing the theoretical curves calculated based on Eq. (13) with experimental data of A_d vs. $[A]_0$ of 2,2-methyl-3-ethyl-3-pentanol in tetrachloroethylene at different temperatures: (1) 278 K, (2) 288 K, (3) 298 K, (4) 308 K.

Prokopenko and Bethea in studying the effect of ring size on the dimerization of lactams [25] adopted to fit the data of $y = A_m$ against $x = [A]_0$ to the equation

$$A_m = \varepsilon_m b \frac{\sqrt{1 + 8K[A]_0} - 1}{4K} \quad (17)$$

to obtain K and ε_m using the Levenberg-Marquardt non-linear method. Luck [26] in his paper of studying the monomer–dimer self-association of lactams fitted the data of $y = A_m/[A]_0$ versus $x = A_m^2/[A]_0$ to the linear equation

$$\frac{A_m}{[A]_0} = \varepsilon_m - \frac{2K}{\varepsilon_m} \left(\frac{A_m^2}{[A]_0} \right) \quad (18)$$

to obtain ε_m and K . All the above three methods leave the data of the dimer band unattended. Our approach, on the contrary, seems more comprehensive and thoughtful, in the sense that two independent sources, i.e. the data from monomer and dimer bands, are employed to determine K , with the obtainment of ε_m and ε_d as a bonus. The values of K determined either from the data of monomer or from the dimer are expected to be identical, since the same entity is referred to. Hence, the disparity between two K values is a good criterion for the merit of determinations. In the same token, ΔH° and ΔS° of dimerization determined from the data of monomer bands and dimer bands serve the same purpose.

5. Conclusion

In addition to Eq. (9), which treats the integrated absorbances of monomer band to obtain ε_m and K , we employed Eq. (13) to treat those of the dimer band to obtain ε_d and K . Thus K can be obtained from two independent sources and the disparity between the respective determined values provides a vehicle to assess the goodness of determination. The standard enthalpy (ΔH°) and entropy (ΔS°) determined from the temperature-dependent K of two independent sources also have the same function. Dilute solution of 2,2-dimethyl-3-ethyl-3-pentanol in tetrachloroethylene was used as an example to illustrate the usage of Eqs. (9) and (13). It is hoped that this new approach would facilitate the IR study of monomer–dimer self-association.

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