TÜBİTAK

Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2017) 41: 658 – 671

doi:10.3906/kim-1701-76

Novel bis(aminoalcohol)oxalamide organogelators and their diglycolylamide analogs: evaluation of gelation efficiency in various organic fluids

Mehmet ÇOLAK[1], **Deniz BARIŞ**[2], **Necmettin PİRİNÇÇİOĞLU**[1], **Halil HOŞGÖREN**[1,*]
[1]Department of Chemistry, Faculty of Science, Dicle University, Diyarbakir, Turkey
[2]Department of Chemistry, Faculty of Science and Arts, Batman University, Batman, Turkey

Received: 30.01.2017 • **Accepted/Published Online:** 20.03.2017 • **Final Version:** 10.11.2017

Abstract: Three modular types of bis(aminoalcohol)oxalamides (**1**, **4**, and **7**) and bis(aminoalcohol)diglycolylamide (**8**) gelators have been prepared by the reaction of the respective aminoalcohols with oxalyl and digycolyl methylesters as potential low-molecular-weight organogelators. The gelation properties of these amides have been evaluated in various aromatic organic solvents (xylene, toluene, isopropyl benzene, and aromatic ether type organic fluids such as anisole or α-phenylethylmethylether) as well as the long-chain aliphatic alcohols (1-hexanol, 1-octanol, 2-octanol, and aromatic 1-phenylethanol). The compounds with *sec*-butyl and ethyl side chains produce good gelation properties in both aromatic and other organic fluids. Furthermore, the common oxalamide linker present in the gelators was replaced by an extended diglycolylamide linker (**8**) and its behaviors were compared with the benzylic oxalamide analog (**3**). The gelator (**8**) gives the best results with aromatic fluid and lauric acid ethyl ester. ^{1}H NMR studies reveal the existence of temperature-dependent network assembly/dissolution equilibrium and produce K_{gel}. FTIR was employed to see the effect of hydrogen bonding in the formation of gel network. Thermodynamic parameters regarding gel-to-sol transition were collected with van't Hoff relationships.

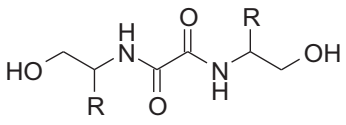
Key words: Gelation, self-assembly, low-molecular-weight organogels, infrared, NMR spectroscopy, hydrogen bonding, chiral amidediols

1. Introduction

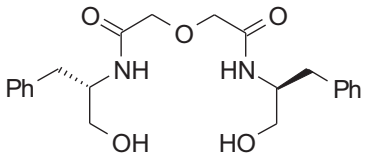
Organogelators are low-molecular-weight organic molecules. They can form gels at low concentrations and thus create a three-dimensional network in organic solvents.[1–5] Because of their soft material properties, they receive significant interest in a variety of applications such as cosmetics, templated materials, drug delivery, enzyme-immobilization matrices, tissue engineering, optical sensors, and phase-selective gelation, as well as in the conservation of art materials.[6–13] The works by Shinkai, Hanabusa, Hamilton and van Esch, and other groups marked the beginning of the design of molecular gelators in the mid-1990,[14] followed by the tailored rational design and synthesis of molecules having versatile gelation ability. Consequently, the emergence of low-molecular-weight gelators (LMWGs) has occupied a key place in immobilization of solvents for a broad spectrum of applications, because of their supramolecular 3D networks, which are gained via noncovalent interactions such as hydrogen bonding, van der Waals, electrostatic, and π-π aggregation.[15] There are two major types of gels based on the nature of the liquid that is immobilized. Gels that cause the immobilization of water are called hydrogels and those causing the immobilization of organic solvents are called organogels.[16]

*Correspondence: hosgoren@dicle.edu.tr

Chiral bis(aminoalcohol)oxalamides **2**, **3**, **5**, and **6** are known as LMWGs for common organic fluids.[17,18] On the other hand, the gelation properties of **1** and **4** have only been tested in pharmaceutical fluids such as fatty acid esters.[13] The present study aims to investigate the gelation behaviors of **1** and **4** (Scheme) not only in common organic solvents but also in unusual solvents such as aromatic ethers and long-chain alcohols. The work also offers the synthesis of two new candidate gelators, **7** and **8** (Scheme), prepared by simple modifications, the former by changing the alkyl chain with the long hexyl group and the latter by alteration of the common oxalamide core with diglycolyldiamide, and involves the first report of the organogelation properties of **7** and **8** in common organic solvents as well as in unusual solvents such as anisole, PhEME (α-phenylethylmethylether), 1-phenyl ethanol, and long-chain alcohols. T_{gel} measurements were employed to determine the thermal stability of these gels. ^{1}H NMR was used to obtain the thermodynamic quantities of the gelation process such as K_{gel} and ΔH_{gel} and FTIR spectroscopy was used to analyze hydrogen bond formation in the gel network.



1-7



8

Scheme. The structures of bis(amino alcohol)oxalamide and diglycoldiamide. R = Ethyl **1** (R,R); R = Phenyl **2** (S,S); R = Benzyl **3** (S,S); R = *sec*-Buthyl **4** (S,S); R = Isobuthyl **5** (S,S); R = Isopropyl **6** (S,S); R = n-Hexyl **7** (rac); **8** R = Benzyl (S,S).

2. Results and discussion

2.1. Determination of minimum gel concentration

The oxalyl types of bis(aminoalcohol)diamide derivative gelators **2**–**6** are well-known as LMWGs for organic fluids and their properties that have been reported in several papers.[17,18] The other oxalyl type gelators, **1** and **4**, containing different alkyl chains, have been evaluated as a gel matrix in pharmaceutically acceptable organic fluids.[13] Current work reports the synthesis of diglycolyldiamide type **8** and oxalyl type **7** gelators and investigation of their potentials as organogelators along with **1**, **2**, **3**, **4**, **5**, and **6**. The result of gelation experiments with gelators **1**, **4**, **7**, and **8** in different nonaromatic solvents are shown in Table 1. The efficiency of gelation is stated by the minimum gel concentration (MGC) in mg/mL. When the gelation properties of gelators are compared, **1**, **4**, **7**, and **8** have striking differences. Derivative **8** was found to form a gel only in lauric acid ethyl ester (LEE) with MGC of 2 mg/mL. Similarly, compound **4** appeared to form a gel in LEE and decalin, whereas racemic gel **7** was formed in almost all the solvents but with higher MGCs (7–30 mg/mL). This may be attributed to its enhanced solvophilicity in the tested solvents caused by the longer site chains (hexyl groups). Gelator **1**, which has the shortest alkyl group, results in stable gel in the majority of tested fluids. Furthermore, it seems that the replacement of the oxalyl core with a diglycolyl linker decreases the gelation ability for gelator **3** with the former linker having better gelation ability compared to that of **8** (Table 1). However, the gelation efficiency of **8** was improved in the aromatic fluids and LEE (Table 2). The gelation behaviors of gelators **1**, **4**, **7**, and **8** in different aromatic solvents are demonstrated in Table 2. They show that **1**, **4**, and **8** function as excellent organogelators in aromatic fluids (See Figure 1 for **4** in xylene gel). However, **7** showed much less efficient gelation in the analogous solvents. Moreover, it was found that **1**, **4**, **7**, and **8**

have remarkably different gelation behaviors in oxygenic aromatic fluids such as anisole, PhEME, and 1-phenyl ethanol. They all showed much less efficient gelation in anisole with MGCs of higher than 13 mg/mL, except **3** with 2 mg/mL, whereas the (*R*)-2-butanol derivative gelator **1** showed efficient gel formation in PhEME and 1-phenyl ethanol with MGCs of 5 mg/mL and 3 mg/mL, respectively, and also **4** with MGC of 3.3 mg/mL in PhEME.

Table 1. Minimum gel concentration (MGC as mg/mL) in the nonaromatic organic fluids.

Solvent	**1**	**4**	**7**	**8**	**3**
Acetonitrile	2.4 (og)	cry	p	sol	cry
$CHCl_3$	sol	sol	7 (og) (4 °C)	sol	-
LEE	4	4	30 (og)	2	2
Hexanol	sol	cry	10 (4 °C)	-	5 (tg)
1-Octanol	8 (og)	cry	20 (og)	N.T.	2.7 (tlg)
2-Octanol	N.T.	N.T.	20 (og)	N.T.	N.T.
1-Decanol	4 (og)	cry	12 (tlg)	N.T.	2 (tlg)
Decalin	-	7	20 (og)	sol	4 (wg)

og: opaque gel, wg: weak gel, sol: soluble, cry: crystal, tg: transparent gel, N.T: not tested, (-): denotes no gelation, tlg: translucent gel.

Table 2. Minimum gelation concentration (MGC as a mg/mL) of **1**, **4**, **7**, and **8** in aromatic solvents.

Solvent	**1**	**4**	**7**	**8**	**3**
o-Xylene	2 (og)	5 (og)	25 (wg)	7	1.22[i]
m-Xylene	2 (og)	5 (og)	25 (wg)	3	1.67[i]
p-Xylene	2 (og)	5 (og)	25 (wg)	3	1.67[i]
Toluene	ins	7 (og)	20 (og)	cry	1.25[i]
Isopropyl benzene	3	7	24 (wg)	7	2 (wg)
PhEME	5	3.3	N.T.	sol	N.T.
Anisole	13 (og)	13 (tg)	21 (wg)	15 (og)	2 (tg)
1-Phenyl ethanol	3	30	sol	sol	15 (tg)

PhEME: α-Phenylethylmethylether, og: opaque gel, wg: weak gel, sol: soluble, ins: insoluble, cry: crystal, tg: transparent gel, N.T: not tested, (-): denotes no gelation. [i]) Taken from the literature.[18]

Figure 1. A typical gel structure of **4** in xylene.

The MGCs of the samples in nonaromatic and aromatic fluids required for gelation are demonstrated in Tables 1 and 2, respectively.

The effect of various alkyl chains on the gelation efficiency indicated that the shorter chain length in **1** has the best scores in aromatic and nonaromatic solvents, while **4** with the *sec*-butyl side chain also had good

gelation efficiency in aromatic fluids. On the other hand, **7** did not demonstrate good gelation efficiency in the two types of tested fluids.

2.2. Gel-to-sol dissociation temperature (T_{gel}) measurement

The temperature dependence of the MGC (mg/mL) required for organogelation in anisole is presented in Figure 2. Dropping ball measurements were employed in the determination of the temperatures of the gel-to-sol transition (T_{gel}) for two types of bis(aminoalcohol)diamide derivatives in anisole and it was found that increasing the concentration of gelators leads to an increase in the thermal stability of the gels (Figure 2). The presence of aromatic side chains on the aminoalcohol part of gelators, such as phenyl and benzyl groups, increases T_{gel} values (see Figure 2). This may be due to π-π interactions between the aromatic phenyl in gelator **2** and the benzyl side chain in gelator **3** with the solvent. Moreover, **3** with an oxalamide linker forms a thermally more stable gel than its diglycolylamide analog **8** in anisole. This is possibly associated with the more rigid character of the oxalyl linker compared with the diglycolyl one. These measurements were not carried out for **7** and **6** due to high MGC (21 mg/mL) and solubility in anisole, respectively.

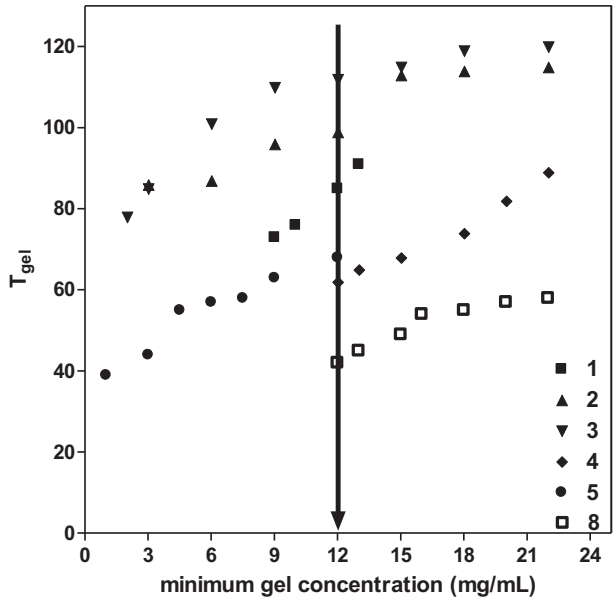


Figure 2. A plot of gel-to-sol transition temperature (T_{gel}) against the minimum gel concentration (mg/mL) of gelators **1**, **2**, **3**, **4**, **5,** and **8** in anisole.

The relative thermal stability order of gelators is found to be **3** > **2** > **1** > **5** > **4** > **8** by considering MGC of 12 mg/mL as a reference. At this concentration, the gel-to-sol melting transition for **2** and **3** reach up to 100 °C (see Figure 2). Furthermore, van't Hoff relationships were employed to obtain thermodynamic parameters for gel-to-sol transitions in order to analyze the detailed thermal behaviors of the gels.[19,20] The melting enthalpy of crystals is estimated by the van't Hoff equation (Eq. (1)):

$$\frac{d\ln C_g}{d1/T_g} = \frac{\Delta H_2}{R} \tag{1}$$

This could also apply to obtaining the gel-sol transition enthalpy. Enthalpies of the gel-sol transition (ΔH_{gel})

obtained from the slope of van't Hoff plots for gels of **1**, **2**, **3**, **4**, **5**, and **8** in anisole are summarized in Table 3 and represented in Figure 3.

Table 3. Gel-sol transition enthalpies from the slope of van't Hoff graphic ΔH_{gel} (kJ/mol).

Solvent	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Anisole	17.64	48.95	61.96	20.95	80.50	-	-	63.33
MGC	13 (og)	3 (og)	2 (tg)	13 (tg)	1	(sol)	21 (wg)	(15)

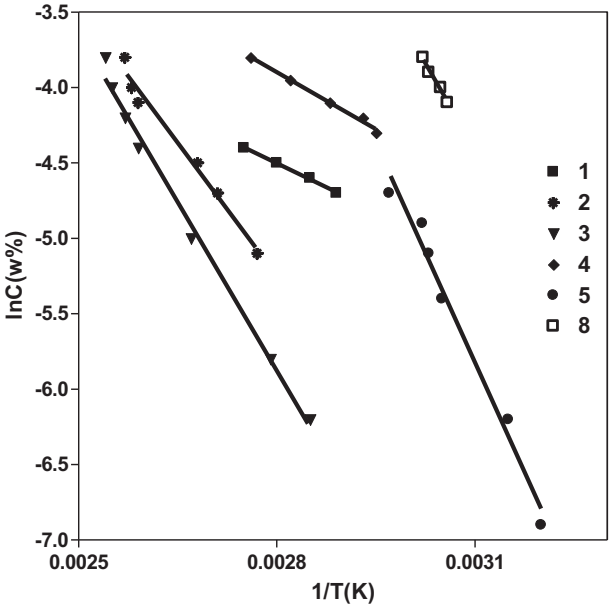


Figure 3. van't Hoff plot of gelators **1**, **2**, **3**, **4**, **5**, and **8** in anisole.

The gel-to-sol transition temperatures (T_{gel}) for the different concentrations of **1** and **4** in PhEME were also determined and it was found that raising the gelator concentration increases the thermal stability of the gels. The results reveal that **1** forms a more thermally stable gel than **4** in their equivalent concentrations (Figure 4).

Furthermore, the gel-to-sol transition enthalpies (ΔH_{gel}) estimated from the slope of van't Hoff plots for **1** and **4** in PhEME were found as 116.36 and 69.18 kJ/mol, respectively (see Figure 5). They demonstrate that these two gels are more stable in PhEME compared with anisole.

2.3. FTIR study

Hydrogen bonding plays a very essential role in the self-assembly of gelators and FTIR spectroscopy is the one of the most powerful tools to study these interactions. [21–24] FTIR spectra of the xerogel state of **4** from xylene and its solid state are demonstrated in Figure 6. The similarity of the spectra is the indication of intermolecular hydrogen bonding in the gel.

The involvement of intramolecular hydrogen bonds was confirmed by the dilution of the xerogel form of the gelator in chloroform (10^{-3} mol/dm^3). The spectrum of **4** in the solid state produces the N-H bands appearing at 3295 cm^{-1} while amide-I is at 1655 cm^{-1}. These stretching bands correspond to the hydrogen-

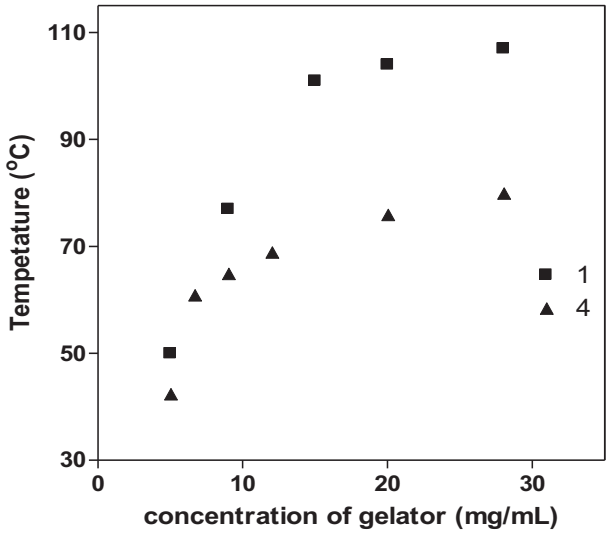


Figure 4. A plot of the gel-to-sol transition temperature (T_{gel}) against the concentration of the gelators (**1** and **4**) in PhEME.

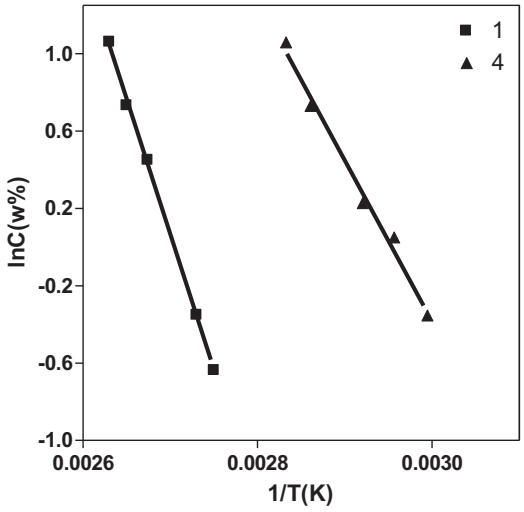


Figure 5. van't Hoff plot of **1** and **4** gelators in PhEME.

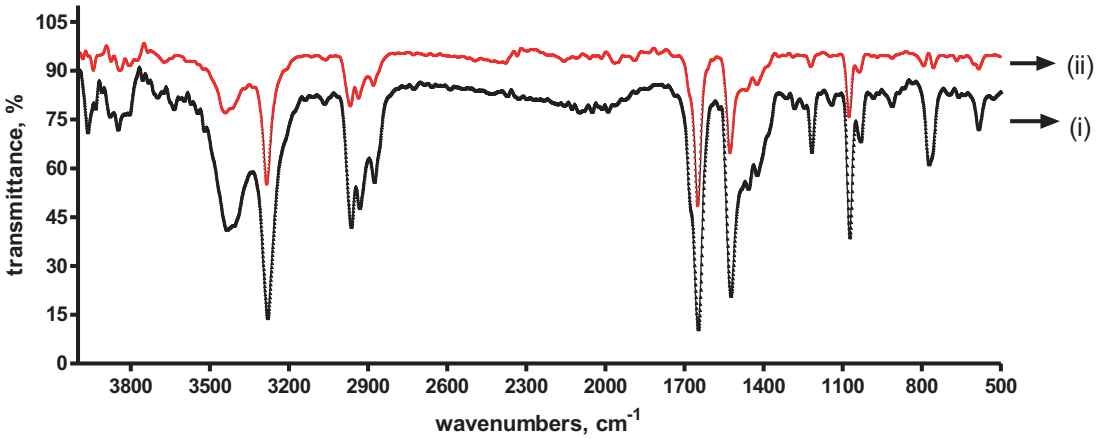


Figure 6. FTIR spectra of **4** in the solid state and the xerogel form from xylene gel.

bonded N-H and C=O in the oxalamide component. These peaks shift to higher wave numbers in the diluted solution of the gelator in chloroform (Figure 7a). The N-H band appears at 3392 and 3387 cm^{-1} and the amide-I band appears at 1680 cm^{-1}. On the other hand, the peak corresponding to the amide-II at 1525 cm^{-1} in the solid state moves down to 1501 cm^{-1} in the solution (Figure 7b). Moreover, a broad band at 3440 cm^{-1} in the solid state appears at a higher wave number with a low intensity in the diluted sample. The IR spectra imply that the OH and oxalamide functions take part in the intermolecular hydrogen bonding, which stabilizes the gel-fiber organization and hence maintains the 3D network.[25–28]

2.4. Temperature- and concentration-dependent ^{1}H NMR spectra

It is usually expected that the gelator molecules collected in the rigid gel network give broadened signals and reach a nonobservable point as a result of the long correlation times. The ^{1}H NMR spectra of the gels of **1** in CD_3CN and **4** in d_8-toluene at room temperature display the residual signals of the nondeuterated solvent and

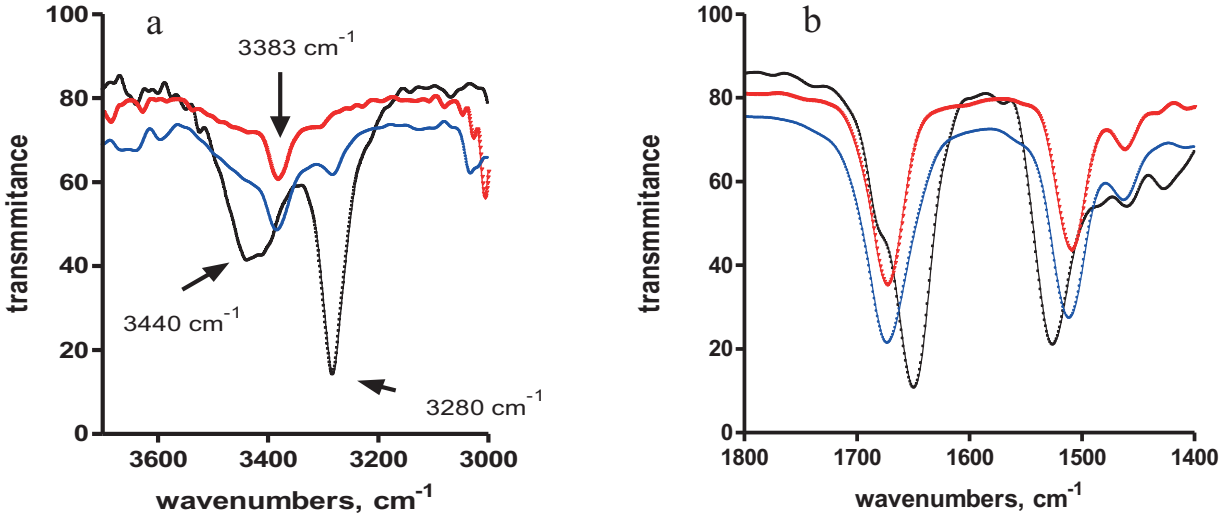


Figure 7. FTIR spectra of **4** in the xerogel form from xylene gel and in the solution diluted by chloroform. (a) 3500–3000 cm^{-1}, (b) 1800–1400 cm^{-1}.

only a trace amount of gelators. When the temperature was raised, the signals of the gelator were intensified and they yielded maximal intensity at temperatures above the gel melting points. Consequently, this may hint that at room temperature the gelator molecules are aggregated in a rigid network, but as a result of heating the network was disrupted and hence solvated smaller entities were formed, which lead to the observable NMR signals.[29–31] Therefore, the signals should correspond to gelators dissolved in the entrapped solvent. The plots of I_{std}/I_{Hi} against temperatures for gelators **1** in CD_3CN and **4** in toluene-d_8 are shown in Figures 8a and 8b, respectively.

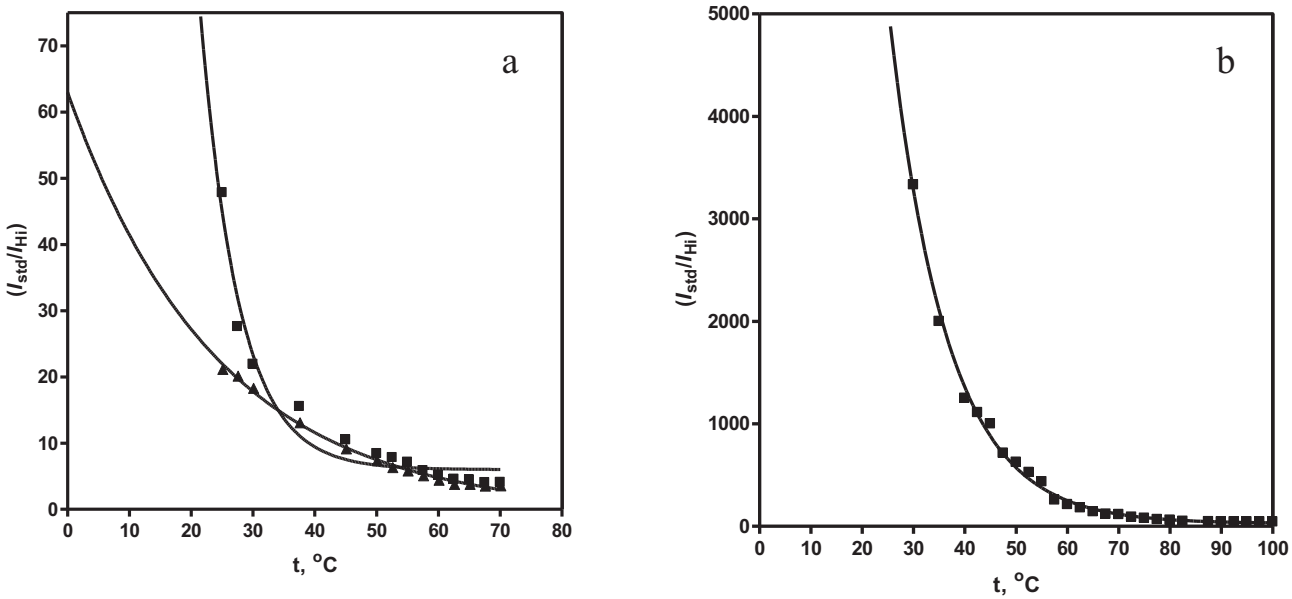


Figure 8. The plot of I_{std}/I_{Hi} against temperatures for the gelators: (a) **1** in CD_3CN where solid squares correspond to the integration in *CH and angles to that in NH and (b) **4** in toluene-d_8 involving the internal standard ($Cl_2CHCHCl_2$).

The plots show that the gelators almost completely exist in the gel form at room temperature, but as the temperature increases the deformation of the gel starts with a final collapse at a temperature corresponding to T_{gel}. The following two hydrogen atoms (*CH or NH) produce similar results (Figure 8).

A similar observation was also found by the dilution of the gel sample. Addition of solvent also leads to the release of entities from the network and hence this could be observed by NMR. The dilution will gradually cause the release of gelator molecules from the network, which could be detected by ^{1}H NMR (Figures 9a and 9b). This also implies that the *CH and NH hydrogen are buried within the gel network since the gelators are in gel form at the initial concentrations and they start to be disrupted by dilution. These two applications will be very useful to collect data to understand some key points regarding the structures of the gels.

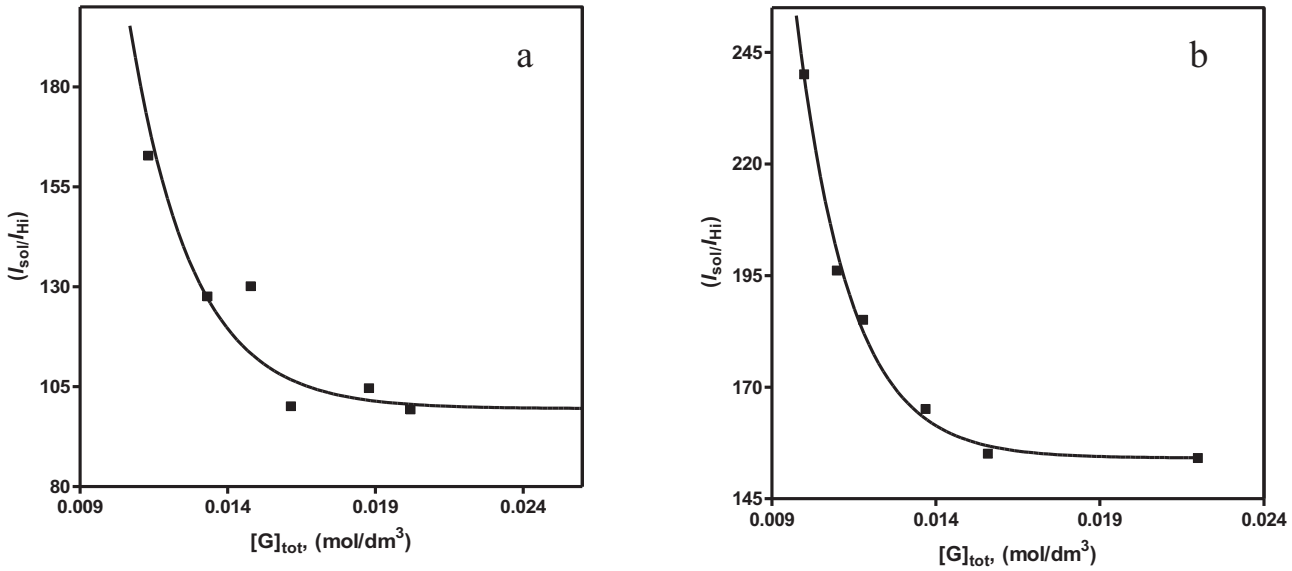


Figure 9. The plot of I_{sol}/I_{Hi} against the concentration of the gelator for the gelators: (a) **1** in CD_3CN and (b) **4** toluene-d_8.

Thermodynamic parameters (ΔH_d and ΔS_d) calculated by plotting $\ln K_d$, determined by NMR, against 1/T for the gels of **1** and **4** (Figures 10a and 10b, respectively) are illustrated in Table 4. It appears that the dissolution process is more likely enthalpy-controlled. The difference in ΔH_d implies that **4**/d_8-toluene gel is thermally more stable than **1**/CD_3CN gel.

Table 4. Thermodynamic parameters calculated by NMR for the gels of **1**/CD_3CN and **4**/d_8-toluene at 25 °C.

Gelator	ΔH_d, kJ mol^{-1}	ΔS_d, JK^{-1} mol^{-1}	ΔG_d, kJ mol^{-1}
1	38.43	0.42	38.31
4	72.53	67.51	52.42

In summary, the present study involves the synthesis of two new oxalamide- and diglycolylamide-based organogelators and investigation of their gelation behaviors in various organic fluids and comparison of these behaviors with already available compounds in the analogous solvents. Data obtained from ^{1}H NMR and FTIR gel spectra produce relevant mechanistic details and highlight the importance of equilibrium between the accumulated network and smaller dissolved gelato aggregates. They also demonstrate that there is a network assembly/dissolution equilibrium depending on the temperature. This work provides useful information in connection with other literature references to develop new soft materials for their use in various applications.

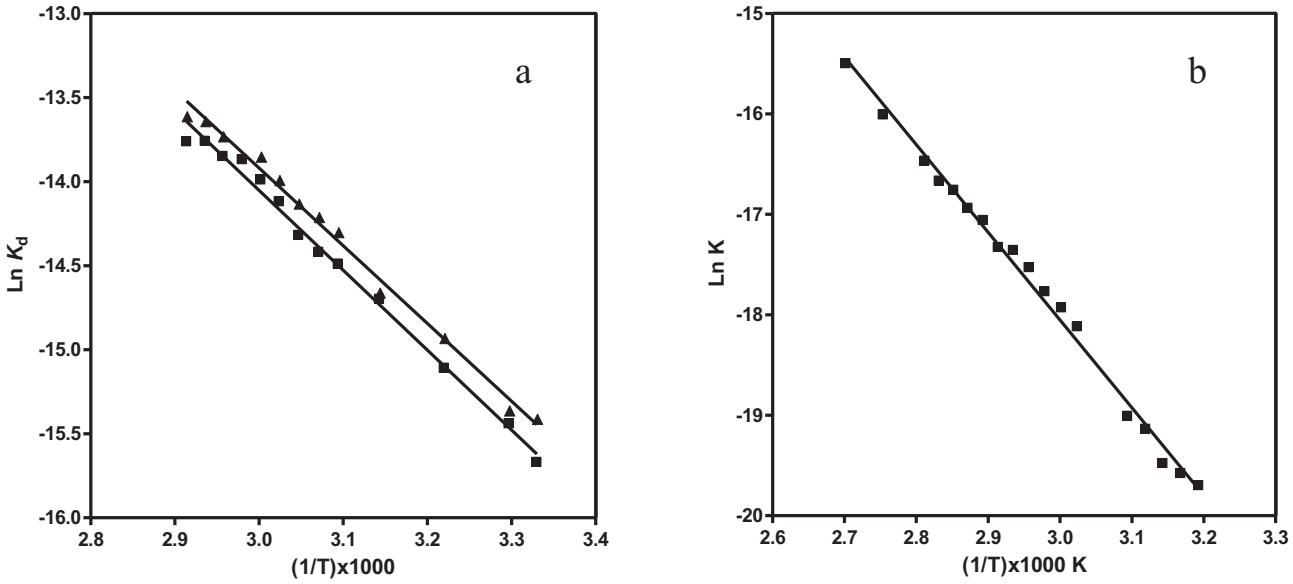


Figure 10. Plots of $\ln K_d$ versus 1/T for the gelators: (a) **1** in CD_3CN and (b) **4** in d_8-toluene at 25 °C.

3. Experimental

3.1. Chemical reagents

All chemicals were of reagent grade and used without further purification unless specified. They were purchased from commercial sources (Sigma-Aldrich or Fluka Chemical Company). Flash column chromatography was performed on silica gel 60 (Merck, 0.040–0.063 mm) and thin-layer chromatography (TLC) was used to follow the course of reactions on silica gel-coated Merck 60 F_{254} silica plates, visualized using a UV lamp (254 nm) or I_2 vapors. Nitrogen or argon gas was supplied to have an inert atmosphere in dry solvents purified according to literature methods and stored over molecular sieves. The purity of the products was proved by elemental analysis and TLC, as well as by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

3.2. Instruments and measurements

A Gallenkamp model apparatus with open capillaries was used to determine melting points and they are uncorrected. A Carlo Erba 1108 model apparatus was used to obtain elemental analyses of C, H, and N within $\pm 0.3\%$ of the theoretical values. A PerkinElmer 341 model polarimeter was employed to measure specific rotations. The concentration "c" has units of g/100 mL. A MATTSON model 1000 spectrophotometer was employed to record infrared spectra. A Bruker AV-400 digital FT-NMR spectrometer was used to record ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra in the solvents mentioned. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards.

3.3. General procedure for the synthesis of aminoalcohols

(*R*)-(-)-2-Amino-1-butanol was commercially available from Fluka and used without further purification. The literature procedures were followed for the synthesis of *L*-leucinol, *L*-isoleucinol, *L*-phenylalanilol, *L*-phenylglycinol, *L*-valinol, and 2-amino-octanol. They were prepared in one step from the reduction of the corresponding amino acids.[32]

3.4. Synthesis of dimethyloxalate and dimethyldiglycolate

The synthetic procedures described in the literature[33] were applied for the preparation of these esters. To a mixture of methanol and pyridine in 500 mL with flux under dry nitrogen, a solution of oxalylchloride (38.0 g, 300 mmol) or diglycolic acid dichloride (17.1 g, 100 mmol) in benzene (250 mL) was added drop-wise via a pressure-controlled dropping funnel for a period of 3 h. The solution was refluxed for 3 h and then kept stirring for 24 h at room temperature. The precipitated salt was removed by filtration and the solvent was removed by evaporation in vacuum. The remaining residue was extracted with ice-cold ether (3 × 50 mL), producing a white solid after evaporation. The products were recrystallized from diethyl ether-petroleum ether (2:1). Mp: 54–54.5 °C, yield: 92% for oxalate ester; mp: 36–37.5 °C, yield: 80% for diglycolate ester.

3.5. General procedure for the synthesis of gelators (1–7)

A general procedure described in the literature was followed for the syntheses of gelators.[18, 34] A solution of aminoalcohol (32 mmol) in MeOH (25 mL) kept cool at 5 °C was slowly added to a solution of dimethyloxalate (1.4 g, 16 mmol) at 0 °C in an ice bath over a period of 30 min. The mixture was kept stirring at 5 °C for a further 30 min and then allowed to warm to room temperature and stirred for 3 h. The precipitate was filtered, washed with ether, and dried in vacuum.

3.6. N,N′-Bis[(1*R*)-1-ethyl-2-hydroxyethyl]ethanediamide (1)

3.68 g (99%), mp 212–213 °C; $[\alpha]_D^{25} = +30.3$ (C 1.0, DMSO). Anal. Calcd. (%) for $C_{10}H_{20}N_2O_4$: C 51.71, H 8.68, N 12.06. Found C 51.69, H 8.71, N 12.02; IR (KBr) ν: 3365 (O-H), 3280 (N-H), 1665 (C=O, first amide band), 1530 (C=O, second amide band), 1048 (C-O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.85 (t, J = 7.4 Hz, 6H, CH_3), 1.42 (m, 2H$_a$, $\underline{CH}_2CH_3$) 1.55 (m, 2H$_b$, $\underline{CH}_2CH_3$), 3.30 (m, 4H, $\underline{CH}_2OH$), 3.71 (m, 2H, CH-N), 4.70 (bs, 2H, OH), 8.2 (d, J = 9.2 Hz, 2H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 11.4 (CH_3), 24.4 (CH_2CH_3), 54.2 (CH-N), 63.7 (CH_2OH), 161.7 (C=O).

3.7. N,N′-Bis[(1*S*)-2-hydroxyethyl-1-(*S*)-sec-buthyl]ethanediamide[34] (4)

White solid, 4.53 g (98%), mp 191–192 °C; $[\alpha]_D^{25} = +25.8$ (c 1.0, DMSO). Anal. Calcd. (%) for $C_{14}H_{28}N_2O_4$: C 58.30, H, 9.79, N, 9.71. Found: C 58.29, H 9.80; N 9.70. IR (KBr) ν: 3435 cm^{-1} (O-H), 3288 cm^{-1} (N-H), 1651 cm^{-1} (C=O, first amide band), 1529 cm^{-1} (C=O, second amide band), 1080 cm^{-1} (C-O ether band); ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 0.90 (t, J= 6.5 Hz, 6H, $\underline{CH}_2\underline{CH}_3$), 0.95 (d, J= 6.4 Hz, 6H, $CH\underline{CH}_3$), 1.38 (m, 2H, $\underline{CH}CH_3$), 1.40 (dd, J= 8.6, J = 4.4 Hz, 2H$_a$, $\underline{CH}_2CH_3$), 1.65 (dd, J= 8.6, J= 4.4 Hz, 2H$_b$, $\underline{CH}_2CH_3$), 3.50 (m, 4H, CH_2O), 3.81 (m, 2H, CHN), 8.2 (d, J= 9.2 Hz 2H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 11.6 ($CH_2\underline{C}H_3$), 15.9 ($CH\underline{C}H_3$), 25.5 ($\underline{C}H_2CH_3$), 35.4 ($\underline{C}HCH_3$), 56.0 (CH-N) 61.3 (CH_2OH), 160.3 (C=O).

3.8. N,N′-Bis [1-Hexyl-2-hydroxyethyl]ethanediamide (7)

3.8.1. Step 1

2-Amino-octanol was prepared by the reduction of 2-amino-octanoic acid as mentioned before.[32,35,36] Mp: 46–47 °C; bp: 124–124.5 °C. Anal. Calcd. (%) for $C_8H_{19}NO$: C 66.15, H 13.18, N 9.64. Found C 66.11, H 13.13,

N 9.61. IR (KBr) ν: 3417 and 3302 cm^{-1} bond respectively free and hydrogen bonded (O-H) stretching, 3280 cm^{-1} (N-H), 2922 and 2853 cm^{-1} C-H stretching, 1081 and 1043 cm^{-1} (C-O stretching); ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 0.79 (t, J = 7.4 Hz, 6H, CH_3), 0.99–1.05 (m, 16H, CH_2CH_2), 1.56 (m, 4H, $C^*H\underline{CH}_2$), 2.52 (m, 2H, $\underline{CH}$-N) 3.15-3.45 (dd, 4H, CH_2OH), 3.60 (bs, 2H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 14.04 (CH_3), 22.59 (CH_2CH_2), 26.07 (CH_2CH_2), 29.36 (CH_2CH_2), 31.76 (CH_2CH_2), 34.35 (CH_2CH_2), 52.85 (CH-N), 66.54 (CH_2OH).

3.8.2. Step 2

A solution of 2-amino-1-octanol (1.7 g, 12 mmol) in MeOH (17 mL) was slowly added to a solution of dimethyloxalate (0.5 g, 5 mmol) over a period of 30 min at 0 °C. The mixture was kept stirring for a further 1 h and the white solid precipitate was collected by filtration and washed with a small portion of the diethyl ether (3.6 g, 99%) of compound **7**. Mp: 152–153 °C. Anal. Calcd. (%) for $C_{18}H_{36}N_2O_4$ (344.49 $gmol^{-1}$): C 62.75, H 10.53, N 8.13. Found C 62.72, H 10.51, N 8.02. IR (KBr) ν: 3417 and 3302 cm^{-1} bond respectively free and hydrogen bonded (O-H) stretching, 3280 cm^{-1} (N-H), 2922 and 2853 cm^{-1} C-H stretching, 1640 cm^{-1} (C=O, first amide band), 1532 cm^{-1} (C=O, second amide band), 1081 and 1043 cm^{-1} (C-O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.79 (t, J = 6.6 Hz, 3H, CH_3), 1.19–1.1.22 (m, 8H, CH_2), 1.43–1.56 (m, 2H, $\underline{CH}_2CHNH$), 3.30 (m, 4H, CH_2OH), 3.74–3.80 (m, 1H, $\underline{CH}$-N), 4.47 (bs, 1H, O$\underline{H}$), 7.83 (t, J = 9.9 Hz, 1H, N$\underline{H}$); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 14.4 (CH3), 22.4 (CH_2CH_3), 25.9 (CH_2CH_2), 29 (CH_2CH_2), 30.8 (CH_2CH_2), 31.6 (CH_2CH_2), 51.8 (CH-N), 63.3 (CH_2OH), 161.2 (C=O).

3.9. N,N′-Bis[(1S)-1-benzyl-2-hydroxyethyl]diglycolyldiamide (8)

The synthesis of **8** has been reported in the literature.[33] Dimethyldiglycolate (0.16 g, 1.2 mmol) was added to a suspension of L-phenylalanilol (0.71 g, 2.5 mmol) in toluene (25 mL) in a 50-mL flat-bottomed one-necked flask with a vigorous stirring. The flask was attached to a reflux condenser and a Dean-Stark trap. The reaction mixture was refluxed with stirring for 2 days and the process was monitored by TLC ether/petroleum ether (2:1). The solvent was removed by evaporation in vacuum and the remaining residue was washed with ether. The purification of the crude material was achieved by column chromatography on silica gel (eluent: ether/petroleum ether 2:1). White crystals were precipitated on standing at 4 °C with slow evaporation. Yield: 72%; mp: 128–130 °C; $[\alpha]_D^{34}$ = –39.2 (c = 0.03, MeOH). Anal. Calcd. for $C_{22}H_{28}N_2O_5$: C, 65.98; H, 7.05; N, 7.00. Found: C, 65.97; H, 7.09; N, 6.97. IR (KBr): ν: 3413, 3316, 3243, 3070, 3031, 2931, 2873, 1643, 1546, 1110, 1045 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.70 (2H, dd, J= 16, J = 8.4 Hz), 2.90 (2H, dd, J = 8.4, J = 7.4 Hz), 3.39–3.46 (4H, m), 3.77–3.89 (4H, m), 3.91–4.06 (2H, m), 4.91 (br s 2H,), 7.15–7.29 (10H, m) 7.91 (2H, d, J = 8.4); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 37.01, 52.71, 62.89, 70.84, 126.46, 128.62, 129.54, 139.50, 169.01.

3.10. Gelation test

A typical gelation experiment as mentioned in the literature[37] was carried out for the gelation test. A weighed amount of gelator was mixed with 1 mL of several polar and nonpolar common organic solvents and unusual solvents such as aromatic ethers and long chain alcohols. In a septum-capped 4-mL glass vial with an internal diameter of 10 mm it was heated until the solid dissolved, followed by cooling in a constant temperature

bath at 25 °C. The appearance of a homogeneous substance was considered an indication of gelation with no gravitational flow upon inversion of the vial.

3.11. Determination of gel-to-sol transition temperatures (T_{gel})

Gel-to-sol transition temperatures (T_{gel}) were determined using the "dropping ball" method reported in the literature.[38] A stainless steel ball (250 mg, 4 mm in diameter) was carefully placed on the top of a gel in a 2-mL glass vial in a heating block. The temperature of the heating block was increased by 1 °C/min. T_{gel} was recorded at the temperature when the steel ball reached the bottom of the vial. Errors in all T_{gel} values are ±3 °C.

3.12. FTIR measurements

FTIR spectroscopy was used to obtain the information regarding hydrogen bonds in the gel network. The samples of solid and xerogel were prepared as KBr pellets. Xerogels were prepared by freeze-drying technique from the gel. A KBr cell (1 mm) was used for the solution samples. $CHCl_3$ (10^{-3} mol/dm^3) was used for the dilution of the samples.

3.13. The ^{1}H NMR determination of K_{gel} and ΔH_{gel}

The gel forms of **1** (1.6 mg) and **4** (3.8 mg) were prepared in 0.6 mL of CD_3CN and d_8-toluene, respectively, including an internal standard, 1,1,2,2-tetrachloroethane (1.9 μL).[39] ^{1}H NMR spectra of each gel were recorded at different temperatures. The ^{1}H NMR intensity ratios of the internal signal (I_{std}) to that of the gelator (I_{Hi}), the hydrogen attached to the chiral centre (*CH), or amide hydrogen (NH) were monitored and they were plotted against the temperature. This allowed estimation of the stability of gels since increasing the temperature increased the release of entities into solution from the gel network and hence the data produced a curve with a limit of I_{std}/I_{Hi} corresponding to a temperature at which the gel network was disrupted. A similar observation was also possible by using the signal of the solvent as a standard by plotting I_{sol}/I_{Hi} against the concentration of the gelator. In this case, the data would also produce a curve with a limit of I_{sol}/I_{Hi} corresponding to a concentration at which the network collapses. The following equation (Eq. (2)) proposed by Duncan describes the equilibrium nature of the gel systems.[31]

$$G_n \rightleftharpoons G_{ma} \rightleftharpoons aG_d \tag{2}$$

Here, G_n stands for the concentration of gelator assembled in the rigid network, G_{ma} stands for the concentration of larger mobile aggregates, and finally G_d stands for the concentration of dissolved gelator molecules. G_{ma} and G_d are observable by ^{1}H NMR. Their concentrations (G_{ma} and G_d) were obtained from the relative intensity of the NMR signal (NH and *CH) of the gelator compared with that of the internal standard as mentioned above.[39] The cumulative dissolution equilibrium may be defined as $K_d = [G_d]$ where $[G_d] = [G_{ma}] + [G_d]$. The K_d values are calculated at different temperatures.[31] Plotting $\ln K_d$ against 1/T gives the cumulative dissolution enthalpy (ΔH_d) and entropy (ΔS_d) as described in Eq. (3).

$$\ln K_d = (\Delta H_d/R)1/T + \Delta S_d/R. \tag{3}$$

Acknowledgments

We would like to express our gratitude to the Scientific and Technological Research Council of Turkey (TÜBİTAK) for financially support (Project No. 113Z142), and also the Dicle University Research Council (13-FF-72 and 13-FF-73).

References

1. Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133-3159.
2. Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237-1247.
3. Fages, F.; Vogtle, F.; Zinic, M. *Top. Curr. Chem.* **2005**, *256*, 77-131.
4. George, M.; Weiss, R. G. *Acc. Chem. Res.* **2006**, *39*, 489-497.
5. Janja, M.; Milan, J.; Berislav, P.; Vladislav, T.; Biserka, K. P.; Mladen, Z. *Tetrahedron* **2011**, *67*, 85-91.
6. Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev.* **2005**, *34*, 821-836.
7. Vintiloiu, A.; Leroux, J. C. J. *Controlled Release* **2008**, *125*, 179-192.
8. Banerjee, S.; Das, R. K.; Maitra, U. *J. Mater. Chem.* **2009**, *19*, 6649-6687.
9. Carretti, E.; Bonini, M.; Dei, L.; Berrie, B. H.; Angelova, L. V.; Baglioni, P.; Weiss, R. G. *Acc. Chem. Res.* **2010**, *43*, 751-760.
10. Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644-656.
11. Srinivasan, S.; Babu, P. A.; Mahesh, S.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2009**, *131*, 15122-15123.
12. Du, X.; Zhou, J.; Shi, J.; Xu, B. *Chem. Rev.* **2015**, *115*, 13165-13307.
13. Uzan, S.; Barış, D.; Çolak, M.; Aydın, H.; Hoşgören, H. *Tetrahedron* **2016**, *72*, 7517-7525.
14. van Esch, J. H.; Feringa, B. L. *Angew. Chem. Int. Ed.* **2000**, *39*, 2263-2266.
15. Tanmoy, K.; Sisir, D.; Dibyendu, D.; Anshupriya, S.; Prasanta, K. D. *Langmuir* **2009**, *25*, 8639-8648.
16. Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133-3160.
17. Frkanec, L.; Žinić. M. *Chem. Commun.* **2010**, *46*, 522-537.
18. Makarevic, J.; Jokic, M.; Raza, Z.; Stefanic, Z.; Kojic-Prodic, B.; Žinić, M. *Chem. Eur. J.* **2003**, *9*, 5567-5580.
19. Seo, S. H.; Chang, J. Y. *Chem. Matter.* **2005**, *17*, 3249-3254.
20. Suzuki, M.; Sato, T.; Kurose, A.; Shirai, H.; Hanabusa, K. *Tetrahedron Lett.* **2005**, *46*, 2741-2745.
21. Suzuki, M.; Owa, S.; Kimura, M.; Kurose, A.; Shiraib, H.; Hanabusa, K. *Tetrahedron Lett.* **2005**, *46*, 303-306.
22. Roy, S.; Das, D.; Dasgupta, A.; Mitra, N. R.; Das, K. P. *Langmuir* **2005**, *21*, 10398-10404.
23. Suzuki, M.; Nakajima, Y.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Langmuir* **2003**, *19*, 8622-8624.
24. Su, L.; Bao, C.; Lu, R.; Chen, Y.; Xu, T.; Song, D.; Tan, C.; Shi, T.; Zhao, Y. *Org. Biomol. Chem.* **2006**, *4*, 2591-2594.
25. Chen, L.; Wu, J.; Yuwen, L.; Shu, T.; Xu, M.; Zhang, M.; Yi, T. *Langmuir* **2009**, *25*, 8434-8438.
26. Luo, X.; Liu, B.; Liang, Y. *Chem Commun.* **2001**, *17*, 1556-1557.
27. Schmidt, R.; Schmutz, M.; Michel, M.; Decher, G.; Mesini, P. J. *Langmuir* **2001**, *18*, 5668-5672.
28. Hafkamp, R. J.; Feiters, M. C.; Nolte, R. J. M. *J. Org. Chem.* **1999**, *64*, 412-426.
29. Menger, F.; Yamasaki, Y.; Catlin, K.; Nishimi, T. *Angew. Chem.* **1995**, *107*, 616-618.
30. Menger, F.; Yamasaki, Y.; Catlin, K.; Nishimi, T. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 585-586.
31. Duncan, C. D.; Whitten, G. D. *Langmuir* **2000**, *16*, 6445-6452.

32. McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. *J. Org. Chem.* **1993**, *58*, 3568-3571.
33. Barış, D.; Şeker, S.; Hoşgören, H.; Toğrul, M. *Tetrahedron-Asymmetry.* **2010**, *21*, 1893-1899.
34. Sunkur, M.; Baris, D.; Hosgoren, H.; Togrul, M. *J. Org. Chem.* **2008**, *73*, 2570-2575.
35. Henry, G.; Lawrence, S.; Robert, W. L. *J. Org. Chem.* **1952**, *17*, 630-640.
36. Umezawa, J.; Takahashi, O.; Furuhashi, K.; Nohira, H. *Tetrahedron-Asymmetry.* **1994,** *5*, 491-498.
37. Yu, X.; Li, Y.; Yin, Y.; Yu, D. *Mater. Sci. Eng. C* **2012**, *32*, 1695-1698.
38. Chung, W. J.; An, K. B.; Park, Y. S. *Chem. Mater.* **2008,** *20*, 6750-6755.
39. Makarevic, J.; Jokic, M.; Peric, B.; Kojic-Prodic, B.; Zinic, M. *Chem. Eur. J.* **2001**, *7,* 3328-3341.