Journal of Chemical & Engineering Data

Enthalpies of Dilution of 1,3-Propanediol and Isomers of 2,3-Butanediol in Dimethylsulfoxide + Water Mixtures at 298.15 K

Aidi Guo,[†] Xingen Hu,^{*,†} Guoyong Fang,[†] Shuang Shao,[‡] and Hejuan Zhang[†]

⁺College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China ⁺Department of Chemistry, Zhejiang International Studies University, Hangzhou 310012, China

ABSTRACT: The dilution enthalpies of three isomers of 2,3-butanediol, namely, meso-2,3-butanediol, (2S,3S)-(+)-2,3-butanediol, (2R,3R)-(-)-2,3-butanediol, as well as 1,3-propanediol in dimethylsulfoxide (DMSO) + water mixtures have been determined, respectively, using an isothermal titration calorimeter (ITC) at 298.15 K. On the basis of the McMillan-Mayer theory, the homochiral enthalpic pairwise interaction coefficients (h_{XX}) of the four diols in the DMSO + water mixtures of various mass fractions (w = 0 to 0.3) have been calculated. The results are discussed from the point of view of solute-solute interaction and solute-solvent interaction. It was found that the method of ITC can differentiate the energies of homochiral interactions between different pairs of optical isomers in aqueous solutions. The variations of h_{XX} with w for the four diols depend largely on the competition equilibrium between hydrophobic-hydrophobic, hydrophilic-hydrophilic, and hydrophobic-hydrophilic interactions in DMSO + water mixtures. The five-membered intramolecular hydrogen bonding of vicinal diols plays an important role on homochiral pairwise interactions. The structure of relative rigid ring favors the forming of preferential configuration in molecular pairwise interaction.

INTRODUCTION

The molecular mechanism of chiral recognition has become a term which pervades a wide range of disciplines such as chemistry, biology, materials, and pharmaceutics.¹⁻⁵ Enantioselective interaction can be studied by various experimental methods, such as UV,⁶ IR,⁷ fluorescence spectrometry,^{8,9} circular dichroism (CD),¹⁰ NMR,¹¹ and microcalorimetry,¹² and so forth. For exploring weak nonbonding interactions in chiral molecular systems, the microcalorimetry is usually very useful.^{13,14} In 1968, by a microcalorimeter Takagi et al.¹⁵ found that there exists a very weak mixed enthalpy between two liquid chiral molecules (R- and S-). Atik et al.¹⁶ determined the excess molar enthalpies between fenchone and α -methyl benzyl amine enantiomers using microcalorimeter, and an obvious chiral discrimination effect was found. Recently, Kimura¹⁷⁻²⁰ and his coworkers determined the mixed enthalpies and the excess molar heat capacities among a series of small organic enantiomers (or their aqueous solutions) by the means of microcalorimetry $^{17-20}$ and differential scanning calorimetry (DSC),^{21,22} respectively. The mixed enthalpies and the apparent molar volumes of some chiral dicarboxylic acids in pure enthanol solutions have also been determined by them.²³ Castronuovo²⁴ had measured the enthalpic pairwise interaction coefficients between enantiometric α -amino acids of different alkyl chain lengths, and approximately a difference of (200 to 300) $J \cdot kg \cdot mol^{-2}$ was found that distinguishes cross-homo- from cross-heterotactic coefficients. In our previous work,²⁵ the enthalpies of dilution of L-alanine

In our previous work,²⁵ the enthalpies of dilution of L-alanine in dimethylsulfoxide (DMSO) + water of various mass fractions have been determined using ITC (VP-ITC, MicroCal). DMSO is a breaker for H_2O structure. Intramolecular hydrogen bond can be formed easily in DMSO + water mixed solvents. Hydrogen bonds can also be formed between DMSO and diols since the latter bears two hydroxyls as an H-donor. As a continuation of our interest in the chiral discrimination effect in the process of molecular pairwise interaction and solvent-mediated solute—solute interaction in aqueous mixed solvents, four aliphatic diols, namely, 1,3-propanediol, meso-2,3-butanediol, (2S,3S)-(+)-2,3-butanediol, and (2R,3R)-(-)-2,3-butanediol, were chosen as research objects in this work. The dilution enthalpies of these diols in DMSO + water mixtures have been determined respectively by isothermal titration calorimetry (ITC; ITC200, Micro-Cal). On the basis of the McMillan–Mayer theory,²⁶ the homochiral enthalpic pairwise interaction coefficients (h_{XX}) have been calculated. The chiral discrimination effect between different pairs of optical isomers has been discussed.

THEORETICAL BACKGROUND

According to Fini and Castagnolo,²⁷ the value of dilution enthalpy per injection in ITC can be expressed as:

$$\Delta H(m_{N-1} \rightarrow m_N) = \Delta H(m_{N-1}, m_N)/n_{\rm p} \qquad (1)$$

where N indicates the number of injections, and n_p is the moles of solute in each injection volume (V_{inj}) , which can be calculated as follows:

$$n_{\rm p} = V_{\rm inj} \rho_{\rm sol} m_0 \tag{2}$$

in which ρ_{sol} and m_0 are the density and the concentration of the solution in the syringe, respectively. m_0 is defined as moles of solute in 1 g of solution. Since the solutions used were at lower concentrations, the densities of them were assumed to be that of pure water.

Received:	January 11, 2011
Accepted:	February 23, 2011
Published:	March 07, 2011





From the McMillan–Mayer framework,²⁶ the thermodynamic formula commonly used to deal with the excess enthalpy of a binary solution containing solute X and solvent Y (Y = pure water or aqueous mixed solvent) can be expressed as follows:

$$H^{Z}(m_{\rm X}) = h_{\rm XX}m_{\rm X} + h_{\rm XXX}m_{\rm X}^{2} + \cdots$$
(3)

in which, h_{XX} , h_{XXX} , and so forth are known as pairwise, triplet, and higher order enthalpic interaction coefficients, respectively. To evaluate these coefficients, the dilution enthalpies of a binary solution (X + Y) are needed. The method of measuring dilution enthalpy by ITC was described in ref 27.

EXPERIMENTAL SECTION

Meso-2,3-butanediol, (2S,3S)-(+)-2,3-butanediol, and (2R,3R)-(-)-2,3-butanediol were purchased from ACROS; 1,3propanediol was purchased from SIGMA. The structures of the four diols can be seen in Scheme 1. All of the diols were used without further purification. DMSO was twice-distilled under reduced pressure over molecular sieves (0.4 nm), collected finally at 314.15 K, and then dried by molecular sieves for 24 h before use. All of the solutions were prepared by mass using a Sartorius balance with precision to 0.00001 g. The Milli-Q water (Millipore Elix5/Milli-Q Academic system) was used in all of the preparations. The dilution enthalpies were determined at 298.15 K by an isothermal titration calorimeter (ITC200, MicroCal), which requires only a 40 μ L sample (one-sixth of that needed by VP-ITC). All of the solutions were degassed before use. The sample cell was loaded with 200 μ L of H₂O (or aqueous mixed solvent), and the 40 μ L syringe was filled with chiral diol solution which was prepared by the same solvent. A titration run consisted of consecutive injections of $2 \,\mu$ L volume and 5 s duration each, with an interval of 2 min between them. The heat effect $\Delta H(m_{N-1}, m_N)$ per injection was determined by automatic peak integration of thermal power versus time curve. The thermal effects relating to the friction from each injection were considered to be negligible in all experiments. Every sample was determined for three times in the same condition, and the average $h_{\rm XX}$ was calculated.

RESULTS AND DISCUSSION

To check the accuracy of apparatus and method in use, dilution experiments of glycine, L-alanine, and L-serine in pure water at 298.15 K were carried out. The values of homochiral enthalpic pairwise interaction coefficients ($h_{\rm XX}$) for the three amino acids are $-370.98 \pm 6.79 \, \text{J} \cdot \text{kg} \cdot \text{mol}^{-2}$, 194.59 $\pm 2.76 \, \text{J} \cdot \text{kg} \cdot \text{mol}^{-2}$, $-610.75 \pm 2.64 \, \text{J} \cdot \text{kg} \cdot \text{mol}^{-2}$, respectively. For the three amino acids in water, the calculated values of $h_{\rm XX}$ differ slightly from those reported previously by us.²⁵ The difference is considered to arise from the experimental systematic errors as the types of microcalorimeters used are different. The method used in this work is also different from that by Palecz,²⁸ so a small difference in the values of $h_{\rm XX}$ can be found.

As an example, the typical titration curve of (2S,3S)-(+)-2,3butanediol in water at 298.15 K can be seen in Figure 1, and the experimental values of $\Delta H(m_{N-1} \rightarrow m_N)$ of (2S,3S)-(+)-2,3butanediol in water plotted as a function of the injection number N are given in Figure 2. The experimental values of $\Delta H(m_{N-1} \rightarrow m_N)$ as a function of N from the dilution experiments of the four diols in DMSO + water mixtures of different mass fractions (w) are listed in Tables 1 and 2. The values of h_{XX} were calculated from the slopes of linear regression of the experimental data based on an equation,²⁵ all with the squares of correlation coefficients $R^2 > 0.95$. The trends of h_{XX} with the mass fraction of DMSO (w) in aqueous mixed solvents are illustrated in Figure 3, and the corresponding values are reported in Table 3.

From Table 3, it can be observed evidently that all of the values of h_{XX} for the four diols are positive, which correspond to negative values of dilution enthalpies (Tables 1 and 2) and that there is a certain difference in energy of interaction between different homochiral pairs of the three diol isomers. However, this difference is still difficult to quantify exactly, because microcalorimetry is a nonspecific test method, and therefore it is impossible to apply it accurately on the level of molecular structure. In addition, the experimental systematic error may also have some impact on the accuracy of the results. Nevertheless, differences of chiral enantiomers in the energy do exist. According to Salam,²⁹ there exists a neutral weak force—the Z_0 particle; Z_0 force interacts with the L-electron or the D-electron in different ways and makes energy by moving which can be responsible for the ultimate optical asymmetry. Recent calculations by Mason³⁰ indicated that alanine, valine, serine, and aspartic acid are all L-stabilized relative to their unnatural D-mirrors for configurations in aqueous media. For the sugars, particularly for D-glyceraldehyde the calculations show that the right-handed variety is more stable.

From the above data which are about the dilution enthalpies and the corresponding values of enthalpic pairwise interaction coefficients, it can be deduced that the energy of pairwise interaction in solutions for *R*-isomers must be less than that of *S*-isomers as the former releases less heat in the process of dilution than the latter, which is characterized directly by the magnitude of h_{XX} . Assuming that the energy shift generated from Z^0 force makes configurations of the *R*-isomer and its molecular pair in condensed phase be also in a lower energy state, less heat will be liberated when diluted by solvent, just as what we have seen in experiments. As for the meso-isomer pair, the values of h_{XX} are the lowest among the three isomers, which implies the lowest energy in its configuration of pairwise interaction.



Figure 1. Typical titration curve of (2S,3S)-2,3-butanediol in water at 298.15 K.



Figure 2. Experimental values of $\Delta H(m_{N-1} \rightarrow m_N)$ of (2*S*,3*S*)-2,3-butanediol in water as a function of injection number *N* at 298.15 K ($R^2 = 0.9984$, SD = 0.87). R^2 is the square of correlation coefficient, and SD is the standard deviation of regression.

From Figure 3, it can be seen that the values of h_{XX} for the three diol isomers are nearly on linear growth with the increasing concentration of DMSO in mixed solvent. As DMSO molecule includes two methyl groups, it is reasonable to infer that the methyl moieties play a pivotal role during the dilution process of aqueous diols solutions. Reported by Lv,³¹ there exist complexes based on hydrogen bonds in DMSO + water mixtures. Hydrogen bonds can also be formed between DMSO and diols since the latter bears two hydroxyl as an H-donor. It has been confirmed by Ma and Wang³² and Wang and Polavarapu³³ that 2,3-butanediol forms an intramolecular hydrogen bond with a five-membered ring structure which is very stable (Scheme 2). On one hand, both hydrophobic—hydrophobic and hydrophobic—hydrophobic residues of

diol and hydrophobic (or hydrophilic) groups of DMSO become predominant on increasing DMSO, which leads to more positive values of h_{XX} for the three diol isomers. On the other hand, the formation of intramolecular hydrogen bonds in vicinal diols provides a relative rigid structure which makes hydrophobic residues go beyond polar moieties in five-membered ring molecule and be exposed more to other apolar species in solvent, namely, another diol molecule of the same five-membered ring structure and the methyls of DMSO, giving an additional contribution to hydrophobic—hydrophobic interaction. Generally the structure of a rigid ring favors the forming of preferential configuration in molecular pairwise interaction. Hence, the values of h_{XX} for the three chiral diols become more positive with the increasing concentration of DMSO (Figure 3).

Table 1. Experimental Dilution Enthalpies of 1,3-Propanediol, Meso-2,3-butanediol, (2S,3S)-(+)-2,3-Butanediol, and (2R,3R)-(-)-2,3-Butanediol in Pure Water at 298.15 K

	m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$		m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$
Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$
	1,3-Propan	nediol; $m_0 = 0.4041 \text{ mol}$	$\cdot kg^{-1}$		Meso-2,3-bu	tanediol; <i>m</i> ₀ = 0.3590 n	$nol \cdot kg^{-1}$
2	0.00121	0.00520	-200.79(-0.15)	2	0.00107	0.00462	-255.10(1.25)
3	0.00520	0.00915	-197.75(0.15)	3	0.00462	0.00813	-251.35(0.68)
4	0.00915	0.01306	-193.61(0.12)	4	0.00813	0.01161	-245.45(0.30)
5	0.01306	0.01694	-190.94(0.21)	5	0.01161	0.01505	-242.34(0.63)
6	0.01694	0.02077	-185.93(0.35)	6	0.01505	0.01845	-234.22(0.16)
7	0.02077	0.02456	-183.68(0.37)	7	0.01845	0.02182	-230.60(0.39)
8	0.02456	0.02832	-178.65(0.05)	8	0.02182	0.02515	-226.33(0.50)
9	0.02832	0.03203	-174.90(-0.23)	9	0.02515	0.02845	-222.14(0.34)
10	0.03203	0.03570	-171.98(0.05)	10	0.02845	0.03171	-217.94(0.35)
11	0.03570	0.03933	-169.00(0.16)	11	0.03171	0.03494	-215.44(0.77)
12	0.03933	0.04293	-164.86(0.21)	12	0.03494	0.03813	-210.93(1.05)
13	0.04293	0.04648	-161.70(0.27)	13	0.03813	0.04129	-206.82(0.64)
14	0.04648	0.04999	-158.46(-0.51)	14	0.04129	0.04441	-204.36(0.82)
15	0.04999	0.05346	-154.01(-0.44)	15	0.04441	0.04749	-198.99(0.76)
16	0.05346	0.05689	-152.08(-0.40)	16	0.04749	0.05054	-196.04(0.72)
17	0.05689	0.06028	-148.82(-0.25)	17	0.05054	0.05355	-191.92(0.87)
18	0.06028	0.06364	-146.18(-0.32)	18	0.05355	0.05653	-188.62(0.9)
20	0.06695	0.07022	-140.57(0.00)	20	0.05947	0.06238	-181.13(0.62)
	(2 <i>R</i> ,3 <i>R</i>)-2,3-B	utanediol; $m_0 = 0.3672$	$mol \cdot kg^{-1}$		(2 <i>S</i> ,3 <i>S</i>)-2,3-Bi	itanediol; $m_0 = 0.3212$	$mol \cdot kg^{-1}$
2	0.00146	0.00508	-294.37(0.16)	2	0.00096	0.00413	-257.29(0.44)
3	0.00508	0.00867	-288.46(0.08)	3	0.00413	0.00727	-252.38(0.94)
4	0.00867	0.01222	-283.11(0.40)	4	0.00727	0.01038	-246.01(0.81)
5	0.01222	0.01574	-278.72(0.09)	5	0.01038	0.01346	-242.58(0.57)
6	0.01574	0.01922	-269.60(0.29)	6	0.01346	0.01651	-234.80(1.04)
7	0.01922	0.02266	-266.65(0.15)	7	0.01651	0.01952	-231.45(1.09)
8	0.02266	0.02607	-262.36(0.89)	8	0.01952	0.02250	-226.06(1.10)
9	0.02607	0.02944	-256.53(-0.12)	9	0.02250	0.02546	-222.47(1.04)
10	0.02944	0.03277	-250.41(-0.11)	10	0.02546	0.02837	-218.46(1.63)
11	0.03277	0.03607	-247.44(0.06)	11	0.02837	0.03126	-214.08(1.36)
12	0.03607	0.03933	-241.34(-0.41)	12	0.03126	0.03412	-208.87(1.06)
13	0.03933	0.04255	-237.37(-0.42)	13	0.03412	0.03694	-205.52(1.29)
14	0.04255	0.04574	-233.65(-0.14)	14	0.03694	0.03973	-202.23(1.12)
15	0.04574	0.04889	-227.97(-0.10)	15	0.03973	0.04249	-198.02(1.74)
16	0.04889	0.05200	-224.99(0.11)	16	0.04249	0.04522	-194.93(1.68)
17	0.05200	0.05508	-220.20(0.07)	17	0.04522	0.04791	-190.72(1.34)
18	0.05508	0.05812	-216.75(0.08)	18	0.04791	0.05058	-186.27(0.39)
19	0.05812	0.06113	-212.85(-0.03)	19	0.05058	0.05321	-182.88(1.21)
20	0.06113	0.06410	-209.84(-0.02)	20	0.05321	0.05581	-179.59(1.21)

It should be pointed that such an intramolecular hydrogen bond in vicinal diol simultaneously makes another bare H atom on one of the two hydroxyls becomes more active. Therefore, intermolecular hydrogen bonding between the bare H atom and the solvent molecule (DMSO and H₂O) can be formed (Scheme 3) and makes a negative contribution on h_{XX} as what typical hydrophilic—hydrophilic interaction does. According to Wang,³³ the *R*-isomer forms an intramolecular hydrogen bond easier than S-isomer in the case of vicinal diols; consequently, (2*R*,3*R*)-2,3butanediol has smaller h_{XX} than (2*S*,3*S*)-2,3-butanediol as expected. The smallest value of h_{XX} for meso-2,3-butanediol should be anticipated reasonably, on the assumption that it does in this way most easily as its two chiral C atoms are mirror images with each other wherefore the two methyls are arranged on the same side of the C_2-C_3 single bond, which are favorable to intramolecular hydrogen bonding. Consequently in the studied mass fraction range of mixed solvents, the values of h_{XX} follow the order: (2S,3S)-2,3-butanediol > (2R,3R)-2,3-butanediol > meso-2,3-butanediol (Figure 3).

The overall sign and magnitude of $h_{\rm XX}$ would be a result of the competitive balance of all interaction factors in the ternary solution mentioned above. The possible interactions between a pair of homochiral diols, which are mediated strongly by DMSO and H₂O in solvent, can be classified as follows:

Table 2. Experimental Dilution Enthalpies of Meso-2,3-but anediol, (2S,3S)-(+)-2,3-Butanediol, (2R,3R)-(-)-2,3-Butanediol, and 1,3-Propanediol in DMSO + Water Mixtures at 298.15 K^a

	m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$		m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$
Ν	$mol \cdot kg^{-1}$	mol·kg ⁻¹	$J \cdot mol^{-1}$	Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$
			Meso-2,3-butanedic	ol in DMSO +	- Water		
	w = 0.05	$502 \cdot m_0 = 0.3627 \text{ mol} \cdot k$	σ^{-1}		w = 0.09	$98 \cdot m_0 = 0.3637 \text{ mol} \cdot k$	σ^{-1}
2	0.00108	0.00467	-276.96(0.07)	2	0.00109	0.00468	-306.85(0.59)
3	0.00467	0.00821	-273.01(0.05)	3	0.00468	0.00824	-302.24(0.39)
4	0.00821	0.01172	-266.34(-0.30)	4	0.00824	0.01176	-296.02(0.39)
5	0.01172	0.01520	-262.55(-0.23)	5	0.01176	0.01524	-291.64(0.24)
6	0.01520	0.01864	-253.28(0.25)	6	0.01524	0.01869	-280.56(0.21)
7	0.01864	0.02204	-251.43(-0.66)	7	0.01869	0.02210	-278.20(0.69)
8	0.02204	0.02541	-245.51(-0.74)	8	0.02210	0.02548	-272.19(0.72)
9	0.02541	0.02874	-240.67(-0.85)	9	0.02548	0.02882	-266.56(0.49)
10	0.02874	0.03204	-236.23(-1.05)	10	0.02882	0.03213	-261.80(0.53)
11	0.03204	0.03530	-232.54(-1.02)	11	0.03213	0.03540	-256.81(0.31)
12	0.03530	0.03852	-227.10(-0.84)	12	0.03540	0.03863	-250.71(0.06)
13	0.03852	0.04171	-222.73(-1.02)	13	0.03863	0.04182	-246.26(0.05)
14	0.04171	0.04486	-219.34(-0.81)	14	0.04182	0.04498	-242.43(0.05)
15	0.04486	0.04798	-213.8(-1.01)	15	0.04498	0.04811	-235.35(-0.31)
16	0.04798	0.05106	-211.13(-0.89)	16	0.04811	0.05120	-232.46(-0.14)
17	0.05106	0.05410	-207.44(-1.00)	17	0.05120	0.05425	-227.94(0.17)
18	0.05410	0.05711	-199.08(1.27)	18	0.05425	0.05727	-224.42(0.25)
19	0.05711	0.06008	-198.86(-1.25)	19	0.05727	0.06025	-218.99(0.32)
20	0.06008	0.06302	-196.41(-1.49)	20	0.06025	0.06319	-215.57(0.23)
	w = 0.15	583; $m_0 = 0.3643 \text{ mol} \cdot \text{k}$	g^{-1}		w = 0.20	$147; m_0 = 0.3918 \text{ mol} \cdot k$	g^{-1}
2	0.00109	0.00469	-329.33(-0.08)	2	0.00117	0.00504	-361.58(-0.08)
3	0.00469	0.00825	-324.69(-0.42)	3	0.00504	0.00887	-356.80(-0.42)
4	0.00825	0.01178	-317.67(-0.32)	4	0.00887	0.01267	-349.13(-0.32)
5	0.01178	0.01527	-313.38(-0.29)	5	0.01267	0.01642	-346.07(-0.29)
6	0.01527	0.01872	-303.08(-0.16)	6	0.01642	0.02014	-333.51(-0.16)
7	0.01872	0.02214	-298.42(-0.33)	7	0.02014	0.02381	-328.43(-0.33)
8	0.02214	0.02552	-292.25(-0.53)	8	0.02381	0.02745	-321.72(-0.53)
9	0.02552	0.02887	-286.79(-0.82)	9	0.02745	0.03105	-314.97(-0.82)
10	0.02887	0.03218	-281.00(-0.74)	10	0.03105	0.03461	-307.85(-0.74)
11	0.03218	0.03546	-275.88(-0.56)	11	0.03461	0.03813	-305.21(-0.56)
12	0.03546	0.03869	-269.77(-0.45)	12	0.03813	0.04162	-297.58(-0.45)
13	0.03869	0.04190	-264.69(-0.45)	13	0.04162	0.04506	-290.40(-0.45)
14	0.04190	0.04506	-260.86(-0.48)	14	0.04506	0.04846	-287.63(-0.48)
15	0.04506	0.04819	-254.03(-0.52)	15	0.04846	0.05183	-279.28(-0.52)
16	0.04819	0.05129	-250.16(-0.44)	16	0.05183	0.05516	-274.99(-0.44)
17	0.05129	0.05434	-245.15(-0.40)	17	0.05516	0.05845	-269.28(-0.40)
18	0.05434	0.05736	-241.55(-0.62)	18	0.05845	0.06169	-264.84(-0.62)
19	0.05736	0.06035	-236.16(-0.54)	19	0.06169	0.06491	-258.92(-0.54)
20	0.06035	0.06330	-233.12(-0.63)	20	0.06491	0.06808	-255.02(-0.63)
	w = 0.24	194; $m_0 = 0.3667 \text{ mol} \cdot \text{k}$	g^{-1}		w = 0.29	$77; m_0 = 0.3681 \text{ mol} \cdot k$	sg^{-1}
2	0.00109	0.00472	-352.14(0.97)	2	0.00110	0.00474	-369.30(0.94)
3	0.00472	0.00830	-345.17(1.01)	3	0.00474	0.00834	-363.99(1.39)
4	0.00830	0.01185	-336.73(1.30)	4	0.00834	0.01190	-355.91(1.73)
5	0.01185	0.01537	-331.79(1.22)	5	0.01190	0.01543	-349.37(1.51)
6	0.01537	0.01885	-320.71(1.36)	6	0.01543	0.01892	-338.05(1.26)
7	0.01885	0.02229	-315.88(1.19)	7	0.01892	0.02237	-332.22(1.31)
8	0.02229	0.02569	-308.51(0.81)	8	0.02237	0.02579	-325.05(0.97)
9	0.02569	0.02906	-303.72(0.69)	9	0.02579	0.02917	-321.41(1.72)

	m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$		m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$			
Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	J·mol ⁻¹	Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	J·mol ⁻¹			
10	0.02906	0.03239	-296.53(0.28)	10	0.02917	0.03252	-314.28(1.69)			
11	0.03239	0.03569	-293.09(0.83)	11	0.03252	0.03583	-309.29(1.82)			
12	0.03569	0.03895	-286.32(0.79)	12	0.03583	0.03910	-302.51(1.86)			
13	0.03895	0.04217	-280.93(0.84)	13	0.03910	0.04234	-296.33(1.79)			
14	0.04217	0.04536	-275.99(1.07)	14	0.04234	0.04553	-292.18(1.81)			
15	0.04536	0.04851	-268.30(1.26)	15	0.04553	0.04870	-284.00(1.85)			
16	0.04851	0.05162	-264.44(1.19)	16	0.04870	0.05182	-279.65(1.71)			
17	0.05162	0.05470	-258.91(1.32)	17	0.05182	0.05491	-273.15(1.55)			
18	0.05470	0.05774	-254.65(1.39)	18	0.05491	0.05797	-268.18(1.78)			
19	0.05774	0.06075	-248.72(1.38)	19	0.05797	0.06098	-260.96(1.67)			
20	0.06075	0.06371	-245.15(1.53)	20	0.06098	0.06396	-257.29(1.96)			
(2R, 3R)-2,3-Butanediol in DMSO + Water										
	w = 0.050	02; $m_0 = 0.3614 \text{ mol} \cdot \text{kg}$	-1		w = 0.09	998; $m_0 = 0.3148 \text{ mol} \cdot \text{kg}$	g^{-1}			
2	0.00108	0.00465	-325.14(-0.06)	2	0.00094	0.00405	-294.52(-0.38)			
3	0.00465	0.00818	-322.66(0.08)	3	0.00405	0.00713	-291.12(0.07)			
4	0.00818	0.01168	-318.81(0.22)	4	0.00713	0.01018	-284.01(-0.12)			
5	0.01168	0.01514	-316.03(1.45)	5	0.01018	0.01319	-281.42(-0.41)			
6	0.01514	0.01857	-305.20(0.43)	6	0.01319	0.01618	-272.10(-0.38)			
7	0.01857	0.02196	-302.25(0.59)	7	0.01618	0.01913	-268.74(-0.47)			
8	0.02196	0.02532	-297.49(1.17)	8	0.01913	0.02205	-262.61(-0.66)			
9	0.02532	0.02864	-287.77(0.57)	9	0.02205	0.02495	-257.47(-0.47)			
10	0.02864	0.03192	-283.30(0.43)	10	0.02495	0.02781	-252.37(-0.56)			
11	0.03192	0.03517	-279.82(0.24)	11	0.02781	0.03064	-249.01(-0.83)			
12	0.03517	0.03838	-273.04(0.05)	12	0.03064	0.03343	-242.66(-0.44)			
13	0.03838	0.04156	-267.91(-0.09)	13	0.03343	0.03620	-238.66(-0.64)			
14	0.04156	0.04470	-263.52(0.17)	14	0.03620	0.03894	-234.96(-0.63)			
15	0.04470	0.04780	-256.47(0.21)	15	0.03894	0.04164	-228.96(-0.77)			
16	0.04780	0.05087	-252.88(0.37)	16	0.04164	0.04431	-223.32(0.42)			
17	0.05087	0.05390	-246.12(0.27)	17	0.04431	0.04695	-221.08(-0.62)			
18	0.05390	0.05690	-243.35(0.09)	18	0.04695	0.04957	-217.74(-0.34)			
19	0.05690	0.05986	-237.86(0.09)	19	0.04957	0.05214	-212.41(-0.37)			
20	0.05986	0.06279	-234.14(0.19)	20	0.05214	0.05469	-208.89(-0.45)			
	w = 0.158	33; $m_0 = 0.3587 \text{ mol} \cdot \text{kg}$	-1		w = 0.19	997; $m_0 = 0.3517 \text{ mol} \cdot \text{kg}$	g ⁻¹			
2	0.00107	0.00461	-357.83(0.42)	2	0.00100	0.00433	-246.03(-1.75)			
3	0.00461	0.00812	-351.90(0.62)	3	0.00433	0.00762	-366.18(-0.12)			
4	0.00812	0.01160	-344.14(0.57)	4	0.00762	0.01088	-358.29(-1.04)			
5	0.01160	0.01503	-339.34(0.65)	5	0.01088	0.01411	-350.52(-1.28)			
6	0.01503	0.01844	-328.47(0.59)	6	0.01411	0.01730	-336.57(-1.23)			
7	0.01844	0.02180	-325.28(0.68)	7	0.01730	0.02046	-328.41(-3.11)			
8	0.02180	0.02513	-319.16(0.42)	8	0.02046	0.02359	-322.83(-0.26)			
9	0.02513	0.02843	-312.83(0.28)	9	0.02359	0.02668	-319.29(-1.94)			
10	0.02843	0.03169	-306.30(0.35)	10	0.02668	0.02974	-312.66(-1.73)			
11	0.03169	0.03491	-299.81(0.43)	11	0.02974	0.03277	-307.23(-2.79)			
12	0.03491	0.03810	-291.75(0.55)	12	0.03277	0.03576	-302.00(-2.21)			
13	0.03810	0.04125	-286.91(0.65)	13	0.03576	0.03872	-294.26(-1.44)			
14	0.04125	0.04437	-282.40(0.59)	14	0.03872	0.04164	-291.77(-2.17)			
15	0.04437	0.04745	-275.20(0.64)	15	0.04164	0.04454	-283.42(-2.34)			
16	0.04745	0.05050	-271.38(0.43)	16	0.04454	0.04740	-279.86(-2.96)			
17	0.05050	0.05351	-265.40(0.40)	17	0.04740	0.05022	-273.54(-2.17)			
18	0.05351	0.05648	-262.33(0.21)	18	0.05022	0.05301	-270.50(-2.38)			
19	0.05648	0.05942	-256.45(0.44)	19	0.05301	0.05577	-259.00(-0.44)			

N mol-lig1 ⁻¹ N mol-lig1 ⁻¹ N mol-lig1 ⁻¹ J.mat ⁻¹ 20 0.0359 ⁻¹ 0.0453 ⁻¹ 0.0457 ⁻¹ 0.0457 ⁻¹ 0.0457 ⁻¹ 0.0457 ⁻¹ 2 0.0014 ⁻¹ 0.049 ⁻¹ 0.057 ⁻¹ 0.0023 ⁻¹ 0.0035 ⁻¹ 0.0035 ⁻¹ 0.0035 ⁻¹ 0.0035 ⁻¹ 0.0035 ⁻¹ 0.0035 ⁻¹ 0.0045 ⁻¹ 0.0045 ⁻¹ 0.0023 ⁻¹ 0.0045 ⁻¹ 0.0045 ⁻¹ 0.0045 ⁻¹ 0.0059 ⁻¹ -0.0045 ⁻¹ 0.0023 ⁻¹ 0.0045 ⁻¹ 0.0178 ⁻¹ 0.0045 ⁻¹ 0.0178 ⁻¹ 0.0045 ⁻¹ 0.0178 ⁻¹ 0.0045 ⁻¹ 0.0178 ⁻¹ 0.0178 ⁻¹ 0.0105 ⁻¹ 0.0116 ¹ 0.0178 ⁻¹ 0.0105 ¹ 0.0116 ¹ 0.0178 ⁻¹ 0.0105 ¹ 0.0116 ¹ <		m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$		m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$	
200.05340.0633-2.32.2(0.6.4)2.00.05370.05370.0538-2.62.7(-0.13)\$	Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	N	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	
μ = 0.2494, μ ₂ = 0.3498 mol. μ ₂ μ = 0.2679, μ ₂ = 0.000830.00384- 0.3638 = 0.3688 (-0.0088)20.000900.01128- 3.41 26 (-0.01)30.000880.00898- 0.3088 (-0.01)30.000900.01128- 3.51 66 (-0.25)40.000980.01168- 3.9088 (-0.01)60.014620.0173- 3.35 7(0.09)60.014830.01689- 2.85 4(-1.02)70.012110.02445- 3.35 7(0.01)70.014290.01497- 2.74 90(-1.81)80.021210.02445- 3.25 5(0.11)80.016970.02242- 2.65 3(-1.62)100.024450.02765- 3.25 52(0.21)110.02320.02455- 3.55 4(-1.02)110.030820.03396- 3.92 36(-0.23)120.027650.03952- 3.25 54(-1.02)120.037060.4013- 3.22 36(-0.23)130.02320.01484- 3.24 24(-1.95)130.037060.4013- 3.20 7(0.03)140.03760.03142- 2.42 24(-1.97)140.04160.4012- 2.063(0.03)150.03180.0348- 2.42 24(-1.97)150.04130.4041- 2.063(0.02)160.44460.40476- 2.42 24(-1.97)160.04140.4047- 2.42 24(-1.97)160.44460.40476- 2.42 24(-1.97)170.04160.40440.40476- 2.42 24(-1.97)160.44460.444712.42 16(-1.01) <trr<td>160.04160.40476<</trr<td>	20	0.05942	0.06233	-252.21(0.64)	20	0.05577	0.05850	-256.27(-0.85)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		w = 0.24	94; $m_0 = 0.3489 \mathrm{mol} \cdot \mathrm{kg}^{-1}$			w = 0.29	77; $m_0 = 0.2779 \text{ mol} \cdot \text{k}$	g^{-1}	
3 000449 000790 -30039(-0.07) 3 00035 00059 -30038(-0.9) 4 000790 0.01128 -351 66(-0.2) 4 000695 0.0166 -3008(-0.9) 6 0.01642 0.01793 -3357(0.0) 6 0.0165 0.01485 0.0168 -3358(-0.2) 7 0.0121 0.01350 0.01375 -3357(0.0) 9 0.01445 0.01687 -3458(-1.6) 9 0.0221 0.02445 0.03760 -33554(0.2) 1 0.01201 0.0235 -2548(-1.7) 10 0.03882 0.03376 -33582(-0.2) 1 0.0205 0.0355 -2548(-1.9) 13 0.03760 0.0401 -2583(-0.2) 1 0.0316 0.0356 -2548(-1.9) 14 0.0416 0.0401 -2583(-0.2) 1 0.0316 0.0318 0.2275(-1.6) 15 0.04316 0.04516 -2588(-0.2) 1 0.0316 0.0318 0.2375(-1.6) 16 0.0401<	2	0.00104	0.00449	-365.79(-0.02)	2	0.00083	0.00358	-316.39(-0.26)	
40.0017900.01128- 751.65(-025)40.008990.00165- 295.94(-0.2)50.011420.014220.014230.014230.014230.014230.014230.0142370.011730.02121-330.57(0.0)60.014380.01690.014470.220490.024450.02765-371.59(0.2)80.01690.01470.0220-249.3(-1.6)100.039820.03980-315.50(-0.2)110.02200.02455-25.99(-1.7)110.039820.03706-292.6(-0.2)120.02760.02705-25.99(-1.7)120.033960.03706-292.6(-0.2)130.029250.03196-24.83(-1.9)130.04130.0413-292.6(-0.2)140.013960.0491-24.83(-1.9)140.04130.0414-22.63(0.0)160.039760.73(-5.43(-1.9)150.041640.04912-26.36(0.0)160.039760.0414-24.44(-1.9)160.04130.0505-27.16(0.05)170.04140.0412-24.84(-1.9)170.04140.0505-26.63(0.02)180.041460.0423-24.44(-1.9)180.05070.0505-25.63(0.02)180.041460.0457-24.84(-1.9)190.05140.0507-25.63(0.02)140.00670.041630.0424-24.64(-2.1)100.05090.0509-25.63(0.12)140.00630.0404	3	0.00449	0.00790	-360.29(-0.07)	3	0.00358	0.00629	-308.86(-0.05)	
50.011280.01462-346.39(-0.12)50.00880.01165-195.94(-0.1)60.0114620.01793-335.71(09)60.011860.01687-285.44(-1.20)70.01210.024450.02121-335.50(0.1)70.014280.01687-274.90(-1.45)90.014450.02765-317.59(0.20)90.019470.02202-764.35(-1.73)110.039620.0396-305.52(-0.21)110.024550.255.92(-1.73)120.03960.0396-298.26(-0.24)120.027550.02552-764.85(-1.75)130.037660.04013-292.96(-0.23)130.029520.03943-248.24(-1.95)140.041610.04014-292.97(0.03)150.031380.03942-248.24(-1.95)150.041360.04012-276.83(0.19100.03972-248.25(-1.79)160.041610.04161-280.92(0.23)180.04460.447-24.87(-1.79)170.041200.0556-271.16(0.05)170.039120.21.65(-2.17)7180.057800.06663-266.82(0.1)200.04640.0493-21.65(-2.17)190.00930.0092-275.47(-3.01)30.004830.0048-342.26(-2.17)100.00930.00892-275.67(-3.01)30.011630.226.21-33.55(-1.01)140.00930.00892-275.67(-3.01)30.011630.226.21-33.55(-	4	0.00790	0.01128	-351.65(-0.25)	4	0.00629	0.00898	-300.85(-0.29)	
6 0.01462 0.01793 -335.7(0.9) 6 0.01165 0.01428 -285.44(-1.6) 7 0.01479 0.02121 -330.59(0.17) 7 0.01489 0.01497 0.2204 9 0.02445 0.02765 -317.59(0.2) 9 0.01497 0.0202 -269.54(-1.6) 11 0.03082 0.0396 -315.60(-0.2) 11 0.02145 0.02755 -259.96(-1.7) 12 0.03366 0.03706 -289.56(-0.2) 12 0.02952 0.03196 -248.34(-1.9) 14 0.04013 0.04161 -289.56(-0.2) 14 0.0396 0.3396 -248.34(-1.9) 15 0.04161 0.04161 -288.16(-0.2) 14 0.0396 0.3396 -248.34(-1.9) 16 0.04161 0.0412 -265.80(.01) 16 0.0376 0.0391 -248.45(-1.9) 17 0.04161 0.0412 -265.80(.01) 16 0.0436 0.0414 -248.45(-1.9) 18 0.04161 0.0412 -266.87(.0.2) 18 0.01165 0.0449 -224.97(-1.7)	5	0.01128	0.01462	-346.99(-0.12)	5	0.00898	0.01165	-295.94(-0.41)	
7 001793 002121 $-330.39(0,T)$ 7 001428 001699 $-281.46(-1.5)$ 8 0032121 002445 $-333.35(0,31)$ 8 001697 002202 $-274.90(-1.43)$ 10 002765 0.30802 $-311.9(0,07)$ 10 002202 002952 $-264.34(-1.73)$ 12 003306 0.30396 $-998.26(-0.24)$ 12 0.02755 0.02952 $-253.46(-1.79)$ 13 0.04013 0.04013 $-292.96(-0.23)$ 13 0.02952 0.03186 $-244.46(-1.90)$ 14 0.04013 0.04014 $-276.33(0,19)$ 16 0.03476 $-237.36(-1.09)$ 15 0.04146 0.04012 $-276.33(0,19)$ 10 0.04376 $-237.36(-1.09)$ 16 0.05205 0.05494 $-266.7(0.28)$ 18 0.04160 0.04176 $-224.97(-1.7)$ 17 0.05170 0.05937 $-226.03(-2.3)$ 10 0.04476 $-224.97(-1.7)$ 18 0.05290 0.06665 $-225.84(-7.53)$ 3 0.0448 0.0607 $-334.24(-7$	6	0.01462	0.01793	-335.71(0.09)	6	0.01165	0.01428	-285.44(-1.20)	
80.021210.02445	7	0.01793	0.02121	-330.59(0.17)	7	0.01428	0.01689	-281.45(-1.63)	
9 0.02445 0.02765 -317.9(0,20) 9 0.01947 0.02202 0.2485 -24843(-1.73) 10 0.03765 0.03960 -305.52(-0.21) 12 0.02705 0.02952 0.23954 -24843(-1.73) 12 0.03396 0.0413 -248.4(-0.21) 13 0.02705 0.02952 0.0396 -248.4(-0.59) 15 0.0416 0.0416 -287.9(0,00) 15 0.03136 0.249.7(-0.21) 24.34.2(-1.95) 16 0.04616 0.041912 -247.8(0,10) 15 0.03136 0.249.7(-0.19) 17 0.04912 0.02635 0.249.7(-1.90) 2.0 0.0464 0.248.7(-1.90) 18 0.05205 0.0593 -266.3(0.23) 18 0.04146 0.04875 -216.6(-1.90) 19 0.05780 0.0693 -266.8(0.19) 20 0.04646 0.04875 -216.6(-1.90) 20 0.05780 0.0693 -252.8(0.19) 3 0.0694 0.382.1(-1.91) 0.01463 0.0163 3.312.2	8	0.02121	0.02445	-323.55(0.31)	8	0.01689	0.01947	-274.90(-1.45)	
10 0.03765 0.03386 -310.6(07) 10 0.02022 0.02455 -2543(-17) 11 0.03082 0.03396 -305.32(-0.21) 11 0.02455 0.29252 23.36(-17) 13 0.03706 0.4013 -228.26(-0.23) 13 0.02952 0.03196 -248.2(-15) 15 0.04116 0.04116 -228.3(-0.23) 15 0.03438 0.03676 -228.2(-17) 16 0.04116 0.04116 -228.3(-0.23) 16 0.03676 0.0312 -243.8(-17) 17 0.0416 0.0416 -228.18(-0.23) 18 0.04146 0.04176 -228.17(-0.20) 18 0.05005 0.05194 -256.38(0.12) 19 0.04146 0.04196 -228.15(-0.21) 19 0.05005 0.05005 -256.38(0.12) 10 0.04180 0.04185 -248.07(-17) 10 0.05005 0.250.47071 3 0.04087 0.01181 -33.12(-0.01181 12 0.00091 0.00183 0.00087 0.01181 0.00181 0.33.12(-0.01181 0.33.12(-0.01181 0.33.12(-0.	9	0.02445	0.02765	-317.59(0.20)	9	0.01947	0.02202	-269.53(-1.62)	
110.030820.03396-305.52(-0.21)110.024550.02705-249.96(-1.78)120.033960.03706-798.82(-0.24)120.027050.02952-243.44(-1.95)140.040130.0416-280.37(0.06)150.034360.03458-244.46(-1.96)150.043160.04912-276.83(1.07)160.036760.03912-244.84(-1.96)160.049120.05205-271.16(0.05)170.039120.04146-228.15(-2.06)170.049120.05205-271.16(0.05)170.039120.04146-228.15(-2.06)180.054940.05780-266.63(0.26)190.046040.04829-21.65(-2.17)190.059780.06692-256.88(0.19)200.046040.04829-21.65(-2.17)190.059780.0692-25.04(-2.33)20.01060.00483-349.20(-0.70)30.00970.00339-26.06(-2.23)40.00870.01423-344.8(-0.83)40.000910.00392-25.54(-7.23)50.011520.01493-344.8(-0.83)50.000930.0093-26.06(-2.53)50.011520.01493-344.2(-0.25)60.012810.015710.158-25.10(-2.79)70.01810.02181-331.12(-0.99)60.012810.015710.1585-25.10(-2.79)70.01810.02181-331.2(-1.65)70.01510.01680.22460.0246 </td <td>10</td> <td>0.02765</td> <td>0.03082</td> <td>-311.06(0.07)</td> <td>10</td> <td>0.02202</td> <td>0.02455</td> <td>-264.83(-1.73)</td>	10	0.02765	0.03082	-311.06(0.07)	10	0.02202	0.02455	-264.83(-1.73)	
120.033960.03706-0.29826(-0.24)120.027050.029520.13396-248.34(-1.95)130.037060.04413-729.96(-0.23)130.029520.03136-248.24(-1.95)150.044160.04416-288.13(-0.23)160.034380.03676-237.58(-2.40)160.044160.04912-76.83(0.19)160.036760.03912-248.28(-1.57)170.05020.05394-266.63(0.26)190.044640.044376-224.57(-1.7)190.054940.05780-266.63(0.26)190.044760.04232-21.663(-2.1)190.059300.0663-25.68(0.13)20.046400.0423-21.65(-2.4)20.009100.0053-25.68(0.13)20.001660.04640-224.57(-1.7)30.005300.0668-25.68(-2.3)30.00160.00458-344.20(-0.7)40.003310.00592-27.54(-7.31)30.00160.00151-345.25(-0.1)50.009880.01281-25.65(-2.5)50.011520.314.2(-1.9)60.01510.05150.25.6(-2.5)50.011520.307.12(-0.8)70.01570.01580.02142-24.06(-2.3)40.00870.0143-33.12(-0.8)80.01580.02142-24.02(-2.3)70.013110.02165-31.542(-1.9)90.01410.028230.02142-24.02(-2.3)100.02464-30.72(11	0.03082	0.03396	-305.52(-0.21)	11	0.02455	0.02705	-259.96(-1.78)	
130.037060.04013-292.96(-0.23)130.029520.03196-248.34(-1.95)140.040130.04616-280.79(0.0)150.031960.03438-244.66(-1.96)160.040160.04912-276.83(0.19)160.036760.03912-234.28(-1.97)170.040120.05205-271.16(0.05)170.039120.04146-228.15(-2.06)180.052050.05494-266.78(0.26)190.043760.04604-221.65(-2.41)200.057800.0663-250.88(0.19)200.046040.0429-21.65(-2.71)190.0057800.0663-250.88(0.19)200.046040.0429-21.65(-2.71)20.000910.00393-280.08(-3.03)20.004680.0087-344.8(-0.83)40.000920.00982-27.547(-3.01)30.004580.0087-344.8(-0.83)40.000920.00983-265.65(-2.55)50.011520.01152-315.42(-1.39)50.0012810.01281-265.25(-2.55)50.011520.01493-331.12(-0.99)60.012810.012810.01283-24.24(-1.23)100.02616-307.1(-1.09)90.021420.02423-24.26(-2.55)50.011510.3147-320.3(-1.09)140.008880.01281-24.25(-2.54)130.021650.2146-307.1(-1.09)150.012840.012850.021640.02164-307.1(-1.09)<	12	0.03396	0.03706	-298.26(-0.24)	12	0.02705	0.02952	-253.64(-1.79)	
140.040130.04316-28.818(-0.22)140.031960.03438-244.46(-1.9)150.044160.04616-280.79(0.06)150.034380.03676-237.58(-2.40)160.046160.04912-276.38(1.9)160.039760.03912-24.32(.5(-2.40)170.049120.052050.04944-266.78(0.28)180.044460.04376-22.4.97(-1.7)190.057900.0663-256.88(0.19)200.046040.04829-21.6.5(-2.1)200.057900.0663-256.88(0.19)200.046040.04829-21.6.5(-2.1)30.003910.00393-280.08(-3.03)20.00160.00458-344.20(-0.70)30.003930.00692-275.47(-3.01)30.04580.00057-344.38(-0.83)40.006920.00988-266.0(-2.23)40.008070.1152-335.58(-1.01)50.000980.01571-255.65(-2.77)60.014930.01831-320.13(-1.29)60.012810.01571-255.65(-2.77)60.014930.01831-320.13(-1.29)70.015710.018880.2142-242.8(-2.53)90.024960.02823-302.52(-1.03)100.024230.024230.242.8(-2.53)90.024960.02823-302.52(-1.04)110.015810.01571-245.8(-2.76)100.034670.03783-248.9(-1.04)120.020750.03247-248.9(-2.	13	0.03706	0.04013	-292.96(-0.23)	13	0.02952	0.03196	-248.24(-1.95)	
150.043160.04616-28079(0.06)150.034380.03676-237.58(-2.4))160.046160.049120.05205-721.16(0.05)170.039120.4146-224.32(-1.7))180.052050.05494-26678(0.28)180.041460.04376-224.97(-1.7))190.054940.05603-256.88(0.19)200.046040.04829-21.66.3(-2.4))200.057000.06603-256.88(0.19)200.040600.04829-21.66.3(-2.4))20.00910.00933-256.88(0.12)30.001060.00458-34920(-707)30.00920.0092-27.57(7-3.01)30.001680.00458-344.38(-0.83)40.000920.0098-266.0(-2.23)40.008070.01152-335.58(-1.01)50.009880.01281-265.2(-2.55)50.011520.01381-331.12(-0.89)60.012810.01571-256.6(-2.77)60.014930.01831-320.13(-1.29)70.015710.01858-21.4280.021650.02496-307.71(-1.09)80.016710.01874-24.9280.021650.02496-307.71(-1.09)90.021420.024740.0271-24.82(-2.42)80.021650.02496-307.71(-1.09)100.02710.02975-24.27(-2.31)110.031470.03467-27.97.7(-1.01)110.027010.02975-24.27(-2.43)13 <t< td=""><td>14</td><td>0.04013</td><td>0.04316</td><td>-288.18(-0.22)</td><td>14</td><td>0.03196</td><td>0.03438</td><td>-244.46(-1.96)</td></t<>	14	0.04013	0.04316	-288.18(-0.22)	14	0.03196	0.03438	-244.46(-1.96)	
160.046160.04912-276.83(0.19)160.036760.03912-234.28(-1.97)170.049120.05205-0.05494-266.75(0.28)180.041460.04756-224.97(-1.79)190.0557800.06063-256.68(0.19)200.046040.04829-21.65(-2.47)200.057800.06063-256.88(0.19)200.046040.04829-21.65(-2.77) $w=0.0502; m_0=0.057 mol·kg^{-1}$ $w=0.0502; m_0=0.3057 mol·kg^{-1}$ $w=0.0998; m_0=0.352 mol·kg^{-1}$ $w=0.0998; m_0=0.352 mol·kg^{-1}$ $w=0.0998; m_0=0.352 mol·kg^{-1}$ $w=0.0092; m_0=0.3057 mol·kg^{-1}$ $w=0.00933$ -260.06(-3.03)20.004580.00807-344.38(-0.63) $a0.00393$ 0.00692-275.47(-3.01)30.004580.00807-344.38(-0.63) $a0.00393$ 0.00692-275.47(-3.01)30.004580.00807-344.38(-0.63) $a0.00393$ 0.00692-275.47(-3.01)30.004580.00807-344.38(-0.63) $a0.00393$ 0.00692-205.95(-2.77)60.014930.0181-314.2(-0.79) $a0.01510.0151-235.58(-1.77)60.014930.0181-315.42(-1.39)a0.018380.021420.2453-246.95(-2.42)80.021650.0246-307.71(-1.09)a0.018380.02142-246.95(-2.42)8$	15	0.04316	0.04616	-280.79(0.06)	15	0.03438	0.03676	-237.58(-2.40)	
170.049120.05205-271.16(0.05)170.039120.04146-224.5(-2.0)180.052050.05494-266.78(0.26)180.041360.04064-221.6(-2.1)190.057800.06663-265.88(0.19)200.046040.04829-21.66.(-2.1) <td rowsspace<="" t<="" td=""><td>16</td><td>0.04616</td><td>0.04912</td><td>-276.83(0.19)</td><td>16</td><td>0.03676</td><td>0.03912</td><td>-234.28(-1.97)</td></td>	<td>16</td> <td>0.04616</td> <td>0.04912</td> <td>-276.83(0.19)</td> <td>16</td> <td>0.03676</td> <td>0.03912</td> <td>-234.28(-1.97)</td>	16	0.04616	0.04912	-276.83(0.19)	16	0.03676	0.03912	-234.28(-1.97)
18 0.05205 0.05494 0.26678(0.28) 18 0.04146 0.04376 0.2407(-1.7)9 19 0.05780 0.05780 -26063(0.26) 19 0.04364 0.04829 -21.65(-2.4)1 20 0.05780 0.05780 -256.88(0.19) 20 0.04604 0.04829 -21.65(-2.4)1 2 0.00091 0.0033 -280.08(-3.03) 2 0.00166 0.00458 -349.20(-0.7)0 3 0.00393 0.00692 -257.47(-3.01) 3 0.00487 0.01152 -335.85(-1.01) 4 0.00692 0.00988 -266.25(-2.55) 5 0.01152 -331.12(-0.89) 6 0.01281 0.01571 -255.65(-2.77) 6 0.01493 0.0181 -320.13(-1.3) 7 0.01571 0.1858 0.02142 -242.05(-2.42) 8 0.02165 0.02463 -307.21(-1.01) 9 0.02142 0.02423 0.2214 -242.05(-2.31) 11 0.03147 0.03567 -291.0(-0.33 10	17	0.04912	0.05205	-271.16(0.05)	17	0.03912	0.04146	-228.15(-2.06)	
19 0.05494 0.05780 -26063(0.26) 19 0.04376 0.04604 -221.65(-2.1) 2 0.05780 0.0663 -256.88(0.19) 20 0.04644 0.04829 -21.63(-2.7) 2 0.00091 0.0393 -26.80(8-0.30) 2 0.0016 0.0483 -349.20(-0.7) 3 0.00092 0.0093 -26.60(-2.23) 4 0.00458 0.00181 -335.58(-1.01) 5 0.00988 0.1281 -265.25(-2.55) 5 0.01183 0.216.1(-2.1) 6 0.01281 0.0171 -255.65(-2.7) 6 0.01493 0.01831 -231.12(-0.89 6 0.01281 0.0171 -255.65(-2.7) 7 0.01831 0.2165 -315.42(-1.29) 7 0.01571 0.0188 -251.00(-2.7) 7 0.01831 0.20165 -315.42(-1.29) 8 0.01888 0.02142 0.24406 0.2823 0.29466 0.2823 -291.10(-0.93 10 0.02701 0.02975 -234.21(-2.3	18	0.05205	0.05494	-266.78(0.28)	18	0.04146	0.04376	-224.97(-1.79)	
20 0.05780 0.06663 $-256.88(.19)$ 20 0.4664 0.4829 $-216.63(-2.7)$ $k = 0.0502, m_0 = 0.3057 mol \cdot kg^{-1}$ $k = 0.0998, m_0 = 0.3562 mol \cdot kg^{-1}$ $k = 0.0998, m_0 = 0.3562 mol \cdot kg^{-1}$ 2 0.00091 0.00393 -280.08(-3.03) 2 0.00106 0.00458 -349.20(-0.70) 3 0.00393 0.00692 -275.47(-3.01) 3 0.00487 0.01152 -335.58(-1.01) 5 0.00988 0.01281 -265.25(-2.55) 5 0.01152 0.01493 -331.12(-0.80) 6 0.01571 0.255.60(-2.77) 6 0.01493 0.2161 -315.42(-1.39) 7 0.01571 0.01581 0.2162 0.2496 0.2232 -307.71(-1.09) 9 0.01542 0.02423 0.02142 0.02496 -295.78(-1.09) 10 0.02423 0.02101 0.2975 0.3247 -228.78(-2.30) 12 0.03467 0.03783 -294.92(-1.02) 13 0.03247 0.03516 0.274.53(-2.40) 13	19	0.05494	0.05780	-260.63(0.26)	19	0.04376	0.04604	-221.65(-2.41)	
2 0.00091 0.00393 -280.08(-3.03) 2 0.00106 0.00458 -349.20(-0.70) 3 0.00393 0.00692 -275.47(-3.01) 3 0.00458 0.0087 -341.38(-0.83) 4 0.00692 0.00988 -266.00(-2.23) 4 0.00493 0.1152 -335.58(-1.01) 5 0.00988 0.1211 -255.65(-2.77) 6 0.01431 0.2165 -301.571 -315.42(-1.39) 6 0.0158 0.02142 0.04233 -240.06(-2.53) 9 0.02465 0.02496 -307.71(-1.09) 10 0.02423 0.02101 -236.13(-2.13) 10 0.02823 0.03147 -295.76(-1.01) 11 0.02474 0.03547 -228.76(-2.42) 13 0.03783 -04907 -249.42(-0.50) 12 0.02975 0.03782 -224.3(-2.44) 13 0.03783 0.0497 </td <td>20</td> <td>0.05780</td> <td>0.06063</td> <td>-256.88(0.19)</td> <td>20</td> <td>0.04604</td> <td>0.04829</td> <td>-216.63(-2.71)</td>	20	0.05780	0.06063	-256.88(0.19)	20	0.04604	0.04829	-216.63(-2.71)	
$\begin{split} & \psi = 0.0502; \ m_0 = 0.3057 \ \text{mol} \cdot \text{kg}^{-1} & \psi = 0.9998; \ m_0 = 0.3562 \ \text{mol} \cdot \text{kg}^{-1} \\ 2 & 0.00091 & 0.00393 & -280.08(-3.03) & 2 & 0.00106 & 0.00458 & -349.20(-0.70) \\ 3 & 0.00393 & 0.00692 & -275.47(-301) & 3 & 0.00458 & 0.00807 & -344.38(-0.83) \\ 4 & 0.00692 & 0.00988 & -266.00(-2.23) & 4 & 0.00807 & 0.01152 & -335.58(-1.01) \\ 5 & 0.00988 & 0.01281 & -265.25(-2.77) & 6 & 0.01493 & 0.01831 & -320.13(-1.29) \\ 6 & 0.01281 & 0.01571 & -255.65(-2.77) & 6 & 0.01493 & 0.01831 & -320.13(-1.29) \\ 7 & 0.01571 & 0.01858 & -251.00(-2.79) & 7 & 0.01831 & 0.02165 & -315.42(-1.39) \\ 9 & 0.02142 & 0.02423 & -242.08(-2.53) & 9 & 0.02496 & 0.02823 & -302.52(-1.05) \\ 10 & 0.02423 & 0.02701 & -236.13(-2.13) & 10 & 0.02823 & 0.03147 & -295.78(-1.04) \\ 11 & 0.02701 & 0.02975 & -234.21(-2.31) & 11 & 0.03147 & 0.03467 & -291.10(-0.93) \\ 12 & 0.02975 & 0.03247 & -228.78(-2.36) & 12 & 0.03667 & 0.03783 & -284.92(-1.02) \\ 13 & 0.03347 & 0.03316 & -224.23(-2.84) & 13 & 0.03783 & 0.4097 & -2775.26(-1.08) \\ 14 & 0.03516 & 0.03782 & -200.80(-2.30) & 14 & 0.04097 & 0.04406 & -275.36(-1.08) \\ 15 & 0.03782 & 0.40444 & -214.43(-2.46) & 15 & 0.04406 & 0.04712 & -286.02(-0.98) \\ 16 & 0.04044 & 0.04364 & -207.68(-2.46) & 17 & 0.05015 & 0.05313 & -228.43(-1.27) \\ 18 & 0.04560 & 0.04814 & -204.52(-2.24) & 18 & 0.05313 & 0.05609 & -253.58(-1.32) \\ 19 & 0.04814 & 0.05664 & -199.05(-2.03) & 19 & 0.5609 & 0.05911 & -247.64(-1.8) \\ 20 & 0.0564 & 0.05312 & -194.79(-1.33) & 20 & 0.00103 & 0.05619 & -243.94(-1.23) \\ 19 & 0.04814 & 0.05664 & -199.05(-2.03) & 19 & 0.05609 & 0.05911 & -247.64(-1.8) \\ 20 & 0.0564 & 0.05812 & -194.79(-0.33) & 20 & 0.00103 & 0.05619 & -243.94(-1.23) \\ 19 & 0.04814 & 0.05664 & -199.05(-2.03) & 19 & 0.05609 & 0.05911 & -247.64(-1.8) \\ 20 & 0.0564 & 0.05312 & -194.79(-0.36) & 3 & 0.00443 & 0.00780 & -385.92(1.34) \\ 4 & 0.00681 & 0.00973 & -315.73(-0.16) & 4 & 0.07080 & 0.1114 & -378.62(075) \\ 5 & 0.00973 & 0.01261 & -310.36(-0.31) & 5 & 0.01114 & 0.01414 & -378.42(10.81) \\ 4 & 0.00681 & 0.00734 & -325.57(-0.12$				(2 <i>S</i> ,3 <i>S</i>)-2,3-Butanedi	ol in DMSO	+ Water			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		= 0.05	$02.m = 0.2057 \text{ mol} ka^{-1}$				08.m = 0.3562 mol	a ⁻¹	
2 0.00091 0.00095 -2.20.00(-3.05) 2 0.00106 0.00455 -3.42.0(-0.7) 3 0.00092 0.00998 -266.00(-2.23) 4 0.00097 0.01152 -335.58(-1.01) 5 0.00988 0.01281 -265.25(-2.55) 5 0.01152 0.01493 -331.12(-0.89) 6 0.01281 0.01571 -255.65(-2.77) 6 0.01493 0.01831 -320.13(-1.29) 7 0.01571 0.0158 -251.00(-2.79) 7 0.01831 0.02165 -315.42(-1.39) 8 0.0142 0.04495 -246.95(-2.42) 8 0.02165 0.02496 -307.71(-1.09) 9 0.02142 0.02423 -0.2701 -236.13(-2.13) 10 0.02823 -0.30.52(-1.05) 10 0.02423 0.02701 -236.78(-2.36) 12 0.03467 -028.79(-1.04) 11 0.02701 0.02975 -234.21(-2.31) 11 0.03147 -295.78(-1.04) 12 0.02975 0.03247 -228.78(-2.36) 12 0.03467 0.03783 -248.92(-1.02) 14 </td <td>2</td> <td>W = 0.03</td> <td>0.00202</td> <td>280.08(-2.02)</td> <td>2</td> <td>W = 0.99</td> <td>$98; m_0 = 0.3302 \text{ more}$</td> <td>8</td>	2	W = 0.03	0.00202	280.08(-2.02)	2	W = 0.99	$98; m_0 = 0.3302 \text{ more}$	8	
5 0.00593 0.00692 $-2734, (-301)$ 5 0.00435 0.00600 $-344, 36, (-35)$ 4 0.00692 0.00988 $-266.0(-2.23)$ 4 0.00807 0.01152 $-3355, 86(-1.01)$ 5 0.00988 0.01281 0.01571 $-2255, 65(-2.77)$ 6 0.01493 0.01831 $-320.13(-1.29)$ 7 0.01571 0.01858 -241.06(-2.79) 7 0.01831 0.02165 $-335.58(-1.09)$ 9 0.02142 0.02423 $-242.08(-2.43)$ 9 0.02496 0.02823 $-302.52(-1.09)$ 10 0.02423 0.02101 $-236.13(-2.13)$ 10 0.02823 0.03147 $-295.78(-1.04)$ 11 0.02701 0.02975 $-234.21(-2.31)$ 11 0.03147 $-295.78(-1.04)$ 12 0.02975 0.03247 0.03247 $-222.87(-2.36)$ 12 0.03467 0.03783 $-284.92(-1.02)$ 13 0.03247 0.03516 $-221.30(-2.30)$ 14 0.04097 0.04406 $-275.36(-1.$	2	0.00091	0.00393	-280.08(-3.03) -275.47(-2.01)	2	0.00108	0.00458	-349.20(-0.70)	
40.009520.007862.0007(2.2.5)40.0081120.011520.011520.011520.0115250.009880.01281-265.25(-2.55)50.011520.01493-331.12(-0.89)70.015710.01858-251.00(-2.79)70.018310.02165-315.42(-1.39)80.018580.02142-246.95(-2.42)80.021650.02496-307.71(-1.09)90.021420.02423-242.08(-2.53)90.024960.02823-302.52(-1.05)100.024230.02701-236.13(-2.13)100.028230.03147-295.78(-1.04)110.027010.02975-234.21(-2.31)110.031470.03467-291.10(-0.93)120.029750.03247-228.78(-2.36)120.034670.03783-284.92(-1.02)130.032470.03516-224.23(-2.84)130.037830.04097-279.72(-1.10)140.035160.03782-220.80(-2.30)140.040970.04466-275.36(-1.08)150.037820.04044-214.4(-2.46)150.0447120.05015-263.89(-1.16)160.040440.04364-212.61(-2.50)160.0447120.05015-263.89(-1.62)170.043660.04814-204.52(-2.24)180.055010.05313-258.43(-1.27)180.045600.04814-204.52(-2.24)180.055090.05901-247.64(-1.88)200.050640.05312	3	0.00393	0.00092	-2/5.4/(-3.01) -266.00(-2.22)	3	0.00458	0.00807	-344.38(-0.83) -325.58(-1.01)	
3 0.0098 0.01281 $-2053(-2.33)$ 3 0.01132 0.01132 0.01133 $-351.12(-0.39)$ 6 0.01281 0.01571 $-255.65(-2.77)$ 6 0.01493 0.01831 $-320.13(-1.29)$ 7 0.01571 0.01888 0.02142 $-246.95(-2.42)$ 8 0.02165 0.02496 $-307.71(-1.09)$ 9 0.02142 0.02423 $-242.08(-2.53)$ 9 0.02496 0.02823 $-302.52(-1.05)$ 10 0.02701 0.02975 $-234.21(-2.31)$ 11 0.03147 0.03467 $-295.78(-1.04)$ 11 0.021975 0.03247 $-228.78(-2.36)$ 12 0.03467 0.03783 $-284.92(-1.02)$ 13 0.03247 0.03516 $-224.23(-2.84)$ 13 0.03467 0.03783 $-284.92(-1.02)$ 14 0.03516 0.03782 $-220.80(-2.30)$ 14 0.04097 0.04406 $-275.36(-1.08)$ 15 0.03782 0.04044 $-212.61(-2.50)$ 16 0.04712 0.05015 0.05131 $-258.43(-1.27)$ 16 0.04404 0.0	4	0.00092	0.00988	-265.00(-2.23)	4	0.00807	0.01132	-333.38(-1.01) -221.12(-0.80)	
0 0.01431 0.01571 0.01571 0.01571 0.01858 -251.00(-2.79) 7 0.01831 0.02165 -315.42(-1.39) 8 0.01581 0.02142 -246.95(-2.42) 8 0.02165 0.02496 -302.52(-1.05) 10 0.02423 0.02701 -236.13(-2.13) 10 0.02823 0.03147 -295.78(-1.04) 11 0.02701 0.02975 -234.21(-2.31) 11 0.03147 0.03467 -291.10(-0.93) 12 0.02975 0.03247 -228.78(-2.36) 12 0.03467 0.03783 -284.92(-1.02) 13 0.03247 0.03516 -224.23(-2.84) 13 0.03783 0.04097 -279.72(-1.10) 14 0.03516 0.03782 -220.80(-2.30) 14 0.0406 0.04712 -268.02(-0.98) 16 0.04044 0.04304 -212.61(-2.50) 16 0.04712 0.5618 -263.89(-1.16) 17 0.04304 0.04560 -207.68(-2.46) 17 0.05015 0.63131 -258.43(-1.27) 18 0.04560 0.04414 -199.05(-2.03)	5	0.00988	0.01231	-255.65(-2.77)	5	0.01132	0.01493	-32012(-120)	
70.013010.013010.013010.0121030.0121030.0121030.01210380.018580.02142-246.95(-2.42)80.021650.02496 $-307.71(-1.09)$ 90.021420.02423-242.08(-2.53)90.024960.02823 $-302.52(-1.05)$ 100.029750.02477-228.78(-2.36)120.034670.03783 $-284.92(-1.02)$ 130.032470.03516-224.23(-2.84)130.037830.04097 $-279.72(-1.10)$ 140.035160.03782-220.80(-2.30)140.040970.04406 $-275.36(-1.08)$ 150.037820.04044-214.43(-2.46)150.044060.04712 $-268.02(-0.98)$ 160.040440.04304-212.61(-2.50)160.047120.05015 $-263.89(-1.6)$ 170.043040.04560-207.68(-2.46)170.050150.05313 $-258.43(-1.27)$ 180.045600.04814-204.52(-2.24)180.055090.05901 $-247.64(-1.38)$ 200.050640.05312-194.79(-1.33)200.059010.06189 $-391.26(2.78)$ 30.003870.00681-322.79(-0.36)30.004430.00780 $-385.92(1.34)$ 40.006810.00973 $-315.73(-0.16)$ 40.007800.01114 $-376.62(0.75)$ 50.009730.01261 $-310.36(-0.31)$ 50.01114 0.01444 $-374.33(1.17)$ 60.012610.01546 $-$	7	0.01571	0.01371	-251.00(-2.77)	7	0.01495	0.02165	-31542(-1.39)	
3 0.02142 0.02141 0.02141 0.02141 0.02141 0.02141 0.02141 0.02141 0.02141 0.02141 0.02141 0.02141	8	0.01858	0.01858	-246.95(-2.79)	8	0.02165	0.02105	-307.71(-1.09)	
00.024230.02701-236.13(-2.13)100.028230.03147-295.78(-1.04)110.027010.02975-234.21(-2.31)110.031470.03467-291.10(-0.93)120.029750.03247-228.78(-2.36)120.034670.03783-284.92(-1.02)130.032470.03516-224.23(-2.84)130.037830.04097-279.72(-1.10)140.035160.03782-220.80(-2.30)140.040970.04406-275.36(-1.08)150.037820.04044-214.43(-2.46)150.044060.04712-268.02(-0.98)160.040440.04304-212.61(-2.50)160.047120.05015-263.89(-1.16)170.043040.04560-207.68(-2.46)170.050150.05313-258.43(-1.27)180.045600.04814-204.52(-2.24)180.055090.05901-247.64(-1.38)200.050640.05312-194.79(-1.33)200.059010.06189-243.94(-1.30)w = 0.1583; m_0 = 0.3009 mol·kg ⁻¹ w = 0.2047; m_0 = 0.3446 mol·kg ⁻¹ 20.000900.0387-325.61(0.08)20.001030.00443-391.26(2.78)30.003870.00681-322.79(-0.36)30.004430.00780-385.92(1.34)40.006810.00973-315.73(-0.16)40.007800.01114-376.62(0.75)50.009730.01261-310.36(-0.31)5	0	0.02142	0.02/142	-242.08(-2.53)	0	0.02496	0.02490	-302.52(-1.05)	
100.024250.024112.0013(-2.15)100.022250.031472.03.072.05.07(-1.07)110.027010.02975-234.21(-2.31)110.031470.03467-291.10(-0.93)120.029750.03247-228.78(-2.36)120.034670.03783-284.92(-1.02)130.032470.03516-224.23(-2.84)130.037830.04097-279.72(-1.10)140.035160.03782-220.80(-2.30)140.040970.04406-275.36(-1.08)150.037820.04044-214.43(-2.46)150.044060.04712-268.02(-0.98)160.040440.04304-212.61(-2.50)160.047120.05015-263.89(-1.16)170.043040.04560-207.68(-2.46)170.050150.05313-258.43(-1.27)180.045600.04814-204.52(-2.24)180.053130.05609-253.58(-1.32)190.048140.05064-199.05(-2.03)190.056090.05901-247.64(-1.38)200.050640.05312-194.79(-1.33)200.059010.06189-243.94(-1.30)w=0.1583; m ₀ =0.3009 mol·kg ⁻¹ w=0.2047; m ₀ =0.3446 mol·kg ⁻¹ 20.000900.0387-325.61(0.08)20.001030.00443-391.26(2.78)30.003870.00681-322.79(-0.36)30.004430.00780-385.92(1.34)40.006810.00973-315.73(-0.16)	10	0.02423	0.02723	-23613(-213)	10	0.02490	0.03147	-295.78(-1.04)	
11 0.02161 0.02175 0.03247 $-228.78(-2.36)$ 11 0.05161 0.03763 $-228.92(-1.02)$ 13 0.03247 0.03516 $-2224.23(-2.84)$ 13 0.03783 0.04097 $-279.72(-1.10)$ 14 0.03516 0.03782 0.04044 $-212.42(-2.30)$ 14 0.04097 0.04406 $-275.36(-1.08)$ 15 0.03782 0.04044 $-214.43(-2.46)$ 15 0.04406 0.04712 $-268.02(-0.98)$ 16 0.04044 0.04304 $-212.61(-2.50)$ 16 0.04712 0.05015 $-263.89(-1.16)$ 17 0.04304 0.04560 $-207.68(-2.46)$ 17 0.05015 0.05313 $-258.43(-1.27)$ 18 0.04560 0.04814 $-204.52(-2.24)$ 18 0.05609 0.05901 $-247.64(-1.38)$ 20 0.05064 0.05312 $-199.05(-2.03)$ 19 0.05609 0.05901 $-247.64(-1.38)$ 20 0.05064 0.05312 $-194.79(-1.33)$ 20 0.05901 0.06189 $-243.94(-1.30)$ $w=0.1583; m_0=0.3009 mol·kg^{-1}$ $w=0.2047; m_0=0.3446 mol·kg^{-1}$ 2 0.00090 0.00387 $-325.61(0.08)$ 2 0.00103 0.00443 $-391.26(2.78)$ 3 0.00387 0.00681 $-322.79(-0.36)$ 3 0.00443 0.00780 $-385.92(1.34)$ 4 0.00681 0.00973 $-315.73(-0.16)$ 4 0.00780 0.01114 $-378.62(0.75)$ 5 0.00973 0.012	11	0.02701	0.02975	-23421(-231)	11	0.03147	0.03467	-291.10(-0.93)	
12 0.03247 0.03517 $1.222.70$ 1.2 0.03763 0.00763 0.00163 1.20176 1.20176 13 0.03247 0.03516 $-224.23(-2.84)$ 13 0.03783 0.04097 $-279.72(-1.10)$ 14 0.03516 0.03782 $-220.80(-2.30)$ 14 0.04097 0.04406 $-275.36(-1.08)$ 15 0.03782 0.04044 $-214.43(-2.46)$ 15 0.04406 0.04712 $-268.02(-0.98)$ 16 0.04044 0.04304 $-212.61(-2.50)$ 16 0.04712 0.05015 $-263.89(-1.16)$ 17 0.04304 0.04560 $-207.68(-2.46)$ 17 0.05015 0.05313 $-258.43(-1.27)$ 18 0.04560 0.04814 $-204.52(-2.24)$ 18 0.05609 0.5901 $-247.64(-1.38)$ 20 0.05064 0.05312 $-194.79(-1.33)$ 20 0.05901 0.06189 $-243.94(-1.30)$ $w=0.1583; m_0=0.3009 mol \cdot kg^{-1}$ $w=0.3087$ 0.30087 $-325.61(0.08)$ 2 0.00103 0.00443 $-391.26(2.78)$ 3 0.00387 0.00681 $-322.79(-0.36)$ 3 0.00443 0.00780 $-385.92(1.34)$ 4 0.00681 0.00973 $-315.73(-0.16)$ 4 0.00780 0.01114 $-378.62(0.75)$ 5 0.00973 0.01261 $-310.36(-0.31)$ 5 0.01114 $-374.33(1.17)$ 6 0.01261 0.01546 $-300.99(-0.11)$ 6 0.01444 0.02714 $-353.58(0.$	12	0.02975	0.03247	-22878(-2.31)	12	0.03467	0.03783	-284.92(-1.02)	
150.032170.03010224.20 (2.07)150.040070.040072.040712.7.36 (-1.08)140.035160.03782-220.80(-2.30)140.040970.04406-275.36(-1.08)150.037820.04044-214.43 (-2.46)150.044060.04712-268.02 (-0.98)160.040440.04304-212.61 (-2.50)160.047120.05015-263.89 (-1.16)170.043040.04560-207.68 (-2.46)170.050150.05313-258.43 (-1.27)180.045600.04814-204.52 (-2.24)180.056090.05901-247.64 (-1.38)200.050640.05312-194.79 (-1.33)200.059010.06189-243.94 (-1.30)w=0.1583; m_0 =0.3009 mol·kg ⁻¹ w=0.2047; m_0 =0.3446 mol·kg ⁻¹ 20.000900.00387-325.61 (0.08)20.001030.00443-391.26 (2.78)30.003870.00681-322.79 (-0.36)30.004430.00780-385.92 (1.34)40.006810.00973-315.73 (-0.16)40.007800.01114-374.33 (1.17)60.012610.01546-300.99 (-0.11)60.014440.01771-364.67 (0.62)70.015460.01829-295.57 (-0.12)70.017710.02094-361.25 (-0.11)80.018290.02108-289.81 (-0.05)80.020440.02731-348.71 (0.81)	12	0.03247	0.03516	-224.23(-2.84)	12	0.03783	0.04097	-27972(-110)	
150.037820.04044-214.43(-2.46)150.04060.04712-268.02(-0.98)160.040440.04304-212.61(-2.50)160.047120.05015-263.89(-1.16)170.043040.04560-207.68(-2.46)170.050150.05313-258.43(-1.27)180.045600.04814-204.52(-2.24)180.053130.05609-253.58(-1.32)190.048140.05064-199.05(-2.03)190.056090.05901-247.64(-1.38)200.050640.05312-194.79(-1.33)200.059010.06189-243.94(-1.30)w=0.1583; m_0 =0.3009 mol·kg ⁻¹ w=0.2047; m_0 =0.3446 mol·kg ⁻¹ 20.000900.00387-325.61(0.08)20.001030.00443-391.26(2.78)30.003870.00681-322.79(-0.36)30.004430.00780-385.92(1.34)40.006810.00973-315.73(-0.16)40.007800.01114-378.62(0.75)50.009730.01261-310.36(-0.31)50.011140.01444-374.33(1.17)60.012610.01546-300.99(-0.11)60.014440.01771-364.67(0.62)70.015460.01829-295.57(-0.12)70.017710.02094-361.25(-0.11)80.018290.02108-289.81(-0.05)80.020940.02414-353.58(0.37)90.021080.02384-284.18(-0.15)9	14	0.03516	0.03782	-220.80(-2.30)	14	0.04097	0.04406	-275.36(-1.08)	
160.00020.0101111000 (2.00)100.0111212000 (2.00)160.040440.04304-212.61 (-2.50)160.047120.05015-263.89 (-1.16)170.043040.04560-207.68 (-2.46)170.050150.05313-258.43 (-1.27)180.045600.04814-204.52 (-2.24)180.053130.05609-253.58 (-1.32)190.048140.05064-199.05 (-2.03)190.056090.05901-247.64 (-1.38)200.050640.05312-194.79 (-1.33)200.059010.06189-243.94 (-1.30)w=0.1583; $m_0=0.3009$ mol·kg ⁻¹ w=0.2047; $m_0=0.3446$ mol·kg ⁻¹ 20.000900.00387-325.61 (0.08)20.001030.00443-391.26 (2.78)30.003870.00681-322.79 (-0.36)30.004430.00780-385.92 (1.34)40.006810.00973-315.73 (-0.16)40.007800.01114-378.62 (0.75)50.009730.01261-310.36 (-0.31)50.011140.01444-374.33 (1.17)60.012610.01546-300.99 (-0.11)60.014440.01771-364.67 (0.62)70.015460.01829-295.57 (-0.12)70.017710.02094-361.25 (-0.11)80.018290.02108-289.81 (-0.05)80.020940.02414-353.58 (0.37)90.021080.02384-284.18 (-0.15)90.02414	15	0.03782	0.04044	-21443(-246)	15	0.04406	0.04712	-268.02(-0.98)	
170.043040.04560-207.68(-2.46)170.050150.05313-258.43(-1.27)180.045600.04814-204.52(-2.24)180.053130.05609-243.58(-1.32)190.048140.05064-199.05(-2.03)190.056090.05901-247.64(-1.38)200.050640.05312-194.79(-1.33)200.059010.06189-243.94(-1.30) $w=0.1583; m_0=0.3009 \text{mol·kg}^{-1}$ $w=0.2047; m_0=0.3446 \text{mol·kg}^{-1}$ 20.000900.00387-325.61(0.08)20.001030.00443-391.26(2.78)30.003870.00681-322.79(-0.36)30.004430.00780-385.92(1.34)40.006810.00973-315.73(-0.16)40.007800.01114-378.62(0.75)50.009730.01261-310.36(-0.31)50.011140.01444-374.33(1.17)60.012610.01546-300.99(-0.11)60.014440.01771-364.67(0.62)70.015460.01829-295.57(-0.12)70.017710.02094-361.25(-0.11)80.018290.02108-289.81(-0.05)80.020940.02144-353.58(0.37)90.021080.02384-284.18(-0.15)90.024140.02731-348.71(0.81)	16	0.04044	0.04304	-212.61(-2.50)	16	0.04712	0.05015	-263.89(-1.16)	
1.0.0 100 10.0 10001.0 10001.0 10001.0 10001.0 10001.0 1000180.045600.04814-204.52(-2.24)180.053130.05609-253.58(-1.32)190.048140.05064-199.05(-2.03)190.056090.05901-247.64(-1.38)200.050640.05312-194.79(-1.33)200.059010.06189-243.94(-1.30) $w = 0.1583; m_0 = 0.3009 \text{ mol·kg}^{-1}$ $w = 0.2047; m_0 = 0.3446 \text{ mol·kg}^{-1}$ 20.000900.00387-325.61(0.08)20.001030.00443-391.26(2.78)30.003870.00681-322.79(-0.36)30.004430.00780-385.92(1.34)40.006810.00973-315.73(-0.16)40.007800.01114-378.62(0.75)50.009730.01261-310.36(-0.31)50.011140.01444-374.33(1.17)60.012610.01546-300.99(-0.11)60.014440.01771-364.67(0.62)70.015460.01829-295.57(-0.12)70.017710.02094-361.25(-0.11)80.018290.02108-289.81(-0.05)80.020940.02414-353.58(0.37)90.021080.02384-284.18(-0.15)90.024140.02731-348.71(0.81)	17	0.04304	0.04560	-2.07.68(-2.46)	17	0.05015	0.05313	-25843(-1.27)	
101010101010101010190.048140.05064-199.05(-2.03)190.056090.05901-247.64(-1.38)200.050640.05312-194.79(-1.33)200.059010.06189-243.94(-1.30) $w = 0.1583; m_0 = 0.3009 \text{ mol·kg}^{-1}$ 20.000900.00387-325.61(0.08)20.001030.00443-391.26(2.78)30.003870.00681-322.79(-0.36)30.004430.00780-385.92(1.34)40.006810.00973-315.73(-0.16)40.007800.01114-378.62(0.75)50.009730.01261-310.36(-0.31)50.011140.01444-374.33(1.17)60.012610.01546-300.99(-0.11)60.014440.01771-364.67(0.62)70.015460.01829-295.57(-0.12)70.017710.02094-361.25(-0.11)80.018290.02108-289.81(-0.05)80.020940.02414-353.58(0.37)90.021080.02384-284.18(-0.15)90.024140.02731-348.71(0.81)	18	0.04560	0.04814	-2.0452(-2.24)	18	0.05313	0.05609	-253.58(-1.32)	
15 0.0511 0.05021 $1.550(-2.05)$ 1.5 0.00501 0.05101 $1.5101(-1.05)$ 20 0.05064 0.05312 $-194.79(-1.33)$ 20 0.05901 0.06189 $-243.94(-1.30)$ $w = 0.1583; m_0 = 0.3009 \text{ mol·kg}^{-1}$ 2 0.00090 0.00387 $-325.61(0.08)$ 2 0.00103 0.00443 $-391.26(2.78)$ 3 0.00387 0.00681 $-322.79(-0.36)$ 3 0.00443 0.00780 $-385.92(1.34)$ 4 0.00681 0.00973 $-315.73(-0.16)$ 4 0.00780 0.01114 $-378.62(0.75)$ 5 0.00973 0.01261 $-310.36(-0.31)$ 5 0.01114 0.01444 $-374.33(1.17)$ 6 0.01261 0.01546 $-300.99(-0.11)$ 6 0.01444 0.01771 $-364.67(0.62)$ 7 0.01546 0.01829 $-295.57(-0.12)$ 7 0.01771 0.02094 $-361.25(-0.11)$ 8 0.01829 0.02108 $-289.81(-0.05)$ 8 0.02094 0.02414 $-353.58(0.37)$ 9 0.02108 0.02384 $-284.18(-0.15)$ 9 0.02414 0.02731 $-348.71(0.81)$	19	0.04814	0.05064	-199.05(-2.03)	19	0.05609	0.05901	-247.64(-1.38)	
$w = 0.1583; m_0 = 0.3009 \text{ mol·kg}^{-1}$ $w = 0.2047; m_0 = 0.3446 \text{ mol·kg}^{-1}$ 2 0.00090 0.00387 $-325.61(0.08)$ 2 0.00103 0.00443 $-391.26(2.78)$ 3 0.00387 0.00681 $-322.79(-0.36)$ 3 0.00443 0.00780 $-385.92(1.34)$ 4 0.00681 0.00973 $-315.73(-0.16)$ 4 0.00780 0.01114 $-378.62(0.75)$ 5 0.00973 0.01261 $-310.36(-0.31)$ 5 0.01114 0.01444 $-374.33(1.17)$ 6 0.01261 0.01546 $-300.99(-0.11)$ 6 0.01444 0.01771 $-364.67(0.62)$ 7 0.01546 0.01829 $-295.57(-0.12)$ 7 0.01771 0.02094 $-361.25(-0.11)$ 8 0.01829 0.02108 $-289.81(-0.05)$ 8 0.02094 0.02414 $-353.58(0.37)$ 9 0.02108 0.02384 $-284.18(-0.15)$ 9 0.02414 0.02731 $-348.71(0.81)$	20	0.05064	0.05312	-194.79(-1.33)	20	0.05901	0.06189	-243.94(-1.30)	
2 0.00090 0.00387 -325.61(0.08) 2 0.00103 0.00443 -391.26(2.78) 3 0.00387 0.00681 -322.79(-0.36) 3 0.00443 0.00780 -385.92(1.34) 4 0.00681 0.00973 -315.73(-0.16) 4 0.00780 0.01114 -378.62(0.75) 5 0.00973 0.01261 -310.36(-0.31) 5 0.01114 0.01444 -374.33(1.17) 6 0.01261 0.01546 -300.99(-0.11) 6 0.01444 0.01771 -364.67(0.62) 7 0.01546 0.01829 -295.57(-0.12) 7 0.01771 0.02094 -361.25(-0.11) 8 0.01829 0.02108 -289.81(-0.05) 8 0.02094 0.02414 -353.58(0.37) 9 0.02108 0.02384 -284.18(-0.15) 9 0.02414 0.02731 -348.71(0.81)			$82.m = 0.2000 \text{ mol} \text{ km}^{-1}$			w=0.20	47.m = 0.3446 mol k	a ⁻¹	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	w = 0.15	$m_0 = 0.3009 \text{ mol} \cdot \text{kg}$	-225.61(0.08)	2	w = 0.20	$47; m_0 = 0.5440 \text{ more k}$	8 	
3 0.0037 0.00081 $322.79(-0.30)$ 3 0.00443 0.00780 $333.32(1.34)$ 4 0.00681 0.00973 $-315.73(-0.16)$ 4 0.00780 0.01114 $-378.62(0.75)$ 5 0.00973 0.01261 $-310.36(-0.31)$ 5 0.01114 0.01444 $-374.33(1.17)$ 6 0.01261 0.01546 $-300.99(-0.11)$ 6 0.01444 0.01771 $-364.67(0.62)$ 7 0.01546 0.01829 $-295.57(-0.12)$ 7 0.01771 0.02094 $-361.25(-0.11)$ 8 0.01829 0.02108 $-289.81(-0.05)$ 8 0.02094 0.02414 $-353.58(0.37)$ 9 0.02108 0.02384 $-284.18(-0.15)$ 9 0.02414 0.02731 $-348.71(0.81)$	2	0.00090	0.00387	-222.70(-0.26)	2	0.00103	0.00740	-285.02(1.24)	
7 0.00071 0.00073 0.01261 -310.36(-0.31) 5 0.01114 -374.33(1.17) 5 0.00973 0.01261 -310.36(-0.31) 5 0.01114 0.01444 -374.33(1.17) 6 0.01261 0.01546 -300.99(-0.11) 6 0.01444 0.01771 -364.67(0.62) 7 0.01546 0.01829 -295.57(-0.12) 7 0.01771 0.02094 -361.25(-0.11) 8 0.01829 0.02108 -289.81(-0.05) 8 0.02094 0.02414 -353.58(0.37) 9 0.02108 0.02384 -284.18(-0.15) 9 0.02414 0.02731 -348.71(0.81)	3	0.00587	0.00001	-31573(-0.16)	Л	0.00445	0.00/80	-37862(1.34)	
5 0.00773 0.01201 510.50(-0.51) 5 0.01114 0.01444 5/4.53(1.17) 6 0.01261 0.01546 -300.99(-0.11) 6 0.01444 0.01771 -364.67(0.62) 7 0.01546 0.01829 -295.57(-0.12) 7 0.01771 0.02094 -361.25(-0.11) 8 0.01829 0.02108 -289.81(-0.05) 8 0.02094 0.02414 -353.58(0.37) 9 0.02108 0.02384 -284.18(-0.15) 9 0.02414 0.02731 -348.71(0.81)	+ 5	0.00072	0.009/3	-310.36(-0.10)	4 c	0.00780	0.01114	-37422(1.17)	
0 0.01201 0.01300 300.97(-0.11) 0 0.01444 0.01771 -364.87(0.82) 7 0.01546 0.01829 -295.57(-0.12) 7 0.01771 0.02094 -361.25(-0.11) 8 0.01829 0.02108 -289.81(-0.05) 8 0.02094 0.02414 -353.58(0.37) 9 0.02108 0.02384 -284.18(-0.15) 9 0.02414 0.02731 -348.71(0.81)	6	0.00975	0.01546	-300.99(-0.11)	5	0.01114	0.01771	-36467(062)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	0.01201	0.01340	-295 57(-0.12)	7	0.01771	0.01//1	-361.25(-0.11)	
9 0.02108 0.02384 $-284.18(-0.15)$ 9 0.02414 $-355.58(0.57)$, 8	0.01340	0.01027	-289.81(-0.05)	/ Q	0.02004	0.02094	-35258(0.27)	
	9	0.02108	0.02384	-284.18(-0.15)	9	0.02414	0.02731	-348.71(0.81)	

	m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$		m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$
Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	J∙mol ⁻¹
10	0.02384	0.02658	-278.31(-0.25)	10	0.02731	0.03044	-338.30(1.45)
11	0.02658	0.02928	-273.99(-0.17)	11	0.03044	0.03354	-332.52(3.87)
12	0.02928	0.03196	-267.63(-0.15)	12	0.03354	0.03660	-325.05(1.45)
13	0.03196	0.03460	-262.51(-0.18)	13	0.03660	0.03963	-319.25(1.67)
14	0.03460	0.03722	-257.97(0.11)	14	0.03963	0.04263	-313.85(1.84)
15	0.03722	0.03980	-252.12(-0.01)	15	0.04263	0.04559	-304.92(1.90)
16	0.03980	0.04236	-248.43(0.01)	16	0.04559	0.04851	-300.98(1.59)
17	0.04236	0.04488	-242.89(-0.14)	17	0.04851	0.05140	-294.23(1.75)
18	0.04488	0.04738	-238.77(0.24)	18	0.05140	0.05426	-288.51(2.20)
19	0.04738	0.04984	-232.72(0.02)	19	0.05426	0.05709	-282.37(2.52)
20	0.04984	0.05228	-228.33(0.30)	20	0.05709	0.05988	-277.49(0.66)
	w = 0.24	94; $m_0 = 0.2847 \text{ mol} \cdot \text{kg}$	g ⁻¹		w = 0.29	77; $m_0 = 0.3091 \text{ mol} \cdot \text{k}$	g^{-1}
2	0.00085	0.00366	-336.74(0.87)	2	0.00092	0.00398	-417.84(-1.50)
3	0.00366	0.00645	-327.87(0.45)	3	0.00398	0.00700	-412.24(-0.83)
4	0.00645	0.00920	-315.13(-0.98)	4	0.00700	0.00999	-401.60(-0.89)
5	0.00920	0.01193	-317.13(0.94)	5	0.00999	0.01295	-396.30(-0.35)
6	0.01193	0.01463	-304.45(0.13)	6	0.01295	0.01589	-383.78(-0.50)
7	0.01463	0.01731	-300.23(0.18)	7	0.01589	0.01879	-377.17(-0.54)
8	0.01731	0.01995	-294.18(0.14)	8	0.01879	0.02166	-368.50(-0.81)
9	0.01995	0.02256	-289.06(0.54)	9	0.02166	0.02450	-362.19(-0.68)
10	0.02256	0.02515	-282.99(0.51)	10	0.02450	0.02731	-35452(-0.48)
11	0.02515	0.02771	-278.02(0.13)	11	0.02731	0.03008	-34832(-0.30)
12	0.02771	0.03024	-27051(0.02)	12	0.03008	0.03283	-340.77(-0.27)
13	0.03024	0.03274	-26614(0.25)	13	0.03283	0.03555	-33445(-0.28)
14	0.03274	0.03527	-262.10(0.13)	14	0.03555	0.03823	-326.09(0.68)
15	0.03522	0.03766	-25473(0.04)	15	0.03823	0.04089	-321.43(-0.38)
16	0.03766	0.04008	-251.44(0.33)	16	0.04089	0.04351	-31671(-0.29)
17	0.04008	0.04247	-245.77(0.52)	17	0.04351	0.04611	-30941(-0.20)
18	0.04247	0.04483	-242.01(0.59)	18	0.04611	0.04867	-304.11(-0.38)
10	0.04483	0.04717	-23572(0.70)	19	0.04867	0.05121	-29746(-0.18)
20	0.04717	0.04947	-231.75(0.78)	20	0.05121	0.05271	-297.70(-0.13)
20	0.04/1/	0.07747	1.2 Dropon adialia	DMSO + M	0.03121	0.05571	291.75(0.52)
			-1	1 DIVISO + V	vater		-1
	w = 0.48	$64; m_0 = 0.4579 \text{ mol} \cdot \text{kg}$, - , - , - , - , - , - , - , - , - , -		w = 0.10	$03; m_0 = 0.4078 \text{ mol} \cdot \text{k}$	g
3	0.00589	0.01037	-226.22(1.28)	3	0.00549	0.00967	-199.97(-0.47)
4	0.01037	0.01480	-222.85(1.31)	4	0.00967	0.01381	-194.63(0.06)
5	0.01480	0.01919	-219.00(1.25)	5	0.01381	0.01790	-192.70(-0.36)
6	0.01919	0.02353	-213.78(0.69)	6	0.01790	0.02195	-185.47(-0.41)
7	0.02353	0.02783	-209.71(0.83)	7	0.02195	0.02596	-182.90(-0.09)
8	0.02783	0.03208	-205.91(0.55)	8	0.02596	0.02992	-177.24(0.89)
9	0.03208	0.03629	-202.38(0.81)	9	0.02992	0.03385	-174.57(0.40)
10	0.03629	0.04045	-197.97(0.98)	10	0.03385	0.03773	-171.73(0.73)
11	0.04045	0.04457	-194.02(1.62)	11	0.03773	0.04157	-167.99(0.09)
12	0.04457	0.04864	-189.85(1.13)	12	0.04157	0.04536	-164.53(0.37)
13	0.04864	0.05266	-186.14(1.61)	13	0.04536	0.04912	-161.05(0.61)
14	0.05266	0.05664	-181.15(0.86)	14	0.04912	0.05283	-158.69(0.37)
15	0.05664	0.06057	-179.55(0.93)	15	0.05283	0.05650	-154.38(0.74)
16	0.06057	0.06446	-176.07(1.27)	16	0.05650	0.06012	-151.50(1.14)
17	0.06446	0.06830	-172.37(1.03)	17	0.06012	0.06371	-148.73(0.71)
18	0.06830	0.07210	-168.83(1.45)	18	0.06371	0.06725	-146.42(0.44)
19	0.07210	0.07585	-165.45(1.79)	19	0.06725	0.07075	-142.87(0.32)
20	0.07585	0.07956	-163.64(0.62)	20	0.07075	0.07421	-140.33(0.63)

	m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$		m_{N-1}	m_N	$\Delta H(m_{N-1} \rightarrow m_N)$
Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$	Ν	$mol \cdot kg^{-1}$	$mol \cdot kg^{-1}$	$J \cdot mol^{-1}$
	w = 0.15	02; $m_0 = 0.4049 \text{ mol} \cdot \text{k}$	g^{-1}		w = 0.20	000; $m_0 = 0.4128 \text{ mol} \cdot \text{k}$	cg^{-1}
2	0.00121	0.00521	-181.62(0.60)	2	0.00123	0.00531	-171.07(-0.81)
3	0.00521	0.00917	-180.48(0.09)	3	0.00531	0.00935	-168.11(-0.94)
4	0.00917	0.01309	-174.76(-0.62)	4	0.00935	0.01335	-164.08(-1.09)
5	0.01309	0.01697	-172.30(-0.75)	5	0.01335	0.01730	-161.58(-1.34)
6	0.01697	0.02081	-166.12(-0.60)	6	0.01730	0.02122	-155.64(-0.87)
7	0.02081	0.02461	-164.30(-0.33)	7	0.02122	0.02509	-153.59(-0.94)
8	0.02461	0.02837	-160.97(-0.70)	8	0.02509	0.02892	-150.06(-0.81)
9	0.02837	0.03209	-157.37(-0.69)	9	0.02892	0.03272	-147.22(-0.82)
10	0.03209	0.03577	-154.62(-0.42)	10	0.03272	0.03647	-144.38(-1.18)
11	0.03577	0.03941	-151.88(-0.78)	11	0.03647	0.04018	-141.92(-0.99)
12	0.03941	0.04301	-148.38(-0.62)	12	0.04018	0.04385	-138.48(-1.12)
13	0.04301	0.04657	-145.72(-0.45)	13	0.04385	0.04747	-136.26(-1.27)
14	0.04657	0.05009	-143.82(-0.50)	14	0.04747	0.05106	-134.07(-1.13)
15	0.05009	0.05356	-139.78(-0.43)	15	0.05106	0.05461	-130.35(-0.80)
16	0.05356	0.05700	-137.62(-0.54)	16	0.05461	0.05811	-128.57(-0.99)
17	0.05700	0.06040	-134.94(-0.45)	17	0.05811	0.06158	-125.81(-1.10)
18	0.06040	0.06376	-133.07(-0.68)	18	0.06158	0.06500	-123.50(-1.13)
19	0.06376	0.06708	-129.65(-0.49)	19	0.06500	0.06838	-120.99(-0.97)
20	0.06708	0.07036	-126.36(-1.26)	20	0.06838	0.07173	-120.04(-1.44)
	w = 0.24	96; $m_0 = 0.5390 \text{ mol} \cdot \text{k}$	g^{-1}		w = 0.29	77; $m_0 = 0.4124 \mathrm{mol} \cdot \mathrm{k}$	sg^{-1}
2	0.00161	0.00693	-199.92(-0.83)	2	0.00123	0.00531	-133.77(0.56)
3	0.00693	0.01221	-196.76(-0.99)	3	0.00531	0.00934	-132.27(0.05)
4	0.01221	0.01742	-191.41(-0.57)	4	0.00934	0.01333	-129.31(-0.27)
5	0.01742	0.02259	-188.58(-0.43)	5	0.01333	0.01729	-127.53(-0.50)
6	0.02259	0.02770	-182.66(-0.76)	6	0.01729	0.02120	-123.63(-0.02)
7	0.02770	0.03276	-180.35(-0.82)	7	0.02120	0.02507	-121.79(-0.11)
8	0.03276	0.03776	-175.89(-1.00)	8	0.02507	0.02890	-119.81(-0.06)
9	0.03776	0.04272	-172.81(-1.01)	9	0.02890	0.03269	-116.50(0.32)
10	0.04272	0.04761	-169.12(-0.96)	10	0.03269	0.03643	-114.75(-0.39)
11	0.04761	0.05246	-166.08(-0.96)	11	0.03643	0.04014	-113.13(-0.46)
12	0.05246	0.05725	-162.21(-0.81)	12	0.04014	0.04381	-110.28(-0.36)
13	0.05725	0.06199	-159.12(-0.54)	13	0.04381	0.04743	-108.11(-0.25)
14	0.06199	0.06667	-156.58(-0.67)	14	0.04743	0.05102	-106.48(-0.04)
15	0.06667	0.07130	-152.50(-0.77)	15	0.05102	0.05456	-103.25(0.37)
16	0.07130	0.07588	-149.81(-0.68)	16	0.05456	0.05806	-101.79(0.32)
17	0.07588	0.08040	-146.75(-0.27)	17	0.05806	0.06152	-99.90(-0.27)
18	0.08040	0.08487	-144.73(0.62)	18	0.06152	0.06494	-98.07(-0.29)
19	0.08487	0.08929	-140.89(0.28)	19	0.06494	0.06832	-95.46(0.30)
20	0.08929	0.09365	-139.09(-0.31)	20	0.06832	0.07166	-94.00(0.16)

^{*a*} The values in parentheses are the evaluated uncertainties: $100[\Delta H(exptl) - \Delta H(calcd)/\Delta H(exptl)]$.

- (a) Hydrophobic—hydrophobic interactions of CH₃- (or -CH₂-) residues of one diol molecule with those of another, along with similar interactions with CH₃- of DMSO, all of which make positive contributions on h_{XX}. The formation of intramolecular hydrogen bond in diols strengthens such an interaction greatly with the help of preferential configuration.
- (b) Hydrophobic-hydrophilic interactions of CH_3 (or $-CH_2$ -) residues of one diol molecule with the HO-residues of another, along with similar interactions with

>S=O in DMSO (or HO- in H₂O), all of which usually make positive contributions to h_{XX} .

(c) Hydrophilic—hydrophilic interactions of HO— residues of one diol molecule with those of another, along with similar interactions with >S=O in DMSO (or HO— in H₂O), which are mainly in the form of intermolecular hydrogen bonds. All bring about the broken structure of water and make negative contributions to h_{XX}. As a double-edged sword, the formation of intramolecular hydrogen bond in diols is in favor of such an interaction.



Figure 3. Homochiral enthalpic pairwise interaction coefficients (h_{XX}) of the four diols in DMSO + H₂O mixtures as a function of mass fraction *w* at 298.15 K (\blacktriangle , (25,35)-2,3-butanediol; \Box , (2*R*,3*R*)-2,3-butanediol; \blacksquare , meso-2,3-butanediol; \bigtriangleup , 1,3-propanediol).

Table 3.	Homochiral Enthalp	oic Pairwise In	teraction Coeffici	ients of Meso-	2,3-butanediol,	(2S,3S)-(+)	-2,3-Butanediol,
(2R, 3R)-((-)-2,3-Butanediol,	and 1,3-Propa	nediol in DMSO	+ Water Mix	tures at 298.15	K ^a	

			$h_{\rm XX}$					
w		J·kg·mol ⁻² w						
Meso	-2,3-butanediol	(2R,3R)-2,3-Butanediol	(2 <i>S</i> ,3 <i>S</i>)-2,3-Butanediol	1,3	-Propanediol			
0	569.74(±6.42)	643.22(±7.04)	$663.76(\pm 4.65)$	0	$422.97(\pm 5.03)$			
0.0502	629.94(±11.88)	$738.40(\pm 13.22)$	$777.85(\pm 8.51)$	0.0486	$416.29(\pm 2.26)$			
0.0998	$705.22(\pm 11.06)$	$769.05(\pm 13.28)$	$826.41(\pm 0.28)$	0.1003	$401.05(\pm 4.47)$			
0.1583	$748.41(\pm 3.43)$	$829.72(\pm 6.41)$	$911.32(\pm 8.62)$	0.1502	384.73(±9.93)			
0.1997	$771.00(\pm 9.16)$	$854.05(\pm 8.34)$	$941.55(\pm 1.38)$	0.2000	$348.31(\pm 5.76)$			
0.2494	$806.47(\pm 2.57)$	$876.96(\pm 18.40)$	$993.21(\pm 3.12)$	0.2496	315.73(± 5.79)			
0.2977	$845.73(\pm 1.15)$	$954.79(\pm 16.69)$	$1138.49(\pm 25.97)$	0.2987	$272.53(\pm 1.64)$			
^{<i>a</i>} The values in	n parentheses are the evalua	ated errors: $\pm (\Sigma_{i=1}^{3} h_{XXi} - \overline{h}_{XX})$	/3).					





Considering the values of h_{XX} obtained are all positive for the four diols, it is concluded that interactions (a) and (b) play an magistral role in the pairwise interaction. However, as for 1, 3-propanediol, the tendency of h_{XX} is on a linear decrease with the mass fraction of mixed solvent. Out of question, 1,3-propanediol forms a stable six-membered ring comprised by three C atoms, two O atoms, and one H atom through an intramolecular hydrogen bond bridge (Scheme 4).³⁴ The six atoms on the rigider ring are out of freedom, and it becomes more stable with the increase of DMSO content as the active bare H atom of hydroxyl associates freely with O atoms in DMSO or H₂O molecules. The strong intermolecular hydrogen bonds make a considerably negative contribution to h_{XX} , resulting in the smallest values of h_{XX} in the diol series under study. Though

Scheme 3. Solvated 2,3-Butanediol in DMSO + Water Mixture³⁴ (B Represents the >S=O Group in DMSO or the O Atom in H_2O)



Scheme 4. Solvated 1,3-Propanediol in DMSO + H₂O Mixtures³⁵ (B Represents the >S=O Group in DMSO or the O Atom in H₂O)



interactions (a) and (b) ever become stronger, 1,3-propanediol is quite different from the 2,3-butanediol molecule in which CH_3 — is completely free. Interactions (c) must be playing a dominate role in pairwise interaction of 1,3-propanediol, thereby a decreasing tendence of h_{XX} can be seen.

In addition to the solvent effect, the substituent effect is another obvious factor in molecular pairwise interplay process. According to Castronuovo,²⁴ on the increasing alkyl chain length, the values of $h_{\rm XX}$ of α -amino acids are on the linear growth. This phenomenon has been explained satisfactorily by the SWAG statistical principle. Because of the shorter hydrophobic carbon chain, 1,3-propanediol has a lower $h_{\rm XX}$ value than all 2,3-butanediol isomers.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hxgwzu@126.com. Fax: +86-0577-86689360.

Funding Sources

This work was financially supported by the National Natural Science Foundation of China (No. 21073132).

REFERENCES

(1) Cintas, P. Chirality and Chemical Processes: A Few Afterthoughts. *Chirality* **2008**, *20*, 2–4.

(2) Ariga, K.; Michinobu, T.; Nakanishi, T.; Hill, J. P. Chiral Recognition at the Air-Water Interface. *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 23–30.

(3) Amemiya, R.; Yamaguchi, M. Chiral Recognition in Noncovalent Bonding Interactions between Helicenes: Right-handed Helix favors Right-handed Helix over Left-handed Helix. *Org. Biomol. Chem.* **2008**, *6*, 26–35. (4) Blankenburg, S.; Schmidt, W. G. Long-Range Chiral Recognition due to Substrate Locking and Substrate-Adsorbate Charge Transfer. *Phys. Rev. Lett.* **2007**, *99*, 196107/1–196107/4.

(5) Huang, W. H.; Zavalij, P. Y.; Isaacs, L. Chiral Recognition inside a Chiral Cucurbituril. *Angew. Chem., Int. Ed.* **200**7, *46*, 7425–7427.

(6) Tran, C. D.; Shao, F. Y. Spectroscopic Investigations of Solvent Effect on Chiral Interactions. J. Phys. Chem. B 2005, 109, 12627–12635.

(7) Iwahashi, M.; Ikumi, M.; Matsuzawa, H.; Moroi, Y.; Czarnecki, M. A.; Ozaki, Y. Molecular Self-assembling of Chiral and Racemic Butan-2-ol in Carbon Tetrachloride Solutions. *Vib. Spectrosc.* **1999**, *20* (2), 113–119.

(8) Xu, Y. F.; McCarroll, M. E. Fluorescence Anisotropy as a Method to Examine the Thermodynamics of Enantioselectivity. *J. Phys. Chem. B* **2005**, *109*, 8144–8152.

(9) Xu, Y. F.; McCarroll, M. E. Chiral Recognition and Behavior of [1,1'-Binaphthalene]-2,2'-Diol in Aqueous Solution by Fluorescence Spectroscopy. J. Photochem. Photobiol., A **2006**, 178, 50–56.

(10) Fini, P.; Catucci, L.; Castagnolo, M.; Cosma, P.; Pluchinotta, V.; Agostiano, A. Spectroscopic Investigation of Rose Bengal/cyclodextrin Interactions in Aqueous Solution: the Case of the Hydroxypropylcyclodextrins. J. Inclusion Phenom. Macrocyclic Chem. 2007, 57, 663–668.

(11) Bombelli, C.; Borocci, S.; Cruciani, O.; Mancini, G.; Monti, D.; Segre, A. L.; Sorrenti, A.; Venanzi, M. Chiral Recognition of Dipeptides in Bio-membrane Models: the Role of Amphiphile Hydrophobic Chains. *Tetrahedron: Asymmetry* **2008**, *19*, 124–130.

(12) Liu, Y.; Zhang, Q.; Chen, Y. Spectrophotometric and Calorimetric Titration Studies on Molecular Recognition of Camphor and Borneol by Nucleobase-Modified β -Cyclodextrins. *J. Phys. Chem. B* **2007**, *111*, 12211–12218.

(13) Rekharsky, M.; Yamamura, H.; Kawai, M.; Inoue, Y. Critical Difference in Chiral Recognition of N-Cbz-D/L-aspartic and -glutamic Acids by Mono- and Bis(Trimethylammonio)-β-cyclodextrins. J. Am. Chem. Soc. 2001, 123, 5360–5361.

(14) Liu, Y.; Yang, Y. W.; Cao, R.; Song, S. H.; Zhang, H. Y.; Wang, L. H. Thermodynamic Origin of Molecular Selective Binding of Bile Salts by Aminated β -Cyclodextrins. *J. Phys. Chem. B* **2003**, *107*, 14130–14139.

(15) Takagi, S.; Fujishiro, R; Amaya, K. Heats of Mixing of Optical Isomers in Solution: Calorimetric Evidence of the Stereospecific Effect. *Chem. Commun. (Cambridge, U.K.)* **1968**, *8*, 480.

(16) Atik, Z.; Ewing, M. B.; McGlashan, M. L. Chiral Discrimination in Liquids. II. Excess Molar Enthalpies of $\{(1-x)A_+ + xA_-\}$, Where A Denotes Fenchone or α -Methylbenzylamine. *J. Chem. Thermodyn.* **1983**, 15, 159–163.

(17) Kimura, T.; Matsushita, T.; Ueda, K.; Aktar, F.; Matsuda, T.; Kamiyama, T.; Fujisawa, M. Enthalpic Changes on Mixing two Couples of S- and R-Enantiomers of Heptane-2-ol, Octane-2-ol, Nonane-2-ol, 3-Chloro-propane-1,2-diol, 2-Methyl-1,4-Butanediol at 298.15 K. *Thermochim. Acta* **2004**, *414*, 209–214.

(18) Kimura, T.; Khan, M. A.; Kamiyama, T. Enthalpic Changes on Mixing Two Couples of S- and R-enantiomers which Contained Amino Groups at 298.15 K. J. Therm. Anal. Calorim. **2006**, *85*, 575–580.

(19) Kimura, T.; Khan, M. A.; Ishii, M.; Ueda, K.; Matsushita, T.; Kamiyama, T.; Fujisawa, M. Enthalpic Changes on Mixing two Couples of S- and R-enantiomers of Benzyl-(1-phenyl-ethyl)-amine, 1-Phenyl-ethylamine, 1-Phenyl-ethanol, Butyric Acid Oxiranylmethyl Ester, 4-Methyl-[1,3]dioxolan-2-one, 2-Chloro-methyloxirane and 3-Hydro-xyisobutyric Acid Methyl Ester at T = 298.15 K. *J. Chem. Thermodyn.* **2006**, 38, 1042–1048.

(20) Kimura, T.; Khan, M. A.; Ishii, M. Enthalpy Change on Mixing a Couple of *S*- and *R*-Enantiomers of Some Chiral Compounds at 298.15 K. *Chirality* **2006**, *18*, 581–586.

(21) Fujisawa, M.; Matsushita, T.; Kimura, T. Excess Molar Heat Capacities of $((R)-(+)-\alpha$ -Pinene+ $(S)-(-)-\alpha$ -Pinene) at Temperatures between 293.15–308.15 K. J. Therm. Anal. Calorim. 2005, 81, 137–139.

(22) Fujisawa, M.; Matsushita, T.; Khan, M. A.; Kimura, T. Excess Molar Heat Capacities of (L-glutamine Aqueous Solution + D-glutamine Aqueous Solution) at Temperatures between 293.15 and 303.15 K. J. Therm. Anal. Calorim. 2005, 82, 319–321.

(23) Kimura, T.; Khan, M. A.; Kamiyama, T. Enthalpies of Mixing and Apparent Molar Volumes of Ethanol Solution of Chiral Dicarboxylic Acids. J. Therm. Anal. Calorim. 2006, 85, 559–565.

(24) Castronuovo, G.; Elia, V.; Magliulo, M. Chiral Recognition in Aqueous Solutions at 25 °C. A Calorimetric Study of the Interaction between Enantiomeric α -Amino Acids of Different Alkyl Chain Length. *Can. J. Chem.* **1991**, *69*, 794–797.

(25) Zhang, H. J.; Hu, X. G.; Shao, S. Enthalpies of Dilution of L-Alanine in Dimethylsulfoxide + Water and Dimethylformamide + Water Mixtures at 298.15 K. J. Chem. Eng. Data **2010**, *52*, 941–946.

(26) McMillan, W. G.; Mayer, J. E. The Statistical Thermodynamics of Multicomponent Systems. J. Chem. Phys. 1945, 13, 276–305.

(27) Fini, P.; Castagnolo, M. Determination of Enthalpic Interaction Coefficients by ITC Measurements. *J. Therm. Anal. Calorim.* 2001, 66, 91–102.

(28) Palecz, B. Enthalpies of Solution and Dilution of Some L-α-Amino Acids in Water at 298.15 K. J. Therm. Anal. Calorim. **1998**, 4, 257–263.

(29) Salam, A. The Role of Chirality in the Origin of Life. *J. Mol. Evol.* **1991**, 33, 105–113.

(30) Mason, S. F. Universal Dissymmetry and the Origin of Biomolecular Chirality. *Biosystems* **1987**, *20*, 27–35.

(31) Lv, S. The Influence of Hydrogen Bond on the Raman Spectrum of S=O in DMSO Aqueous Solution. M.S. Ji Lin University, China, 2007.

(32) Ma, X. Y.; Wang, J. P. Differentiating Subtle Variation of Weak Intramolecular Hydrogen Bond in Vicinal Diols by Linear Infrared Spectroscopy. J. Phys. Chem. A **2009**, *113*, 6070–6076.

(33) Wang, F.; Polavarapu, P. L. Predominant Conformations of (2R,3R)-(-)-2,3-Butanediol. J. Phys. Chem. A 2001, 105, 6991-6997.

(34) Wang, Y. X.; Li, H. P.; Wang, J. B.; Zhang, F. Q.; Zhao, J. P.; Dai, M. Infrared Spectroscopic Studies of Interactions of the Diols with Aprotic Solvent. *Acta. Phys. Chim.* **1998**, *14*, 514–519.

(35) Busfield, W. K.; Ennis, M. P.; Mcewen, I. J. An Infrared Study of Intramolecular Hydrogen Bonding in α , ω Diols. *Spectrochim. Acta, Part A* **1973**, *29*, 1259–1264.