

Evaluation of viscosity in binary mixtures of dimethyl sulphoxide at 298.15K

Abstract

The viscosity of binary mixtures of dimethyl sulphoxide with different alcohols such as methanol, ethanol, 1-propanol, iso-propanol, 1-butanol, iso-butanol, tertiary butanol has been determined at 298.15K. The experimental values are compared with theoretical values evaluated by different theories. It is observed that for some theories, values are in agreement with the experimental values. Further, an attempt has been made to study the intermolecular interactions in studied solutions in terms of excess free energy of mixing, strength of interaction parameters and interaction energy. The viscosity data of pure liquids and their mixtures are needed to design various chemical processes where heat and mass transfer are important.

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Introduction

Transport properties of binary solution have proven to be a useful tool in elucidating the interactions occurring in solutions. Viscosity is an important transport property.¹ The determination of viscosity of liquid mixtures are of interest in chemical industries and chemical engineering involving fluid transportation, process design, pump operations, heat exchange, mixing agitation etc.²⁻⁹

In the present work, densities and viscosities of binary mixtures of dimethyl sulphoxide with some alcohols such as methanol, ethanol, 1-propanol, iso-propanol, 1-butanol, iso-butanol, ter-butanol have been measured at 298.15 K. For binary and non-electrolytic solutions, various theories have been developed such as Bingham, Kendall-Munroe, Arrhenius- Eyring, Katti and Chaudhari, Grunberg-Nissan etc. These theories are tested for these studied binary mixtures using experimental data of viscosities. Further, some excess parameters such as excess volume and excess viscosities have also been evaluated.

Experimental

The studied liquids used in the present study were of analytical grade and were supplied by S. D. Fine Chemicals Pvt. Mumbai. These liquids were purified by standard method.¹⁰ The purified liquids were stored in air tight bottles over 0.4 nm molecular sieves.

All the binary mixtures were prepared by volume and were stored in stoppered bottles to minimize the error due to evaporation. The densities of all the pure liquids and their binary solutions were measured by Anton Paar densitometer (model No. DSA 5000) at 298.15 K with accuracy of $\pm 0.005 \text{ kg/m}^3$. The viscosities of pure liquids and solutions were measured by Ubbelohde viscometer at 298.15 K. An electronic digital stop watch was used for the flow time measurements. The flow time measurements were done at least three times so that each data reproducible to $\pm 0.05 \text{ s}$ was obtained, and the results were averaged. The uncertainties in dynamic viscosities are of the order of $\pm 0.003 \text{ mPa}\cdot\text{s}$.

Theory

The viscosity deviations ($\Delta\eta$) are obtained by the equation:

$$\Delta\eta = \eta_{12} - x_1\eta_1 + x_2\eta_2$$

where η_{12} is the viscosity of the mixture and x_1 , η_1 , x_2 and η_2 are the mole fraction and viscosity of pure components 1 and 2 respectively. Figure 1 shows the variation of viscosity deviation in studied solutions. It is evident from Figure 1 that as CH_2 group in alcohol series increases, deviation increases and deviation is more in branched alcohols.

For binary liquid mixtures, ideal viscosity can be evaluated by the following equation proposed by Bingham:¹¹

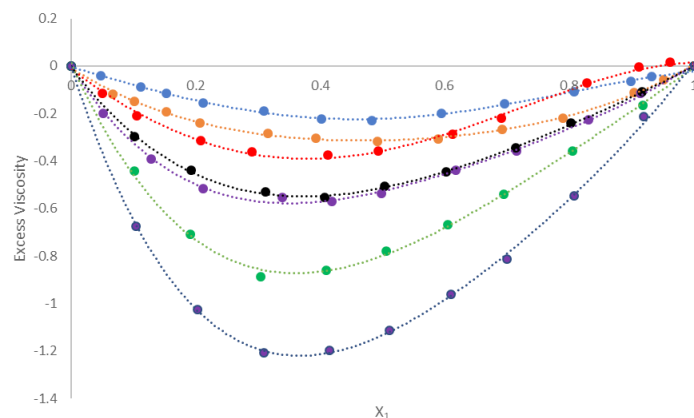


Figure 1 The variation of viscosity deviation for different binary solutions of DMSO with alcohols at 298.15K.

••: Methanol; ••: Ethanol; •: Prop-1-ol; •: Prop-2-ol; •: Butan-1-ol; •: Butan-2-ol; •: Ter-Butanol.

$$\eta = \sum x_i \eta_i$$

where x_i and η_i are the mole fraction and viscosity of the i-component respectively.

The viscosity of binary solution can also be evaluated by an additive relation based on Arrhenius and Eyring model¹² as follows:

$$\ln \eta V = \sum x_i \ln \eta_i V_i$$

Where V_i is the molar volume of the i-component.

Kendall and Munroe¹³ gave another equation for multi-component systems which is:

$$\ln \eta = \sum x_i \ln \eta_i$$

The following relation was proposed by Katti and Chaudhari¹⁴ for binary solutions:

$$\ln \eta V = \sum x_i \ln \eta_i V_i + (W_{vis} / RT) x_1 x_2$$

where W_{vis} is the interaction energy parameter and is given by:

$$W_{vis} = (RT / x_1 x_2) \ln (V / \sum V_i x_i) + dRT$$

where V is the molar volume of the mixture and d is the Grunberg-Nissan interaction parameter, which is given by:

$$d = -(\alpha F_m / x_1 x_2 RT)$$

and

$$F_m = -RT (\ln \eta_{exp} - \ln \eta_{Bring})$$

where η_{exp} is the experimental viscosity and η_{Bring} is the viscosity calculated by Bringam relation.

The Grunberg-Nissan relation¹⁵ for viscosity of non-ideal mixture is given as:

$$\ln \eta = \sum x_i \ln \eta_i + x_1 x_2 d$$

Results and discussion

The purity of the samples and accuracy of data were checked by comparing the measured densities and viscosities of the pure compounds with the literature values, which are given in Table 1. The experimental values are in agreement with literature values.

Table 1 Experimental Density and viscosity of pure liquids at 298.15 K along with literature values in parenthesis

Liquid	Density	Viscosity
Dimethyl sulphoxide	1.0959 (1.0960) ¹⁶	1.991 (1.991) ¹⁰
Methanol	0.7868 (0.7867) ¹⁷	0.557 (0.553) ¹⁹
Ethanol	0.7854 (0.7855) ¹⁸	1.074 (1.0825) ²⁰
Prop-1-ol	0.7996 (0.7998) ¹⁸	1.934 (1.943) ¹⁰
Prop-2-ol	0.7816 (0.78126) ¹⁰	2.049 (2.0436) ¹⁰
But-1-ol	0.8067 (0.8059) ¹⁸	2.568 (2.571) ²⁰
But-2-ol	0.7987 (0.7998) ¹⁰	3.333 (3.333) ¹⁰
Ter-Butanol	0.7809 (0.7812) ¹⁰	4.439 (4.438) ¹⁰

The experimental values of viscosities for the studied binary solutions are given in Table 2.

Table 2 Experimental and theoretical viscosities in different binary solutions at 298.15 K

x_1	η_{exp}	H_{Bring}	η_{Arr}	H_{Ken}	H_{Katti}	H_{Grun}
DMSO+Methanol						
0.0473	0.5853	0.6248	0.5886	0.5916	0.5492	0.5542
0.1114	0.6297	0.7167	0.6349	0.6419	0.5536	0.564
0.1528	0.6611	0.7761	0.6665	0.6767	0.5629	0.5765
0.2119	0.7065	0.8609	0.7173	0.7296	0.5813	0.5988
0.3098	0.8114	1.0013	0.8079	0.8265	0.6459	0.6698
0.4014	0.9114	1.1326	0.9042	0.9288	0.7185	0.7474
0.4824	1.0196	1.2487	1.0017	1.0298	0.808	0.8408
0.5949	1.2114	1.4101	1.1565	1.1885	0.984	1.0209
0.6956	1.3956	1.5545	1.3188	1.3512	1.1754	1.2129
0.8072	1.6052	1.7145	1.5314	1.5576	1.4256	1.458
0.8995	1.7828	1.8469	1.7356	1.752	1.6689	1.6908
0.932	1.8507	1.8935	1.8139	1.8261	1.7679	1.7844
DMSO+Ethanol						
0.0668	1.0155	1.1353	1.1197	1.1192	0.9991	1.0011
0.1009	1.0185	1.1665	1.1434	1.1431	0.9954	0.998
0.153	1.0213	1.2143	1.1809	1.1804	0.9895	0.9928
0.2062	1.0239	1.2631	1.2205	1.2198	0.9848	0.9888
0.3164	1.0792	1.3641	1.3064	1.3057	1.0278	1.0329

Table Continued...

x_1	η_{exp}	H_{Bing}	η_{Arr}	H_{Ken}	H_{Katti}	H_{Grun}
0.3926	1.1302	1.434	1.3692	1.3686	1.0728	1.0786
0.4913	1.2088	1.5245	1.4549	1.4546	1.1469	1.1532
0.5898	1.3088	1.6148	1.5459	1.5458	1.246	1.2527
0.6921	1.4408	1.7086	1.6472	1.6466	1.3817	1.3882
0.7894	1.5801	1.7978	1.7484	1.7485	1.5305	1.5364
0.9044	1.7904	1.9033	1.8765	1.8772	1.7612	1.7654
0.9518	1.8903	1.9468	1.932	1.9329	1.8733	1.8763
DMSO+Prop-1-ol						
0.0505	1.8161	1.9369	1.8926	1.9366	1.8143	1.8159
0.1049	1.7185	1.94	1.8971	1.9397	1.7167	1.7183
0.2086	1.6125	1.9459	1.9059	1.9455	1.6106	1.6122
0.2908	1.5593	1.9506	1.9133	1.9502	1.5574	1.559
0.4128	1.5396	1.9575	1.9254	1.9571	1.5376	1.5393
0.4932	1.5532	1.9621	1.9335	1.9617	1.5512	1.5529
0.6126	1.6192	1.9689	1.9457	1.9685	1.6171	1.6189
0.6914	1.6825	1.9734	1.9544	1.973	1.6804	1.6822
0.8277	1.8277	1.9812	1.9699	1.9808	1.8256	1.8274
0.9123	1.8896	1.986	1.9796	1.9857	1.8877	1.8893
0.962	1.9471	1.9888	1.9855	1.9886	1.9053	1.9068
DMSO+Prop-2-ol						
0.0516	1.848	2.046	2.0428	2.0463	1.8461	1.8478
0.1282	1.6498	2.0415	2.4266	2.0418	1.6478	1.6496
0.2124	1.5202	2.0366	2.031	2.0369	1.5181	1.52
0.3389	1.475	2.0293	2.0227	2.0295	1.4727	1.4748
0.4183	1.4551	2.0247	2.0181	2.0248	1.4527	1.4549
0.4989	1.4831	2.0201	2.0135	2.0202	1.4807	1.4828
0.618	1.5753	2.0131	2.0072	2.0133	1.5728	1.575
0.7156	1.6505	2.0075	2.0024	2.0077	1.648	1.6502
0.8309	1.7745	2.0008	1.9972	2.001	1.7721	1.7742
0.9141	1.8801	1.9959	1.9936	1.9962	1.878	1.8798
DMSO+But-1-ol						
0.1008	2.2114	2.5097	1.7351	2.5025	1.5283	2.205
0.192	2.017	2.457	1.75598	2.4451	1.4405	2.0072
0.3117	1.7572	2.3878	1.7538	2.3718	1.3867	1.8446
0.4075	1.7783	2.3325	1.8086	2.3147	1.3775	1.7645
0.5031	1.7721	2.2772	1.8328	2.2591	1.4256	1.7577
0.6021	1.7738	2.2199	1.8623	2.2029	1.4858	1.7597
0.7144	1.8117	2.1551	1.8939	2.1408	1.5912	1.7992
0.8032	1.8648	2.1038	1.9247	2.093	1.7025	1.8546
0.9174	1.9295	2.0377	1.9628	2.033	1.8548	1.9242

Table Continued...

x_1	η_{exp}	H_{Bing}	η_{Arr}	H_{Ken}	H_{Katti}	H_{Grun}
DMSO+But-2-ol						
0.1017	2.7536	3.1965	3.1498	3.1638	2.7139	2.7241
0.1917	2.366	3.0757	2.9998	3.0203	2.3088	2.3224
0.3048	2.0366	2.9239	2.8241	2.8494	1.9683	1.9839
0.4099	1.9219	2.7829	2.6724	2.6991	1.8467	1.8634
0.5056	1.874	2.6545	2.5426	2.5692	1.7962	1.8132
0.6044	1.8538	2.5218	2.4175	2.4416	1.7779	1.7942
0.6946	1.8599	2.4008	2.3102	2.3308	1.79	1.805
0.8047	1.8945	2.2531	2.1877	2.2022	1.8391	1.8511
0.9181	1.934	2.1009	2.0706	2.0772	1.9048	1.9116
DMSO+Ter-Butanol						
0.1038	3.5097	4.1847	4.065	4.086	3.41	3.4248
0.2023	2.9199	3.9435	3.7448	3.7756	2.7744	2.7939
0.3096	2.4754	3.6807	3.4236	3.4643	2.3072	2.3285
0.4154	2.2247	3.4216	3.1385	3.1825	2.0464	2.068
0.5113	2.073	3.1868	2.9029	2.9469	1.895	1.9159
0.6098	1.9855	2.9455	2.6845	2.723	1.815	1.8344
0.6994	1.9155	2.7261	2.5017	2.5342	1.7625	1.7796
0.8082	1.9131	2.4597	2.3003	2.3225	1.7918	1.8052
0.9198	1.9755	2.1864	2.1128	2.1236	1.9097	1.9174

In Figure 1, deviation plots of excess viscosity are given for all the studied solutions. It is evident from Figure 1 that for all the solutions, values are negative. Further, at equimolar concentrations of studied solutions, the order is: methanol > ethanol > prop-1-ol > butan-1-ol > prop-2-ol > butan-2-ol > tertiary butanol. Thus, as CH_2 group increases, interactions decrease which causes more negative values with higher or branched alcohols.

Using above relations, the theoretical viscosities and some thermodynamic parameters such as excess free energy of mixing, strength of interaction parameter and interaction energy etc., have been evaluated for all the studied binary mixtures. The theoretical velocities evaluated by Bingham, Arrhenius and Eyring model, Kendall and Munroe, Katti and Chaudhari and Grunberg-Nissan relations are also given in Table 1. The validity of these relations has been checked by calculating percentage deviations for all the studied binary liquid mixtures and the results are shown in Table 3. It is observed that for some binary solutions, some of the relations give better results than others. Further, in most of the solutions, deviations are higher in intermediate compositions. The limitations and approximations incorporated in these theories are responsible for the deviations. The deviations are different for different solutions for different theories. In DMSO + methanol system, there is good agreement between experimental and theoretical values evaluated by Arrhenius and Kendell relations. In all the other solutions except DMSO + But-1-ol, values evaluated by Katti and Grunberg relations are close to experimental values. In DMSO + But-1-ol solutions, experimental values are in good agreement with those evaluated by Grunberg relation. Additive property is considered in some theories,

which gives better results in ideal solutions which is not the case in studied solutions. This is one of the reasons for discrepancy between experimental and theoretical values.

Table 3 Deviation between experimental and theoretical values of viscosity in studied binary solutions

x_1	H_{Bing}	η_{Arr}	H_{Ken}	H_{Katti}	H_{Grun}
DMSO+Methanol					
0.0473	-6.75	-0.56	-1.06	6.17	5.31
0.1114	-13.82	-0.82	-1.93	12.09	10.43
0.1528	-17.4	-0.81	-2.35	14.85	12.8
0.2119	-21.85	-1.53	-3.26	17.72	15.24
0.3098	-23.4	0.43	-1.86	20.4	17.45
0.4014	-24.27	0.79	-1.91	21.16	17.99
0.4824	-22.48	1.76	-1	20.75	17.54
0.5949	-16.4	4.53	1.89	18.77	15.72
0.6956	-11.39	5.51	3.18	15.78	13.09
0.8072	-6.81	4.6	2.96	11.19	9.17
0.8995	-3.59	2.65	1.73	6.39	5.16
0.932	-2.31	1.99	1.33	4.47	3.58

Table Continued...

x_1	H_{Bing}	η_{Arr}	H_{Ken}	H_{Katti}	H_{Grun}
DMSO+Ethanol					
0.0668	-11.79	-10.22	-10.26	1.61	1.41
0.1009	-14.53	-12.23	-12.26	2.27	2.02
0.153	-18.9	-15.58	-15.63	3.12	2.79
0.2062	-23.36	-19.14	-19.2	3.81	3.43
0.3164	-26.4	-20.99	-21.05	4.77	4.29
0.3926	-26.88	-21.1	-21.15	5.08	4.57
0.4913	-26.12	-20.34	-20.36	5.12	4.6
0.5898	-23.38	-18.11	-18.12	4.8	4.29
0.6921	-18.59	-14.28	-14.32	4.11	3.65
0.7894	-13.78	-10.66	-10.65	3.14	2.77
0.9044	-6.31	-4.85	-4.81	1.63	1.4
0.9518	-2.99	-2.26	-2.21	0.9	0.74
DMSO+Prop-1-ol					
0.0505	-6.65	-4.22	-6.64	0.1	0.01
0.1049	-12.89	-10.39	-12.87	0.1	0.01
0.2086	-20.68	-18.2	-20.65	0.12	0.02
0.2908	-25.09	-22.7	-25.07	0.12	0.02
0.4128	-27.15	-25.06	-27.12	0.13	0.02
0.4932	-26.33	-24.49	-26.3	0.13	0.02
0.6126	-21.6	-20.17	-21.57	0.13	0.02
0.6914	-17.29	-16.16	-17.27	0.12	0.02
0.8277	-8.4	-7.78	-8.38	0.11	0.02
0.9123	-5.1	-4.77	-5.09	0.1	0.01
0.962	-4.29	-4.11	-4.27	0.1	0.01
DMSO+Prop-2-ol					
0.0516	-10.71	-10.55	-10.73	0.1	0.01
0.1282	-23.75	-47.08	-23.76	0.12	0.01
0.2124	-33.97	-33.6	-33.99	0.14	0.01
0.3389	-37.58	-37.14	-37.59	0.16	0.02
0.4183	-39.15	-38.69	-39.16	0.16	0.02
0.4989	-36.21	-35.77	-36.22	0.16	0.02
0.618	-27.8	-27.42	-27.81	0.16	0.02
0.7156	-21.63	-21.32	-21.64	0.15	0.02
0.8309	-12.75	-12.55	-12.77	0.13	0.02
0.9141	-6.16	-6.04	-6.18	0.11	0.01

Table Continued...

x_1	H_{Bing}	η_{Arr}	H_{Ken}	H_{Katti}	H_{Grun}
DMSO+But-1-ol					
0.1008	-13.49	21.54	-13.17	30.89	0.29
0.192	-21.82	12.94	-21.23	28.58	0.49
0.3117	-35.89	5.57	-27.71	25.34	0.68
0.4075	-31.16	-1.7	-30.16	22.54	0.77
0.5031	-28.5	-3.42	-27.48	19.55	0.81
0.6021	-25.15	-4.99	-24.19	16.24	0.79
0.7144	-18.95	-4.54	-18.17	12.17	0.69
0.8032	-12.81	-3.21	-12.24	8.7	0.55
0.9174	-5.61	-1.73	-5.37	3.87	0.27
DMSO+But-2-ol					
0.1017	-16.09	-14.39	-14.9	1.44	1.07
0.1917	-30	-26.79	-27.66	2.42	1.84
0.3048	-43.57	-38.67	-39.91	3.35	2.59
0.4099	-44.8	-39.05	-40.44	3.91	3.05
0.5056	-41.65	-35.68	-37.1	4.15	3.25
0.6044	-36.04	-30.41	-31.71	4.1	3.21
0.6946	-29.08	-24.21	-25.32	3.76	2.95
0.8047	-18.93	-15.48	-16.24	2.92	2.29
0.9181	-8.63	-7.06	-7.4	1.51	1.16
DMSO+Ter-Butanol					
0.1038	-19.24	-15.82	-16.42	2.84	2.42
0.2023	-35.06	-28.25	-29.31	4.98	4.31
0.3096	-48.69	-38.31	-39.95	6.79	5.93
0.4154	-53.8	-41.08	-43.05	8.01	7.04
0.5113	-53.73	-40.03	-42.16	8.59	7.58
0.6098	-48.36	-35.21	-37.15	8.59	7.61
0.6994	-42.32	-30.61	-32.3	7.99	7.1
0.8082	-28.57	-20.24	-21.4	6.34	5.64
0.9198	-10.68	-6.95	-7.5	3.33	2.94

Further, in studied binary solutions, some thermodynamic parameters such as interaction parameter d , interaction energy (W_{vis}) and excess free energy of mixing (αF_m) have also been evaluated for quantitative estimation of interactions in solutions. The evaluated values are listed in Table 4.

It is evident from Table 4 that for all the studied solutions, interaction parameter (d) values are negative which suggest weak interactions in these solutions.²¹ This is further supported by interaction energy which is again negative for these solutions. αF_m is a measure of excess free energy of mixing. For studied solutions, these values are positive. Thus, excess free energy of mixing is reverse of interaction parameter and interaction energy. The negative

αF_m suggests strong interaction between molecules whereas positive values are due to weak interactions. Thus, in the studied solutions, weak interactions exist. This is further confirmed by negative excess viscosity which is shown in Figure 1.

Thus, it concluded that in studied binary solutions, some theories require modifications to give better results. Further, in studied solutions, weak interactions between molecules exist.

Table 4 Evaluated thermodynamic parameters for the studied binary solutions at 298.15K

x_1	d	W_{vis}	α_{Fm}
DMSO+Methanol			
0.0473	-1.4503	-3806.76	161.9963
0.1114	-1.308	-3431.43	320.9581
0.1528	-1.239	-3232.61	397.5923
0.2119	-1.1833	-3121.24	489.8494
0.3098	-0.9833	-2595.82	521.1631
0.4014	-0.9044	-2371.6	538.6374
0.4824	-0.812	-2133	502.5606
0.5949	-0.6302	-1661.76	376.4692
0.6956	-0.5092	-1347.45	267.2746
0.8072	-0.4234	-1139.85	163.3234
0.8995	-0.3906	-1073.08	87.53749
0.932	-0.3607	-1004.54	56.65759
DMSO+Ethanol			
0.0668	-1.7883	-4530.75	276.3306
0.1009	-1.4958	-3787.71	336.3721
0.153	-1.3357	-3383.97	429.0644
0.2062	-1.2826	-3248.79	520.3998
0.3164	-1.0833	-2749.76	580.7955
0.3926	-0.9984	-2536.73	590.1648
0.4913	-0.9285	-2360.01	575.217
0.5898	-0.8685	-2210.03	520.8725
0.6921	-0.8001	-2044.95	422.6595
0.7894	-0.7767	-1984.54	320.065
0.9044	-0.7075	-1817.91	151.6255
0.9518	-0.642	-1667.05	73.00559
DMSO+Prop-1-ol			
0.0505	-1.3428	-2185.26	159.602
0.1049	-1.2911	-2637.89	300.496
0.2086	-1.1384	-2528.24	465.8539
0.2908	-1.0856	-2474.09	554.9766
0.4128	-0.9908	-2300.44	595.3148
0.4932	-0.935	-2185.38	579.3108
0.6126	-0.824	-1932.64	484.7382

Table Continued...

x_1	d	W_{vis}	α_{Fm}
0.6914	-0.7475	-1755.28	395.3273
0.8277	-0.5654	-1322.63	199.8764
0.9123	-0.6219	-1475.11	123.341
0.962	-1.148	-2798.29	104.0231
DMSO+Prop-2-ol			
0.0516	-2.0799	-5132.61	-1778.19
0.1282	-1.9063	-8585.42	252.3096
0.2124	-1.7484	-4313.93	528.1429
0.3389	-1.4241	-3511.91	725.0038
0.4183	-1.3577	-3349.25	790.8784
0.4989	-1.236	-3048.65	818.9175
0.618	-1.0389	-2561.89	765.9417
0.7156	-0.9621	-2373.26	607.95
0.8309	-0.8543	-2109.58	485.3763
0.9141	-0.7617	-1887.21	297.5384
DMSO+But-1-ol			
0.1008	-1.39666	-3472.25	313.8001
0.192	-1.27255	-3165.29	489.3629
0.3117	-1.17202	-2714.69	623.2957
0.4075	-1.12425	-2795.98	672.8568
0.5031	-1.00406	-2491.83	622.1981
0.6021	-0.93769	-2337.45	556.8618
0.7144	-0.85228	-2116.81	431.0472
0.8032	-0.76517	-1924.26	299.8121
0.9174	-0.72623	-1852.42	136.4142
DMSO+But-2-ol			
0.1017	-1.6326	-4042.72	369.7236
0.1917	-1.6931	-4189.18	650.3041
0.3048	-1.7068	-4223.87	896.4812
0.4099	-1.5304	-3788.31	917.6201
0.5056	-1.3929	-3446.85	863.0638
0.6044	-1.2872	-3186.68	762.9138
0.6946	-1.2035	-2981.62	632.8395
0.8047	-1.103	-2738.01	429.7003
0.9181	-1.1009	-2752.25	205.1969
DMSO+Ter-Butanol			
0.1038	-1.89143	-4683.2	436.1524
0.2023	-1.86267	-4607.98	745.1024
0.3096	-1.85644	-4577.46	983.6187
0.4154	-1.7733	-4366.07	1067.46
0.5113	-1.72164	-4231.91	1066.361

Table Continued...

x_i	d	W_{vis}	α_{Fm}
0.6098	-1.65858	-4078.38	978.2627
0.6994	-1.67987	-4130.68	875.4577
0.8082	-1.62342	-3996.29	623.7957
0.9198	-1.38082	-3397.3	252.4923

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Conflicts of interest

The author declares there is no conflict of interest.

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