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Hydrogen Bonding and Interaction between Diethylene Glycol and Water: Density, Excess Molar Volume and Spectral Studies

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Density was determined over the whole concentration range for diethylene glycol (DEG) + water (DEGW) in the range of 298.15-323.15 K. The density (ρ) values was used to calculate the excess molar volume (V_m^E), which was used to discuss hydrogen bonding and interaction of DEG with water. The computed results are fitted to a Redlich-Kister equation to obtain the coefficients and estimate the standard deviations between the experimental and calculated quantities. These results suggest that the likely complex of 1 DEG molecule bonding with 2 water molecules is formed at maximal excess molar volume, which displayed lower absorption capabilities for SO_2 (122 mg L^{-1}) when the concentration of SO_2 arrived at $\Phi_1 = 5 \times 10^{-4}$ in the gas phase. When conventional spectroscopic techniques were used for inspection of spectral changes of various DEGWs, the results suggest that DEG can interact with water by hydrogen bonding and interaction.

Key Words: Density, Spectroscopy, Hydrogen Bonding and Interaction, Diethylene Glycol.

INTRODUCTION

Natural resources are limited, so coal with high sulfur content is commonly the most important consumption resource. The combustion of coal, due to its high sulfur content[1], means it is necessary to dedicate particular attention to eliminating the resulting emission of sulfur dioxide. Sulfur dioxide is an important atmospheric pollutant and therefore it is severe in environmental protection. Among the many procedures employed to desulfurize exhaust gases, organic solvents used as absorbents have been identified as an option among the regenerative processes[2-6] because regeneration can be done by pressure reduction, by temperature increase and by use of a carrier gas. Of the numerous organic solvents, alcohols show favourable absorption and desorption capabilities for acid gases in industrial processes[7]; therefore, our research group has paid attention to the alcohol + water system for SO_2 removal for several years[8-12].

Diethylene glycol (DEG) is an important industrial solvent, which has been used in the absorption processes of SO_2[13] because of its favourable properties, such as low toxicity, low vapour pressure and low melting point. DEG and DEGW presents native hydrogen bonding sites for the absorption of SO_2 so that the scrubbing and desorption properties may be related to strong hydrogen bonding and interaction[14-19] between DEG and water. In actual use, the physical properties of DEG + water mixtures are extremely important. Especially, the density (ρ) data and excess property of aqueous solutions are significant from the practical and theoretical viewpoint. Previously published data[20,21] showed the density data of pure water and pure DEG, but the density and viscosity data over the whole concentration range for the binary mixtures of DEG + water are generally limited to ambient temperatures.

In addition, FTIR spectroscopy and UV spectroscopy are very successful methods to probe the molecular association effects among molecules, since the FTIR spectroscopy gives precise information about water sensitive bonds[22,23] and the UV spectroscopy gives information about various electronic transitions. Generally, FTIR spectral technique[24,25] and UV spectral technique offer the advantages to measure the association properties and hydrogen bonding capability to assess interaction of DEG with water by analyzing band shifts and changes of band shape. Furthermore, FTIR is also advantageous to evaluate the vibrational properties of bonds through very thin solution films, which are usually difficult to handle for the floating properties of solution.

Our previous results[13] show that the addition of H_2O into DEG decreased the solubilities of SO_2 in DEGW (Fig. 1). In the entire composition range, $w_1 = 0.60$ DEGW exhibits an extreme minimum value of 122 mg/L to dissolve SO_2 when SO_2 concentration is designed at $\Phi_1 = 5 \times 10^{-4}$ in the gas phase and pure DEG shows the strongest capabilities to dissolve SO_2 and the solubility is 259 mg/L at the same gas composition. The above results may be related to the excess properties of aqueous DEG solutions because maximum excess volume value (V_m^E) presents at about $x_1 = 0.33$ ($w_1 = 0.60$) DEGW, which exhibited an extreme minimum value and may be related to the hydrogen bonding and interactions among DEG, H_2O and SO_2 and the similar hydrogen bonding and interactions among DEG, H_2O and SO_2 had been published in our previous work[16]. The study of absorption processes of SO_2 in DEGW includes the following three steps: (1) gas-liquid equilibrium data for mixture gas of $SO_2 + N_2$ with DEG aqueous solutions, (2) density, viscosity and excess properties for DEG aqueous solutions and (3) spectral properties of DEG + SO_2 + H_2O interactions. Our previous article covers the first step of this study[13]. The present work was mainly focused on investigating the second step and the possible hydrogen bonding and interaction mechanism between DEG and H_2O by FTIR and UV spectroscopic techniques. In our future work, we will publish the possible hydrogen bonding and interaction among DEG, H_2O and SO_2 in the absorption processes of SO_2 by FTIR, UV, fluorescence and ^1H NMR spectroscopic techniques.

EXPERIMENTAL

The analytical grade DEG was purchased from Beijing Reagent Company. It was used after drying over molecular sieves (type 4A) and decompression filtration

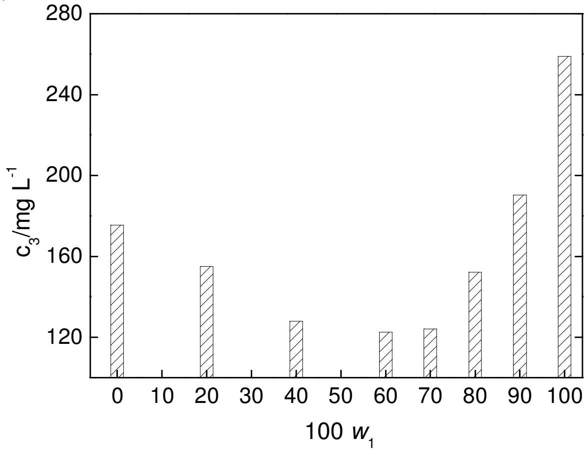


Fig. 1. Solubility of SO_2 at various DEGW when the concentration of SO_2 in the gas phase arrives at 5 × 10^{-4}

before measurements. The purity of the sample was checked by density determination at 298.15 K. The density of DEG at 298.15 K was found to be 1.1132 g cm^{-3}, in good agreement with the literatures[20,21]. Bidistilled water was used in this work.

General procedure: Densities of pure liquids and their mixtures were determined using a bicapillary pycnometer having a bulb volume of 10 cm^3. The volume of the pycnometer was calibrated as a function of temperature using distilled, deionized and desgassed water at various temperatures[26-28]. The pycnometer filled with liquid was kept in a thermostatically controlled and well-stirred water bath (maintained constant to ± 0.01 K) for (10-15) min to attain thermal equilibrium. The density measurements were carried out at temperatures 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K. Each experimental density value was an average of at least three measurements. The uncertainty of the density measurement was estimated to be ± 0.1 %.

The experimental densities (ρ) of pure DEG are compared with the available literature values are given in Table-1.

TABLE-1
COMPARISON OF EXPERIMENTAL DENSITIES (ρ) OF DEG WITH LITERATURE VALUES AT VARIOUS TEMPERATURES

T (K)	ρ/(g cm^{-3})	
	Expt.	Lit.
298.15	1.1132	1.11303[20], 1.11297[21]
303.15	1.1088	1.10947[20]
308.15	1.1066	1.10578[21]
313.15	1.1016	–
318.15	1.0986	1.09851[21]
323.15	1.0946	–

The excess molar volume, V_m^E, was calculated from density measurements according to the following equation

$$V_m^E = \frac{x_1M_1 + x_2M_2}{\rho_m} - \left(x_1\frac{M_1}{\rho_1} + x_2\frac{M_2}{\rho_2} \right) \quad (1)$$

where ρ_m = density of the mixture and x_1, ρ_1, M_1, x_2, ρ_2, M_2 are the mole fractions, densities and molecular weights of pure DEG and pure water, respectively.

A Redlich-Kister relation was used to correlate the excess volume data.

$$\frac{V_m^E}{cm^3\ mol^{-1}} = x_1x_2\sum_{i=0}^{n} A_i(2x_1 - 1)^i \quad (2)$$

where x_1 = mole fraction of DEG and x_2 = mole fraction of water, A_i are the polynomial coefficients which were evaluated from the least - squares method and n = polynomial degree.

The standard deviation values, σ, between the calculated and experimental data points are obtained by the following equation

$$\sigma_{V_m^E} = \left[\frac{\Sigma(V_{calc}^E - V_m^E)^2}{(N - m)} \right]^{1/2} \quad (3)$$

where N = total number of experimental points and m = number of A_i coefficients considered.

Detection method: FTIR spectra were recorded on a Bruker VECTOR22 FTIR spectrometer with a resolution of 1 cm^{-1} at 298 K in the range from 4000-400 cm^{-1}. The spectrometer possesses auto-align energy optimization and a dynamically aligned interferometer and fitted with a constringent $BaSO_4$ pellet for the measurement of aqueous solution, an OPUS/IR operator and IR source. A base line correction was made for the spectra that were recorded in air and then 20 mL solution was used to performance on the FTIR spectrometer in every one of measurements and the thin layer of samples are less than typically 2 micrometer thickness. UV spectra were recorded using a Varian CARY 1E UV-vis spectrometer with a resolution of 0.2 nm at room temperature in the region of 190-900 nm. A base line correction was made for the spectra recorded in deionized water.

RESULTS AND DISCUSSION

Density and excess volume: Experimental densities of the binary solutions of DEG + water at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K throughout the whole concentration range are summarized in Table-2. The values of the measured density at different temperatures are shown in Fig. 2. Table-2 and Fig. 2 show that the density values increase with the increasing DEG concentration in binary solutions over the whole concentration range and the values quickly increase between $x_1 = 0$ and $x_1 = 0.33$. The density values decrease with the augment of temperature at the same concentration. The results of V_m^E are listed in Table-3 and the dependence of V_m^E at various temperatures is shown in Fig. 3.

TABLE-2
EXPERIMENTAL DENSITIES (ρ) OF DEG (1) + WATER (2)
AT DIFFERENT TEMPERATURE (K)

x_1	ρ/(g cm^{-3})					
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0.0000	0.9971	0.9952	0.9941	0.9922	0.9903	0.9881
0.0500	1.0310	1.02830	1.0265	1.0239	1.0215	1.0191
0.1000	1.0552	1.0519	1.0493	1.0463	1.0435	1.0404
0.1429	1.0694	1.0656	1.0632	1.0598	1.0565	1.0532
0.2002	1.0826	1.0785	1.0758	1.0722	1.0689	1.0655
0.2504	1.0904	1.0864	1.0835	1.0796	1.0761	1.0725
0.2999	1.0962	1.0919	1.0888	1.0850	1.0815	1.0779
0.3340	1.0990	1.0946	1.0918	1.0879	1.0844	1.0806
0.3995	1.1033	1.0987	1.0958	1.0920	1.0883	1.0846
0.4498	1.1055	1.1011	1.0977	1.0939	1.0906	1.0866
0.5000	1.1072	1.1026	1.0997	1.0957	1.0923	1.0885
0.5499	1.1086	1.1041	1.1020	1.0976	1.0935	1.0900
0.5998	1.1096	1.1051	1.1030	1.0984	1.0948	1.0911
0.6494	1.1103	1.1060	1.1039	1.0993	1.0956	1.0920
0.6995	1.1110	1.1069	1.1046	1.0999	1.0962	1.0926
0.7497	1.1117	1.1074	1.1051	1.0998	1.0968	1.0932
0.7997	1.1120	1.1078	1.1057	1.1002	1.0975	1.0936
0.8500	1.1124	1.1081	1.1059	1.1007	1.0975	1.0942
0.8999	1.1127	1.1084	1.1063	1.1010	1.0979	1.0944
0.9493	1.1130	1.1086	1.1065	1.1014	1.0982	1.0945
1.0000	1.1132	1.1088	1.1066	1.1016	1.0986	1.0946

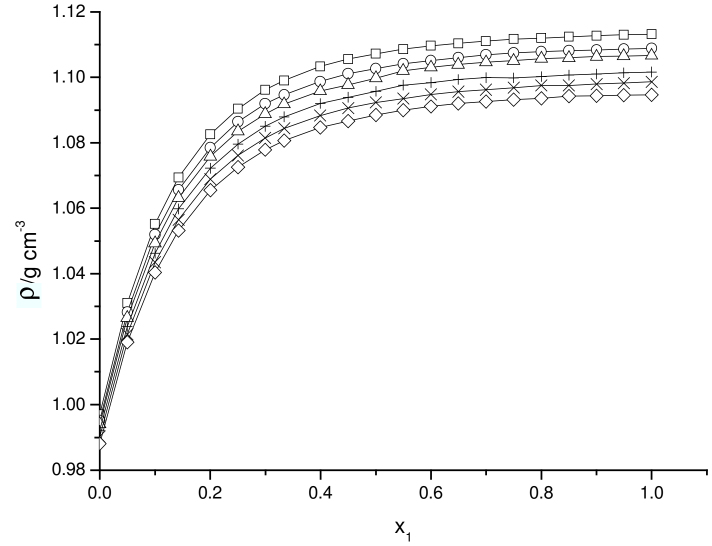


Fig. 2. Experimental densities with mole fraction for DEG (1) + water (2): □, 298.15 K; ○, 303.15 K; △, 308.15 K; +, 313.15 K; ×, 318.15 K; ◇, 323.15 K

TABLE-3
EXCESS MOLAR VOLUMES (V_m^E) FOR DEG (1) + WATER (2)
AT DIFFERENT TEMPERATURE (K)

x_1	V_m^E/(cm^3 mol^{-1})					
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0500	-0.1852	-0.1794	-0.1706	-0.1683	-0.1645	-0.1676
0.1000	-0.3721	-0.3609	-0.3404	-0.3357	-0.3247	-0.3208
0.1429	-0.4889	-0.4700	-0.4503	-0.4496	-0.4292	-0.4222
0.2002	-0.6013	-0.5796	-0.5500	-0.5547	-0.5349	-0.5290
0.2504	-0.6593	-0.6469	-0.6262	-0.6103	-0.5825	-0.5739
0.2999	-0.7010	-0.6784	-0.6422	-0.6452	-0.6169	-0.6132
0.3340	-0.7034	-0.6823	-0.6521	-0.6586	-0.6279	-0.6202
0.3995	-0.6946	-0.6713	-0.6361	-0.6582	-0.6207	-0.6160
0.4498	-0.6746	-0.6574	-0.6154	-0.6238	-0.6001	-0.5876
0.5000	-0.6426	-0.6179	-0.6010	-0.5982	-0.5733	-0.5696
0.5499	-0.5998	-0.5818	-0.5765	-0.5918	-0.5256	-0.5429
0.5998	-0.5463	-0.5282	-0.5237	-0.5341	-0.4961	-0.5013
0.6494	-0.4907	-0.4786	-0.4767	-0.4893	-0.4442	-0.4575
0.6995	-0.4378	-0.4277	-0.4189	-0.4301	-0.3809	-0.4000
0.7497	-0.3769	-0.3685	-0.3590	-0.3265	-0.3260	-0.3430
0.7997	-0.2991	-0.2996	-0.3043	-0.2590	-0.2751	-0.2827
0.8500	-0.2228	-0.2247	-0.2241	-0.2015	-0.1879	-0.2351
0.8999	-0.1495	-0.1576	-0.1581	-0.1324	-0.1248	-0.1614
0.9493	-0.0792	-0.0754	-0.0865	-0.0747	-0.0548	-0.0815
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

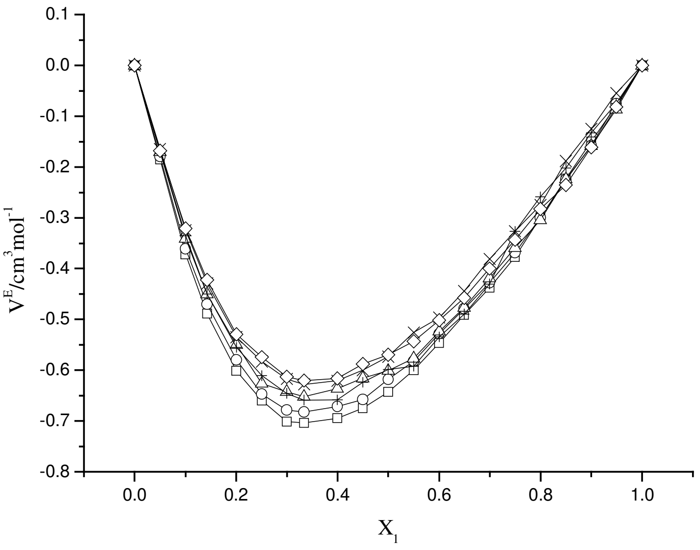


Fig. 3. Excess molar volumes with mole fraction for DEG (1) + water (2): □, 298.15 K; ○, 303.15 K; △, 308.15 K; +, 313.15 K; ×, 318.15 K; ◇, 323.15 K

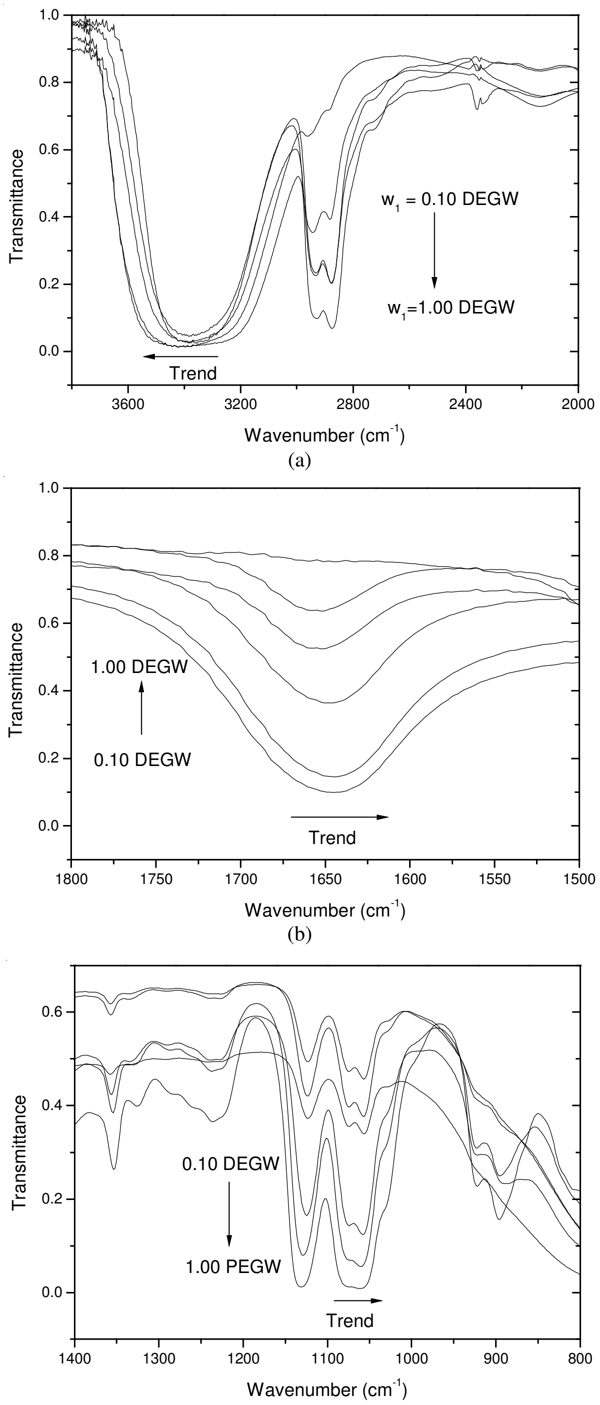
Fig. 3 shows that V_m^E is negative for all the mixtures over the entire mole fraction range at each temperature, as is common for other completely miscible (water + organic solvents). The maximum is at about $x_1 = 0.33$. Additionally, these V_m^E values become less negative with increasing temperature. The coefficients A_i and corresponding standard deviations, σ, are listed in Table-4.

TABLE-4
COEFFICIENTS AND STANDARD DEVIATIONS OF EXCESS MOLAR VOLUMES, V^E, FOR DEG (1) + WATER (2)

T (K)	A_0	A_1	A_2	A_3	σ/cm^3 mol^{-1}
298.15	-2.585	1.582	-0.584	-0.152	0.00776
30315	-2.505	1.532	-0.650	-0.273	0.00761
308.15	-2.417	1.339	-0.636	-0.125	0.00994
313.15	-2.464	1.355	-0.226	-0.193	0.01310
318.15	-2.312	1.370	-0.424	-0.048	0.00842
323.15	-2.299	1.275	-0.640	-0.250	0.00667

Fig. 3 shows that V_E in different DEGW is negative value and the extremum of V_E appeared nearby 0.33 (mole fraction) keeps increasing with increasing temperatures at the same DEG molar fraction. These results suggest that the likely complex of 1 DEG molecule bonding with 2 water molecules is formed at maximal excess molar volume in DEGW, which may be related to the low absorption of SO_2 in w_1 = 0.6 DEGW. On the basis of these findings, it is considered that hydrogen bonding interaction is formed between DEG and water over the whole concentration range of DEGW. At the maximal excess molar volume, there presents the closest aggregates.

FTIR spectral properties of DEG + H_2O: The recorded FTIR spectra of DEG + H_2O are shown in Fig. 4. From Fig. 4 (a) the stretching vibrational band of hydroxyl in DEGW is found to shift toward higher frequency from 3422-3356 cm^{-1} with increasing H_2O concentration. The fact that the stretching vibrational band of hydroxyl in DEGW shifts toward higher frequency indicates that the interactions are due to the variational property of hydroxyl in DEG. From Fig. 4(b) the bending vibrational frequency of water changes from 1645-1652 cm^{-1}, which has been reported to appear at 1645 cm^{-1} in water saturated low density polyethylene[22]. The fact that H-O-H bending vibrational band shifts towards lower frequency indicates that the interactions result from the variational property of hydrogen atom in H_2O. Meanwhile, the stretching vibrational band of C-O-C in DEG is found to shift toward lower frequency from 1061-1057 cm^{-1} (Fig. 4c). The fact that the stretching vibrational band of C-O-C in DEG shifts toward lower frequency indicates that interactions can be related to the oxygen in C-O-C. According above results, it present that the interactions between DEG and water result from the following two ways: (1) hydrogen bonding and interaction of hydrogen atom in H_2O with hydroxyl oxygen atom in DEG by cross-linking as the formations of $-CH_2CH_2O(H)\cdots HOH\cdots$ and $-CH_2CH_2OH\cdots(H)OH\cdots$ and (2) weak hydrogen bonding and interaction of hydrogen atom in water with ether oxygen atom in DEG as the formation of $-CH_2-CH_2-O(CH_2-CH_2-)\cdots HOH\cdots$.



(a)

(b)

(c)

Fig. 4. FTIR spectra of DEGW at various mass fractions: (a) 3800-2000 cm^{-1}, (b) 1800-500 cm^{-1} and (c) 1400-800 cm^{-1}

UV-Vis spectral properties of DEG + H_2O: Fig. 5 shows that the electronic transitions blue shift from 200-210 nm with increasing H_2O concentration in DEGW. The absorption band can be due to the n→σ* electronic transition of unshared electronic pair of hydroxyl oxygen in DEG because the n→σ* electronic transition of water and the n→σ* electronic transition of ether oxygen in DEG are often found at the vacuum ultraviolet region. With increasing water concentration, hydrogen bonding and interaction of hydroxyl oxygen of DEG with hydrogen of water happened easily. However, the hydrogen bonding and interaction makes the n→σ* electronic transition of hydroxyl oxygen in DEG become more difficulty. Above results show that the hydrogen bonding and interaction in the DEGW be formed as $-CH_2CH_2O(H)\cdots HOH\cdots$.

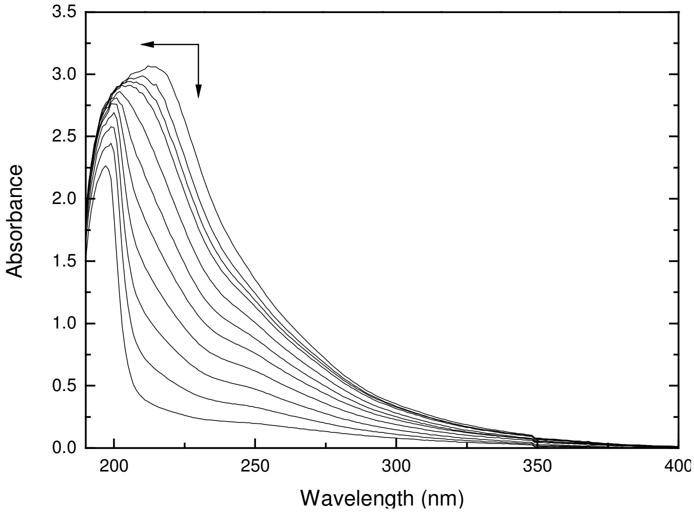


Fig. 5. Absorption spectral changes with increasing H_2O concentration at various concentrations of DEGW

Conclusion

This paper reports experimental data for the densities of the aqueous DEG solutions over a range of temperature from (298.15-323.15) K. The calculated V_m^E values for the aqueous DEG solutions were negative at all temperatures and compositions. The density analyses of DEGW show that the maximal excess molar volume of DEGW was displayed at about 0.33. These results suggest that the likely complex of 1 DEG molecule bonding with 2 water molecules is formed at maximal excess molar volume in DEGW. The spectral results of various DEGWs present the strong hydrogen bonding interaction of the water hydrogen with the hydroxyl oxygen of DEG from the following two ways: (1) hydrogen bonding and interaction of hydrogen atom in H_2O with hydroxyl oxygen atom in DEG by cross-linking as the formations of $-CH_2CH_2O(H)\cdots HOH\cdots$ and $-CH_2CH_2OH\cdots(H)OH\cdots$ and (2) weak hydrogen bonding and interaction of hydrogen atom in water with ether oxygen atom in DEG as the formation of -CH_2-CH_2-O(CH_2-CH_2-)···HOH···.

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REFERENCES

1. M.A. Siddiqi, J. Krissmann, P. Peters-Gerth, M. Luckas and K. Lucas, *J. Chem. Thermodyn.*, **28**, 685 (1996).
2. X. Esteve, A. Conesa and A. Coronas, *J. Chem. Eng. Data*, **48**, 392 (2003).
3. H.C. Ku and C.H. Tu, *J. Chem. Eng. Data*, **45**, 391 (2000).
4. A. Valtz, C. Coquelet and D. Richon, *Fluid Phase Equilib.*, **220**, 77 (2004).
5. D. Nagel, R. de Kermadec, H.G. Lintz, C. Roizard and F. Lapicque, *Chem. Eng. Sci.*, **57**, 4883 (2002).
6. R. de Kermadec, F. Lapicque, D. Roizard and C. Roizard, *Ind. Eng. Chem. Res.*, **41**, 153 (2002).
7. C.N. Schubert and W.I. Echter, CN. Patent. 1364096A (2002).
8. X.X. Li, Y.X. Liu and X.H. Wei, *Chin. J. Chem. Eng.*, **13**, 234 (2005).
9. X.H. Wei, CN. Patent. 02130605. 2 (2002).
10. X.H. Wei, J.B. Zhang, P.Y. Zhang, L.W. Zhang and X.B. Li, CN. Patent. 101053746 (2007).
11. J.B. Zhang, P.Y. Zhang, G.H. Chen, F. Han and X.H. Wei, *J. Chem. Eng. Data*, **53**, 1479 (2008).
12. J.B. Zhang, P.Y. Zhang, F. Han, G.H. Chen, X.H. Wei, *J. Chem. Eng. Data*, **53**, 2372 (2008).
13. J.B. Zhang, G.H. Chen, P.Y. Zhang, F. Han and X.H. Wei, *J. Chem. Eng. Data*, **48**, 1287 (2009).
14. P. Ivopoulos, M. Sotiropoulou, G. Bokias and G. Staikos, *Langmuir*, **22**, 9181 (2006).
15. D.P. Schofield, J.R. Lane and H.G. Kjaergaard, *J. Phys. Chem. A*, **111**, 567 (2007).
16. J.B. Zhang, P.Y. Zhang, F. Han, G.H. Chen, L.W. Zhang and X.H. Wei, *Ind. Eng. Chem. Res.*, **48**, 1287 (2009).
17. J.B. Zhang, P.Y. Zhang, K. Ma, F. Han, G.H. Chen and X.H. Wei, *Sci. China Ser. B-Chem.*, **51**, 420 (2008).
18. J.L. Dashnau, N.V. Nucci and K.A. Sharp, *J. Phys. Chem. B*, **110**, 13670 (2006).
19. A. Nose, T. Hamsaki, M. Hojo, R. Kato, K. Uetara and T. Ueda, *J. Agric. Food. Chem.*, **53**, 7074 (2005).
20. A. Cwilinska, M. Klimczak, W.J.J. Kinart and C.M. Kinart, *J. Chem. Themodyn.*, **40**, 476 (2008).
21. L.F. Chen, A.N. Soriano and M.H. Li, *J. Chem. Thermodyn.*, **41**, 724 (2009).
22. A. Lasgabaster, M.J. Abad, L. Barral and A. Ares, *Eur. Polym. J.*, **42**, 3121 (2006).
23. K. Dharmalingam and K.P. Ramachandran, *Physica B.*, **4**, 1 (2006).
24. F. Palombo, M. Paolantoni, P. Sassi and A. Morresi, *J. Mol. Liq.*, **125**, 139 (2006).
25. B. Yuan and X.M. Dou, *Spectrosc. Spect. Anal.*, **11**, 1319 (2004) in Chinese.
26. A. Henni, J.J. Hromek, P. Tontiwachwuthikul and A. Chakma, *J. Chem. Eng. Data*, **48**, 551 (2003).
27. J.F. Comesana, J.J. Otero, E. García and A. Correa, *J. Chem. Eng. Data*, **48**, 362 (2003).
28. E. Alvarez, A. Cancela, R. Maceiras, J.M. Navaza and R. Taboas, *J. Chem. Eng. Data*, **51**, 940 (2006).

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