



Excess Molar Properties and Viscosities of Glycerol + Water System at 298.15 to 318.15 K

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In this study, the experimental densities for the binary system of glycerol + water at the temperature range from (298.15 to 318.15) K at intervals of 5 K are reported. Densities of pure liquids and their mixtures were determined using a bicapillary pycnometer. The viscosities were determined with an Ubbelohde capillary viscometer. The experimental results are compared with data published in the previous literatures. The density (ρ) and viscosity (η) values, the excess molar volumes V_m^E , viscosity deviations ($\Delta\eta$) of the experimental data, which the calculated results are fitted to a Redlich-Kister equation to obtain the coefficients and estimated the standard deviations between the experimental and calculated values. The calculated V_m^E values for the glycerol + water system were negative cover whole compositions at all temperatures, while, the viscosity deviations ($\Delta\eta$) of the aqueous glycerol solutions were positive over the major composition range.

Key Words: Glycerol, Density, Excess molar volume, Viscosity deviations.

INTRODUCTION

Sulfur dioxide (SO_2) is a hazardous gas to atmosphere, is mainly emitted from the burning of fossil fuels that contributes to acid rain and other environmental problems such as corrosion and ground-level ozone formation and is linked to several respiratory diseases^{1,2}. The flue gas comes from the burning of fuels with high sulfur content from 0.03 mg m^{-3} in the air up to several mg m^{-3} in a typical flue gas³. Up to now, flue gas desulfurization is one of the most effective techniques for SO_2 control of the combustion of fossil fuels. The wet desulfurization method has been taken in commercial. Although the processes mainly based on limestone scrubbing and its high desulfurization efficiency, its has some disadvantages, such as high operating cost, huge magnitude of capital investment, huge magnitude water requirement and even causing secondary pollution. In recent years, the large part of organic solvents has been used in SO_2 removal^{4,5}. In the most of organic solvents, alcohols show favourable absorption and desorption properties for acid gases in industrial processes^{6,7}. Thus, in present research studies, great attention has been paying attention to alcohol + water systems for the SO_2 scrubbing⁸⁻¹³.

Glycerol is an important solvent in the pharmaceutical and food industries, available as a industrial organic solvent in the removal of SO_2 from flue gas^{14,15}. Because of its favourable properties, such as low vapour pressure, low toxicity, low melting point and high chemical stability. The

physical properties of glycerol + water binary system may be benefit to solubility and desorption capability for SO_2 . Especially, the previous literatures¹⁶⁻²² of density (ρ) and viscosity (η) data prove that only the partly mixing properties of glycerol + water have reported. Therefore, we have to implement the measurements for densities and viscosities of glycerol + water.

In present work, the densities and viscosities of glycerol + water are presented at the temperature range of (298.15 to 318.15) K. Based on these results, the excess molar volume and the deviation of the viscosity were discussed.

EXPERIMENTAL

Analytical grade was purchased from Beijing Reagent Company. Glycerol was dried over 0.4 nm molecular sieves decompression filtration before measurements and through the ultrasonic model degassing just before the experiments. The purity of the sample was checked by density determination at 298.15 K. The density of glycerol at 298.15 K was found to be 1.2580 g cm^{-3} , in good agreement with the literatures²³. Meanwhile, bi-distilled water and high-performance liquid chromatography (HPLC) grade ethanol were used at present work.

Measurements: The solutions of binary mixtures were prepared by mass using an electronic analytical balance (Sartorius BS 224S), which shows a precision of $\pm 0.0001 \text{ g}$. The uncertainty in the mole fraction for each binary mixture was approximated to be ± 0.0001 .

Densities of pure liquids and their mixtures were determined using a bicapillary pycnometer having a bulb volume of 10 cm³. The volume of the pycnometer was calibrated as a function of temperature using distilled, deionized and degassed water at various temperatures of T = (298.15 to 318.15) K at intervals of 5 K. Each experimental density and viscosity value was controlled to ± 0.01 K in a thermostatically controlled and well-stirred water bath. The pycnometer filled with liquid was kept in the water bath for 20 min to accomplish thermal equilibrium. The density value of experimental was an average of at least three measurements; however, the uncertainty of the density measurement was approximated to be lower than ± 0.03 %.

The kinematic viscosity in both the pure components and their mixtures was made with a commercial capillary viscometer for has a capillary diameter of 0.90 mm of the Ubbelohde type, which was calibrated with bi-distilled water and ethanol (HPLC grade) at the temperatures of (298.15, 303.15, 308.15, 313.15 and 318.15) K. The flow time was determined with a hand-held digital stopwatch capable of measuring time within ± 0.01 s; furthermore, the measurements of density and viscosity were accomplished in a transparent glasswalled water bath with the thermal stability 0.01 K.

The kinematic viscosity (ν) was calculated from the following equation:

$$\nu = A t \frac{B}{t} \quad (1)$$

where, ν shows the kinematic viscosity; t shows its flow time of liquids; and A and B shows viscometer constants. A and B are calculated from measurements with the calibration fluids bi-distilled water and ethanol. The absolute viscosity (η) was obtained by multiplying the determined ν by the measured density ($\eta = \nu\rho$). Each experimental point was the average of 16 sets, which has a maximum deviation of ± 0.3 % in the flow time.

RESULTS AND DISCUSSION

Experimental values of the densities the binary solutions of glycerol + water over the temperature range from (298.15 to 318.15) K with a step of 5 K throughout the whole concentration range are presented in Table-1 (Fig. 1).

Table-1 (Fig. 1) display that the density values increase with the increasing glycerol concentrations in binary solutions over the whole concentration range and the values quickly increase between $x_1 = 0$ and $x_1 = 0.2$. Moreover, under the same concentration with temperature increasing density value decreases.

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

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - \left(x_1 \frac{M_1}{\rho_1} + x_2 \frac{M_2}{\rho_2} \right) \quad (2)$$

where, ρ_m shows that the density of the mixture and x_1 , ρ_1 , M_1 , x_2 , ρ_2 and M_2 are the mole fractions, densities and molecular weights of the pure glycerol and pure water, respectively. The results of V_m^E are listed in Table-2 and the dependence of V_m^E at various temperatures (Fig. 2).

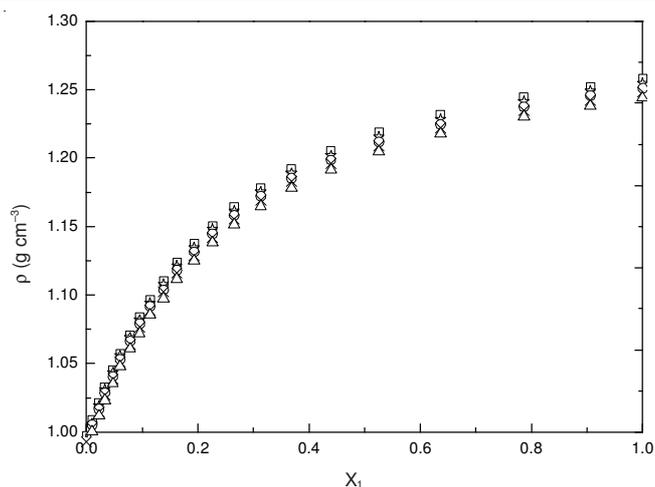


Fig. 1. Experimental densities with mole fraction for glycerol (1) + water (2): □, 298.15 K; ☆, 303.15 K; ○, 308.15 K; ×, 313.15 K; and △, 318.15 K

x_1	$\rho/(g\ cm^{-3})$				
	T (K) = 298.15	T (K) = 303.15	T (K) = 308.15	T (K) = 313.15	T (K) = 318.15
0.0000	0.9971	0.9950	0.9933	0.9930	0.9892
0.0101	1.0087	1.0060	1.0052	1.0028	1.0004
0.0220	1.0211	1.0190	1.0169	1.0147	1.0117
0.0328	1.0329	1.0309	1.0287	1.0270	1.0231
0.0472	1.0452	1.0433	1.0407	1.0386	1.0353
0.0608	1.0574	1.0557	1.0531	1.0509	1.0478
0.0782	1.0708	1.0689	1.0663	1.0639	1.0607
0.0952	1.0839	1.0817	1.0790	1.0765	1.0721
0.1144	1.0964	1.0942	1.0917	1.0890	1.0855
0.1384	1.1102	1.1078	1.1037	1.1023	1.0975
0.1627	1.1235	1.1213	1.1182	1.1161	1.1119
0.1935	1.1375	1.1345	1.1315	1.1286	1.1249
0.2265	1.1507	1.1479	1.1445	1.1420	1.1382
0.2652	1.1644	1.1616	1.1583	1.1556	1.1514
0.3128	1.1782	1.1753	1.1720	1.1690	1.1648
0.3683	1.1921	1.1888	1.1853	1.1830	1.1782
0.4394	1.2056	1.2019	1.1986	1.1958	1.1913
0.5257	1.2188	1.2153	1.2118	1.2088	1.2046
0.6364	1.2316	1.2284	1.2246	1.2220	1.2175
0.7863	1.2447	1.2413	1.2374	1.2347	1.2303
0.9060	1.2522	1.2490	1.2457	1.2422	1.2379
1.0000	1.2580	1.2546	1.2510	1.2483	1.2440

Table-2 (Fig. 2) display that the values of V_m^E are negative for all the mixtures over the entire mole fraction range at all temperature. The maximum is found at approximately $x_1 = 0.38$, along with the increase of the temperature that the value of V_m^E become less negative.

A Redlich-Kister relation was used to correlate the excess volume data according to the following equation:

$$V_m^E (\text{cm}^3 \text{mol}^{-1}) = x_1 x_2 \sum_{i=0}^n A_i (2x_1 - 1)^i \quad (3)$$

where, x_1 shows the mole fraction of glycerol; x_2 shows the mole fraction of water; and A_i shows the polynomial coefficients; and n shows that the polynomial degree.

The standard deviation values, σ , between the calculated and experimental data according to the following equation:

TABLE-2
EXCESS MOLAR VOLUMES (V_m^E) FOR
GLYCEROL (1) + WATER (2)

x_1	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$				
	T (K) = 298.15	T (K) = 303.15	T (K) = 308.15	T (K) = 313.15	T (K) = 318.15
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0101	-0.0220	-0.0113	-0.0309	0.0065	-0.0189
0.0220	-0.0413	-0.0425	-0.0377	-0.0051	-0.0216
0.0328	-0.0816	-0.0859	-0.0814	-0.0601	-0.0581
0.0472	-0.0878	-0.0967	-0.0832	-0.0554	-0.0677
0.0608	-0.1231	-0.1366	-0.1252	-0.0960	-0.1122
0.0782	-0.1443	-0.1545	-0.1466	-0.1147	-0.1305
0.0952	-0.1891	-0.1956	-0.1855	-0.1519	-0.1430
0.1144	-0.2139	-0.2211	-0.2184	-0.1810	-0.1936
0.1384	-0.2357	-0.2407	-0.2022	-0.1966	-0.1804
0.1627	-0.2758	-0.2866	-0.2716	-0.2535	-0.2494
0.1935	-0.2965	-0.2908	-0.2810	-0.2426	-0.2531
0.2265	-0.3194	-0.3198	-0.3019	-0.2753	-0.2827
0.2652	-0.3454	-0.3492	-0.3349	-0.3046	-0.3043
0.3128	-0.3560	-0.3577	-0.3466	-0.3102	-0.3121
0.3683	-0.3753	-0.3680	-0.3522	-0.3414	-0.3212
0.4394	-0.3534	-0.3333	-0.3267	-0.3026	-0.2919
0.5257	-0.3210	-0.3092	-0.3006	-0.2673	-0.2721
0.6364	-0.2522	-0.2549	-0.2373	-0.2247	-0.2164
0.7863	-0.1562	-0.1516	-0.1302	-0.1212	-0.1167
0.9060	-0.0414	-0.0477	-0.0613	-0.0138	-0.0165
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

TABLE-3
COEFFICIENTS AND STANDARD DEVIATIONS OF EXCESS
MOLE VOLUMES (V_m^E) FOR GLYCEROL (1) + WATER (2)

T/K	A_0	A_1	A_2	A_3	A_4	$\sigma/(\text{cm}^3\cdot\text{mol}^{-1})$
298.15	-1.331	0.808	-0.314	0.205	0.486	0.0074
303.15	-1.436	0.670	-0.546	0.313	0.515	0.0088
308.15	-1.254	0.913	-0.047	-0.136	-0.213	0.0117
313.15	-1.139	0.736	-0.609	0.256	1.435	0.0144
318.15	-1.119	0.730	-0.481	0.325	1.053	0.0112

TABLE-4
EXPERIMENTAL VISCOSITIES (η) OF
GLYCEROL (1) + WATER (2)

x_1	$\eta/(\text{mPa}\cdot\text{s})$				
	T (K) = 298.15	T (K) = 303.15	T (K) = 308.15	T (K) = 313.15	T (K) = 318.15
0.0000	0.893	0.792	0.723	0.652	0.596
0.0101	0.920	0.828	0.741	0.677	0.618
0.0220	0.957	0.863	0.779	0.708	0.647
0.0328	1.01	0.907	0.821	0.741	0.677
0.0472	1.08	0.969	0.875	0.787	0.718
0.0608	1.18	1.05	0.958	0.847	0.769
0.0782	1.32	1.17	1.06	0.930	0.840
0.0952	1.51	1.31	1.19	1.03	0.928
0.1144	1.75	1.51	1.36	1.17	1.05
0.1384	2.10	1.79	1.61	1.36	1.21
0.1627	2.58	2.18	1.95	1.62	1.43
0.1935	3.28	2.73	2.41	1.98	1.73
0.2265	4.33	3.53	3.09	2.50	2.16
0.2652	5.89	4.75	4.10	3.28	2.78
0.3128	8.48	6.69	5.71	4.47	3.73
0.3683	13.0	10.0	8.24	6.35	5.23
0.4394	21.2	15.4	12.5	9.46	7.61
0.5257	36.6	26.1	20.6	15.1	11.9
0.6364	70.0	47.8	37.0	26.4	20.2
0.7863	153.0	101.1	74.6	51.4	38.1
0.9060	259.1	170.1	119.8	80.7	58.5
1.0000	396.5	253.9	178.8	118.6	84.2

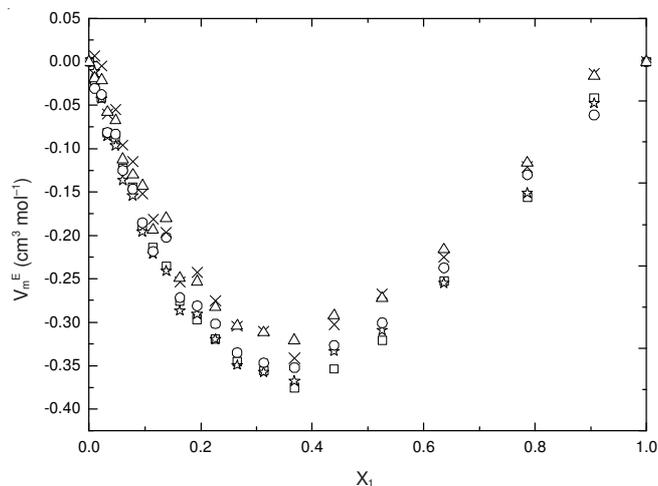


Fig. 2. Excess molar volumes with mole fraction for glycerol (1) + water (2): \square , 298.15 K; \star , 303.15 K; \circ , 308.15 K; \times , 313.15 K; and \triangle , 318.15 K

$$\sigma_{V_m^E} = \left[\frac{\sum (V_{\text{calc}}^E - V_m^E)^2}{(N - m)} \right]^{1/2} \quad (4)$$

where, N shows the total number of experimental points and m shows the number of A_i coefficients considered. The coefficients A_i and corresponding standard deviations (σ) are listed in Table-3.

The experimental values of viscosities of the binary solutions of glycerol + water at (298.15, 303.15, 308.15, 313.15 and 318.15) K are listed in Table-4 (Fig. 3). In all cases, along with the increase of the glycerol concentration that the value of the viscosities increased, at the same time, the viscosities decrease with the increasing temperature.

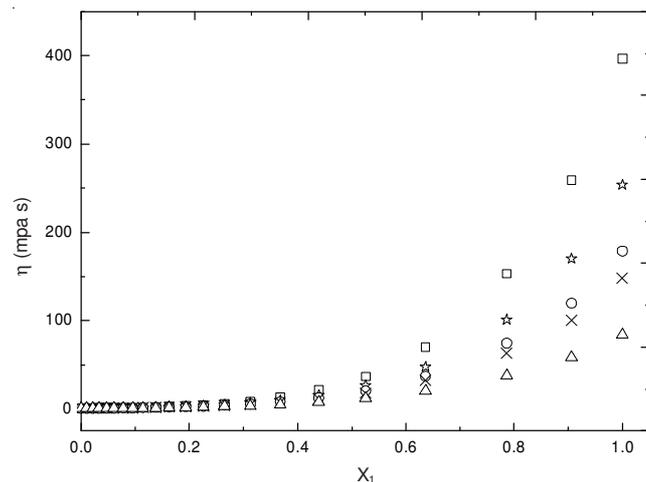


Fig. 3. Experimental viscosities with mole fraction for glycerol (1) + water (2): \square , 298.15 K; \star , 303.15 K; \circ , 308.15 K; \times , 313.15 K; and \triangle , 318.15 K

The experimental values of η for the various mixtures have been used to calculate the viscosity deviation, $\Delta\eta$, which is obtained by the following equation.

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (5)$$

where, η show the viscosity of the mixture; η_1 and η_2 are respectively show the viscosities of pure glycerol and pure water and x_1 and x_2 are the mole fractions of the pure components. The results of the viscosity deviation ($\Delta\eta$) are listed in Table-5 (Fig. 4).

x_1	$\Delta\eta$ /(mPa.s)				
	T (K) = 298.15	T (K) = 303.15	T (K) = 308.15	T (K) = 313.15	T (K) = 318.15
0.0000	0.000	0.000	0.000	0.000	0.000
0.0101	0.026	0.020	0.018	0.021	0.022
0.0220	0.062	0.054	0.056	0.050	0.050
0.0328	0.112	0.096	0.096	0.082	0.079
0.0472	0.179	0.154	0.146	0.125	0.116
0.0608	0.270	0.227	0.222	0.179	0.162
0.0782	0.393	0.332	0.309	0.253	0.225
0.0952	0.557	0.456	0.422	0.340	0.300
0.1144	0.759	0.619	0.567	0.453	0.398
0.1384	1.036	0.845	0.765	0.606	0.526
0.1627	1.42	1.15	1.03	0.809	0.698
0.1935	1.92	1.55	1.36	1.07	0.91
0.2265	2.66	2.10	1.83	1.43	1.20
0.2652	3.66	2.89	2.48	1.92	1.61
0.3128	5.21	4.04	3.42	2.61	2.15
0.3683	7.67	5.81	4.75	3.59	2.92
0.4394	11.4	8.18	6.62	4.93	3.94
0.5257	16.9	12.0	9.43	6.87	5.37
0.6364	25.1	17.1	13.1	9.36	7.12
0.7863	32.5	21.4	15.7	10.8	8.01
0.9060	24.2	15.9	11.2	7.52	5.44
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000

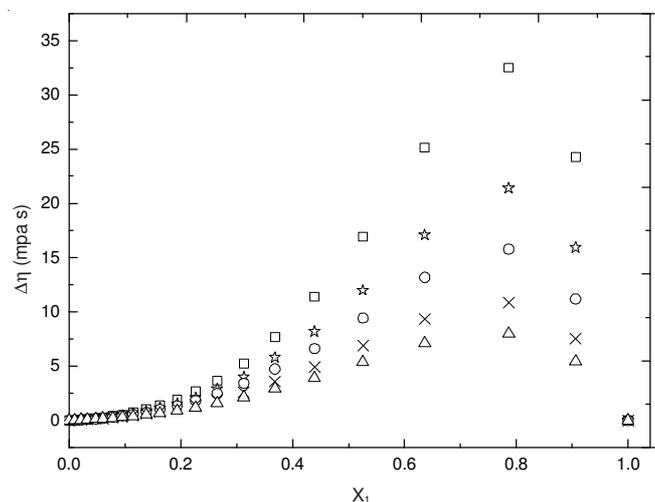


Fig. 4. Viscosity deviations with mole fraction for glycerol (1) + water (2): \square , 298.15 K; \star , 303.15 K; \circ , 308.15 K; \times , 313.15 K; and \triangle , 318.15 K

Fig. 4 shows that the large of the $\Delta\eta$ values are positive over the main composition range for all mixtures in all cases. The $\Delta\eta$ versus x_1 curves shift toward the water-rich region and the observed results are similar to the V_m^E results. The viscosity deviations, $\Delta\eta$, decrease with the increasing temperatures.

The viscosity deviations, $\Delta\eta$, were also displayed by the Redlich-Kister equation as follows:

$$\Delta\eta / \text{mPa.s} = x_1 x_2 \sum_{i=0}^n B_i (2x_1 - 1)^i \quad (6)$$

The coefficients B_i and the standard deviation are presented in Table-6.

T (K)	B_0	B_1	B_2	B_3	B_4	$\sigma / (\text{m}^2\text{s})$
298.15	60.862	138.39	129.24	52.195	1.018	0.0906
303.15	43.296	89.609	77.378	34.513	4.799	0.0488
308.15	34.410	67.595	54.313	16.475	-3.978	0.0407
313.15	25.252	46.362	33.868	9.059	-2.771	0.0285
318.15	19.850	33.926	22.513	5.397	-1.877	0.0225

Conclusion

This paper reports the densities and viscosities of the binary system of aqueous glycerol solutions of the experimental data at $T = (298.15 \text{ to } 318.15) \text{ K}$. These data have been used to compute excess properties of the system. The calculated V_m^E values for the glycerol + water system were negative at each temperatures and compositions, whereas the viscosity deviations ($\Delta\eta$) of the aqueous glycerol solutions were positive at all temperatures and compositions.

REFERENCES

- J.L. Llanos, A.E. Fertitta, E.S. Flores and E.J. Bottani, *J. Phys. Chem. B*, **107**, 8448 (2003).
- S.H. Ren, Y.C. Hou, W.Z. Wu and M.J. Jin, *Ind. Eng. Chem. Res.*, **50**, 998 (2011).
- M. Siddiqi, A. Krissmann, J. Peters-Gerth, M. Luckas and K. Lucas, *J. Chem. Thermodyn.*, **28**, 685 (1996).
- M.H.H. van Dam, A.S. Lamine, D. Roizard, P. Lochon and C. Roizard, *Ind. Eng. Chem. Res.*, **36**, 4628 (1997).
- X. Esteve, A. Conesa and A. Coronas, *J. Chem. Eng. Data*, **48**, 392 (2003).
- C.N. Schubert and W.I. Echter, The Method of Polymer Ethylene Glycol for Removal Pllution from Gases, CN Patent 1364096A (2002).
- J.B. Zhang, P.Y. Zhang, G.H. Chen, F. Han and X.H. Wei, *J. Chem. Eng. Data*, **53**, 1479 (2008).
- J.B. Zhang, G.H. Chen, P.Y. Zhang, F. Han, J.F. Wang and X.H. Wei, *J. Chem. Eng. Data*, **55**, 1446 (2010).
- 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).
- J.B. Zhang, Q. Li, Z.H. Guo, K.X. Li, M.D. Xu, N. Zhang, T. Zhang and X.H. Wei, *Ind. Eng. Chem. Res.*, **50**, 674 (2011).
- J.B. Zhang, F. Han, X.H. Wei, L.K. Shui, H. Gong and P.Y. Zhang, *Ind. Eng. Chem. Res.*, **49**, 2025 (2010).
- J.B. Zhang, P.Y. Zhang, F. Han, G.H. Chen, R.H. Deng and X.H. Wei, *J. Chem. Eng. Data*, **53**, 2372 (2008).
- J.B. Zhang, F. Han, P.Y. Zhang, G.H. Chen and X.H. Wei, *J. Chem. Eng. Data*, **55**, 959 (2010).
- Y.G. Zheng, X.L. Chen and Y.C. Shen, *Chem. Rev.*, **108**, 5253 (2008).
- C.W. Chiu, M.A. Dasari, W.R. Sutterlin and G.J. Suppes, *Ind. Eng. Chem. Res.*, **45**, 791 (2006).
- M.T. Sanz, B. Blanco, S. Beltran and J.L. Cabezas, *J. Chem. Eng. Data*, **46**, 635 (2001).
- C.S. Liu, K.G.H. Desai, X.X. Tang and X.G. Chen, *J. Chem. Eng. Data*, **50**, 2061 (2005).
- M.-C. Hu, W.-J. Zhang, S.-N. Li, Q.-G. Zhai, Y.-C. Jiang, Y. Li, J. Wang, and N. Chen, *J. Chem. Thermodyn.*, **41**, 1016 (2009).
- A.S. Alkindi, Y.M. Al-Wahaibi and A.H. Muggerridge, *J. Chem. Eng. Data*, **53**, 2793 (2008).
- A. Hammadi, *J. Chem. Eng. Data*, **43**, 1004 (1998).
- S. Magazu, F. Migliardo, N.P. Malomuzh and I.V. Blazhnov, *J. Phys. Chem. B*, **111**, 9563 (2007).
- J.B. Secur and E. Helen, *Eng. Ind. Chem.*, **43**, 2117 (1951).
- L.A.J. Verhoeve and E. Lauwers, *J. Chem. Eng. Data*, **14**, 306 (1969).