Densities and excess volumes of aqueous monoethanolamine and diisopropanolamine systems at atmospheric pressure from 303.15 K to 333.15 K

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Abstract−The densities of water+monoethanolamine (MEA), water+diisopropanolamine (DIPA), DIPA+MEA binary systems and water+DIPA+MEA ternary system were measured over the full range of composition at temperatures from 303.15 K to 333.15 K by using an Anton Paar digital vibrating tube density meter (DMA4500). The experimental excess volumes were obtained from the experimental density results and fitted using the Redlich-Kister-Muggianu expression. The parameters obtained from the binary excess volume data were used for the correlation of ternary system with one additional ternary parameter for each isotherm. All investigated binary and ternary systems are completely miscible, because the values of excess volume are negative under the examined conditions.

Keywords: Density, Excess Volume, Monoethanolamine, Diisopropanolamine

INTRODUCTION

Energy production from fossil fuel combustion results in the emission of green gases, the dominant contributor being carbon dioxide. Public awareness has led to a policy of reduction of greenhouse gas emission with the regulations driven by initiatives such as Kyoto protocol [1]. Carbon dioxide capture and storage (CCS) technology contributes to mitigating climate change by reducing industrial CO_2 emissions. Current capture technologies include oxyfuel combustion, pre-combustion using integrated gasification combined cycles, chemical looping combustion or post-combustion capture via flue gas scrubbing [2-5]. Mixture-containing amine absorbents are well known for the removal of acidic gases from natural gas, combustion gases from thermal power station by post combustion capture. Alkanolamines and their mixtures used for CO_2 capture from exhaust gases to avoid the emission of global warming gas have caused an increased interest in amine absorbents due to their high affinity for CO_2 [6]. Densities of amine solutions are necessary to perform various engineering calculations; it is also necessary for the application of activity coefficient models [7,8]. The volumetric properties of aqueous amines and amine solutions are essential for the design and operation of new chemical absorption processes of CO_2.

Although physical properties of amine solutions are rarely available, density data for aqueous monoethanolamine (MEA) solution have previously been reported [9-16]. In the present study, we investigated the density of the binary mixture of water+MEA to assess the reliability of our measurement by comparison with literature data and extension for the ternary mixtures containing MEA. Furthermore, the densities of water+diisopropanolamine (DIPA), DIPA+MEA binary systems and water+MEA+DIPA ternary mixture were measured. The excess volumes were obtained from the experimental density results of the binary systems, and ternary system were fitted by the Redlich-Kister-Muggianu equation [17].

EXPREMENTAL SESSION

1. Materials

The monoethanolamines were obtained from Daejung at 99+% purity by mass, and diisopropanolamines were obtained from Aldrich Chemistry at 98+% purity by mass. The water, obtained from Samchun Chemicals, had a minimum purity of 99.99 mass%. Reagents were used without further purification. During the course of the experiments, the purity of the solvents was monitored by density measurements.

2. Apparatus and Procedure

Binary samples were prepared directly in a glass vial equilibrium cell, using a digital microbalance (Ohaus Co. PAG214) with the accuracy of $\pm 1.0 \times 10^{-4}$ g. Every precaution was taken to minimize contamination by water. The density of pure compounds and mixtures was measured by means of an Anton Paar DMA 4500 vibrating-tube densitometer with the estimated accuracy of ± 0.056 kg m^{-3}.

The following procedure was applied to the preparation and loading of pure components and mixtures into the vibration tube. An empty glass bottle of 20 ml was closed airtight with a septum and then evacuated with a vacuum pump. The empty bottle was weighed and the less volatile component was introduced by a syringe. After the bottle loaded with the first component was weighed, a second component was added similarly, and the bottle was weighed again. All weighing involved using an analytical balance with the accuracy
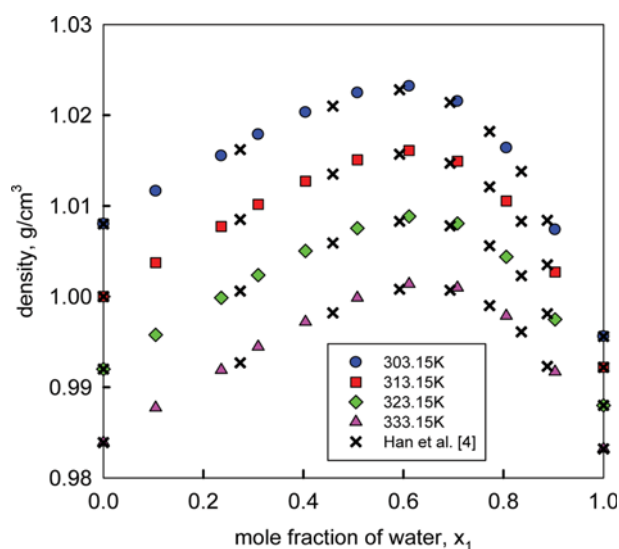
Fig. 1. Comparison of measured densities for water(1)+MEA(2) system with literature data.

Fig. 2. Densities of water(1)+DIPA(2) system.

of 0.0001 g. Therefore, the average uncertainty in mole fraction is estimated to below 0.0001 for the binary systems.

RESULTS AND DISCUSSION

The results of the density measurement of water(1)+MEA(2) binary system from 303.15 K to 333.15 K are shown in Table 1 and Fig. 1. In Fig. 1, the measured density data are compared with literature data [9]. The measured data are in good agreement with literature data for all temperatures and composition regions. The densities have the maximum value near the composition range from x_1=0.5 to 0.7. The densities become lower when the temperature increases for all compositions. The measured density values of water(1)+DIPA(2) system from 303.15 K to 333.15 K are shown in Table 2 and Fig. 2. The densities have the maximum value near the composition range from x_1=0.8 to 0.9. The densities became lower when the temperature is increased for all compositions. The measured densities of DIPA(1)+MEA(2) system are presented in Table 3 and Fig. 3. The density of the mixture decreased with the
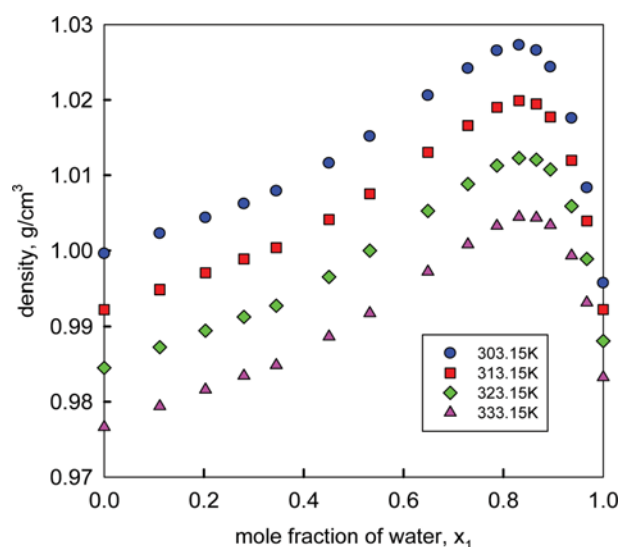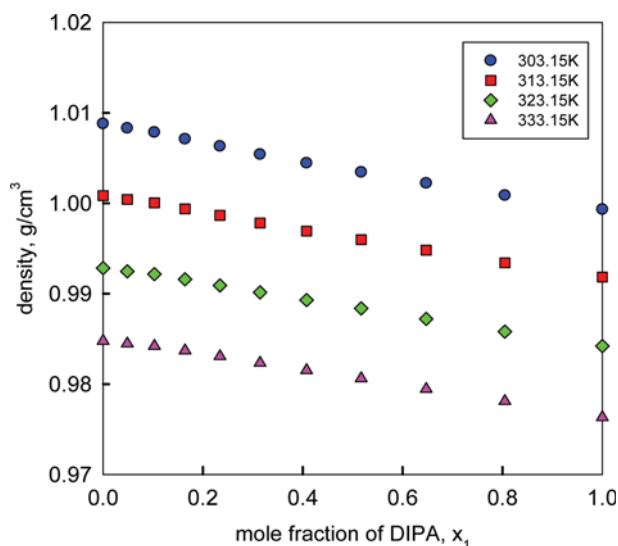

Fig. 3. Densities of DIPA(1)+MEA(2) system.

Table 1. Experimental densities and excess volumes of the water(1)+MEA(2) system

x_1	Density (g/cm³)				Excess volume (cm³/mol)			
	303.15 K	313.15 K	323.15 K	333.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.0000	1.0080	1.0000	0.9920	0.9848	0.0000	0.0000	0.0000	0.0000
0.1046	1.0116	1.0037	0.9958	0.9877	−0.1817	−0.1797	−0.1781	−0.1764
0.2357	1.0155	1.0077	0.9999	0.9919	−0.3922	−0.3875	−0.3842	−0.3817
0.3095	1.0179	1.0102	1.0024	0.9945	−0.4891	−0.4825	−0.4784	−0.4750
0.4042	1.0203	1.0127	1.0050	0.9972	−0.5841	−0.5753	−0.5698	−0.5650
0.5079	1.0225	1.0151	1.0075	0.9999	−0.6400	−0.6294	−0.6222	−0.6163
0.6112	1.0232	1.0161	1.0088	1.0014	−0.6292	−0.6177	−0.6098	−0.6039
0.7079	1.0215	1.0149	1.0081	1.0010	−0.5455	−0.5347	−0.5284	−0.5237
0.8057	1.0164	1.0105	1.0044	0.9979	−0.3876	−0.3807	−0.3783	−0.3759
0.9031	1.0074	1.0027	0.9975	0.9917	−0.1828	−0.1826	−0.1842	−0.1841
1.0000	0.9956	0.9922	0.9880	0.9832	0.0000	0.0000	0.0000	0.0000

Table 2. Experimental densities and excess volumes of water(1)+DIPA(2) system

x_1	Density (g/cm^3)				Excess volume (cm^3/mol)			
	303.15 K	313.15 K	323.15 K	333.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.0000	0.9996	0.9922	0.9845	0.9766	0.0000	0.0000	0.0000	0.0000
0.1114	1.0023	0.9949	0.9872	0.9794	−0.3310	−0.3194	−0.3319	−0.3335
0.2032	1.0044	0.9970	0.9894	0.9816	−0.5278	−0.5256	−0.5360	−0.5360
0.2801	1.0062	0.9989	0.9913	0.9834	−0.6841	−0.6761	−0.6817	−0.6809
0.3450	1.0079	1.0004	0.9928	0.9849	−0.8103	−0.7929	−0.7944	−0.7912
0.4507	1.0116	1.0041	0.9965	0.9887	−0.9980	−0.9691	−0.9636	−0.9511
0.5324	1.0151	1.0075	1.0000	0.9918	−1.1235	−1.0908	−1.0781	−1.0560
0.6489	1.0206	1.0130	1.0053	0.9972	−1.2491	−1.2100	−1.1828	−1.1514
0.7289	1.0242	1.0166	1.0088	1.0008	−1.2555	−1.2096	−1.1737	−1.1413
0.7871	1.0265	1.0190	1.0113	1.0033	−1.1838	−1.1358	−1.0982	−1.0672
0.8314	1.0273	1.0199	1.0123	1.0045	−1.0682	−1.0234	−0.9887	−0.9594
0.8661	1.0266	1.0195	1.0121	1.0043	−0.9327	−0.8945	−0.8649	−0.8373
0.8942	1.0244	1.0177	1.0108	1.0034	−0.7912	−0.7608	−0.7370	−0.7115
0.9365	1.0176	1.0120	1.0059	0.9993	−0.5218	−0.5062	−0.4931	−0.4828
0.9672	1.0083	1.0039	0.9989	0.9932	−0.2853	−0.2799	−0.2743	−0.2611
1.0000	0.9957	0.9923	0.9881	0.9832	0.0000	0.0000	0.0000	0.0000

Table 3. Experimental densities and excess volumes of DIPA(1)+MEA(2) system

x_1	Density (g/cm^3)				Excess volume (cm^3/mol)			
	303.15 K	313.15 K	323.15 K	333.15 K	303.15 K	313.15 K	323.15 K	333.15K K
0.0000	1.0080	1.0008	0.9928	0.9848	0.0000	0.0000	0.0000	0.0000
0.0485	1.0083	1.0004	0.9925	0.9845	−0.0418	−0.0424	−0.0458	−0.0484
0.1029	1.0078	1.0000	0.9922	0.9842	−0.0659	−0.0675	−0.0756	−0.0815
0.1643	1.0071	0.9994	0.9916	0.9837	−0.0949	−0.0986	−0.1112	−0.1208
0.2342	1.0063	0.9987	0.9909	0.9831	−0.1325	−0.1390	−0.1552	−0.1687
0.3145	1.0054	0.9978	0.9901	0.9823	−0.1615	−0.1701	−0.1895	−0.2068
0.4076	1.0044	0.9969	0.9893	0.9815	−0.1567	−0.1656	−0.1881	−0.2087
0.5170	1.0034	0.9960	0.9884	0.9806	−0.1167	−0.1255	−0.1499	−0.1721
0.6472	1.0022	0.9948	0.9872	0.9795	−0.0848	−0.0960	−0.1180	−0.1381
0.8050	1.0009	0.9934	0.9858	0.9781	−0.0365	−0.0455	−0.0631	−0.0766
1.0000	0.9993	0.9918	0.9842	0.9763	0.0000	0.0000	0.0000	0.0000

Table 4. Experimental densities and excess volumes of water(1)+(DIPA(2)+MEA(3)=5 : 5 weight fraction) system

x_1	x_2	Density (g/cm^3)				Excess volume (cm^3/mol)			
		303.15 K	313.15 K	323.15 K	333.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.0000	0.3860	1.0053	0.9977	0.9900	0.9822	−0.1210	−0.1210	−0.1210	−0.1210
0.1256	0.3376	1.0088	1.0013	0.9937	0.9859	−0.3387	−0.3312	−0.3301	−0.3295
0.2291	0.2976	1.0121	1.0046	0.9970	0.9892	−0.5170	−0.5063	−0.5048	−0.5039
0.3145	0.2646	1.0150	1.0076	1.0000	0.9922	−0.6544	−0.6428	−0.6412	−0.6402
0.4235	0.2226	1.0189	1.0115	1.0039	0.9961	−0.8038	−0.7927	−0.7912	−0.7903
0.5099	0.1892	1.0219	1.0145	1.0069	0.9992	−0.8870	−0.8774	−0.8761	−0.8753
0.6022	0.1536	1.0247	1.0173	1.0098	1.0020	−0.9221	−0.9146	−0.9136	−0.9129
0.7068	0.1132	1.0258	1.0186	1.0113	1.0037	−0.8653	−0.8406	−0.8599	−0.8595
0.8064	0.0748	1.0226	1.0162	1.0094	1.0023	−0.6879	−0.6856	−0.6852	−0.6850
0.9067	0.0360	1.0121	1.0071	1.0016	0.9956	−0.3776	−0.3770	−0.3769	−0.3769
1.0000	0.0000	0.9956	0.9922	0.9880	0.9832	0.0000	0.0000	0.0000	0.0000

Fig. 4. Densities of water(1)+(DIPA(2)+MEA(3)=5:5 weight fraction) system.
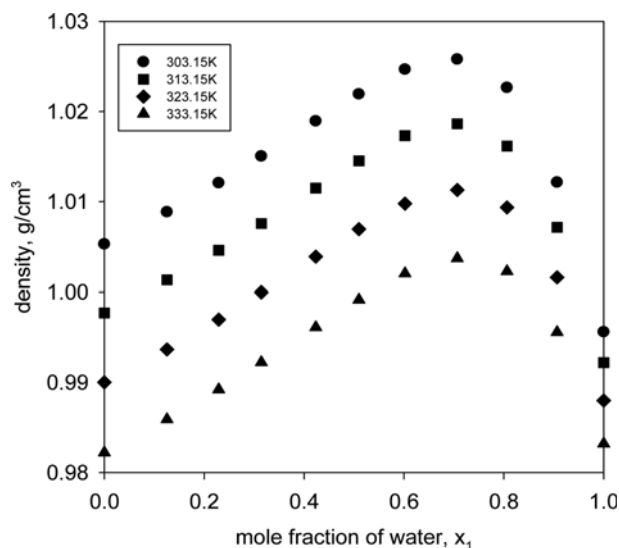
Fig. 6. Excess volumes of water(1)+DIPA(2) system.

increasing mole fraction of DIPA. For the ternary system of water (1)+DIPA(2)+MEA(3), water was mixed with previously prepared equal masses of absorbent mixture (MEA(2)+DIPA(3)=5:5 weight fraction). The measured density of the ternary system is tabulated in Table 4. Several weight fractions of water and absorbent mixture (MEA+DIPA) from 303.15 K to 333.15 K were examined for density measurement. The density had a maximum value near the composition range from x_1=0.4 to 0.7.

The excess molar volumes of the mixtures were calculated from the densities of the pure liquids and their mixtures (see Eq. (1)):

$$V^E = \Sigma_{i=1}^n \frac{x_i M_i}{\rho} - \Sigma_{i=1}^n \frac{x_i M_i}{\rho_i} \qquad (1)$$

where ρ is the density of the mixture and x_i, ρ_i and M_i are the mole fraction, density and molecular weight of pure component i,
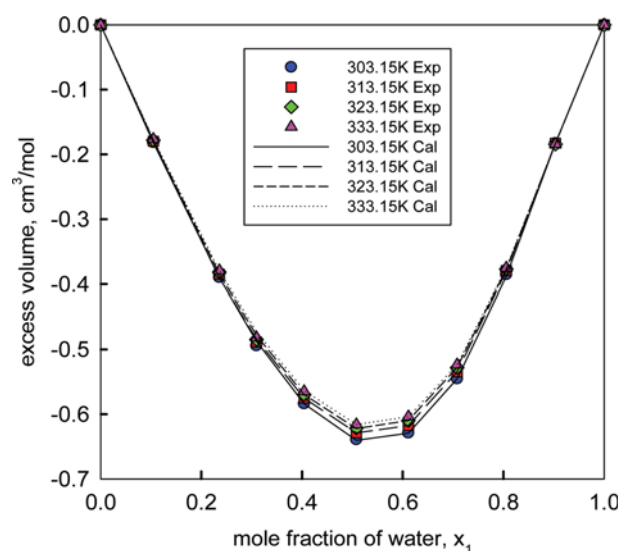
respectively. The excess volumes of water(1)+MEA(2), water(1)+ DIPA(2), DIPA(1) +MEA(2) and water(1) +MEA(2)+DIPA(3) are displayed from Table 1 to Table 4, respectively. The V^E values are negative for the water(1)+MEA(2) (Fig. 5), water(1)+DIPA(2) (Fig. 6), DIPA(1)+MEA(2) (Fig. 7) binary systems and water(1)+MEA(2) +DIPA(3) (Fig. 8) ternary system at the investigated temperature over the whole composition range. As shown in Figs. 5-6, for the aqueous solution of water(1)+MEA(2) and water(1)+DIPA(2), V^E values became more negative when temperature decreased. The minimum values in V^E for water(1)+MEA(2) were observed at around x_1=0.5 and the minimum values in V^E for water(1)+DIPA (2) were observed at around x_1=0.7. In the case of DIPA(1)+MEA(2) of Fig. 7, V^E values became more negative when temperature increased and the minimum values in V^E were observed at around x_1=0.5. The V^E values for water(1)+MEA(2)+DIPA(3) ternary sys-

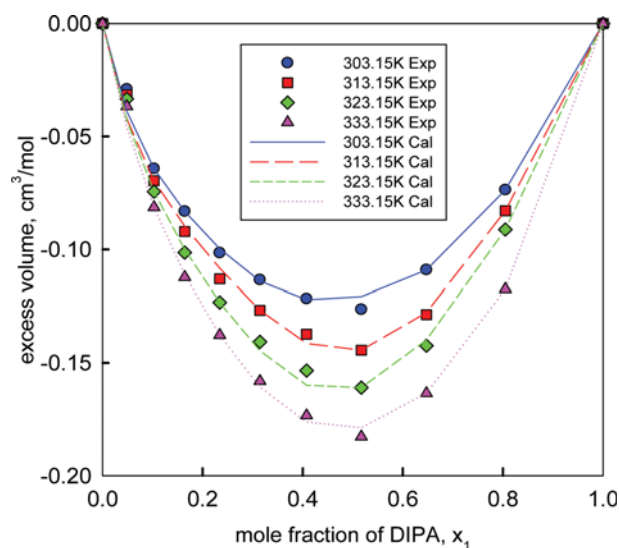Fig. 5. Excess volumes of water(1)+MEA(2) system.

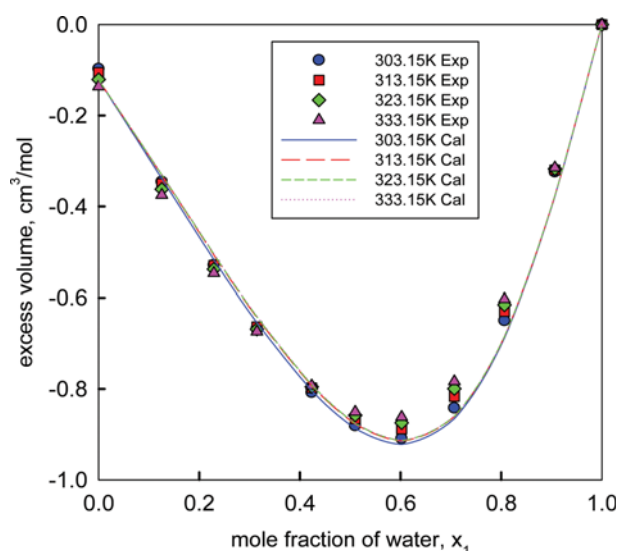Fig. 7. Excess volumes of DIPA(1)+MEA(2) solution at selected temperature.

Fig. 8. Excess volumes of water(1)+(DIPA(2)+MEA(3)=5 : 5 weight fraction) system.

tem of Fig. 8 were observed to have nearly the same value according to the temperature changes and had the minimum value of around $x_1=0.6$.

The Redlich-Kister-Muggianu expression was applied for the description of dependence of the excess volume with mole fraction for binary and ternary systems. In the case of the binary system, the following expression was applied for the excess volume of components 1 and 2 (see Eq. (2)):

$$V^E=x_1x_2[A_0+A_1(x_1-x_2)+A_2(x_1-x_2)^2+A_3(x_1-x_2)^3 \\ +A_4(x_1-x_2)^4+A_5(x_1-x_2)^5] \qquad (2)$$

For the ternary system, the following equation was used (see Eq. (3)):

$$V^E=x_1x_2[A_0+A_1(x_1-x_2)+A_2(x_1-x_2)^2+A_3(x_1-x_2)^3+A_4(x_1-x_2)^4 \\ +A_5(x_1-x_2)^5]+x_2x_3[B_0+B_1(x_2-x_3)+B_2(x_2-x_3)^2+B_3(x_2-x_3)^3 \qquad (3) \\ +B_4(x_2-x_3)^4+B_5(x_2-x_3)^5]+x_1x_3[C_0+C_1(x_1-x_3)+C_2(x_1-x_3)^2$$

Table 6. Redlich-Kister-Muggianu model parameters for water(1)+ (DIPA(2)+MEA(3)=5 : 5 weight fraction) ternary system

	Temp (K)	F_{123}	*SD
Water	303.15	2.9052	0.0244
+	313.15	3.2367	0.0328
(DIPA+MEA	323.15	3.2829	0.0410
=5 : 5 wt fraction)	333.15	3.3107	0.0499

*SD=standard deviation

$$+C_3(x_1-x_3)^3+C_4(x_1-x_3)^4+C_5(x_1-x_3)^5]+x_1x_2x_3f_{123}$$

The parameters A_i, B_i, C_i of Eq. (3) were obtained from binary data fitting shown in Table 5, together with the standard deviation, S_d, calculated as follows (see Eq. (4)):

$$S_d=\left[\frac{\Sigma_i(V_{calc}^E-V_{exp}^E)_i^2}{(N-n)}\right]^{1/2} \qquad (4)$$

where N is the number of experimental data points and n is the number of parameters.

Additional ternary parameters for each temperature in Table 6, f_{123}, were obtained from ternary experimental data.

CONCLUSION

Density values of water+MEA, water+DIPA, DIPA+MEA and water+DIPA+MEA were measured by using a vibrating tube densimeter over the whole range of composition. These systems are completely miscible, because the values of V^E are negative under the examined conditions. The Redlich-Kister-Muggianu expression was used to correlate the excess volume of the binary and ternary systems. In the calculation of excess volume of the ternary system, parameters of the correlation model obtained from the binary system were used with one additional ternary parameter for each isotherm. The new density data can be used as basic data for the design of new carbon dioxide absorption process with new complex absorbents.

Table 5. Redlich-Kister-Muggianu model parameters for binary systems

	Temp. (K)	A_0	A_1	A_2	A_3	A_4	A_5	*SD
Water + MEA	303.15	−2.5538	−0.5864	0.5405	0.7227	0.4607	0.0369	0.0028
	313.15	−2.5077	−0.5648	0.4503	0.9644	0.5278	−0.4245	0.0031
	323.15	−2.4817	−0.5320	0.5015	0.7544	0.3926	−0.2124	0.0031
	333.15	−2.4564	−0.5340	0.4985	0.7188	0.3623	−0.1838	0.0034
Water + DIPA	303.15	−4.3154	−2.9825	−2.5352	−1.8482	0.0551	2.7130	0.0143
	313.15	−4.1692	−2.9654	−2.6387	−0.6450	0.4422	1.0421	0.0141
	323.15	−4.1441	−2.8550	−2.3335	−0.0061	0.0384	0.3524	0.0138
	333.15	−4.0513	−2.6780	−2.3938	0.0704	0.1960	0.1540	0.0127
MEA + DIPA	303.15	−0.4863	0.0866	−0.1490	−0.2571	0.1257	0.7157	0.0154
	313.15	−0.5801	0.0499	0.0992	−0.0905	−0.2433	0.4592	0.0154
	323.15	−0.6483	0.0992	0.1206	−0.0960	−0.2891	0.2805	0.0151
	333.15	−0.7175	0.0539	−0.1057	−0.2087	−0.0809	0.4026	0.0145

*SD=standard deviation

ACKNOWLEDGEMENTS

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