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Excess Molar Enthalpies of *N*,*N*-Dimethylethanolamine with (Methanol, Ethanol, 1-Propanol, and 2-Propanol) at T = (298.2, 313.2, and 328.2) K and p = (0.1 and 10.0) MPa

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A high-pressure flow-mixing isothermal calorimeter was used to determine the excess molar enthalpies of four binary systems for *N*,*N*-dimethylethanolamine + (methanol, ethanol, 1-propanol, and 2-propanol) at T = (298.2, 313.2, and 328.2) K and p = (0.1 and 10.0) MPa. The experimental data were correlated by the Redlich−Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC).

Introduction

The excess thermodynamic properties of solutions are of great fundamental and practical importance. The experimental data of excess enthalpies are particularly important to develop the thermodynamic models and to understand the feature of the structure and interactions of mixed solvents. In continuation of our studies,[1–3] the excess molar enthalpies of four binary systems for *N*,*N*-dimethylethanolamine (DMEA) + (methanol, ethanol, 1-propanol, and 2-propanol) at T = (298.2, 313.2, and 328.2) K and p = (0.1 and 10.0) MPa were determined by a high-pressure flow-mixing isothermal calorimeter in this work. DMEA has been widely applied as an absorbent in the scrubbing of H_2S, CO_2, and SO_2 from gas streams.[4,5] Up to now, very limited data of excess molar enthalpies of mixtures containing DMEA were found in the literature.[6–8] The experimental data were correlated by the Redlich−Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC).

Experimental Section

Materials. *N*,*N*-Dimethylethanolamine (DMEA, 99.0 + mass %) was purchased from Chemical Plant of Zhejiang University (China). DMEA was purified by fractional distillation twice through a 1 m column under reduced pressure and collected the middle fraction. The purity of DMEA is greater than 0.999 mass fraction, determined by gas chromatography. Alcohols (99.85 + mass %, HPLC reagent) were purchased from Tianjin Saifu Technologies Co., Ltd. All chemicals above were dried with the help of molecular Sieves (3 to 4) Å and filtrated by a Millipore filter (0.45 μm).

Apparatus. A commercial isothermal calorimeter (model: 4400 IMC, Calorimeter Science Corporation, USA) with a refrigerating/heating circulator (model: 9501, PolyScience Inc., USA) was used to measure the H^E values. The flow-mixing system is comprised of a sample cell and a reference cell (model: CSC 4442), two syringe pumps (model: 260D, ISCO Inc., USA) with the resolution of 0.1 $\mu L \cdot min^{-1}$, and a back pressure regulator (model: CSC 4448). A high-pressure flow-mixing isothermal calorimeter can be used to measure heat of mixing at temperatures from (−20 to 200) °C and at pressure up to 15 MPa. The IMC data acquisition software was provided by Calorimeter Science Corporation. The uncertainty of composition on a mole fraction basis was 0.0005. The uncertainties of temperature and pressure were 0.1 K and 0.1 KPa, respectively. The uncertainty of the H_m^E value was less than 1.0 %. The experimental procedure and the reliability of the apparatus have been described in detail elsewhere.[3]

Results and Discussion

The excess molar enthalpies of four binary systems for DMEA + (methanol, ethanol, 1-propanol, and 2-propanol) have been measured at T = (298.2, 313.2, and 328.2) K and p = (0.1 and 10.0) MPa in this work. The experimental data were listed in Tables 1 to 4. As a typical example, experimental data from Table 2 were plotted in Figure 1. It can be seen from the figure that the influence of pressure on the excess molar enthalpy is very small, but the influence of temperature on the excess molar enthalpy is more distinct. Figure 2 shows the excess molar enthalpies of DMEA + (methanol, ethanol, 1-propanol, and 2-propanol) at T = 298.2 K and p = 0.1 MPa. The peak values of H_m^E for the systems DMEA + methanol, + ethanol, + 1-propanol, and + 2-propanol are (−910, −410, −255, and 50) $J \cdot mol^{-1}$, respectively. The excess molar enthalpies of two systems DMEA + (ethanol, and + 2-propanol) are in good agreement with the literature data,[8] but the excess molar enthalpies of two systems DMEA + (methanol, and + 2-propanol) have small deviations.

The experimental data of excess molar enthalpies were correlated by the Redlich−Kister equation and three local composition H_m^E models (Wilson, NRTL, and UNIQUAC). Analytical expressions of H_m^E derived from the G^E model were developed through the Gibbs−Helmholtz equation.

Redlich−Kister Equation. The Redlich−Kister expression was commonly used because of its simplicity

$$H_m^E = x_1(1 - x_1)\sum_{i=0}^{n} A_i(1 - 2x_1)^i \tag{1}$$

where x_1 is the mole fraction of DMEA; A_i is the adjustable parameter; and n is the number of fitted parameters. The parameters A_i were obtained by the least-squares fit method, which were listed in Table 5 together with the root-mean-square deviation (σ).

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Table 1. Excess Molar Enthalpies for the System DMEA (1) + Methanol (2)

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
T = 298.2 K, p = 0.10 MPa					
0.0499	−251.8	0.3968	−906.3	0.7506	−532.2
0.0990	−452.8	0.4466	−897.2	0.8007	−438.2
0.1495	−603.0	0.4972	−867.3	0.8477	−343.3
0.1981	−719.2	0.5483	−825.6	0.8977	−236.0
0.2479	−805.7	0.5992	−767.0	0.9512	−113.0
0.2982	−864.8	0.6494	−700.6		
0.3481	−896.1	0.6981	−622.0		
T = 298.2 K, p = 10.00 MPa					
0.0500	−275.7	0.3976	−905.7	0.7452	−540.9
0.0993	−468.7	0.4474	−895.1	0.7948	−450.8
0.1479	−612.6	0.4981	−867.4	0.8481	−342.3
0.1986	−731.0	0.5447	−827.0	0.8980	−235.1
0.2485	−812.6	0.5952	−771.5		
0.2961	−865.4	0.6450	−704.7		
0.3458	−896.2	0.6988	−621.3		
T = 313.2 K, p = 0.10 MPa					
0.0499	−259.4	0.3968	−916.6	0.7506	−544.9
0.0990	−456.5	0.4466	−909.1	0.8007	−445.4
0.1495	−621.3	0.4972	−881.4	0.8477	−347.7
0.1981	−739.7	0.5483	−833.9	0.8977	−236.7
0.2479	−822.7	0.5992	−781.4	0.9512	−117.3
0.2982	−880.5	0.6494	−710.2		
0.3481	−908.6	0.6981	−632.0		
T = 313.2 K, p = 10.00 MPa					
0.0502	−260.9	0.3983	−927.9	0.7458	−558.5
0.0996	−463.3	0.4482	−917.1	0.7953	−463.9
0.1484	−617.7	0.4989	−890.0	0.8485	−354.3
0.1992	−742.4	0.5455	−851.1	0.8983	−241.7
0.2491	−829.1	0.5960	−794.7		
0.2968	−884.0	0.6457	−727.2		
0.3465	−917.6	0.6995	−640.0		
T = 328.2 K, p = 0.10 MPa					
0.1479	−591.9	0.3469	−894.1	0.5465	−822.4
0.1972	−714.2	0.3974	−902.6	0.5963	−765.9
0.2469	−802.6	0.4466	−894.9	0.6473	−699.9
0.2976	−859.9	0.4956	−865.3		
T = 328.2 K, p = 10.00 MPa					
0.1487	−592.7	0.3465	−903.0	0.5455	−839.6
0.1983	−717.2	0.3970	−911.1	0.5979	−782.8
0.2481	−809.9	0.4460	−906.1	0.6457	−720.2
0.2973	−867.9	0.4972	−879.8	0.6973	−642.2

Table 2. Excess Molar Enthalpies for the System DMEA (1) + Ethanol (2)

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
T = 298.2 K, p = 0.10 MPa					
0.0717	−146.6	0.4916	−404.4	0.8157	−203.6
0.1392	−242.1	0.5427	−390.4	0.8553	−168.2
0.2054	−319.3	0.5925	−370.9	0.8911	−129.8
0.2665	−365.7	0.6409	−343.8	0.9281	−85.0
0.3264	−392.4	0.6874	−311.7	0.9663	−37.2
0.3845	−407.8	0.7314	−278.3		
0.4399	−411.4	0.7727	−247.6		
T = 298.2 K, p = 10.00 MPa					
0.0721	−155.3	0.4933	−409.6	0.8118	−211.4
0.1399	−256.5	0.5443	−395.1	0.8511	−171.2
0.2039	−321.0	0.5941	−372.6	0.8917	−127.8
0.2678	−367.2	0.6383	−349.2	0.9285	−84.7
0.3279	−399.6	0.6845	−319.0	0.9665	−37.8
0.3829	−413.4	0.7283	−286.1		
0.4381	−417.3	0.7739	−247.1		
T = 313.2 K, p = 0.10 MPa					
0.0717	−154.3	0.4916	−418.8	0.8108	−214.6
0.1392	−259.9	0.5427	−403.1	0.8553	−168.0
0.2028	−328.8	0.5925	−381.3	0.8911	−129.4
0.2665	−381.2	0.6409	−353.9	0.9281	−87.5
0.3264	−409.4	0.6830	−324.9	0.9663	−41.2
0.3845	−424.6	0.7270	−290.7		
0.4399	−426.4	0.7727	−251.7		
T = 313.2 K, p = 10.00 MPa					
0.0699	−154.6	0.4933	−422.4	0.8118	−216.4
0.1399	−264.9	0.5443	−406.8	0.8511	−175.8
0.2039	−335.7	0.5902	−386.3	0.8917	−130.2
0.2650	−383.8	0.6383	−358.2	0.9285	−88.0
0.3249	−413.8	0.6845	−327.1	0.9665	−41.4
0.3829	−428.3	0.7283	−293.1		
0.4381	−430.5	0.7739	−253.0		
T = 328.2 K, p = 0.10 MPa					
0.2034	−311.3	0.4385	−402.5	0.6393	−334.2
0.2654	−357.2	0.4924	−393.1	0.6848	−304.2
0.3253	−385.1	0.5427	−382.0	0.7296	−271.8
0.3839	−398.6	0.5910	−358.5		
T = 328.2 K, p = 10.00 MPa					
0.2044	−314.8	0.3835	−402.6	0.5421	−380.5
0.2667	−359.9	0.4381	−403.8	0.5926	−359.0
0.3267	−387.6	0.4919	−395.3	0.6383	−332.5

Wilson Model. The model proposed by Wilson[9] is based on the concept of local composition

$$G_m^E/RT = -x_1 \ln(x_1 + \Lambda_{21}x_2) - x_2 \ln(x_2 + \Lambda_{12}x_1) \qquad (2)$$

The expression of excess molar enthalpies of the binary mixture developed through eq 2 is as follows

$$H_m^E = x_1\left(\frac{\Lambda_{21}x_2}{x_1 + \Lambda_{21}x_2}\right)(\lambda_{21} - \lambda_{22}) + x_2\left(\frac{\Lambda_{12}x_1}{x_2 + \Lambda_{12}x_1}\right)(\lambda_{12} - \lambda_{11})$$

$$\Lambda_{12} = \frac{V_{m1}}{V_{m2}} \exp[-(\lambda_{12} - \lambda_{11})/RT], \qquad (3)$$

$$\Lambda_{21} = \frac{V_{m2}}{V_{m1}} \exp[-(\lambda_{21} - \lambda_{22})/RT]$$

in which $V_{m,i}$ is the molar liquid volume of pure component solvent i (see Table S1 in the Supporting Information). λ_{ij} and λ_{ii} are the energies of interaction between the molecules designated in the subscripts. The parameters of the Wilson equation ($\lambda_{ij} - \lambda_{ii}$)and the root-mean-square deviation were listed in Table 6.

NRTL Model. The NRTL (nonrandom two-liquid) equation was given by Renon and Prasunitz,[10] based on Scott's two-liquid theory and on an assumption of nonrandomness similar to that used by Wilson. This equation contains a nonrandomness parameter α which makes it applicable to a large variety of mixtures.

$$G_m^E/RT = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right) \qquad (4)$$

According to the G^E model for the binary system, the formula of excess molar enthalpies is given

$$H_m^E = x_1x_2\left[\frac{G_{21}(g_{21} - g_{11})(x_1 + x_2G_{21} - x_1\tau_{21}\alpha_{12})}{(x_1 + x_2G_{21})^2} + \frac{G_{12}(g_{12} - g_{22})(x_2 + x_1G_{12} - x_2\tau_{12}\alpha_{12})}{(x_2 + x_1G_{12})^2}\right] \qquad (5)$$

$$\tau_{12} = g_{12} - g_{22}/RT, \qquad \tau_{21} = g_{21} - g_{11}/RT$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), \qquad G_{21} = \exp(-\alpha_{12}\tau_{21})$$

where ($g_{21} - g_{11}$) and ($g_{21} - g_{22}$) are the interaction energy parameters and α_{12} is the nonrandomness parameter, obtained by nonlinear least-squares fit. The parameters of the NRTL equation and the root-mean-square deviation were listed in Table 7.

Table 3. Excess Molar Enthalpies for the System DMEA (1) + 1-Propanol (2)

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
T = 298.2 K, p = 0.10 MPa					
0.2007	−191.4	0.3999	−250.8	0.6000	−234.4
0.2509	−213.8	0.4507	−251.9	0.6505	−219.3
0.3008	−230.9	0.4990	−253.7		
0.3505	−243.8	0.5509	−245.0		
T = 298.2 K, p = 10.00 MPa					
0.2001	−191.1	0.3995	−251.7	0.5994	−234.4
0.2503	−213.9	0.4504	−254.7	0.6497	−220.5
0.3004	−231.2	0.5007	−253.0		
0.3502	−243.4	0.5504	−245.4		
T = 313.2 K, p = 0.10 MPa					
0.2984	−251.2	0.5004	−277.1	0.6986	−216.7
0.3505	−266.9	0.5488	−268.6	0.7488	−190.4
0.4012	−276.2	0.5985	−256.5	0.8005	−157.8
0.4501	−279.4	0.6497	−238.9	0.8495	−124.4
T = 313.2 K, p = 10.00 MPa					
0.2492	−231.3	0.4986	−280.2	0.7501	−189.4
0.2998	−255.5	0.5504	−271.8	0.8015	−156.7
0.3489	−270.1	0.6001	−258.4	0.8503	−122.8
0.3995	−279.2	0.6512	−239.6		
0.4484	−282.0	0.7000	−216.6		
T = 328.2 K, p = 0.10 MPa					
0.2007	−264.4	0.3999	−333.0	0.6000	−295.7
0.2509	−291.2	0.4507	−333.3	0.6505	−272.1
0.3008	−312.9	0.4990	−326.9	0.7001	−244.8
0.3505	−326.9	0.5509	−313.3		
T = 328.2 K, p = 10.00 MPa					
0.2001	−263.6	0.3995	−338.2	0.5994	−302.2
0.2503	−293.2	0.4504	−339.3	0.6497	−279.2
0.3004	−316.7	0.5007	−331.8		
0.3502	−330.6	0.5504	−319.5		

Table 4. Excess Molar Enthalpies for the System DMEA (1) + 2-Propanol (2)

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
T = 298.2 K, p = 0.10 MPa					
0.1008	16.2	0.3005	46.7	0.5010	42.0
0.1502	27.9	0.3504	48.0	0.5505	37.3
0.1994	37.2	0.3999	47.6	0.5993	32.8
0.2501	43.3	0.4507	45.4		
T = 298.2 K, p = 10.00 MPa					
0.0998	13.6	0.3500	44.7	0.5501	37.2
0.2005	34.5	0.3995	44.6	0.6009	33.0
0.2496	40.1	0.4504	43.1		
0.3000	43.3	0.5006	40.6		
T = 313.2 K, p = 0.10 MPa					
0.0496	−16.9	0.2501	−2.7	0.4507	3.0
0.1008	−17.3	0.3005	0.9	0.5010	2.0
0.1502	−12.7	0.3504	2.9	0.5505	−0.5
0.1994	−7.0	0.3999	3.4	0.5993	−1.2
T = 313.2 K, p = 10.00 MPa					
0.0499	−18.4	0.2496	−5.6	0.4504	−0.4
0.0998	−19.4	0.3000	−2.5	0.5006	−1.3
0.1494	−19.1	0.3500	−0.7	0.5501	−2.6
0.2005	−9.9	0.3995	−0.1		
T = 328.2 K, p = 0.10 MPa					
0.0499	−35.9	0.3018	−55.3	0.5522	−48.1
0.1014	−51.1	0.3519	−54.3	0.6009	−45.8
0.1511	−56.6	0.4015	−53.3	0.6508	−42.9
0.2005	−57.4	0.4524	−51.8		
0.2513	−56.6	0.5026	−50.1		
T = 328.2 K, p = 10.00 MPa					
0.0499	−39.2	0.3000	−58.3	0.5006	−51.3
0.0998	−53.9	0.3500	−56.6	0.5501	−49.2
0.2005	−60.7	0.3995	−55.0	0.6009	−46.6
0.2496	−59.8	0.4504	−53.2	0.6508	−45.7

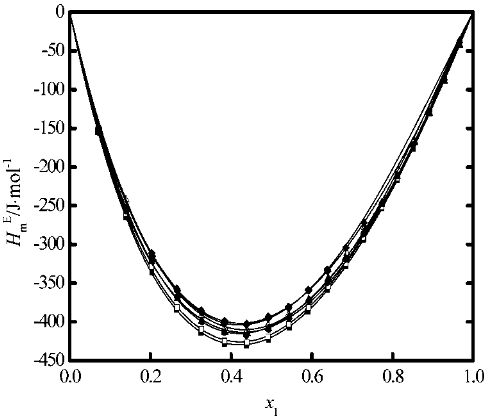

Figure 1. Excess molar enthalpies for the system DMEA (1) + ethanol (2) as a function of mole fraction x_1. △, 298.2 K, 0.1 MPa; ▲, 298.2 K, 10.0 MPa; □, 313.2 K, 0.1 MPa; ■, 313.2 K, 10.0 MPa; ◇, 328.2 K, 0.1 MPa; ◆, 328.2 K, 10.0 MPa. The curves were calculated by the Redlich−Kister equation (parameters taken from Table 5).

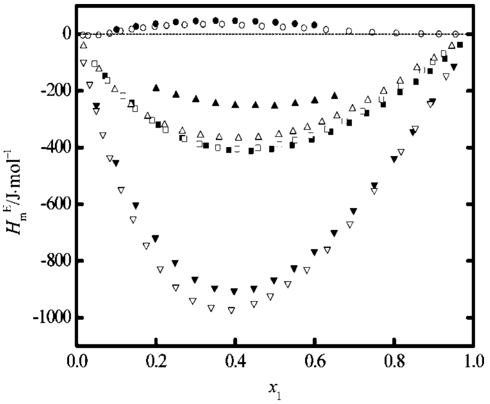

Figure 2. Excess molar enthalpies for the system DMEA (1) + alkanols (2) as a function of mole fraction x_1. At 298.2 K, 0.1 MPa, methanol: ▼ in this work; ▽, ref 8. Ethanol: ■, in this work; □, ref 8. 1-Propanol: ▲, in this work; △, ref 8. 2-Propanol: ●, in this work; ○, ref 8.

UNIQUAC Model. The universal quasi-chemical (UNIQUAC) equation uses only two adjustable parameters for each binary system. This equation gives good representation of both vapor−liquid and liquid−liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolyte components.[11]

$$G_m^E = G_{\text{com.}}^E + G_{\text{res.}}^E$$

$$\begin{aligned} G_{\text{com.}}^E/RT &= x_1 \ln\frac{\varphi_1}{x_1} + \\ &\quad x_2 \ln\frac{\varphi_2}{x_2} + \frac{z}{2}\left(q_1 x_1 \ln\frac{\theta_1}{\varphi_1} + q_2 x_2 \ln\frac{\theta_2}{\varphi_2}\right) \\ G_{\text{res.}}^E/RT &= -q_1 x_1 \ln(\theta_1 + \theta_2\tau_{21}) - \\ &\quad q_2 x_2 \ln(\theta_2 + \theta_1\tau_{12}) \end{aligned} \tag{6}$$

The equation of excess molar enthalpies of the binary mixture is developed through the G^E model

$$\begin{gathered} H_m^E = q_1 x_1\left(\frac{\theta_2}{\theta_1 + \theta_2\tau_{21}}\right)\tau_{21}\Delta u_{21} + q_2 x_2\left(\frac{\theta_1}{\theta_2 + \theta_1\tau_{12}}\right)\tau_{12}\Delta u_{12} \\ \tau_{21} = \exp(-\Delta u_{21}/RT), \quad \tau_{12} = \exp(-\Delta u_{12}/RT) \\ \theta_1 = x_1 q_1/(x_1 q_1 + x_2 q_2), \quad \theta_2 = x_2 q_2/(x_1 q_1 + x_2 q_2) \end{gathered} \tag{7}$$

in which q_i is a pure component structural parameter.[12] Δu_{12} and Δu_{21} are the interaction energy parameters, which were

Table 5. Parameters of the Redlich−Kister Equation 1 and Standard Deviations

	A_0/J·mol^{-1}	A_1/J·mol^{-1}	A_2/J·mol^{-1}	A_3/J·mol^{-1}	σ^a/J·mol^{-1}
		DMEA + methanol			
298.2 K, 0.10 MPa	−3459.1	1408.1	−516.14	229.04	2.26
298.2 K, 10.0 MPa	−3434.1	1314.9	−736.26	652.57	6.39
313.2 K, 0.10 MPa	−3508.7	1454.0	−573.92	221.16	1.84
313.2 K, 10.0 MPa	−3551.6	1418.1	−550.59	252.98	1.33
328.2 K, 0.10 MPa	−3449.4	1474.4	−523.95	−135.91	1.04
328.2 K, 10.0 MPa	−3508.2	1419.4	−536.88	−238.22	1.39
		DMEA + ethanol			
298.2 K, 0.10 MPa	−1612.6	405.11	−146.78	200.71	2.65
298.2 K, 10.0 MPa	−1624.5	405.71	−213.49	288.13	2.24
313.2 K, 0.10 MPa	−1663.4	489.7	−194.64	136.72	0.92
313.2 K, 10.0 MPa	−1678.2	491.25	−220.38	162.14	0.89
328.2 K, 0.10 MPa	−1569.9	468.73	−147.06	100.41	0.93
328.2 K, 10.0 MPa	−1576.1	496.04	−72.717	189.94	0.56
		DMEA + 1-propanol			
298.2 K, 0.10 MPa	−1007.3	149.1	−92.213	287.92	0.85
298.2 K, 10.0 MPa	−1009.6	152.98	−95.765	258.56	0.69
313.2 K, 0.10 MPa	−1107.1	206.39	−41.821	33.614	0.30
313.2 K, 10.0 MPa	−1119.7	221.14	−17.332	26.608	0.36
328.2 K, 0.10 MPa	−1304.4	359.8	−142.39	327.41	0.96
328.2 K, 10.0 MPa	−1329.5	355.04	−102.23	297.18	0.71
		DMEA + 2-propanol			
298.2 K, 0.10 MPa	164.05	−165.43	134.79	389.67	0.72
298.2 K, 10.0 MPa	158.13	−133.16	164.71	421.16	2.07
313.2 K, 0.10 MPa	−2.9199	−63.387	307.83	886.45	1.62
313.2 K, 10.0 MPa	−10.388	4.1330	432.32	979.1	1.23
328.2 K, 0.10 MPa	−208.52	14.276	60.152	778.86	1.73
328.2 K, 10.0 MPa	−213.20	9.6331	12.613	811.39	2.16

[a] $\sigma = [\Sigma(H^{E}_{\text{calcd}} - H^{E}_{\text{exptl}})^2/n\ ]^{1/2}$, n is the number of data for each data set.

Table 6. Parameters Used in Equation 3 for Calculating Excess Enthalpies

	Wilson		
	$(\lambda_{12} - \lambda_{11})$/J·mol^{-1}	$(\lambda_{21} - \lambda_{22})$/J·mol^{-1}	σ^a/J·mol^{-1}
	DMEA + Methanol		
0.10 MPa	−1179.77	−1764.30	13.4
10.0 MPa	−1186.99	−1779.58	15.1
	DMEA + Ethanol		
0.10 MPa	−731.58	−694.17	7.0
10.0 MPa	−745.46	−690.59	7.7
	DMEA + 1-Propanol		
0.10 MPa	−728.33	−238.96	26.1
10.0 MPa	−738.54	−229.15	27.5
	DMEA + 2-Propanol		
0.10 MPa	223.28	−294.86	31.1
10.0 MPa	286.20	−371.00	31.4

[a] $\sigma = [\Sigma(H^{E}_{\text{calcd}} - H^{E}_{\text{exptl}})^2/n\ ]^{1/2}$, n is the number of data for each data set.

Table 7. Parameters Used in Equation 5 for Calculating Excess Enthalpies

	NRTL			
	$(g_{12} - g_{11})$/J·mol^{-1}	$(g_{21} - g_{22})$/J·mol^{-1}	α_{12}	σ^a/J·mol^{-1}
	DMEA + Methanol			
0.10 MPa	−2362.98	−48.37	0.51	10.4
10.0 MPa	−2233.78	−207.16	0.57	12.7
	DMEA + Ethanol			
0.10 MPa	−918.34	−271.31	1.24	7.0
10.0 MPa	−847.01	−317.97	1.53	7.4
	DMEA + 1-Propanol			
0.10 MPa	−930.24	−11.22	0.63	26.9
10.0 MPa	−1035.05	94.72	0.53	28.2
	DMEA + 2-Propanol			
0.10 MPa	−397.79	63.41	−4.79	31.4
10.0 MPa	−341.15	198.73	−1.67	31.0

[a] $\sigma = [\Sigma(H^{E}_{\text{calcd}} - H^{E}_{\text{exptl}})^2/n\ ]^{1/2}$, n is the number of data for each data set.

Table 8. Parameters Used in Equation 7 for Calculating Excess Enthalpies

	UNIQUAC		
	Δu_{21}/J·mol^{-1}	Δu_{12}/J·mol^{-1}	σ*/J·mol^{-1}
	DMEA + Methanol		
0.10 MPa	−759.44	−728.37	8.4
10.0 MPa	−767.27	−731.98	10.8
	DMEA + Ethanol		
0.10 MPa	−229.04	−382.85	7.1
10.0 MPa	−222.29	−395.93	8.1
	DMEA + 1-Propanol		
0.10 MPa	−33.75	−342.87	25.7
10.0 MPa	−30.7	−348.18	27.1
	DMEA + 2-Propanol		
0.10 MPa	−2.49	−6.88	31.0
10.0 MPa	−2.72	−10.03	31.2

[a] $\sigma = [\Sigma(H^{E}_{\text{calcd}} - H^{E}_{\text{exptl}})^2/n\ ]^{1/2}$, n is the number of data for each data set.

obtained by nonlinear least-squares fit and given in Table 8 together with root-mean-square deviation.

As can be seen from the calculated results, good agreement between experimental and calculated values is achieved for the binary systems studied in this work. The best fitting results have been obtained with the Redlich−Kister approach. However, the Redlich−Kister approach has too many parameters, comparing the other three approaches (Wilson, NRTL, and UNIQUAC). The explanation of the experimental results is thought to be molecular interactions in solutions. Negative molar excess enthalpies indicate an exothermic mixing process between DMEA and *n*-alkanol molecules. The exothermic mixing is due to the strong interaction between the −OH group in *n*-alkanols with the amine ($-N(CH_3)_2$) group of DMEA. From Figure 2, the negative values of excess enthalpies decrease with the increase of molecular size of *n*-alkahols, and this may be closely owing to the increasing difficulty to form crossed associations between DMEA and alcohols with increasing steric hindrance when the aliphatic chain of *n*-alkanol was increased.[13] Table 4 gives the molar fraction dependence of molar excess enthalpies for the system DMEA + 2-propanol. At 298.2 K, the values of molar excess enthalpy are slightly positive with a minimum at around $x_1 = 0.35$. But at (313.2 and 328.2) K, the values of molar excess enthalpy are small negative with a minimum at around $x_1 = 0.38$. It means that the increase of temperature is propitious to the crossed associations between the $-$OH group in 2-propanol with the amine ($-N(CH_3)_2$) group of DMEA.

Supporting Information Available:

Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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