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Measurement and Correlation of Excess Molar Enthalpies for Ethylene Glycol + Alkanol Systems at the Temperatures (298.15, 308.15, and 323.15) K

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Excess molar enthalpies for a series of ethylene glycol + alkanol (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol) systems were measured over the entire molar composition range at (298.15, 308.15, and 323.15) K under atmospheric pressure using a flow-type isothermal microcalorimeter. The values of H^E increase slightly with increasing temperature for all of the ethylene glycol + *n*-alkanol (methanol, ethanol, 1-propanol, and 1-butanol) systems over the entire composition range. In addition, a dependence of H^E on the chain length of the *n*-alkanol was observed. However, the same temperature dependency as in the ethylene glycol + *n*-alkanol systems was not observed for ethylene glycol + 2-alkanol (2-propanol and 2-butanol) systems. The experimental results were compared with values correlated using the Redlich−Kister equation.

Introduction

The excess molar enthalpy (H^E) is an important property for the evaluation and prediction of phase equilibrium. Industrially, its role is of the basic physical properties for energy calculation. For these purposes, an advanced measurement technique is useful for determining H^E values. So far, we have measured H^E for binary systems containing supercritical carbon dioxide using a flow microcalorimeter.[1−5] This calorimeter is also useful for determining the excess enthalpies at low pressures.

In this study, we focus our attention on the systems with different viscosities between the two components, specifically ethylene glycol + alkanol (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol). The H^E values of the ethylene glycol + *n*-alkanol systems have been measured by Kracht et al.[6] and Jimenez et al.[7] They have used the H^E values to study the parameter optimization of different group contribution methods.[8−10] However, the literature data do not contain a sufficient number of H^E values to consider the temperature dependency of H^E in a system containing a viscous component. Therefore, we measured H^E for systems composed of ethylene glycol and an alkanol (methanol, ethanol, and propanol) over the entire composition range between (298.15 and 323.15 K) at atmospheric pressure. The experimental data were also compared with calculated values from the Redlich−Kister equation.[11]

Experimental Section

Apparatus and Procedure. The flow isothermal microcalorimeter (Calorimetry Sciences Corporation model 4400) was used for the measurement of H^E. It consists of a mixing unit, a constant temperature water bath, two high-pressure ISCO syringe pumps for sample supply, a cooling circulation system for the syringe, a degassing unit, and a personal computer for data processing. Measurement is possible from (273 to 353) K and from (0.1 to 20) MPa. Details of the experimental apparatus and procedure have been described elsewhere.[2,3] In this study, a modified model of the mixing cell was used. The improved mixing cell uses both a mixing wire and concentric tubes to enhance mixing of difficult systems. The degassing of liquids was carried out by combining a vacuum line and an ultrasonic wave unit. The water bath temperature was kept constant within ±0.0005 K. In the present study, the reproducibility of our measurements can be estimated to be within ±1.0% (maximum absolute accuracy is 4 J·mol^{-1}), the uncertainty being due primarily to the high sensitivity of H^E values to small changes in temperature. Additionally, the large difference in viscosity of the pure substances required a calibration of the optimal total flow rate of the pump for our measurements. This calibration resulted in the use of a total flow rate of (0.05 to 0.10) cm^3·min^{-1} for all cases studied.

For our measurements, each pure component was charged into the ISCO syringe after degassing. The syringes and their contents were kept in a water thermostat. The pure components were then delivered to the mixing cell. Pumping rates of the liquids were calibrated by weighing the liquids delivered as a function of time.

Prior to this study, the apparatus was checked with the systems hexane + cyclohexane at 298.15 K and methanol + water at (298.15 and 323.15) K. The pre-experimental results of H^E for hexane + cyclohexane and methanol + water systems are compared with literature values in Figures 1 and 2, respectively. For hexane + cyclohexane at 298.15 K, the values calculated from the equation of Marsh and Stokes[12] are also shown for the sake of comparison. As can be seen from these figures, the H^E values measured by this apparatus are well in agreement with the literature values.

Materials. The methanol, ethanol, propanol, butanol, and ethylene glycol used in this study were special grade pure reagents (Wako Pure Chemical Industry, Ltd., Japan) and were used after removing trace water with molecular

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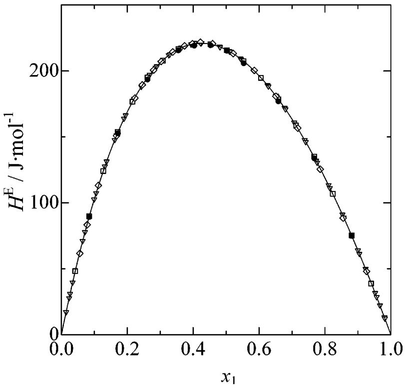

Figure 1. Comparison of excess molar enthalpies for hexane (1) + cyclohexane (2) with the literature at 298.15 K: (▽) Marsh and Stokes;[12] (□) Christensen et al.;[13] (◇) Raal and Webley;[14] (●) this work; (—) calculated values of H^E from the expression of Marsh and Stokes.

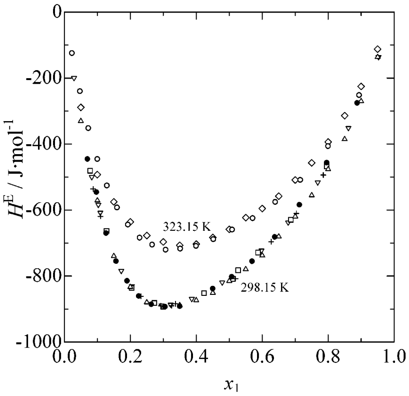

Figure 2. Comparison of excess molar enthalpies for methanol (1) + water (2) with the literature at 298.15 and 323.15 K: (+) Fenby and Chand;[15] (□) Abello;[16] (▽) Benjamin and Benson;[17] (◇) Friese et al.;[18] (●, ○) this work.

Table 1. Densities ρ and Viscosities η at 298.15 K, and Normal Boiling Points T_b of the Pure Components

	$10^{-3}\rho$/kg·m^{-3}		$10^3\eta$/Pa·s	T_b/K	
component	exptl	lit.	lit.	exptl	lit.
ethylene glycol	1.110	1.1100[a]	15.312[c]	470.38	470.69[a]
methanol	0.7864	0.78637[a]	0.5513[a]	337.62	337.696[a]
ethanol	0.7852	0.78509[b]	1.0826[a]	351.41	351.443[a]
1-propanol	0.7998	0.79975[b]	1.9430[a]	370.31	370.301[a]
2-propanol	0.7811	0.78126[a]	2.0436[a]	355.35	355.392[a]
1-butanol	0.8059	0.80575[a]	2.5710[a]	390.86	390.875[a]
2-butanol	0.8024	0.80241[a]	2.998[a]	372.68	372.662[a]

[a] Reference 19. [b] Reference 20. [c] Reference 21.

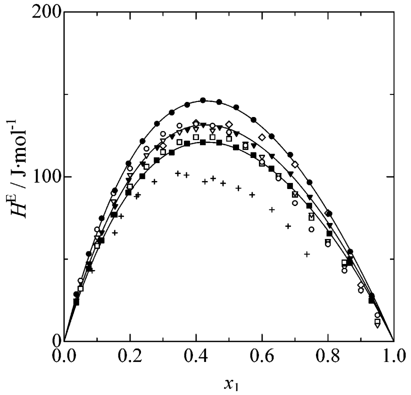

Figure 3. Experimental excess molar enthalpies for ethylene glycol (1) + methanol (2). This work: (■) 298.15 K; (▼) 308.15 K; (●) 323.15 K. Kracht et al.:[8] (□) 298.15 K; (▽) 308.15 K; (○) 323.15 K. Jimenez et al.:[7] (+) 298.15 K. Cratin and Gradden:[22] (◇) 298.15 K. (—) Calculated values from eqs 1 and 2.

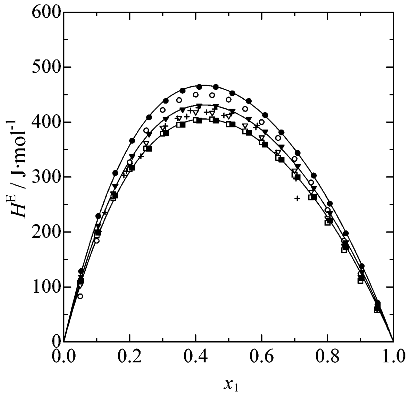

Figure 4. Experimental excess molar enthalpies for ethylene glycol (1) + ethanol (2). This work: (■) 298.15 K; (▼) 308.15 K; (●) 323.15 K. Kracht et al.:[8] (□) 298.15 K; (▽) 308.15 K; (○) 323.15 K. Jimenez et al.:[7] (+) 298.15 K. (—) Calculated values from eqs 1 and 2.

sieves. The purity of all substances was checked by gas chromatography and found to be better than 99.9 mol %. Liquid densities and normal boiling points of pure components were measured, and viscosities of pure components were taken from the literature. The properties of materials are listed in Table 1.

Results and Discussion

The measured excess molar enthalpies for six binary systems containing ethylene glycol (ethylene glycol + methanol, + ethanol, + 1-propanol, + 2-propanol, + 1-butanol, and + 2-butanol) are listed in Table 2 and shown in Figures 3−8.

***Ethylene Glycol* + *Methanol*.** The experimental excess molar enthalpies for this system are compared with values reported by Kracht et al.,[6] Jimenez et al.,[7] and Cratin and Gradden[22] in Figure 3. As can be seen from the figure, the discrepancy between our data and the literature values increases with increasing ethylene glycol composition. This tendency reflects the difference in the temperature dependency of H^E in the ethylene glycol rich region. It is supposed that these discrepancies depend on the effects of mixing the liquids in the high viscosity region.

***Ethylene Glycol* + *Ethanol*.** The experimental values of H^E for this system are compared with the literature values[6,7] in Figure 4. For this system, the discrepancy between our data and the literature values is also observed, but not to the same degree as that for the ethylene glycol + methanol system.

***Ethylene Glycol* + *1-Propanol*.** The literature data[7] for this system at 298.15 K are shown in Figure 5 with our results. As can be seen from the figure, the discrepancy between our data and the literature values is too large to compare them to each other.

***Ethylene Glycol* + *2-Propanol*.** The experimental results of H^E for this system are shown in Figure 6. The temperature dependency of the H^E values for this system is different from that for the ethylene glycol + 1-propanol system. The H^E values for the 2-propanol system decrease slightly with increasing temperature.

***Ethylene Glycol* + *1-Butanol*.** The literature data[7] for this system at 298.15 K are shown in Figure 7 with our results. Again, the discrepancy between our data and the literature values is very large.

Table 2. Experimental Excess Molar Enthalpies H^E for the Binary Systems with Ethylene Glycol at Different Temperatures

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
Ethylene Glycol (1) + Methanol (2) at 298.15 K						Ethylene Glycol (1) + Ethanol (2) at 298.15 K					
0.0370	23.59	0.3262	114.73	0.6851	94.39	0.0526	111.48	0.4109	402.55	0.7581	263.67
0.0748	44.20	0.3726	120.06	0.7436	82.38	0.1045	198.73	0.4611	402.66	0.8069	220.90
0.1137	61.32	0.4206	120.87	0.8042	65.53	0.1561	266.30	0.5112	395.57	0.8554	172.39
0.1538	77.07	0.4701	120.71	0.8670	47.72	0.2075	317.12	0.5610	380.72	0.9037	116.01
0.1950	90.30	0.5212	117.85	0.9321	24.74	0.2587	351.41	0.6106	358.98	0.9518	61.53
0.2374	100.27	0.5740	113.05			0.3096	379.42	0.6600	331.99		
0.2811	110.03	0.6286	104.86			0.3604	395.46	0.7092	299.66		
Ethylene Glycol (1) + Methanol (2) at 308.15 K						Ethylene Glycol (1) + Ethanol (2) at 308.15 K					
0.0372	24.87	0.3274	124.55	0.6863	101.86	0.0526	118.54	0.4109	430.09	0.7581	280.22
0.0752	47.30	0.3739	128.54	0.7447	87.74	0.1045	211.70	0.4611	429.57	0.8069	234.96
0.1143	66.19	0.4219	131.58	0.8051	70.61	0.1561	283.66	0.5112	420.64	0.8554	180.95
0.1545	82.08	0.4715	130.00	0.8676	50.43	0.2075	337.85	0.5610	406.24	0.9037	127.53
0.1958	98.06	0.5226	126.26	0.9325	26.44	0.2587	378.22	0.6106	382.75	0.9518	65.08
0.2384	108.06	0.5754	119.09			0.3096	406.15	0.6600	355.50		
0.2822	117.82	0.6299	112.68			0.3604	422.80	0.7092	320.07		
Ethylene Glycol (1) + Methanol (2) at 323.15 K						Ethylene Glycol (1) + Ethanol (2) at 323.15 K					
0.0371	28.72	0.3266	138.94	0.6856	113.34	0.0526	128.62	0.4109	464.20	0.7581	302.72
0.0750	53.17	0.3732	143.63	0.7441	96.57	0.1045	228.89	0.4611	463.86	0.8069	251.59
0.1140	74.76	0.4211	146.40	0.8046	77.55	0.1561	307.15	0.5112	452.44	0.8554	197.48
0.1540	91.62	0.4706	144.13	0.8673	54.55	0.2075	366.00	0.5610	438.38	0.9037	137.78
0.1953	108.08	0.5218	142.15	0.9323	27.95	0.2587	408.55	0.6106	412.60	0.9518	70.90
0.2378	121.57	0.5746	134.53			0.3096	438.54	0.6600	381.32		
0.2815	132.21	0.6292	124.52			0.3604	457.19	0.7092	343.92		
Ethylene Glycol (1) + 1-Propanol (2) at 298.15 K						Ethylene Glycol (1) + 2-Propanol (2) at 298.15 K					
0.0664	208.45	0.4718	613.42	0.8005	375.27	0.0678	217.83	0.4776	601.07	0.8042	341.05
0.1300	355.33	0.5229	604.22	0.8425	310.13	0.1326	366.60	0.5287	585.30	0.8455	283.45
0.1915	455.90	0.5725	577.03	0.8834	243.26	0.1951	469.05	0.5782	561.91	0.8857	218.84
0.2511	528.06	0.6207	553.53	0.9232	167.51	0.2555	535.06	0.6262	530.81	0.9248	150.76
0.3089	572.82	0.6676	517.24	0.9619	87.45	0.3138	578.22	0.6727	493.08	0.9628	77.34
0.3648	602.44	0.7131	477.12			0.3702	600.33	0.7178	446.27		
0.4191	613.98	0.7574	426.18			0.4248	607.69	0.7617	397.86		
Ethylene Glycol (1) + 1-Propanol (2) at 308.15 K						Ethylene Glycol (1) + 2-Propanol (2) at 308.15 K					
0.0664	223.68	0.4718	654.34	0.8005	394.24	0.0675	211.69	0.4783	602.57	0.8049	346.59
0.1300	381.56	0.5229	641.45	0.8425	328.12	0.1325	365.60	0.5294	588.01	0.8462	285.19
0.1915	489.29	0.5725	619.53	0.8834	255.66	0.1953	466.94	0.5890	563.82	0.8863	220.66
0.2511	564.92	0.6207	588.71	0.9232	178.03	0.2558	535.01	0.6270	533.16	0.9252	153.09
0.3089	613.15	0.6676	551.13	0.9619	91.21	0.3143	576.60	0.6735	495.54	0.9631	78.51
0.3648	636.46	0.7131	506.68			0.3708	600.71	0.7186	449.36		
0.4191	648.53	0.7574	453.98			0.4254	607.27	0.7624	401.09		
Ethylene Glycol (1) + 1-Propanol (2) at 323.15 K						Ethylene Glycol (1) + 2-Propanol (2) at 323.15 K					
0.0644	236.73	0.4718	697.70	0.8005	421.15	0.0678	196.20	0.4775	583.76	0.8042	341.23
0.1300	404.32	0.5229	682.32	0.8425	350.71	0.1326	340.85	0.5286	570.75	0.8456	281.66
0.1915	524.70	0.5725	660.49	0.8833	272.39	0.1951	437.98	0.5781	549.29	0.8858	218.48
0.2511	600.98	0.6207	629.31	0.9231	187.55	0.2555	508.06	0.6261	517.90	0.9248	150.48
0.3089	652.95	0.6676	589.22	0.9619	96.02	0.3138	549.83	0.6727	484.63	0.9628	79.27
0.3648	684.02	0.7131	540.87			0.3702	578.89	0.7178	440.95		
0.4192	699.01	0.7574	486.90			0.4247	584.53	0.7617	392.71		
Ethylene Glycol (1) + 1-Butanol (2) at 298.15 K						Ethylene Glycol (1) + 2-Butanol (2) at 298.15 K					
0.0803	296.08	0.5224	732.52	0.8308	429.37	0.0810	273.90	0.5235	690.46	0.8314	389.28
0.1548	482.24	0.5730	710.11	0.8675	358.57	0.1557	457.66	0.5741	668.62	0.8680	324.90
0.2250	603.08	0.6212	681.06	0.9026	284.18	0.2260	570.84	0.6222	635.40	0.9029	252.28
0.2912	675.15	0.6671	644.87	0.9362	194.89	0.2923	642.77	0.6681	601.55	0.9365	176.27
0.3537	718.45	0.7109	599.33	0.9686	101.52	0.3549	685.66	0.7117	556.02	0.9687	93.34
0.4129	736.89	0.7527	554.38			0.4142	700.78	0.7535	510.72		
0.4691	740.03	0.7926	488.89			0.4703	700.82	0.7933	449.45		
Ethylene Glycol (1) + 1-Butanol (2) at 308.15 K						Ethylene Glycol (1) + 2-Butanol (2) at 308.15 K					
0.0803	311.81	0.5223	773.06	0.8308	452.02	0.0810	243.74	0.5235	665.39	0.8314	382.80
0.1548	511.62	0.5730	752.34	0.8675	382.12	0.1557	421.23	0.5741	646.07	0.8680	321.87
0.2250	634.83	0.6211	720.77	0.9026	299.30	0.2260	537.30	0.6222	620.61	0.9029	251.75
0.2912	714.20	0.6671	682.86	0.9362	203.05	0.2923	606.55	0.6681	584.18	0.9365	172.57
0.3537	757.88	0.7109	637.57	0.9686	108.84	0.3549	649.31	0.7117	545.12	0.9687	92.42
0.4129	780.13	0.7527	579.64			0.4142	671.97	0.7535	498.30		
0.4691	783.53	0.7926	519.15			0.4703	673.83	0.7933	441.76		
Ethylene Glycol (1) + 1-Butanol (2) at 323.15 K						Ethylene Glycol (1) + 2-Butanol (2) at 323.15 K					
0.0798	324.41	0.5224	819.75	0.8309	483.26	0.0810	176.38	0.5235	580.46	0.8314	355.91
0.1552	519.89	0.5730	796.85	0.8675	394.92	0.1557	325.06	0.5741	570.50	0.8680	297.25
0.2253	667.09	0.6211	769.46	0.9026	313.19	0.2260	432.64	0.6222	552.96	0.9029	230.02
0.2914	749.40	0.6671	719.05	0.9363	218.09	0.2923	502.00	0.6681	525.23	0.9365	155.95
0.3540	797.30	0.7108	671.43	0.9687	111.51	0.3549	546.81	0.7117	490.71	0.9687	80.49
0.4131	824.29	0.7527	616.38			0.4142	572.39	0.7535	453.89		
0.4692	831.23	0.7926	553.07			0.4703	583.30	0.7933	409.62		

Table 3. Parameters and Deviations of the Correlation by Using Eqs 1 and 2[a]

	$k = 0$	$k = 1$	$k = 2$		298.15 K	308.15 K	323.15 K
			Ethylene Glycol (1) + Methanol (2) System				
a_{k0}	1.7200×10^3	-5.9478×10^2	6.9059×10^{-1}	δ_1	0.61	0.68	0.69
a_{k1}	-3.7113×10^5	1.4019×10^5	1.6366×10^4	δ_2	0.5	0.5	0.5
			Ethylene Glycol (1) + Ethanol (2) System				
a_{k0}	4.6678×10^3	-1.4365×10^3	8.9668×10^2	δ_1	2.11	1.97	1.86
a_{k1}	-9.1779×10^5	2.9922×10^5	-1.9500×10^5	δ_2	0.5	0.5	0.4
			Ethylene Glycol (1) + 1-Propanol (2) System				
a_{k0}	6.7393×10^3	-5.9478×10^3	1.5055×10^3	δ_1	2.53	3.84	3.52
a_{k2}	-1.2831×10^6	-1.6666×10^5	-2.8046×10^5	δ_2	0.4	0.6	0.5
			Ethylene Glycol (1) + 2-Propanol (2) System				
a_{k0}	-2.3051×10^4	1.5061×10^4	-1.7430×10^4	δ_1	2.63	2.50	1.27
a_{k1}	1.5519×10^7	-9.1850×10^6	1.0776×10^7	δ_2	0.4	0.4	0.2
a_{k2}	-2.3660×10^9	1.3415×10^9	-1.6166×10^9				
			Ethylene Glycol (1) + 1-Butanol (2) System				
a_{k0}	7.5314×10^3	-3.1763×10^2	6.3796×10^2	δ_1	2.47	3.62	2.97
a_{k1}	-1.3661×10^6	-3.7031×10^4	9.1650×10^4	δ_2	0.3	0.5	0.4
			Ethylene Glycol (1) + 2-Butanol (2) System				
a_{k0}	-5.7241×10^4	4.0344×10^4	-3.1482×10^4	δ_1	1.51	2.09	3.98
a_{k1}	3.5430×10^7	-2.3292×10^7	1.8493×10^7	δ_2	0.2	0.3	0.7
a_{k1}	-5.2274×10^9	3.3157×10^9	-2.6496×10^9				

[a] δ_1: average absolute deviation = $\{\sum_{i=1}^{N}|(H^{E}_{cal} - H^{E}_{exp})_i|\}/N$ (J·mol^{-1}), where N is the number of data points. δ_2: average relative deviation = $\{\sum_{i=1}^{N}|(H^{E}_{cal} - H^{E}_{exp})_i/H^{E}_{(exp)max}| \times 100\%\}/N$ (%), where N is the number of data points.

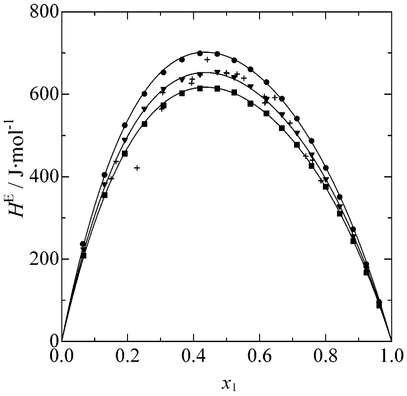

Figure 5. Experimental excess molar enthalpies for ethylene glycol (1) + 1-propanol (2). This work: (■) 298.15 K; (▼) 308.15 K; (●) 323.15 K. Jimenez et al.:[7] (+) 298.15 K. (—) Calculated values from eqs 1 and 2.

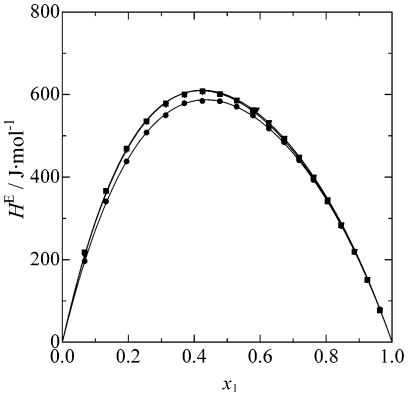

Figure 6. Experimental excess molar enthalpies for ethylene glycol (1) + 2-propanol (2). This work: (■) 298.15 K; (▼) 308.15 K; (●) 323.15 K. (—) Calculated values from eqs 1 and 2.

Ethylene Glycol + 2-Butanol. The experimental values of H^E for this system are shown in Figure 8. By comparing Figure 6 with Figure 5, it can be seen that the H^E values for the 2-butanol system decrease with increasing temperature, while the 1-butanol system shows the opposite effect.

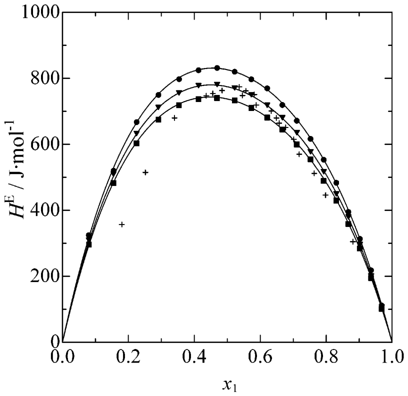

Figure 7. Experimental excess molar enthalpies for ethylene glycol (1) + 1-butanol (2). This work: (■) 298.15 K; (▼) 308.15 K; (●) 323.15 K. Jimenez et al.:[7] (+) 298.15 K. (—) Calculated values from eqs 1 and 2.

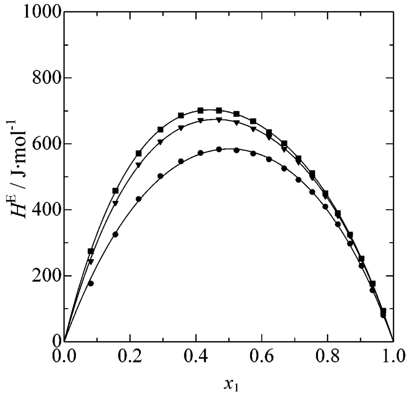

Figure 8. Experimental excess molar enthalpies for ethylene glycol (1) + 2-butanol (2). This work: (■) 298.15 K; (▼) 308.15 K; (●) 323.15 K. (—) Calculated values from eqs 1 and 2.

All the systems in Figures 3−8 show endothermic, slightly asymmetrical parabolic curves. For the systems containing an *n*-alkanol, the H^E values rise with increasing temperature and with the increase in the chain length of the *n*-alkanol. However, the systems containing 2-propanol and 2-butanol show a temperature dependency opposite to that for the systems containing *n*-alkanols.

Data Reduction

In this work, the experimental results of H^E were correlated with values calculated using the Redlich−Kister polynomial.

$$H^E\ (\mathrm{J{\cdot}mol^{-1}}) = x(1-x)\sum_{k=0}^{N-1} A_k(2x-1)^k \tag{1}$$

$$A_k = \sum_{i=0}^{n-1} a_{ki}T^{-i} \tag{2}$$

where A_k is the temperature-dependent parameter, a_{ki} is the adjustable parameter, x is the mole fraction of ethylene glycol, T is the temperature, N is the number of A_k parameters, and n is the number of a_{ki} parameters. An algorithm suggested by Marquardt,[23] based on an earlier suggestion of Levenberg,[24] was used in the data reduction. A suitable objective function to be minimized is

$$\mathrm{OF} = \sum_{k=1}^{\mathrm{NDP}} (H^E_{\mathrm{cal}} - H^E_{\mathrm{exp}})^2_k \tag{3}$$

where NDP is the number of experimental data points, and H^E_{cal} and H^E_{exp} are the calculated and measured excess molar enthalpies, respectively.

The estimated adjustable parameters a_{ki} and the relative average deviations are listed in Table 3. The calculated results are shown in Figures 3−8.

Conclusion

Excess molar enthalpies were determined for ethylene glycol + alkanol (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol) systems over the entire composition range at 298.15, 308.15, and 323.15 K. In all systems, H^E was endothermic, with values of H^E increasing with the increase in temperature over the full composition range for the systems containing an *n*-alkanol. In addition, the excess molar enthalpies greatly increased with increasing carbon number of the *n*-alkanol. In contrast to those systems, the ethylene glycol + 2-alkanol systems showed decreasing H^E values with increasing temperature.

The experimental results of excess molar enthalpies were correlated with calculated values from the Redlich−Kister equation. The strong correlation between the experimental and calculated values demonstrates this model provided a good description of the systems in this study.

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