Excess Molar Enthalpies and Volumes of Diethylamine or Dipropylamine + an Ether at 298.15 K

Trevor M. Letcher and Penny U. Govender

Department of Chemistry, Natal University, Durban 4041, South Africa

Urszula Domańska*

Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Excess molar enthalpies H_m^E and volumes V_m^E were measured as a function of mole fraction at 298.15 K and atmospheric pressure for each of the 12 binary mixtures: diethylamine or dipropylamine + di-1-methylethyl ether, 1,1-dimethylethyl methyl ether, 1,1-dimethylpropyl methyl ether, tetrahydrofuran, tetrahydropyran, and 1,4-dioxane. The results were compared to H_m^E and V_m^E for related mixtures and the specific interactions noted. The NRTL, UNIQUAC, and UNIQUAC ASM models of liquid mixtures were fitted to the results. The experimental results have been correlated and compared with the results from the extended real associated solution (ERAS) theory.

Introduction

We have previously reported H_m^E and V_m^E values for tributylamine (Letcher and Domańska, 1994a,b), for dibutylamine (Letcher et al., 1994a,b), or for *n*-butylamine (Letcher and Gołdon,1996a,b) + di-1-methylethyl ether, 1,1-dimethylethyl methyl ether, 1,1-dimethylpropyl methyl ether, tetrahydrofuran, tetrahydropyran, and 1,4-dioxane. The aim of the work was to investigate whether there was any evidence for hydrogen bonding between the amine and the ether. In all but one of the mixtures investigated the H_m^E's were small (<105 J·mol^{-1}). However for dibutyl amine + 1,4-dioxane, H_m^E(max) > 1000 J·mol^{-1}. Taking the dissociation effect into account, it was shown that there was some evidence for a week interaction between the amine and the ether. The V_m^E(max) results for dibutylamine ranged between −0.4 and +0.45 cm^3·mol^{-1} and did not show any pattern which could be associated with hydrogen bonds. In this work, shorter chain amines together with the same ethers were used to further investigate the hydrogen bonding effect between secondary amines and ethers.

* To whom correspondence should be addressed.

Experimental Section

The preparation and purities of the liquids used, with the exception of diethylamine and dipropylamine, have

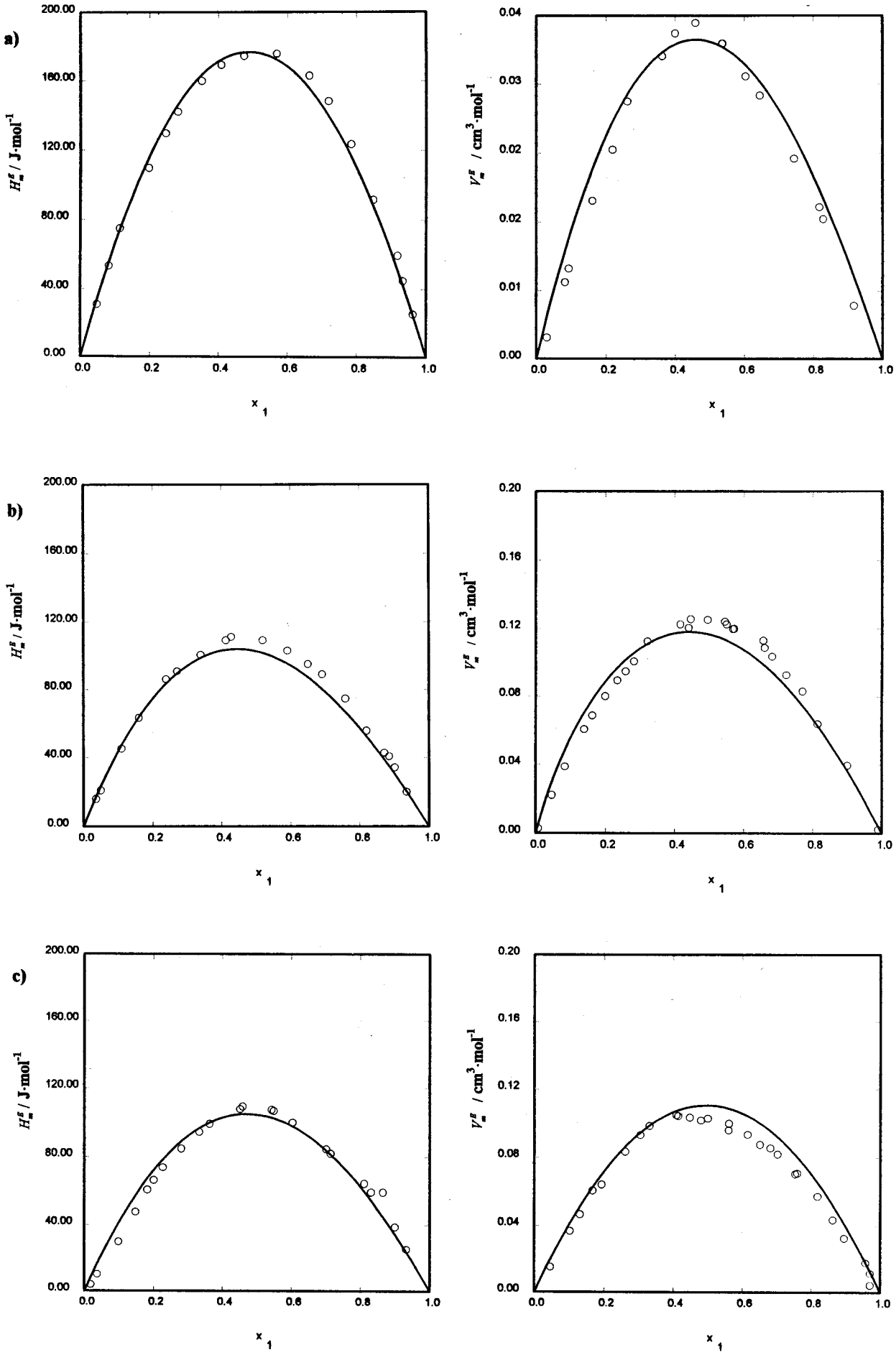
Table 1. Excess Molar Enthalpies H_m^E for Diethylamine or Dipropylamine (1) + an Ether (2) and the Deviations δH_m^E, Calculated from Equation 1 and Table 3 at 298.15 K

x_1	H_m^E/(J·mol^{-1})	δH_m^E/(J·mol^{-1})	x_1	H_m^E/(J·mol^{-1})	δH_m^E/(J·mol^{-1})	x_1	H_m^E/(J·mol^{-1})	δH_m^E/(J·mol^{-1})
Diethylamine (1) + Di-1-methylethyl Ether (2)								
0.048	31.0	−0.9	0.351	159.9	−0.2	0.784	123.5	−0.4
0.082	53.5	0.4	0.408	169.2	−1.0	0.848	91.8	−3.5
0.114	74.9	4.0	0.474	174.5	−1.8	0.918	59.6	3.2
0.198	109.9	−1.3	0.569	176.0	1.2	0.933	45.0	−1.8
0.247	129.7	−0.9	0.663	163.0	2.3	0.962	25.3	−2.4
0.282	142.3	0.2	0.719	148.4	1.8			
Diethylamine (1) + 1,1-Dimethylethyl Methyl Ether (2)								
0.036	16.0	−0.1	0.413	109.2	0.1	0.820	55.6	−2.1
0.050	20.9	1.1	0.429	111.2	1.4	0.871	42.8	0.1
0.110	45.2	−0.6	0.520	109.2	−0.3	0.885	40.7	2.2
0.160	63.2	0.5	0.592	103.0	−0.7	0.901	34.2	0.7
0.239	86.1	1.8	0.651	95.1	−0.4	0.935	20.1	−2.1
0.271	90.8	−0.3	0.692	88.9	0.7			
0.340	100.5	−2.0	0.759	74.6	1.0			
Diethylamine (1) + 1,1-Dimethylpropyl Methyl Ether (2)								
0.018	4.13	−2.4	0.333	94.5	0.7	0.714	82.0	−4.6
0.037	10.3	−3.1	0.363	99.2	0.9	0.811	64.3	1.0
0.099	30.0	−4.5	0.452	108.0	1.4	0.831	59.4	1.9
0.148	47.8	−2.3	0.459	109.5	2.6	0.865	59.3	3.9
0.182	60.7	0.9	0.543	107.6	0.5	0.900	39.0	2.9
0.201	66.2	1.0	0.549	106.9	0.0	0.932	25.6	0.6
0.227	73.7	1.8	0.604	100.1	−2.9			
0.281	84.8	0.7	0.701	84.6	−4.4			

10.1021/je980142x CCC: $18.00
Published on Web 02/17/1999

Table 1. (Continued)

x_1	H_m^E/(J·mol^{-1})	δH_m^E/(J·mol^{-1})	x_1	H_m^E/(J·mol^{-1})	δH_m^E/(J·mol^{-1})	x_1	H_m^E/(J·mol^{-1})	δH_m^E/(J·mol^{-1})
				Diethylamine (1) + Tetrahydrofuran (2)				
0.045	13.7	2.2	0.306	51.8	−1.3	0.746	22.2	0.7
0.052	16.3	3.2	0.339	54.6	−0.2	0.769	18.7	0.4
0.053	14.1	0.8	0.352	55.6	0.4	0.815	11.9	−0.4
0.063	16.5	0.7	0.434	57.7	2.9	0.856	7.92	0.2
0.099	23.9	0.1	0.439	57.6	3.0	0.925	2.75	0.9
0.159	34.1	−1.5	0.506	52.3	1.5	0.947	1.46	0.7
0.222	43.8	−1.3	0.540	46.6	−1.3	0.966	0.29	0.2
0.227	44.3	−1.4	0.607	39.0	−1.5			
0.267	48.6	−1.4	0.659	30.9	−2.7			
				Diethylamine (1) + Tetrahydropyran (2)				
0.037	1.13	−0.4	0.328	34.0	0.2	0.733	2.10	0.1
0.095	9.64	−3.1	0.333	33.8	−0.1	0.824	−1.21	−0.5
0.148	19.6	−0.4	0.369	33.9	−1.0	0.846	−1.83	−0.3
0.163	21.4	−0.4	0.445	29.7	−1.5	0.849	−1.95	−0.4
0.202	27.5	1.3	0.496	25.4	−2.2	0.899	−2.45	−0.2
0.218	30.1	2.3	0.577	20.0	−0.2	0.934	−2.30	−0.3
0.299	33.9	0.9	0.637	15.4	1.4	0.971	−1.60	−0.5
0.314	34.5	1.0	0.698	10.1	2.0			
				Diethylamine (1) + 1,4-Dioxane (2)				
0.040	77.7	−18.0	0.223	457.0	−2.9	0.634	551.3	0.2
0.083	187.1	−7.5	0.275	522.1	−7.1	0.734	451.8	5.5
0.097	207.1	−18.4	0.307	565.1	2.1	0.795	376.7	10.7
0.145	334.4	9.6	0.376	620.0	7.2	0.806	353.0	2.7
0.147	356.3	27.6	0.421	629.0	0.3	0.865	260.1	0.9
0.174	378.8	−0.3	0.437	627.0	−4.3	0.899	190.4	−10.8
			0.542	601.0	−11.5	0.939	118.1	−9.1
				Dipropylamine (1) + Di-1-methylethyl Ether (2)				
0.062	3.75	−0.3	0.374	24.0	0.3	0.715	22.0	0.0
0.124	7.78	−0.7	0.437	25.8	0.1	0.773	18.3	−0.3
0.160	11.7	0.6	0.494	26.2	−0.4	0.834	14.8	0.5
0.185	12.8	0.0	0.619	25.5	−0.2	0.853	13.2	−0.3
0.238	16.7	0.4	0.679	23.8	0.2	0.944	4.38	−0.8
0.330	21.3	−0.6						
				Dipropylamine (1) + 1,1-Dimethylethyl Methyl Ether (2)				
0.050	5.48	−0.5	0.265	27.2	0.7	0.593	24.3	0.1
0.062	6.76	−0.4	0.322	25.2	0.1	0.628	22.8	−0.2
0.100	9.98	−0.8	0.384	27.0	−0.7	0.709	18.9	−0.3
0.153	16.2	0.6	0.453	26.6	−1.6	0.773	16.1	0.5
0.157	16.1	0.0	0.525	26.1	−1.4	0.827	12.5	0.3
0.183	18.5	0.5	0.528	25.6	−1.5	0.919	5.39	−0.4
0.184	18.3	0.2						
				Dipropylamine (1) + 1,1-Dimethylpropyl Methyl Ether (2)				
0.080	5.88	−0.3	0.294	17.5	0.8	0.598	12.5	0.0
0.140	10.1	−0.3	0.360	17.2	−0.1	0.670	10.6	0.5
0.181	12.5	−0.2	0.390	16.7	−0.5	0.751	7.63	0.0
0.230	15.2	0.3	0.479	15.2	−0.8	0.856	4.70	−0.2
0.268	16.5	0.4	0.594	12.9	0.3	0.922	2.95	−0.1
				Dipropylamine (1) + Tetrahydrofuran (2)				
0.030	3.68	−0.3	0.442	57.4	1.8	0.722	50.9	−1.0
0.097	13.7	0.2	0.497	59.8	1.4	0.775	45.3	−0.6
0.126	17.8	−0.1	0.523	60.0	0.7	0.846	36.0	1.2
0.145	20.5	−0.1	0.600	58.5	−0.8	0.893	26.9	1.3
0.257	35.4	−1.2	0.607	58.3	−0.8	0.961	11.0	0.9
0.353	47.9	−0.1	0.651	56.0	−1.4			
				Dipropylamine (1) + Tetrahydropyran (2)				
0.040	7.01	−1.6	0.366	23.1	−0.7	0.753	−4.90	0.6
0.066	11.2	−2.0	0.473	15.3	−0.9	0.863	−6.50	1.2
0.105	19.9	1.3	0.549	9.39	−0.2	0.932	−6.84	−1.3
0.157	25.4	1.7	0.654	1.47	0.8	0.938	−7.03	−1.9
0.224	27.3	0.5	0.752	−5.14	0.3	0.961	−4.20	−0.6
0.296	26.2	−0.4						
				Dipropylamine (1) + 1,4-Dioxane (2)				
0.053	134.5	−17.9	0.258	595.0	8.6	0.636	633.7	7.4
0.088	252.4	7.0	0.319	649.7	−8.4	0.709	538.3	−7.8
0.123	342.3	9.5	0.410	713.9	1.1	0.773	455.0	−1.7
0.153	402.8	2.8	0.413	716.6	2.9	0.836	361.5	6.8
0.192	468.4	−10.0	0.492	711.5	−3.2	0.936	150.4	4.3


a)
H_m^E / J·mol^{-1}
200.00
160.00
120.00
80.00
40.00
0.00
0.0
0.2
0.4
0.6
0.8
1.0
x_1
V_m^E / cm^3·mol^{-1}
0.04
0.03
0.02
0.02
0.01
0.00
b)
H_m^E / J·mol^{-1}
V_m^E / cm^3·mol^{-1}
0.20
0.16
0.12
0.08
0.04
0.00
c)
H_m^E / J·mol^{-1}
V_m^E / cm^3·mol^{-1}

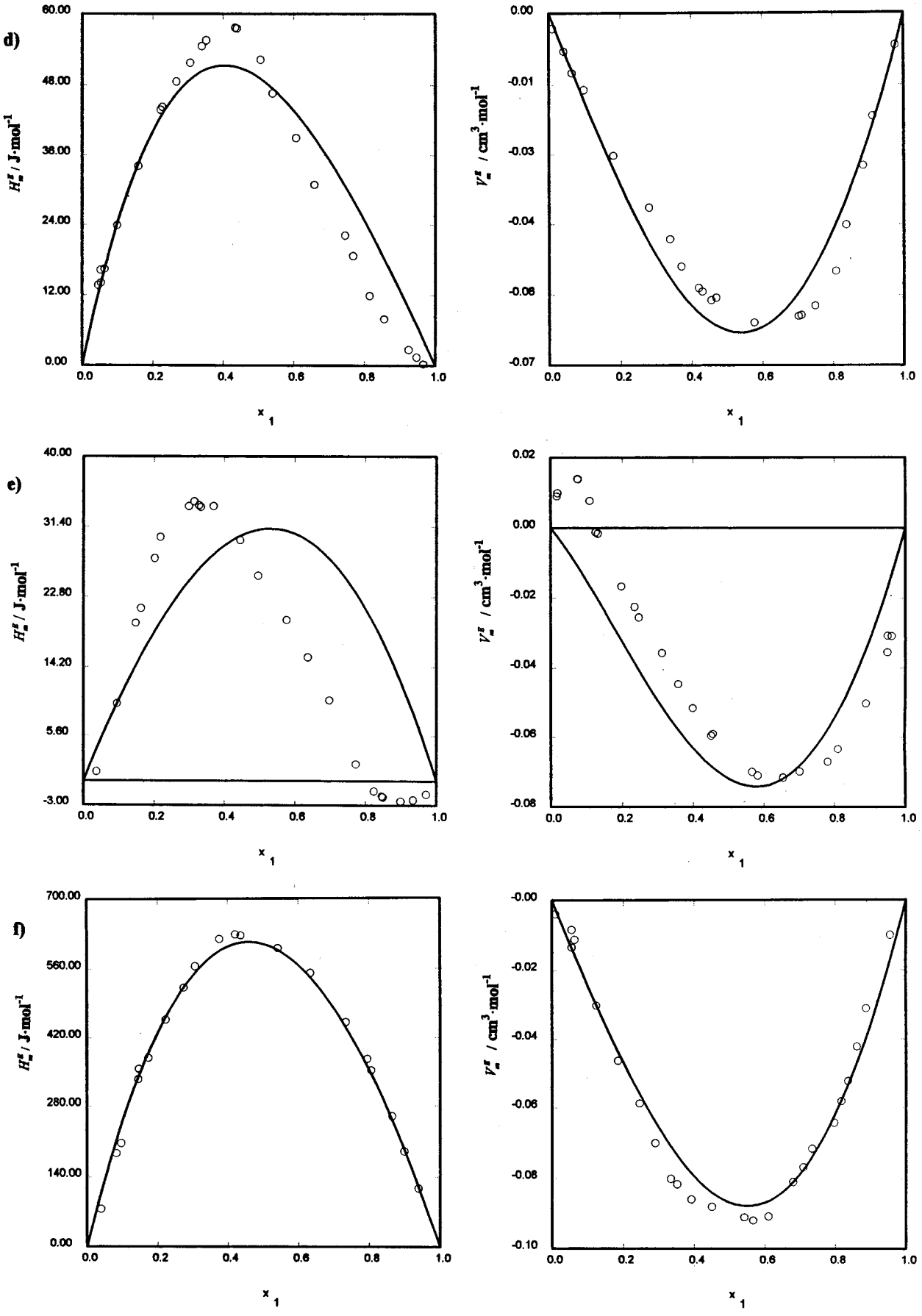
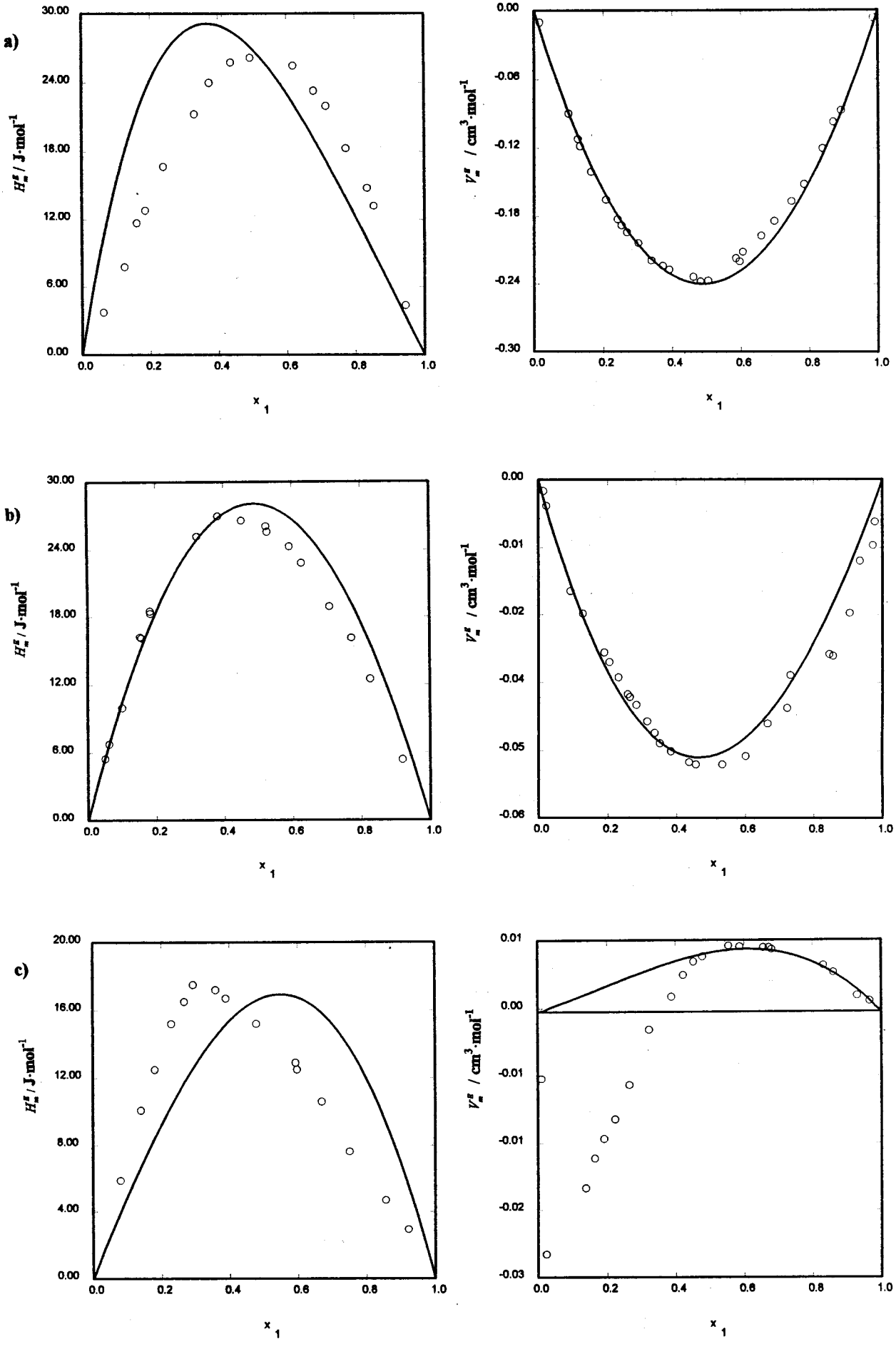


Figure 1. Excess molar functions, H_m^E and V_m^E, for binary mixture of diethylamine (1) + an ether (2) at 298.15 K: (a) di-1-methylethyl ether; (b) 1,1-dimethylethyl ether; (c) 1,1-dimethylpropyl ether; (d) tetrahydrofuran; (e) tetrahydropyran; (f) 1,4-dioxane. Solid line estimated from ERAS theory.


a)
H_m^E / J·mol^{-1}
V_m^E / cm^3·mol^{-1}
x_1
b)
H_m^E / J·mol^{-1}
V_m^E / cm^3·mol^{-1}
x_1
c)
H_m^E / J·mol^{-1}
V_m^E / cm^3·mol^{-1}
x_1

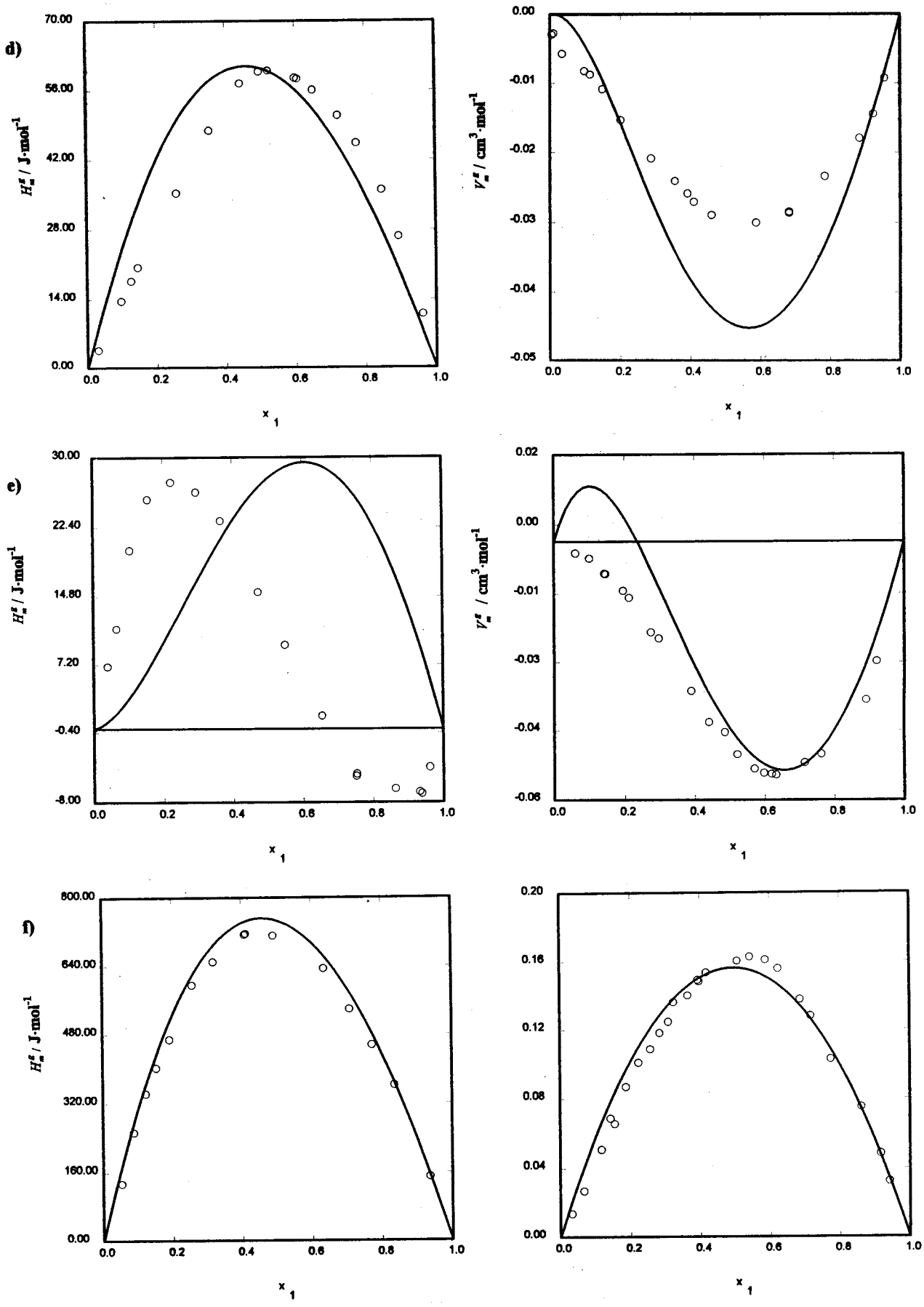


Figure 2. Excess molar functions, H_m^E and V_m^E, for binary mixture of dipropylamine (1) + an ether (2) at 298.15 K: (a) di-1-methylethyl ether; (b) 1,1-dimethylethyl ether; (c) 1,1-dimethylpropyl ether; (d) tetrahydrofuran; (e) tetrahydropyran; (f) 1,4-dioxane. Solid line estimated from ERAS theory.

Table 2. Excess Volumes V_m^E for Diethylamine or Dipropylamine (1) + an Ether (2) and the Deviations δV_m^E Calculated from Equation 1 and Table 4 at 298.15 K

x_1	V_m^E/ (cm^3·mol^{-1})	δV_m^E/ (cm^3·mol^{-1})	x_1	V_m^E/ (cm^3·mol^{-1})	δV_m^E/ (cm^3·mol^{-1})	x_1	V_m^E/ (cm^3·mol^{-1})	δV_m^E/ (cm^3·mol^{-1})
				Diethylamine (1) + Di-1-methylethyl Ether (2)				
0.030	0.0025	−1.0	0.363	0.0353	−0.2	0.645	0.0307	−1.1
0.082	0.0090	−0.7	0.400	0.0380	1.1	0.744	0.0234	−0.3
0.093	0.0106	−0.4	0.459	0.0392	1.2	0.817	0.0178	1.3
0.161	0.0185	−0.4	0.536	0.0368	−0.4	0.828	0.0164	1.0
0.219	0.0244	−0.6	0.537	0.0368	−0.3	0.917	0.0063	−0.4
0.262	0.0300	1.3	0.604	0.0329	−1.5			
				Diethylamine (1) + 1,1-Dimethylethyl Methyl Ether (2)				
0.007	0.0030	−0.5	0.321	0.1126	2.2	0.656	0.1130	4.4
0.046	0.0221	1.0	0.416	0.1225	−0.1	0.660	0.1088	1.0
0.083	0.0388	1.9	0.440	0.1205	−3.6	0.682	0.1036	0.2
0.139	0.0605	1.1	0.446	0.1256	1.2	0.723	0.0925	−1.6
0.162	0.0687	0.9	0.495	0.1252	0.2	0.770	0.0830	1.4
0.199	0.0801	0.2	0.545	0.1242	1.3	0.814	0.0637	−4.4
0.234	0.0893	−1.1	0.550	0.1225	−0.1	0.900	0.0396	1.0
0.258	0.0947	−1.9	0.568	0.1199	−1.0	0.989	0.0024	−2.1
0.282	0.1007	−1.6	0.572	0.1200	−0.6			
				Diethylamine (1) + 1,1-Dimethylpropyl Methyl Ether (2)				
0.046	0.0152	−3.7	0.414	0.1044	2.5	0.702	0.0820	0.2
0.102	0.0370	−2.5	0.448	0.1036	0.4	0.753	0.0704	−1.0
0.131	0.0468	−2.4	0.480	0.1019	−1.6	0.759	0.0708	0.7
0.167	0.0606	0.5	0.500	0.1030	−0.2	0.818	0.0573	1.7
0.193	0.0641	−3.0	0.560	0.0961	−4.2	0.862	0.0437	0.1
0.261	0.0836	0.8	0.561	0.1000	−0.2	0.895	0.0328	−1.2
0.305	0.0932	2.8	0.615	0.0935	−1.5	0.957	0.0179	3.4
0.331	0.0986	4.5	0.651	0.0876	−2.6	0.970	0.0114	1.2
0.409	0.1049	3.3	0.681	0.0856	0.1	0.970	0.0044	0.7
				Diethylamine (1) + Tetrahydrofuran (2)				
0.009	−0.0029	−1.5	0.371	−0.0504	−0.4	0.710	−0.0600	−1.5
0.041	−0.0073	−1.1	0.420	−0.0546	−0.1	0.749	−0.0581	−3.1
0.064	−0.0117	−2.0	0.430	−0.0553	0.0	0.808	−0.0513	−3.7
0.097	−0.0150	−0.3	0.455	−0.0570	0.1	0.837	−0.0421	0.7
0.180	−0.0283	−1.6	0.469	−0.0565	1.6	0.885	−0.0302	2.9
0.280	−0.0386	1.3	0.577	−0.0615	0.8	0.912	−0.0202	6.4
0.339	−0.0450	1.8	0.702	−0.0602	−1.2	0.975	−0.0061	2.2
				Diethylamine (1) + Tetrahydropyran (2)				
0.017	0.0090	4.5	0.247	−0.0254	1.0	0.655	−0.0716	1.0
0.019	0.0099	4.8	0.312	−0.0357	2.1	0.702	−0.0699	1.2
0.075	0.0140	1.3	0.358	−0.0446	0.1	0.782	−0.0671	−1.9
0.076	0.0139	1.4	0.399	−0.0515	−1.0	0.811	−0.0634	−1.2
0.109	0.0077	1.3	0.451	−0.0595	−1.9	0.889	−0.0502	1.6
0.126	−0.0012	−3.7	0.456	−0.0590	−0.8	0.949	−0.0355	−1.1
0.132	−0.0016	−2.4	0.567	−0.0700	0.2	0.950	−0.0307	3.1
0.198	−0.0166	−0.7	0.583	−0.0710	0.8	0.961	−0.0308	−2.5
0.235	−0.0224	1.6						
				Diethylamine (1) + 1,4-Dioxane (2)				
0.009	−0.0039	−1.9	0.334	−0.0800	−3.2	0.709	−0.0768	0.9
0.055	−0.0084	4.4	0.352	−0.0815	−1.8	0.738	−0.0716	0.9
0.055	−0.0134	−0.5	0.392	−0.0858	−0.6	0.797	−0.0643	−4.8
0.063	−0.0112	3.6	0.450	−0.0879	2.9	0.817	−0.0582	−3.8
0.124	−0.0302	−0.3	0.542	−0.0909	2.6	0.836	−0.0523	−2.8
0.185	−0.0463	−1.1	0.567	−0.0918	1.1	0.861	−0.0422	0.6
0.246	−0.0588	0.7	0.610	−0.0906	−0.3	0.887	−0.0311	4.3
0.290	−0.0700	−1.3	0.680	−0.0809	1.5	0.955	−0.0100	4.6
				Dipropylamine (1) + Di-1-methylethyl Ether (2)				
0.016	−0.0102	5.5	0.301	−0.2036	3.2	0.605	−0.2114	4.4
0.099	−0.0893	1.4	0.339	−0.2191	−1.0	0.659	−0.1971	3.1
0.126	−0.1118	−0.2	0.372	−0.2237	1.7	0.697	−0.1840	2.9
0.132	−0.1182	−2.1	0.391	−0.2271	1.4	0.747	−0.1665	−0.4
0.164	−0.1407	−2.3	0.461	−0.2335	0.1	0.784	−0.1514	−3.4
0.207	−0.1653	−0.6	0.482	−0.2375	−4.2	0.838	−0.1199	−0.9
0.241	−0.1825	0.0	0.504	−0.2367	−4.6	0.869	−0.0966	3.0
0.252	−0.1880	−0.5	0.585	−0.2171	3.2	0.892	−0.0866	−2.4
0.268	−0.1942	0.2	0.596	−0.2198	−2.0	0.986	−0.0063	6.3
				Dipropylamine (1) + 1,1-Dimethylethyl Methyl Ether (2)				
0.014	−0.0019	1.3	0.283	−0.0400	0.7	0.665	−0.0433	3.3
0.023	−0.0045	0.7	0.314	−0.0429	0.1	0.722	−0.0405	2.7
0.092	−0.0198	−1.6	0.336	−0.0449	−0.7	0.732	−0.0347	2.1
0.128	−0.0238	0.1	0.351	−0.0467	−1.6	0.845	−0.0310	−0.6
0.190	−0.0307	1.2	0.383	−0.0481	−1.4	0.856	−0.0313	−2.4
0.205	−0.0324	1.1	0.436	−0.0500	−1.5	0.905	−0.0237	2.7
0.231	−0.0351	1.1	0.456	−0.0504	−1.4	0.934	−0.0144	1.0
0.258	−0.0381	0.6	0.533	−0.0504	−0.7	0.972	−0.0116	−4.6
0.264	−0.0386	0.6	0.601	−0.0489	−0.1	0.978	−0.0074	−1.8

Table 2. (Continued)

x_1	V_m^E/(cm^3·mol^{-1})	δV_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})	δV_m^E/(cm^3·mol^{-1})	x_1	V_m^E/(cm^3·mol^{-1})	δV_m^E/(cm^3·mol^{-1})
			Dipropylamine (1) + 1,1-Dimethylpropyl Methyl Ether (2)					
0.010	−0.0075	3.0	0.323	−0.0020	0.1	0.657	0.0072	−1.6
0.023	−0.0274	−6.5	0.388	0.0017	1.6	0.673	0.0072	−1.4
0.024	−0.0274	−5.8	0.423	0.0041	2.3	0.681	0.0070	−1.4
0.138	−0.0199	6.5	0.453	0.0056	3.1	0.832	0.0052	2.8
0.164	−0.0165	3.8	0.479	0.0062	4.0	0.861	0.0044	2.1
0.191	−0.0143	0.00	0.555	0.0074	7.1	0.930	0.0018	−2.0
0.223	−0.0121	−3.4	0.588	0.0073	8.2	0.966	0.0012	−2.6
0.265	−0.0082	−4.7						
			Dipropylamine (1) + Tetrahydrofuran (2)					
0.005	−0.0028	−2.4	0.287	−0.0208	0.4	0.682	−0.0284	0.3
0.010	−0.0026	−1.8	0.355	−0.0240	0.4	0.682	0.0286	0.1
0.034	−0.0056	−3.0	0.391	−0.0258	0.1	0.784	−0.0233	1.9
0.097	−0.0082	−0.4	0.409	−0.0270	−0.5	0.884	−0.0179	−0.2
0.113	−0.0087	0.4	0.460	−0.0289	−1.0	0.923	−0.0144	−1.3
0.148	−0.0108	1.1	0.587	−0.0300	−0.6	0.955	−0.0092	−0.8
0.200	−0.0153	0.4						
			Dipropylamine (1) + Tetrahydropyran (2)					
0.061	−0.0026	−1.6	0.275	−0.0211	0.4	0.597	−0.0538	−1.0
0.100	−0.0038	−0.6	0.297	−0.0225	1.6	0.619	−0.0540	−0.3
0.143	−0.0073	−0.5	0.390	−0.0348	0.4	0.632	−0.0542	−0.1
0.145	−0.0074	−0.4	0.440	−0.0421	−1.4	0.714	−0.0514	2.8
0.146	−0.0074	−0.4	0.485	−0.0444	0.6	0.762	−0.0494	2.6
0.196	−0.0113	0.8	0.521	−0.0495	−1.4	0.891	−0.0369	−2.6
0.213	−0.0130	1.2	0.570	−0.0528	−1.4	0.921	−0.0278	−0.9
			Dipropylamine (1) + 1,4-Dioxane (2)					
0.033	0.0138	−2.6	0.309	0.1247	−2.6	0.588	0.1609	3.2
0.067	0.0271	−4.7	0.324	0.1361	4.0	0.624	0.1557	4.0
0.117	0.0508	−2.3	0.365	0.1400	−3.6	0.687	0.1375	0.6
0.143	0.0687	4.7	0.394	0.1491	−1.2	0.717	0.1279	−0.3
0.155	0.0655	−3.4	0.397	0.1482	−2.9	0.774	0.1028	−6.6
0.187	0.0868	5.0	0.418	0.1535	−1.5	0.861	0.0750	−1.0
0.223	0.1010	4.9	0.507	0.1603	−2.7	0.916	0.0484	−2.5
0.257	0.1088	−0.3	0.543	0.1626	0.5	0.941	0.0326	0.7
0.284	0.1182	−0.8						

Table 3. Coefficients A_r and Standard Deviation σ^a for H_m^E of Diethylamine or Dipropylamine (1) + an Ether (2) at 298.15 K Calculated Using Equation 1

ether	A_0	A_1	A_2	A_3	σ^a/(J·mol^{-1})
		Diethylamine			
di-1-methylethyl	708.5	26.7	24.9		2.2
1,1-dimethylethyl methyl	440.8	−58.2	−30.3		1.3
1,1-dimethylpropyl methyl	431.6	7.2	−60.3		2.7
tetrahydrofuran	204.9	−148.8	−80.4	10.5	1.7
tetrahydropyran	109.3	−164.2	−74.6	86.2	1.3
1,4-dioxane	2508.9	−482.6	−174.8	401.2	11.7
		Dipropylamine			
di-1-methylethyl	106.7	15.4	−30.2		0.4
1,1-dimethylethyl methyl	105.7	−27.1	−6.9		0.5
1,1-dimethylpropyl methyl	61.6	−51.3	2.2	37.2	0.5
tetrahydrofuran	234.3	70.9	−34.2		1.1
tetrahydrofuran	55.5	−173.1	10.2		1.3
1,4-dioxane	2850.8	−547.2	−28.6	370.7	9.1

[a] $\sigma = \{\sum[H^E_{m(expt)} - H^E_{m(calc)}]^2/(n-k)\}^{1/2}$, where n is the number of experimental points.

been described previously (Letcher and Domańska, 1994c). In this work the diethylamine and dipropylamine were obtained from Aldrich Chemical Co. and were used without further purification. Gas−liquid chromatography analysis indicated a purity of 99.5 and 99.6 mol % for diethylamine and dipropylamine, respectively.

Analysis by Karl Fischer titration showed that the water contamination of each of the ethers was less than 0.002 mol %.

A thermometric flow calorimeter (TAM) 2277 was used to determine the H_m^E values. The temperature was accurate to 0.01 K and was monitored by a calibrated quartz thermometer fixed into the cell compartment. The estimated uncertainty of the excess enthalpy (H_m^E) and mole fraction (x) is less than 4% and 0.3%, respectively, as judged from reproducibility experiments conducted on cyclohexane + heptane mixtures.

The V_m^E's were calculated from molar masses and densities of pure liquids and mixtures measured using an Anton-Paar DMA 602 vibrating-tube densimeter, thermostated at the temperature (298.15 ± 0.01) K. The estimated uncertainties of the excess volumes V_m^E and mole fractions (x) are less than 1% and 0.1%, respectively, as judged from a comparison with well-documented results for cyclohexane + heptane mixtures.

Results and Discussion

The measured excess molar enthalpies H_m^E and volumes V_m^E are given in Tables 1 and 2, respectively. To each of

Table 4. Coefficients B_r and Standard Deviation σ^a for V_m^E of Diethylamine or Dipropylamine (1) + an Ether (2) at 298.15 K Calculated Using Equation 1

ether	B_0	B_1	B_2	B_3	$\sigma^a \times 10^3/(cm^3 \cdot mol^{-1})$
		Diethylamine			
di-1-methylethyl	0.1515	−0.0246	−0.0623		1.0
1,1-dimethylethyl methyl	0.4997	−0.0406	−0.0614		1.9
1,1-dimethylpropyl methyl	0.4129	−0.0451	−0.0254		2.3
tetrahydrofuran	−0.2393	−0.1003	0.0144		2.3
tetrahydropyran	−0.2560	−0.1300	0.0230	−0.4270	3.5
1,4-dioxane	−0.3730	−0.0514	0.1021		2.8
		Dipropylamine			
di-1-methylethyl	−0.9294	0.1364	−0.0276	−0.0773	3.0
1,1-dimethylethyl methyl	−0.1985	−0.0161	−0.0486		1.8
1,1-dimethylpropyl methyl	0.0193	0.0808	0.0760	−0.3323	3.7
tetrahydrofuran	−0.1146	−0.0324	−0.0294	−0.0345	1.4
tetrahydropyran	−0.1854	−0.1710	−0.0174	−0.0467	1.5
1,4-dioxane	0.6450	0.0600	−0.1590		3.2

[a] $\sigma = \{\sum[V^E_{m(expt)} - V^E_{m(calc)}]^2/(n-k)\}^{1/2}$, where n is the number of experimental points.

Table 5. Excess Molar Volumes V_m^E of $0.5CH_3(CH_2)_nNH(CH_2)_nCH_3 + 0.5$Ether for $n = 1$, 2, or 3 at 298.15 K

	$V^E_m(0.5)/(cm^3 \cdot mol^{-1})$				$V^E_m(0.5)/(cm^3 \cdot mol^{-1})$		
ether	$n = 1^a$	$n = 2^a$	$n = 3^b$	ether	$n = 1^a$	$n = 2^a$	$n = 3^b$
di-1-methylethyl	0.04	−0.23	−0.38	tetrahydrofuran	−0.06	−0.03	0.09
1,1-dimethylethyl methyl	0.12	−0.05	−0.14	tetrahydropyran	−0.06	−0.05	0.13
1,1-dimethylpropyl methyl	0.10	0.00	−0.02	1,4-dioxane	−0.09	0.16	0.48

[a] This work. [b] Letcher et al., 1994b.

Table 6. Excess Molar Enthalpies H_m^E for $0.5CH_3(CH_2)_nNH(CH_2)_nCH_3 + 0.5$Ether for $n = 1$, 2, or 3 at 298.15 K

	$H^E_m(0.5)/(J \cdot mol^{-1})$				$H^E_m(0.5)/(J \cdot mol^{-1})$		
ether	$n = 1^a$	$n = 2^a$	$n = 3^b$	ether	$n = 1^a$	$n = 2^a$	$n = 3^b$
di-1-methylethyl	177	27	32	tetrahydrofuran	51	59	104
1,1-dimethylethyl methyl	110	26	80	tetrahydropyran	27	14	63
1,1-dimethylpropyl methyl	108	15	45	1,4-dioxane	629	713	981

[a] This work. [b] Letcher et al, 1994a.

Table 7. Excess Molar Enthalpies H_m^E at $x_1 = 0.5$ and 298.15 K for an Ether (2) + a Hydrocarbon and the Interaction Value c,[a] Where $H_m^E(0.5)$ for Diethylamine (1) + Heptane is 716 $J \cdot mol^{-1}$ [b] and $H_m^E(0.5)$ for Dipropylamine (1) + Heptane is 452 $J \cdot mol^{-1}$ [c]

ether (2)	$H^E_m(0.5)/(J \cdot mol^{-1})$ (2) + hydrocarbon	hydrocarbon	c^a(diethylamine)/ $(J \cdot mol^{-1})$	c^a(dipropylamine)/ $(J \cdot mol^{-1})$
di-1-methylethyl	256[d]	heptane	−795	−681
1,1-dimethylethyl methyl	283[e]	heptane	−889	−709
1,1-dimethylpropyl methyl	290[f]	heptane	−898	−727
tetrahydrofuran	718[g]	hexane	−1383	−1111
tetrahydropyran	608[d]	cyclopentane	−1297	−1046
1,4-dioxane	1809[g]	heptane	−1896	−1548

[a] $c = H^E_m[0.5(1) + 0.5(2)] - H^E_m[0.5(1) + 0.5\text{hydrocarbon}] - H^E_m[0.5(2) + 0.5\text{hydrocarbon}]$. [b] Funke et al., 1989. [c] Our unpublished data. [d] Christiansen et al., 1988. [e] Tusel-Langer et al., 1991. [f] Kammerer and Lichtenthaler, 1996. [g] Christiansen et al., 1982.

the 24 sets of experimental values, a Redlich−Kister polynomial of the type

$$\delta X^E_m = X^E_m - x_1(1 - x_1)\sum_{r=0}^{r=k} Y_r(1 - 2x_1)^r \qquad (1)$$

was fitted by a method of unweighted least squares, where X_m^E refers to $H_m^E/(J \cdot mol^{-1})$ and $V_m^E/(cm^3 \cdot mol^{-1})$ and Y_r refers to A_r and B_r, respectively (see Tables 3 and 4).

To our knowledge, no measurements of H_m^E or V_m^E have been reported for the mixtures discussed in this work.

H_m^E(max) for each of the mixtures reported here was less than 200 $J \cdot mol^{-1}$ except for the 1,4-dioxane mixtures, for which H_m^E(max) was greater than 600 $J \cdot mol^{-1}$. A similar observation was seen previously (Letcher et al., 1994a) for mixtures of dibutylamine + an ether. V_m^E's for each of the mixtures reported here were small and ranged between −0.23 and +0.16 $cm^3 \cdot mol^{-1}$ (Table 5). As in the case of the H_m^E results reported here, there is no obvious evidence from the V_m^E results that hydrogen bonding occurs between the amines and the ethers.

However, some evidence can be obtained from a consideration of the assumption made in an earlier paper (Letcher et al., 1994a) that a measure of [(1) + (2)] interactions can be ganged from the magnitude of $c = H^E_m[0.5(1) + 0.5(2)] - H^E_m[0.5(1) + 0.5n\text{-}C_6H_{14}$ or $0.5n\text{-}C_7H_{16}) - H^E_m[0.5(2) + 0.5n\text{-}C_6H_{14}$ or $0.5n\text{-}C_7H_{16}]$. The assumption is that the magnitude of $H^E_m[0.5(1) + 0.5(2)]$ is due to the dissociation enthalpy of (1), the dissociation enthalpy of (2), and the association enthalpy of (1) and (2) in the mixture. Using the data in Table 6 together with the data in Table 7, the interaction between diethylamine or dipropylamine and an

Table 8. Correlation of the Excess Molar Enthalpies for Diethylamine or Dipropylamine (1) + an Ether (2) by Means of the NRTL, UNIQUAC, and UNIQUAC ASM Equations: Values of Parameters and Measures of Deviations

	param/(J·mol^{-1})			σ^c dev(J·mol^{-1})		
	NRTL	UNIQUAC	UNIQUAC ASM[b]			
ether	$g_{12} - g_{11}$ $g_{12} - g_{22}$	Δu_{12} Δu_{21}	Δu_{12} Δu_{11}	NRTL	UNIQUAC	UNIQUAC ASM
			Diethylamine			
di-1-methylethyl	533.9	−121.3	−1016.5	2.2	2.3	24.9
	218.8	386.6	845.8			
1,1-dimethylethyl methyl	−259.8	−301.2	−1079.8	1.7	1.7	16.1
	775.8	528.4	888.9			
1,1-dimethylpropyl methyl	288.5	−149.3	−1102.4	3.3	3.3	20.2
	146.2	315.6	906.8			
tetrahydrofuran	−983.1	−506.0	−1198.6	3.8	4.8	7.3
	1594.7	765.3	1027.6			
tetrahydropyran	−1112.0	−635.0	−1001.9	3.7	4.5	7.6
	1702.7	927.4	545.5			
1,4-dioxane	1084.8	695.2	1522.4	19.9	19.5	32.2
	1985.4	532.7	−680.7			
			Dipropylamine			
di-1-methylethyl	545.9	264.8	−896.4	1.1	1.2	10.9
	−390.1	−212.5	760.2			
1,1-dimethylethyl methyl	−534.1	−251.4	−889.3	0.5	0.6	8.5
	738.9	317.2	756.4			
1,1-dimethylpropyl methyl	−764.3	−408.5	−628.4	0.7	0.8	1.3
	1022.2	513.3	347.7			
tetrahydrofuran	−1260.0	−686.4	−502.9	1.7	4.6	5.5
	1962.4	1017.5	135.0			
tetrahydropyran	1066.4	773.4	−840.8	1.8	1.3	15.9
	−649.5	−523.2	716.6			
1,4-dioxane	1287.5	978.2	1307.5	13.1	12.0	17.3
	2450.2	312.5	−329.3			

[a] Calculated for $\alpha_{12} = 0.2$. [b] Calculated using data from Table 9. [c] Given by the equation $\sigma = \{\sum[H^E_{m(expt)} - H^E_{m(calc)}]^2/(n - k)\}^{1/2}$.

Table 9. Pure Component Properties for the ERAS Model at 298.15 K

component	Δh/(kJ·mol^{-1})	Δv/(cm^3·mol^{-1})	K	component	Δh/(kJ·mol^{-1})	Δv/(cm^3·mol^{-1})	K
diethylamine	−8.5[a]	−4.7[a]	0.84[b]	dipropylamine	−7.5[c]	−4.2[c]	0.55[c]

[a] Funke et al., 1989. [b] Nath and Bender, 1981. [c] Letcher and Bricknell, 1996.

Table 10. Characteristic Parameters of Pure Components for the ERAS Model at 298.15 K

component	V_m/(cm^3·mol^{-1})	$\alpha \times 10^4$/K^{-1}	$\kappa_T \times 10^4$/MPa^{-1}	V^*/(cm^3·mol^{-1})	T^*/K	p^*/(J·cm^{-3})
diethylamine	104.5	15.30[a]	14.71[a]	78.76	4397	511.3
dipropylamine	138.0	13.10[b]	12.20[b]	106.81	4706	505.4
di-1-methylethyl ether	142.2	14.50[c]	17.19[c]	106.66	4348	447.0
1,1-dimethylethyl methyl ether	119.9	14.20[c]	15.39[c]	90.29	4389	485.1
1,1-dimethylpropyl methyl ether	133.4	12.20[d]	13.29[d]	103.32	4715	456.3
tetrahydrofuran	81.56	8.77	9.60	66.75	5637	406.7
tetrahydropyran	98.19	7.76	9.46	81.83	6070	352.1
1,4-dioxane	85.70	7.17	7.39	72.22	6380	407.3

[a] Funke et al., 1989. [b] Letcher and Bricknell, 1996. [c] Spanedda et al., 1991. [d] Zhu et al., 1994.

ether can be described and decreases in the following sequence: 1,1-dimethylpropyl methyl ether > 1,1-dimethylethyl methyl ether > di-1-methylethyl ether for the branched ethers and 1,4-dioxane > tetrahydrofuran > tetrahydropyran for the cyclic ethers. The same order was observed for dibutylamine and branched ethers (Letcher et al., 1994a). For the $-NH_2$ group in butylamine + an ether systems the interaction is much higher, especially for cyclic ethers. Negative values of c in Table 7 indicate an interaction between the −NH group of the amine molecule and the oxygen atom of the ether molecule.

The experimental results of H^E_m have in the first instance been correlated using the NRTL equation (Renon and Prausnitz, 1968), UNIQUAC equation (Abrams and Prausnitz, 1975), and UNIQUAC ASM model (Nagata, 1985) with the Krestchmer−Wiebe model of association. The exact mathematical forms of the pure component structural parameter r (volume parameter) and q (surface

Table 11. ERAS Model Parameters Characterizing Mixture Properties of Diethylamine or Dipropylamine (1) + an Ether (2) at 298.15 K

ether	$-h_{12}$*/(kJ·mol^{-1})	$-\Delta v_{12}$*/(cm^3·mol^{-1})	K_{12}
	Diethylamine		
di-1-methylethyl	6.1	4.1	0.83
1,1-dimethylethyl methyl	5.7	2.9	0.95
1,1-dimethylpropyl methyl	6.9	4.1	0.75
tetrahydrofuran	5.4	4.6	0.84
tetrahydropyran	7.0	7.6	0.82
1,4-dioxane	0.1	4.3	0.80
	Dipropylamine		
di-1-methylethyl	7.2	4.5	0.70
1,1-dimethylethyl methyl	4.5	2.5	0.75
1,1-dimethylpropyl methyl	5.0	2.95	0.75
tetrahydrofuran	3.8	3.8	0.75
tetrahydropyran	5.7	7.3	0.60
1,4-dioxane	0.1	4.0	0.70

Table 12. Exchange Interaction Coefficient X_{12} and Summary of Calculations for 0.5Diethylamine or Dipropylamine (1) + 0.5Ether (2) at 298.15 K Using ERAS

ether	X_{12}/ (J·mol^{-1})	$H^E_{m(calc)}$/ (J·mol^{-1})	σ^a/ (J·mol^{-1})	$V^E_{m(calc)}$/ (cm^3·mol^{-1})	σ^b/ (cm^3·mol^{-1})
		Diethylamine			
di-1-methylethyl	1.1	177	5	0.04	0
1,1-dimethylethyl methyl	1.2	103	5	0.12	0.01
1,1-dimethylpropyl methyl	1.2	105	6	0.11	0.01
tetrahydrofuran	1.0	60	5	−0.06	0
tetrahydropyran	1.0	31	12	−0.07	0.01
1,4-dioxane	0.8	609	16	−0.09	0
		Dipropylamine			
di-1-methylethyl	0.8	27	6	−0.24	0.01
1,1-dimethylethyl methyl	1.0	28	2	−0.05	0
1,1-dimethylpropyl methyl	0.7	17	4	0.01	0.01
tetrahydrofuran	0.8	60	7	−0.04	0.01
tetrahydropyran	0.7	28	18	−0.04	0.01
1,4-dioxane	12.5	748	30	0.16	0.01

[a] $\sigma = \{\sum[H^E_{m(expt)} - H^E_{m(calc)}]^2/(n-k)\}^{1/2}$. [b] $\sigma = \{\sum[V^E_{m(expt)} - V^E_{m(calc)}]^2/(n-k)\}^{1/2}$.

parameter) have been presented earlier (Domańska, 1989). The results are shown in Table 8.

The UNIQUAC ASM calculations were carried out with the association equilibrium constants and the molar enthalpy of hydrogen bond formation presented in Table 9 neglecting the solvation effect between amine and ether. The enthalpy was assumed to be independent of temperature, and the equilibrium constant was calculated by the van't Hoff relation.

The results of the correlation of experimental points with the two parameter NRTL and UNIQUAC equations are in the same range as the Redlich−Kister equation with three or four parameters. For the all of the systems presented here, the best description of excess molar enthalpy was given by the NRTL model with average standard deviations $\langle\sigma\rangle = 2.9$ J·mol^{-1} and $\langle\sigma\rangle = 1.2$ J·mol^{-1} for the diethylamine and dipropylamine systems (with the exception of 1,4-dioxane), respectively. The standard deviations obtained for the UNIQUAC ASM model are much larger than those obtained by simple NRTL and UNIQUAC models ($\langle\sigma\rangle$ = 15.2 J·mol^{-1} and 8.4 J·mol^{-1} for diethylamine and dipropylamine systems). This is evidence of much stronger interaction between amine and ether than in amine itself.

The extended real associated solution (ERAS) theory (Funke et al., 1989) combines the real associated solution model with a free volume contribution using Flory's equation of state (Orwoll and Flory, 1967). Values of characteristic parameters for the pure components are shown in Tables 9 and 10. The ERAS binary parameters Δh_{12}*, Δv_{12}*, and K_{12} were adjusted simultaneously to the experimental H^E_m and V^E_m data for a certain value of the interaction parameter X_{12} and are presented in Table 11. In the systems studied here ethers were assumed to be inert components not showing self-association ($K_2 = 0$), but cross-association with an amine was assumed. The exchange interaction parameter X_{12} for each system and the values of H^E_m and V^E_m calculated at the equimolar composition together with the standard deviations are presented in Table 12.

A comparison of the calculated and experimental H^E_m and V^E_m functions presented in Figures 1 and 2 for the systems diethylamine or dipropylamine (1) + an ether (2) indicates that the ERAS model adequately describes the excess properties quantitatively. However, for the mixtures containing diethylamine and tetrahydropyran the model fails to predict the s-shaped V^E_m in the dilute amine region and H^E_m in the amine rich region (see Figure 1e). For the dipropylamine + tetrahydropyran mixtures, the calculated H^E_m values are symmetrical around $x = 0.5$. This is in contrast to the experimental H^E_m curves, which are skewed toward the dilute amine region and give an s-shaped curve.

Conclusions

The H^E_m and V^E_m results for the mixtures diethylamine or dipropylamine + an ether seem to indicate that as the aliphatic chain length of the secondary amine increases, (a) the packing and the association effects between the amine and the ether become less dominant and (b) the breakdown of the self-association, in both the amine and the ether, dictates the thermodynamic behavior of the system. Our molecular interpretation of the possible cross-association between an amine and an ether is based on the picture that the hydrogen atom of the amine interacts as a proton donor with the oxygen of the ether molecule, which results in small negative values of V^E_m.

Finally, it should be noted that estimates of excess molar volumes and enthalpies, based on the interchange energy parameters, obtained from the present analysis of excess functions show that ERAS model properly describe these functions. For all the mixtures the H^E_m and V^E_m values are of the same sign as the experimental values. However, some deviations in the symmetry of the predictive curves were observed.

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−124.

Christiansen, J. J.; Hanks, R. W.; Izatt, R. M. *Handbook of Heats of Mixing*; Wiley-Interscience: New York, 1982.

Christiansen, J. J.; Rowley, R. L.; Izatt, R. M. *Handbook of Heats of Mixing*; Wiley-Interscience: New York, 1988; Supplementary Volume.

Domańska, U. Solubility of n-Alkanols (C_{16}, C_{18}, C_{20}) in Binary Solvent Mixtures. *Fluid Phase Equilib.* **1989**, *46*, 223−248.

Funke, H.; Wetzel, M.; Heintz, A. New Applications of the ERAS Model. Thermodynamics of Amine + Alkane and Alcohol + Amine Mixtures. *Pure Appl. Chem.* **1989**, *61*, 1429−1439.

Kammerer, K.; Lichtenthaler, R. N. Excess Enthalpy H^E of Binary Mixtures Containing Alkanes, Methanol and tert-Amyl Methyl Ether (TAME). *Thermochim. Acta* **1996**, *49*, 271−278.

Letcher, T. M.; Bricknell, B. C. Excess Molar Volumes of Some Hydrogen-Bonded Complexes at 298.15 K and the Application of the ERAS Model. *J. Chem. Eng. Data* **1996**, *41*, 639−643.

Letcher, T. M.; Domańska, U. The Excess Enthalpies of (Tributylamine + an Ether) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994a**, *26*, 553−560.

Letcher, T. M.; Domańska, U. The Excess Volumes of (Tributylamine + an Ether) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994b**, *26*, 1241−1247.

Letcher, T. M.; Domańska, U. The Excess Enthalpies of (Acetonitryle + an Ether) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994c**, *26*, 15−84.

Letcher, T. M.; Gołdon, A. The Excess Molar Volumes of (n-Butylamine + an Ether) at the Temperature 298.15 K and the Application of the ERAS Model. *Fluid Phase Equilib.* **1996a**, *114*, 147−159.

Letcher, T. M.; Gołdon, A. The Excess Molar Enthalpies of (n-Butylamine + an Ether) at the Temperature 298.15 K. *J. Chem. Eng. Data* **1996b**, *41*, 629−633.

Letcher, T. M.; Domańska, U.; Govender, P. U. The Excess Enthalpies of (Dibutylamine + an Ether) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994a**, *26*, 681−689.

Letcher, T. M.; Domańska, U.; Govender, P. U. The Excess Volumes of (Dibutylamine + an Ether) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994b**, *26*, 1019−1023.

Nagata, I. On the Thermodynamics of Alcohol Solutions. Phase Equilibrium of Binary and Ternary Mixtures Containing Any Number of Alcohols. *Fluid Phase Equilib.* **1985**, *19*, 153−174.

Nath, A.; Bender, E. On the Thermodynamics of Associated Solutions. I. An Analytical Method for Determining the Enthalpy and Entropy of Association and Equilibrium Constant for Pure Liquid Substances. *Fluid Phase Equilib.* **1981**, *7*, 275−281.

Orwoll, R. A.; Flory, P. J. Thermodynamic Properties of Binary Mixtures of *n*-Alkanes. *J. Am. Chem. Soc.* **1967**, *89*, 6822−6825.

Renon, H.; Prausnitz, J. M. Local Composition Model in Thermodynamic Excess Function for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−138.

Spanedda, A.; Lepori, L.; Matteoli, E. Volumes of Mixing of Ethers with Tetrachloromethane at 298.15 K. *Fluid Phase Equilib.* **1991**, *69*, 209−214.

Tusel-Langer, E.; Garcia Alonso, J. M.; Villamaňan Olfos, M. A.; Lichtenthaler, R. N. Excess Enthalpies of Mixtures Containing n-Heptane, Methanol and Methyl tert-Butyl Ether (MTBE). *J. Solution Chem.* **1991**, *20*, 153−163.

Zhu, S.; Shen, S.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies of (Methyl 1,1-Dimethylpropyl Ether + an n-Alkane) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 35-39.

Received June 26, 1998. Accepted December 4, 1998. T.M.L. and P.U.G. wish to thank the FRD (South Africa) and Natal University for financial help.

JE980142X