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Excess Molar Enthalpies of (Butylamine + an Ether) at 298.15 K

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The excess molar enthalpies H_m^E of butylamine + diethyl ether, +dipropyl ether, +bis(1-methylethyl) ether, +dibutyl ether, +1,1-dimethylethyl methyl ether, +1,1-dimethylpropyl methyl ether, +tetrahydrofuran, +tetrahydropyran, and +1,4-dioxane have been measured over the whole composition range at 298.15 K in order to investigate interactions between butylamine and the three classes of ethers, namely straight chain, branched chain, and cyclic. All the mixtures show endothermic behavior. The results reported here are compared to H_m^E results for related systems involving dibutylamine published recently by our group. The experimental results have been correlated using the NRTL and UNIQUAC equations.

Introduction

In continuation of our work on the thermodynamics of nonelectrolyte mixtures containing polar organic substances (Letcher and Domańska, 1994a,b; Letcher *et al.*, 1994a,b) we have determined the excess molar enthalpies of the binary liquid mixtures of butylamine + diethyl ether, +dipropyl ether, +bis(1-methylethyl) ether, +dibutyl ether, +1,1-dimethylethyl methyl ether, +1,1-dimethylpropyl methyl ether, +tetrahydrofuran, +tetrahydropyran, and +1,4-dioxane, over the whole composition range at 298.15 K. These results complement our previous work on excess molar enthalpies H_m^E and excess molar volumes V_m^E of dibutylamine or tributylamine with ROR′, a straight-chain, branched-chain, or cyclic ether (Letcher and Domańska, 1994a,b; Letcher *et al.*, 1994a,b). The ethers used in the previous work are identical to the ethers used in the work reported here and include all three types of ethers—straight chain, branched, and cyclic. The results reported in this work are compared to these earlier results. Of the nine systems presented in this work only H_m^E(butylamine + 1,4 dioxane) has previously been reported by Acevedo *et al.* (1988).

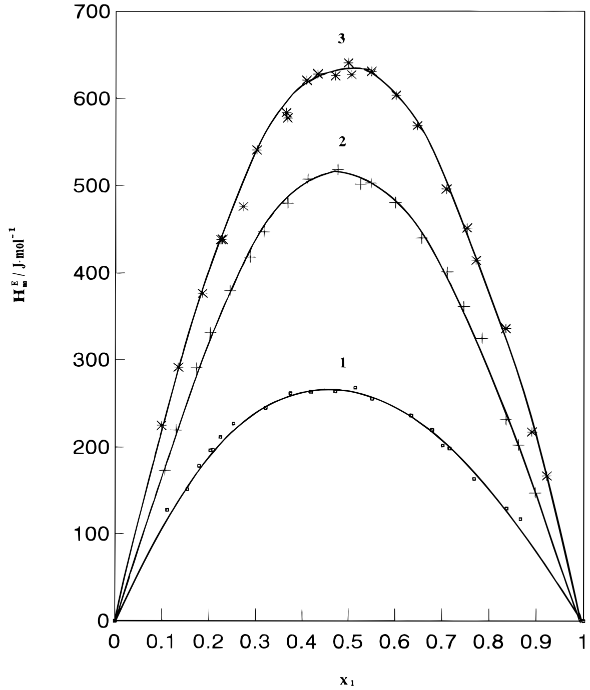

Figure 1. Excess enthalpies of butylamine (1) + straight chain ether (2). Experimental results at 298.15 K: (1) diethyl ether, (2) dipropyl ether, (3) dibutyl ether. The curves are calculated from the Redlich−Kister equation.

Experimental Section

Materials. The chemicals (with the exception of 1,1-dimethylpropyl methyl ether) were supplied by Janssen Chimica. The 1,1-dimethylpropyl methyl ether was supplied by Aldrich Chemicals Co. Each of the solvents was distilled, dried, and degassed before use as previously described (Letcher and Domańska, 1994a). The mole fraction of water in each of the liquids was determined by a Karl−Fischer titration to be <0.001. The solvents were kept in a drybox before use.

***Procedure*.** A ThermoMetric 2277 thermal activity monitor microcalorimeter was used to determine the molar enthalpies of mixing. All measurements were made at (298.15 ± 0.01) K. The method has been described (Letcher and Scoones, 1982).

The performance of the calorimeter was regularly checked by measuring H_m^E of the test mixtures (benzene + cyclohexane). Agreement with the literature results (Battler *et al.*, 1985) was within ±1% for every one of the 9 mixtures tested between $x = 0.1$ and $x = 0.9$ mole fraction.

Results and Discussion

The H_m^E results are shown in Figures 1−3 and are given in Table 1 together with the deviations δH_m^E, calculated from the smoothing equation:

$$\delta H_m^E/(\mathrm{J{\cdot}mol^{-1}}) = H_m^E/(\mathrm{J{\cdot}mol^{-1}}) - x(1-x)\sum_{r=0}^{r=k} A_r(1-2x)^r \tag{1}$$

where x refers to the butylamine.

The values of the parameters A_r are given in Table 2. The results of H_m^E (butylamine + 1,4-dioxane) previously reported (Acevedo *et al.*, 1988) differ from ours results by

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Table 1. Excess Molar Enthalpies, for Binary Mixtures of Butylamine (1) + an Ether (2), and the Deviations, δH_m^E, Calculated from Eq 1 and Table 2 at 298.15 K

x	H_m^E/ J·mol^{-1}	δH_m^E/ J·mol^{-1}	x	H_m^E/ J·mol^{-1}	δH_m^E/ J·mol^{-1}	x	H_m^E/ J·mol^{-1}	δH_m^E/ J·mol^{-1}
Butylamine (1) + Diethyl Ether (2)								
0.1110	127.18	4.2	0.3214	244.39	−4.5	0.6787	219.22	4.1
0.1536	151.19	−8.2	0.3744	261.19	0.2	0.7014	201.86	−3.4
0.1790	178.30	0.0	0.4185	262.95	−3.0	0.7160	198.37	−0.1
0.2028	196.09	1.8	0.4711	263.25	−2.8	0.7684	163.39	−8.3
0.2090	196.70	−1.4	0.5141	267.81	6.0	0.8370	128.99	−1.3
0.2243	211.16	4.0	0.5502	254.80	−0.8	0.8662	117.03	6.6
0.2524	226.41	4.4	0.6345	235.80	3.7			
Butylamine (1) + Dipropyl Ether (2)								
0.1058	173.28	−10.2	0.3686	479.54	−2.9	0.7102	401.19	6.5
0.1301	218.92	−2.9	0.4110	507.42	5.6	0.7457	361.12	4.8
0.1732	290.48	5.1	0.4763	518.66	3.5	0.7846	324.54	15.0
0.2023	331.17	6.4	0.5254	501.38	−9.7	0.8354	231.12	−11.1
0.2443	379.28	3.5	0.5478	502.75	−2.5	0.8624	202.46	−1.7
0.2873	418.07	−2.5	0.6001	480.14	−2.3	0.8978	147.23	−5.3
0.3174	446.63	−0.4	0.6556	439.89	−4.6			
Butylamine (1) + Dibutyl Ether (2)								
0.0987	224.32	5.5	0.3678	577.52	−10.2	0.6463	568.68	−0.5
0.1343	291.35	4.1	0.4085	621.25	9.6	0.7087	495.78	−11.0
0.1857	376.44	0.4	0.4322	628.44	6.9	0.7527	451.10	0.1
0.2246	437.91	2.9	0.4706	626.37	−4.5	0.7717	414.51	−9.6
0.2283	438.23	−2.0	0.4983	641.20	8.7	0.8353	335.85	13.3
0.2727	475.68	−22.1	0.5052	627.58	−4.7	0.8905	217.21	−4.9
0.3014	540.62	10.8	0.5481	631.41	6.6	0.9222	166.83	6.5
0.3651	583.73	−2.1	0.6006	603.72	2.1			
Butylamine (1) + Bis(1-methylethyl) Ether (2)								
0.1081	155.99	2.7	0.3564	345.22	−8.1	0.7175	302.17	3.1
0.1453	194.36	−1.4	0.3772	360.28	−1.2	0.7564	266.86	−1.2
0.1716	222.13	−0.8	0.4219	385.64	10.9	0.7857	238.42	−3.5
0.1963	249.26	2.9	0.5085	388.12	5.8	0.8181	206.00	−4.3
0.2309	280.25	4.2	0.5483	375.63	−2.0	0.8612	169.01	4.5
0.2818	307.63	−5.4	0.6244	355.88	1.9	0.8926	132.70	3.8
0.3222	333.41	−3.5	0.6621	329.25	−5.9			
Butylamine (1) + 1,1-Dimethylpropyl Methyl Ether (2)								
0.0805	102.44	−4.3	0.3134	279.87	−2.0	0.6300	304.93	−2.4
0.1214	151.04	1.9	0.3417	287.65	−6.7	0.6664	278.95	−1.2
0.1532	185.99	8.2	0.3737	299.89	−6.5	0.7567	222.12	−1.0
0.1694	196.11	4.8	0.4521	330.37	4.4	0.8078	189.93	1.4
0.1879	208.38	2.7	0.4951	338.70	8.6	0.8431	155.04	0.0
0.2419	235.64	−7.1	0.5355	339.67	1.0	0.8720	131.19	5.1
0.2942	267.64	−4.8	0.5661	332.16	6.9	0.9231	80.24	6.5

x	H_m^E/ J·mol^{-1}	δH_m^E/ J·mol^{-1}	x	H_m^E/ J·mol^{-1}	δH_m^E/ J·mol^{-1}	x	H_m^E/ J·mol^{-1}	δH_m^E/ J·mol^{-1}
Butylamine (1) + 1,1-Dimethylethyl Methyl Ether (2)								
0.1087	122.03	−3.2	0.4616	275.36	−4.1	0.7001	222.69	1.2
0.1331	144.84	−2.1	0.4871	274.61	−4.6	0.7271	197.29	−9.9
0.2039	203.62	4.7	0.5076	276.20	−1.8	0.7542	187.98	−3.4
0.2589	232.68	3.4	0.5489	274.49	1.8	0.7977	166.84	3.8
0.3053	251.33	2.1	0.5511	276.03	3.7	0.8499	124.91	0.0
0.3067	246.77	−3.0	0.5754	267.15	−0.2	0.8949	88.45	−6.6
0.3542	262.05	0.5	0.6253	259.66	6.6	0.9062	81.21	1.4
0.3869	270.66	−1.2	0.6657	241.70	4.2			
Butylamine (1) + 1,4-Dioxane (2)								
0.0604	121.00	−0.7	0.3115	469.56	−6.2	0.6400	476.55	1.7
0.0893	178.20	0.7	0.3597	503.85	−0.4	0.6871	452.21	5.0
0.1192	234.74	2.5	0.4245	524.26	0.4	0.7447	393.84	−11.6
0.1582	299.33	1.6	0.4627	531.60	5.0	0.8033	343.28	−8.5
0.1829	335.90	0.5	0.4766	521.83	−4.3	0.8314	314.10	−6.6
0.2056	372.92	5.9	0.5343	520.31	3.4	0.8876	250.32	6.3
0.2570	419.77	−8.1	0.6009	500.70	6.9	0.9214	199.87	14.0
Butylamine (1) + Tetrahydrofuran (2)								
0.0765	47.02	1.3	0.3230	145.10	1.6	0.6245	131.21	−5.5
0.0989	60.43	1.7	0.3397	145.33	−1.2	0.7030	118.62	0.2
0.1265	70.95	−1.9	0.4108	158.30	3.9	0.7587	104.36	1.5
0.1362	79.60	1.8	0.4305	162.51	7.3	0.8286	87.08	7.3
0.1634	90.28	−0.5	0.4778	153.88	−0.9	0.8913	54.08	−1.1
0.2182	111.75	−1.9	0.5099	151.01	−1.9	0.9211	35.97	−6.0
0.3002	133.93	−4.7	0.5489	147.36	−1.6			
Butylamine (1) + Tetrahydropyran (2)								
0.0776	69.73	−5.3	0.3874	235.46	8.8	0.6634	182.37	0.5
0.1069	98.24	−1.9	0.3929	234.65	7.6	0.6718	186.28	7.4
0.1480	138.80	6.9	0.3986	232.01	4.6	0.7608	147.58	3.9
0.1870	165.16	7.2	0.4541	223.79	−3.7	0.8084	117.50	−4.3
0.2467	186.41	−3.2	0.4858	220.93	−3.9	0.8404	102.29	−3.5
0.2539	186.49	−6.3	0.5043	226.09	3.6	0.8999	73.14	0.9
0.3050	204.26	7.0	0.5418	205.84	−10.0	0.9321	54.00	1.8
0.3420	217.09	−3.1	0.5863	203.48	−2.0			

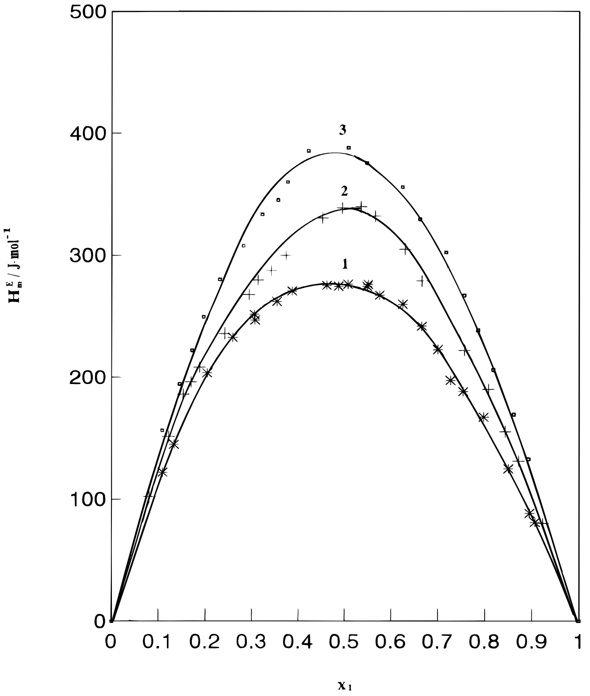

Figure 2. Excess enthalpies of butylamine (1) + branched chain ether (2). Experimental results at 298.15 K: (1) 1,1-dimethylethyl methyl ether, (2) 1,1-dimethylpropyl methyl ether, (3) bis(1-methylethyl) ether. The curves are calculated from the Redlich−Kister equation.

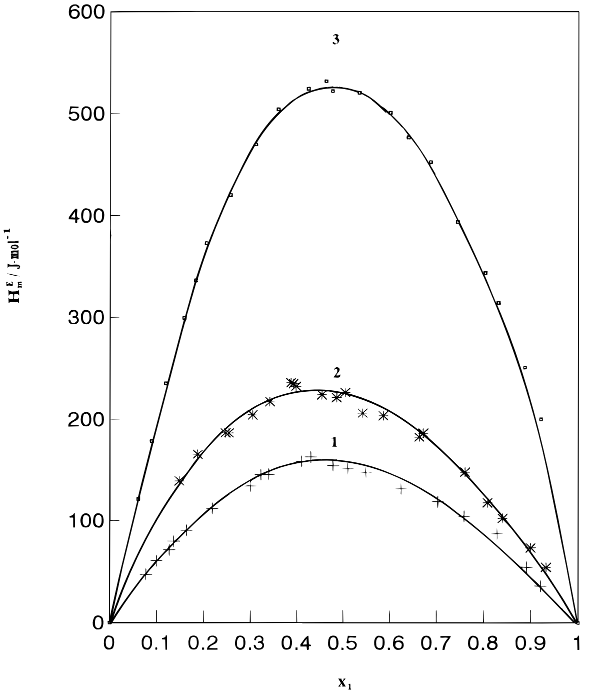

Figure 3. Excess enthalpies of butylamine (1) + cyclic ether (2). Experimental results at 298.15 K: (1) tetrahydrofuran, (2) tetrahydropyran, (3) 1,4-dioxane. The curves are calculated from the Redlich−Kister equation.

about 120 J·mol^{-1} at $x = 0.5$. Our results were made with great care and repeated many times, and the purity was checked before each run. It is possible that Acevedo and co-workers did not degas the mixtures before taking measurements and also were not careful in excluding atmospheric moisture from the butylamine.

H_m^E values have been reported for many binary mixtures containing butylamine. Negative H_m^E values, which were symmetrical about mole fraction $x = 0.5$, were observed for (butylamine + an alkanol) systems by Christiansen *et al.* (1982, 1988) with minima ranging from −2595 J·mol^{-1} for propan-1-ol to −3901 J·mol^{-1} for butan-1-ol at 298.15 K. Endothermic H_m^E effects were observed for (butylamine + a straight-chain alkane) with maxima of 1012 J·mol^{-1} and of 1218 J·mol^{-1} at 298.15 K for hexane and hexadecane, respectively.

Table 2. Parameters A_r and Standard Deviations *s* for H_m^E of Butylamine (1) + an Ether (2) at 298.15 K by Eq 1

ether	A_0	A_1	A_2	A_3	*s*
diethyl	1055	223	74	−57	4.4
dipropyl	2058	160	−410	19	7.2
dibutyl	2530	52	−261	109	8.9
bis(1-methylethyl)	1533	49	−102	175	5.1
1,1-dimethylpropyl methyl	1321	−45	−108	400	7.1
1,1-dimethylethyl methyl	1114	130	12	145	4.0
1,4-dioxane	2094	287	384	−735	6.7
tetrahydrofuran	615	135	−3	132	3.9
tetrahydropyran	892	276	52	−190	5.9

Table 3. Excess Enthalpies H_m^E at $x = 0.5$, Where $A = H_m^E$(Butylamine + an Ether), $B = H_m^E$(Butylamine + Hexane) = 986 J·mol^{-1},[c] and $C = H_m^E(C_kH_l$ + an Ether) (All Measurements Refer to 298.15 K)

ether	A^a/J·mol^{-1}	*C*/J·mol^{-1}	ref	C_kH_l	$A - B - C$/J·mol^{-1}
diethyl	264	439	*c*	cyclohexane	−1161
dipropyl	512	205	*d*	heptane	−676
dibutyl	633	93	*c*	hexane	−446
bis(1-methylethyl)	383	256	*d*	heptane	−859
1,1-dimethylpropyl methyl	330	268	*b*	heptane	−924
1,1-dimethylethyl methyl	279	383	*e*	heptane	−1090
1,4-dioxane	524	1809	*c*	heptane	−2271
tetrahydrofuran	154	718	*c*	hexane	−1532
tetrahydropyran	223	608	*d*	cyclopentane	−1369

[a] Refers to this work. [b] Our unpublished data. [c] Christiansen *et al.* (1982). [d] Christiansen *et al.* (1988). [e] Tusel-Langer *et al.* (1991).

H_m^E(a primary or a secondary amine + an alkanol) shows the strongest negative values found for organic mixtures in the literature (Christiansen *et al.*, 1982, 1988; Tusel-Langer *et al.*, 1991). This is due to strong intermolecular interactions between the NH group of the amine molecule and the OH group of the alkanol molecule. In contrast to this, H_m^E(butylamine + ROR′) was found in this work to be positive. This was also true for H_m^E(dibutylamine or tributylamine + ROR′) reported previously by Letcher and Domańska (1994a) and Letcher et al. (1994a).

The magnitude of the interaction between butylamine and ROR′ can be obtained by subtracting from $A = H_m^E$(butylamine + ROR′) the enthalpic contributions resulting from dissociation of butylamine on the one hand and ROR′ on the other. These contributions can be estimated from $B = H_m^E(\text{butylamine} + C_kH_l)$ and $C = H_m^E(\text{ROR}' + C_kH_l)$ where C_kH_l relates to nonpolar alkane. The result of such an analysis at $x = 0.5$ is given in Table 3.

Negative values of $(A - B - C)$ indicate an interaction between the NH_2 group of the amine molecule and the O atom of the ether molecule. Results in Table 3 show that the interaction decreases in the following order: diethyl ether > dipropyl ether > dibutyl ether for straight-chain ethers, 1,1-dimethylpropyl methyl ether > 1,1-dimethylethyl methyl ether > bis(1-methylethyl) ether for the

Table 4. Correlation of the Excess Molar Enthalpies H_m^E of (Butylamine + an Ether) by Means of the NRTL, UNIQUAC, and UNIQUAC ASM Equations: Values of Parameters and Measures of Deviations

	parameters/J·mol^{-1}			deviations		
ether	NRTL[a] g_{12} - g_{11}, g_{12} - g_{22}	UNIQUAC Δu_{12}, Δu_{21}	UNIQUAC ASM Δu_{12}, Δu_{21}	NRTL σ[b]	UNIQUAC σ[c], σ_r[d]	UNIQUAC ASM σ_r[d]
diethyl	−114.34, 1419.88	−235.41, 772.71	−1292.62, 1026.49	4.7, 3.0	4.7, 3.0	25.9, 15.1
dipropyl	849.39, 1497.69	−123.85, 979.22	−1079.82, 895.05	16.4, 7.7	15.2, 7.2	44.5, 16.5
dibutyl	1388.07, 1663.30	−168.32, 1190.08	−1013.22, 850.68	13.7, 3.7	11.5, 2.9	36.3, 9.3
bis(1-methylethyl)	−567.97, 1137.49	−216.40, 870.47	−1238.78, 997.89	6.5, 2.4	6.1, 2.1	32.5, 13.5
1,1-dimethylpropyl methyl	446.18, 999.36	−212.66, 777.70	−1291.91, 1034.74	9.7, 4.4	9.5, 4.2	31.2, 15.1
1,1-dimethylethyl methyl	34.09, 1275.47	−269.19, 812.12	−1299.81, 1032.32	4.3, 2.3	4.3, 2.2	21.8, 12.3
1,4-dioxane	1185.20, 1350.18	792.90, 298.35	−784.56, 675.79	16.4, 6.7	16.9, 6.8	78.1, 30.3
tetrahydrofuran	−183.68, 899.80	156.81, 132.98	−1440.89, 1117.96	4.2, 4.3	4.3, 4.5	16.0, 21.0
tetrahydropyran	−287.51, 1449.19	−191.47, 661.77	−1364.56, 1075.86	6.3, 5.3	6.3, 5.3	14.4, 14.1

[a] Calculated for $\alpha_{12} = 0.3$. [b] Given by $\sigma = (\delta H_m^E/H_m^E)$. [c] Given by $\sigma = [\Sigma(H_m^E - H_{m(calc)}^E)^2/(n - k)]^{1/2}$. [d] Given by $\sigma_r = 100[\Sigma(H_m^E - H_{m(calc)}^E)^2/(H_m^E)^2 (n - k)]^{1/2}$.

branched-chain ethers, and 1,4-dioxane > tetrahydrofuran > tetrahydropyran for cyclic ethers. In general, the longer the alkyl group of the ether, the weaker is the association with butylamine. A similar effect was seen with (dibutylamine + an ether) (Letcher *et al.*, 1994a). The fact that the ($A - B - C$) values calculated for (dibutylamine + ROR′) are much more positive than for (butylamine + ROR′), reported here, where ROR′ are the straight-chain ethers, indicates that the association between the butylamine and the ether is much greater than between the dibutylamine and the ether.

For the branched-chain ethers the value of ($A - B - C$) decreases with the increasing number of CH_3 groups attached to the carbon adjacent to the ether oxygen. This is probably due to the inductive effect of the CH_3 group in the branched-chain ethers which increases the electron density in the oxygen atom, resulting in an enhanced cross-association. The fact that the ($A - B - C$) values for (butylamine + ROR′) where ROR′ are cyclic ethers are much more negative than for (butylamine + ROR′) where ROR′ are straight-chain or branched-chain ethers could be due to the larger dipole or quadrupole moments of cyclic ethers (Riddick *et al.*, 1986). As expected, the greatest association is between the butylamine and the ring compound containing two ether oxygen atoms. A similar effect was seen with (dibutylamine + an ether).

The experimental results have been correlated using the NRTL equation (Renon and Prausnitz, 1968), the simple UNIQUAC equation (Abrams and Prausnitz, 1975), and the UNIQUAC ASM model (Nagata, 1985). The calculations with the UNIQUAC ASM (Kretshmer and Wiebe model of association) were carried out by assuming that the association equilibrium constant for the pure butylamine was $K_A = 0.96$ and that the molar enthalpy of formation for the cyclic dimer of butylamine was $h_A = -13.2$ kJ·mol^{-1} at 298.15 K (Funke *et al.*, 1989). The molar volume of butylamine was calculated to be 99.86 cm^3·mol^{-1} at 298.15 K (Letcher and Gołdon, in press) and the molar volumes of the ethers were taken from previous work (Letcher and Domańska, 1994a). The binary parameters and the absolute arithmetic-mean deviations obtained by minimizing the sum of the deviations between the experimental and calculated H_m^E values (using the Marquardt maximum neighborhood method (Marquardt, 1963) for minimization) are presented in Table 4.

The results of the correlation of experimental points with the two-parameter NRTL and UNIQUAC equations are in the same range as the four-parameter Redlich−Kister equation. The correlation of experimental points in binary mixtures with the results obtained by means of the UNIQUAC ASM model are not as good as those obtained by the simple NRTL and UNIQUAC models. A better description by the UNIQUAC ASM model was obtained with the association constant as the third adjustable parameter.

The optimized value of the association constant is, however, smaller than that used by Funke *et al.* (1989) and results in values ranging between (0.00 and 0.26) at 298.15 K. For the nine mixtures presented in Table 4, the description of excess molar enthalpy is given by the two-parameter UNIQUAC model and the NRTL with an average standard deviation $\langle\sigma\rangle = 8.1$ J·mol^{-1} and $\langle\sigma\rangle = 9.7$ J·mol^{-1}, respectively. The description obtained by means of the UNIQUAC ASM model with the association constant as the third adjustable parameter is also in the same range.

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*, 116−128.

Acevedo, I. L.; Postigo, M. A.; Katz, M. Excess thermodynamic properties and vapor-liquid equilibrium data for the n-butylamine + p-dioxane system at 25 °C. *J. Solution Chem.* **1988**, *17*, 977−986.

Battler, J. R.; Clark, W. M.; Rowley, R. L. Excess Enthalpy and Liquid−Liquid Surfaces for the Cyclohexane−2-Propanol−Water System from 293.15 to 323.15 K. *J. Chem. Eng. Data* **1985**, *30*, 254−259.

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.

Funke, H.; Wetzel, M.; Heintz, A. New application of the ERAS model. Thermodynamics of amine + alkane and alcohol + amine mixtures. *Pure Appl. Chem.* **1989**, *61*, 1429−1439.

Letcher, T. M.; Scoones, B. W. H. The excess enthalpies of bicyclohexyl + a cycloalkane and an n-alkane at two temperatures. *J. Chem. Thermodyn.* **1982**, *14*, 703−706.

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.; 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.*, in press.

Letcher, T. M.; Domańska, U.; Govender, P. 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. The excess volumes of (dibutylamine + an ether) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1994b**, *26*, 1019−1023.

Marquardt, D. An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Appl. Math.* **1963**, *11*, 431−441.

Nagata, I. On thermodynamics of alcohol solutions. Phase equilibria of binary and ternary mixtures containing any numbers of alcohols. *Fluid Phase Equilib*. **1985**, *19*, 153−174.

Renon, H.; Prausnitz, J. M. Local compositions in thermodynamics excess functions for liquid mixtures. *AIChE J*. **1968**, *14*, 135−141.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*; Wiley-Interscience: New York, 1986.

Tusel-Langer, E.; Garcia Alonso, J. M.; Villamañan 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.

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