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Excess Properties and Vapor Pressure of 2-Diethylaminoethylamine + *n*-Heptane

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ABSTRACT: The vapor pressures of liquid [2-diethylaminoethylamine (2-DEEA) + *n*-heptane] mixtures were measured by a static method between T = (273.15 and 363.15) K at 10 K intervals. The excess molar enthalpies H^E at 303.15 K were also measured. The molar excess Gibbs energies G^E were obtained with Barker's method and fitted to the Redlich—Kister equation. The Wilson equation was also used. The molar excess Gibbs energies and the molar excess enthalpies were used to test the applicability of group-contribution models, including the modified UNIFAC model in the versions of Larsen and Gmehling and the Disquac model. Particularly, the proximity effect of N atoms was analyzed.

1. INTRODUCTION

Diamines are an important class of compounds used in different fields of industry[1,2] and represent a particularly interesting family of molecules for the purpose of testing group-contribution models and analyzing intramolecular effects, especially the proximity effect. This effect renders methods such as the UNIFAC model inaccurate. The Disquac model is a group-contribution model that improves the predictions by using structure-dependent group parameters.[3] Previous studies[4−7] have shown that the occurrence of a functional group in a cyclic compound and/or the proximity of another group may change the interaction parameters considerably.

(Vapor + liquid) phase equilibria measurements have great importance in thermodynamics, not only for their direct use in process design but also for testing and extension of fluid-mixture theories. Following our systematic study of the thermodynamic properties of mixtures of symmetric diamines with *n*-alkanes or cyclohexane[8−12] and of linear or aromatic diamines with aromatics,[13] polyaromatics,[14−16] and supercritical CO_2,[17] we present in this paper a complete set of data on vapor pressures for [2-diethylaminoethylamine (2-DEEA) + *n*-heptane] mixtures at 10 temperatures between T = (273.15 and 363.15) K as well as the excess molar enthalpies H^E at 303.15 K.

From a theoretical point of view, mixtures of unsymmetrical diamines are of interest because of their complexity resulting from the heteroproximity effect. The treatment of this class of mixtures is thus a test for any theoretical model. These data are examined on the basis of group-contribution models (UNIFAC and Disquac) in order to examine the influence of the proximity effect of N atoms on the thermodynamic properties H^E and G^E.

2. EXPERIMENTAL PROCEDURES

2.1. Materials. *n*-Heptane (Merck, mass-fraction purity greater than 0.99) was fractionally distilled on a 40-plate column, and the vapor pressure was determined and found to agree with literature values.[18] 2-DEEA (Aldrich, mass-fraction purity greater than 0.99) was also distilled under nitrogen in the presence of sodium, and the purity was checked by GC.

Table 1. Molar Volumes V^* and Virial Coefficients B_{ij} for [2-DEEA (1) + *n*-Heptane (2)]

	2-DEEA		*n*-heptane		
	V^*	$-B_{11}$	V^*	$-B_{22}$	$-B_{12}$
T/K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
273.15	125.56	7236	141.61	3840	5216
283.15	126.89	6135	143.31	3377	4504
293.15	128.27	5280	145.08	3004	3943
298.15	128.98	4923	145.99	2844	3705
303.15	129.70	4604	146.93	2698	3491
313.15	131.18	4061	148.85	2443	3122
323.15	132.71	3618	150.87	2227	2815
333.15	134.31	3251	152.98	2042	2557
343.15	135.97	2943	155.19	1882	2337
353.15	137.69	2681	157.53	1742	2147
363.15	139.50	2456	159.99	1619	1981

2.2. Apparatus and Procedure. The total vapor pressure measurements were obtained by a static method whose experimental details and procedure have been described elsewhere.[19] The static apparatus allows reliable measurements over a very large pressure range (0.5 Pa to 200 kPa).

Vapor pressures were measured using a fused quartz gauge (model 145.01, Texas Instruments, Bedford, U.K.) protected

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Table 2. Values of Vapor Pressure p, Deviations $\Delta p = 100 \cdot (p - p_{\text{calcd}})/p$, Activity Coefficients γ_1 and γ_2, and Excess Molar Gibbs Energies G^E for [2-DEEA (1) + n-heptane (2)]

x_1	p kPa	Δp	γ_1	γ_2	G^E J·mol^{-1}
$T = 273.15$ K					
0.0000	1.5355	0.00	2.9205	1.0000	0.0
0.1186	1.4158	0.30	2.1752	1.0185	246.0
0.1978	1.3396	−0.07	1.8460	1.0503	364.8
0.3215	1.2352	−0.28	1.4982	1.1296	483.0
0.4404	1.1341	−0.33	1.2813	1.2397	525.6
0.5444	1.0293	−0.54	1.1670	1.3630	511.4
0.6554	0.8999	0.38	1.0837	1.5222	448.5
0.7527	0.7548	−0.35	1.0422	1.6662	368.1
0.8469	0.5580	2.03	1.0132	1.8567	240.5
0.9311	0.3289	−1.54	1.0024	2.0218	115.3
1.0000	0.1291	0.00	1.0000	2.1609	0.0
$T = 293.15$ K					
0.0000	4.7595	0.00	2.4716	1.0000	0.0
0.1186	4.3987	0.45	1.9459	1.0150	216.9
0.1978	4.1461	−0.10	1.7016	1.0409	323.3
0.3215	3.8096	−0.07	1.4298	1.1061	431.8
0.4404	3.4734	−0.12	1.2566	1.1973	474.1
0.5444	3.1402	−0.25	1.1535	1.3007	465.0
0.6554	2.7345	0.36	1.0794	1.4363	411.7
0.7527	2.3072	−0.39	1.0411	1.5617	340.5
0.8469	1.7153	0.76	1.0134	1.7329	224.7
0.9311	1.1041	−0.54	1.0025	1.8879	108.6
1.0000	0.5288	0.00	1.0000	2.0249	0.0
$T = 298.15$ K					
0.0000	6.1353	0.00	2.3804	1.0000	0.0
0.1186	5.6731	0.47	1.8986	1.0142	219.3
0.1978	5.3447	−0.10	1.6703	1.0389	327.4
0.3215	4.9079	−0.02	1.4145	1.1010	438.2
0.4404	4.4694	−0.08	1.2495	1.1880	482.2
0.5444	4.0384	−0.19	1.1502	1.2871	473.9
0.6554	3.5153	0.35	1.0783	1.4175	420.5
0.7527	2.9711	−0.40	1.0408	1.5387	348.5
0.8469	2.2298	0.49	1.0134	1.7055	230.5
0.9311	1.4549	−0.30	1.0026	1.8578	111.7
1.0000	0.7256	0.00	1.0000	1.9938	0.0
$T = 303.15$ K					
0.0000	7.8288	0.00	2.2977	1.0000	0.0
0.1186	7.2423	0.49	1.8543	1.0135	214.3
0.1978	6.8209	−0.09	1.6415	1.0369	320.4
0.3215	6.2602	0.02	1.4004	1.0961	429.8
0.4404	5.6948	−0.03	1.2429	1.1794	474.0
0.5444	5.1435	−0.13	1.1473	1.2744	466.9
0.6554	4.4763	0.34	1.0773	1.4000	415.3
0.7527	3.7902	−0.42	1.0405	1.5175	344.8
0.8469	2.8556	0.23	1.0134	1.6802	228.6
0.9311	1.8988	−0.05	1.0026	1.8302	111.0
1.0000	0.9831	0.00	1.0000	1.9654	0.0
$T = 313.15$ K					
0.0000	12.392	0.00	2.1497	1.0000	0.0
0.1186	11.474	0.50	1.7735	1.0121	204.5
0.1978	10.804	−0.06	1.5884	1.0333	306.6
0.3215	9.907	0.11	1.3739	1.0870	413.3
0.4404	8.998	0.05	1.2304	1.1632	458.0
0.5444	8.123	−0.02	1.1416	1.2507	453.1
0.6554	7.069	0.32	1.0754	1.3677	404.9
0.7527	6.009	−0.47	1.0399	1.4782	337.5
0.8469	4.564	−0.25	1.0134	1.6334	224.9
0.9311	3.148	0.43	1.0026	1.7789	109.6
1.0000	1.741	0.00	1.0000	1.9122	0.0
$T = 323.15$ K					
0.0000	18.960	0.00	2.0205	1.0000	0.0
0.1186	17.569	0.51	1.7014	1.0108	194.8
0.1978	16.545	−0.02	1.5403	1.0299	293.0
0.3215	15.163	0.20	1.3496	1.0786	397.0
0.4404	13.756	0.14	1.2189	1.1483	442.1
0.5444	12.417	0.07	1.1362	1.2291	439.3
0.6554	10.813	0.29	1.0735	1.3382	394.6
0.7527	9.228	−0.54	1.0394	1.4423	330.2
0.8469	7.072	−0.93	1.0134	1.5907	221.1
0.9311	5.050	1.34	1.0026	1.7319	108.2
1.0000	2.957	0.00	1.0000	1.8633	0.0
$T = 333.15$ K					
0.0000	28.140	0.00	1.9063	1.0000	0.0
0.1186	26.093	0.50	1.6363	1.0096	185.2
0.1978	24.585	0.04	1.4964	1.0267	279.4
0.3215	22.522	0.28	1.3270	1.0708	380.6
0.4404	20.418	0.22	1.2080	1.1345	426.1
0.5444	18.435	0.15	1.1311	1.2092	425.5
0.6554	16.070	0.25	1.0717	1.3110	384.1
0.7527	13.771	−0.62	1.0388	1.4094	322.8
0.8469	10.650	−1.09	1.0133	1.5413	217.3
0.9311	7.862	1.44	1.0026	1.6885	106.8
1.0000	4.833	0.00	1.0000	1.8179	0.0
$T = 343.15$ K					
0.0000	40.640	0.00	1.8044	1.0000	0.0
0.1186	37.709	0.50	1.5770	1.0085	175.5
0.1978	35.557	0.11	1.4560	1.0238	265.8
0.3215	32.564	0.37	1.3059	1.0635	364.1
0.4404	29.513	0.30	1.1977	1.1217	410.0
0.5444	26.658	0.22	1.1262	1.1906	411.4
0.6554	23.270	0.20	1.0699	1.2858	373.5
0.7527	20.024	−0.72	1.0382	1.3788	315.3
0.8469	15.634	−1.46	1.0133	1.5048	213.3
0.9311	11.915	1.97	1.0027	1.6481	105.3
1.0000	7.634	0.00	1.0000	1.7754	0.0
$T = 353.15$ K					
0.0000	57.270	0.00	1.7127	1.0000	0.0
0.1186	53.170	0.49	1.5226	1.0075	165.6

Table 2. Continued

	p				G^E
x_1	kPa	Δp	γ_1	γ_2	$\mathrm{J\cdot mol^{-1}}$
0.1978	50.187	0.02	1.4185	1.0210	251.9
0.3215	45.957	0.45	1.2861	1.0567	347.3
0.4404	41.649	0.38	1.1878	1.1097	393.5
0.5444	37.645	0.28	1.1215	1.1733	397.1
0.6554	32.914	0.14	1.0682	1.2622	362.5
0.7527	28.443	−0.83	1.0376	1.3503	307.4
0.8469	22.422	−1.80	1.0132	1.4806	209.1
0.9311	17.615	2.52	1.0027	1.6101	103.7
1.0000	11.696	0.00	1.0000	1.7353	0.0
		$T = 363.15$ K			
0.0000	78.937	0.00	1.6296	1.0000	0.0
0.1186	73.325	0.47	1.4723	1.0065	155.7
0.1978	69.292	0.29	1.3835	1.0183	237.8
0.3215	63.451	0.54	1.2672	1.0502	330.2
0.4404	57.512	0.45	1.1783	1.0983	376.7
0.5444	52.027	0.33	1.1169	1.1570	382.2
0.6554	45.572	0.07	1.0664	1.2401	351.1
0.7527	39.549	−0.96	1.0370	1.3234	299.1
0.8469	31.482	−2.11	1.0131	1.4484	204.6
0.9311	25.461	3.09	1.0027	1.5741	101.9
1.0000	17.429	0.00	1.0000	1.6970	0.0

by a differential-pressure null indicator (Validyne, Northridge, CA). The gauge was checked periodically by means of a Hg manometer and a cathetometer (type 7000, Bouty, Paris, France).

Temperatures were measured with a copper−constantan thermocouple calibrated with a platinium resistance thermometer and a Leeds and Northrup bridge. The uncertainties in our measurements are estimated to be ± 0.02 K for the temperature range, 1 % for the pressure range $700 \leq P/\text{Pa} \leq 1300$, and 0.3 % for the pressure range $1300 \leq P/\text{Pa} \leq 200\,000$.

Excess molar enthalpies were measured at $T = 303.15$ K with a C 80 calorimeter (Setaram, France), a Calvet-type microcalorimeter with no vapor space. Mercury was used to separate the two cells, which contained the liquids under study. The performance of the apparatus was checked by determining H^E for (n-hexane + cyclohexane) at $T = 298.15$ K; our results differed from those reported by Marsh[20] by less than 2 %.

3. RESULTS AND DISCUSSION

Table 1 shows the molar volumes of the pure compounds 2-DEEA and n-heptane estimated with the Rackett correlation using the literature data for acentric factor and critical properties together with the mixed virial coefficients. The virial coefficients of the pure compounds were evaluated using the Pitzer correlation.[21] The mixed virial coefficients were obtained using Lorentz−Berthelot combining rules.

Table 3. Coefficients A_i and Pressure Standard Deviations $\sigma(p)$ for the Least-Squares Representation of [2-DEEA (1) + n-heptane (2)] Mixture Using Equation 1

T/K	A_0	A_1	$\sigma(p)$/kPa
273.15	0.9249	−0.1337	0.005341
283.15	0.8622	−0.1134	0.007747
293.15	0.8055	−0.0955	0.01105
298.15	0.7790	−0.0873	0.01331
303.15	0.7536	−0.0795	0.01626
313.15	0.7056	−0.0652	0.02603
323.15	0.6608	−0.0522	0.04553
333.15	0.6186	−0.0404	0.08258
343.15	0.5786	−0.0296	0.1481
353.15	0.5406	−0.0197	0.2577
363.15	0.5041	−0.0106	0.4320

Table 4. Coefficients Λ_{ij} and Pressure Standard Deviations $\sigma(p)$ for the Least-Squares Representation of the [2-DEEA (1) + n-heptane (2)] Mixture Using Equation 2

T/K	Λ_{12}	Λ_{21}	$\sigma(p)$/kPa
273.15	0.2168	0.5884	0.00656
283.15	0.2039	0.5536	0.009131
293.15	0.1945	0.5195	0.01227
298.15	0.1909	0.5027	0.01421
303.15	0.1879	0.4859	0.01666
313.15	0.1839	0.4524	0.02489
323.15	0.1823	0.4185	0.04269
333.15	0.1831	0.3840	0.07844
343.15	0.1864	0.3484	0.1432
353.15	0.1925	0.3110	0.2524
363.15	0.2017	0.2711	0.4267

The results of vapor pressure measurements for the [2-DEEA (1) + n-heptane (2)] mixture at different temperatures are given in Table 2 together with the activity coefficients γ_1 and γ_2 and the values of the excess molar Gibbs energies G^E calculated using Barker's method[22] with the Redlich−Kister equation (eq 1):

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

where x_1 is the mole fraction of 2-DEEA. The values of the parameters A_i and the standard deviation of the pressure $\sigma(p)$ are given in Table 3. The Wilson equation was also used:

$$\frac{G^E}{RT} = -x_1 \ln[x_1 + \Lambda_{12}(1 - x_1)] - (1 - x_1)\ln[(1 - x_1) + \Lambda_{21}x_1] \tag{2}$$

where x_1 is the mole fraction of the diamine. The parameters Λ_{ij} and the corresponding standard deviations $\sigma(p)$ are reported in Table 4. The vapor pressures of n-heptane and 2-DEEA reported in Table 2 were fitted by the least-squares method to the Antoine equation:

$$\log(P/\text{mmHg}) = A - \frac{B}{(T + C)}$$

The values of the Antoine constants and the standard deviation of the fit, σ, are given in Table 5.

Experimental molar excess enthalpies H^E at $T = 303.15$ K for the [2-DEEA (1) + n-heptane (2)] systems are reproduced in

Table 5. Values of the Constants in the Antoine Equation and the Standard Deviation of the Fit

compound	A	B	C	σ
n-heptane	6.947529	1292.684	219.61357	0.10
2-DEEA	7.282963	1592.636	218.25656	0.07

Table 6. Experimental Molar Excess Enthalpies H^E of [2-DEEA (1) + n-Heptane (2)] Mixtures at 303.15 K

x_1	$H^E/J\cdot mol^{-1}$	x_1	$H^E/J\cdot mol^{-1}$
0.0612	283.9	0.5068	998.3
0.1118	482.7	0.6156	905.7
0.1488	600.0	0.7084	766.8
0.2038	749.1	0.7471	686.1
0.2452	840.0	0.8058	562.8
0.3051	927.8	0.8841	362.5
0.4078	1003.8		

Table 7. Coefficients a_i and Standard Deviations $\sigma(H^E)$ for the Least-Squares Representation of H^E of [2-DEEA (1) + n-Heptane (2)] Mixtures at T = 303.15 K Using Equation 4

a_0	a_1	a_2	$\sigma(H^E)/J\cdot mol^{-1}$
4002.1	853.1	304.8	3.0

Table 6. The results obtained were fitted to the smoothing equation

$$H^E_{i,\,calcd} = x_1(1 - x_1)\sum_{i=0}^{n-1} a_i(2x_1 - 1)^i \tag{3}$$

The values of the coefficients a_i and the standard deviation $\sigma(H^E)$, which is given by

$$\sigma(H^E) = \left[\frac{\sum_{i=1}^{N}(H^E_{i,\,calcd} - H^E_{i,\,exptl})^2}{(N - n)}\right]^{1/2} \tag{4}$$

where N is the number of experimental points and n the number of coefficients a_i, were determined by least-squares analysis and are reported in Table 7. The quality of the prediction is expressed in terms of the standard deviation $\sigma(H^E)$ between the experimental and calculated values. The consistency of the model with the measured data can be seen from the small value of $\sigma(H^E)$.

When the $G^E(x_1 = 0.5)/T$ data was fitted with a second-degree polynomial in $1/T$, the derivative at 303.15 K gave H^E = 934 J·mol^{-1} for [2-DEEA (1) + n-heptane (2)]. This result can be compared with the value 998 J·mol^{-1} measured calorimetrically. The agreement is reasonable since the quantitative evaluation of H^E from vapor pressure involves considerable uncertainty.[23]

Group-contribution methods can be used for semiquantitative predictions of activity coefficients of the liquid mixture. The basic idea of the group-contribution methods is that the number of functional groups is much smaller than the number of chemical compounds. Because of the availability of large tables of group-interaction parameters, the UNIFAC group-contribution method has gained widespread popularity in chemical engineering computations. Modified UNIFAC models differ from the original UNIFAC method with respect to the combinatorial term and the temperature dependence of the group-interaction parameters. Using the parameters of the Larsen[29] and Gmehling[30] versions of modified UNIFAC, we calculated values of G^E and H^E. Figure 1 shows the experimental and theoretical G^E and H^E curves at 303.15 K for (2-DEEA + n-heptane). As can be seen, the mixtures exhibit positive deviations. The Gmehling version of the modified UNIFAC model gives slightly better results than the other version.

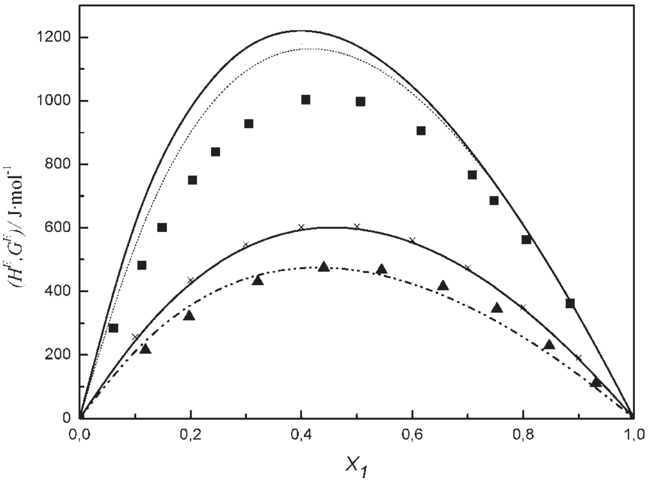

Figure 1. Experimental and predicted molar excess Gibbs energies G^E and molar excess enthalpies H^E at T = 303.15 K for the [2-DEEA (1) + n-heptane (2)] system: ■, experimental values of H^E; ▲, experimental values of G^E; —, modified UNIFAC (Larsen version) for H^E; ----, modified UNIFAC (Gmehling version) for H^E; −×−, modified UNIFAC (Larsen version) for G^E; −·· −, modified UNIFAC (Gmehling version) for G^E.

The difficulties in representing complex systems such unsymmetrical diamines are not surprising because a simple group-contribution method is not able to account for the proximity effect. Disquac, a physical model based on the rigid lattice theory developed by Guggenheim, has been applied to several systems containing complex molecules by considering structure-dependent interaction parameters. In the framework of Disquac, mixtures of a diamine and an alkane are regarded as possessing three types of surfaces: type a, alkane ($-CH_3$ or $-CH_2-$) group; type n, nitrogen ($-N<$) group; type h, nitrogen ($-NH_2$) group. The solvent n-heptane (surface type a) is regarded as a homogeneous molecule and was estimated previously.[24] The relative molecular volume r_1, the surface q_1, and the surface fractions α_{s1} (s = a, n, h) for 2-DEEA (1) are 4.8557, 4.0034, 0.8303, 0.0198, and 0.1498, respectively. The three types of surfaces a, n, and h generate three pairs of contacts: (a, n), (a, h), and (n, h). The equations used to calculate G^E and H^E are the same as in other publications.[25,26] The temperature dependence of the interchange parameters are expressed in terms of dispersive (dis) and/or quasichemical (quac) interchange coefficients $C^{dis}_{st,l}$ and $C^{quac}_{st,l}$, respectively, where s and t are the surfaces types and l = 1 for Gibbs energy and l = 2 for enthalpy. For the contact (a, n), we used the same interaction parameters as reported previously in the literature.[9] For the contact (a, h), the interaction parameters were taken from the literature.[27] For the contact (n, h), we reduced the dispersive coefficients

Table 8. Dispersive ($C^{dis}_{st,l}$) and Quasichemical [$C^{quac}_{st,l}$] Interchange Energy Coefficients for Contacts (a, n), (a, h), and (n, h) for [$(C_2H_5)_2N(CH_2)_uNH_2$] (1) + *n*-Heptane (2)] Mixtures (u = 2, 2-DEEA; u = 3, 3-DEPA)

contact (s, t)	u	$C^{dis}_{st,1}$	$C^{dis}_{st,2}$	$C^{quac}_{st,1}$	$C^{quac}_{st,2}$
(a, n)	2	40	100	2.05	5.9
	3	40	100	3.7	8.2
(a, h)	2	1.2	2.4	2.11	4.9
	3	1.2	2.4	4.19	6.10
(n, h)	2	13	67	0.45	0.005
	3	13	67	0.75	0.009
(n, h) for tertiary amine $(CH_3)_2NCH_2CH_3$ + primary amine $CH_3(CH_2)_3NH_2$		13	67	1.0	0.15

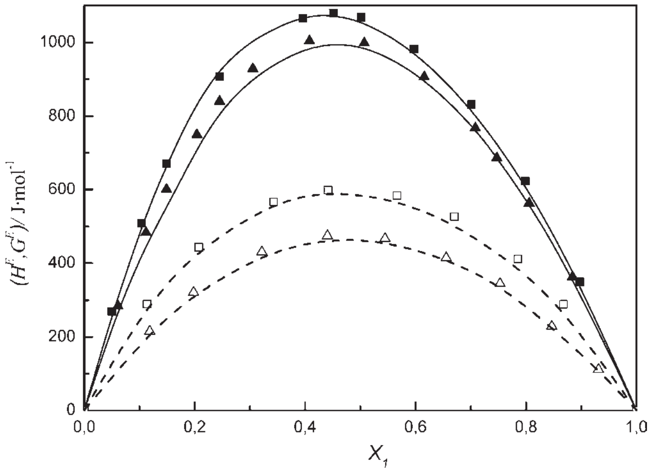

Figure 2. Experimental and predicted molar excess Gibbs energies G^E and molar excess enthalpies H^E at T = 303.15 K: experimental values for the [2-DEEA (1) + *n*-heptane (2)] system (△, G^E; ▲, H^E); experimental values for the [3-DEPA (1) + *n*-heptane (2)] system[28] (□, G^E; ■, H^E); —, Disquac model for H^E; ----, Disquac model for G^E.

$C^{dis}_{nh,l}$ to 13 (l = 1) and 67 (l = 2), and the quasichemical coefficients $C^{quac}_{nh,l}$ were adjusted by fitting the equimolar values of G^E and H^E for our experimental data and that for [3-diethylaminopropylamine (3-DEPA) (1) + *n*-heptane (2)] mixtures reported in the literature.[28] The quasichemical parameters increase with the "distance" between the N atoms and tend toward the limiting values for the monoamines, as shown in Table 8.

As shown in Figure 2, the experimental values of G^E and H^E are in good agreement with those obtained using the Disquac model. The interesting result of this study is the confirmation of the proximity effect in group-contribution methods.

4. CONCLUSION

The vapor pressures of liquid [2-diethylaminoethylamine (2-DEEA) + *n*-heptane] mixtures were measured by a static method between T = (273.15 and 363.15) K at 10 K intervals. The excess molar enthalpies H^E at 303.15 K were also measured. The experimental results have been carefully analyzed and compared with group-contribution models (UNIFAC and Disquac). The experimental values of G^E and H^E were observed to be in good agreement with the results obtained using Disquac model. The proximity effect of N atoms in group-contribution methods has also been demonstrated.

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