

THERMODYNAMIC PROPERTIES OF DIMETHYL SULFOXIDE + BENZENE OR + ISOPROPYLBENZENE MIXTURES

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ABSTRACT

The vapor pressure of binary mixtures of dimethyl sulfoxide + benzene or + isopropyl benzene and of the three pure components were measured by means of a static apparatus at temperatures between 293.15 K and 363.15 K. Molar excess Gibbs energies G^E were calculated for several constant temperatures, and fitted to a third-order Redlich-Kister equation. Calorimetric excess enthalpy H^E measurements for the binary mixtures are also reported at 298.15 K. The data on excess molar Gibbs energies and excess molar enthalpies are examined on the basis of the DISQUAC and Modified UNIFAC group contribution models which provide a fairly consistent description of phase equilibria and the related excess functions.

Keywords: Vapor-liquid equilibria; Excess enthalpy; DISQUAC; UNIFAC; Dimethyl sulfoxide.

INTRODUCTION

The present paper is part of a research program on vapor-liquid equilibria (VLE) and excess enthalpies H^E in mixtures of strongly polar non hydrogen bonded compounds with saturated, unsaturated, and aromatic hydrocarbons [1-7].

The purpose of the present work is to investigate VLE and excess enthalpy H^E in binary mixtures of dimethyl sulfoxide + benzene or + isopropylbenzene and to examine the applicability of the DISQUAC and modified UNIFAC models to the results.

A survey of the literature [8-11] shows that no VLE data are available for dimethyl sulfoxide + isopropylbenzene mixture. Dimethyl sulfoxide + benzene has been investigated isothermally by Kenttämaa et al. [12,13] and Heinrich [14].

Excess enthalpies, H^E , for dimethyl sulfoxide + benzene have been measured by Absood et al. [15], Fenby et al. [16], Kenttämäa et al. [13] and Tanaka [17]. For dimethyl sulfoxide + isopropylbenzene, no calorimetric data are available except molar enthalpies of solution at infinite dilution of isopropylbenzene, as well as benzene, in dimethyl sulfoxide [18,19].

EXPERIMENTAL TECHNIQUE

The experimental vapor pressure, P , data were taken with an apparatus described in detail by Blondel-Telouk et al. [20,21], as a function of the temperature, T , for given constant values of the mole fraction composition, x_i . The apparatus allows measurements in the P range from 27 Pa to $200 \cdot 10^3$ Pa and from 258.15 to 468.15 K. Vapor pressures are measured by means of pressure gauges (Rosemount, Model 1151 DPE 22S2, Minneapolis, Minn., USA), protected by a differential pressure indicator (MKS, Model 615D, MKS Instruments, USA). The pressure gauges were checked periodically by means of a Hg or oil manometer and a Bouty (Paris, France) Type 70298 cathetometer, readings accurate to within 1 Pa. Temperature of oil thermostat was maintained constant to within 0.01 K and was measured by means of a copper-constantan thermocouple calibrated against a Leeds and Northrup standard Pt resistance thermometer 8163-B, provided with the National Bureau of Standards (Washington D.C., USA) certificate, and connected to Mueller type G2 bridge (precision 10^{-4} W). All temperatures are on ITS-90. The estimated uncertainties in P and T are, respectively: $\sigma(P) = 0.15 P$ (if $P/\text{Pa} < 13.3$), $\sigma(P) = 0.05 P$ (in the range $13.3 < P/\text{Pa} < 200$), $\sigma(P) = 0.005 P$ (in the range $200 < P/\text{Pa} < 1000$), $\sigma(P) = 0.002 P$ (in the range $1000 < P/\text{Pa} < 200 \cdot 10^3$), and $\sigma(T) = 0.01$ K.

Mixtures were prepared by mass and thoroughly degassed by distillation as described by Blondel-Tellouk et al. [20,21]. The final composition of the liquid was determined after each measurement of P by GLC on a column filled with Carbowax as stationary phase, using a thermal conductivity detector.

The experimental H^E data were taken at atmospheric pressure by means of a microcalorimeter, model C 80II (SETARAM, Lyon, France). The temperature T (ITS-90) was maintained constant at (298.15 ± 0.02) K. Check measurements on cyclohexane + heptane are in agreement to within 2 % (over the entire range of concentration) with the data reported by Marsh [22]. The estimated uncertainties in the mole fraction composition x_i and H^E are, respectively, $\sigma(x_i) = 0.0002$ and $\sigma(H^E) = 5 \text{ J mol}^{-1}$.

MATERIALS

The chemical substances were supplied by Janssen Chimica (Geel, Belgium) and Aldrich Chem. (Milwaukee, WI, USA) and were used without further purification. The mole fraction purities, tested by GLC, were: dimethyl sulfoxide (Janssen, > 99 %), benzene (Janssen, ~ 99 %) and isopropylbenzene (Aldrich, > 99 %).

RESULTS

Table 1 lists, for the pure components dimethyl sulfoxide, benzene and isopropylbenzene, the vapor pressures measured in this work, between 293.15 K and 363.15 K, together with the molar volumes extrapolated from the densities [23-27] and the second molar virial coefficients estimated by the method of Tsonopoulos [28,29] using the literature data for acentric factor and critical properties of pure compounds [23-27].

Our vapor pressure data for the pure liquid components agree with those reported in the literature [30-33]

Table 2 gives, for dimethyl sulfoxide + benzene or + isopropylbenzene mixtures, experimental data for total vapor pressures at different temperatures together with the corresponding compositions of the liquid and vapor phases, the activity coefficients γ_1 and γ_2 , and the values of the excess molar Gibbs energies G^E calculated by Barker's method [34], using the Redlich-Kister equation (1)

$$G^E = x_1 x_2 \sum_{j=1}^m R T G_j (x_1 - x_2)^{j-1} \quad (1)$$

where x_1 is the molar fraction for dimethyl sulfoxide

Table 3 lists the values G_j for the two binary mixtures.

All binary mixtures exhibit positive deviations. The equimolar G^E of dimethyl sulfoxide + benzene increases with increasing temperature from 804 J mol⁻¹ (293.15 K) to 850 J mol⁻¹ (363.15 K). The equimolar G^E of dimethyl sulfoxide + isopropylbenzene is almost independent from temperature, 1325 J mol⁻¹ at 293.15 K and 1336 J mol⁻¹ at 363.15 K (Figures 1 and 2).

Our excess Gibbs energy, G^E , for dimethyl sulfoxide + benzene, at 298.15 K agree to within 2 % with literature data [12, 14].

Table 1 : Molar volumes V^ ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$), vapor pressures P^* (kPa) and second molar virial Coefficients, B_{ii} ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$) for pure compounds.*

T (K)	Dimethyl sulfoxide			Benzene			Isopropylbenzene		
	V^*	P^*	B_{ii}	V^*	P^*	B_{ii}	V^*	P^*	B_{ii}
293.15	71.0	0.056	-6422	88.9	10.029	-1624	139.5	0.456	-5151
298.15	71.4	0.082	-5870	89.4	12.707	-1543	140.2	0.622	-4802
303.15	71.7	0.115	-5386	89.9	15.946	-1469	140.9	0.838	-4491
313.15	72.3	0.224	-4583	91.0	24.452	-1340	142.2	1.472	-3963
323.15	73.0	0.414	-3952	92.1	36.312	-1230	143.7	2.481	-3535
333.15	73.7	0.733	-3449	93.2	52.403	-1135	145.1	4.030	-3182
343.15	74.5	1.248	-3043	94.4	73.714	-1053	146.7	6.332	-2887
353.15	75.6	2.054	-2711	95.7	101.332	-980	148.3	9.659	-2637
363.15	76.8	3.276	-2436	97.0	136.436	-916	149.9	14.340	-2424

Experimental molar excess enthalpies H^E of the binary mixtures are listed in Table 4. The results have been fitted to the smoothing equation:

$$H_{i,\text{exp}}^E = x_1 (1 - x_1) \sum_{i=0}^{n-1} H_i (2x_1 - 1)^i \quad (2)$$

The values of the coefficients H_i and the standard deviations $\sigma(H^E)$ are given by :

$$\sigma(H^E) = \left[\sum_{i=1}^N (H_{i,\text{exp}}^E - H_{i,\text{calc}}^E)^2 / (N - n) \right]^{1/2} \quad (3)$$

where N is the number of experimental points and n the number of coefficients H_i ; they are determined by least-square analysis and are reported in Table 5.

The molar excess enthalpy, H^E , of dimethyl sulfoxide + isopropylbenzene is considerably larger than for dimethyl sulfoxide + benzene, due to the partially aliphatic character of isopropylbenzene (Figure 3).

Our H^E data for dimethyl sulfoxide + benzene at 298.15 K are in good agreement with those reported by Kenttämaa et al. [13].

Table 2 : Values of the vapor pressure P (Pa), standard deviations $\delta P/P$ (%), activity coefficients γ_1 and γ_2 and excess molar Gibbs energies G^E (J mol^{-1}).

T(K)	x_1	y_1	P	$\delta P / P$	γ_1	γ_2	G^E
Dimethyl sulfoxide (1) + benzene (2)							
293.15	0,1114	0,0022	9325,2	0,55	3,2621	1,0388	403,4
	0,2165	0,0031	8823,4	-0,04	2,1943	1,1208	632,5
	0,3197	0,0037	8361,9	-0,23	1,7154	1,2252	757,3
	0,4107	0,0044	7911,0	-0,02	1,4767	1,3349	805,1
	0,5132	0,0052	7288,3	0,00	1,3009	1,4879	800,6
	0,6260	0,0064	6493,1	0,41	1,1675	1,7171	729,1
	0,7400	0,0084	5343,0	-0,56	1,0754	2,0498	586,0
	0,8362	0,0121	4040,2	0,36	1,0271	2,4311	409,2
	0,9060	0,0196	2636,9	-0,10	1,0079	2,7592	250,0
298.15	0,1114	0,0025	11803,8	0,51	3,2147	1,0381	404,8
	0,2165	0,0035	11162,8	-0,04	2,1746	1,1189	635,1
	0,3197	0,0043	10569,1	-0,22	1,7048	1,2219	760,7
	0,4107	0,0050	9993,2	0,00	1,4695	1,3302	808,8
	0,5132	0,0060	9196,1	0,00	1,2961	1,4813	804,1
	0,6260	0,0074	8178,3	0,39	1,1646	1,7067	732,0
	0,7400	0,0097	6715,3	-0,55	1,0740	2,0321	588,0
	0,8362	0,0139	5065,6	0,37	1,0266	2,4031	410,4
	0,9060	0,0225	3301,0	-0,10	1,0078	2,7209	250,6
303.15	0,1114	0,0028	14799,8	0,46	3,1694	1,0375	406,3
	0,2165	0,0039	13988,7	-0,04	2,1557	1,1171	637,8
	0,3197	0,0048	13232,7	-0,22	1,6945	1,2187	764,1
	0,4107	0,0057	12503,9	0,02	1,4627	1,3257	812,5
	0,5132	0,0068	11493,7	0,00	1,2916	1,4748	807,7
	0,6260	0,0084	10204,1	0,37	1,1619	1,6965	735,0

Table 2 (continued)

T(K)	x_1	y_1	P	$\delta P / P$	γ_1	γ_2	G^E
Dimethyl sulfoxide (1) + benzene (2)							
313.15	0,7400	0,0110	8361,7	-0,55	1,0728	2,0151	590,2
	0,8362	0,0159	6294,0	0,38	1,0261	2,3765	411,7
	0,9060	0,0258	4096,5	-0,11	1,0076	2,6850	251,4
	0,1114	0,0035	22661,6	0,37	3,0794	1,0365	409,2
	0,2165	0,0049	21396,9	-0,05	2,1157	1,1138	642,4
	0,3197	0,0061	20206,1	-0,19	1,6735	1,2125	769,9
	0,4107	0,0072	19067,5	0,11	1,4498	1,3162	818,8
	0,5132	0,0086	17448,7	-0,13	1,2837	1,4608	814,1
323.15	0,6260	0,0107	15476,3	0,42	1,1574	1,6755	740,8
	0,7400	0,0142	12634,5	-0,54	1,0704	1,9826	594,5
	0,8362	0,0206	9476,1	0,37	1,0251	2,3279	414,3
	0,9060	0,0334	6158,5	-0,11	1,0073	2,6190	252,7
	0,1114	0,0043	33613,3	0,32	3,0064	1,0353	412,2
	0,2165	0,0061	31703,4	-0,04	2,0854	1,1105	648,3
	0,3197	0,0076	29891,7	-0,20	1,6563	1,2071	777,5
	0,4107	0,0090	28166,1	0,06	1,4378	1,3089	826,9
333.145	0,5132	0,0108	25780,1	0,00	1,2756	1,4502	821,8
	0,6260	0,0135	22745,1	0,31	1,1528	1,6581	747,2
	0,7400	0,0179	18505,6	-0,55	1,0686	1,9525	599,3
	0,8362	0,0261	13840,7	0,42	1,0246	2,2818	417,7
	0,9060	0,0423	8991,0	-0,13	1,0072	2,5601	254,9
	0,1114	0,0052	48462,6	0,27	2,9337	1,0343	415,2
	0,2165	0,0074	45660,4	-0,05	2,0530	1,1077	653,3
	0,3197	0,0093	42987,4	-0,18	1,6387	1,2018	783,8
343.15	0,4107	0,0110	40444,0	0,07	1,4264	1,3011	833,8
	0,5132	0,0134	36944,0	0,00	1,2685	1,4386	828,5
	0,6260	0,0168	32503,3	0,29	1,1488	1,6403	753,2
	0,7400	0,0224	26363,7	-0,55	1,0668	1,9242	603,9
	0,8362	0,0326	19675,3	0,44	1,0240	2,2399	420,8
	0,9060	0,0528	12785,8	-0,14	1,0070	2,5057	256,7
	0,1114	0,0062	68118,1	0,23	2,8656	1,0335	418,1
	0,2165	0,0090	64111,9	-0,06	2,0221	1,1050	658,1
353.15	0,3197	0,0113	60275,4	-0,17	1,6218	1,1969	789,8
	0,4107	0,0134	56619,8	0,08	1,4156	1,2937	840,2
	0,5132	0,0163	51621,2	0,01	1,2618	1,4276	834,9
	0,6260	0,0206	45297,1	0,28	1,1451	1,6233	758,9
	0,7400	0,0275	36638,1	-0,55	1,0651	1,8974	608,2
	0,8362	0,0402	27298,5	0,46	1,0233	2,2007	423,6
	0,9060	0,0649	17757,9	-0,15	1,0068	2,4547	258,4
	0,1114	0,0074	93581,6	0,18	2,8012	1,0327	420,8
363.15	0,2165	0,0107	87986,8	-0,07	1,9922	1,1025	662,6
	0,3197	0,0135	82614,4	-0,15	1,6054	1,1921	795,4
	0,4107	0,0162	77479,9	0,09	1,4052	1,2865	846,2
	0,5132	0,0198	70510,6	0,01	1,2554	1,4169	840,8
	0,6260	0,0249	61720,2	0,26	1,1414	1,6070	764,1
	0,7400	0,0335	49793,9	-0,56	1,0633	1,8720	612,1
	0,8362	0,0489	37056,8	0,49	1,0227	2,1634	426,2
	0,9060	0,0788	24143,3	-0,16	1,0066	2,4060	259,9
363.15	0,1114	0,0086	125938,4	0,15	2,7398	1,0319	423,4
	0,2165	0,0127	118289,1	-0,08	1,9632	1,1001	666,7
	0,3197	0,0161	110931,2	-0,13	1,5894	1,1876	800,4
	0,4107	0,0193	103869,3	0,09	1,3950	1,2796	851,5

Table 2 (continued)

T(K)	x_1	y_1	P	$\delta P / P$	γ_1	γ_2	G^E
Dimethyl sulfoxide (1) + benzene (2)							
	0,5132	0,0237	94361,0	0,02	1,2490	1,4066	846,1
	0,6260	0,0299	82406,5	0,25	1,1378	1,5914	768,6
	0,7400	0,0402	66326,8	-0,57	1,0615	1,8478	615,5
	0,8362	0,0588	49320,4	0,51	1,0219	2,1278	428,2
	0,9060	0,0944	32196,9	-0,18	1,0064	2,3587	260,9
Dimethyl sulfoxide (1) + isopropylbenzene (2)							
293.15	0,1050	0,0823	469,7	0,85	6,4790	1,0477	579,8
	0,2687	0,0973	458,5	-0,27	2,9524	1,2451	1099,8
	0,4278	0,1044	448,9	-0,41	1,9525	1,5480	1307,2
	0,5235	0,1085	443,7	-0,01	1,6320	1,8216	1321,5
	0,6089	0,1114	439,8	0,44	1,4211	2,1829	1265,8
	0,7510	0,1170	423,0	-0,25	1,1722	3,2999	1015,4
	0,9000	0,1562	333,9	0,04	1,0284	6,1816	505,5
298.15	0,1050	0,0845	641,5	0,77	6,3049	1,0470	581,1
	0,2687	0,1010	626,2	-0,28	2,9042	1,2414	1102,1
	0,4278	0,1092	612,6	-0,34	1,9315	1,5388	1309,4
	0,5235	0,1140	604,2	0,03	1,6188	1,8061	1323,4
	0,6089	0,1175	596,8	0,33	1,4128	2,1580	1267,4
	0,7510	0,1245	571,8	-0,20	1,1692	3,2392	1016,5
	0,9000	0,1675	448,7	0,03	1,0280	6,0065	506,1
303.15	0,1050	0,0866	865,5	0,69	6,1387	1,0462	582,2
	0,2687	0,1047	845,0	-0,29	2,8584	1,2376	1104,2
	0,4278	0,1140	825,9	-0,28	1,9114	1,5297	1311,6
	0,5235	0,1195	813,0	0,05	1,6061	1,7912	1325,3
	0,6089	0,1237	800,4	0,25	1,4049	2,1341	1269,0
	0,7510	0,1322	763,9	-0,16	1,1663	3,1815	1017,6
	0,9000	0,1790	596,4	0,03	1,0276	5,8411	506,6
313.15	0,1050	0,0906	1522,3	0,55	5,8271	1,0447	583,8
	0,2687	0,1120	1487,0	-0,30	2,7732	1,2300	1107,7
	0,4278	0,1237	1451,0	-0,17	1,8739	1,5119	1315,4
	0,5235	0,1306	1423,5	0,09	1,5823	1,7626	1328,7
	0,6089	0,1362	1393,7	0,10	1,3896	2,0889	1271,8
	0,7510	0,1478	1320,8	-0,09	1,1606	3,0739	1019,3
	0,9000	0,2027	1021,5	0,01	1,0268	5,5352	507,5
323.15	0,1050	0,0944	2569,0	0,42	5,5400	1,0432	584,6
	0,2687	0,1193	2511,3	-0,29	2,6950	1,2224	1110,2
	0,4278	0,1333	2446,9	-0,07	1,8393	1,4947	1318,4
	0,5235	0,1417	2393,1	0,11	1,5600	1,7355	1331,3
	0,6089	0,1489	2332,8	-0,01	1,3752	2,0467	1273,9
	0,7510	0,1637	2196,5	-0,03	1,1551	2,9752	1020,5
	0,9000	0,2270	1685,7	0,01	1,0260	5,2570	507,9
333.145	0,1050	0,0978	4177,9	0,30	5,2738	1,0416	584,7
	0,2687	0,1265	4087,9	-0,27	2,6224	1,2148	1111,7
	0,4278	0,1430	3977,7	0,02	1,8069	1,4780	1320,4
	0,5235	0,1529	3879,6	0,11	1,5390	1,7097	1333,0
	0,6089	0,1616	3768,6	-0,09	1,3614	2,0070	1275,0
	0,7510	0,1800	3527,5	0,01	1,1497	2,8838	1020,7
	0,9000	0,2519	2689,9	0,00	1,0251	5,0013	507,7
343.15	0,1050	0,1010	6572,4	0,20	5,0259	1,0401	584,1
	0,2687	0,1335	6438,0	-0,24	2,5542	1,2073	1112,0
	0,4278	0,1526	6256,6	0,09	1,7764	1,4619	1321,2

Table 2 (continued)

T(K)	x_1	y_1	P	$\delta P / P$	γ_1	γ_2	G^E
Dimethyl sulfoxide (1) + isopropylbenzene (2)							
353.15	0,5235	0,1641	6087,2	0,10	1,5189	1,6850	1333,6
	0,6089	0,1744	5897,0	-0,15	1,3480	1,9695	1275,1
	0,7510	0,1964	5489,5	0,05	1,1443	2,7986	1019,9
	0,9000	0,2772	4164,1	-0,01	1,0242	4,7638	506,9
	0,1050	0,1040	10034,5	0,11	4,7942	1,0386	582,7
	0,2687	0,1404	9841,3	-0,21	2,4897	1,2000	1111,1
	0,4278	0,1621	9553,1	0,16	1,7473	1,4461	1320,8
	0,5235	0,1752	9273,8	0,08	1,4995	1,6612	1332,9
	0,6089	0,1871	8965,2	-0,18	1,3350	1,9338	1273,9
	0,7510	0,2130	8303,7	0,07	1,1388	2,7187	1017,9
363.15	0,9000	0,3028	6271,6	-0,01	1,0233	4,5417	505,3
	0,1050	0,1066	14911,3	0,03	4,5770	1,0371	580,7
	0,2687	0,1471	14643,4	-0,18	2,4282	1,1928	1109,0
	0,4278	0,1716	14199,8	0,21	1,7193	1,4308	1318,9
	0,5235	0,1863	13756,7	0,04	1,4807	1,6383	1330,8
	0,6089	0,1999	13278,4	-0,20	1,3222	1,8998	1271,3
	0,7510	0,2296	12241,3	0,09	1,1333	2,6433	1014,6
	0,9000	0,3287	9213,0	-0,02	1,0223	4,3325	502,7

Table 3 : Coefficients G_j and standard deviations, σ (kPa) for least-squares representations by Eq. (1)

T (K)	G_1	(σ)	G_2	(σ)	G_3	(σ)	G_4	(σ)
Dimethyl sulfoxide (1) + benzene (2)								
293,15	1,32010	(0,004)	-0,20962	(0,009)	0,20013	(0,015)	-0,14487	(0,026)
298,15	1,30377	(0,004)	-0,20862	(0,008)	0,19466	(0,014)	-0,14108	(0,025)
303,15	1,28798	(0,004)	-0,20738	(0,008)	0,18976	(0,014)	-0,13754	(0,024)
313,15	1,25671	(0,004)	-0,20172	(0,008)	0,18199	(0,013)	-0,13654	(0,024)
323,15	1,22946	(0,004)	-0,20094	(0,008)	0,17432	(0,013)	-0,12568	(0,023)
333,15	1,20238	(0,004)	-0,19723	(0,007)	0,16823	(0,013)	-0,12118	(0,023)
343,15	1,17637	(0,004)	-0,19348	(0,007)	0,16272	(0,013)	-0,11764	(0,023)
353,15	1,15113	(0,004)	-0,18982	(0,008)	0,15742	(0,013)	-0,11509	(0,023)
363,15	1,12644	(0,004)	-0,18640	(0,008)	0,15206	(0,013)	-0,11354	(0,024)
Dimethyl sulfoxide (1)+ isopropylbenzene (2)								
293,15	2,17502	(0,008)	-0,05085	(0,016)	0,38679	(0,031)	-0,15170	(0,057)
298,15	2,14184	(0,007)	-0,05278	(0,014)	0,38155	(0,028)	-0,14755	(0,051)
303,15	2,10962	(0,006)	-0,05440	(0,013)	0,37588	(0,025)	-0,14337	(0,045)
313,15	2,04763	(0,005)	-0,05690	(0,010)	0,36340	(0,019)	-0,13499	(0,036)
323,15	1,98839	(0,004)	-0,05863	(0,008)	0,34962	(0,016)	-0,12687	(0,029)
333,15	1,93131	(0,003)	-0,05984	(0,007)	0,33476	(0,013)	-0,11923	(0,024)
343,15	1,87598	(0,003)	-0,06076	(0,006)	0,31899	(0,012)	-0,11229	(0,022)
353,15	1,82203	(0,003)	-0,06160	(0,006)	0,30246	(0,011)	-0,10623	(0,021)
363,15	1,76918	(0,003)	-0,06242	(0,006)	0,28526	(0,011)	-0,10119	(0,021)

Table 4 : Experimental molar excess enthalpies at 298.15 K

Dimethyl sulfoxide (1) + benzene (2)		Dimethyl sulfoxide(1)+isopropylbenzene (2)	
x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)
0.1334	314.8	0.1045	537.5
0.2377	451.2	0.2153	871.2
0.3566	546.1	0.3249	1049.5
0.4018	567.3	0.4383	1132.0
0.4540	581.7	0.5178	1152.2
0.4975	594.0	0.6062	1128.2
0.5397	589.2	0.6062	1125.7
0.5604	581.1	0.6836	1045.5
0.6517	542.8	0.7862	865.7
0.7472	462.2	0.9176	426.3
0.8330	349.6		
0.9191	198.6		

Table 5 : Coefficients H_i and standard deviations, $\sigma(H^E)$ (J mol⁻¹) for least-squares representations by Eq. (2) of H^E at 298.15 K.

Mixtures	H_1	H_2	H_3	H_4	H_5	$\sigma(H^E)$
Dimethyl sulfoxide(1) + benzene (2)	2360.5	47.7	239.6	-295.5	549.6	0.2
Dimethylsulfoxide(1)+isopropylbenzene(2)	4606.5	128.3	1663.7	-393.5		0.3

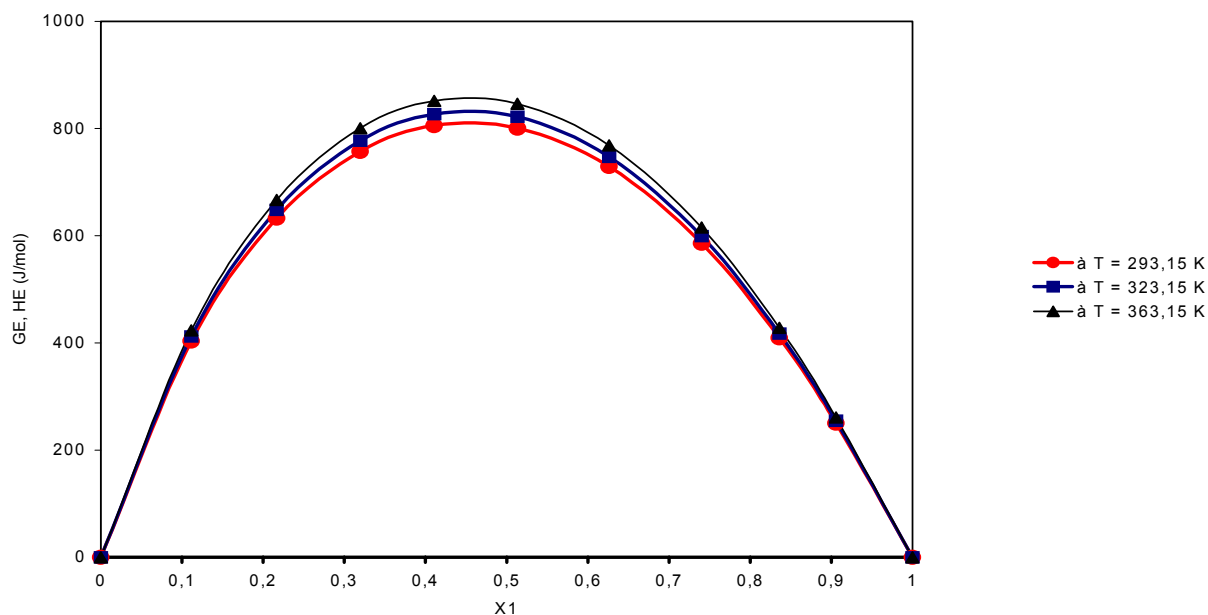


Figure 1 : Experimental molar excess Gibbs energy, G^E , of dimethyl sulfoxide + benzene mixtures as a function of the mole fraction, x_1 , of dimethyl sulfoxide at different temperatures.

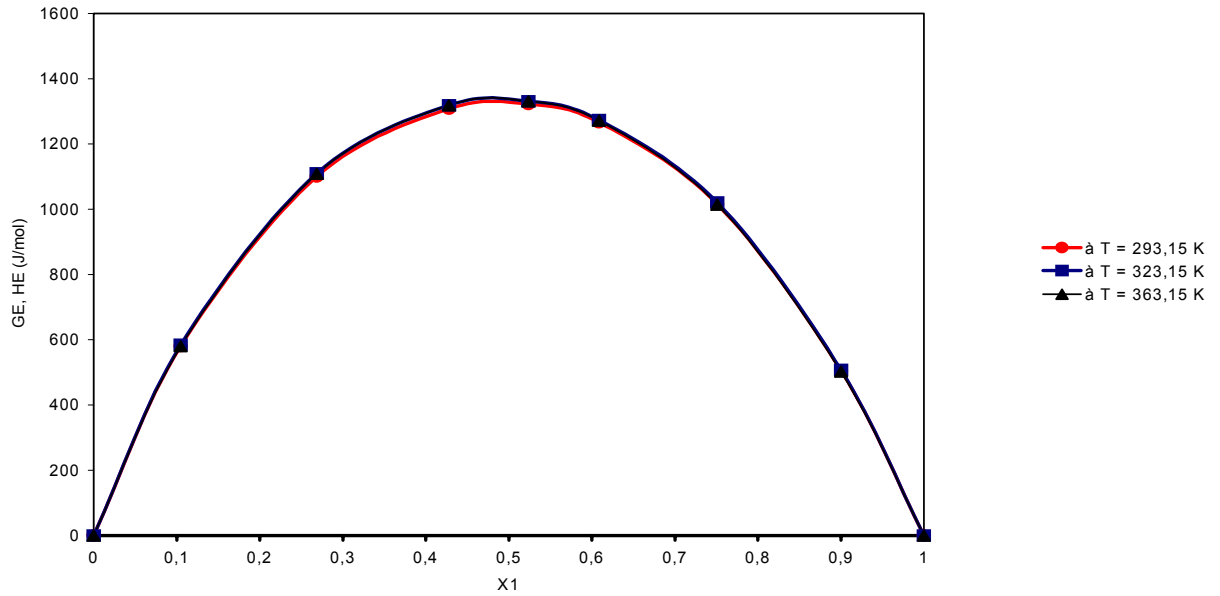


Figure 2 : Experimental molar excess Gibbs energy, G^E , of dimethyl sulfoxide + isopropylbenzene mixtures as a function of the mole fraction, x_1 , of dimethyl sulfoxide at different temperatures.

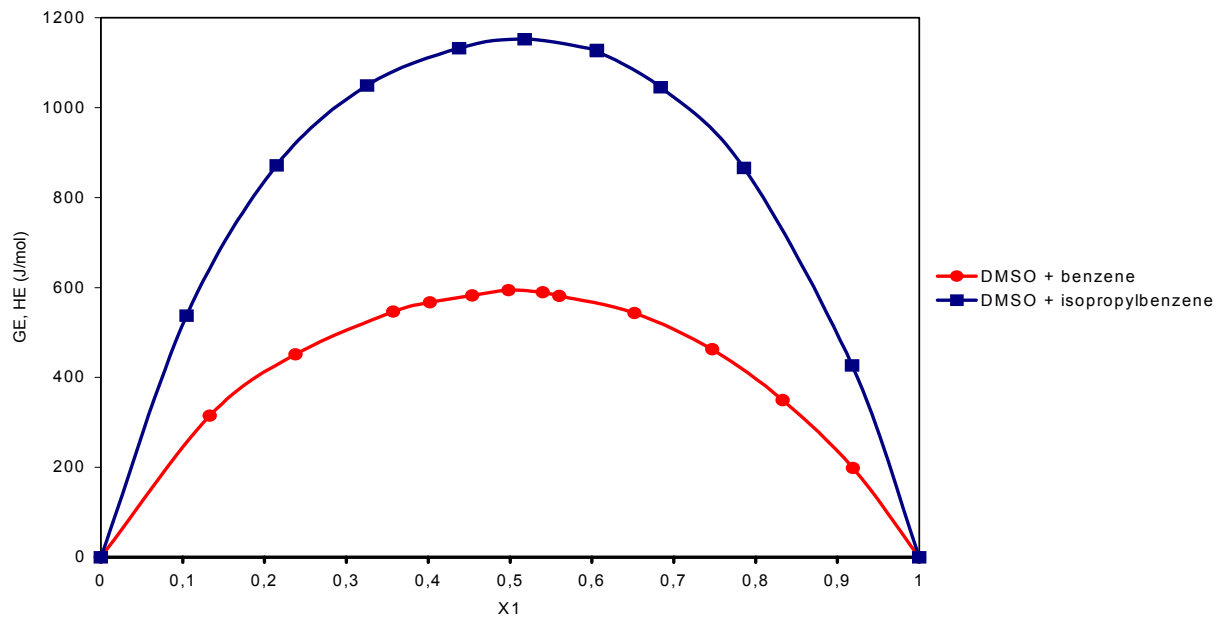


Figure 3 : Experimental molar excess enthalpy, H^E , of dimethyl sulfoxide + benzene or + isopropylbenzene mixtures as a function of the mole fraction, x_1 , of dimethyl sulfoxide at 298,15 K

THEORY

Application of the DISQUAC model

The molecules under study, i.e., dimethyl sulfoxide, benzene or isopropylbenzene are regarded as possessing four types of surfaces: (1) type a (CH₃ and CH groups in dimethyl sulfoxide and isopropylbenzene); (2) type b (C₆H₆ in benzene); (3) type p (C₆H₅ in isopropylbenzene); (4) type n (SO group in dimethyl sulfoxide).

Table 6 : Relative group increments for molecular volumes, $r_G = V_G / V_{CH_4}$, and areas, $q_G = A_G / V_{CH_4}$, calculated by the method of Bondi [38], ($V_{CH_4} = 17.12 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$; $A_{CH_4} = 2.90 \times 10 \text{ m}^2 \text{ mol}^{-1}$).

Group	r_G	q_G
-H	0.20094	0.26552
-CH ₃	0.79848	0.73103
C ₆ H ₆	2.82480	2.07240
C ₆ H ₅	2.67757	1.83793
SO	0.90771	0.66897

The equations used to calculate excess Gibbs energies and excess enthalpies, G^E and H^E are the same as in other publications [35-37]. The temperature dependence of the interaction parameters is expressed in terms of the dispersive (DIS) or quasichemical (QUAC) interchange coefficients $C_{st,l}^{DIS}$ and $C_{st,l}^{QUAC}$, where s, t = a, b, p or n and l = 1 (Gibbs energy) or l = 2 (enthalpy). Heat capacity coefficients, l = 3, have not been considered.

The relative molecular volumes, r_i , the surfaces, q_i , and the surface fractions, α_{si} , of all the molecular species have been calculated on the basis of the group volumes and surfaces recommended by Bondi (38), taking arbitrarily the volume and surface of methane as unity [35]. The applied values are shown in Tables 6 and 7.

The dispersive (a,b) and (a,p) interaction parameters were taken as determined before [39, 3] and the (a,n) model parameters were estimated from infinite dilution activity coefficients data of dimethyl sulfoxide + heptane [14].

The (b,n) and (p,n) interaction parameters, i.e., for dimethyl sulfoxide + benzene or + isopropylbenzene, were adjusted to the equimolar G^E and H^E values obtained in this work. All quasichemical interchange coefficients were assumed equal to zero (Table 8).

Table 7: Volumes r_i , total surfaces q_i , and molecular surface fractions α_{si} , calculated from the group increments r_G and q_G given in Table 6

Compound	r_i	q_i	α_{ai}	α_{bi}	α_{pi}	α_{ni}
Dimethyl sulfoxide	2.5047	2.1310	0.6861	0.0000	0.0000	0.3139
Benzene	2.8248	2.0724	0.0000	1.0000	0.0000	0.0000
Isopropylbenzene	4.6706	3.4965	0.4744	0.000	0.5256	0.0000

Table 8 : Interchange energy coefficients, dispersive $C_{sn,l}^{DIS}$ and quasichemical $C_{sn,l}^{QUAC}$, ($l = 1$, Gibbs energy; $l = 2$, enthalpy) for contacts (s,n), $s = b$ or p (type b , C_6H_6 in benzene; type p , C_6H_5 in isopropylbenzene; type n , SO in dimethyl sulfoxide)

System	$C_{bn,1}^{DIS}$	$C_{bn,2}^{DIS}$	$C_{bn,1}^{QUAC}$	$C_{bn,2}^{QUAC}$
Dimethyl sulfoxide (1) + benzene (2)	10.30	15.02	0.00	0.00
Dimethyl sulfoxide (1) + isopropylbenzene (2)	10.13	12.19	0.00	0.00

As expected [40], the enthalpic parameter decreases from benzene (15.02) to isopropylbenzene (12.19) due to the increasing inductive effect of the alkyl group (stronger dipole-induced dipole interaction). The Gibbs energy parameter changes but slightly from 10.30 (benzene) to 10.13 (isopropylbenzene).

Application of the Modified UNIFAC (Dortmund) model

The modified UNIFAC [41-44] group contribution method based on the local composition concept has temperature-dependent parameters and needs four parameters per contact (two for Gibbs energy and two for enthalpy) to reproduce G^E and H^E . The equations used to calculate the excess properties are the same as in other applications [43, 44]. The group interaction parameters are all available.

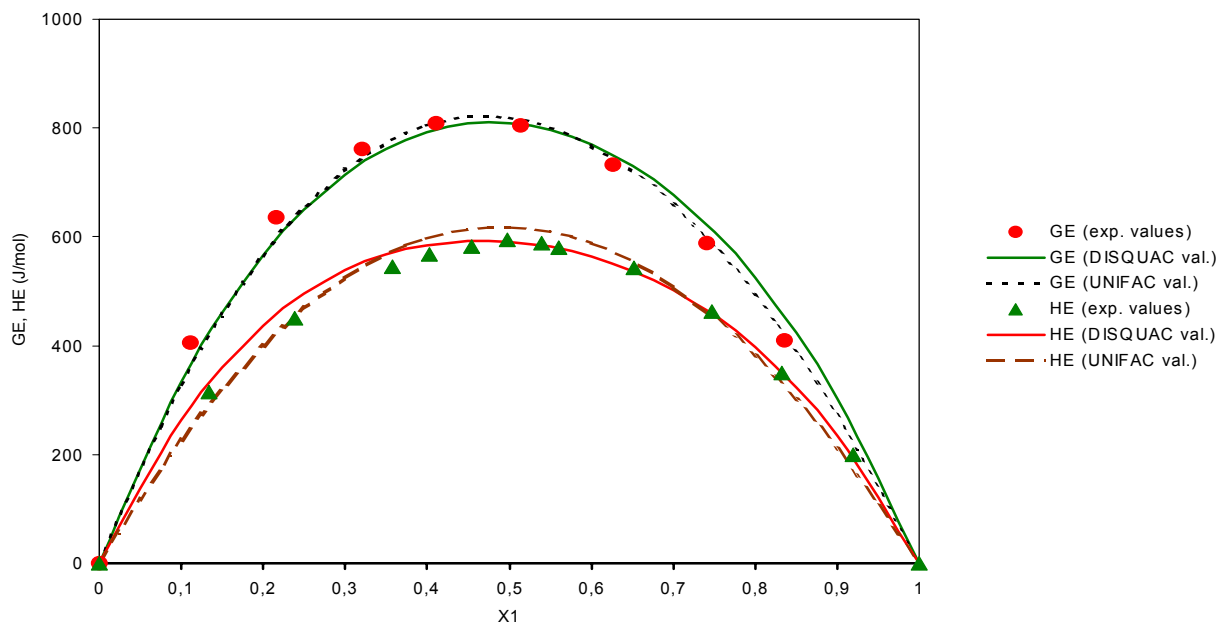


Figure 4. Comparison of theory with experiment for the molar excess Gibbs energy G^E and the molar excess enthalpy H^E , at 298.15 K, of dimethyl sulfoxide + benzene mixtures versus x_1 , the mole fraction of dimethyl sulfoxide.

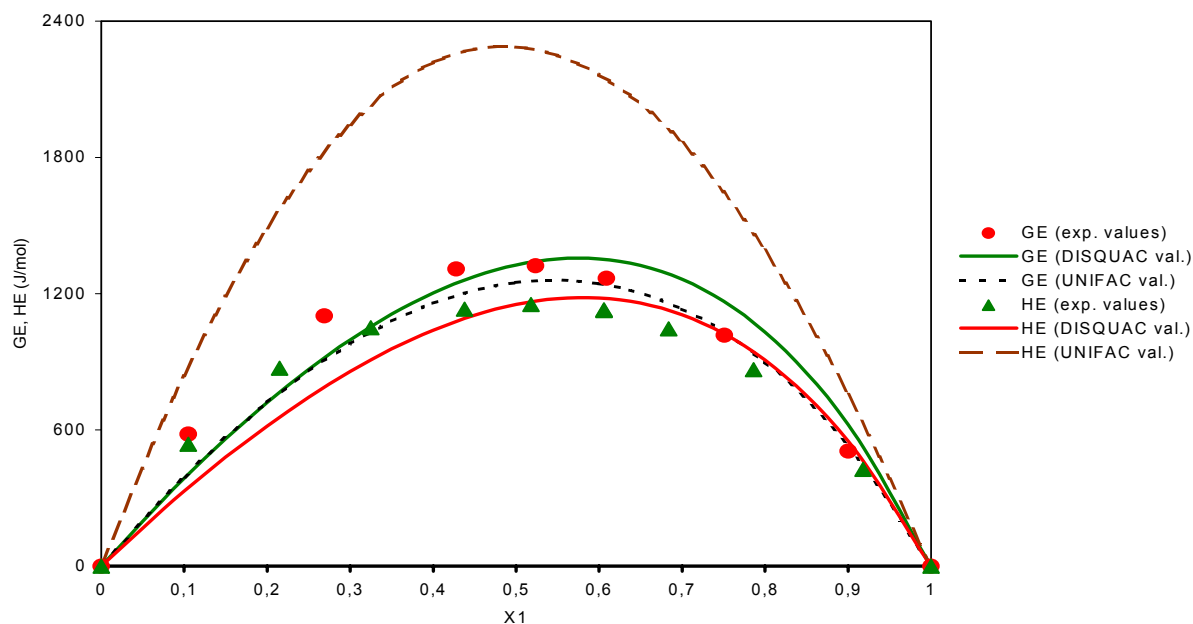


Figure 5. Comparison of theory with experiment for the molar excess Gibbs energy G^E and the molar excess enthalpy H^E , at 298.15 K, of dimethyl sulfoxide + isopropylbenzene mixtures versus x_1 , the mole fraction of dimethyl sulfoxide.

COMPARISON WITH EXPERIMENT AND DISCUSSION

The G^E and H^E properties are represented by DISQUAC within better 2 % over central range of concentration: The difference between G^E (exp) and G^E (cal) rarely exceed 20 J mol^{-1} . The calculated excess enthalpies H^E agree within 60 J mol^{-1} with the measurements. The model reproduces fairly well the shapes of both excess functions.

The prediction of G^E by UNIFAC is quite satisfactory for the two systems. The difference between G^E (experimental) and G^E (calculated) doesn't exceed 70 J mol^{-1} . For H^E , the experimental values are 20 to 1000 J mol^{-1} different than those obtained by the model.

The comparison between experimental data, DISQUAC and Modified UNIFAC results is presented in a graphical way in Figures 4 and 5.

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