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Activity coefficients and excess Gibbs free energies for binary mixtures of N,N-dimethylformamide with substituted benzenes

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Abstract

Vapour–liquid equilibrium (VLE) and boiling point data have been measured for binary mixtures of *N,N*-dimethylformamide with substituted benzenes, of different compositions, in a Swietoslawski-type ebulliometer. The mixtures include *N,N*-dimethylformamide with ethylbenzene; as well as chlorobenzene, and bromobenzene, with aniline. The measurements were made at 712 mm Hg. The experimental temperature–mole fraction data were used to estimate Wilson parameters, These, in turn, were used to calculate vapour compositions, boiling points and activity coefficients, from which the excess Gibbs free energies G^E were calculated. The observed and calculated values are interpreted in terms of specific interaction.

Keywords: Activity coefficients; Binary mixtures; Boiling points; Excess Gibbs free energies; *N,N*-Dimethylformamide; Substituted benzenes; Vapour–liquid equilibrium; Wilson parameters

1. Introduction

Vapour–liquid equilibria are required both for practical use, such as in the design and operation of distillation equipment, and for theoretical use, to determine the thermodynamic properties of mixtures. Evaporation has been employed as an effective means of separation in chemical processing. An accurate and complete knowledge of

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VLE data on the mixtures under consideration is necessary for the design of distillation equipment. Generally, VLE data are obtainable under two fixed conditions, isothermal and isobaric. Most distillation processes are conducted at constant pressure rather than constant temperature. Therefore, isobaric vapour–liquid equilibria data for the binary mixtures *N*,*N*-dimethylformamide with ethylbenzene, bromobenzene, chlorobenzene and aniline at 712 mm Hg are presented in this communication. It has been noticed that the specific interactions between unlike molecules are related to chemical properties and structures of liquids and liquid mixtures [1,2].

2. Experimental

All the chemicals used were of analytical grade. *N*,*N*-dimethylformamide, ethylbenzene, bromobenzene, chlorobenzene and aniline were purified as described previously [3,4]. The purity of the samples was checked by measuring densitites and boiling points. The densities were measured using a standard bicapillary pycnometer, giving an accuracy of two parts in 10^5. Boiling points were measured using a Swietoslawski-type ebulliometer, giving an accuracy of $\pm 0.2°C$. The measured values are in good agreement with literature values [5,6] and are included in Table 1.

The vapour–liquid equilibrium measurements were studied in a Swietoslawski-type ebulliometer [7] connected to a vacuum system. Pressures were measured using a mercury manometer which gave an accuracy of ± 1 mm Hg. The temperatures were measured using a PT100 thermometer with an accuracy of $\pm 0.1°C$. The detailed experimental procedures have been described previously [7,8].

The boiling points of mixtures of *N*,*N*-dimethylformamide with enthylbenzene, chlorobenzene, bromobenzene or aniline were determined at 712 mm Hg over the entire range of compositions, mixtures of different composition being prepared by taking quantities (by weight) of the pure compounds.

3. Results

In the present work, isobaric T–x measurements were usd for data reduction. The model chosen for expressing the composition–temperature dependence was the Wilson

Table 1
Boiling points and densities of pure components at 303.15 K

Component	Boiling point/K		Density, ρ/(g cm^{-3})	
	Experimental	Literature	Experimental	Literature
N,*N*-Dimethylformamide	426.05	426.15	0.94119	0.94120
Ethylbenzene	409.25	409.34	0.85818	0.85820
Chlorobenzene	404.75	404.85	1.09547	1.09550
Bromobenzene	429.20	429.19	1.48147	1.48150
Aniline	457.35	457.55	1.01314	1.01317

equation [9]:

$$\ln v_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \quad (1)$$

$$\ln v_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_1 + \Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right) \quad (2)$$

where

$$\Lambda_{12} = \frac{V_2^{\mathrm{L}}}{V_1^{\mathrm{L}}}\exp\left(\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \quad (3)$$

and

$$\Lambda_{21} = \frac{V_1^{\mathrm{L}}}{V_2^{\mathrm{L}}}\exp\left(\frac{\lambda_{12} - \lambda_{22}}{RT}\right) \quad (4)$$

where x_1 and x_2 are the mole fractions of the components of the mixture, v_1 and v_2 are the corresponding activity coefficients, V_1^{L} and V_2^{L} are the liquid molal volumes; $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are the (to some extent) temperature-independent Wilson parameters; and λ is the energy of interaction between the molecules designated by the subscripts. The optimum Wilson parameters Λ_{12} and Λ_{21} are obtained by minimizing the objective function ϕ

$$\phi = \sum\left(\frac{P_{\mathrm{cal}}}{P_{\mathrm{exp}}} - 1.0\right)^2 \quad (5)$$

The optimum Wilson parameters were obtained by minimizing the above objective function using Nelder–Mead optimization techniques. The Wilson parameters so obtained, with standard deviations, are presented in Table 2.

4. Discussion

Since the prediction of vapour–liquid equilibrium data involves measurement of the vapour pressures of the pure compounds, these were measured for *N*,*N*-dimethylformamide, ethylbenzene, chlorobenzene, bromobenzene and aniline. The Antoine

Table 2
Wilson parameters with standard deviation $\sigma(t)$ at 712 mm Hg

N,*N*-Dimethylformamide +	Λ_{12}	Λ_{21}	σ
Ethylbenzene	648.72	−138.00	0.4
Chlorobenzene	175.94	13.41	0.5
Bromobenzene	154.52	98.95	0.2
Aniline	−463.61	479.59	0.4

Table 3
Antoine constants for the pure compounds

Compound	A	B	C
N,*N*-Dimethylformamide	7.1085	1537.78	210.80
Ethylbenzene	6.9572	1424.26	211.60
Chlorobenzene	6.9781	1431.05	217.55
Bromobenzene	6.8606	1438.82	204.60
Aniline	7.5717	1941.70	230.00

Table 4
Temperature–mole fraction, T–x, data for the binary systems *N*,*N*-dimethylformamide (1) + substituted benzenes (2) at 712 mm Hg

x_1	Boiling point/°C		Mole fraction of component 1 in vapour	Activity coefficients		ΔT^b/°C
	Exp.	Calc.^{a}		Component 1	Component 2	
N,N-Dimethylformamide (1) + ethylbenzene (2)						
0.0887	133.4	133.0	0.1346	2.5036	1.0149	−0.4
0.1555	132.7	132.3	0.1916	2.0731	1.0419	−0.4
0.2383	131.8	132.2	0.2424	1.7235	1.0898	0.4
0.3751	132.4	132.4	0.3095	1.3840	1.1994	0.0
0.4652	133.4	132.9	0.3528	1.2493	1.2911	−0.5
0.5210	132.9	133.5	0.3819	1.1876	1.3558	0.6
0.5675	134.0	134.2	0.4085	1.1458	1.4144	0.2
0.6410	135.2	135.3	0.4562	1.0939	1.5167	0.1
0.7623	138.6	138.2	0.5602	1.0376	1.7132	−0.4
0.8430	141.1	141.1	0.6587	1.0157	1.8653	0.0
0.9310	146.0	145.6	0.8146	1.0029	2.0533	−0.4
N,N-Dimethylformamide (1) + chlorobenzene (2)						
0.0750	130.5	129.9	0.0598	1.4458	1.0023	−0.6
0.1575	131.1	130.6	0.1207	1.3607	1.0103	−0.5
0.2342	131.7	131.3	0.1743	1.2922	1.0229	−0.4
0.3302	132.6	132.4	0.2395	1.2188	1.0463	−0.2
0.3902	133.1	133.1	0.2802	1.1795	1.0656	0.0
0.4535	133.5	134.0	0.3241	1.1428	1.0900	0.5
0.5164	134.2	135.1	0.3696	1.1110	1.1188	0.8
0.5986	136.5	136.5	0.4336	1.0760	1.1639	0.0
0.6846	137.9	138.4	0.5096	1.0467	1.2213	0.5
0.7465	139.7	140.0	0.5728	1.0302	1.2699	0.3
0.8344	143.4	142.8	0.6814	1.0129	1.3506	−0.6
0.9149	146.3	146.0	0.8108	1.0034	1.4382	−0.3
N,N-Dimethylformamide (1) + bromobenzene (2)						
0.0828	151.6	152.1	0.1317	1.5231	1.0029	0.5
0.1682	150.3	150.3	0.2398	1.4293	1.0123	0.0
0.2505	149.2	149.2	0.3261	1.3486	1.0283	0.0
0.3157	148.5	148.5	0.3858	1.2912	1.0464	0.0

Table 4 (*Continued*)

x_1	Boiling point/°C		Mole fraction of component 1 in vapour	Activity coefficients		ΔT^b/°C
	Exp.	Calc.[a]		Component 1	Component 2	
0.3951	148.0	147.8	0.4514	1.2289	1.0757	−0.2
0.5017	147.5	147.3	0.5320	1.1573	1.1298	−0.2
0.5990	147.1	147.1	0.6027	1.1037	1.1977	0.0
0.6819	146.8	147.1	0.6644	1.0665	1.2730	0.3
0.7648	147.4	147.5	0.7310	1.0373	1.3688	0.1
0.8545	148.1	148.1	0.8140	1.0147	1.5023	0.0
0.9206	149.2	148.9	0.8877	1.0045	1.6262	−0.3
N,N-Dimethylformamide (1) + aniline (2)						
0.0850	179.6	179.6	0.1255	0.7078	0.9984	0.0
0.1549	178.6	178.3	0.2270	0.7276	0.9944	−0.3
0.2473	175.6	176.0	0.3573	0.7549	0.9842	0.4
0.3173	173.9	174.3	0.4518	0.7768	0.9721	0.4
0.4039	171.9	171.9	0.5624	0.8053	0.9503	0.0
0.5283	167.9	167.9	0.7052	0.8492	0.9022	0.0
0.6033	165.5	165.4	0.7802	0.8772	0.8607	−0.1
0.6861	162.6	162.4	0.8517	0.9091	0.8011	−0.2
0.7653	158.7	159.2	0.9079	0.9394	0.7277	0.5
0.8322	157.2	156.7	0.9455	0.9636	0.6514	−0.5
0.9133	154.3	153.5	0.9788	0.9880	0.5398	−0.8

[a] From the Wilson equation.

[b] $\Delta T = T_{\mathrm{cal}} - T_{\mathrm{exp}}$.

constants for the pure components were obtained by non-linear regression analyses of the experimental data, and are presented in Table 3. The measured boiling points, calculated boiling points from the Wilson equation, calculated vapour composition, activity coefficients and ΔT values are presented in Table 4. The excess Gibbs free energies were calculated using the equation:

$$\frac{G^E}{RT} = x_1 \ln v_1 + x_2 \ln v_2 \tag{6}$$

The temperature versus mole fraction curves are presented graphically in Figs. 1–4. Activity coefficients, excess Gibbs free energies and mole fractions of *N,N*-dimethylformamide are given in Table 5. The excess Gibbs free energies are calculated at 298.15 K from the activity coefficients, using Eq. (6). Plots of excess Gibbs free energies versus mole fraction of *N,N*-dimethylformamide are presented graphically in Figs. 5 to 8.

The activity coefficients presented in Table 4 reveal that all the systems are non-ideal. The non-ideality falls in the order:

Ethylbenzene > bromobenzene > chlorobenzene > aniline.

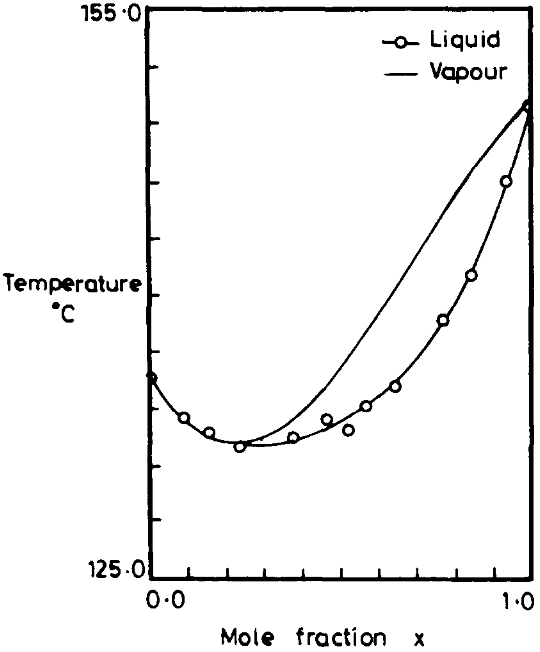

Fig. 1. *N*,*N*-Dimethylformamide (x) + ethylbenzene (1-x).

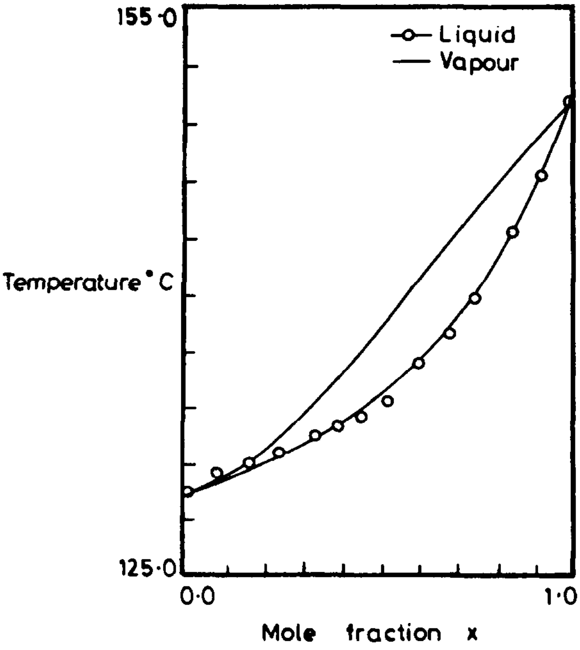

Fig. 2. *N*,*N*-Dimethylformamide (x) + chlorobenzene (1-x).

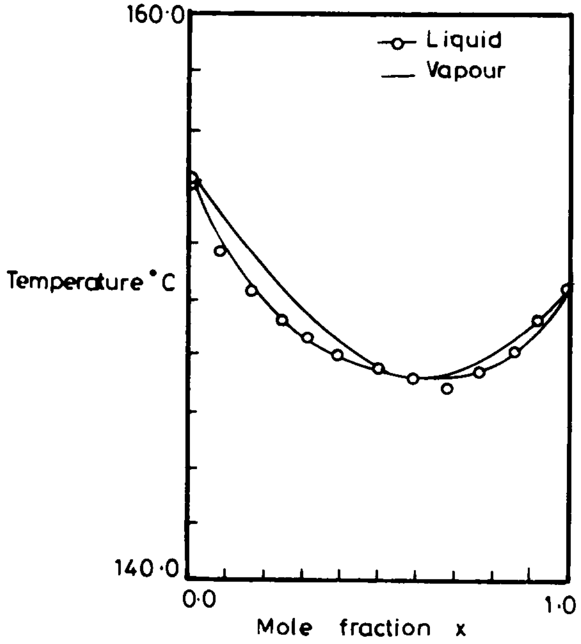

Fig. 3. *N*,*N*-Dimethylformamide (x) + bromobenzene (1-x).

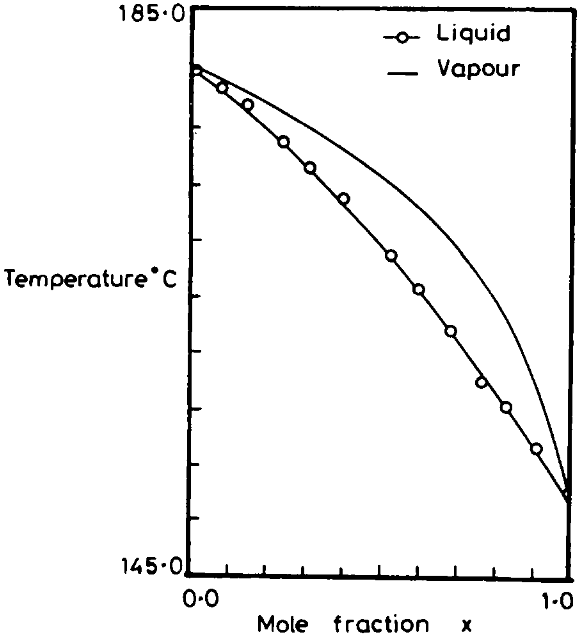

Fig. 4. *N*,*N*-Dimethylformamide + aniline (1-x).

Table 5

Activity coefficients, v, and excess Gibbs free energies, G^E, for the systems *N*,*N*-dimethylformamide (l) + substituted benzenes (2) at 298.15 K

x_1	v_1	v_2	$G^E/(\mathrm{J\ mol^{-1}})$
N,N-Dimethylformamide (1) + ethylbenzene (2)			
0.0500	3.8140	1.0092	183.3
0.1000	2.9044	1.0314	326.0
0.1500	2.3599	1.0622	436.7
0.2000	2.0047	1.0994	521.2
0.2500	1.7586	1.1419	583.5
0.3000	1.5805	1.1889	626.8
0.3500	1.4473	1.2403	653.3
0.4000	1.3454	1.2957	664.8
0.4500	1.2660	1.3552	662.8
0.5000	1.2034	1.4188	648.6
0.5500	1.1536	1.4865	623.2
0.6000	1.1139	1.5585	587.4
0.6500	1.0824	1.6348	542.0
0.7000	1.0574	1.7158	487.6
0.7500	1.0380	1.8016	424.8
0.8000	1.0233	1.8924	354.0
0.8500	1.0126	1.9884	275.8
0.9000	1.0054	2.0900	190.5
0.9500	1.0013	2.1975	98.5
N,N-Dimethylformamide(1) + chlorobenzene (2)			
0.0500	1.6935	1.0015	67.3
0.1000	1.6039	1.0059	127.4
0.1500	1.5239	1.0133	180.4
0.2000	1.4524	1.0237	226.4
0.2500	1.3885	1.0371	265.3
0.3000	1.3314	1.0538	297.2
0.3500	1.2805	1.0738	322.0
0.4000	1.2350	1.0973	339.9
0.4500	1.1946	1.1246	350.7
0.5000	1.1588	1.1560	354.5
0.5500	1.1273	1.1918	351.3
0.6000	1.0997	1.2324	341.0
0.6500	1.0758	1.2783	323.6
0.7000	1.0554	1.3301	299.2
0.7500	1.0384	1.3885	267.5
0.8000	1.0246	1.4542	228.7
0.8500	1.0138	1.5282	182.6
0.9000	1.0062	1.6116	129.1
0.9500	1.0015	1.7057	68.3
N,N-Dimethylformamide (1) + bromobenzene (2)			
0.0500	1.8644	1.0015	79.0
0.1000	1.7632	1.0060	150.7
0.1500	1.6711	1.0138	215.0
0.2000	1.5874	1.0249	271.8
0.2500	1.5113	1.0396	321.1

Table 5 (*Continued*)

x_1	v_1	v_2	$G^E/(\mathrm{J\ mol^{-1}})$
0.3000	1.4420	1.0583	362.5
0.3500	1.3791	1.0813	396.0
0.4000	1.3221	1.1091	421.4
0.4500	1.2705	1.1422	438.6
0.5000	1.2239	1.1814	447.2
0.5500	1.1822	1.2277	447.1
0.6000	1.1450	1.2820	437.9
0.6500	1.1121	1.3459	419.5
0.7000	1.0834	1.4210	391.6
0.7500	1.0588	1.5096	353.6
0.8000	1.0384	1.6147	305.4
0.8500	1.0221	1.7398	246.4
0.9000	1.0101	1.8900	176.2
0.9500	1.0026	2.0717	94.3
N,N-Dimethylformamide (1) + aniline (2)			
0.0500	0.4576	0.9992	−96.7
0.1000	0.4732	0.9964	−189.3
0.1500	0.4899	0.9915	−277.2
0.2000	0.5078	0.9839	−360.1
0.2500	0.5270	0.9734	−437.4
0.3000	0.5475	0.9593	−508.7
0.3500	0.5697	0.9412	−573.2
0.4000	0.5935	0.9183	−630.2
0.4500	0.6193	0.8898	−678.7
0.5000	0.6471	0.8551	−717.7
0.5500	0.6771	0.8131	−745.8
0.6000	0.7097	0.7630	−761.5
0.6500	0.7448	0.7038	−762.6
0.7000	0.7825	0.6349	−746.8
0.7500	0.8228	0.5559	−710.7
0.8000	0.8652	0.4672	−650.0
0.8500	0.9084	0.3706	−559.0
0.9000	0.9500	0.2702	−429.4
0.9500	0.9843	0.1730	−249.3

The G^E values are positive over the entire range of composition for the mixtures of *N*,*N*-dimethylformamide with ethylbenzene, chlorobenzene and bromobenzene. Excess Gibbs free energies versus composition curves are almost symmetrical for mixtures of *N*,*N*-dimethylformamide with ethylbenzene, chlorobenzene and bromobenzene. The G^E values are negative over the entire range of composition for the mixture of *N*,*N*-dimethylformamide with aniline and the G^E versus x_1 curve is skewed, with a maximum occurring at 0.65 mole fraction of *N*,*N*-dimethylformamide.

The algebraic values of G^E for mixtures of *N*,*N*-dimethylformamide with the four substituted benzenes fall in the order:

Ethylbenzene > bromobenzene > chlorobenzene > aniline.

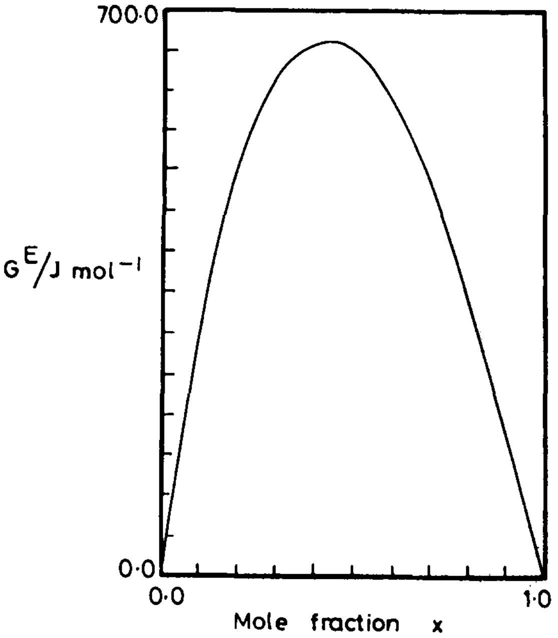

Fig. 5. Excess Gibbs free energies (G) for *N*,*N*-Dimethylformamide (x) ethylbenzene (1-x) at 298.15 K.

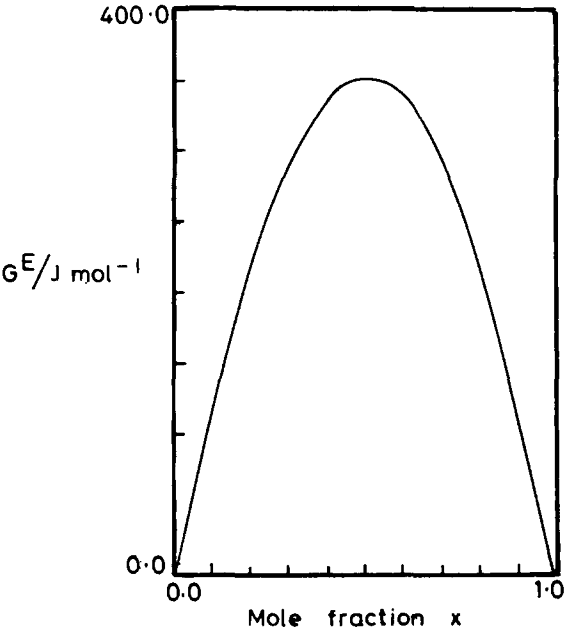

Fig. 6. Excess Gibbs free energies (G) for *N*,*N*-Dimethylformamide (x) chlorobenzene (1-x) at 298.15 K.

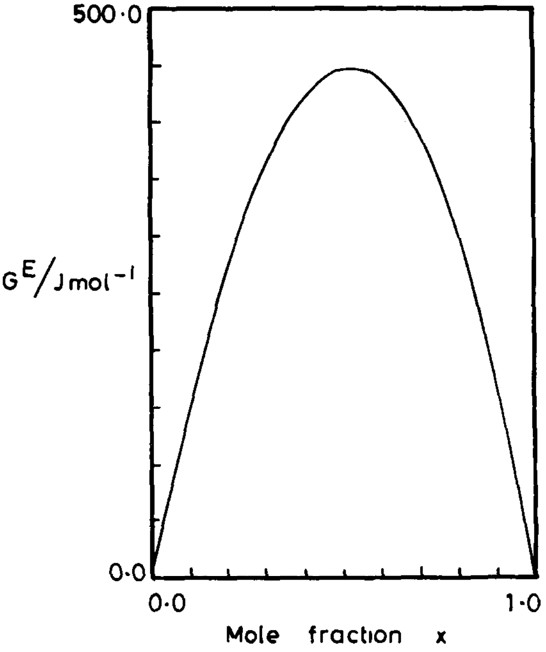

Fig. 7. Excess Gibbs free energies (G^E) for *N*,*N*-Dimethylformamide (x) bromobenzene (1-x) at 298.15 K.

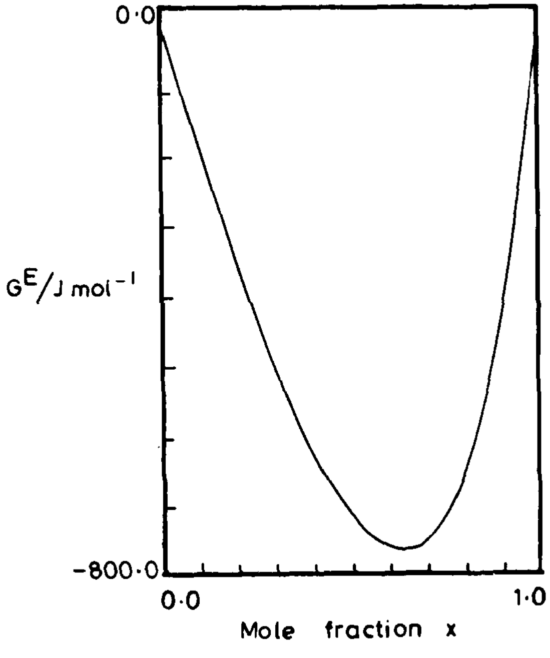

Fig. 8. Excess Gibbs free energies (G^E) for *N*,*N*-Dimethylformamide (x) aniline (1-x) at 298.15 K.

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