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Excess molar Gibbs free energies of ethyl iodide plus aromatic hydrocarbons at 308.15 K

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Abstract

Excess molar Gibbs free energies G_m^E for (ethyl iodide plus benzene, toluene, *o*-xylene, *m*-xylene or *p*-xylene) over the whole range of composition have been measured experimentally at 308.15 K from the measured vapour pressures. The results for G_m^E values of these mixtures suggest the existence of weak specific interactions of electron donor–acceptor type in which aromatic hydrocarbons behave as electron donors. The values of G_m^E have also been computed from the statistical theory of Flory. The Flory theory gave poor agreement between experimental and calculated values.

INTRODUCTION

The study of excess heats of mixing and excess volumes of mixing of 1-haloalkane plus *n*-alkane mixtures [1,2] and those of 1,2-dibromoethane plus an aromatic hydrocarbon [3] and our earlier studies of ethyl iodide plus aromatic hydrocarbon mixtures [4–6] have revealed the specific interactions of electron donor–acceptor type, where aromatic hydrocarbons behave as electron donors and also cause disruption of the favourable orientational order of the pure components. In the present investigations, excess molar Gibbs free energies G_m^E for the same set of mixtures have been obtained by measuring the vapour pressures at a temperature of 308.15 K. The G_m^E values have also been estimated using the theory of Flory [7,8].

EXPERIMENTAL

Ethyl iodide, benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene (BDH, A.R. grade) were purified by standard procedures [9]. The purities of the final samples were checked by measuring their densities at 298.15 ± 0.01 K (293.15 K in the case of *m*-xylene), which agreed to within $\pm 5 \times 10^{-5}$ g cm^{-3} with the corresponding literature values [10,11]. Total vapour pres-

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sures of mixtures of ethyl iodide plus an aromatic hydrocarbon were measured as a function of the liquid-phase mole fraction of ethyl iodide at 308.15 ± 0.01 K using the static vapour pressure method in the manner described in the literature [12]. Pressures were calculated from the heights of the mercury column. The density of mercury and the acceleration of free fall

TABLE 1

Measured total vapour pressure P, partial pressures P_1 and P_2, activity coefficients γ, residual vapour pressure $R = P_{expt} - P_{calc}$, and excess molar Gibbs free energy of mixing G_m^E for different mole fractions x_A of ethyl iodide at 308.15 K

x_A	P (Torr)	P_1 (Torr)	P_2 (Torr)	γ_1	γ_2	R (Torr)	G_m^E (J mol^{-1})
Ethyl iodide (A) + benzene (B)							
0.00	149.90						
0.1346	162.65	27.36	129.84	1.1924	0.9994	+0.26	59.28
0.2451	172.95	49.91	113.36	1.1804	1.0020	+0.45	107.98
0.3396	180.75	69.19	99.21	1.1577	1.0102	+0.43	144.61
0.4224	185.35	86.08	86.80	1.1323	1.0242	−1.02	169.88
0.5159	191.80	105.17	72.78	1.1011	1.0500	−0.42	187.88
0.6150	197.01	125.41	57.90	1.0688	1.0903	−0.16	191.48
0.6810	200.20	138.89	47.98	1.0493	1.1296	+0.26	183.52
0.7215	201.50	147.16	41.89	1.0385	1.1575	+0.19	174.08
0.8407	202.5	171.49	23.96	1.0134	1.2604	−1.49	124.16
1.0	204.00						
Ethyl iodide (A) + toluene (B)							
0.00	48.05						
0.1329	66.80	25.93	40.74	1.0343	1.0023	−0.85	16.63
0.2182	87.20	45.66	38.71	1.0215	1.0049	+1.45	21.73
0.3874	107.95	78.68	29.61	1.0105	1.0093	−1.44	24.95
0.4651	119.75	94.52	25.88	1.0088	1.0106	−1.75	24.85
0.5788	140.70	117.77	20.42	1.0073	1.0121	+1.39	23.88
0.6820	156.60	138.89	15.44	1.0058	1.0148	+1.23	22.13
0.7643	167.80	155.75	11.46	1.0042	1.0192	−0.28	19.69
0.9082	188.00	185.29	4.07	1.0010	1.0372	−1.70	10.88
1.00	204.00						
Ethyl iodide (A) + o-xylene (B)							
0.00	12.67						
0.1213	33.15	24.21	11.18	0.9381	0.9985	−0.73	−23.15
0.2950	66.74	59.63	9.00	0.9554	0.9939	+0.82	−45.40
0.3217	70.42	64.70	8.68	0.9573	0.9931	−0.14	−48.00
0.4209	89.13	85.01	7.43	0.9635	0.9893	−0.13	−56.04
0.5113	105.85	103.32	6.29	0.9691	0.9842	−0.47	−60.95
0.5914	120.70	119.63	5.27	0.9746	0.9774	−1.05	−62.88
0.7006	144.04	142.11	3.87	0.9829	0.9621	+0.63	−60.50
0.8108	166.15	164.65	2.46	0.9915	0.9362	+0.59	−49.66
0.9015	183.60	183.12	1.30	0.9973	0.9040	−0.19	−31.80
1.0	203.7						

TABLE 1 (continued)

x_A	P (Torr)	P_1 (Torr)	P_2 (Torr)	γ_1	γ_2	R (Torr)	G_m^E (J mol^{-1})
Ethyl iodide (A) + m-xylene (B)							
0.00	14.09						
0.1010	35.05	20.41	12.70	1.0673	0.9921	+0.67	1.24
0.2150	60.53	43.51	11.13	1.1541	0.9788	−0.58	35.80
0.3850	97.90	78.07	8.76	1.1464	0.9845	−0.22	110.17
0.5024	119.85	102.01	7.11	1.0990	1.0189	+0.49	145.41
0.6244	139.86	126.92	5.38	1.0496	1.0815	+0.82	152.89
0.7250	153.42	147.48	3.95	1.0204	1.1466	−1.80	113.80
0.8015	168.60	163.18	2.85	1.0071	1.1954	+0.41	105.36
0.9418	192.60	192.0	0.84	0.9999	1.2463	−0.42	32.52
1.0	204.0						
Ethyl iodide (A) + p-xylene (B)							
0.00	15.48						
0.2060	46.40	41.68	12.34	0.8486	1.0152	−1.50	−55.89
0.2912	60.94	58.97	11.04	0.8358	1.0201	+0.39	−97.74
0.4851	93.72	98.40	8.05	0.8637	0.9955	+0.72	−188.06
0.5740	108.10	116.51	6.67	0.8918	0.8154	−1.24	−213.08
0.6101	117.94	123.91	6.12	0.9044	0.9405	+0.12	−218.32
0.6921	135.90	140.69	4.84	0.9336	0.8860	+0.26	−217.24
0.7541	151.15	153.42	3.87	0.9546	0.8380	+1.45	−202.66
0.9107	183.16	185.58	1.41	0.9931	0.6842	−2.11	−102.90
1.00	204.0						

were taken as 13 509.09 kg m^{-3} and 9.8009 m s^{-2} respectively. The composition of the liquid phase was obtained by capacitance measurements (capacitance cell fitted in the vapour pressure still) using a dipolemeter (S&I Instruments, India). The measured vapour pressures were reproducible within ± 0.003 kPa. The uncertainty in the liquid phase composition was 0.01%. The agreement between experimentally observed and literature values [10–12] of vapour pressures was within 0.3%.

RESULTS AND DISCUSSION

The total vapour pressures for ethyl iodide plus benzene or ethyl iodide plus toluene or ethyl iodide plus *o*-, *m*- or *p*-xylene over the whole mole fraction range are reported in Table 1. The G_m^E values of these mixtures were calculated using Barker's [13,14] method and assuming that the results for G_m^E could be expressed in the form

$$G_m^E \text{ (J mol}^{-1}) = x(1-x)RT\left[A + (2x-1)B + (2x-1)^2C\right] \quad (1)$$

where x is the mole fraction of ethyl iodide; A, B and C are parameters and are presented in Table 2. In these calculations the second virial

TABLE 2

Adjustable parameters A, B and C for excess molar Gibbs free energies G_m^E from eqn. (1) for ethyl iodide (A) plus aromatic hydrocarbons (B) at 308.15 K

System	A	B	C
Ethyl iodide (A) + benzene (B)	0.28995	0.11490	−0.01373
Ethyl iodide (A) + toluene (B)	0.03848	−0.00557	0.02550
Ethyl iodide (A) + *o*-xylene (B)	−0.09442	−0.03398	−0.02802
Ethyl iodide (A) + *m*-xylene (B)	0.22629	0.15534	−0.16907
Ethyl iodide (A) + *p*-xylene (B)	−0.30180	−0.26450	0.03730

coefficients of the pure components were calculated from Berthelot's equation [15] using values of critical constants from the literature [16]. The values of β_{12} were assumed to be equal to $0.5(\beta_{11} + \beta_{22})$. The activity coefficients

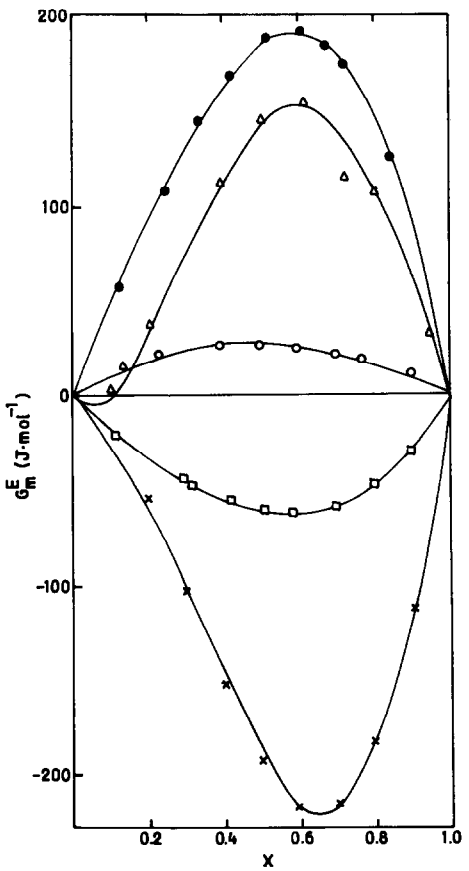

Fig. 1. Excess molar Gibbs free energies G_m^E, of ethyl iodide + benzene (●), ethyl iodide + toluene (○), ethyl iodide + *o*-xylene (□), ethyl iodide + *m*-xylene (△) and ethyl iodide + *p*-xylene (×) systems at 308.15 K.

γ_1 and γ_2 of the components and G_m^E values as a function of x for the same set of mixtures are recorded in Table 1. Since no values of G_m^E were available in the literature for these mixtures, it was not possible to compare the results. The plots of G_m^E against x for these mixtures are shown in Fig. 1. The G_m^E values for ethyl iodide plus benzene or toluene or *m*-xylene systems are positive throughout the mole fraction range. However, for ethyl iodide plus *o*-xylene and ethyl iodide plus *p*-xylene, G_m^E values are negative. The order of variation of G_m^E values at $x = 0.5$ is benzene > *m*-xylene > toluene > *o*-xylene > *p*-xylene. The variation in magnitude of G_m^E values may be explained if it is assumed that (1) there are specific interactions of electron-donor–acceptor type where aromatic hydrocarbons behave as electron donors; and (2) disruption occurs in the orientational order of the pure components.

The introduction of one $-CH_3$ group into benzene (as in toluene) would increase the electron donating capacity of the benzene ring, and hence toluene would interact more strongly than benzene. This is supported by the less positive values for toluene than for benzene. However, when two methyl groups are introduced into the benzene ring (as in the case of xylenes), there is an increase in the electron-donating capacity and the strength of electron donor–acceptor interactions, and at the same time there is steric repulsion

TABLE 3

Comparison of the measured excess molar Gibbs free energies G_m^E for ethyl iodide (A) + aromatic hydrocarbons (B) at 308.15 K with values evaluated from Flory theory

x_A	G_m^E (J mol^{-1})		x_A	G_m^E (J mol^{-1})	
	Expt.	Flory		Expt.	Flory
Ethyl iodide (A) + benzene (B)			*Ethyl iodide (A) + toluene (B)*		
0.1	43.63	48.03	0.1	13.66	27.03
0.3	130.09	113.43	0.3	24.10	64.85
0.5	185.71	136.64	0.5	24.64	79.62
0.7	179.54	116.23	0.7	21.70	69.03
0.9	86.02	50.46	0.9	11.61	30.54
Ethyl iodide (A) + o-xylene (B)			*Ethyl iodide (A) + m-xylene (B)*		
0.1	−19.64	56.19	0.1	−1.43	66.06
0.3	−45.89	137.24	0.3	73.76	161.84
0.5	−60.48	171.38	0.5	145.20	202.75
0.7	−60.53	151.34	0.7	140.62	179.75
0.9	−32.17	68.36	0.9	55.88	81.16
Ethyl iodide (A) + p-xylene (B)					
0.1	−15.29	60.24			
0.3	−102.24	147.65			
0.5	−193.30	184.93			
0.7	−216.08	164.01			
0.9	−112.87	74.47			

between the atoms of ethyl iodide and the two bulky methyl groups. This hinders the proper orientation of the ethyl iodide molecules for interaction with xylenes. Among the xylenes, *p*-xylene, being a symmetrical molecule, offers the least steric hindrance to ethyl iodide molecules, and thus the electron donor–acceptor interactions are stronger in these mixtures and the G_m^E value is lower than those of the *o*-xylene and *m*-xylene mixtures. The G_m^E data support this conjecture. The positions of the methyl groups in *m*-xylene are such that the steric repulsion is at a maximum and the G_m^E value for the *m*-xylene mixtures should be the highest, and this expectation is supported by our experimental results.

The G_m^E values were calculated using the theory of Flory [7,8] (see Table 3). The Flory theory is able to predict the sign and to some extent the magnitude of G_m^E values for ethyl iodide plus benzene or toluene or *m*-xylene systems.

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