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SOME PROPERTIES OF BINARY MIXTURES OF *N*-FORMYLMORPHOLINE AND AN AROMATIC HYDROCARBON

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ABSTRACT

Densities and viscosities at 298.15 K are presented for seven binary liquid systems of *N*-formylmorpholine with benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene. The viscosity and the derived excess molar Gibbs free energy of activation of viscous flow showed a negative deviation from ideal mixing behaviour. The results indicate that a weak A–B interaction occurs.

INTRODUCTION

As a part of our research program on studying the efficiency of morpholine derivatives for the extraction of aromatic hydrocarbons (C_6–C_9) from petroleum feedstocks, a number of thermodynamic properties of *N*-formylmorpholine with co-solvents [1–3] has been studied. In a recent work, the volumetric behaviour of *N*-formylmorpholine with aromatic hydrocarbons was studied [4]. The present work deals with the study of viscosity, density and the derived excess molar Gibbs free energy for activation of viscous flow at 298.15 K for *N*-formylmorpholine with benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene.

EXPERIMENTAL

The *N*-formylmorpholine and aromatic hydrocarbons were obtained from different sources. The purification procedure has been described in detail previously [4]. The purity was estimated by glc analysis to be better than 99.5 mol%.

Density was determined with an Anton Paar digital densimeter (DMA 55)

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at 298.15 ± 0.01 K and the overall precision of the density measurements is estimated to be better than 4×10^{-5} g cm^{-3}.

Viscosity was determined using a suspended-level Ubbeholde viscometer. The flow times were determined electronically with an electronic timer of precision ±0.01 s and the temperature of the water bath was controlled to be better than ±0.01 K.

RESULTS AND DISCUSSION

Experimental viscosities at 298.15 K for the mixture in the seven systems are listed in Table 1 and plotted in Fig. 1 as a function of mole fraction, x, of aromatic hydrocarbon.

The excess molar Gibbs free energy of activation of viscous flow is defined through the Eyring viscosity equation [5] as

$$\eta = \frac{hN}{M}\exp\left(\frac{\Delta G^*}{RT}\right) \tag{1}$$

By definition

$$\Delta G^{*\mathrm{E}} = \Delta G_{\mathrm{s}}^* - \Delta G_{\mathrm{i}}^* \tag{2}$$

Where ΔG_{s}^* and ΔG_{i}^* are the molar Gibbs free energy of activation of viscous flow of binary mixture and ideal, respectively. For an ideal mixture

$$\Delta G_{\mathrm{i}}^* = x_1 \Delta G_1^* - (1 - x_1)\Delta G_2^* \tag{3}$$

Thus, for a binary mixture [6–8]

$$\Delta G^{*\mathrm{E}} = RT\left[\ln \eta V - x_1 \ln \eta_1 V_1 - (1 - x_1) \ln \eta_2 V_2\right] \tag{4}$$

Where η and V are the viscosity and molar volume of the mixture, respectively. η_{i} and V_{i} represent the viscosity and molar volume of ith component. R and T have their usual meanings. The excess molar Gibbs free energy of activation of viscous flow values, $\Delta G^{*\mathrm{E}}$, calculated from eqn. (4) are listed in Table 1 and plotted in Fig. 2. Each set of results was fitted to a Redlich–Kister equation of the type given in eqn. (5)

$$\frac{\Delta G^{*\mathrm{E}}}{RT} = x_1(1 - x_1) \sum_{n=1}^{m} a_i x_1^{n-1} \tag{5}$$

Where x_1 is the mole fraction of an aromatic hydrocarbon and a_i is the coefficient of order i obtained from a least-squares fit of the results presented in Table 1. The standard deviations, s, associated with this analysis are presented in Table 2, along with the values of the product $a_i s$.

The experimental viscosity (Fig. 1) and computed $\Delta G^{*\mathrm{E}}$ values (Fig. 2) show significant negative deviations from ideal mixing behaviour over the whole mole fraction range, x, of an aromatic hydrocarbon.

TABLE 1

Densities, viscosities and excess molar Gibbs free energies of activation for viscous flow of an aromatic hydrocarbon (1) + *N*-formylmorpholine (2)

x_1	ρ (g cm^{-3})	η (cP)	ΔG^{*E} (J mol^{-1})
$C_6H_6(1)+C_5H_9O_2N(2)$			
0.00000	1.14637	7.613	—
0.03787	1.13817	6.858	−22
0.07912	1.12899	6.137	−39
0.13087	1.11730	5.329	−66
0.22005	1.09656	4.199	−98
0.34826	1.06490	2.992	−134
0.43143	1.04377	2.381	−179
0.55264	1.01149	1.734	−204
0.63515	0.98824	1.413	−192
0.71763	0.96447	1.157	−168
0.75359	0.95397	1.058	−164
0.82996	0.92996	0.880	−136
0.89398	0.90932	0.767	−69
0.95058	0.89064	0.671	−41
1.00000	0.87361	0.601	—
$C_6H_5CH_3(1)+C_5H_9O_2N(2)$			
0.01784	1.14110	7.177	−32
0.06829	1.12731	6.102	−165
0.18812	1.09473	4.224	−247
0.26752	1.07276	3.336	−319
0.34660	1.05088	2.653	−376
0.42465	1.02875	2.155	−384
0.50944	1.00451	1.701	−419
0.59556	0.98028	1.359	−417
0.68494	0.95438	1.099	−359
0.77224	0.92912	0.879	−341
0.84794	0.90710	0.759	−211
0.91783	0.88636	0.646	−149
1.00000	0.86220	0.552	—
$C_6H_5C_2H_5(1)+C_5H_9O_2N(2)$			
0.03224	1.13588	6.848	−66
0.06252	1.12623	6.122	−160
0.08602	1.11894	5.678	−199
0.15841	1.09632	4.430	−380
0.27043	1.06228	3.151	−546
0.35122	1.03827	2.527	−601
0.47013	1.00384	1.841	−665
0.55689	0.97949	1.511	−627
0.63728	0.95716	1.261	−589
0.68876	0.94333	1.137	−533
0.77708	0.91976	0.986	−348
0.86361	0.89717	0.829	−252
0.93172	0.87958	0.713	−212
1.00000	0.86225	0.657	—
m-$C_6H_4(CH_3)_2(1)+C_5H_9O_2N(2)$			
0.05737	1.12901	6.316	−149
0.12969	1.10490	4.989	−267
0.23120	1.07357	3.617	−414

TABLE 1 (continued)

x_1	ρ (g cm^{-3})	η (cP)	ΔG^{*E} (J mol^{-1})
0.51606	0.98950	1.652	−530
0.59976	0.96628	1.343	−506
0.68775	0.94141	1.088	−462
0.77671	0.91837	0.908	−341
0.95233	0.87185	0.635	−100
1.00000	0.86013	0.584	—
o-$C_6H_4(CH_3)_2(1)+C_5H_9O_2N(2)$			
0.03245	1.13658	7.014	−20
0.06364	1.12728	6.442	−55
0.09907	1.11622	5.890	−76
0.16080	1.09774	5.016	−125
0.28056	1.06361	3.707	−200
0.35608	1.04215	3.033	−270
0.47442	1.00956	2.278	−302
0.57012	0.98367	1.829	−314
0.65560	0.96097	1.511	−305
0.69838	0.94995	1.380	−290
0.78188	0.92882	1.159	−250
0.87605	0.90535	0.961	−182
0.93368	0.89122	0.875	−90
1.00000	0.87539	0.780	—
p-$C_6H_4(CH_3)_2(1)+C_5H_9O_2N(2)$			
0.02757	1.13731	6.848	−89
0.05782	1.12776	6.120	−187
0.09608	1.11521	5.439	−230
0.16532	1.09333	4.378	−333
0.27694	1.05846	3.140	−455
0.35498	1.03477	2.505	−523
0.47084	1.00037	1.842	−558
0.54708	0.97838	1.542	−517
0.63772	0.95288	1.231	−508
0.68707	0.93915	1.093	−491
0.77450	0.91557	0.899	−425
0.85539	0.89407	0.772	−295
0.93195	0.87395	0.668	−169
1.00000	0.85649	0.602	—
$C_6H_3(CH_3)_3(1)+C_5H_9O_2N(2)$			
0.02898	1.13583	7.041	−67
0.06010	1.12416	6.315	−143
0.08748	1.11399	5.789	−189
0.14531	1.09331	4.838	−277
0.25039	1.05813	3.530	−412
0.31968	1.03625	2.903	−473
0.44259	0.99948	2.093	−534
0.52741	0.97555	1.701	−532
0.61673	0.95150	1.375	−517
0.66103	0.94005	1.264	−457
0.75030	0.91767	1.058	−359
0.83483	0.89750	0.877	−314
0.94765	0.87177	0.731	−90
1.00000	0.86064	0.667	—

TABLE 2

Coefficients, a_i, and standard deviations, s, for least-squares representations of ΔG^{*E} of x mole fraction of an aromatic hydrocarbon (1)+ *N*-formylmorpholine (2) at 298.15 K by eqn. (5)

	C_6H_6	$C_6H_5CH_3$	$C_6H_5C_2H_5$	m-$C_6H_4(CH_3)_2$	o-$C_6H_4(CH_3)_2$	p-$C_6H_4(CH_3)_2$	$C_6H_3(CH_3)_3$
a_1	-3.295×10^{-3}	-1.447×10^{-2}	1.868×10^{-2}	-9.874×10^{-3}	1.667×10^{-3}	-2.252×10^{-2}	-4.832×10^{-3}
a_2	-0.1506	-0.554	-1.381	-0.913	-0.337	-0.810	-0.884
a_3	-0.136	0.427	1.967	1.078	3.623×10^{-3}	0.820	0.961
a_4	-0.298	0.136	-0.631	-0.159	0.331	-7.503×10^{-3}	-6.987×10^{-2}
s	3.8×10^{-3}	9.7×10^{-3}	1.2×10^{-3}	4.9×10^{-3}	3.6×10^{-3}	7.2×10^{-3}	6.9×10^{-3}

The results obtained here can be explained qualitatively by postulating that such behaviour may be attributed to the disruption of dipole–dipole and dipole–induced dipole interactions. The viscometric behaviour suggests

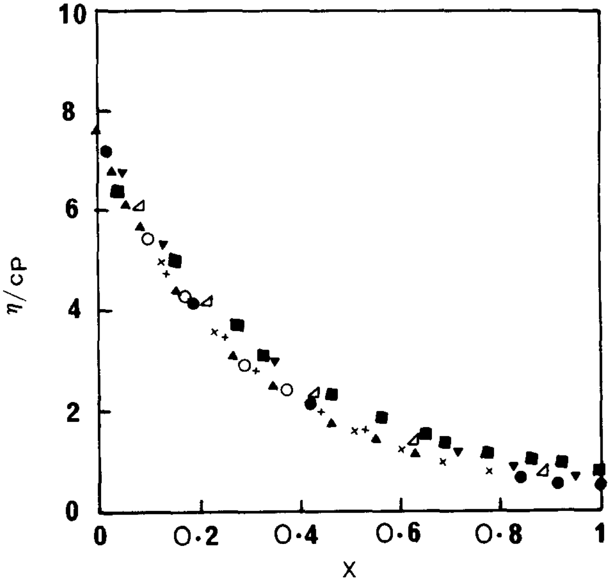

Fig. 1. Viscosities of an aromatic hydrocarbon (1) + *N*-formylmorpholine (2) at 298.15 K. (▼) benzene; (×) toluene; (△) ethylbenzene; (●) *m*-xylene; (■) *o*-xylene; (+) *p*-xylene; (○) mesitylene.

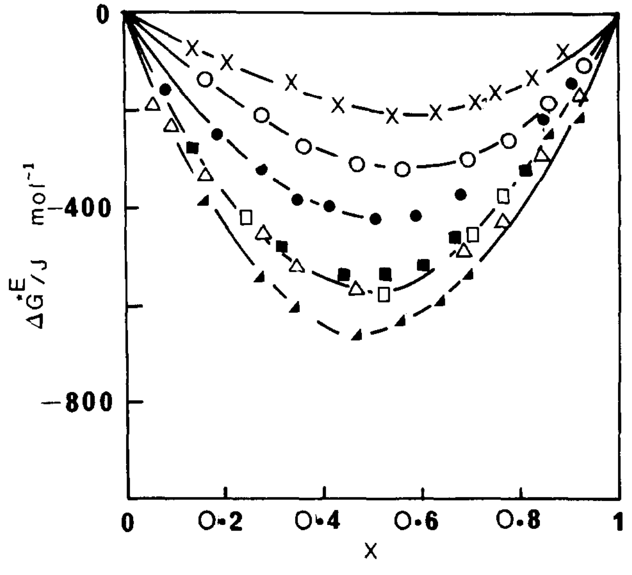

Fig. 2. Excess molar Gibbs free energy of activation of viscous flow of an aromatic hydrocarbon (1) + *N*-formylmorpholine (2) at 298.15 K. (×) Benzene; (●) toluene; (▲) ethylbenzene; (○) *o*-xylene; (□) *m*-xylene; (△) *p*-xylene; (■) mesitylene.

that the dipole–induced dipole interactions between the formyl group (N–CHO) of *N*-formylmorpholine and the benzene ring is greater than the dipole–dipole breaking interaction. This hypothesis is substantiated by the considerable volume contraction on mixing [4]. Also, such behaviour reflects the extent to which the dipole–induced dipole interactions are destabilized as the mole fraction, x, of the aromatic hydrocarbon increases and the dipole–dipole interaction predominates. This enhances flow due to the cooperative translational movement of adjacent molecules.

ΔG^{*E} behaviour does not follow the volumetric [4] sequence. This may reflect the importance of the inductive, steric and geometrical factors. ΔG^{*E} values for the *N*-formylmorpholine + aromatic hydrocarbon systems are fairly large and negative. It is apparent that the magnitudes of ΔG^{*E} for benzene are smaller than for the toluene and ethylbenzene systems: the minimum value ($x = 0.5$) is -200 J mol^{-1} for the benzene system; -410 J mol^{-1} for the toluene system; and -625 J mole^{-1} for the ethylbenzene system. Because of the inductive effect of methyl and ethyl in toluene and ethylbenzene, the electrostatic interactions and dispersive forces in pure toluene and ethylbenzene are considered to be weaker than those in pure benzene. Therefore, the degree to which such intermolecular interactions are lessened as a result of introducing *N*-formylmorpholine molecules may be smaller in the benzene system than in toluene and ethylbenzene. This enhances the dipole–induced dipole interaction to give the highest negative ΔG^{*E} value for ethylbenzene.

For *m*-xylene, *p*-xylene and mesitylene, ΔG^{*E} values are similar, which is another effect that may be attributed to the geometrical factor of the pure components. For *o*-xylene, ΔG^{*E} behaviour is different, which may be attributed to an additional factor: steric hindrance of methyl groups.

The above interpretation of ΔG^{*E} behaviour is not certain, because the function cannot be measured directly. More data for different systems are under investigations and will be published in the near future.

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