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EXCESS MOLAR VOLUMES OF AN AROMATIC HYDROCARBON + *N*-METHYLPYRROLIDONE AT 298.15 K

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ABSTRACT

Excess molar volumes at 298.15 K are reported for seven binary mixtures of *N*-methylpyrrolidone with benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene. The excess molar volumes are negative over the whole mole fraction range. The results are discussed in terms of the complex-forming ability. The experimental results are compared with values predicted from the Flory theory and found to be in poor agreement.

INTRODUCTION

N-Methlylpyrrolidone (NMP) is a highly dense, highly polar and selective solvent. It has been used in the petroleum industry for the extraction of low-molar mass, monocyclic aromatic hydrocarbons (C_6–C_9) from petroleum feedstocks [1]. As part of our research program on studying the efficiency of *N*-methylpyrrolidone for the extraction of aromatic hydrocarbons from different petroleum cuts, a number of thermodynamic properties with a cosolvent [2–4] have been studied. In previous studies [3,4] the volumetric and viscometric behaviour of *N*-methylpyrrolidone with *n*-alkanol has been reported. In a continuation of this work, we report here the excess molar volumes of *N*-methylpyrrolidone with benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene at 298.15 K derived from precise density measurements. The excess molar volumes of the systems under investigation were predicted using the Flory theory and compared with values obtained experimentally.

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EXPERIMENTAL

The N-methylpyrrolidone and aromatic hydrocarbons were obtained from Fluka AG (purium grade). The purification procedures have been described previously in detail [3,5]. The purity was estimated by GLC analysis to be better than 99.5 mol%. Densities of the pure component liquids were measured and are listed in Table 1, together with literature values [6,7].

Densities of the pure liquids and binary mixtures were determined with an Anton Paar digital densimeter (DMA 601) at 298.15 K. The overall precision of density measurements is estimated to be better than 3×10^{-6} g cm^{-3}. Binary mixtures were prepared on a weight basis and the mole fraction error is less than 4×10^{-4}.

RESULTS AND DISCUSSION

The experimental V^{E} results obtained from density measurements at 298.15 K are listed in Table 2. Each set of results was fitted to an empirical equation of the form

$$V^{\mathrm{E}}(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = x(1-x)\sum_{i=1}^{m} a_i(1-2x)^{i-1} \tag{1}$$

The values of the coefficients a_i are listed in Table 3, together with the standard deviations, s, of the fits.

The excess molar volumes, V^{E}, for all the binary mixtures (Fig. 1) are negative over the whole mole fraction range at 298.15 K. The V^{E} values for benzene + , and toluene + N-methylpyrrolidone reported by other authors [8] at 298.15 K are more negative than ours in each case. For example, at $x = 0.5$ they obtained -0.765 and -0.886 compared to our values of -0.634 and -0.830 cm^3 mol^{-1} for the systems containing benzene and toluene, respectively.

TABLE 1

Densities (g cm^{-3}) of the pure component liquids at 298.15 K

Component	Obs.	Lit.
Benzene	0.87372	0.87363
Toluene	0.86240	0.86222
Ethylbenzene	0.86236	0.86264
o-Xylene	0.87483	0.87596
m-Xylene	0.85984	0.85990
p-Xylene	0.85667	0.85669
Mesitylene	0.86109	0.86111
N-Methylpyrrolidone	1.02805	–

TABLE 2

Experimental excess molar volumes V_m^E (cm^3 mol^{-1}), of an aromatic hydrocarbon (1)+ *N*-methylpyrrolidone (2) at 298.15 K

x	V_m^E	x	V_m^E
Benzene (1)+ *N*-methylpyrrolidone (2)			
0.09550	−0.11495	0.55612	−0.65446
0.20352	−0.26546	0.64802	−0.66541
0.28016	−0.38159	0.72578	−0.63895
0.36027	−0.50882	0.82221	−0.50794
0.48095	−0.64252	0.92120	−0.28212
Toluene (1)+ *N*-methylpyrrolidone (2)			
0.08133	−0.22179	0.61143	−0.82401
0.16241	−0.41005	0.70751	−0.72389
0.24987	−0.57364	0.79682	−0.61661
0.34045	−0.70679	0.89914	−0.36540
0.42613	−0.79673	0.95842	−0.21126
Ethylbenzene (1)+ *N*-methylpyrrolidone (2)			
0.06245	−0.14745	0.48284	−0.65293
0.14539	−0.29491	0.58103	−0.67687
0.22540	−0.42394	0.67433	−0.62886
0.31354	−0.55184	0.78138	−0.48651
0.39883	−0.60991	0.89276	−0.28900
o-Xylene (1)+ *N*-methylpyrrolidone (2)			
0.07315	−0.17010	0.58326	−0.63246
0.14792	−0.31646	0.58035	−0.58217
0.22985	−0.45068	0.78144	−0.46072
0.30853	−0.52884	0.88726	−0.26038
0.39358	−0.61009	0.94509	−0.14122
0.48195	−0.63987		
m-Xylene (1)+ *N*-methylpyrrolidone (2)			
0.07236	−0.17234	0.57477	−0.65692
0.14774	−0.33187	0.67848	−0.60551
0.19876	−0.38564	0.73496	−0.54446
0.22901	−0.45319	0.76956	−0.49699
0.30539	−0.54904	0.84501	−0.37972
0.39400	−0.62401	0.87326	−0.30927
0.47754	−0.66723	0.89639	−0.27491
p-Xylene (1)+ *N*-methylpyrrolidone (2)			
0.06377	−0.19542	0.48068	−0.75399
0.14343	−0.35750	0.57417	−0.76371
0.22137	−0.52501	0.67152	−0.69637
0.30574	−0.62802	0.77829	−0.56552
0.39369	−0.73728	0.89204	−0.31198
Mesitylene (1)+ *N*-methylpyrrolidone (2)			
0.05996	−0.07840	0.54872	−0.39132
0.12836	−0.18675	0.64512	−0.37234
0.19852	−0.26521	0.75977	−0.29988
0.28193	−0.32759	0.87210	−0.17892
0.36561	−0.36772	0.95144	−0.06981
0.45289	−0.39242		

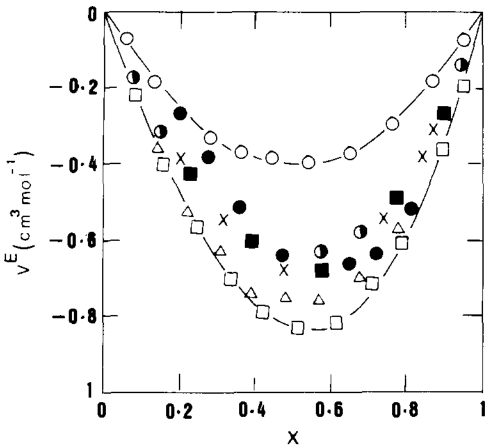

Fig. 1. Excess molar volumes of an aromatic hydrocarbon (1)+ *N*-methylpyrrolidone (2) at 298.15 K. (■) Benzene; (□) toluene; (×) ethylbenzene; (◑) *o*-xylene; (●) *m*-xylene; (△) *p*-xylene; (○) mesitylene.

The excess molar volumes for the systems studied here were predicted using the theory of Flory [9–12] from the following equation

$$V^E = (v^0)^{7/3}(4/3 - v^{01/3})^{-1}(\tilde{T} - T^0)(x_1 V_1^* + x_2 V_2^*) \tag{2}$$

where v^0, $\tilde{T}$, T^0, x_i and V_i^* are, respectively, the ideal reduced volume, the reduced temperature of the mixture, the ideal reduced temperature, the mole fraction of the *i*th component and the characteristic volume. These quantities can be evaluated from the following equations

$$\tilde{v}^0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \tag{3}$$

$$T^0 = (\tilde{v}^{01/3} - 1)/\tilde{v}^{04/3} \tag{4}$$

$$\tilde{v}_i = \left[(1 + 4/3\alpha_i T)/(1 + \alpha T)\right]^3 \tag{5}$$

TABLE 3

Coefficients, a_i, and standard deviations, s, for least-squares representations of V_m^E (cm^3 mol^{-1}) for aromatic hydrocarbons (1)+NMP (2) by eqn. (1)

Aromatic hydrocarbon	a_1	a_2	a_3	a_4	s
Benzene	−2.538	1.491	−0.035	–	0.06
Toluene	−3.321	0.487	−0.051	–	0.03
Ethylbenzene	−2.657	0.516	−0.100	−0.287	0.06
o-Xylene	−2.593	0.232	0.042	−0.264	0.03
m-Xylene	−2.663	0.196	−0.122	–	0.04
p-Xylene	−3.067	0.392	−0.174	−0.509	0.08
Mesitylene	−1.614	−0.122	0.023	0.319	0.07

$$\phi_i = (x_i V_i^*)/(x_i V_i^* + x_j V_j^*) \tag{6}$$

The reduced temperature, $\tilde{T}$, for the binary mixture is given by

$$\tilde{T} = \left(\frac{\phi_1 P_1^* \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2}{\phi_1 P_1^* + \phi_2 P_2^*}\right)\left(1 - \frac{\phi_1 \theta_2 X_{12}}{\phi_1 P_1^* + \phi_2 P_2^*}\right)^{-1} \tag{7}$$

where X_{12} is a constant characterising the difference in interaction energy between sites on neighbouring molecules of species 1 and 2. The reduced temperature, $\tilde{T}$, of the mixture is dependent on the parameter X_{12}, which can be evaluated from the excess heat of mixing. Since the excess heat of mixing values for our systems are not available in the literature, $\tilde{T}$ values of the binary mixtures were obtained from

$$\tilde{T} = \phi_1 \tilde{T}_1 + \phi_2 \tilde{T}_2 \tag{8}$$

which is a reasonable approximation of eqn. (7). The parameters of the pure liquids used for computing the excess molar volumes, V^E, of the binary mixtures in this study are listed in Table 4. Predicted V^E values and the experimental values at $x = 0.5$ are listed in Table 5 for comparison.

The poor agreement between the experimental and predicted values is mostly attributed to the specific interaction between *N*-methylpyrrolidone and an aromatic hydrocarbon which is not taken into account in the Flory theory.

The excess molar volume obtained here can be explained by the dipole–induced-dipole interaction between the carbonyl group of NMP and the benzene ring of an aromatic hydrocarbon, which is greater than the dispersive and dipole–dipole breaking interactions. Due to the electron donor ability of the aromatic hydrocarbon and the weak acceptor ability of NMP, a weak charge-transfer complex will be formed. Toluene has a greater electron donor ability than benzene (inductive effect of the methyl group), thus giving a stronger charge-transfer complex, which is supported by the

TABLE 4

Parameters of the pure component liquids at 298.15 K

Component	V (cm^3 mol^{-1})	$\alpha \times 10^{-3}$ (K^{-1})	V^* (cm^3 mol^{-1})	$\tilde{v}$ (cm^3 mol^{-1})	T^* (K)
Benzene	89.41	1.235	69.10	1.294	4658
Toluene	106.84	1.072	84.64	1.262	5053
Ethylbenzene	123.12	1.016	98.42	1.213	5231
o-Xylene	121.36	0.952	98.05	1.238	5421
m-Xylene	123.48	0.991	99.11	1.246	5231
p-Xylene	123.93	1.003	99.28	1.248	5231
Mesitylene	139.59	0.942	112.97	1.236	5421
N-Methylpyrrolidone	96.43	0.837	79.47	1.213	5801

TABLE 5

Summary of calculations for mixtures of NMP with seven aromatic hydrocarbons using the Flory theory

	V^{E}_{exp} (cm^3 mol^{-1}) (at $x = 0.5$)	V^{E}_{pred} (cm^3 mol^{-1})
Benzene	−0.634	−0.179
Toluene	−0.830	−0.074
Ethylbenzene	−0.664	−0.047
o-Xylene	−0.648	−0.020
m-Xylene	−0.666	−0.036
p-Xylene	−0.767	−0.041
Mesitylene	−0.403	−0.018

largest negative V^{E} value. As the substitution of the methyl group in the benzene ring (xylene and mesitylene) increases, the negative effect decreases, probably due to the steric effect.

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