Thermochimica Acta, 237 (1994) 35–41
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01617-C

Excess volumes and excess viscosities of benzene with picolines

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(Received 30 July 1993; accepted 28 September 1993)

Abstract

From density and viscosity measurements at 298.15 and 313.15 K, excess volumes V^E and excess viscosities η^E of the binary mixtures of benzene with picolines were determined. Both the V^E and η^E values are slightly negative over the whole composition range. The results are discussed in terms of molecular interactions.

INTRODUCTION

This work continues our study of the molecular interactions between benzene or cyclohexane and some aromatic heterocycles [1–5].

The volumetric properties of some of the mixtures of benzene with picolines have already been studied [6–8], but no literature η^E data are available for these mixtures. We report here excess volumes V^E and excess viscosities η^E for binary mixtures of benzene with picolines at 298.15 and 313.15 K.

EXPERIMENTAL

Materials

Benzene (better than 99.9 mol%) and β-picoline (better than 99 mol%) were obtained from Aldrich. α-Picoline (better than 99 mol%) and γ-picoline (better than 99 mol%) were provided by TCI. All the liquids were used without further purification.

Table 1 shows the experimental values of density and viscosity for the pure components at 298.15 K compared with those found in the literature [9].

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TABLE 1

Densities ρ and viscosities η of pure compounds at 298.15 K, and comparison with literature data [9]

Component	$\rho/\mathrm{g\ cm^{-3}}$		η/cP	
	This study	Lit.	This study	Lit.
Benzene	0.87366	0.87360	0.5925	0.6028
α-Picoline	0.93981	0.93981	0.7483	0.753
β-Picoline	0.95178	0.95197	0.8661	0.8723
γ-Picoline	0.95029	0.95020	0.8369	

TABLE 2

Excess volumes V^E of binary mixtures of benzene(1) + picolines(2) at 298.15 and 313.15 K

x_1	$V^E/\mathrm{cm^3\ mol^{-1}}$	x_1	$V^E/\mathrm{cm^3\ mol^{-1}}$	x_1	$V^E/\mathrm{cm^3\ mol^{-1}}$
Benzene + α-picoline at 298.15 K					
0.1085	−0.0100	0.3998	−0.0251	0.6968	−0.0255
0.1906	−0.0148	0.5033	−0.0273	0.7878	−0.0218
0.2983	−0.0207	0.6023	−0.0275	0.9114	−0.0108
Benzene + β-picoline at 298.15 K					
0.1141	−0.0273	0.4033	−0.0908	0.6997	−0.0945
0.1884	−0.0494	0.4987	−0.0971	0.7803	−0.0817
0.3066	−0.0720	0.5928	−0.1029	0.9002	−0.0466
Benzene + γ-picoline at 298.15 K					
0.0990	−0.0310	0.3990	−0.0818	0.6937	−0.0777
0.1870	−0.0516	0.5041	−0.0864	0.7920	−0.0658
0.2852	−0.0669	0.6072	−0.0859	0.9024	−0.0357
Benzene + α-picoline at 313.15 K					
0.1096	−0.0120	0.3970	−0.0356	0.6948	−0.0371
0.1988	−0.0204	0.5047	−0.0407	0.7971	−0.0311
0.2979	−0.0287	0.5963	−0.0403	0.9080	−0.0164
Benzene + β-picoline at 313.15 K					
0.1133	−0.0487	0.4123	−0.1285	0.7055	−0.1226
0.1981	−0.0801	0.5003	−0.1292	0.7964	−0.0981
0.2994	−0.1059	0.6000	−0.1342	0.8976	−0.0586
Benzene + γ-picoline at 313.15 K					
0.0990	−0.0340	0.4012	−0.1125	0.6938	−0.1066
0.1961	−0.0636	0.5016	−0.1200	0.7900	−0.0794
0.2993	−0.0936	0.6076	−0.1170	0.9088	−0.0405

TABLE 3

Excess viscosities η^E of binary mixtures of benzene(1) + picolines(2) at 298.15 and 313.15 K

x_1	η^E/cP	x_1	η^E/cP	x_1	η^E/cP
Benzene + α-picoline at 298.15 K					
0.1010	−0.0021	0.4077	−0.0053	0.7056	−0.0046
0.2038	−0.0039	0.5085	−0.0060	0.8064	−0.0032
0.3050	−0.0049	0.6172	−0.0056	0.9046	−0.0020
Benzene + β-picoline at 298.15 K					
0.1007	−0.0031	0.4007	−0.0083	0.7030	−0.0069
0.2003	−0.0056	0.5030	−0.0084	0.8031	−0.0044
0.3013	−0.0076	0.6053	−0.0082	0.9045	−0.0024
Benzene + γ-picoline at 298.15 K					
0.1012	−0.0032	0.4034	−0.0097	0.7029	−0.0079
0.2012	−0.0050	0.5067	−0.0096	0.8020	−0.0063
0.3025	−0.0082	0.6059	−0.0090	0.9004	−0.0040
Benzene + α-picoline at 313.15 K					
0.1005	−0.0016	0.4077	−0.0041	0.7056	−0.0033
0.1990	−0.0025	0.5085	−0.0040	0.8064	−0.0024
0.3050	−0.0035	0.6172	−0.0039	0.9001	−0.0013
Benzene + β-picoline at 313.15 K					
0.0995	−0.0022	0.4007	−0.0059	0.7006	−0.0049
0.2002	−0.0038	0.5030	−0.0060	0.8057	−0.0033
0.3010	−0.0050	0.6033	−0.0056	0.9044	−0.0019
Benzene + γ-picoline at 313.15 K					
0.1001	−0.0021	0.4034	−0.0068	0.7029	−0.0048
0.2012	−0.0037	0.5067	−0.0069	0.8047	−0.0036
0.3025	−0.0057	0.6059	−0.0060	0.9004	−0.0020

Measurements

Densities were measured with an Anton Paar DMA-58 vibrating tube densimeter, and viscosities were determined using an Ubbelhode viscosimeter with a Schott-Geräte automatic measuring unit model AVS-440. The procedure has been previously described [4].

RESULTS AND DISCUSSION

Measured data of density and viscosity are used to calculate V^E and η^E using the equations

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \quad (1)$$

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

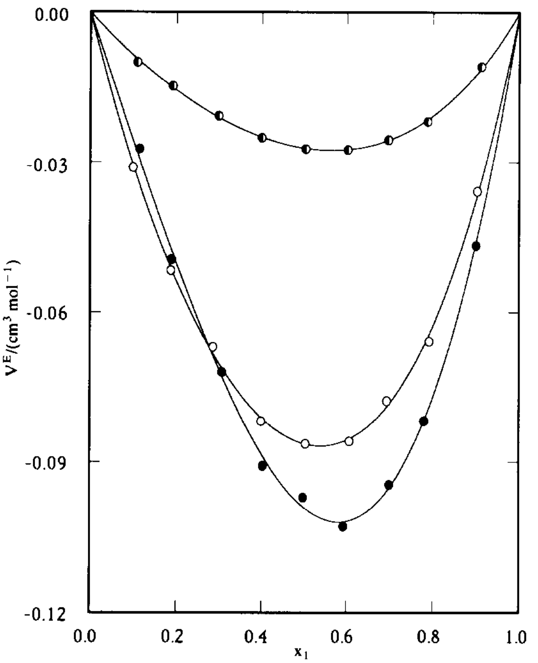

Fig. 1. Excess volumes V^E of benzene(1) + a picoline(2) at 298.15 K as a function of mole fraction x_1: ◐, α-picoline; ●, β-picoline; ○, γ-picoline.

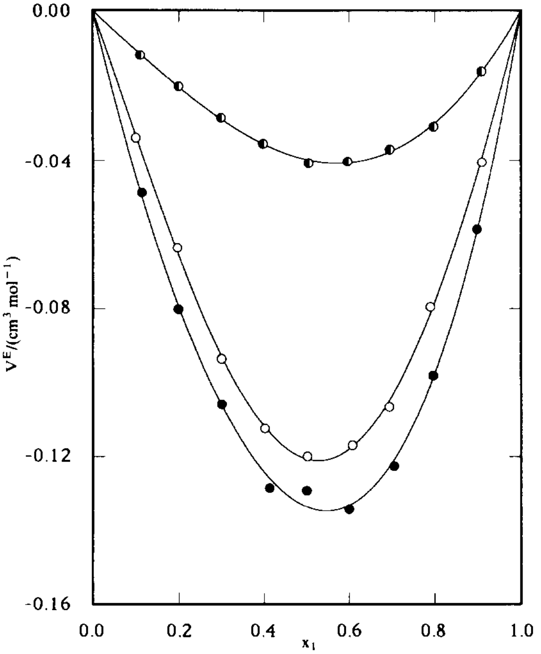

Fig. 2. Excess volumes V^E of benzene(1) + a picoline(2) at 313.15 K as a function of mole fraction x_1: ◐, α-picoline; ●, β-picoline; ○, γ-picoline.

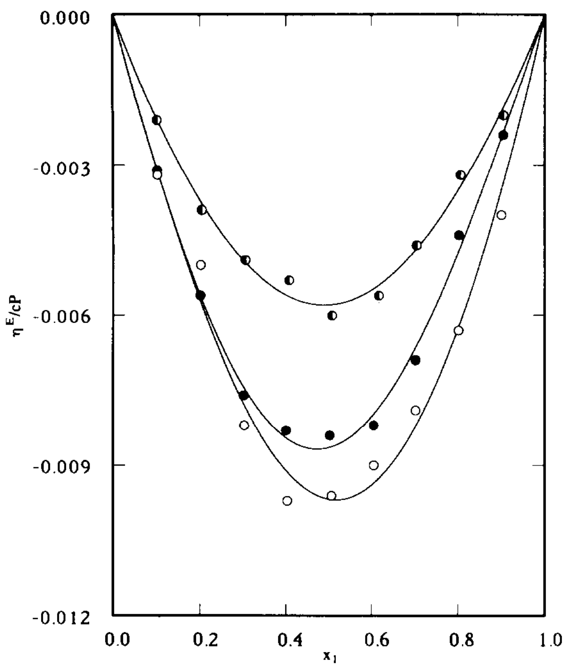

Fig. 3. Excess viscosities η^E of benzene(1) + a picoline(2) at 298.15 K as a function of mole fraction x_1: ◐, α-picoline; ●, β-picoline; ○, γ-picoline.

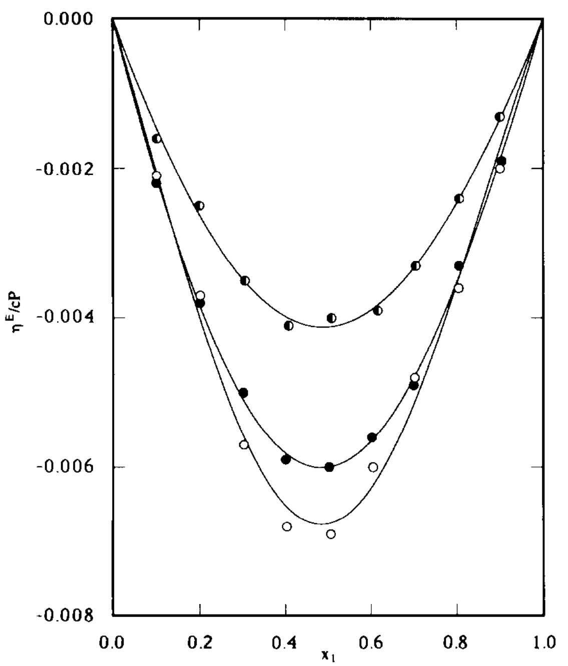

Fig. 4. Excess viscosities η^E of benzene(1) + a picoline(2) at 313.15 K as a function of mole fraction x_1: ◐, α-picoline; ●, β-picoline; ○, γ-picoline.

TABLE 4

Coefficients a_i of eqn. (3) and standard deviations σ determined by the method of least squares

Function	a_1	a_2	a_3	σ
Benzene + α-picoline at 298.15 K				
V^E/cm³ mol⁻¹	−0.1087	−0.0260	−0.0138	0.0004
η^E/cP	−0.0232	−0.0101	−0.0016	0.0002
Benzene + β-picoline at 298.15 K				
V^E/cm³ mol⁻¹	−0.3964	−0.1402	−0.0042	0.0017
η^E/cP	−0.0346	0.0043	0.0060	0.0002
Benzene + γ-picoline at 298.15 K				
V^E/cm³ mol⁻¹	−0.3455	−0.0469	−0.0523	0.0011
η^E/cP	−0.0387	−0.0030	−0.0033	0.0005
Benzene + α-picoline at 313.15 K				
V^E/cm³ mol⁻¹	−0.1591	−0.0496	0.0011	0.0006
η^E/cP	−0.0165	0.0008	0.0015	0.0001
Benzene + β-picoline at 313.15 K				
V^E/cm³ mol⁻¹	−0.5340	−0.0929	−0.0565	0.0023
η^E/cP	−0.0240	0.0016	0.0027	0.0001
Benzene + γ-picoline at 313.15 K				
V^E/cm³ mol⁻¹	−0.4826	−0.0638	0.4826	0.0013
η^E/cP	−0.0270	0.0023	0.0094	0.0003

where ρ, ρ_1 and ρ_2 are the densities (g cm^{-3}) of the mixtures and of the pure components, η, η_1 and η_2 are the absolute viscosities (cP) of the mixtures and of the pure components, and x_i is the mole fraction of component i in the mixture.

Excess volumes and excess viscosities are given in Tables 2 and 3. They are plotted in Figs. 1–4.

The results of eqns. (1) and (2) have been fitted by the method of least squares to a polynomial equation of the type

$$Y^E = x_1(1 - x_1)[a_1 + a_2(2x_1 - 1) + \ldots]$$

where a_1, a_2, etc., are adjustable parameters and x_1 is the mole fraction of benzene. The values of the parameters a_i, together with standard deviations $\sigma(Y^E)$ are given in Table 4.

The V^E values for benzene + α-picoline or β-picoline are in reasonable agreement with those of Wóycicky and Sadowska [6] and Garrett and Pollock [7]. The V^E results of Botros et al. [8] are not in good agreement, either with our results or with those of the abvoe-mentioned authors. The excess volumes are negative over the whole composition range and become more negative with temperature. For a given temperature, V^E decreases in the sequence α-picoline > γ-picoline > β-picoline.

The excess viscosities are slightly negative and become less negative with temperature; η^E decreases in the sequence α-picoline > β-picoline > γ-picoline. A change was observed in the sequence between β-picoline and γ-picoline for η^E compared with V^E. However, the mixtures with β-picoline and γ-picoline display similar values for these magnitudes.

The low values obtained for both V^E and η^E compared with those of the mixtures of cyclohexane and picolines [4] could be due to opposite effects. One of these effects could be attributed to the existence of molecular associations of charge-transfer-type between benzene and picoline molecules which lead to negative deviations from the ideal behaviour. In addition to this, the addition of benzene causes the picolines to disassociate due to a weakening of the dipole–dipole interactions in picolines. The disassociation of the picolines compensates for the charge transfer effect to a considerable extent and, consequently, the deviations from ideality are minimal. This behaviour is similar to that observed for the mixtures of benzene with 2,4-lutidine or 2,6-lutidine previously investigated in our laboratory [5].

ACKNOWLEDGEMENT

The authors are grateful for financial assistance from Diputación General de Aragón (Proyecto PCB5/90).

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