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Excess volumes and excess viscosities of binary mixtures of cyclohexane + picoline

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Abstract

The densities and viscosities of binary mixtures of cyclohexane + picoline have been measured at 298.15 and 313.15 K over the whole composition range. From these, excess volumes V^E, excess viscosities η^E and excess energies of activation for viscous flow G^{*E} have been calculated. V^E is positive and both η^E and G^{*E} are negative. These results are consistent with the self-association of picolines and the non-polar character of cyclohexane, which produces the dissociation of the picolines.

INTRODUCTION

This paper is a continuation of previous work [1–3] in which we showed how the introduction of a heteroatom in an aromatic ring influences the interaction of the molecule with benzene or cyclohexane molecules.

Several properties of mixtures of cyclohexane with isomeric picolines have previously been investigated [1, 4, 5]. In this paper the values of excess volumes V^E, excess viscosities η^E and excess energies of activation for viscous flow G^{*E} are reported for binary mixtures of cyclohexane + picoline at 298.15 and 313.15 K.

EXPERIMENTAL

Materials

The liquids used were cyclohexane (Fluka; better than 99.5 mol%) α-picoline (TCI; better than 99 mol%), β-picoline (Aldrich; better than 99 mol%) and γ-picoline (TCI; better than 99 mol%). No further purification was attempted.

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TABLE 1

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

Component	$\rho/(\mathrm{g\,cm^{-3}})$		$\eta/(\mathrm{cp})$	
	This paper	Ref. 6	This paper	Ref. 7
Cyclohexane	0.77371	0.77375	0.8997	0.8936 [a]
α-Picoline	0.92963	0.93981	0.7703	0.7602 [a]
β-Picoline	0.95232		0.8960	
γ-Picoline	0.94900		0.8628	

[a] Interpolated value.

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. Densities were taken from Ref. 6 and viscosities from Ref. 7, using the suggested interpolation equations.

Measurements

Densities were measured by means of an Anton Paar DMA-58 vibrating tube densimeter. Calibration was carried out with deionized doubly-distilled water and dry air. The uncertainty of density measurements was $\pm 1 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$.

The viscosities of the pure components and of the mixtures were determined using a Ubbelhode viscosimeter with a Schott–Geräte automatic measuring unit model AVS-440. The accuracy of the time flow measurement is ±0.01%. A thermostatically-controlled bath (constant to ±0.01 K) was used. Mixtures were made by mass.

RESULTS AND DISCUSSION

The excess thermodynamic functions were calculated from our density and viscosity measurements with the equations

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

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

$$G^{*E} = RT\,|\ln \nu M - (x_1 \ln \nu_1 M_1 + x_2 \ln \nu_2 M_2)| \tag{3}$$

TABLE 2

Excess volumes V^E of the binary mixtures cyclohexane(1) + a picoline(2) at 298.15 and 313.15 K

x_1	$V_E/(cm^3\,mol^{-1})$	x_1	$V^E/(cm^3\,mol^{-1})$	x_1	$V^E/(cm^3\,mol^{-1})$
Cyclohexane + α-picoline at 298.15 K					
0.0890	0.1356	0.4012	0.5855	0.6981	0.6677
0.2100	0.3305	0.5031	0.6617	0.8073	0.5501
0.3068	0.4735	0.6029	0.6995	0.8860	0.3937
Cyclohexane + β-picoline at 298.15 K					
0.0877	0.1151	0.4021	0.4954	0.6994	0.5652
0.2127	0.2862	0.5007	0.5665	0.8087	0.4776
0.3025	0.3945	0.6003	0.5906	0.8890	0.3458
Cyclohexane + γ-picoline at 298.15 K					
0.0951	0.1269	0.4031	0.5191	0.7003	0.5980
0.2074	0.2805	0.5002	0.5880	0.8165	0.4923
0.3017	0.4123	0.5994	0.6230	0.8909	0.3503
Cyclohexane + α-picoline at 313.15 K					
0.0972	0.1528	0.4051	0.5949	0.7102	0.6834
0.2093	0.3295	0.5029	0.6807	0.8043	0.5726
0.3070	0.4815	0.6046	0.7129	0.8929	0.3840
Cyclohexane + β-picoline at 313.15 K					
0.0865	0.1080	0.4021	0.4991	0.7026	0.5926
0.1995	0.2680	0.5006	0.5731	0.8094	0.4985
0.2984	0.3939	0.6006	0.6083	0.8914	0.3524
Cyclohexane + γ-picoline at 313.15 K					
0.0994	0.1290	0.3984	0.5195	0.7174	0.6025
0.2092	0.2858	0.4997	0.5952	0.8161	0.4998
0.3002	0.4084	0.5992	0.6351	0.8903	0.3580

where M_1 and M_2 are the molecular masses of the components, ρ, ρ_2 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, v, v_1 and v_2 are the corresponding kinematic viscosities ($m^2\,s^{-1}$), M is the molar mass of the mixture and x_i is the mole fraction of component i in the mixture.

Tables 2–4 show the excess thermodynamic functions for the three mixtures at both temperatures. Excess volumes and excess viscosities are graphically presented in Figs. 1–4.

The values of V^E, η^E and G^{*E} were fitted to the polynomial expression

$$Y = x_1(1 - x_1)[a_1 + a_2(2x_1 - 1) + \ldots] \quad (4)$$

where a_1, a_2, etc. are adjustable parameters and x_1 is the mole fraction of cyclohexane. The values of the parameters a_i computed by the method of

TABLE 3

Excess viscosities η^E of the binary mixtures cyclohexane(1) + picoline(2) at 298.15 and 313.15 K

x_1	$\eta^E/(cp)$	x_1	$\eta^E/(cp)$	x_1	$\eta^E/(cp)$
Cyclohexane + α-picoline at 298.15 K					
0.0997	−0.0429	0.3982	−0.1262	0.6988	−0.1411
0.1992	−0.0735	0.4989	−0.1403	0.7981	−0.1238
0.2999	−0.1046	0.5983	−0.1467	0.8986	−0.0794
Cyclohexane + β-picoline at 298.15 K					
0.1037	−0.0408	0.3998	−0.1163	0.6980	−0.1270
0.2009	−0.0704	0.5014	−0.1270	0.7990	−0.1089
0.2992	−0.0967	0.5980	−0.1312	0.8984	−0.0726
Cyclohexane + γ-picoline at 298.15 K					
0.1011	−0.0379	0.3993	−0.1096	0.6970	−0.1216
0.1974	−0.0686	0.4994	−0.1201	0.7990	−0.1038
0.2990	−0.0938	0.5991	−0.1261	0.8981	−0.0718
Cyclohexane + α-picoline at 313.15 K					
0.0957	−0.0270	0.4020	−0.0875	0.6996	−0.0967
0.2031	−0.0532	0.5083	−0.0976	0.8003	−0.0831
0.2993	−0.0725	0.6041	−0.1006	0.9002	−0.0530
Cyclohexane + β-picoline at 313.15 K					
0.0971	−0.0261	0.3993	−0.0790	0.6976	−0.0856
0.2024	−0.0495	0.5003	−0.0867	0.7959	−0.0741
0.2959	−0.0653	0.6044	−0.0893	0.9005	−0.0470
Cyclohexane + γ-picoline at 313.15 K					
0.0956	−0.0244	0.3997	−0.0765	0.7000	−0.0815
0.2026	−0.0478	0.4996	−0.0834	0.7974	−0.0714
0.2978	−0.0642	0.6019	−0.0857	0.8998	−0.0460

least squares are shown in Table 5, together with standard deviations $\sigma(Y^E)$

$$\sigma(Y^E) = \left[\sum (Y^E_{\text{calc}} - Y^E_{\text{exp}})^2/(n-p)\right]^{1/2} \qquad (5)$$

where n is the number of experimental data and p is the number of parameters.

Our V^E results for cyclohexane + α-picoline are approximately 4% lower than those of Wóycicky and Sadowska [4]. The excess volumes are positive over the whole composition range and increase with increasing temperature. Maximum V^E values are slightly shifted towards higher concentrations of cyclohexane. V^E increases in the sequence β-picoline < γ-picoline < α-picoline, although the values for β-picoline and γ-picoline are similar. The picolines are associated liquids and the addition of cyclohexane (which is

TABLE 4

Excess energies of activation for viscous flow G^{*E} of the binary mixtures cyclohexane(1) + picoline(2) at 298.15 and 313.15 K

x_1	$G^{*E}/(\text{kJ mol}^{-1})$	x_1	$G^{*E}/(\text{kJ mol}^{-1})$	x_1	$G^{*E}/(\text{kJ mol}^{-1})$
Cyclohexane + α-picoline at 298.15 K					
0.0997	−0.1319	0.3982	−0.3905	0.6988	−0.4232
0.1992	−0.2277	0.4989	−0.4322	0.7981	−0.3588
0.2999	−0.3241	0.5983	−0.4468	0.8986	−0.2216
Cyclohexane + β-picoline at 298.15 K					
0.1037	−0.1116	0.3998	−0.3291	0.6980	−0.3609
0.2009	−0.1961	0.5014	−0.3631	0.7990	−0.3073
0.2992	−0.2712	0.5980	−0.3748	0.8984	−0.1998
Cyclohexane + γ-picoline at 298.15 K					
0.1011	−0.1064	0.3993	−0.3167	0.6970	−0.3483
0.1974	−0.1939	0.4994	−0.3480	0.7990	−0.2932
0.2990	−0.2680	0.5991	−0.3629	0.8981	−0.1983
Cyclohexane + α-picoline at 313.15 K					
0.0957	−0.1091	0.4020	−0.3576	0.6996	−0.3851
0.2031	−0.2166	0.5083	−0.3971	0.8003	−0.3237
0.2993	−0.2959	0.6041	−0.4057	0.9002	−0.1995
Cyclohexane + β-picoline at 313.15 K					
0.0971	−0.0929	0.3993	−0.2943	0.6976	−0.3236
0.2024	−0.1794	0.5003	−0.3261	0.7959	−0.2789
0.2959	−0.2401	0.6044	−0.3376	0.9005	−0.1742
Cyclohexane + γ-picoline at 313.15 K					
0.0956	−0.0902	0.3997	−0.2913	0.7000	−0.3104
0.2026	−0.1791	0.4996	−0.3189	0.7974	−0.2698
0.2978	−0.2426	0.6019	−0.3274	0.8998	−0.1708

non polar) disrupts the molecular order and dissociation of picolines and gives rise to a positive value of V^E.

The excess viscosities and excess energies of activation for viscous flow are negative and decrease in absolute value as the temperature is increased. Here also the minimum η^E and G^{*E} values are shifted in the same direction. Both η^E and G^{*E} increase in absolute value in the sequence γ-picoline < β-picoline < α-picoline. There is a inversion in the order for β-picoline and γ-picoline compared with the V^E sequence although the values for these last mixtures are still approximately the same. The values of η^E and G^{*E} can also be interpreted in the same way as the V^E values. According to Fort and Moore [8] this viscosity behaviour corresponds to systems in which there is an associated component and in which solute–solvent complexes are not formed or have low stability. According to Meyer et al. [9] negative values of G^{*E} correspond to the existence of

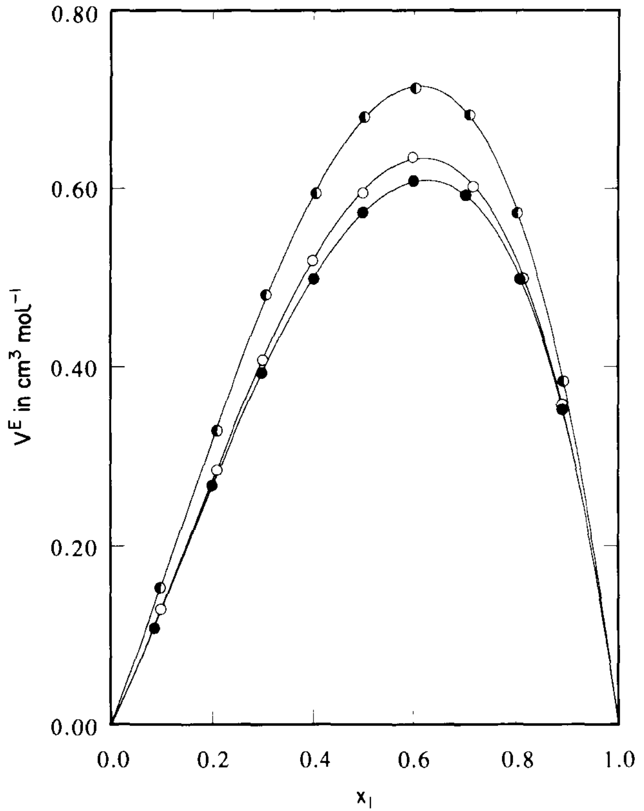

Fig. 1. Excess molar volumes V^E of cyclohexane(1) + picoline(2) at 298.15 K as a function of mole fraction x_1: (◐) α-picoline; (●) β-picoline; (○) γ-picoline.

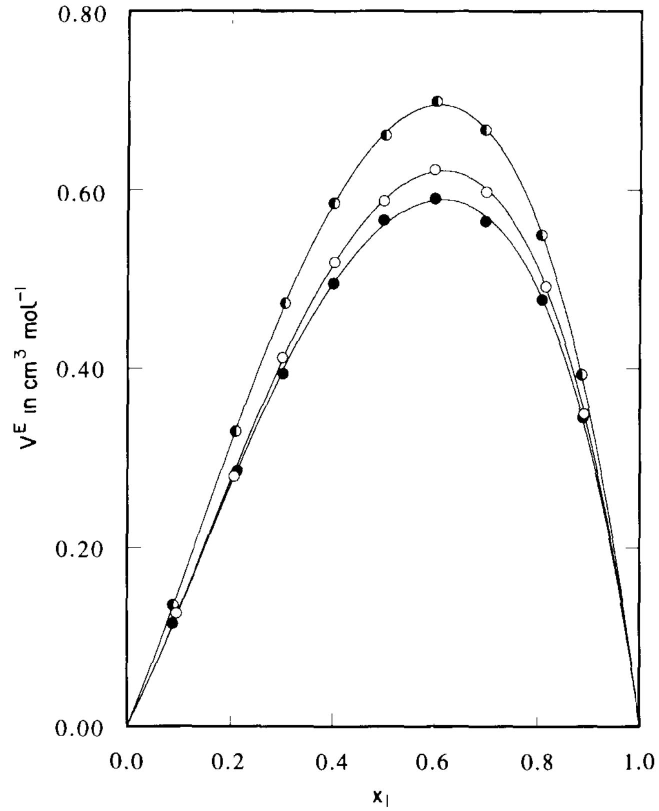

Fig. 2. Excess molar volumes V^E of cyclohexane(1) + picoline(2) at 313.15 K as a function of mole fraction x_1: (◐) α-picoline; (●) β-picoline; (○) γ-picoline.

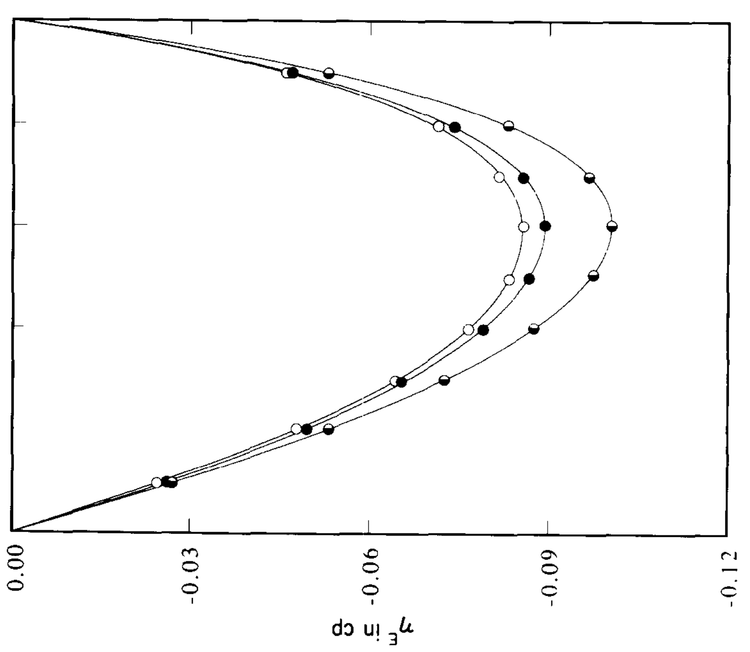

Fig. 4. Excess molar viscosities η^E of cyclohexane(1) + picoline(2) at 313.15 K as a function of mole fraction x_1; (◐) α-picoline; (●) β-picoline; (○) γ-picoline.

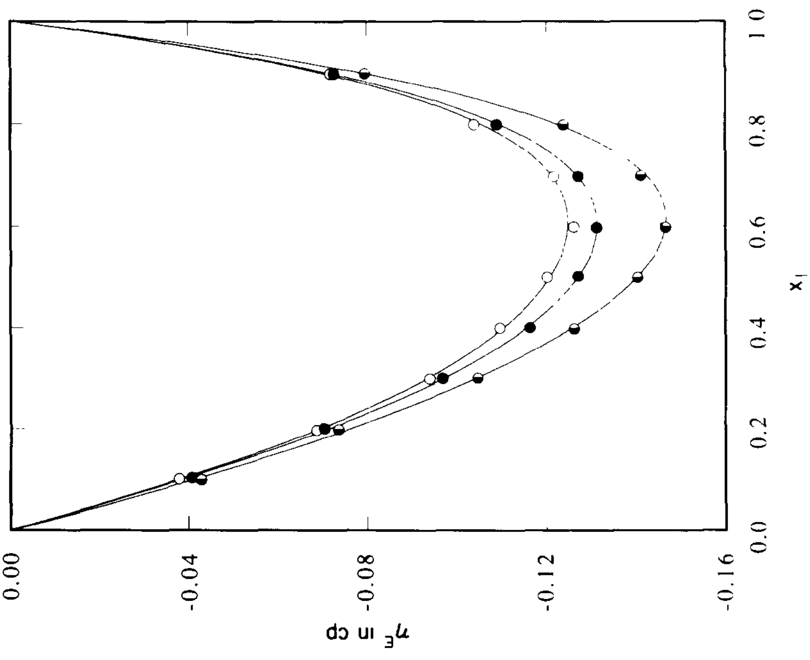

Fig. 3. Excess molar viscosities η^E of cyclohexane(1) + picoline(2) at 298.15 K as a function of mole fraction x_1; (◐) α-picoline; (●) β-picoline; (○) γ-picoline.

TABLE 5

Coefficients a_i of Eq. (4) and standard deviations σ determined by the method of least squares

Function	a_1	a_2	a_3	a_4	σ
Cyclohexane + α-picoline at 298.15 K					
$V^E/(cm^3\ mol^{-1})$	2.6530	1.1505	0.2614	0.3933	0.0029
$\eta^E/(cp)$	−0.5609	−0.2149	−0.1636	−0.0712	0.0016
$G^{*E}/(kJ\ mol^{-1})$	−1.7299	−0.6014	−0.3113	−0.0609	0.0040
Cyclohexane + β-picoline at 298.15 K					
$V^E/(cm^3\ mol^{-1})$	2.2421	0.9572	0.3651	0.5348	0.0048
$\eta^E/(cp)$	−0.5078	−0.1596	−0.1568	−0.1059	0.0009
$G^{*E}/(kJ\ mol^{-1})$	−1.4499	−0.4895	−0.3560	−0.2219	0.0018
Cyclohexane + γ-picoline at 298.15 K					
$V^E/(cm^3\ mol^{-1})$	2.3551	1.0776	0.3029	0.4613	0.0034
$\eta^E/(cp)$	−0.4829	−0.1447	−0.1753	−0.1206	0.0013
$G^{*E}/(kJ\ mol^{-1})$	−1.3976	−0.4235	−0.4001	−0.2844	0.0030
Cyclohexane + α-picoline at 313.15 K					
$V^E/(cm^3\ mol^{-1})$	2.7098	1.2671	0.2759	0.2772	0.0029
$\eta^E/(cp)$	−0.3876	−0.1355	−0.0998	−0.0611	0.0002
$G^{*E}/(kJ\ mol^{-1})$	−1.5794	−0.5098	−0.2670	−0.1495	0.0011
Cyclohexane + β-picoline at 313.15 K					
$V^E/(cm^3\ mol^{-1})$	2.2892	1.1040	0.4056	0.4768	0.0016
$\eta^E/(cp)$	−0.3462	−0.1066	−0.0994	−0.0550	0.0003
$G^{*E}/(kJ\ mol^{-1})$	−1.3026	−0.4513	−0.3096	−0.1614	0.0010
Cyclohexane + γ-picoline at 313.15 K					
$V^E/(cm^3\ mol^{-1})$	2.3898	1.1586	0.2780	0.4006	0.0019
$\eta^E/(cp)$	−0.3334	−0.0906	−0.0981	−0.0833	0.0003
$G^{*E}/(kJ\ mol^{-1})$	−1.2752	−0.3623	−0.3091	−0.2756	0.0013

solute–solute association like that mentioned for picolines. This association is also confirmed by the positive excess enthalpy for these mixtures [1].

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