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Viscosities and densities for binary mixtures of cresols

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Abstract

This work reports the measured density and viscosity values of mixtures of 2-, 3- and 4-methylphenol (*o*-, *m*- and *p*-cresol), at temperatures in the range 313.15–333.15 K over a range of mole fractions. Viscosities were fitted to the McAllister three-body interaction model and to the Ausländer equation. The results showed mixtures containing *o*-cresol to be more fluid when compared to the pure liquids and positive viscosity deviations for *m*- and *p*-cresol mixtures. The results indicated an increase in the average degree of cross-association of mixtures containing *o*-cresol. The activation energy, enthalpy and entropy of flow were determined by applying Eyring's theory of rate processes.

Keywords: Density; Viscosity; *o*-Cresol; *m*-Cresol; *p*-Cresol; Liquid mixture; Molecular interactions; Viscosity deviations; Eyring's theory

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1. Introduction

Experimental data of physical properties such as density and viscosity in binary mixtures give information on the existence of specific molecular interactions. Transport and thermodynamic properties also provide insight into the molecular arrangement of liquids. Thermophysical properties are required for the design of industrial processes, but such data are scarce in the literature.

In this work, the densities and viscosities of, 2-, 3- and 4-methylphenol (*o*-, *m*- and *p*-cresol) binary mixtures were measured at 313.15, 323.15 and 333.15 K, at atmospheric pressure. Results were fitted to the empirical equations of McAllister [1] and Ausländer [2], based on Eyring theory [3,4], which were proposed to describe viscosities of mixtures in terms of pure-component data. The aim of this work was to determine the properties of viscous flow in the absence of expansion or contraction effects due to interaction of unlike molecules. Viscosity deviations should only reflect the degree of intermolecular association.

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2. Experimental

The chemicals employed were of analytical grade and provided by Merck. The mass fraction purities assumed by the manufacturer were: *o*-cresol (>0.990), *m*-cresol (>0.990), *p*-cresol (>0.980). Their actual purity, tested by gas chromatography, were as follows: *o*-cresol (0.997), *m*-cresol (0.994), *p*-cresol (>0.992).

Densities of the pure components and mixtures were measured using capillary pycnometers with an accuracy of ±0.0001. Weights were determined using a digital balance (Ohaus Galaxy 160D) accurate to 0.1 mg.

Kinematic viscosities were measured using Canon–Fenske-type Ostwald capillary viscometers for transparent liquids supplied by Proton. Sizes 50 and 75 were used according to the viscosity of the mixture. All the measurements were carried out according to ASTM test methods D445 and D2515. The viscometer was submerged in a thermostatic bath at 313.15, 323.15 and 333.15 K with a resolution of ±0.1 K and allowed to attain thermal equilibrium. The efflux time was measured with a hand-held digital stopwatch capable of measuring time within ±0.01 s. At least four sets of readings were taken with a reproducibility of the viscosity measurements within ±0.004 mPa s, representing an average uncertainty of ±0.5%. The observed viscosities were close to available data found in the literature [5].

3. Results

The densities and dynamic viscosities of pure liquids and binary mixtures over the whole composition range are listed in Table 1. Dynamic viscosities were obtained from the measured kinematic viscosity. Positive contributions (hydrogen bond rupture and dispersive interactions between unlike molecules) and negative contributions (intermolecular dipole interactions and geometrical fitting between components) to molar excess volumes should be virtually absent from the system studied in this work. As expected, densities were almost linear with composition, and in all cases, excess molar volumes did not exceed experimental errors.

Data were fitted using the correlating equations of McAllister [1] and Ausländer [2], both based on Eyring's theory of absolute reaction rates. The two-parameter McAllister three-body-interaction model is given as follows:

$$\begin{aligned}\ln \nu = {} & x_A^3 \ln \nu_A + 3x_A^2 x_B \ln Z_{AB} + 3x_A x_B^2 \ln Z_{BA} + x_B^3 \ln \nu_B - \ln\left(x_A + x_B\frac{M_B}{M_A}\right) \\ & + 3x_A^2 x_B \ln\left(\frac{2}{3} + \frac{M_B}{3M_A}\right) + 3x_A x_B^2 \ln\left(\frac{1}{3} + \frac{2M_B}{3M_A}\right) + x_B^3 \ln\left(\frac{M_B}{M_A}\right)\end{aligned} \quad (1)$$

where Z_{AB} and Z_{BA} are interaction parameters and M_i and n_i the molecular mass and kinematic viscosity of pure component *i*, respectively. In systems where both components have the same molecular mass, the last four terms vanish.

The Ausländer equation depends on three parameters representing binary interactions:

$$\eta = \frac{x_A \eta_A (x_A + B_{AB} x_B) + x_B \eta_B A_{BA} (B_{BA} x_A + x_B)}{x_A (x_A + B_{AB} x_B) + x_B A_{BA} (B_{BA} x_A + x_B)} \quad (2)$$

Table 1
Experimental densities and viscosities for *o*-, *m*- and *p*-cresol binary systems

	ρ (g cm^{-3})			η (mPa s)		
	313.15	323.15	333.15	313.15	323.15	333.15
$m + p$ (x_m)						
0.0000	1.0168	1.0092	1.0017	6.661	4.480	3.232
0.1000	1.0167	1.0090	1.0016	6.798	4.564	3.316
0.2000	1.0166	1.0089	1.0014	6.861	4.653	3.363
0.3000	1.0165	1.0086	1.0012	6.878	4.653	3.396
0.4000	1.0163	1.0085	1.0011	6.855	4.618	3.359
0.5000	1.0162	1.0084	1.0008	6.750	4.540	3.307
0.6000	1.0161	1.0082	1.0007	6.625	4.439	3.222
0.7000	1.0161	1.0080	1.0006	6.547	4.337	3.160
0.8000	1.0160	1.0078	1.0005	6.409	4.246	3.088
0.9000	1.0160	1.0077	1.0005	6.321	4.175	3.046
1.0000	1.0160	1.0077	1.0004	6.252	4.111	3.007
$m + o$ (x_m)						
0.0000	1.0260	1.0174	1.0085	4.243	3.020	2.274
0.1000	1.0246	1.0160	1.0076	4.379	3.086	2.301
0.2000	1.0234	1.0150	1.0067	4.539	3.145	2.346
0.3000	1.0227	1.0143	1.0060	4.689	3.235	2.396
0.4000	1.0215	1.0134	1.0054	4.861	3.320	2.449
0.5000	1.0207	1.0122	1.0044	5.048	3.417	2.518
0.6000	1.0194	1.0117	1.0038	5.248	3.543	2.604
0.7000	1.0188	1.0104	1.0031	5.462	3.666	2.702
0.8000	1.0180	1.0098	1.0023	5.693	3.805	2.801
0.9000	1.0167	1.0085	1.0013	5.966	3.949	2.904
1.0000	1.0160	1.0077	1.0004	6.252	4.111	3.007
$o + p$ (x_o)						
0.0000	1.0168	1.0092	1.0017	6.661	4.480	3.232
0.1000	1.0173	1.0097	1.0023	6.380	4.318	3.119
0.2000	1.0185	1.0107	1.0028	6.086	4.147	3.005
0.3000	1.0190	1.0113	1.0034	5.766	3.929	2.857
0.4000	1.0199	1.0119	1.0042	5.425	3.727	2.733
0.5000	1.0209	1.0127	1.0047	5.125	3.555	2.609
0.6000	1.0217	1.0135	1.0055	4.847	3.401	2.510
0.7000	1.0228	1.0146	1.0062	4.616	3.235	2.400
0.8000	1.0239	1.0153	1.0069	4.435	3.112	2.326
0.9000	1.0244	1.0165	1.0073	4.300	3.047	2.280
1.0000	1.0260	1.0174	1.0085	4.243	3.020	2.274

The coefficients in Eqs. (1) and (2) were regressed by the least-square fit method employing the Powell algorithm [6]. Results are listed in Table 2 together with their 95% level confidence intervals. In all cases a strong correlation was detected between the parameters of Ausländer equation, showing that some of them were not relevant. This was attributed to the difficulty of statistically splitting the effect of BA interactions into significant parameters. Therefore, as indicated in Table 2, for the mixtures containing *o*-cresol A_{BA}

Table 2
Values of parameters and confidence intervals for the models of McAllister and Ausländer

	McAllister equation		Ausländer equation		
	Z_{AB}	Z_{BA}	B_{AB}	B_{BA}	A_{BA}[a]
$m + p$					
313.15	6.330 ± 0.020	7.183 ± 0.044	−1.385 ± 0.007	4.1 ± 1.2	0.414 ± 0.086
323.15	4.229 ± 0.037	4.960 ± 0.042	−1.267 ± 0.033	3.23 ± 0.56	0.462 ± 0.054
333.15	3.076 ± 0.030	3.669 ± 0.035	−1.455 ± 0.052	3.66 ± 0.74	0.413 ± 0.057
$m + o$					
313.15	5.211 ± 0.015	4.628 ± 0.014	0.683 ± 0.017	1.530 ± 0.024	
323.15	3.554 ± 0.013	3.162 ± 0.012	0.490 ± 0.032	1.520 ± 0.50	
333.15	2.656 ± 0.016	2.327 ± 0.015	0.291 ± 0.044	1.464 ± 0.69	
$o + p$					
313.15	4.240 ± 0.016	5.802 ± 0.021	1.067 ± 0.023	0.183 ± 0.015	
323.15	3.004 ± 0.030	3.996 ± 0.034	1.032 ± 0.074	0.156 ± 0.050	
333.15	2.250 ± 0.019	2.919 ± 0.022	1.064 ± 0.080	0.098 ± 0.049	

[a] A_{BA} was not significant for $m + o$ and $o + p$ mixtures.

was taken as unity to get parameters significantly different from zero. The fitting to McAllister equation yielded in all cases significant interaction parameters that monotonically decreased with temperature as expected.

The viscosity deviations from linear dependence on mole fraction were calculated by means of Eq. (3):

$$\Delta\eta = \eta - (x_A\eta_A + x_B\eta_B) \tag{3}$$

where η, η_A and η_B are the dynamic viscosities of the mixture and of pure components A and B, respectively. The experimental viscosity deviations and the values predicted by McAllister according to Eq. (1) are plotted in Figs. 1–3 as a function of the mole fraction of the mixture. Calculating the standard percentage deviations between the experimental an calculated viscosity also tested the correlating ability of both equations:

$$\sigma\,(\%) = \left[\frac{1}{n-p}\sum\left(100 \times \frac{\nu_{\mathrm{exp}} - \nu_{\mathrm{calc}}}{\nu_{\mathrm{exp}}}\right)^2\right]^{1/2} \tag{4}$$

where n represents the number of data points and p the number of coefficients in the equation. In all cases, the deviations are below 0.3% and tend to slightly increase with temperature.

4. Discussion

In mixtures containing *o*-cresol, viscosity deviations were negative over the whole range of mole fractions and slightly skewed as shown in Figs. 1 and 3. For the *m*–*p* system, deviations were positive with a maximum in viscosity at about 0.35 mole fraction of *m*-cresol. Elsewhere it has been shown [7] that intermolecular hydrogen interactions are not the only factor determining viscosity deviations in

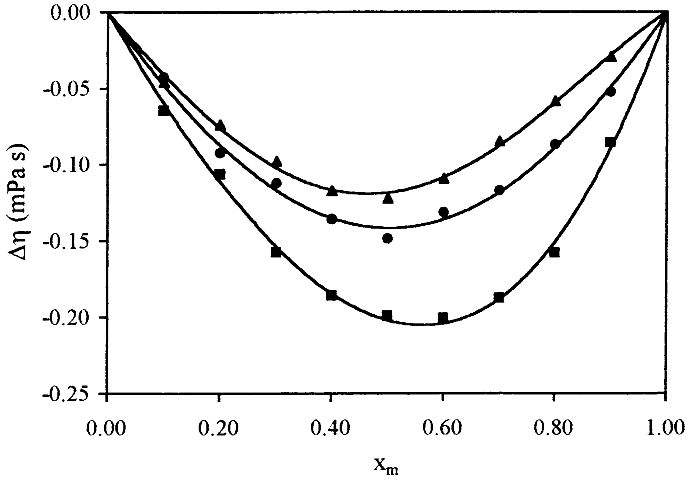

Fig. 1. Variation of viscosity deviations $\Delta\eta$ with mole fraction for *m*- and *o*-cresol mixtures at 313.15 (■), 323.15 (●) and 333.15 (▲). Solid lines correspond to McAllister equation.

liquid mixtures. The average degree of association and the shape and size of the molecules are factors of importance. Negative viscosity deviations obtained in mixtures of *o*-cresol may be explained by a lower formation of multimer species that decreased the average degree of cross-association of mixtures of *o*-cresol with the other two isomers. This hypothesis [8] is supported by the difference in dipole moments, similar for *m*-cresol (1.54 D at 15 °C) and *p*-cresol (1.54 D at 20 °C) and somewhat lower for *o*-cresol (1.41 D at 20 °C). In all cases, with rising temperature from 313.15 to 333.15 K, the magnitude of deviations decreased. It has been established that methyl group can not behave as hydrogen bond acceptor in substituted hydroxibenzenes [9]. It has also been stated that aromatic–aromatic interactions

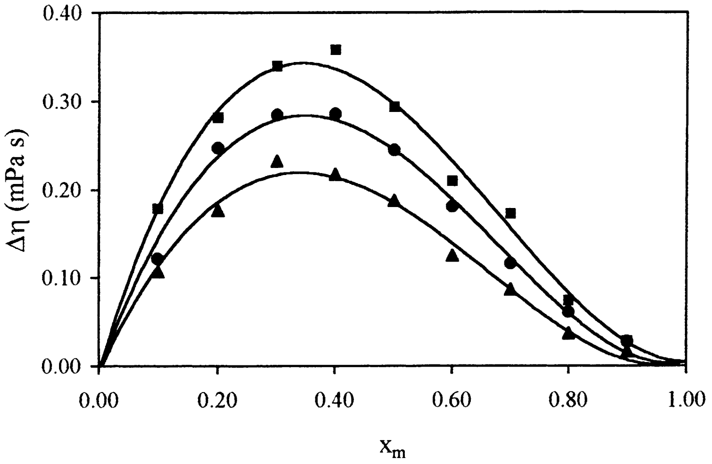

Fig. 2. Variation of viscosity deviations $\Delta\eta$ with mole fraction for *m*- and *p*-cresol mixtures at 313.15 (■), 323.15 (●) and 333.15 (▲). Solid lines correspond to McAllister equation.

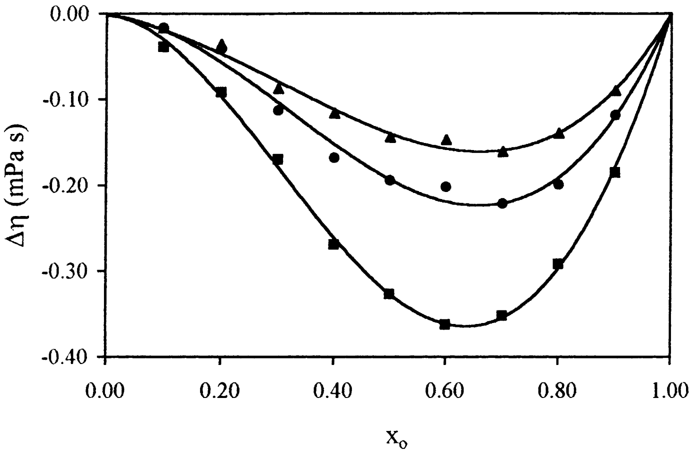

Fig. 3. Variation of viscosity deviations $\Delta\eta$ with mole fraction for *o*- and *p*-cresol mixtures at 313.15 (■), 323.15 (●) and 333.15 (▲). Solid lines correspond to McAllister equation.

can be described as a competition between the stacked and T-shaped geometry [10]. Available data suggest that electrostatic interactions and hydrogen bonds lead to a higher binding energy for T-shaped structures, which are supposed to dominate condensed mixtures [11]. The enthalpy of viscous flow reflects the energy of hydrogen bonds between cresols. Moreover, the viscosity of *o*-cresol, the weakest dipole, is lower for all temperatures than the corresponding of the other two isomers. The combination of *o*-cresol with either *m*- or *p*-cresol, may result in lower interaction due to the breaking of the liquid structure combined with repulsive the effect of the more exposed methyl group in *m*- and *p*-cresol. The molar volumes of *m*- and *p*-cresol suggest a similar intermolecular interaction due to the aliphatic groups in both isomers. The increase in viscosity observed in *m*- and *p*-cresol mixtures may be linked to a better accommodation of methyl groups in T-shaped structures.

The absolute reaction rate theory of Eyring relates kinematic viscosity with the free energy of activation of viscous flow:

$$\nu = \frac{hN_A}{M}\exp\left(\frac{\Delta G^*}{RT}\right) \tag{5}$$

where h, N_A and M are Planck's constant, Avogradro's number and molar mass, respectively. In ideal binary mixtures, the free energy of flow can be determined from pure component data:

$$\Delta G^* = x_A\,\Delta G^*_A + x_B\,\Delta G^*_B \tag{6}$$

Otherwise, there exists an excess molar free energy of activation related to viscosity as follows [12,13]:

$$\Delta G^{*E} = RT\left[\ln\left(\frac{\nu M}{\nu_B M_B}\right) - x_A \ln\left(\frac{\nu_A M_A}{\nu_B M_B}\right)\right] \tag{7}$$

where

$$M = x_A M_A + x_B M_B \tag{8}$$

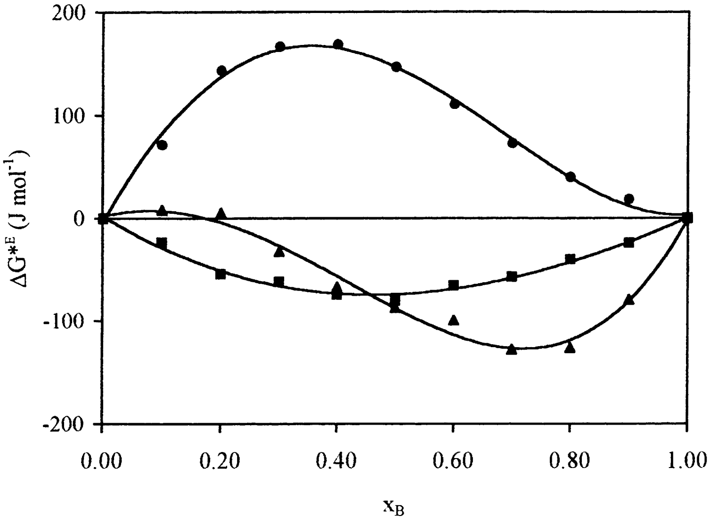

Fig. 4. Excess energy of activation of the flow process for cresol mixtures at 323.15 K. Mole fraction refers to the first component in *m*- and *o*-cresol (■), *m*- and *p*-cresol (●) and *o*- and *p*-cresol (▲). Solid lines correspond to a Redlich–Kister fitting.

Moreover, the activation parameters ΔH^* and ΔS^* can be derived by fitting viscosity data at several temperatures [14–16]:

$$\nu = \frac{hN_A}{M} \exp\left(\frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}\right) \tag{9}$$

The uncertainty in the determination of the activation energy from Eq. (7) limits the precision of ΔG^* to about ±30 J mol^{-1} resulting in deviations from ideal behavior close to the accuracy of the data presented in this work. The values of enthalpy and entropy of flow for the pure components obtained by least-square fitting of Eq. (9) were respectively 26.3 kJ mol^{-1} and -31.7 J K^{-1} mol^{-1} for *o*-cresol, 31.3 kJ mol^{-1} and -19.6 J K^{-1} mol^{-1} for *m*-cresol and 30.7 kJ mol^{-1} and -21.4 J K^{-1} mol^{-1} for *p*-cresol. The enthalpy of flow is lower from *o*-cresol, in agreement with its weaker dipole–dipole interactions. Fig. 4 plots the excess energy of activation of viscous flow. The solid line in Fig. 4 were obtained by least-square fitting of experimental deviations to a conventional Redlich–Kister polynomial equation:

$$\Delta G^{*E} = x_A x_B \sum_{i=0}^{m=3} A_i (x_A - x_B)^i \tag{10}$$

Excess energies of activation and viscosity deviations follow a similar pattern. The higher positive deviations took place in *m*- and *p*-cresol mixtures whereas for liquids containing *o*-cresol, excess free energies were negative over the whole concentration range.

List of symbols

A_i	parameter of Redlich–Kister equation (Eq. (10))
A_{BA}, B_{AB}, B_{BA}	interaction parameters of Ausländer equation (Eq. (2))
ΔG^*	free energy of activation of viscous flow

ΔG^*_A, ΔG^*_B	free energy of activation of viscous flow for components A and B
ΔG^{*E}	excess free energy of activation of viscous flow
ΔH^*	enthalpy of viscous flow
M	molecular mass of a mixture
M_A, M_B	molecular mass of pure components A and B
ΔS^*	entropy of viscous flow
x_A, x_B	mole fraction of components A and B
Z_{AB}, Z_{BA}	interaction parameters of McAllister equation (Eq. (1))

Greek letters

η	dynamic viscosity of a mixture
$\Delta\eta$	viscosity deviation
η_A, η_B	dynamic viscosity of components A and B
ν	kinematic viscosity of a mixture
ν_A, ν_B	kinematic viscosity of components A and B
σ (%)	percentage standard deviations

References

[1] R.A. McAllister, AIChE J. 6 (1960) 427–431.
[2] G. Ausländer, Br. Chem. Eng. 10 (1965) 196.
[3] H. Eyring, J. Chem. Phys. 4 (1936) 283–291.
[4] S. Glasstone, K.J. Laidler, H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.
[5] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 80th ed., CRC Press, Boca Raton, 1999.
[6] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical Recipes in Fortran, Cambridge University Press, Cambridge, 1992.
[7] S.L. Oswal, H.S. Desai, Fluid Phase Equilib. 149 (1998) 359–376.
[8] J.A. Dean (Ed.), Lange's Handbook of Chemistry, McGraw-Hill, New York, 1998.
[9] I. Rozas, I. Alkorta, J. Elguero, J. Phys. Chem. A 105 (2001) 10462–10467.
[10] F.L. Gervasio, P. Procacci, G. Cardini, A. Guarna, A. Giolitti, V. Schettino, J. Phys. Chem. B 104 (2000) 1108–1114.
[11] F.L. Gervasio, R. Chelli, P. Procacci, V. Schettino, J. Proteins: Struct. Funct. Genet. 48 (2002) 117–125.
[12] R.J. Bearman, P.F. Jones, J. Chem. Phys. 33 (1960) 1432–1438.
[13] J.L. Chevalier, P. Petrino, Y.G. Bonhomme, Chem. Eng. Sci. 43 (1988) 1303–1309.
[14] H. Eyring, M.S. John, Significant Liquid Structure, Wiley, New York, 1969.
[15] A. Ali, A.K. Nairn, S. Hyder, J. Indian Chem. Soc. 75 (1998) 501–505.
[16] K. Hickey, W.E. Waghorne, J. Chem. Eng. Data 46 (2001) 851–857.