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EXCESS MOLAR VOLUMES AND EXCESS VISCOSITIES OF THE *n*-PENTANOL–CUMENE–1,4-DIOXANE SYSTEM AT 298.15 K

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ABSTRACT

Densities and viscosities were determined for the *n*-pentanol–cumene–1,4-dioxane system at 298.15 K. From the experimental results, molar excess volumes and excess viscosities were calculated. Different expressions exist in the literature to predict these excess properties from the binary data. The empirical correlation of Cibulka is shown to be the best for this system.

INTRODUCTION

Data of excess volumes and excess viscosities are known for a number of binary liquid mixtures of non-electrolytes, and such data can be found in several articles. On the other hand, experimental data on excess volumes or densities and viscosities of mixtures of more than two components are quite rare in the literature. It is therefore interesting to estimate excess volumes and excess viscosities for mixtures with more than two components from binary data. Data for ternary systems can be found in the works of Heric and Brewer [1], Rastogi et al. [2], Radojkovič et al. [3], Cibulka [4], Singh et al. [5], Tsao and Smith [6], Kohler [7], and Jacob and Fitzner [8].

It is the aim of this work to determine molar excess volumes V^E and excess viscosities η^E for the *n*-pentanol (1)–cumene (2)–1,4-dioxane (3) system at 298.15 K, and for the three corresponding binary systems, as well as to consider some methods for empirical correlations if interactions in a ternary mixture are assumed to be closely dependent on the interactions of the constituents in binary mixtures.

EXPERIMENTAL

The methods used in our laboratory have been described previously [9,10]. Densities were determined with an AP digital densimeter, model DMA 45.

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All weighings were made on a Mettler H315 balance. A thermostatically controlled bath (constant to ±0.01° C) was used. Temperatures were read from calibrated thermometers. Density calibration was carried out with air and doubly distilled water with an error of ±0.1 kg m^{-3}.

Viscosities of the pure liquids and the mixtures were determined with a Cannon–Fenske viscosimeter calibrated with doubly distilled water and benzene. Kinetic energy corrections were applied to viscosity data. The estimated error was ±0.005 mPa s.

Materials and solutions

n-Pentanol (Merck, puriss.) was distilled over calcium oxide; cumene (Fluka, puriss.) and 1,4-dioxane (Fluka, puriss.) were distilled over sodium at reduced pressure. In all cases, the middle fractions were collected. Mixtures were prepared by weighing adequate amounts of the pure components. Caution was taken to prevent evaporation.

RESULTS AND DISCUSSION

The experimental results for the pure liquids are reported in Table 1, together with literature values for comparison.

Densities and viscosities of the binary mixtures can be calculated from the experimental data, the mole fraction being known, by using the following equation

$$P = x_i P_i + x_j P_j + x_i x_j \sum_{\substack{k=0 \\ i<j}}^{n} a_k (x_i - x_j)^k \qquad (1)$$

where P_i and P_j are properties of the pure components. Table 2 shows the values of the coefficients a_k, as well as their standard deviations, calculated by the method of least squares using a VAX 11/780 computer.

TABLE 1

Properties characterizing the pure components at 298.15 K

Substance	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)	
	Exp.	Lit.	Exp.	Lit.
n-Pentanol	0.8121	0.8115 [a]	3.384	3.35 [a]
Cumene	0.8580	0.85743 [c]	0.728	0.739 [b]
1,4-Dioxane	1.0292	1.02693 [d]	1.193	1.197 [d]

[a] Ref. 11. [b] Ref. 12. [c] Ref. 13. [d] Ref. 14.

TABLE 2

Coefficients a_k for eqn. (1) and standard deviations σ for the binary systems at 298.15 K

System	a_0	a_1	a_2	a_3	a_4	a_5	σ
(1)+(2)							
$\rho \times 10^{-3}$ (kg m^{-3})	0.00732	0.00083	−0.00108	0.00143	0.00130	–	1.4×10^{-5}
η (mPa s)	−3.54130	−1.58951	−0.71313	−0.11362	0.78737	0.88649	3.2×10^{-3}
(2)+(3)							
$\rho \times 10^{-3}$ (kg m^{-3})	−0.08566	0.21216	−0.00713	0.00098	0.00238	–	1.8×10^{-5}
η (mPa s)	−0.21999	−0.1087	−1.0601	1.42644	1.49679	−1.65407	6.7×10^{-3}
(1)+(3)							
$\rho \times 10^{-3}$ (kg m^{-3})	−0.06464	0.01268	−0.00281	0.002725	–	–	2.7×10^{-5}
η (mPa s)	−3.56402	−1.30866	−0.25744	0.142486	−0.46494	–	4.6×10^{-3}

The excess function of a binary system can be represented by a Redlich–Kister expression of the type

$$X^E = x_i x_j \sum_{k=0}^{n} a_k (x_i - x_j)^k \tag{2}$$

where X^E represents V^E or η^E, x_i and x_j are the mole fractions of components i and j, and a_k are polynomial coefficients. The method of least squares was used to determine the values of the coefficients. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate with n

$$\sigma = \left[\sum \left(X^E_{\mathrm{obs}} - X^E_{\mathrm{cal}} \right)^2 / \left(n_{\mathrm{obs}} - n \right) \right]^{1/2} \tag{3}$$

The values adopted for the coefficients and the standard error of estimate associated with the use of eqn. (3) are summarized in Table 3.

Figure 1 shows the experimental values of V^E and η^E for the three systems. The continuous curves were calculated from eqn. (2) using these values for the coefficients.

The experimental values of densities and viscosities of the ternary system are obtained by adding the third component to a constant relationship of the other two. Molar excess volume is calculated using the following equation

$$V^E = x_1 M_1 \left(\rho^{-1} - \rho_1^{-1} \right) + x_2 M_2 \left(\rho^{-1} - \rho_2^{-1} \right) + x_3 M_3 \left(\rho^{-1} - \rho_3^{-1} \right) \tag{4}$$

where M_1, M_2 and M_3 are the molecular weights of the components, ρ_1, ρ_2 and ρ_3 are the densities of the pure components and ρ is the density of the solution. The excess viscosity is defined by the following equation:

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3) \tag{5}$$

TABLE 3

Coefficients a_k from eqn. (2) and standard deviations for the binary systems at 298.15 K

System	a_0	a_1	a_2	a_3	a_4	a_5	σ
(1)+(2)							
$V^E \times 10^6$ (m^3 mol^{-1})	0.649	0.001	0.158	−0.152	−0.180	-	0.001
η^E (mPa s)	−1.592	−1.100	−0.605	−0.068	0.762	0.836	0.004
(2)+(3)							
$V^E \times 10^6$ (m^3 mol^{-1})	0.384	−0.040	0.148	0.016	−0.220	-	0.001
η^E (mPa s)	−0.158	0.134	0.045	−0.131	0.056	0.089	0.001
(1)+(3)							
$V^E \times 10^6$ (m^3 mol^{-1})	1.430	−0.374	0.114	0.350	–	–	0.004
η^E (mPa s)	−2.447	−1.114	−0.240	0.130	−0.455	-	0.006

where η, η_1, η_2 and η_3 are the viscosities of the mixture and of the pure components.

Table 4 shows the experimental values of densities and viscosities at different mole fractions.

Figures 2 and 3 show the experimental constant values of V_{123}^E and η_{123}^E.

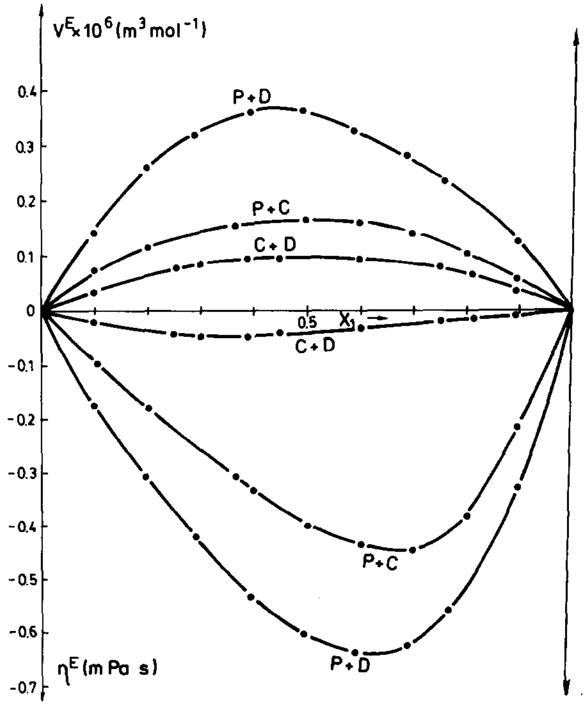

Fig. 1. Excess molar volumes and excess viscosities for binary systems at 298.15 K. Points, experimental results; continuous curves calculated from eqn. (2).

TABLE 4

Densities and viscosities for the *n*-pentanol (1)–cumene (2)–1,4-dioxane (3) system at 298.15 K

x_1	x_2	x_3	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)
0.0219	0.7786	0.1995	0.8793	0.803
0.0400	0.5956	0.3644	0.9002	0.858
0.0560	0.4339	0.5101	0.9217	0.925
0.0696	0.2967	0.6337	0.9422	0.978
0.0817	0.1747	0.7436	0.9635	1.034
0.0922	0.0689	0.8389	0.9842	1.101
0.0736	0.7867	0.1397	0.8704	0.780
0.1349	0.6094	0.2557	0.8819	0.851
0.1901	0.4494	0.3605	0.8941	0.932
0.2378	0.3111	0.4511	0.9057	1.003
0.2803	0.1880	0.5317	0.9172	1.071
0.3214	0.0689	0.6097	0.9297	1.156
0.1147	0.8036	0.0817	0.8620	0.787
0.2243	0.6161	0.1596	0.8667	0.874
0.2511	0.5702	0.1787	0.8678	0.909
0.3954	0.3233	0.2813	0.8751	1.112
0.4703	0.1950	0.3347	0.8794	1.255
0.5399	0.0758	0.3843	0.8838	1.411
0.1387	0.8007	0.0606	0.8588	0.791
0.2593	0.6273	0.1134	0.8598	0.890
0.3685	0.4704	0.1611	0.8609	1.028
0.4688	0.3263	0.2049	0.8620	1.191
0.5596	0.1958	0.2446	0.8631	1.388
0.6355	0.0867	0.2778	0.8642	1.581
0.1707	0.8100	0.0193	0.8530	0.797
0.3260	0.6372	0.0368	0.8485	0.937
0.4654	0.4822	0.0524	0.8411	1.142
0.5933	0.3398	0.0669	0.8399	1.143
0.7139	0.2957	0.0804	0.8357	1.768
0.8274	0.0794	0.0932	0.8316	2.236
0.0102	0.0922	0.8976	1.0002	1.113
0.0211	0.1910	0.7879	0.9743	1.020
0.0342	0.3086	0.6572	0.9475	0.953
0.0483	0.4362	0.5155	0.9224	0.896
0.0649	0.5865	0.3486	0.8969	0.841
0.0843	0.7816	0.1541	0.8715	0.791
0.0324	0.0757	0.8919	0.9983	1.114
0.0665	0.1555	0.7780	0.9710	1.057
0.1034	0.2419	0.6547	0.9450	1.000
0.1489	0.3485	0.5026	0.9169	0.948
0.1976	0.4624	0.3400	0.8908	0.920
0.2517	0.5891	0.1592	0.8654	0.894
0.0558	0.0560	0.8882	0.9970	1.112
0.1134	0.1137	0.7729	0.9688	1.071
0.1812	0.1817	0.8371	0.9394	1.034
0.2524	0.2531	0.4945	0.9122	1.029
0.3372	0.3381	0.3247	0.8834	1.065

TABLE 4 (continued)

x_1	x_2	x_3	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)
0.4312	0.4324	0.1364	0.8552	1.117
0.0664	0.0488	0.8888	0.9969	1.115
0.1396	0.0942	0.7662	0.9666	1.064
0.2185	0.1474	0.6341	0.9377	1.057
0.3054	0.2060	0.4886	0.9093	1.083
0.4048	0.2731	0.3221	0.8803	1.134
0.5125	0.3458	0.1417	0.8523	1.255
0.0966	0.0246	0.8788	0.9937	1.128
0.1914	0.0487	0.7599	0.9641	1.102
0.2338	0.0594	0.7068	0.9517	1.113
0.4191	0.1066	0.4743	0.9027	1.230
0.5503	0.1399	0.3098	0.8724	1.389
0.6909	0.1737	0.1334	0.8430	1.692
0.8251	0.0188	0.1561	0.8393	2.221
0.6608	0.0364	0.3028	0.8667	1.655
0.5087	0.0527	0.4386	0.8936	1.376
0.3568	0.0690	0.5742	0.9222	1.191
0.2267	0.0830	0.6903	0.9484	1.094
0.0896	0.0977	0.8127	0.9782	1.064
0.8443	0.0474	0.1083	0.8325	2.311
0.6854	0.0958	0.2188	0.8540	1.700
0.5891	0.1251	0.2858	0.8674	1.475
0.3822	0.1877	0.4301	0.8971	1.151
0.2419	0.2308	0.5273	0.9180	1.036
0.0958	0.2752	0.6290	0.9408	0.969
0.8079	0.0822	0.1099	0.8345	2.128
0.6992	0.1287	0.1721	0.8474	1.721
0.5366	0.1983	0.2651	0.8669	1.355
0.3966	0.2583	0.3451	0.8839	1.132
0.2487	0.3216	0.4297	0.9021	0.999
0.2107	0.4515	0.3378	0.9069	0.915
0.8586	0.0965	0.0449	0.8245	2.420
0.7257	0.1871	0.0872	0.8359	1.810
0.5768	0.2887	0.1345	0.8485	1.385
0.5028	0.3392	0.1580	0.8546	1.255
0.3068	0.4730	0.2202	0.8706	0.987
0.1101	0.6072	0.2827	0.8864	0.855
0.8726	0.1143	0.0131	0.8203	2.495
0.7438	0.2299	0.0263	0.8282	1.852
0.6008	0.3582	0.0410	0.8367	1.406
0.4531	0.4907	0.0562	0.8451	1.119
0.2958	0.6319	0.0723	0.8537	0.919
0.1407	0.7710	0.0883	0.8618	0.798

If interaction in a ternary system i–j–k is assumed to be closely dependent on the interaction of the constituent mixtures $i+j$, $j+k$ and $i+k$, it

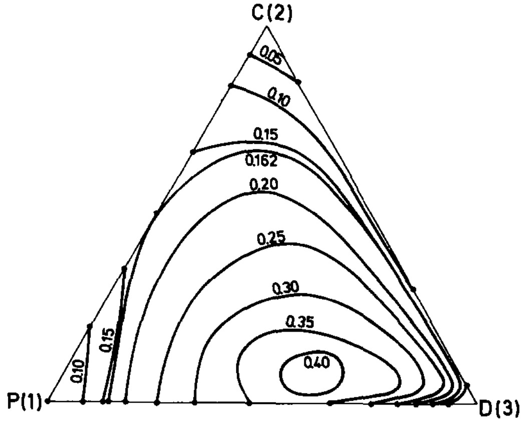

Fig. 2. Lines of constant excess molar volumes (10^6 m^3 mol^{-1}) for the *n*-pentanol (1)–cumene(2)–1,4-dioxane (3) system at 298.15 K.

should be possible to evaluate thermodynamic excess functions for ternary mixtures of non-electrolytes when the corresponding functions for the binary $i+j$, $j+k$ and $i+k$ mixtures are known.

Rastogi et al. [2] suggested an expression for predicting the excess volume of a ternary solution

$$V_{123}^{E} = \tfrac{1}{2}(x_1 + x_2)V_{12}^{E} + (x_1 + x_3)V_{13}^{E} + (x_2 + x_3)V_{23}^{E} \tag{6}$$

in which V_{ij}^{E} represents the excess molar volume of the binary mixtures at composition x_i^0, x_j^0 such that

$$x_i^0 = 1 - x_j^0 = \frac{x_i}{x_i + x_j} \tag{7}$$

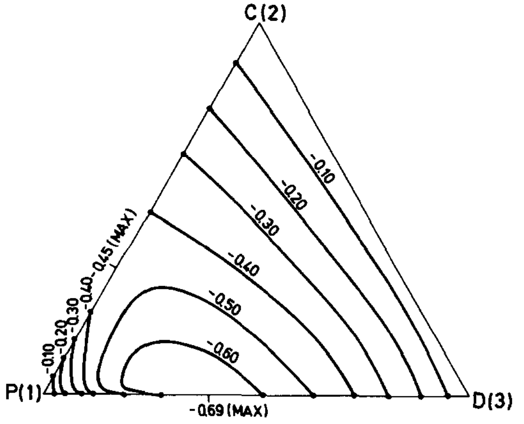

Fig. 3. Lines of constant excess viscosities (mPa s) for the *n*-pentanol (1)–cumene (2)–1,4-dioxane (3) system at 298.15 K.

This expression is inappropriate for describing the system near infinite dilution.

Radojkovič et al. [3] considered an expression proposed by Redlich and Kister for the excess free energy:

$$V_{123}^{\mathrm{E}} = V_{12\star}^{\mathrm{E}} + V_{23\star}^{\mathrm{E}} + V_{13\star}^{\mathrm{E}} \tag{8}$$

where $V_{12\star}^{\mathrm{E}}$, $V_{23\star}^{\mathrm{E}}$ and $V_{13\star}^{\mathrm{E}}$ represent the excess molar volumes with x_1, x_2 and x_3 mole fractions of the ternary system calculated from eqn. (2), using the coefficients of Table 3.

Kohler [7] proposed an equation for a ternary system of the following form

$$V_{123}^{\mathrm{E}} = (x_1 + x_2)^2 V_{12}^{\mathrm{E}} + (x_1 + x_3) V_{13}^{\mathrm{E}} + (x_2 + x_3) V_{23}^{\mathrm{E}} \tag{9}$$

Kohler's equation is symmetrical in that all three binary systems are treated identically. In this equation, V_{ij}^{E} refers to the excess volumes of x_i^0, x_j^0 in the binary mixtures obtained using eqn. (7).

Jacob and Fitzner [8] suggested an equation for estimating the properties of a ternary solution based on the binary data at composition nearest the ternary composition, taking the form for excess molar volume

$$V_{123}^{\mathrm{E}} = \frac{x_1 x_2 V_{12}^{\mathrm{E}}}{[x_1 + (x_3/2)][x_2 + (x_3/2)]} + \frac{x_1 x_3 V_{13}^{\mathrm{E}}}{[x_1 + (x_2/2)][x_3 + (x_2/2)]} + \frac{x_2 x_3 V_{23}^{\mathrm{E}}}{[x_2 + (x_1/2)][x_3 + (x_1/2)]} \tag{10}$$

so that, for the binary system at composition x_i^0, x_j^0

$$x_i - x_j = x_i^0 - x_j^0 \tag{11}$$

Tsao and Smith [6] proposed an equation for predicting the excess enthalpy of a ternary system. For excess molar volume this equation is

$$V_{123}^{\mathrm{E}} = \left(\frac{x_2}{1 - x_1}\right) V_{12}^{\mathrm{E}} + \left(\frac{x_3}{1 - x_1}\right) V_{13}^{\mathrm{E}} + (1 - x_1) V_{23}^{\mathrm{E}} \tag{12}$$

in which V_{ij}^{E} refers to the excess volume for the binary mixtures at compositions x_i^0, x_j^0, such that $x_i^0 = x_i$ for the 1,2 and 1,3 binary systems and $x_2^0 = x_2/(x_2 + x_3)$ for the 2,3 binary system.

Singh et al. [5] proposed an equation of the following form

$$V_{123}^{\mathrm{E}} = V_{12\star}^{\mathrm{E}} + V_{13\star}^{\mathrm{E}} + V_{23\star}^{\mathrm{E}} + x_1 x_2 x_3 \left[A + B x_1 (x_2 - x_3) + C x_1^2 (x_2 - x_3)^2\right] \tag{13}$$

where A, B and C are parameters characteristic of the mixtures, evaluated by fitting this equation by the least squares method with a standard deviation defined as in eqn. (3).

TABLE 5

Standard deviations for the *n*-pentanol (1)–cumene (2)–1,4-dioxane (3) system at 298.15 K

Equation	$\sigma(V^{E})\times10^{6}$ (m^3 mol^{-1})	$\sigma(\eta^{E})$ (mPa s)
(8)	0.062	0.046
(9)	0.062	0.051
(10)	0.062	0.025
(12)	0.060	0.046
(13)	0.055	0.026
(14)	0.045	0.026

The parameters obtained for V_{123}^{E} of this system are $A = 0.8683$, $B = -13.9313$ and $C = 21.9703$, and for η_{123}^{E} are $A = 1.9198$, $B = 3.4339$ and $C = 8.3469$.

Finally, Cibulka [4] proposed the following equation

$$V_{123}^{E} = V_{12\star}^{E} + V_{13\star}^{E} + V_{23\star}^{E} + x_1x_2x_3(A + Bx_1 + Cx_2) \qquad (14)$$

The parameters obtained for V_{123}^{E} are $A = 9.2411$, $B = -12.5988$ and $C = -12.0916$, and for η^{E} are $A = 1.0074$, $B = 1.1999$ and $C = 1.6890$.

The last two equations are modifications of Radojkovič's equation.

Table 5 shows the standard deviations calculated by using all the above-mentioned equations for molar excess volumes and excess viscosities for the ternary system. Equation (14) shows the best agreement with the experimental data.

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