

## Densities and viscosities of mixing for the binary system of methyl benzoate with *n*-nonane at different temperatures

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### Abstract

Viscosity and density measurements are reported for the binary liquid mixtures of methyl benzoate with *n*-nonane at six different temperatures between 288.15 and 318.15 K. Excess volumes, excess viscosities, excess free energies of activation for viscous flow, and the contact interaction parameters were calculated. The system studied exhibits positive–negative excess molar volumes depending on the ester concentration; however, the excess viscosities and excess activation energies of viscous flow are negative over the entire range of compositions. The behavior of the mixtures is also discussed.

### INTRODUCTION

Density and viscosity are thermophysical properties needed in the evaluation of the effects brought about in mixtures of pure liquids. Several methods for predicting such properties have been suggested [1,2] in an attempt to verify the behavior of liquid mixtures. In most cases, however, development and further application of any theoretical method require the availability and knowledge of a proper data base that includes the species to be investigated. Therefore, as part of an ongoing program that aims at determining the thermodynamic properties of alkyl esters [3–5] and benzyl esters [6,7], the purpose of this work is to extend and systematize the investigations already done, in order to observe the behavior of the binary liquid system of methyl benzoate with *n*-alkanes.

The use of *n*-alkanes as the second component in binary mixtures is thought worthwhile and also advisable in the field of liquid mixtures. In this work, the choice of *n*-nonane seemed obvious, since this species has an acceptable chemical stability, is commercially available at high purity levels,

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and is frequently used as a good reference for calibration of equipment [8]. In order to provide insight into the structure of the system, as well as on the interactions among components, the purpose of this work is to report densities, viscosities and related quantities for the binary mixture methyl benzoate plus *n*-nonane, for which no information was found in the literature, at 288.15, 293.15, 298.15, 303.15, 308.15 and 318.15 K; only  $v^E$  data for alkyl benzoates plus *n*-heptane [9] and alkyl benzoates plus *n*-alkanes [10] have been reported.

## EXPERIMENTAL

The pure liquids were commercially available from Fluka AG, and prior to use they were degassed with ultrasound and dried over Union Carbide molecular sieve 4 Å, also from Fluka AG. All samples were prepared by direct weighing. The maximum average error of mole fractions was estimated at  $\pm 5 \times 10^{-5}$ .

Densities of the pure components and their mixtures were measured with an Anton Paar 60/602 digital densimeter ( $\pm 0.002 \text{ kg m}^{-3}$ ), which operates by determining the period of oscillation of the sample in a U-shaped tube. The instrument was calibrated at every operating temperature for each set of readings with doubly distilled water and *n*-nonane as reference compounds, which were previously degassed. A more detailed description of the experimental procedure has already been reported [8]. The reference values for water and *n*-nonane were taken, respectively, from Riddick et al. [11] and Ortega and Matos [12].

Viscosities were measured with a Cannon–Fenske viscometer calibrated with doubly distilled water at different temperatures [7] using a precision thermostat which was controlled to within  $\pm 0.01 \text{ K}$ ; the flow times were observed with a precision of  $\pm 0.01 \text{ s}$ . Five readings were made for each sample, and the maximum error of the averaged value was estimated as  $\pm 0.003 \text{ mPa s}$ .

In order to check the quality of the products used, Table 1 lists the physical properties measured by us and their comparison with those available from the literature.

## PRESENTATION AND TREATMENT OF THE RESULTS

In Table 2 the results are collected for the experimental densities  $\rho$  and viscosities  $\eta$  obtained at different temperatures for the binary system  $\{x_1\text{C}_6\text{H}_5\text{COOCH}_3 + x_2n\text{-C}_9\text{H}_{20}\}$ , along with the corresponding excess properties  $v^E$  and  $\eta^E$ , calculated as

$$v^E \times 10^6 (\text{m}^3 \text{mol}^{-1}) = x_1 M_1 (\rho^{-1} - \rho_1^{-1}) + x_2 M_2 (\rho^{-1} - \rho_2^{-1}) \quad (1)$$

$$\eta^E (\text{mPa s}) = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (2)$$

TABLE 1

Properties characterizing the pure components at several temperatures

$T$ (K)	$\rho$ (kg m <sup>-3</sup> )		$\eta$ (mPa s)		$n_D$	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
<b>Methyl benzoate</b>						
288.15	1091.848	1093.34 [11]	2.250	2.298 [11]	1.5190	
293.15	1088.318	1089.2 [7]	2.010		1.5167	1.51679 [11]
298.15	1083.518	1082.65 [9]	1.809		1.5144	1.51457 [11]
303.15	1078.067	1079.01 [11] 1080.0 [7]	1.630	1.673 [11]	1.5124	
308.15	1073.286		1.476		1.5102	
318.15	1063.504		1.224		1.5056	
<b><i>n</i>-Nonane</b>						
288.15	723.151		0.750		1.4077	
293.15	717.978	717.63 [11]	0.696	0.716 [11]	1.4057	1.40542 [11]
298.15	713.855	713.81 [11] 713.86 [12]	0.650	0.6696 [4]	1.4034	1.40311 [11]
303.15	709.896	709.91 [12]	0.607		1.4010	1.4011 [12]
308.15	705.959	705.96 [12]	0.569		1.3988	1.3987 [12]
318.15	698.063	698.06 [12]	0.498		1.3942	1.3939 [12]

where  $M_i$ ,  $x_i$  and  $\eta_i$  represent, respectively, the molecular weight, mole fraction, density and viscosity of the component  $i$  in the mixture, and the quantities without subscript ( $\rho$  and  $\eta$ ) refer to the solution. Excess free energies of activation of flow (see Table 2) were calculated from the densities and viscosities by means of the equation

$$\Delta g^{*E} (\text{J mol}^{-1}) = RT \left[ \ln \eta (x_1 M_1 + x_2 M_2) \rho^{-1} - (x_1 \ln \eta_1 M_1 \rho_1^{-1} + x_2 \ln \eta_2 M_2 \rho_2^{-1}) \right] \quad (3)$$

where  $T$  represents the absolute temperature and  $R$  is the gas constant. The excess quantities calculated from eqns. (1), (2) and (3) were fitted at each temperature to the empirical equation (eqn. 4) by the method of unweighted least-squares:

$$Y^E = x_1 x_2 \sum_i A_i \left[ x_1 / (x_1 + k x_2) \right]^i \quad i = 0, 1, 2, \dots \quad (4)$$

where  $Y^E$  represents  $v^E$ ,  $\eta^E$  and  $\Delta g^{*E}$ . Coefficients  $A_i$  were determined for each property by choosing the value of  $k$  that minimizes the standard deviations,  $s(Y^E)$ , of the property considered. Table 3 summarizes the values of all the parameters obtained.

The calculation of excess properties is important for a better understanding of the behavior of liquid mixtures and of interactions among components; nevertheless, some definitions such as those in eqns. (2) and (3) have

TABLE 2

Densities,  $\rho$ , viscosities,  $\eta$ , and excess properties for the system  $\{x_1$  methyl benzoate +  $x_2$  *n*-nonane $\}$  at several temperatures

$x_1$	$\rho$ ( $\text{kg m}^{-3}$ )	$v^E \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )	$\eta$ ( $\text{mPa s}$ )	$\eta^E$ ( $\text{mPa s}$ )	$\Delta g^{*E}$ ( $\text{kJ mol}^{-1}$ )
288.15 K					
0.05240	736.55	0.095	0.758	-0.070	-0.105
0.12274	755.36	0.185	0.776	-0.155	-0.221
0.20597	778.92	0.235	0.813	-0.241	-0.323
0.31243	811.16	0.250	0.879	-0.333	-0.408
0.40219	840.30	0.231	0.951	-0.394	-0.451
0.48501	868.90	0.197	1.032	-0.437	-0.472
0.61031	915.56	0.129	1.189	-0.466	-0.464
0.68991	947.50	0.085	1.319	-0.457	-0.429
0.78496	988.28	0.026	1.518	-0.401	-0.350
0.87862	1031.34	-0.005	1.778	-0.284	-0.227
0.94965	1066.09	-0.011	2.032	-0.139	-0.104
293.15 K					
0.05251	731.25	0.091	0.705	-0.059	-0.096
0.12539	750.82	0.176	0.724	-0.134	-0.210
0.19613	770.83	0.223	0.752	-0.198	-0.292
0.22353	778.86	0.232	0.764	-0.221	-0.322
0.26403	791.02	0.241	0.785	-0.253	-0.357
0.32876	811.20	0.239	0.824	-0.298	-0.402
0.44798	850.93	0.202	0.915	-0.363	-0.450
0.57962	898.97	0.135	1.050	-0.400	-0.456
0.64799	925.82	0.096	1.141	-0.398	-0.432
0.71450	953.29	0.058	1.245	-0.382	-0.395
0.81091	995.66	0.011	1.437	-0.318	-0.303
0.90828	1041.71	-0.012	1.692	-0.193	-0.169
0.91721	1046.10	-0.012	1.719	-0.178	-0.154
0.94582	1060.40	-0.013	1.811	-0.125	-0.106
0.96351	1069.40	-0.011	1.873	-0.087	-0.072
298.15 K					
0.05357	727.57	0.087	0.660	-0.051	-0.090
0.13127	748.44	0.172	0.679	-0.120	-0.206
0.23680	778.71	0.227	0.716	-0.204	-0.331
0.26295	786.56	0.234	0.730	-0.220	-0.347
0.35693	816.07	0.227	0.780	-0.278	-0.415
0.44623	846.02	0.198	0.842	-0.318	-0.449
0.52641	874.63	0.157	0.910	-0.343	-0.459
0.58757	897.61	0.121	0.972	-0.352	-0.452
0.67381	931.84	0.071	1.078	-0.346	-0.418
0.76388	970.04	0.024	1.219	-0.310	-0.349
0.81920	994.84	0.002	1.325	-0.268	-0.288
0.87824	1022.46	-0.013	1.457	-0.207	-0.209
0.93302	1049.22	-0.014	1.601	-0.129	-0.122

TABLE 2 (continued)

$x_1$	$\rho$ ( $\text{kg m}^{-3}$ )	$v^E \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )	$\eta$ ( $\text{mPa s}$ )	$\eta^E$ ( $\text{mPa s}$ )	$\Delta g^{*E}$ ( $\text{kJ mol}^{-1}$ )
303.15 K					
0.04786	722.08	0.076	0.618	-0.037	-0.066
0.13079	744.23	0.165	0.633	-0.106	-0.201
0.20747	765.88	0.212	0.657	-0.159	-0.289
0.30340	794.74	0.225	0.694	-0.218	-0.382
0.41012	829.24	0.204	0.755	-0.267	-0.430
0.49213	857.64	0.167	0.816	-0.288	-0.437
0.61150	902.16	0.099	0.927	-0.300	-0.414
0.66128	921.94	0.068	0.983	-0.294	-0.393
0.78921	976.23	0.007	1.156	-0.253	-0.312
0.87440	1015.42	-0.015	1.307	-0.191	-0.225
0.93678	1045.78	-0.016	1.448	-0.115	-0.131
308.15 K					
0.04992	718.67	0.074	0.574	-0.039	-0.091
0.09944	731.72	0.129	0.583	-0.074	-0.165
0.23111	768.72	0.212	0.622	-0.154	-0.306
0.30325	790.52	0.221	0.652	-0.188	-0.355
0.40435	823.04	0.202	0.704	-0.227	-0.400
0.48602	851.13	0.165	0.754	-0.251	-0.422
0.60669	895.87	0.094	0.847	-0.267	-0.421
0.68540	927.26	0.052	0.924	-0.262	-0.394
0.78282	968.80	0.006	1.044	-0.230	-0.327
0.88004	1013.44	-0.020	1.203	-0.161	-0.212
0.93067	1038.02	-0.019	1.306	-0.105	-0.133
318.15 K					
0.05308	711.51	0.073	0.503	-0.033	-0.091
0.16740	742.20	0.181	0.525	-0.093	-0.234
0.19051	748.72	0.192	0.532	-0.102	-0.251
0.33425	791.78	0.207	0.580	-0.158	-0.352
0.40315	814.06	0.189	0.611	-0.176	-0.375
0.49727	846.38	0.145	0.659	-0.196	-0.397
0.56734	871.94	0.105	0.703	-0.203	-0.393
0.64472	901.75	0.060	0.759	-0.203	-0.377
0.67808	915.15	0.041	0.787	-0.199	-0.363
0.74636	943.67	0.004	0.851	-0.185	-0.323
0.79491	964.84	-0.012	0.904	-0.168	-0.283
0.85504	992.19	-0.028	0.980	-0.136	-0.221
0.89180	1009.54	-0.031	1.033	-0.110	-0.174
0.93863	1032.36	-0.026	1.109	-0.069	-0.104
0.95067	1038.35	-0.022	1.130	-0.057	-0.086

not been totally accepted by all the researchers in this field. For this reason, it was thought useful to determine the activation thermodynamic properties,  $\Delta g^*$ ,  $\Delta h^*$  and  $\Delta s^*$ , according to Eyring's activated complex theory [13]

TABLE 3

Coefficients  $A_i$  and standard deviations,  $s$ , obtained for eqn. (4)

$T$ (K)	$k$	$A_0$	$A_1$	$A_2$	$A_3$	$s$
$v^E \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )						
288.15	0.972	2.168	-4.184	3.986	-2.376	0.001 <sub>s</sub>
293.15	1.171	1.996	-3.877	3.127	-1.650	0.001
298.15	0.884	1.863	-2.501	0.858	-0.609	0.001
303.15	0.956	1.744	-2.140			0.001
308.15	0.733	1.632	-1.286	-0.777		0.001
318.15	1.097	1.624	-2.192			0.001
$\eta^E$ (mPa s)						
288.15	3.145	-1.309	-1.957			0.003
293.15	2.717	-1.123	-1.541			0.002
298.15	2.386	-0.972	-1.283			0.001
303.15	4.150	-0.900	-1.320			0.002
308.15	3.310	-0.765	-1.109			0.002
318.15	2.956	-0.604	-0.734			0.001
$\Delta g^{*E}$ ( $\text{kJ mol}^{-1}$ )						
288.15	0.617	-2.320	1.684	-1.623		0.002
293.15	0.617	-2.047	0.946	-0.992		0.001
298.15	0.664	-1.847	0.293	-0.465		0.003
303.15	0.863	-1.394	-3.143	7.548	-5.435	0.003
308.15	0.667	-2.048	1.629	-1.746		0.001
318.15	0.590	-1.936	1.423	-1.372		0.001

(where  $h$  is the Planck constant and  $N$  is the Avogadro number)

$$\ln \left[ \frac{\eta(x_1 M_1 + x_2 M_2)}{\rho h N} \right] = \frac{\Delta g^*}{RT} \quad (5)$$

and the well-known equation

$$\Delta g^* = \Delta h^* - T\Delta s^* \quad (6)$$

which allow those functions to be calculated. A plot of the lefthand side of eqn. (5) vs.  $1/T$  provides  $\Delta h^*$  and  $\Delta s^*$ ; the corresponding results are listed in Table 4.

## DISCUSSION

Inspection of the data in Table 2 reveals that excess volumes of mixtures  $\{x_1$  methyl benzoate +  $x_2$   $n$ -nonane $\}$  display a sigmoid distribution, with negative values at high ester compositions ( $x_1 \rightarrow 1$ ); the variations observed with increasing temperature were small within the entire composition range, demonstrating close to ideal behavior. Although the positive-negative shape of the curve  $v^E$  vs.  $x_1$  might be attributed to dipole-induced dipole interac-

TABLE 4

Activation parameters for the system  $\{x_1 \text{ methyl benzoate} + (1-x) \text{ } n\text{-nonane}\}$ 

$x$	$\Delta g^* \text{ (kJ mol}^{-1}\text{)}$							$\Delta h^* \text{ (kJ mol}^{-1}\text{)}$	$\Delta s^* \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	318.15 K	318.15 K		
0.09830	63.6	64.5	65.4	66.4	67.3	69.2	69.2	9.5	-187.6
0.19734	63.6	64.5	65.5	66.4	67.4	69.2	69.2	9.6	-187.6
0.29886	63.7	64.6	65.6	66.5	67.4	69.3	69.3	9.8	-186.8
0.39706	63.8	64.7	65.7	66.6	67.5	69.4	69.4	10.4	-185.2
0.49805	64.0	64.9	65.8	66.7	67.6	69.5	69.5	10.8	-184.5
0.59490	64.2	65.1	66.0	66.9	67.8	69.6	69.6	11.4	-183.1
0.69230	64.4	65.3	66.2	67.1	68.0	69.8	69.8	11.9	-182.0
0.79853	64.6	65.5	66.4	67.3	68.2	70.1	70.1	12.6	-180.7
0.89907	65.0	65.9	66.7	67.6	68.5	70.3	70.3	13.8	-177.7

tions between the aromatic ester and *n*-nonane (the effect being larger at low proportions of *n*-nonane), the interstitial accommodation of hydrocarbon molecules among the ester molecules may be considered more relevant, the result being a decrease in the volume of the mixture,  $v^E < 0$ .

Excess viscosities were negative at all compositions, and decreased noticeably with increasing temperature. Attempts have been made to describe the behavior of binary liquid mixtures by using a characteristic parameter [14–16] that is related to the viscosities of the pure components; the determination of such a parameter denotes “typical” behavior of the mixture investigated, similar to that of other species of very different size [17]. Dispersion forces are thought to be responsible for the greatest part of the discrepancies in  $\eta^E$ , and also permit justifying the variations observed in  $v^E$ . The negative values calculated for energies of activation of viscous flow and their decrease with increasing temperature also point to a prevalence of dispersion forces [18,19]. Similar behavior has already been reported for binary mixtures of alkyl benzoate and acetonitrile [6]. The highly negative values calculated for activation entropies  $\Delta s^*$  indicate the small mobility of the pure components in the mixture; on the other hand, the high values of  $\Delta h^*$  in the ester-rich region also explain the geometrical effects and the molecular interaction, which support the above statements.

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