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Excess Thermodynamic Properties of Mixtures of Alkyl Benzoates with *n*-Heptane

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The paper reports h^E values at 298.15 K and v^E and $\delta\eta$ values at various temperatures for binary mixtures of propyl or butyl benzoate and *n*-heptane. The excess Gibbs energy of viscous flow, Δg^{*E}, and the thermodynamic activation properties were calculated from these values. The results are compared with those for similar mixtures and interpreted on the basis of the characteristic dipole-dipole interactions of alkyl esters.

KEY WORDS: binary mixtures; *n*-heptane; methyl esters; thermodynamic properties; viscosity.

1. INTRODUCTION

The present study is a continuation of the ongoing work that we have been conducting for some time on the thermodynamic behavior of ester-containing mixtures [1-3]. This research is of considerable interest because of the usefulness of esters as solvents, and work on mixtures of components of differing types may furnish information on the structural changes in the pure ester that take place during the mixing process. Specifically, to date the behavior of such systems has been investigated by means of such functions as h^E, v^E, and g^E for alkyl esters + *n*-alkanes. However, the viscosity of binary mixtures and, hence, the corresponding apparent excess magnitude also reveal important information about the molecular structure of the components and the intermolecular interactions taking place in the mixtures. We have not previously been able to furnish values of η for alkyl ester-containing mixtures, for which relatively few literature values

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Table 1. Characteristics of Alkyl Benzoates at Different Temperatures

	288.15 K		298.15 K		308.15 K	318.15 K	
Property	Exp.	Lit.	Exp.	Lit.	Exp.	Exp.	Lit.
			Propyl benzoate				
n_D	1.5022	1.50139[9]	1.4982		1.4936	1.4895	1.5056[1]
ρ (kg · m^{-3})	1026.60	1027.4[9]	1017.75	1017.87[8]	1008.83	999.81	1063.50[1]
η (mPa · s)	2.960		2.311		1.867	1.527	
$\bar{\alpha}_p$ (K^{-1})	0.00088						
			Butyl benzoate				
n_D	1.4985		1.4945		1.4904	1.4863	
ρ (kg · m^{-3})	1008.39		999.78	1003.56[8]	991.29	982.65	
η (mPa · s)	3.437		2.647		2.099	1.708	
α (K^{-1})	0.00086						

are available, [4] although earlier work at our laboratory has dealt with mixtures of methyl or ethyl benzoate and *n*-nonane [5] or *n*-heptane [6].

This paper presents experimental values for the excess volume, v^E, and apparent excess viscosity, $\delta\eta$, over the temperature range from 288.15 to 318.15 K and enthalpy, h^E, at 298.15 K for the binary system propyl or butyl benzoate + *n*-heptane. The literature consulted did not yield any h^E or $\delta\eta$ values; however, v^E values at 298.15 K for the mixtures propyl benzoate + *n*-heptane have been published by Grolier et al. [7] and Dussart et al. [8] and for butyl benzoate + *n*-heptane by Dussart et al. [8].

2. EXPERIMENTAL

The *n*-heptane employed in this study was supplied by Fluka (purity, >99.5 mol %); the alkyl benzoates, by Aldrich (+99 mol %); these components were not subjected to any further purification. However, they were degassed with ultrasound and stored on 0.3-nm molecular sieves (from Fluka) to eliminate all traces of moisture prior to use. The physical characteristics of the hydrocarbon did not differ significantly from the values published earlier [6]. The values for the aromatic esters, for which not many literature values were available for comparison, over the temperature range from 288.15 to 318.15 K are presented in Table I. The values for the density ρ as a function of the temperature T were used to calculate the mean coefficients of the isobaric thermal expansion over the aforementioned temperature range, via the expression $\bar{\alpha} = -(\partial \ln \rho/\partial T)_p$.

The ρ measurements for the pure components and for the mixtures were made with an Anton–Paar Model 60/602 vibrating-tube densimeter with an accuracy of $\pm 0.002\ \mathrm{kg \cdot m^{-3}}$. The kinematic viscosity, ν, were measured by one of us [10] with a Cannon–Fenske viscosimeter with an accuracy of $\pm 0.003\ \mathrm{mPa \cdot s}$. The h^E values were measured with a Calvet Model MS80D microcalorimeter from Setaram with an accuracy of about 1%. The concentrations of mixture ponents for the excess magnitudes v^E, $\delta\eta$, and h^E were calculated with an accuracy of $\pm 2 \times 10^{-4}$. Additional information on the measurement procedures can be found in Refs. 1, 2, 5, and 10.

3. RESULTS

Table II presents the excess enthalpy, h^E, at 298.15 K for the binary systems x_1 propyl or butyl benzoate + x_2 *n*-heptane and clearly demonstrates the endothermal behavior of these mixtures. The results for these systems displays a good agreement with the values calculated by extrapolation of the values published by Grolier et al. [7] for mixtures of methyl and ethyl benzoate and the same hydrocarbon. The excess properties v^E and $\delta\eta$ ($\delta\eta = \eta - x_1\eta_1 - x_2\eta_2$) for the mixtures at various temperatures between 288.15 and 318.15 K were calculated from the direct measurements of density, ρ, and viscosity, η, as a function of the concentration of the aromatic ester. All these values, together with the excess Gibbs energy of viscous flow calculated with Eq. (1), are presented in Table III.

$$\Delta g^{*E} = RT\left(\ln \eta v - \sum_{i=1}^{2} x_i \ln \eta_i v_i\right) \tag{1}$$

where the subscript i indicates the pure components of the mixture. Letting Y^E represent a generic excess function, the excess magnitudes could be correlated with the polynomial equation:

$$Y^E = x_1 x_2 \sum A_i [x_1/(x_1 + k x_2)]^i \tag{2}$$

where the coefficients A_i were calculated for a fixed value of k by a method of least squares with the standard deviation, $s(Y^E)$, as the target function. The fitting procedure was iterated, varying the values of k appropriately until the lowest value of $s(Y^E)$ was attained. Table IV gives the values for fits for all the excess properties (Tables II and III). Those same excess magnitudes have been plotted in Figs. 1, 2, and 3 for comparison.

Table II. Excess Molar Enthalpies for the Binaries x_1 Propyl or Butyl Benzoate + x_2 n-Heptane at 298.15 K

x_1	h^E ($J \cdot mol^{-1}$)	x_1	h^E ($J \cdot mol^{-1}$)	x_1	h^E ($J \cdot mol^{-1}$)
		Propyl benzoate + n-heptane			
0.0485	234.4	0.3930	1028.9	0.6763	850.8
0.1059	457.6	0.4228	1040.8	0.7392	734.0
0.1664	652.5	0.4631	1045.6	0.8118	595.3
0.2269	800.4	0.5078	1038.5	0.8690	413.7
0.2851	904.9	0.5624	1001.3	0.9374	219.1
0.3403	991.1	0.6174	940.7	—	—
		Butyl benzoate + n-heptane			
0.0476	236.4	0.3789	905.9	0.6429	787.9
0.0994	415.5	0.4252	918.9	0.6908	721.2
0.1558	586.8	0.4673	921.4	0.7307	659.4
0.2139	721.3	0.5068	909.4	0.7941	533.7
0.2714	816.5	0.5421	879.1	0.8650	367.8
0.3268	877.1	0.5899	831.3	0.9330	198.9

Table III. Densities (ρ), Viscosities (η), and Excess Properties for the System x_1 Propyl or Butyl Benzoate + x_2 n-Heptane at Several Temperatures

x_1	ρ ($kg \cdot m^{-3}$)	$v^E \times 10^6$ ($m^3 \cdot mol^{-1}$)	η ($mPa \cdot s$)	$\delta\eta$ ($mPa \cdot s$)	Δg^{*E} ($kJ \cdot mol^{-1}$)
Propyl benzoate (1) + n-heptane (2)					
288.15 K					
0.0990	726.4	−0.118	0.501	−0.189	−0.148
0.1965	762.0	−0.209	0.589	−0.347	−0.205
0.2952	797.3	−0.282	0.700	−0.485	−0.243
0.3950	832.3	−0.338	0.825	−0.611	−0.306
0.4959	866.9	−0.375	0.997	−0.694	−0.313
0.5924	899.2	−0.389	1.214	−0.719	−0.279
0.6991	934.0	−0.371	1.527	−0.675	−0.217
0.7981	965.5	−0.310	1.878	−0.573	−0.172
0.8973	996.1	−0.195	2.330	−0.372	−0.107
298.15 K					
0.0990	716.3	−0.142	0.444	−0.141	−0.145
0.1965	752.0	−0.260	0.516	−0.255	−0.196
0.2952	787.5	−0.359	0.603	−0.357	−0.244
0.3950	822.6	−0.435	0.707	−0.445	−0.291
0.4959	857.4	−0.485	0.842	−0.503	−0.298
0.5924	889.9	−0.501	1.017	−0.514	−0.256
0.6991	924.9	−0.471	1.254	−0.480	−0.202
0.7981	956.5	−0.389	1.526	−0.399	−0.150
0.8973	987.2	−0.240	1.853	−0.262	−0.101
308.15 K					
0.0990	707.6	−0.181	0.399	−0.104	−0.111
0.1965	743.3	−0.321	0.466	−0.185	−0.132
0.2952	778.8	−0.428	0.531	−0.269	−0.217
0.3950	813.8	−0.505	0.614	−0.337	−0.272
0.4959	848.6	−0.548	0.734	−0.370	−0.247
0.5924	881.0	−0.555	0.874	−0.376	−0.212
0.6991	916.0	−0.513	1.051	−0.360	−0.194
0.7981	947.6	−0.418	1.248	−0.313	−0.176
0.8973	978.2	−0.255	1.525	−0.187	−0.084
318.15 K					
0.0990	698.9	−0.208	0.358	−0.080	−0.101
0.1965	734.5	−0.357	0.408	−0.148	−0.162
0.2952	769.9	−0.485	0.472	−0.203	−0.190
0.3950	805.0	−0.587	0.550	−0.246	−0.201
0.4959	839.8	−0.647	0.638	−0.280	−0.226
0.5924	872.3	−0.651	0.754	−0.281	−0.186
0.6991	907.2	−0.587	0.897	−0.266	−0.167
0.7981	938.6	−0.464	1.064	−0.219	−0.124
0.8973	969.2	−0.279	1.266	−0.137	−0.074

Table III. *(Continued)*

x_1	ρ (kg·m^{-3})	$v^E \times 10^6$ (m^3·mol^{-1})	η (mPa·s)	$\delta\eta$ (mPa·s)	Δg^{*E} (kJ·mol^{-1})
		Butyl benzoate (1) + *n*-heptane (2)			
		288.15 K			
0.0994	727.9	−0.139	0.517	−0.222	−0.108
0.1959	763.6	−0.249	0.614	−0.415	−0.170
0.2964	799.3	−0.339	0.750	−0.579	−0.183
0.3986	833.9	−0.405	0.911	−0.724	−0.219
0.4963	865.7	−0.442	1.128	−0.800	−0.187
0.5965	896.8	−0.448	1.407	−0.821	−0.151
0.6954	926.2	−0.417	1.710	−0.814	−0.171
0.7986	955.5	−0.336	2.158	−0.676	−0.122
0.8973	982.2	−0.204	2.698	−0.432	−0.074
		298.15 K			
0.0994	718.0	−0.218	0.457	−0.161	−0.103
0.1959	754.0	−0.372	0.536	−0.299	−0.162
0.2964	789.8	−0.480	0.645	−0.417	−0.176
0.3986	824.6	−0.544	0.777	−0.515	−0.198
0.4963	856.5	−0.571	0.950	−0.562	−0.161
0.5965	887.8	−0.567	1.162	−0.576	−0.135
0.6954	917.4	−0.526	1.411	−0.549	−0.120
0.7986	946.8	−0.433	1.731	−0.462	−0.101
0.8973	973.6	−0.272	2.122	−0.294	−0.064
		308.15 K			
0.0994	709.2	−0.221	0.410	−0.117	−0.072
0.1959	745.2	−0.387	0.476	−0.219	−0.127
0.2964	781.0	−0.514	0.571	−0.300	−0.121
0.3986	815.9	−0.595	0.686	−0.363	−0.118
0.4963	847.8	−0.629	0.811	−0.409	−0.135
0.5965	879.1	−0.616	0.978	−0.417	−0.114
0.6954	908.7	−0.554	1.176	−0.392	−0.093
0.7986	938.1	−0.432	1.413	−0.335	−0.094
0.8973	964.9	−0.254	1.727	−0.193	−0.032
		318.15 K			
0.0994	700.5	−0.256	0.368	−0.089	−0.059
0.1959	736.5	−0.454	0.426	−0.164	−0.099
0.2964	772.4	−0.605	0.501	−0.230	−0.120
0.3986	807.3	−0.700	0.598	−0.275	−0.106
0.4963	839.3	−0.735	0.697	−0.311	−0.134
0.5965	870.6	−0.711	0.835	−0.312	−0.100
0.6954	900.1	−0.630	0.991	−0.294	−0.087
0.7986	929.4	−0.481	1.192	−0.236	−0.057
0.8973	956.2	−0.276	1.426	−0.140	−0.022

Table IV. Coefficients k and A_i and Standard Deviations Obtained for Eq. (2)

T (K)	k	A_0	A_1	A_2	$s(Y^E)$
		Propyl benzoate + n-heptane			
		$v^E \times 10^6$ ($m^3 \cdot mol^{-1}$)			
288.15	0.642	−1.489	1.132	−1.905	0.004
298.15	2.344	−1.512	−1.443	—	0.005
308.15	0.906	−2.071	0.484	−1.384	0.006
318.15	0.204	−3.080	3.285	−3.241	0.006
		$\delta\eta$ (mPa · s)			
288.15	2.141	−1.961	−2.486	—	0.007
298.15	2.056	−1.469	−1.583	—	0.006
308.15	2.137	−1.085	−1.237	—	0.006
318.15	2.060	−0.850	−0.780	—	0.002
		Δg^{*E} ($J \cdot mol^{-1}$)			
288.15	0.001	−57.493	56.380	—	0.015
298.15	0.501	−1.532	−0.624	—	0.015
308.15	0.754	−1.072	−0.140	—	0.022
318.15	0.132	−1.466	−0.713	—	0.008
		h^E ($J \cdot mol^{-1}$)			
298.15	0.600	5071.9	−1479.1	—	7.3
		Butyl benzoate + n-heptane			
		$v^E \times 10^6$ ($m^3 \cdot mol^{-1}$)			
288.15	2.122	−1.472	−0.942	—	0.004
298.15	1.356	−2.558	1.696	−2.508	0.005
308.15	4.812	−2.422	−0.572	—	0.006
318.15	2.482	−2.874	−0.207	—	0.006
		$\delta\eta$ (mPa · s)			
288.15	2.622	−2.371	−3.047	—	0.008
298.15	2.874	−1.764	−1.893	—	0.003
308.15	1.979	−1.237	−1.168	—	0.006
318.15	1.307	−0.925	−0.712	—	0.002
		Δg^{*E} ($J \cdot mol^{-1}$)			
288.15	0.096	−1.917	1.239	—	0.016
298.15	0.199	−1.610	1.113	—	0.013
308.15	0.078	−1.525	1.091	—	0.013
318.15	0.971	−0.695	0.433	—	0.009
		h^E ($J \cdot mol^{-1}$)			
298.15	0.334	5268.7	−2187.9	—	5.8

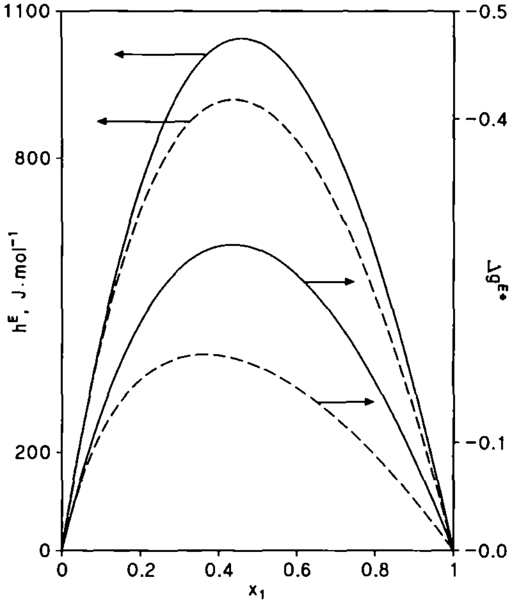

Fig. 1. Representation of excess enthalpies, h^E, and excess free activation energy of viscous flow, Δg^{*E}, at 298.15 K for the binaries $x_1 C_6H_5COOC_nH_{2n+1}$ ($n = 3, 4$) + $x_2 n$-C_7H_{16} obtained with Eq. (2) and coefficients in Table IV. (——) $n = 3$; (- - -) $n = 4$.

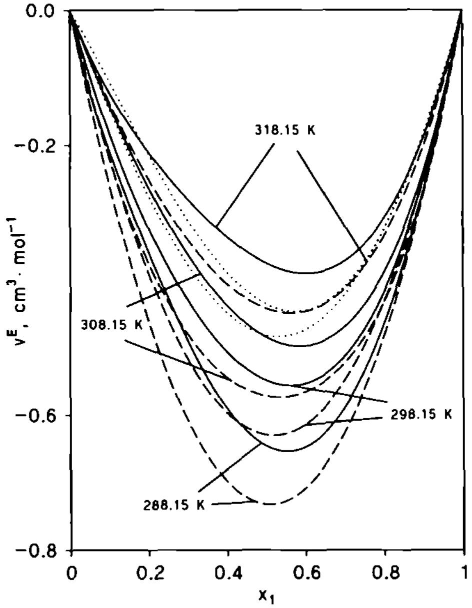

Fig. 2. Representation of excess molar volumes, v^E, for $x_1$propyl (——) or butyl (- - -) benzoate + $x_2 n$-heptane at different temperatures. (···) Values from Dussart et al. [8] for the same mixtures.

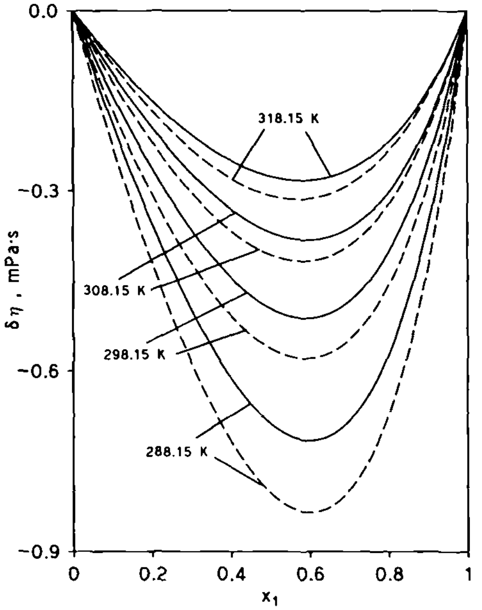

Fig. 3. Representation of apparent excess viscosities, $\delta\eta$, for $x_1$propyl (——) or butyl (- - -) benzoate + x_2n-heptane at different temperatures.

Some excess volumes at 298.15 K have been found in the literature for the mixtures considered. Our values for propyl benzoate + *n*-heptane show a difference of approximately 16% with respect to those reported by Dussart et al. [8]; for the values for butyl benzoate + *n*-heptane the difference with respect to those reported by Grolier et al. [7] and Dussart et al. [8] is somewhat higher, about 23%. These differences correspond to discrepancies of about ±0.008 $\text{cm}^3 \cdot \text{mol}^{-1}$ between the values for v^E calculated from the density by those authors [7, 8] and those calculated by us.

Since v^E and $\delta\eta$ values were available for the mixtures over a range of temperatures, we were able to extend our analysis by calculating the thermodynamic activation properties, Δh^* and Δs^*, and consequently Δg^*, based on the activated complex theory of Eyring et al. [11], using the equation

$$\eta = -\frac{hN}{v}\exp[(\Delta h^*/RT) - (\Delta s^*/R)] \tag{3}$$

where $\Delta g^* = \Delta h^* - T\,\Delta s^*$. The values for these properties are presented in Table V.

Table V. Activation Parameters for x_1 Propyl or Butyl Benzoate + x_2*n*-Heptane

	Δg^* (kJ · mol^{-1})				Δs^*	Δh^*
x_1	288.15 K	298.15 K	308.15 K	318.15 K	(J · K^{-1} · mol^{-1})	(kJ · mol^{-1})
Propyl benzoate (1) + *n*-heptane (2)						
0.0000	61.8	63.7	65.6	67.5	−189.2	7.3
0.0990	62.1	64.0	65.9	67.8	−189.7	7.5
0.1965	62.6	64.4	66.3	68.2	−188.5	8.2
0.2952	63.0	64.9	66.7	68.6	−187.0	9.1
0.3950	63.4	65.3	67.1	69.0	−187.0	9.5
0.4959	63.9	65.7	67.6	69.4	−185.4	10.4
0.5924	64.4	66.2	68.1	69.9	−184.2	11.3
0.6991	64.9	66.8	68.6	70.4	−181.0	12.8
0.7981	65.5	67.2	69.0	70.8	−179.2	13.8
0.8973	66.0	67.8	69.6	71.3	−177.8	14.8
1.0000	66.6	68.3	70.1	71.9	−175.2	16.1
Butyl benzoate (1) + *n*-heptane (2)						
0.0000	61.8	63.7	65.6	67.5	−189.2	7.3
0.0994	62.2	64.1	66.0	67.9	−189.5	7.6
0.1959	62.7	64.6	66.5	68.4	−188.7	8.3
0.2964	63.2	65.1	67.0	68.8	−187.1	9.3
0.3986	63.7	65.6	67.5	69.4	−187.3	9.8
0.4963	64.3	66.1	68.0	69.8	−183.5	11.4
0.5965	64.9	66.7	68.5	70.3	−181.8	12.5
0.6954	65.4	67.2	69.0	70.8	−181.3	13.1
0.7986	66.0	67.8	69.6	71.4	−178.9	14.4
0.8975	66.6	68.3	70.1	71.9	−177.3	15.5
1.0000	67.2	68.9	70.7	72.4	−173.8	17.1

4. DISCUSSION

The values for the different excess properties presented in this paper highlight important aspects of the behavior of alkyl benzoate + *n*-heptane mixtures. First, the endothermal nature of the mixtures due to the formation of induced dipole–dipole complexes between the benzoate and the hydrocarbon. The values of h^E, like those of v^E and $\delta\eta$, decrease with increasing chain length of the aromatic ester. The volume contracts, i.e., $v^E < 0$, considerably as the temperature increases, thereby facilitating interstitial accommodation of the hydrocarbon molecules among the benzoate molecules. The opposite effect was recorded for the $\delta\eta$ values.

The Δg^{*E} values for these mixtures, like those for the mixtures considered in previous works [5, 6], are negative and decrease slightly with increasing temperature. The negative Δg^{*E} values also decrease with increasing hydrocarbon chain length of the benzoate, which is a clear indicator that a breakdown of the dipolar order of the alkyl benzoate $C_6H_5COO\text{–}R_1$ requires less energy as the chain length of R_1 increases, as discussed previously by Oswal and Dave [4]. Our data do not provide a sufficient basis for establishing the specific effects that may be brought about by the presence of an aromatic ring.

As for the activation properties, the negative entropy values, $\Delta s^{\neq}$, yield a picture of increasing molecular order or arrangement, and these values decrease slightly as the *n*-alkane concentration is increased. In contrast, the activation enthalpy, $\Delta h^{\neq}$, for the mixtures increases as the ester concentration rises and is somewhat higher as R_1 increases due to the geometric effects caused by the voluminosity of the alkyl benzoate.

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NOMENCLATURE

A_i	Parameters in Eq. (2)
Δg^{*E}	Gibbs free energy of viscous flow ($J \cdot mol^{-1}$)
$\Delta g^{\neq}$	Activation free energy ($kJ \cdot mol^{-1}$)
K	Parameter in Eq. (2)
h	Planck constant
h^E	Excess enthalpy ($J \cdot mol^{-1}$)
$\Delta h^{\neq}$	Activation enthalpy ($kJ \cdot mol^{-1}$)
N	Avogadro number
R	Universal gas constant ($J \cdot K^{-1} \cdot mol^{-1}$)
s	Standard deviation
$\Delta s^{\neq}$	Activation entropy ($J \cdot K^{-1} \cdot mol^{-1}$)
T	Temperature (K)
v	Molar volume of pure component ($m^3 \cdot mol^{-1}$)
v^E	Excess volume ($m^3 \cdot mol^{-1}$)
x_i	Mole fraction of component i

Greek Letters

α	Expansion coefficient (K^{-1})
ρ	Density ($kg \cdot m^{-3}$)
η	Viscosity ($mPa \cdot s$)
$\delta\eta$	Apparent excess viscosity ($mPa \cdot s$)

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