The Viscosity of Gaseous n-Butane and Its Initial Density Dependence[1]

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ABSTRACT

New relative high-precision measurements of the viscosity η of gaseous n-butane were carried out in an oscillating-disk viscometer. Seven series of measurements were performed between 298 and 627 K in the density range from 0.01 up to 0.05 $\mathrm{mol \cdot L^{-1}}$. Isotherms recalculated from the original experimental data were analysed with a first-order expansion, in terms of density, for the viscosity. Reduced values of the second viscosity virial coefficient deduced from the zero-density and initial-density viscosity coefficients for n-butane are in good agreement with the representation of the Rainwater-Friend theory. The new experimental data and some data sets from literature were used to develop a representation for the viscosity of n-butane in the limit of zero density on the basis of the extended principle of corresponding states. It has been proven that an individual correlation is needed to represent the experimental data between 293 and 627 K with an uncertainty of ± 0.4 %.

KEY WORDS: n-alkanes; n-butane; second viscosity virial coefficient; transport properties; viscosity.

1. INTRODUCTION

In a programm initiated under the auspices of IUPAC the viscosity surfaces of ethane [1] and propane [2] were studied in the series of the n-alkanes. This program is now extended to n-butane, which belongs as natural gas and environmentally friendly alternative refrigerant to those fluids, for which thermophysical properties are required over the widest range of thermodynamic states possible.

Earlier viscosity measurements on n-butane in the low-density range suffered from three problems. First, the measurements were not extended to higher temperatures. Second, there exist only a limited number of reliable values to be included in the primary data sets for the correlation. Third, isotherms with a sufficient number of precise data were not measured to evaluate them with a first-order expansion, in terms of density, for the viscosity. Such data are needed, because the correlation of a transport-property surface should be started at low densities.

The new viscosity measurements at relatively low densities are suitable to determine both leading terms in the density series of the viscosity. The viscosity in the limit of zero density is to be correlated on the basis of the extended theorem of corresponding states. But, the specific interactions between n-butane molecules require an individual correlation. Individual parameters are also needed for the description of the initial density dependence of viscosity. The representation proposed in this paper for the low-density range differs from the earlier correlation given by Younglove and Ely [3] by considering the initial density dependence of viscosity in a novel and correct way [4].

2. METHODOLOGY OF DATA CORRELATION

The viscosity η of a moderately dense gas may be represented at temperature T and molar density ρ by a density expansion limited to the first power:

$$\eta(T,\rho) = \eta_0(T) + \eta_1(T)\rho + \cdots = \eta_0(T)\left[1 + B_\eta(T)\rho + \cdots\right] \tag{1}$$

Here, η_0 and η_1 are the zero-density and initial-density viscosity coefficients, and B_η is the second viscosity virial coefficient.

$\eta_0(T)$ is not directly experimentally accessible, but it follows from extrapolation of the results of low-density measurements. According to the well-established kinetic theory of dilute gases, $\eta_0(T)$ is given in practical engineering form [5] by

$$\eta_0(T) = \frac{0.021357(MT)^{1/2}}{\sigma^2 \mathfrak{S}_\eta^*(T^*)} \tag{2}$$

$$T^* = k_\mathrm{B} T/\varepsilon \tag{3}$$

The notation $\mathfrak{S}_\eta^*$ represents the reduced effective collision cross section $\mathfrak{S}^*(2000)$ and the correction factor for higher approximations. T^* is the reduced temperature, and ε/k_B is an energy scaling parameter or the well-depth of an assumed intermolecular potential in K. σ is a length scaling parameter or the collision diameter in nm.

The temperature dependence of $\mathfrak{S}_\eta$ may be represented in the reduced functional form

$$\ln \mathfrak{S}_\eta^* = \sum_{i=0}^{n} a_i \left(\ln T^*\right)^i \tag{4}$$

To develop a viscosity correlation the available experimental data are divided into primary and secondary data sets based on a critical assessment of the methods of measurements with regard to the completeness of the measuring theory and to the achieved precision. Then, experimental $\mathfrak{S}_\eta$ values ($\mathfrak{S}_\eta = \pi\sigma^2\mathfrak{S}_\eta^*$) are derived from given η data and fitted, using appropriate statistical weights, to Eq. (4). Since the kinetic theory for polyatomic gases like n-butane is still in its formative stages, a modified analysis has to be performed in two steps based on an empirical extension of the extended corresponding-states principle. We adopted a universal correlation on the basis of this principle derived by Bich et al. [6], who determined simultaneously the coefficients a_i of Eq. (4) as well as σ and ε/k_B in Eqs. (2) and (3) for the noble gases in the temperature range $1.2 < T^* < 10$. In the first step σ and ε/k_B are determined from $\eta_0(T)$ using the known coefficients a_i. In the second step, the determined scaling factors are assumed to be fixed and new coefficients

a_i are deduced by fitting the quasi-experimental $\mathfrak{S}_\eta$ values to Eq. (4). The resulting representation is specific for the considered substance and is called individual correlation.

The temperature function $B_\eta(T)$, which characterizes the viscosity of moderately dense gases, can be represented by a microscopically based theoretical model derived by Rainwater and Friend [7, 8] using the Lennard-Jones 12-6 potential. In this theory two potential parameter ratios δ and θ had to be determined by fitting the theoretical expressions to experimental B_η data for monatomic and polyatomic gases as well as to experimental B_λ values for monatomic gases (λ - thermal conductivity). Bich and Vogel [9] presented tables of B_η^* (Eq. (5)) as a function of T^* (see Eq. (3)) for two sets of δ and θ. For practical applications in computer codes B_η^* can be represented using the correlation

$$B_\eta^* = \frac{B_\eta}{N_\mathrm{A}\sigma^3} = \sum_{i=0}^{n} c_i \left(T^*\right)^{-i/2} \tag{5}$$

The coefficients c_i are given in Table 5.3. of Ref. [9] for the optimized parameter ratios $\delta = 1.04$ and $\theta = 1.25$ by Bich and Vogel [4] (B_η in units of $\mathrm{L \cdot mol^{-1}}$).

3. EXPERIMENTAL RESULTS

The experiments were carried out in a quartz-glass oscillating-disk viscometer with small gaps. The basic principles of design and construction [10] as well as details of performance of the relative measurements [11, 12] have been described previously. In accordance with the experiments on propane [13], the uncertainty of the viscosity data has been estimated to be ± 0.15 % at room temperature and ± 0.2-0.3 % at the highest temperatures, whereas the reproducibility has been found to be about ± 0.1 % covering the whole temperature range. Seven series of measurements were performed on n-butane for densities between 0.009 and 0.047 $\mathrm{mol \cdot L^{-1}}$ in a temperature range from 298 up to 627 K. The actual densities were determined during the filling process by $p\rho T$ measurements taking into account the real-gas behavior [3]. The certified purity of n-butane supplied by UCAR, USA, amounts to 99.95 %. Table I summarizes the experimental data.

As the values of Table I are not exactly isothermal, the isochoric data were recalculated into isothermal values by means of a first-order Taylor series, in terms of temperature:

$$\eta(T_{\rm int}) = \eta(T_{\rm exp}) + \left(\frac{\partial \eta}{\partial T}\right)_{\rho} \Delta T + R_{\rm n} \tag{6}$$

$$\Delta T = T_{\rm int} - T_{\rm exp} \tag{7}$$

The interpolation temperature $T_{\rm int}$ corresponds to the mean temperature for the points of the seven series. The temperature derivative of η needed in Eq. (6) was evaluated with the coefficients of Eq. (8), which were obtained by a fit to the original isochoric data.

$$\eta(T) = S\ \exp(A \ln T_{\rm R} + \frac{B}{T_{\rm R}} + \frac{C}{T_{\rm R}^2} + D), \qquad T_{\rm R} = \frac{T}{298.15} \tag{8}$$

Then, η_0 and η_1 were deduced by fitting Eq. (1) to the quasi-experimental viscosity values of the isotherms. In Table II the least-squares values of η_0 and η_1 are given, together with their individual standard deviations s_{η_0} and s_{η_1} and with the standard deviation s_η for each isotherm.

4. ANALYSIS OF $B_\eta(T)$

Our experimental results and the values by Kestin and Yata [14] are the only data at moderate densities that are suitable for an exact evaluation in the limit of zero density. Both data sets are characterized by a sufficient number of low-density points of high accuracy along isotherms to resolve both slope η_1 and zero-density limit η_0. In order to compare B_η (Eq. (1)) with predicted reduced values B_η^* (Eq. (5)) due to the Rainwater-Friend theory, Lennard-Jones 12-6 potential parameters for n-butane are needed. They have been determined from $\eta_0(T)$ of this paper using Eqs. (2) and (3) to be

$$\varepsilon/k_{\rm B} = 328.68\,{\rm K} \qquad\qquad \sigma = 0.53272\,{\rm nm}.$$

Fig. 1 compares the curves of the theoretical results for the ratios δ and θ, obtained originally by Rainwater and Friend [7, 8] and more recently by Bich and Vogel [4], with B_η^*

values for n-butane of this paper and of Kestin and Yata [14] as well as for ethane [15] and propane [13]. The comparision shows that the B_η^* values for the three n-alkanes, all reduced with Lennard-Jones 12-6 parameters from $\eta_0(T)$, do not completely agree with one of the theoretical curves. The disagreement is due to the uncertainty of the experimental data and to the fact that the Lennard-Jones 12-6 potential model is inadequate to represent the intermolecular interactions of polyatomic gases. Since the experimental information is to be used for a viscosity surface correlation with the aim of extrapolating to temperatures outside the measuring ranges, it is advisable to derive scaling factors ε/k_B and σ in a fit of one of the theoretical curves to the experimental $B_\eta(T)$ data. Thus, we chose $B_\eta^*(T^*)$ according to Eq (5) with the coefficients c_i by Bich and Vogel [9] and obtained using the data of this paper and those by Kestin and Yata for n-butane:

$$\varepsilon/k_\mathrm{B} = 280.51\,\mathrm{K} \qquad\qquad \sigma = 0.57335\,\mathrm{nm}$$

The temperature dependence of the experimental B_η^* values resulting this way agrees now very reasonable with that of the Rainwater-Friend theory. But, Fig. 1 shows also that the B_η^* values due to the Younglove-Ely correlation [3] are in disagreement with that theory.

5. ZERO-DENSITY CORRELATION

Our data cover a larger temperature range than those of all other sources together. A list of data from literature on viscosity measurements of n-butane at low densities can be obtained from the authors. The list includes the method of measurement, the temperature range, number of data points at densities up to 0.10 $\mathrm{mol \cdot L^{-1}}$, the ascribed accuracy of the data and the classification in primary and secondary data sets.

In order to compare our data with that from literature on a common basis the last-mentioned values were corrected to the limit of zero density using the information on the initial density dependence of viscosity given in the foregoing section. Although for the temperature range under discussion this effect is small compared with the experimental

uncertainties of most authors, the correction was performed because it is a systematic one. In this procedure the densities were calculated with the MBWR equation of state [3] for temperatures corresponding to the IPTS-68 from the information given in the papers followed by a correction of the temperatures to ITS-90.

In principle, only data by Kestin and coworkers [14, 16, 17, 18, 19, 20] might be classified as primary ones. But, there are two problems with that data. First, several data sets exist in the same temperature range, so that their influence would be overrated. Second, the deviations between different data sets amount to about 1 %, although Kestin and coworkers claimed an accuracy of $\pm 0.1 - 0.3\,\%$ for their data. Thus, we were forced to increase the ascribed accuracy to $\pm 0.2 - 0.6\,\%$ and to include only the data at room temperature [14, 16] and the most recent data by Abe et al. [20] between 298 and 468 K into the primary data sets.

According to the methodology described in Section 2. the scaling factors of the universal correlation have been determined in the first step to be:

$$\varepsilon/k_{\mathrm{B}} = 330.51\,\mathrm{K} \qquad\qquad \sigma = 0.53649\,\mathrm{nm}$$

It emerges clearly that the universal correlation is not suitable to represent the primary data sets within their errors in the temperature range covered by the experiments (see Fig. 2). For this reason an individual correlation was carried out with ε/k and σ to be fixed. The following coefficients a_i of Eq. (4) were derived:

$$a_0 = 0.2229039 \quad a_1 = -0.4809052 \quad a_2 = 0.1339312 \quad a_3 = -0.2548478 \quad a_4 = 0.1941395$$

The deviations of the primary and secondary data sets from the individual correlation are shown in Fig. 2 including a comparison with the universal correlation and with the recommended data by Younglove and Ely [3] and by Tarzimanov et al. [32]. The values by Tarzimanov et al. turn out to be generally too high. The agreement with the Younglove-Ely correlation is quite reasonable, although it is based on experimental data only up to 480 K. However, there is a tendency to higher values at low temperatures. The uncertainty

of the new correlation for the zero-density viscosity between 293 and 625 K is estimated to be $\pm 0.4\,\%$.

6. CONCLUSIONS

The representation of the viscosity surface should separately take into account both leading terms of the density series. In the case of polyatomic gases the representation of the viscosity in the limit of zero density is preferably to be based on an individual correlation instead of a universal one according to the extended principle of corresponding states. The initial density dependence of viscosity is to be modelled due to the Rainwater-Friend theory including optimized scaling factors. Only a small body of experimental values for n-butane from literature could be characterized as primary data.

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FIGURE CAPTIONS

Fig. 1. Reduced second viscosity virial coefficient B_η^* as a function of the reduced temperature T^* for the Lennard-Jones 12-6 potential. (□) Ethane [15]; (○) propane [13]; (▽) n-butane, present paper; (△) n-butane, Kestin and Yata [14]; (▼) n-butane, optimized scaling factors, present paper; (▲) n-butane, optimized scaling factors, Kestin and Yata [14]; (-·-·-·-·-) n-butane, optimized scaling factors, Younglove-Ely correlation [3], (- - - - -) Rainwater-Friend theory [7, 8] ($\delta = 1.02$, $\theta = 1.15$); (———) Rainwater-Friend theory, Bich and Vogel [4] ($\delta = 1.04$, $\theta = 1.25$).

Fig. 2. Deviations of viscosity data from the present correlation. Primary data: (●) Kestin and Yata [14], (⧫) Kestin et al. [16], (■) Abe et al. [20], (○) present paper. Correlations: (———) universal correlation, (-·-·-·-·-) Younglove and Ely [3], (- - - - -) Tarzimanov et al. [32]. Secondary data (in the inner part of the figure): (+) Kuenen and Visser [21], (∗) Titani [22], ($) Sage et al. [23], (x) Wobser and Mueller [24], (<) Senftleben and Gladisch [25], (>) Senftleben [26], (◊) Lambert et al. [27], (□) Carmichael and Sage [28], (ϕ) Dolan et al. [29], (#) Diaz Pena and Cheda [30], (&) Diaz Pena and Cheda [31], (▼) Kestin et al. [17], (▽) Abe et al. [18], (△) Abe et al. [19].
$\Delta = 100 \cdot (\eta_{\rm exp} - \eta_{\rm corr})/\eta_{\rm exp}$.

Table I. Viscosity of n-Butane

Temperature T (K)	Viscosity η (μPa · s)	Temperature T (K)	Viscosity η (μPa · s)
Series 1 $\rho = 8.79 \times 10^{-3}$ mol · L^{-1}		Series 2 $\rho = 8.98 \times 10^{-3}$ mol · L^{-1}	
298.75	7.432	298.24	7.426
325.44	8.093	325.68	8.103
353.67	8.769	353.92	8.782
382.95	9.471	382.81	9.474
410.83	10.136	410.00	10.131
438.85	10.805	440.11	10.842
470.13	11.541	467.36	11.481
496.47	12.140	496.84	12.158
526.82	12.845	527.31	12.841
546.66	13.313	547.92	13.327
568.13	13.810	568.78	13.802
597.66	14.490	597.47	14.454
626.84	15.136	627.13	15.116
298.15	7.419	330.04	8.198
Series 3 $\rho = 17.72 \times 10^{-3}$ mol · L^{-1}		Series 4 $\rho = 27.28 \times 10^{-3}$ mol · L^{-1}	
298.87	7.420	298.45	7.418
325.02	8.087	325.17	8.076
353.55	8.779	353.06	8.758
381.52	9.457	383.28	9.496
409.78	10.140	410.45	10.136
438.45	10.822	438.82	10.821
466.85	11.481	467.00	11.477
495.83	12.156	495.93	12.146
526.76	12.860	525.26	12.802
546.87	13.320	546.27	13.295
568.04	13.801	567.18	13.771
595.83	14.438	595.75	14.436
625.29	15.100	626.10	15.118
325.20	8.092	297.68	7.397

Table I. *(Continued)*

Temperature T (K)	Viscosity η (μPa · s)	Temperature T (K)	Viscosity η (μPa · s)
Series 5 $\rho = 34.19 \times 10^{-3}$ mol · L^{-1}		Series 6 $\rho = 40.26 \times 10^{-3}$ mol · L^{-1}	
299.36	7.433	299.12	7.433
325.43	8.080	324.89	8.070
353.36	8.757	352.94	8.766
384.10	9.515	381.88	9.463
409.63	10.126	409.87	10.141
438.90	10.819	438.55	10.824
467.43	11.488	467.14	11.494
496.15	12.156	496.29	12.165
527.60	12.872	525.60	12.844
546.69	13.325	545.96	13.324
568.33	13.815	568.43	13.846
598.25	14.498	596.55	14.482
626.87	15.123	625.15	15.142
298.27	7.407	297.77	7.397
Series 7 $\rho = 46.47 \times 10^{-3}$ mol · L^{-1}			
297.85	7.392		
324.49	8.054		
354.14	8.792		
381.44	9.449		
409.67	10.135		
437.94	10.812		
466.46	11.488		
496.03	12.175		
525.50	12.854		
546.71	13.346		
567.43	13.832		
595.92	14.491		
625.74	15.155		
297.72	7.390		

Table II. Zero-Density and Initial-Density Viscosity Coefficients of n-Butane for the Isotherms According to Eq. (1)

Temperature T (K)	Zero-density viscosity $\eta_0 \pm s_{\eta_0}$ (μPa $\cdot$ s)	Initial-density viscosity $\eta_1 \pm s_{\eta_1}$ (μPa $\cdot$ s $\cdot$ L $\cdot$ mol^{-1})	Standard deviation $10^3\ s_\eta$ (μPa $\cdot$ s)
298.52	7.437 ± 0.005	-0.588 ± 0.158	5.78
325.16	8.094 ± 0.003	-0.497 ± 0.109	4.01
353.52	8.768 ± 0.006	0.132 ± 0.204	7.50
382.57	9.467 ± 0.005	0.301 ± 0.170	6.25
410.03	10.124 ± 0.008	0.435 ± 0.259	9.49
438.80	10.807 ± 0.007	0.527 ± 0.221	8.11
467.48	11.476 ± 0.005	0.636 ± 0.182	6.68
496.22	12.135 ± 0.007	0.820 ± 0.249	9.14
526.41	12.819 ± 0.011	1.018 ± 0.355	13.01
546.73	13.295 ± 0.008	0.998 ± 0.275	10.10
568.05	13.780 ± 0.012	1.199 ± 0.415	15.23
596.78	14.438 ± 0.012	1.225 ± 0.417	15.31
626.16	15.091 ± 0.016	1.388 ± 0.529	19.40
297.92	7.417 ± 0.003	-0.459 ± 0.078	2.27

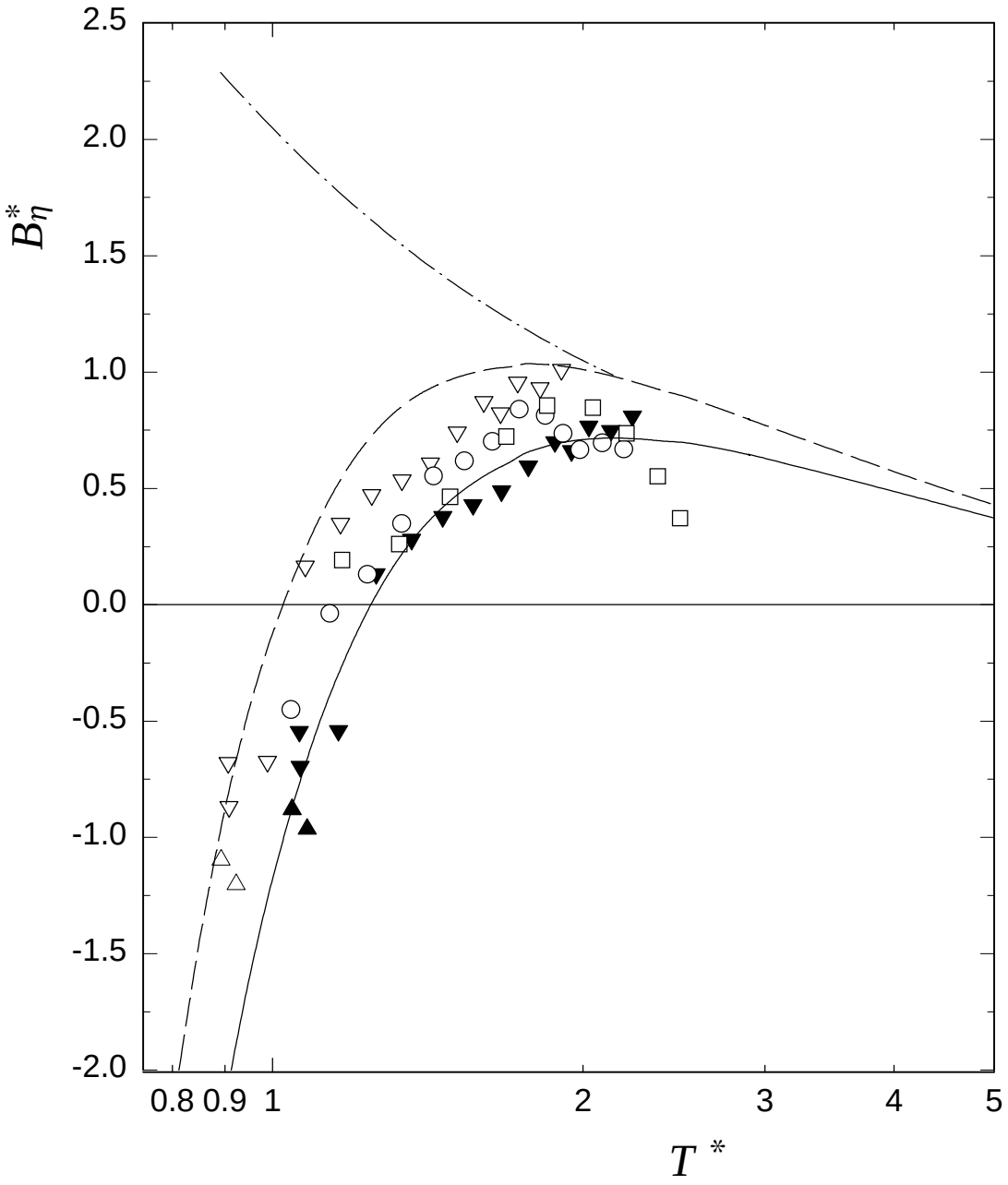

Fig. 1 E. Vogel and C. Küchenmeister

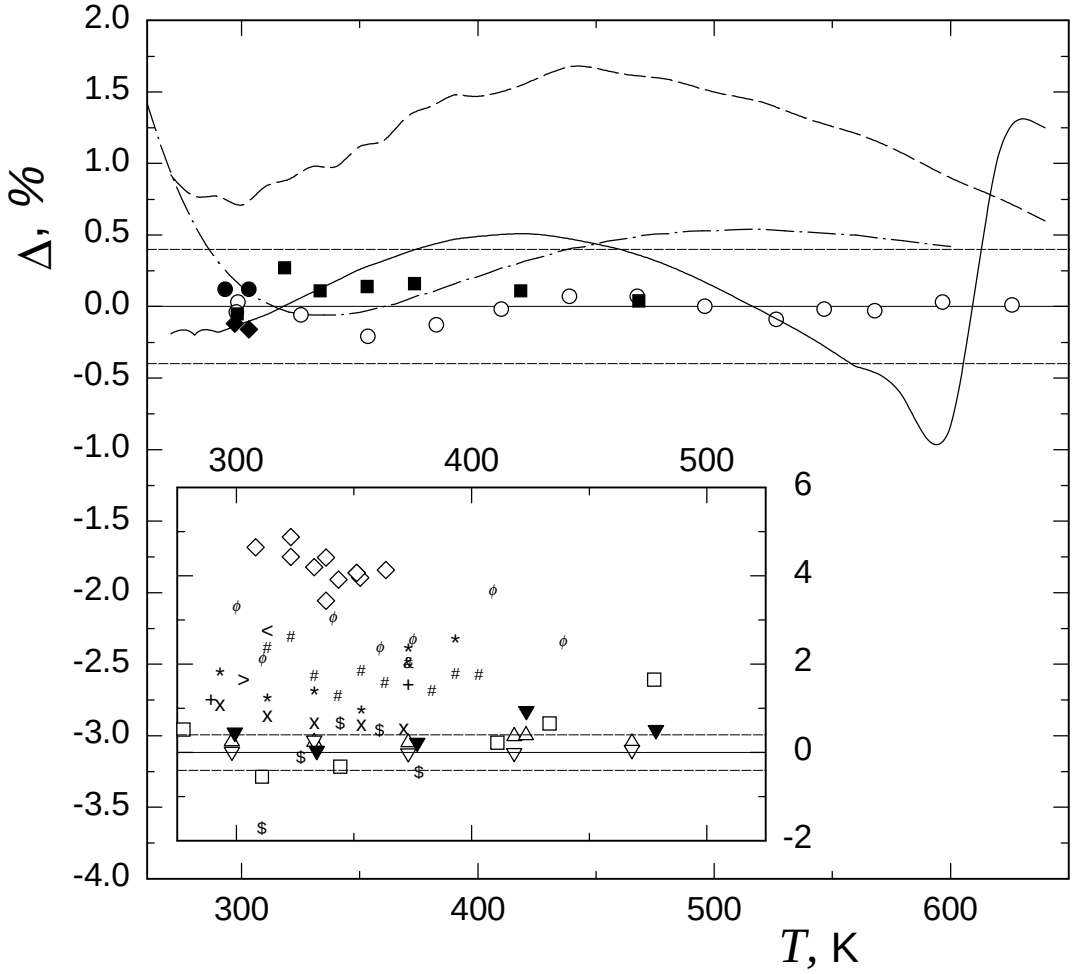

Fig. 2 E. Vogel and C. Küchenmeister