

## Vapor-Phase Viscosity of Phenol<sup>1</sup>

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Received January 8, 1993

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New measurements of the vapor-phase viscosity of phenol were performed from 437 up to 624 K and for densities between 0.006 and 0.023 mol · L<sup>-1</sup> in an all-quartz oscillating-disk viscometer with small gaps. Thus, including our own measurements reported earlier, experimental data are available in the temperature range between 376 and 639 K and in the density range from 0.001 up to 0.023 mol · L<sup>-1</sup>. The data were evaluated with a density series for the viscosity in which only a linear density contribution is included. The values of the second viscosity virial coefficient obtained for phenol as well as for benzene, toluene, and *p*-xylene were compared with results of the Rainwater-Friend theory and of the modified Enskog theory on the basis of the Lennard-Jones 12-6 potential. The agreement is reasonable, when the potential parameter ratios determined by Bich and Vogel are used. The influence of bound dimers seems to be already taken into account in the three-monomer contribution according to Hoffman and Curtiss.

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**KEY WORDS:** phenol; second viscosity virial coefficient; transport properties; viscosity.

### 1. INTRODUCTION

The viscosity of a moderately dense gas may be represented at temperature  $T$  and density  $\rho$  by a density expansion limited to the first power,

$$\eta(T, \rho) = \eta_0(T) + \eta_1(T) \rho + \dots = \eta_0(T) [1 + B_\eta(T) \rho + \dots] \quad (1)$$

The collisional process between pairs of monomers in the limit of zero density is taken into account in the  $\eta_0$  term and is described by means of the kinetic theory of dilute gases [1, 2]. Although this theory originated by

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Chapman and Enskog has reached a very high level, exact calculations on the basis of a well-established intermolecular potential model are available only for monatomic gases. In order to calculate  $\eta_0$  in the case of polyatomics, some approximations have to be made with respect to the formal kinetic theory as well as to the intermolecular potential surface. There seems to be some progress in the evaluation of the cross sections needed for  $\eta_0$  for the diatomic nitrogen gas [3].

In addition, collisional processes between pairs of monomers contribute to the linear-in-density correction  $\eta_1$  through collisional transfer. But collisions among three monomers and between a monomer and a dimer also contribute to this initial density viscosity coefficient  $\eta_1$ . The theoretical basis of  $\eta_1$  is less well developed, although certain improvements were reached during the last 10 years. Rainwater and Friend [4-6] developed a microscopically based theoretical model for the second transport virial coefficients  $B_\eta$  and  $B_\lambda$  which is limited to monatomic gases in the case of thermal conductivity  $\lambda$ . Unfortunately, the calculations were restricted to the Lennard-Jones 12-6 potential and to pure fluids. This model includes ideas by Stogryn and Hirschfelder [7] as well as by Hoffman and Curtiss [8]. The most important problem, which has to be taken into consideration for real molecules with both repulsive and attractive forces, is the formation of bound states. The progress achieved by Rainwater and Friend consists in that the two-monomer collisional transfer contribution is evaluated only for the free phase space so that bound states can be considered separately. But the three-monomer contribution proposed originally by Hoffman and Curtiss and used by Rainwater and Friend could possibly also include effects of the formation of bound states. To advance the understanding of the approximation procedure, an experimental determination of the viscosity of polyatomic gases or vapors with polar interactions could be helpful, because a formation of dimers should occur to a larger extent.

The present paper reports results of the vapor-phase viscosity of phenol at low and moderate densities in a comparably large temperature range. The experimental data were evaluated in order to obtain values of the reduced second viscosity virial coefficient  $B_\eta^*$  as a function of the reduced temperature  $T^*$  on the basis of the Lennard-Jones 12-6 potential distance and energy parameters  $\sigma$  and  $\epsilon$ .

$$B_\eta^* = \frac{B_\eta}{\sigma^3} \quad (2)$$

$$T^* = \frac{kT}{\epsilon} \quad (3)$$

Here  $k$  is Boltzmann's constant. The results for phenol have been compared with the Rainwater-Friend theory, including improved potential parameter ratios for well depth and collision diameter due to Bich and Vogel [9], with the modified Enskog theory, and with results for some other aromatic vapors.

## 2. EXPERIMENTAL RESULTS

The experiments were performed in an all-quartz oscillating-disk viscometer. Its characteristics have already been described previously [10]. The basic principles of design and construction [11] and details of calibration and of performance and evaluation of the measurements have been described previously, too [12, 13]. The viscometer was recalibrated at room temperature for a relatively large range of the boundary-layer thickness according to the quasi-absolute theory originated by Newell [14]. Reference values of carbon dioxide stated with an uncertainty of less than  $\pm 0.15\%$  by Kestin et al. [15, 16] were used. Measurements on carbon dioxide at low and moderate densities between room temperature and 683 K were carried out as a test of the performance of the viscometer. The uncertainty of the experimental data has been estimated to be between  $\pm 0.15\%$  at room temperature and  $\pm 0.2\text{--}0.3\%$  at the highest temperatures, whereas the reproducibility is even better.

Phenol of analytical reagent quality supplied by Berlin-Chemie was used as initial product for a rectification. The middle fractions were additionally purified by zone melting repeated five times. In a special glass apparatus the final product was dried by a molecular sieve, 4 A, and its melting point at atmospheric pressure as a criterion of purity was determined to be  $40.82 \pm 0.03^\circ\text{C}$ . Then, the substance was degassed by repeated freezing and evacuation and filled into small glass ampoules in the same apparatus. Finally, the evacuated viscometer was filled by sublimation of the weighed samples.

Four series of measurements each differing in density were performed. The temperature range was started at a temperature at which the substance existed completely as a vapor and continued to approximately 623 K. In order to test whether there is any thermal decomposition, a check measurement was carried out at a lower temperature after the highest temperature had been attained. But the result of the check measurement of a series cannot be considered sufficient, because the temperature at which the decomposition started may have not turned up clearly enough or a reversible process may have remained concealed. As any thermal alteration of the substance is largely increased at high temperatures and at relatively low

Table I. Viscosity of Phenol Vapor

Temperature $T$ (K)	Viscosity $\eta$ ( $\mu\text{Pa} \cdot \text{s}$ )
Series 1 old, $\rho' = 0.116 \text{ kg} \cdot \text{m}^{-3}$ $\rho = 1.23 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	
375.75	9.046
403.76	9.677
434.54	10.387
465.41	11.098
500.23	11.912
537.32	12.799
566.81	13.528
596.38	14.270
639.02	15.316
500.16	11.928
Series 2 old, $\rho' = 0.271 \text{ kg} \cdot \text{m}^{-3}$ $\rho = 2.88 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	
391.74	9.391
410.47	9.823
439.43	10.492
482.49	11.493
528.92	12.580
576.52	13.725
632.94	15.091
390.96	9.370
Series 3 old, $\rho' = 0.278 \text{ kg} \cdot \text{m}^{-3}$ $\rho = 2.95 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	
393.54	9.445
410.03	9.832
440.06	10.525
466.42	11.139
497.27	11.860
541.22	12.904
588.19	14.033
629.73	15.047
395.56	9.492

Table I. (Continued)

Temperature $T$ (K)	Viscosity $\eta$ ( $\mu\text{Pa} \cdot \text{s}$ )
Series 4, $\rho' = 0.591 \text{ kg} \cdot \text{m}^{-3}$ $\rho = 6.28 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	
437.22	10.421
464.94	11.050
493.83	11.743
522.71	12.421
543.44	12.925
564.94	13.451
594.00	14.167
622.45	14.867
436.25	10.398
Series 5, $\rho' = 1.103 \text{ kg} \cdot \text{m}^{-3}$ $\rho = 11.72 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	
437.28	10.384
465.12	11.047
494.14	11.734
523.10	12.412
544.26	12.931
565.70	13.450
594.25	14.162
623.61	14.887
436.85	10.379
Series 6, $\rho' = 1.527 \text{ kg} \cdot \text{m}^{-3}$ $\rho = 16.23 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	
437.24	10.373
466.06	11.069
495.08	11.747
522.34	12.398
543.11	12.910
564.69	13.451
593.43	14.165
622.62	14.880
436.35	10.359
Series 7, $\rho' = 2.170 \text{ kg} \cdot \text{m}^{-3}$ $\rho = 23.06 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	
465.32	10.989
494.03	11.672
522.99	12.363
544.40	12.893
565.96	13.421
594.53	14.158
623.96	14.885
465.71	10.997

densities, the highest isotherms of viscosity as a function of density have to be inspected strictly [10, 17, 18].

Three series of measurements at low densities were carried out several years ago [19]. These data were included here after a slight correction of the viscosity values due to an improved evaluation by means of the Newell procedure. In Table I the results are recorded, together with the density, as the first three series of measurements, marked "old," whereas the new data correspond to the last four series. A comparison of the data points for the highest isotherms proved the existence of a thermal alteration signaled by an excessive increase in the viscosity values of series 1. Therefore, data of this series were excluded from further evaluation for isotherms at temperatures higher than 570 K (see below). The following equation was fitted to the experimental data of each individual series of measurements:

$$\eta(T) = S \exp \left( A \ln T_R + \frac{B}{T_R} + \frac{C}{T_R^2} + D \right) \quad (4)$$

with

$$S = 10 \mu\text{Pa} \cdot \text{s}, \quad T_R = \frac{T}{298.15}$$

In Table II the parameters of Eq. (4), the standard deviations  $\sigma_\eta$ , and the root-mean-square deviations (rms) are listed. Viscosity values calculated at fixed smoothed temperatures are shown as open circles for five isotherms

**Table II.** Parameters of Eq. (4) for the Series of Measurements on Phenol Vapor

Series	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	SD $10^3 \sigma_\eta$ ( $\mu\text{Pa} \cdot \text{s}$ )	Root mean square deviation, $10^2$ rms (%)
1 old	1.28106	0.564311	-0.0753911	-0.796796	9.42	5.67
2 old	1.39032	1.09572	-0.350597	-1.07336	3.39	1.93
3 old	1.42879	1.22434	-0.405412	-1.14846	2.02	1.45
4	0.745065	-1.34152	0.763764	0.315533	5.27	3.33
5	1.82085	2.48517	-0.931243	-1.92083	5.80	3.44
6	1.04699	-0.233188	0.240877	-0.316698	9.34	5.77
7	0.284011	-3.20080	1.65226	1.34050	8.32	4.39
* <sup>a</sup>	1.20347	0.494630	-0.112934	-0.701058	1.88	1.25
** <sup>b</sup>	0.165822	-3.50965	1.72803	1.55890	1.16	0.87

<sup>a</sup> At zero density,  $443 \leq T \leq 623$  K.

<sup>b</sup> At 0.1013 MPa,  $463 \leq T \leq 623$  K.

in Fig. 1. For a comparison error bars of 0.1% at a low and a high temperature are plotted. Equation (1) was fitted to the points of each isotherm in 10 K intervals between 443 and 623 K in order to obtain the zero-density and initial density viscosity coefficients. In Table III some least-squares values of  $\eta_0$  and  $\eta_1$  are given, together with their individual standard deviations  $\sigma_{\eta_0}$  and  $\sigma_{\eta_1}$  as well as with the standard deviation  $\sigma_{\eta}$  for the data set. The straight lines in Fig. 1 represent values calculated via Eq. (1). In Fig. 2 values of the second viscosity virial coefficient  $B_{\eta}$  are plotted as a function of temperature with error bars resulting from  $(\eta_1 \pm \sigma_{\eta_1})/\eta_0$ .

To the best of our knowledge, there are no data in the open literature for the viscosity of phenol vapor. Because experiments are very often performed at atmospheric pressure, viscosity values at 0.1013 MPa were calculated by means of Eq. (1) for a comparison with future measurements. In order to take into account the initial density dependence of viscosity in an accurate manner, the densities needed for pressures of 0.1013 MPa were calculated including the second pressure virial coefficient  $B$ . The temperature function of  $B$  for phenol vapor was analyzed and evaluated by

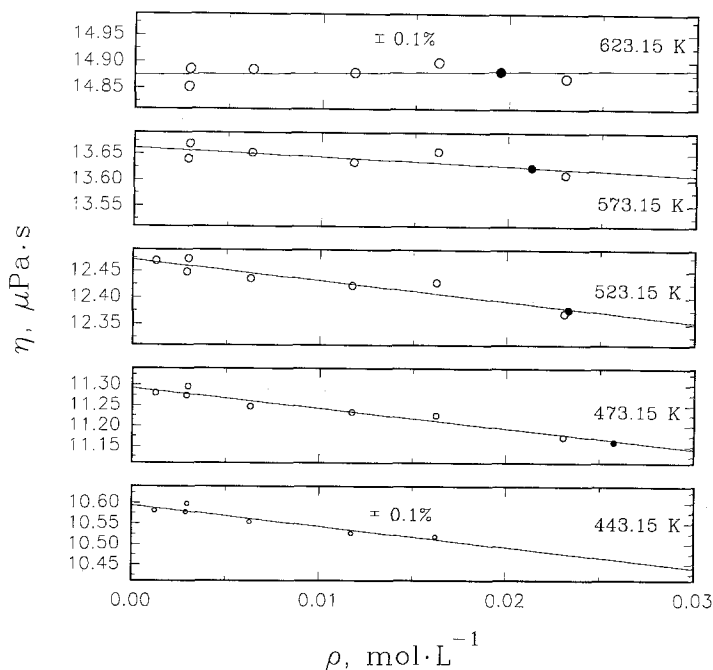
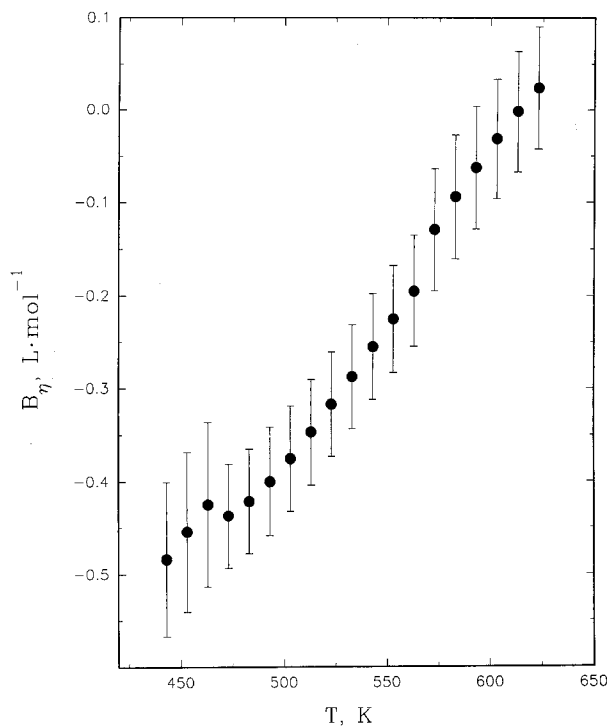


Fig. 1. Viscosity of phenol as a function of density for several isotherms.  $\eta = \eta_0 + \eta_1\rho$ ; (●) at 0.1013 MPa, calculated.

**Table III.** Zero-Density and Initial Density Viscosity Coefficients of Phenol Vapor for Several Isotherms According to Eq. (1)

Temperature $T$ (K)	Number of points ( $n$ )	Zero-density viscosity $\eta_0 \pm \sigma_{\eta_0}$ ( $\mu\text{Pa} \cdot \text{s}$ )	Initial density viscosity $\eta_1 \pm \sigma_{\eta_1}$ ( $\mu\text{Pa} \cdot \text{s} \cdot \text{L} \cdot \text{mol}^{-1}$ )	SD $10^3 \sigma_{\eta}$ ( $\mu\text{Pa} \cdot \text{s}$ )
443.15	6	$10.594 \pm 0.008$	$-5.127 \pm 0.880$	11.6
463.15	6	$11.057 \pm 0.009$	$-4.698 \pm 0.979$	12.9
483.15	7	$11.527 \pm 0.008$	$-4.860 \pm 0.651$	13.0
503.15	7	$11.998 \pm 0.008$	$-4.508 \pm 0.680$	13.6
523.15	7	$12.471 \pm 0.008$	$-3.952 \pm 0.702$	14.0
543.15	7	$12.948 \pm 0.009$	$-3.299 \pm 0.740$	14.8
563.15	7	$13.428 \pm 0.010$	$-2.619 \pm 0.801$	16.0
583.15	6	$13.902 \pm 0.012$	$-1.306 \pm 0.928$	16.7
603.15	6	$14.386 \pm 0.012$	$-0.449 \pm 0.933$	16.8
623.15	6	$14.875 \pm 0.013$	$0.359 \pm 0.988$	17.8



**Fig. 2.** Second viscosity virial coefficient  $B_{\eta}$  of phenol.



Bich and Opel [20] on the basis of experimental data between 477 and 632 K by means of the 12-6-8-3 potential. Values calculated from this potential model for the temperature range from 343 up to 643 K were used to fit the coefficients of the following polynomial in  $1/T$ :

$$B = \sum_{k=0}^4 \frac{a_k}{T^k} \quad (5)$$

The following coefficients  $a_k$  have been obtained, when the second pressure virial coefficient  $B$  is given in  $\text{L} \cdot \text{mol}^{-1}$ :

$$a_0 = -4.43827$$

$$a_1 = 9.49430 \times 10^3$$

$$a_2 = -7.89445 \times 10^6$$

$$a_3 = 2.88043 \times 10^9$$

$$a_4 = -4.32139 \times 10^{11}$$

The parameters of Eq. (4) for the viscosity coefficient at 0.1013 MPa as well as for the zero-density viscosity coefficient are also recorded in Table II including the temperature ranges of validity. The filled circles plotted in Fig. 1 correspond to calculated viscosity values at 0.1013 MPa.

### 3. THEORY OF THE REDUCED SECOND VISCOSITY VIRIAL COEFFICIENT

Apart from the Rainwater-Friend theory, which is the most successful scheme, the modified Enskog theory (MET) can also be used to predict the second viscosity virial coefficient  $B_\eta$  in the case of real gases.

The Enskog theory for a hard-sphere gas [21, 1] takes into account kinetic contributions resulting from the flow of molecules, collisional transfer contributions due to the finite size of the molecules, and the modification of the collisional frequency by a third particle. Thus, collisional processes between two monomers and among three monomers are represented as

$$B_\eta = B_\eta^{(2)} + B_\eta^{(3)} = 0.8b - \chi^{(1)} = 0.8b - \frac{c}{b} \quad (6)$$

Here  $b$  and  $c$  are the second and third pressure virial coefficients of a hard-sphere gas, whereas  $\chi^{(1)}$  is the first density coefficient of the equilibrium radial distribution function at contact. The Enskog theory has to be

modified [21–23] to use it for the treatment of the viscosity of a real moderately dense gas characterized by the formation of bound states as a consequence of attractive forces. Although no theoretical foundation can be given for the modification that the pressure of the hard-sphere fluid is to be replaced by the thermal pressure of the real dense fluid, the MET predicts quite well  $B_\eta$  for real gases [17, 10]. In the MET the reduced second viscosity virial coefficient  $B_\eta^*$  is given by

$$B_\eta^* = \frac{2}{3} \pi \left[ 0.8 \left( B^* + T^* \frac{dB^*}{dT^*} \right) - \frac{C^* + T^* \frac{dC^*}{dT^*}}{B^* + T^* \frac{dB^*}{dT^*}} \right] \quad (7)$$

where  $B^*$  and  $C^*$  are the reduced second and third pressure virial coefficients for the real gas or for an assumed intermolecular potential model. In particular, the MET is useful in the case of real moderately dense gaseous mixtures, because the Rainwater–Friend theory has not been extended to mixtures yet [24].

In the Rainwater–Friend theory [4–6, 9]  $B_\eta$  is represented by means of three contributions, one for the collisional transfer between two monomers and the others for collisional processes among three monomers and between a monomer and a dimer.

$$B_\eta = B_\eta^{(2)} + B_\eta^{(3)} + B_\eta^{(M-D)} \quad (8)$$

Rainwater [4] improved the two-monomer collisional transfer contribution  $B_\eta^{(2)}$  due to Hoffman and Curtiss [8] by limiting the integrations in their expressions, which are similar to the second pressure virial coefficient  $B$ , and in special collision integrals to the free phase and trajectory space. Thus, the effect of bound states is truly excluded from the evaluation of the two-monomer contribution.

The three-monomer contribution  $B_\eta^{(3)}$  was evaluated by Rainwater and Friend [5, 6, 25] in the same manner already applied by Hoffman and Curtiss [8]. Here the main contribution of triple collisions is due to excluded volume effects, whereas the effect of sequences of successive binary collisions is assumed to be negligible for real gases, because it amounts to only about 3% for hard spheres, too. In analogy to hard spheres, the shielding of a colliding pair by a third particle is taken into consideration by an expression connected with the equilibrium radial distribution function.

$$B_\eta^{(3)*} = - \frac{R}{8\pi^2 \sigma^3 \Omega^{(2,2)*}} \quad (9)$$

The multidimensional integral  $R$  in the reduced form of this contribution includes the first density coefficient of the equilibrium radial distribution function [25].

According to the proposal of Stogryn and Hirschfelder [7], Rainwater and Friend [5, 6] modeled a moderately dense gas as a mixture of monomers and dimers via the first approximation for the transport properties of a dilute binary gas mixture [1, 2]. Because of the uncertainty and complexity of the monomer-dimer collisional process, it is assumed that the interaction potential between the monomer and the dimer is known and is of the same form as the monomer-monomer potential and characterized by the potential parameter ratios

$$\delta = \frac{\sigma_{M-D}}{\sigma_M} \quad (10)$$

$$\theta = \frac{\epsilon_{M-D}}{\epsilon_M} \quad (11)$$

Friend and Rainwater [5] determined these potential parameter ratios by fitting the theoretical expressions for the monomer-dimer contributions to experimental data for the second viscosity and second thermal conductivity virial coefficients  $B_\eta$  and  $B_\lambda$  ( $B_\lambda$  only for monatomic gases). They used their calculated values of the two-monomer and three-monomer contributions for the Lennard-Jones 12-6 potential model and obtained the following values for the ratios:

$$\delta = 1.02 \quad \text{and} \quad \theta = 1.15.$$

Bich and Vogel [9] deduced slightly improved values by using additionally own experimental data of  $B_\eta$  for polyatomic gases:

$$\delta = 1.04 \quad \text{and} \quad \theta = 1.25$$

#### 4. ANALYSIS AND CONCLUSIONS

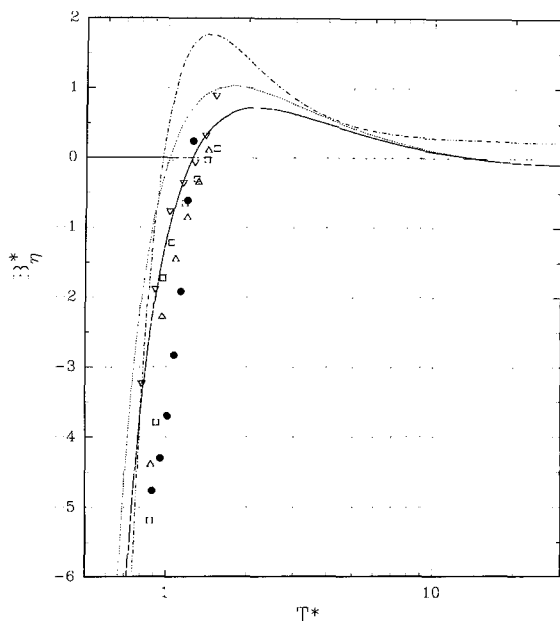
The temperature function of the zero-density viscosity coefficient experimentally found for phenol was used in the framework of the Chapman-Enskog theory [1, 2] to obtain the Lennard-Jones 12-6 potential parameters.

$$\epsilon/k = 497.4 \text{ K} \quad \text{and} \quad \sigma = 0.5527 \text{ nm}$$

They are needed to reduce the second viscosity virial coefficient  $B_\eta$  and the temperature  $T$  according to Eqs. (2) and (3). Figure 3 presents curves of

the modified Enskog theory as well as of the Rainwater-Friend theory for the two different sets of the potential parameter ratios  $\delta$  and  $\theta$  in comparison with the experimental data for phenol vapor. Data for benzene [17], toluene, and *p*-xylene [18] are also included in the comparison.

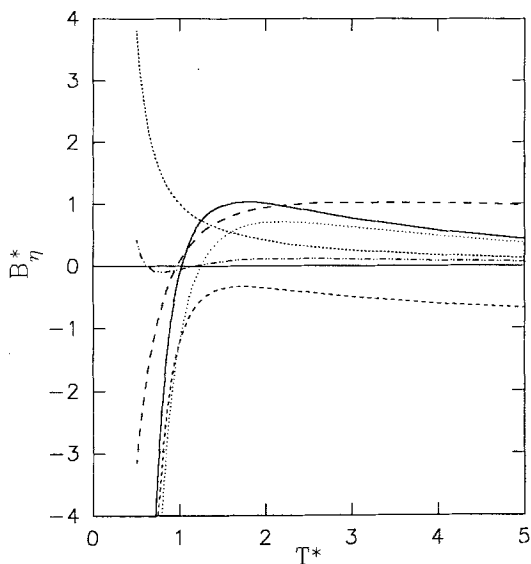
The Rainwater-Friend theory with the parameter ratios  $\delta$  and  $\theta$  obtained by Bich and Vogel [9] represents quite reasonably the experimental  $B_\eta$  data for the aromatic vapors including phenol. In this connection it has to be stressed that the Lennard-Jones 12-6 potential is unsuitable for monatomic gases and, of course, for polyatomics, too. An improvement could be reached only by extending the calculations to other more realistic intermolecular potential models. In addition, the ratios  $\delta$  and  $\theta$  have been optimized by using experimental data for monatomic gases, nitrogen, carbon dioxide, ethane, ethene, sulfur hexafluoride, neopentane, *n*-hexane, cyclohexane, and benzene as the only aromatic vapor [9]. The theorem of corresponding states, which is the basis for the choice of com-



**Fig. 3.** Reduced second viscosity virial coefficient  $B_\eta^*$  as a function of the reduced temperature  $T^*$  for the Lennard-Jones 12-6 potential. (●) Phenol, present work; (▽) benzene [17]; (·) toluene [18]; (△) *p*-xylene [18]; (·-·-·) modified Enskog theory (MET) [21, 22, 23]; (- - - -) Rainwater-Friend theory [5, 6] ( $\delta = 1.02$ ,  $\theta = 1.15$ ); (—) Rainwater-Friend theory, Bich and Vogel [9] ( $\delta = 1.04$ ,  $\theta = 1.25$ ).

mon values for  $\delta$  and  $\theta$ , is a very rough approximation for the behavior of such a wide variety of substances. Therefore, the prediction of  $B_\eta^*$  as a function of  $T^*$  for phenol by means of the Rainwater–Friend theory as well as by the MET is surprisingly good.

As already mentioned in Section 1, effects of the formation of bound states are completely excluded from the two-monomer contribution  $B_\eta^{(2)*}$  of the Rainwater–Friend theory, but they could possibly still be included in the three-monomer contribution. In our opinion, the first density coefficient of the equilibrium radial distribution function in the integral  $R$  of Eq. (9) includes bound states in an analogous manner as in the case of the second pressure virial coefficient for a real gas. Figure 4 represents the different contributions to the reduced second viscosity virial coefficient  $B_\eta^*$ . The numerical values have been given by Rainwater and Friend [6] and by Vogel and Hendl [18]. In both variants of the Rainwater–Friend theory



**Fig. 4.** Contributions to the reduced second viscosity virial coefficient  $B_\eta^*$  according to the Rainwater–Friend theory. (—) Collisional transfer contribution of two monomers; (---) kinetic contribution of three monomers; (-·-·-) monomer–dimer contribution by Rainwater and Friend [5, 6] ( $\delta = 1.02$ ;  $\theta = 1.15$ ); (·-·-·) monomer–dimer contribution by Bich and Vogel [9, 18] ( $\delta = 1.04$ ,  $\theta = 1.25$ ); (—) total contribution by Rainwater and Friend [5, 6] ( $\delta = 1.02$ ,  $\theta = 1.15$ ); (·-·-·) total contribution by Bich and Vogel [9, 18] ( $\delta = 1.04$ ,  $\theta = 1.25$ ).

the same calculated values of  $B_{\eta}^{(2)*}$  and  $B_{\eta}^{(3)*}$  for the Lennard–Jones 12–6 potential have been used, but the contribution for the collisions between a monomer and a dimer  $B_{\eta}^{(M-D)*}$  has been determined by fitting to different experimental data of  $B_{\eta}^*$ . Bich and Vogel [9] were able to use a larger and better experimental material.  $B_{\eta}^{(M-D)*}$  for this variant of the Rainwater–Friend theory is practically zero, whereas the monomer–dimer contribution in the original version by Rainwater and Friend increases to more positive values with decreasing reduced temperature. In principle, the monomer–dimer contribution should become negative for low reduced temperatures. The conclusion from these findings is that the formation of bound states has already been included in the three-monomer contribution and that the monomer–dimer contribution has to be zero for all reduced temperatures. A further consequence should be that the calculation of the three-monomer contribution has to be repeated according to the premise that the integrations in connection with Eq. (9) are to be limited to the free phase space.

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