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A Correlation Between Experimental and Simulation Data for the Self-Diffusion and Shear Viscosity Coefficient of Nonpolar Liquids Along the Saturation Line

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Simple and accurate evaluations for the self-diffusion and shear viscosity coefficients of nonpolar liquids along the saturation line have been obtained from simulation data for the hard-sphere fluid. The obtained deviations are lower than those reported for other correlations.

KEY WORDS: roughness factor; saturation line; self-diffusion; viscosity.

1. INTRODUCTION

Transport properties are important quantities required in several fields of physics, chemistry, and engineering. Unfortunately, our understanding of transport properties lags far behind that of equilibrium properties. There are two main difficulties: one is the inherent problems involved in accurate measurements, and the other is the complexity in theoretical treatments. Most of the available methods for the prediction of transport properties are empirical correlations and are limited to specified state regions of the fluids. A good survey of these methods was given by Reid et al. [1].

Our recent research [2–4] has been devoted to the application of the rough hard-sphere theory, introduced by Chandler [5], to the evaluation of the translational–rotational coupling factor, or simply the roughness factor, of 25 nonpolar liquids, with a special emphasis on the family of alkanes.

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This work increases the number of substances for the self-diffusion coefficient and provides values for the self-diffusion and shear viscosity coefficients whose deviations with respect to the experimental data compare favorably with currently available results.

2. THEORETICAL BACKGROUND

If X is a transport property, X_{RHS} and X_{SHS} are its values for the rough and smooth hard-sphere fluid, respectively, and X_{E} is the Enskog value, Chandler assumed that the transport property X coincides with X_{RHS}, whose relation with X_{SHS} is given by

$$\frac{X}{X_{\mathrm{E}}}=\frac{X_{\mathrm{RHS}}}{X_{\mathrm{E}}}=A_{X}\frac{X_{\mathrm{SHS}}}{X_{\mathrm{E}}} \tag{1}$$

where A_X is the roughness factor and all quantities are referred to the Enskog value, which, in turn, is expressed in terms of the dilute gas X_0 by means of $X_{\mathrm{E}}=(X_{\mathrm{E}}/X_0)\,X_0$.

Starting from the temperature, the pressure (or the volume), the molecular mass and an adequate expression for the hard-sphere diameter, we obtain the ratio V_0/V between the hard-core volume and the actual volume. Then X_{E} and $X_{\mathrm{SHS}}/X_{\mathrm{E}}$ are available with the use of simulation data [6–9]. In addition, X is obtained from the experimental data. Plotting X/X_{E} against $X_{\mathrm{SHS}}/X_{\mathrm{E}}$, the slope of linear fit gives us A_X. Alternatively, we can calculate A_X for each individual state and obtain the arithmetic mean. The two methods provide results that are practically coincident in almost all cases. Details of the procedure are given in our earlier papers [2, 3]. In summary, applying our method, the availability of the simulation data allows us the knowledge of the experimental data.

3. TEST FOR THE CHOICE OF EXPERIMENTAL DATA

Whereas the simulation procedure and the choice for the hard-sphere diameter can be fixed for their application to each group of substances involved in our analysis, the reliability of experimental data for each substance must be given careful consideration and a test must be performed before the procedure is applied.

This can be accomplished from the well-known Stokes–Einstein relation [10], which can be expressed as $D=k_{\mathrm{B}}T/C\pi\eta\sigma$, where σ is the diameter for a brownian particle of mass m in a fluid of shear viscosity coefficient η. Of course, k_{B} is the Boltzmann constant and D is the self-diffusion coefficient. The boundary condition used determines the value of C [11].

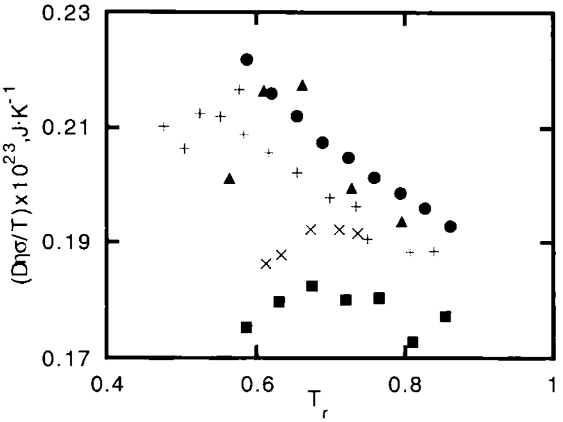

Fig. 1. Test of the Stokes Einstein relation for the atomic and simple molecular liquids. (■) Neon; (▲) argon; (●) xenon; (×) nitrogen; (+) methane.

All values of σ, η, and A_η and the greater part of those corresponding to D and A_D were taken from our earlier works [2, 3].

In Figs. 1 and 2 we plot $D\eta\sigma/T$ against $T_r = T/T_c$, where T_c is the critical temperature, for atomic and simple molecular liquids and for alkanes, respectively. The overwhelming majority of points is in very good agreement with this prediction.

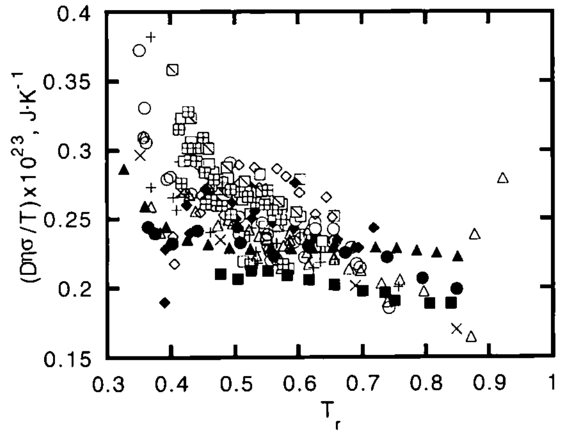

Fig. 2. As for Fig. 1 for the alkanes. (■) methane; (▲) ethane; (●) propane; (×) butane; (+) pentane; (△) hexane; (○) heptane; (□) octane; (◆) nonane; (◇) decane; (⊙) dodecane; (⊡) tetradecane; (⧅) hexadecane; (⊞) octadecane.

Table I. The Coefficients m_D, n_D, and σ_D

Substance	$m_D \times 10^2$	n_D	$\sigma_D \times 10$
Neon	10.79	−1.536	1.642
Argon	5.721	−1.413	1.261
Xenon	2.383	−0.924	1.030
Nitrogen	7.542	−2.319	1.041
Methane	9.434	−3.081	3.485
Ethane	5.215	−2.417	3.576
Propane	2.944	−1.852	2.858
Butane	1.805	−1.419	2.366
Pentane	1.596	−1.527	1.298
Hexane	1.256	−1.416	1.273
Heptane	1.012	−1.310	1.059
Octane	0.925	−1.379	0.687
Nonane	0.772	−1.283	0.930
Decane	0.701	−1.291	0.722
Dodecane	0.470	−1.025	0.534
Tetradecane	0.357	−0.902	0.482
Hexadecane	0.280	−0.804	0.394
Octadecane	0.219	−0.708	0.270

The above relation links the two transport coefficients. To obtain an independent estimate, we have applied the test of Dymond [12], who proposed that the quantities $T^{1/2}/\eta$ and $D/T^{1/2}$ present a linear variation with the molar volume in the context of a hard-sphere theory. Therefore we write

$$(D/T^{1/2} \times 10^5(\mathrm{cm}^2 \cdot \mathrm{s}^{-1} \cdot \mathrm{K}^{-1/2}) = m_D V(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}) + n_D \tag{2}$$

$$T^{1/2}/\eta(\mathrm{K}^{1/2} \cdot \mathrm{mP}^{-1}) = m_\eta V(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}) + n_\eta \tag{3}$$

We have tested these predictions for both transport coefficients analytically and graphically. Tables I and II show the results (m_D, n_D, m_η, n_η and the standard deviations σ_D and σ_η). This test is also verified for the data considered here.

4. REVIEW OF THE SELF-DIFFUSION ROUGHNESS FACTOR

As pointed out above, the analysis of the self-diffusion coefficient has been extended with respect to our earlier work [2]. In particular, we have increased the number of points for the alkanes already considered and we have also analyzed the following paraffins: ethane [13, 14], propane [14],

Table II. The Coefficients m_η, n_η, and σ_η

Substance	$m_\eta \times 10$	$n_\eta \times 10^{-1}$	σ_η
Neon	17.71	−2.549	2.892
Argon	10.83	−2.749	3.351
Krypton	6.921	−2.128	1.850
Xenon	5.169	−2.054	2.208
Nitrogen	13.15	−3.974	4.764
Oxygen	12.66	−3.049	3.675
Methane	18.68	−6.186	7.261
Ethane	9.992	−4.695	6.004
Propane	7.223	−4.691	6.022
Butane	5.847	−4.823	6.166
Pentane	4.739	−4.689	4.673
Hexane	4.000	−4.677	6.662
Heptane	3.752	−5.127	7.179
Octane	3.406	−5.320	7.685
Nonane	2.298	−3.886	2.152
Decane	2.165	−4.080	1.757
Undecane	1.814	−3.736	2.492
Dodecane	1.630	−3.646	1.194
Tridecane	1.497	−3.628	2.058
Tetradecane	1.305	−3.384	0.945
Pentadecane	1.148	−3.180	0.523
Hexadecane	1.193	−3.558	2.265
Heptadecane	1.108	−3.519	3.125
Octadecane	0.772	−2.530	0.392
Eicosane	0.797	−2.947	1.139

butane [15–17], pentane [15, 17–22], tetradecane [15, 23], and octadecane [19, 23].

In Fig. 3, we plot A_D against the chain length. A global decrease is evident. A more detailed analysis seems to suggest some effect on the parity of the chain, depending on the viscosity coefficient [3].

5. RESULTS AND CONCLUSIONS

The main practical application of our study is linked to the predictive power of the two above-mentioned transport coefficients. Its validity has been checked by evaluating the percentage deviation of these quantities by means of the formula

$$D = 100 \frac{X_{\mathrm{exp}} - A_X X_{\mathrm{SHS}}}{X_{\mathrm{exp}}} \tag{4}$$

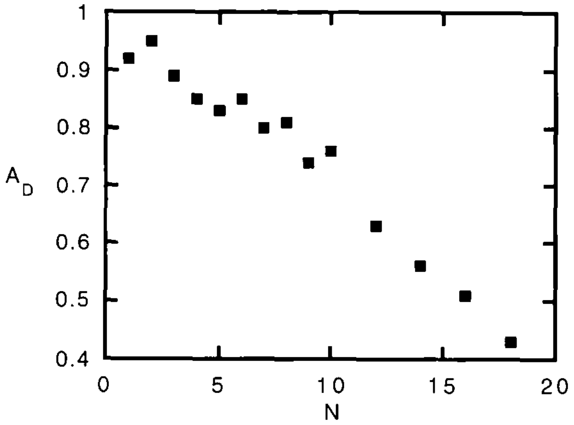

Fig. 3. Plot of the roughness factor A_D against the chain length for alkanes.

In the case of the self-diffusion coefficient we show the results obtained for atomic and simple molecular liquids in Fig. 4 and for alkanes in Fig. 5. The deviations are purely statistical with no dominant trend.

The magnitude of these deviations is satisfactory if one considers the property under analysis. In fact, the comparison with the available methods [24–28] extended to five hydrocarbons (methane, hexane, nonane, dodecane, and octadecane) is clearly encouraging (Fig. 6). The procedures

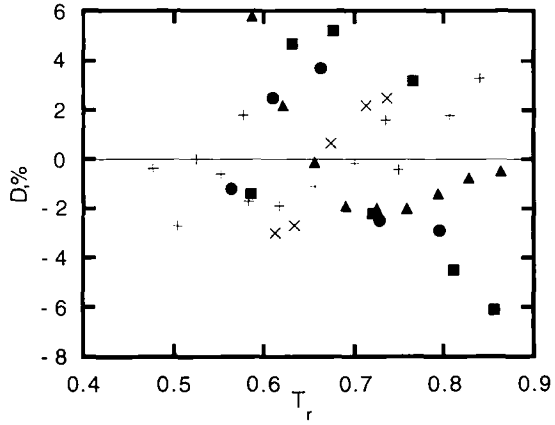

Fig. 4. Percentage deviation in the self-diffusion coefficient for atomic and simple molecular liquids. (■) Neon; (●) argon; (▲) xenon; (×) nitrogen; (+) methane.

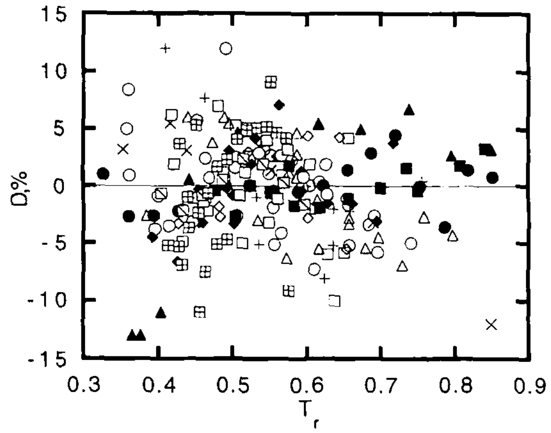

Fig. 5. As for Fig. 4 for the alkanes. (■) methane; (●) ethane; (▲) propane; (×) butane; (+) pentane; (△) hexane; (○) heptane; (□) octane; (◆) nonane; (◇) decane; (⊙) dodecane; (⊡) tetradecane; (⧅) hexadecane; (⊞) octadecane.

based on a hard-sphere theory [24] and this work, seem preferable to the remaining ones.

The shear viscosity coefficient is plotted against T_r for atomic liquids (Fig. 7), simple molecular liquids (Fig. 8), and saturated hydrocarbons (Figs. 9 and 10). The comparison with several correlation methods

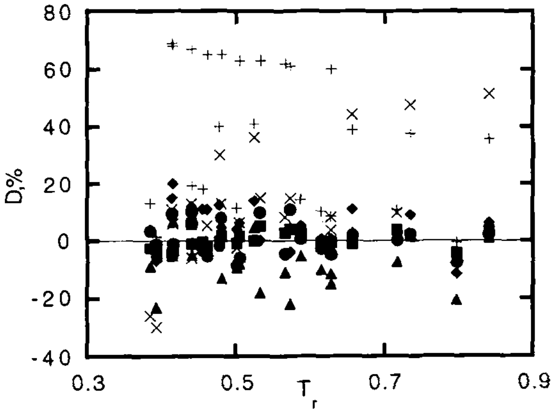

Fig. 6. Percentage deviation in the self-diffusion coefficient for several correlations. (●) Assael et al.; (×) Hayduk and Minhas; (▲) Nakanishi; (◆) Tyn and Calus; (+) Wilke and Chang; (■) our results.

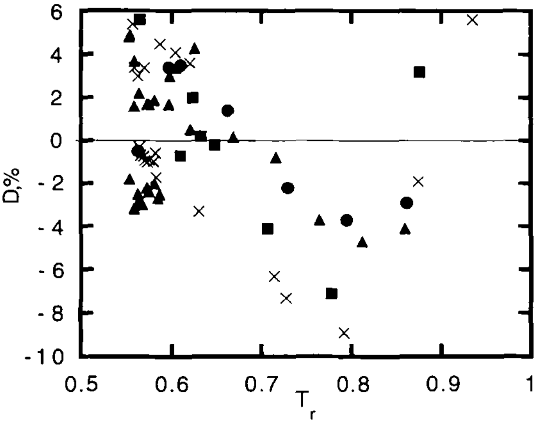

Fig. 7. Percentage deviation in the shear viscosity coefficient for atomic liquids. (■) Neon; (●) argon; (▲) krypton; (×) xenon.

[29–33] is shown in Fig. 11. Again, our results show a clear improvement. In the most unfavorable case our deviation is less than 12%, approximately as in Ref. 29, and much lower than the other predictions.

In contrast to the self-diffusion case, the positive (negative) deviations prevail at lower (higher) temperatures. This can be ascribed to the sharp decrease in the shear viscosity coefficient in the neighborhood of the

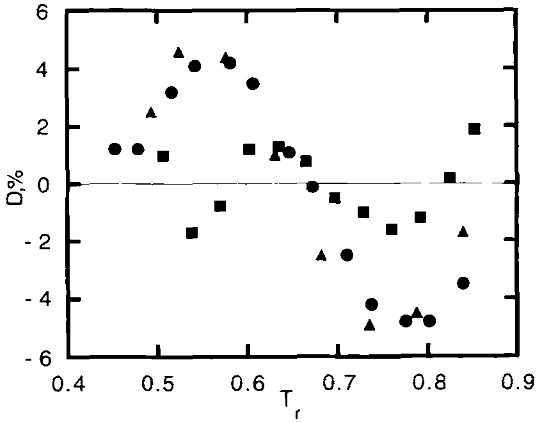

Fig. 8. As for Fig. 7 for simple molecular liquids. (■) Nitrogen; (●) oxygen; (▲) methane.

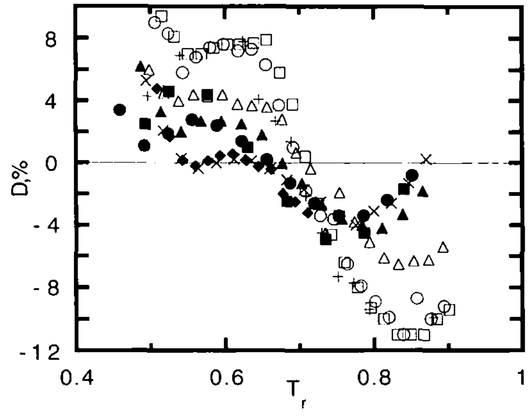

Fig. 9. As for Fig. 7 for the lower alkanes. (■) methane; (●) ethane; (▲) propane; (×) butane; (+) pentane; (△) hexane; (○) heptane; (□) octane; (◆) nonane.

freezing temperature. This behavior restricts the application range of our model and seems predominate over the effects of the attractive forces [4].

From an empirical viewpoint, this feature allows me to subdivide the range in two parts and to apply the method to each. The results found for A_η in the more interesting cases are 1.24 and 1.11 (pentane), 1.23 and 1.13 (hexane), 1.31 and 1.14 (heptane), 1.37 and 1.17 (octane), 1,74 and 1.67

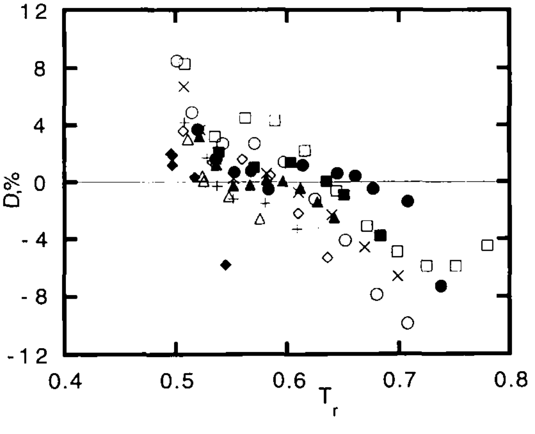

Fig. 10. As for Fig. 7 for the higher alkanes. (■) Decane; (●) undecane; (▲) dodecane; (×) tridecane; (+) tetradecane; (△) pentadecane; (○) hexadecane; (□) heptadecane; (◆) octadecane; (◇) eicosane.

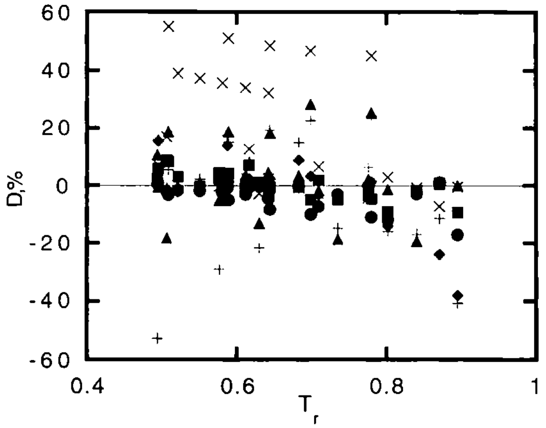

Fig. 11. As for Fig. 6 for the shear viscosity coefficient. (●) Assael et al. [24]; (▲) Brulé and Starling [33]; (+) Orrick and Erbar [30]; (×) Przezdziecki and Sridhar [32]; (◆) van Venzel et al. [31]; (■) our results.

(undecane), 2.42 and 2.20 (hexadecane), and 2.59 and 2.38 (heptadecane). The maximum observed deviation is 6.8 % for one point for octane and the others deviations are less than 6%. In addition to its empirical foundation, the use of a variable parameter A_X has already been considered by other investigators [34].

REFERENCES

1. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987), Chaps. 9-11.
2. J. Amorós, *Mol. Phys.* **83**:771 (1994).
3. J. Amorós, *Chem. Phys.* **200**:281 (1995).
4. J. Amorós, *Chem. Phys.* **206**:301 (1996).
5. D. Chandler, *J. Chem. Phys.* **62**:1358 (1975).
6. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **35**:321 (1984).
7. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **40**:787 (1985).
8. B. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* **53**:3813 (1970).
9. J. J. Erpenbeck and W. W. Wood, *Phys. Rev. A* **43**:4254 (1991).
10. A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956), p. 57.
11. J. P. Hansen and I. R. Mc Donald, *Theory of Simple Liquids*, 2nd. ed. (Academic Press, London, 1986), p. 209.
12. J. H. Dymond, *J. Chem. Phys.* **60**:969 (1974).
13. J. V. Gaven, W. H. Stockmayer, and J. S. Waugh, *J. Chem. Phys.* **37**:1188 (1962).

14. A. Greiner-Schmid, S. Wappmann, M. Has, and H.-D. Lüdemann, *J. Chem. Phys.* **94**:5643 (1991).
15. T. Vardag, F. Bachl, S. Wappmann, M. Has, and H. -D. Lüdemann, *Ber. Bunsenges. Phys. Chem.* **94**:336 (1990).
16. F. Bachl and H.-D. Lüdemann, *Physica B* **139/140**:100 (1986).
17. F. Bachl and H.-D. Lüdemann, *Z. Naturf. A* **41**:963 (1986).
18. E. Fishman, *J. Phys. Chem.* **59**:469 (1955).
19. D. C. Douglass and D. W. Mc Call, *J. Phys. Chem.* **62**:1102 (1958).
20. D. W. Mc Call, D. C. Douglass, and E. W. Anderson, *Phys. Fluids* **2**:87 (1959).
21. D. W. Mc Call, D. C. Douglass, and E. W. Anderson, *J. Chem. Phys.* **31**:1555 (1959).
22. D. W. Mc Call, D. C. Douglass, and E. W. Anderson, *Ber. Bunsenges.* **67**:336 (1963).
23. H. Ertl and F. A. Dullien, *AIChE J.* **19**:1215 (1973).
24. M. J. Assael, J. H. Dymond, and P. M. Patterson, *Int. J. Thermophys.* **13**:729 (1992).
25. C. R. Wilke and P. Chang, *AIChE J.* **1**:264 (1955).
26. M. T. Tyn and W. F. Calus, *J. Chem. Eng. Data* **20**:106 (1975).
27. W. Hayduk and B. S. Minhas, *Can. J. Chem. Eng.* **60**:295 (1982).
28. K. Nakanishi, *Ind. Eng. Chem. Fundam.* **17**:253 (1978).
29. M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, *Int. J. Thermophys.* **13**:269 (1992).
30. C. Orrick and E. J. H. Erbar, quoted in Ref. 1, p. 489.
31. D. van Velzen, R. L. Cardozo, and H. Langenkamp, *Ind. Eng. Chem. Fundam.* **11**:20 (1972).
32. W. Przezdziecki and T. Sridhar, *AIChE J.* **31**:333 (1985).
33. M. R. Brulé and K. E. Starling, *Ind. Eng. Chem. Process Des. Dev.* **23**:833 (1984).
34. F. Bachl, T. Vardag, S. Wappmann, and H.-D. Lüdemann, *J. Mol. Liq.* **54**:193 (1992).