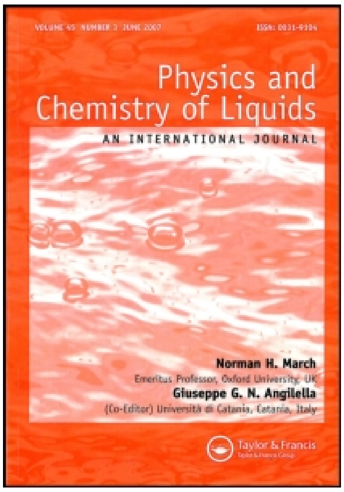

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Density and Viscosity of 1-Bromoalkanes

Syeda K. Begum[a]; Shamim Akhtar[a]; Muhammad Habibullah[a]; Muhammad A. Saleh[a]
[a] Department of Chemistry, University of Chittagong, Chittagong, Bangladesh

To cite this Article Begum, Syeda K. , Akhtar, Shamim , Habibullah, Muhammad and Saleh, Muhammad A.(1995) 'Density and Viscosity of 1-Bromoalkanes', Physics and Chemistry of Liquids, 30: 3, 177 — 185
To link to this Article: DOI: 10.1080/00319109508031652
URL: http://dx.doi.org/10.1080/00319109508031652

Phys. Chem. Liq., 1995, Vol. 30, pp. 177–185
Reprints available directly from the publisher
Photocopying permitted by license only

DENSITY AND VISCOSITY OF 1-BROMOALKANES

SYEDA K. BEGUM, SHAMIM AKHTAR, MUHAMMAD
HABIBULLAH and MUHAMMAD A. SALEH*

Department of Chemistry, University of Chittagong, Chittagong, Bangladesh

(Received 6 March 1995)

Density and Viscosity have been measured for ten 1-bromoalkanes (1-bromoethane to 1-bromoundecane) at temperatures ranging from 292.35 K to 323.15 K. The molar volumes have been found to follow the additive rule, $V_m = V_{CH_3} + xV_{CH_2} + V_{Br}$, for all 1-bromoalkanes. The thermal expansivities have been calculated from the density data. The variation of viscosity of bromoalkanes has been shown as a function of chain length and temperature. Thermodynamic activation parameters for viscous flow, $\Delta H^{\neq}, \Delta G^{\neq}$ and $\Delta S^{\neq}$ have been calculated. $\Delta S^{\neq}$ is found to be negative for all the bromoalkanes and the maximum corresponds distinctively at 1-bromopentane.

KEY WORDS: Density, viscosity, molar volume, additivity rule, thermal expansivity.

1. INTRODUCTION

The primary objective of the present investigation is to determine density and viscosity of 1-bromoalkanes. In an earlier work Smyth *et al*[1]. determined the thermodynamic activation parameters for viscous flow of some normal alkylbromides and graphically compared these with the same parameters for dielectric relaxation. However, absolute data of the viscosity of the bromoalkanes were not shown. The present paper describes systematic studies on the volumetric and viscometric properties of a series of 1-bromoalkanes starting from 1-bromoethane to 1-bromoundecane in a fairly wide range of temperature.

2. EXPERIMENTAL

1-bromalkanes, from 1-bromoethane to 1-bromoundecane, were procured from Aldrich with quoted purities ranging from 98% to 99 + %. The bromoalkanes were used without further purification except that they were allowed to stand over 4A molecular seives for about two weeks before measurements. Densities were measured by a 25 cm^3 density bottle previously calibrated with redistilled water. An analytical balance with an accuracy of ± 0.1 mg was used. Viscosity was measured by U-tube Ostwald viscometers of the British Standard Institution with sufficient efflux times so that no kinetic energy correction was necessary. The flow time of

---

* To whom correspondence should be addressed.

liquids was recorded by a timer to ±0.1 s. The temperature was controlled by a thermostatic water bath fluctuating to ±0.05 K.

The density ($g\,cm^{-3}$) and viscosity (mPa s) measured were considered significant to 4 and 3 decimals, respectively. The overall experimental uncertainties in measured density and viscosity were estimated to be $2 \times 10^{-4}\,g\,cm^{-3}$ and 6×10^{-4} mPa s, respectively.

3. RESULTS AND DISCUSSION

Densities (ρ) of 1-bromoalkanes at different temperatures are given in Table 1. For comparison, literature values so far available are presented in parentheses. For 1-bromopentane to 1-bromoundecane the published data were not available in the temperature range employed; therefore, comparison is made with our extrapolated density data. For all measurements, the variations in densities, however, from different literature values are within 0.4 to 4.7 in 10^3.

The densities varied linearly with temperature and were represented by the equation,

$$\rho/g\,cm^{-3} = A - Bt \tag{1}$$

where, A and B are intercept and slope, respectively, and t is the temperature in °C. The values of A and B are given in Table 2 together with the standard deviation (σ).

Table 1 Densities (ρ) of 1-bromoalkanes at different temperatures $\rho/(g\,cm^{-3})$.

T/K	*292.35*	*295.35*	*298.15*	*300.65*	*303.15*	*308.15*	*313.15*	*318.15*	*323.15*
C_2H_5Br	1.4554	1.4500	1.4439	1.4384	1.4331 $(1.4398)^a$				
C_3H_7Br	–	–	1.3430	–	1.3348	1.3266	1.3180 $(1.3201)^b$	1.3096	1.3007
C_4H_9Br	–	–	1.2687	–	1.2616 $(1.2599)^a$	1.2543	1.2470 $(1.2454)^a$	1.2400	1.2328
$C_5H_{11}Br$	–	–	1.2129^e $(1.21130)^c$	–	1.2056	1.2000	1.1938	1.1873	1.1808
$C_6H_{13}Br$	–	–	1.1683^e $(1.16894)^c$	–	1.1625	1.1568	1.1508	1.1451	1.1394
$C_7H_{15}Br$	–	–	1.1343^e $(1.13480)^c$	–	1.1289	1.1236	1.1181	1.1127	1.1074
$C_8H_{17}Br$	–	–	1.1089^e $(1.10783)^c$	–	1.1038	1.0987	1.0935	1.0885	1.0834
$C_9H_{19}Br$	–	–	1.0809^e $(1.08485)^c$	–	1.0760	1.0712	1.0662	1.0614	1.0565
$C_{10}H_{21}Br$	–	–	1.0639^e $(1.0656)^a$	–	1.0594	1.0547	1.0500	1.0456	1.0410
$C_{11}H_{23}Br$	–	1.0523^{e*} $(1.05209)^d$	–	–	1.0435	1.0389	1.0343	1.0299	1.0257

Superscript a : R. T. Lagemann *et al*., *J. Chem. Phys.* **17**, 369 (1949);
b : ref. 2;
c : L. M. Ellis and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1674 (1932);
d : G. R. Yohe and J. S. Adams, *J. Am. Chem. Soc.*, **50**, 1503 (1928);
e : extrapolated value; and e* at 293.15 K (extrapolated)

Molar volumes (V_m) of 1-bromoalkanes calculated from the density data have been found to vary linearly with the number of CH_2 groups present and can be represented by a general equation of the form,

$$V_m = V_o + xV \qquad (2)$$

where, x is the number of CH_2 groups in the 1-bromoalkanes which varies from 1 to 10, and the slope (V) gives the average volume of a CH_2 group, V_{CH_2}, the latter being estimated to be 16.64 cm^3 mol^{-1} at 303.15 K. The intercept (V_o) gives the combined volume due to a CH_3 group and the Br, represented by V_{CH_3} and V_{Br}, respectively. The slope and the intercept have been calculated by the least squares method. The variation of V_{CH_2} with temperature is shown in Figure 1. The V_{CH_2} values increase with the increase in temperature.

By following Eq. (2), and in the light of the discussion above, molar volumes of 1-bromoalkanes were considered to be made up of the contributions due to V_{CH_3},

Table 2 A and B values of Eq. (1), standard deviations (σ) and molar volume (V_m) of 1-bromoalkanes at 303.15 K.

	A	10^4 *B*	$10^4\,\sigma$ g cm^{-3}	V_m/cm^3 mol^{-1} Eq. (3)	Expt.
C_2H_5Br	1.4973	21.37	3.5	75.53	76.04
C_3H_7Br	1.3855	16.89	2.6	92.18	92.15
C_4H_9Br	1.3047	14.38	0.8	108.82	108.62
$C_5H_{11}Br$	1.2450	12.82	3.1	125.47	125.20
$C_6H_{13}Br$	1.1972	11.58	0.9	142.11	142.00
$C_7H_{15}Br$	1.1613	10.78	2.0	158.76	158.66
$C_8H_{17}Br$	1.1344	10.20	0.5	175.40	174.97
$C_9H_{19}Br$	1.1053	9.76	0.7	192.05	192.53
$C_{10}H_{21}Br$	1.0869	9.18	0.7	208.69	208.79
$C_{11}H_{23}Br$	1.0701	8.92	1.6	225.34	225.41

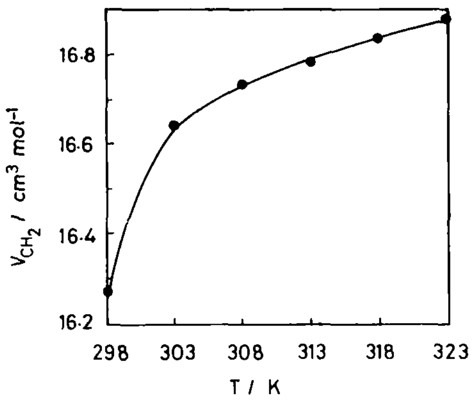

Figure 1 Molar Volume of the CH_2 group in 1-bromoalkanes as a function of temperature.

V_{CH_2} and V_{Br} as given by,

$$V_m = V_{CH_3} + xV_{CH_2} + V_{Br} \tag{3}$$

To find the V_{CH_3} contribution, molar volumes of different *n*-alkanes (*n*-hexane to *n*-undecane) were calculated considering their density values of literature[3–6]. The molar volumes of these hydrocarbons have been found to show similar linear relationship with x as in Eq. (2), the intercept (V_o) now being $2V_{CH_3}$, and thus the value of V_{CH_3} is made available. The value of V_{CH_3} has been found to be 33.82 $cm^3\ mol^{-1}$ at 303.15 K. Plot of the V_m vs. x also yielded V_{CH_2} as 16.17 $cm^3\ mol^{-1}$ for hydrocarbons compared to 16.64 $cm^3\ mol^{-1}$ for 1-bromoalkanes at 303.15 K. Subtracting V_{CH_3} and xV_{CH_2} from V_m for 1-bromoalkanes, equation (3) yielded V_{Br} values for different bromoalkanes, the average being 25.53 $cm^3\ mol^{-1}$ at 303.15 K. From the values of V_{CH_3}, V_{CH_2} and the average value of V_{Br}, molar volumes of 1-bromoalkanes have been calculated. To compare these with the experimental V_m, directly obtained from densities of bromoalkanes, both are shown in Table 2. The maximum deviation between the two sets of V_m values is not more than ± 0.5 $cm^3\ mol^{-1}$.

Thermal expansivity (α) of 1-bromoalkanes has been calculated in order to show its dependence on the chain length. α is originally defined as,

$$\alpha = 1/V_m(\partial V_m/\partial t)_p, \quad \text{which reduces to,} \quad \alpha = -1/\rho(\partial \rho/\partial t)_p \tag{4}$$

Considering the temperature dependency of ρ as shown by Eq. (1), α may easily be calculated from the relation,

$$\alpha = B/(A - Bt) = B/\rho \tag{5}$$

where, $B = -(\partial \rho/\partial t)_p$. Equation (5) clearly indicates that α is a temperature dependent quantity.

Table 3 represents the thermal expansivities calculated at different temperatures and their averages for 1-bromoalkanes. Figure 2 shows the variation of the average expansivity as a function of chain length (n) of the 1-bromoalkanes. Thermal expansivities were found to decrease with the increase in the chain length of alkyl group.

Table 3 Thermal expansivity (α) in the temperature range of 303.15 to 323.15 K and the average ($\bar{\alpha}$) of 1-bromoalkanes.

	$10^4\alpha/K^{-1}$					
T/K	*303.15*	*308.15*	*313.15*	*318.15*	*323.15*	$\bar{\alpha}$
C_2H_5Br	14.91	–	–	–	–	14.91
C_3H_7Br	12.65	12.73	12.81	12.90	12.99	12.82
C_4H_9Br	11.40	11.46	11.53	11.60	11.66	11.53
$C_5H_{11}Br$	10.63	10.68	10.74	10.80	10.86	10.74
$C_6H_{13}Br$	9.96	10.01	10.06	10.11	10.16	10.06
$C_7H_{15}Br$	9.55	9.59	9.64	9.69	9.73	9.64
$C_8H_{17}Br$	9.24	9.28	9.33	9.37	9.41	9.33
$C_9H_{19}Br$	9.07	9.11	9.15	9.20	9.24	9.15
$C_{10}H_{21}Br$	8.67	8.70	8.74	8.78	8.82	8.74
$C_{11}H_{23}Br$	8.55	8.59	8.62	8.66	8.70	8.62

The measured viscosities (η) of 1-bromoalkanes in the range of 292.35 K to 323.15 K are presented in Table 4. Except for 1-bromoethane and 1-bromopropane, as literature values of η were not available for the rest, comparison is shown only for the reported cases. Figure 3 shows the variation of viscosity at 303.15 K, 313.15 K and 323.15 K as a function of chain length of the bromoalkanes. At constant temperature, viscosity has been found to increase as the chain length of the 1-bromoalkanes increases. Figure 4 shows the plots of the viscosity of bromoalkanes as a function of temperature. The fall in η values with respect to temperature was more apparent in case of higher bromoalkanes.

The thermodynamic activation parameters for viscous flow have been calculated by the use of Eyring equation[7],

$$\eta = Nh/V_m \exp(\Delta G^{\neq}/RT) \tag{6}$$

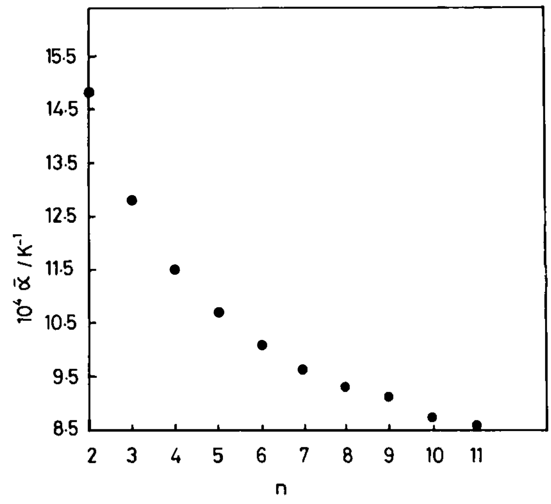

Figure 2 Average thermal expansivity of 1-bromoalkanes as a function of n.

Table 4 Viscosity (η) of 1-bromoalkanes at different temperatures η/mPa s.

T/K	292.35	295.35	298.15	300.65	303.15	308.15	313.15	318.15	323.15
C_2H_5Br	0.4175	0.4068 (0.3959)^b at	0.3985 293.15 K	0.3894	0.3823				
C_3H_7Br	-	-	0.5069	-	0.4833	0.4616	0.4414 (0.4274)^b	0.4257	0.4079
C_4H_9Br	-	-	0.6089	-	0.5795	0.5515	0.5262	0.5038	0.4819
$C_5H_{11}Br$	-	-	-	-	0.7228	0.6859	0.6503	0.6188	0.5918
$C_6H_{13}Br$	-	-	-	-	0.8894	0.8366	0.7882	0.7453	0.7072
$C_7H_{15}Br$	-	-	-	-	1.111	1.037	0.9711	0.9125	0.8607
$C_8H_{17}Br$	-	-	-	-	1.392	1.289	1.198	1.122	1.049
$C_9H_{19}Br$	-	-	-	-	1.703	1.567	1.447	1.343	1.251
$C_{10}H_{21}Br$	-	-	-	-	2.073	1.895	1.739	1.605	1.487
$C_{11}H_{23}Br$	-	-	-	-	2.540	2.305	2.101	1.930	1.779

Superscript b: ref. 2

where, N is the Avogadro number, h the Planck constant, V_m is the molar volume at T, R the gas constant and $\Delta G^{\neq}$ the free energy of activation for viscous flow which is related to enthalpy and entropy of activation as,

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{7}$$

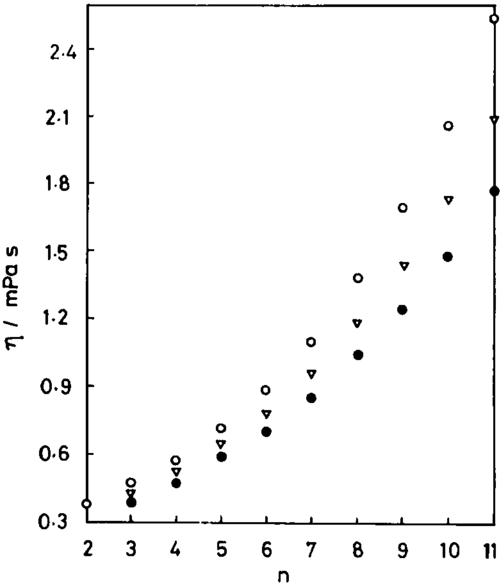

Figure 3 Viscosity of 1-bromoalkanes as a function of n at: ○–303.15 K, ▽ – 313.15 K and ● – 323.15 K.

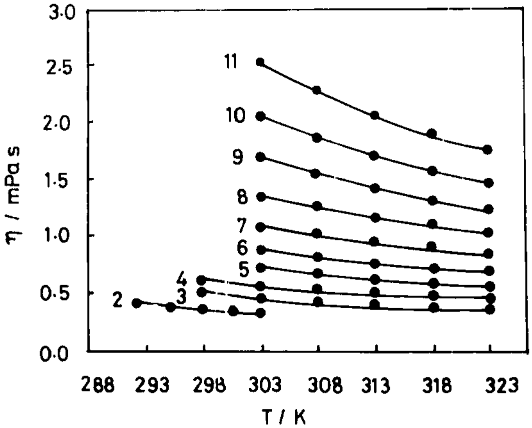

Figure 4 Plots of Viscosity of 1-bromoalkanes as a function of temperature. Each numeral indicates the number of C atoms in 1-bromoalkanes.

Substitution of the value of $\Delta G^{\neq}$ from Eq. (7) into Eq. (6) and by rearrangement we obtain the following equation:

$$\ln(\eta V_m/Nh) = \Delta H^{\neq}/RT - \Delta S^{\neq}/R \tag{8}$$

The plots of ln $(\eta V_m/Nh)$ against $1/T$ yielded excellent straight lines as shown in Figure 5. Thus the slopes and intercepts of such plots determined by the least squares method yielded $\Delta H^{\neq}$ and $\Delta S^{\neq}$ respectively, and hence through Eq. (7) $\Delta G^{\neq}$ is also calculated. Table 5 shows the $\Delta H^{\neq}, \Delta S^{\neq}$ and $\Delta G^{\neq}$ at 303.15 K for the 1-bromoalkanes.

The thermodynamic parameters for viscous flow, $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ drawn against the number of carbon atoms (n), as in Figure 6(a) show some interesting features. Plots of enthalpy show two straight lines intersecting at a point corresponding to 1-bromopentane. The entropy plots also exhibit two straight lines but

Table 5 Enthalpy ($\Delta H^{\neq}$), entropy ($\Delta S^{\neq}$) and free energy ($\Delta G^{\neq}$) of activation for viscous flow of 1-bromoalkanes.

	$\Delta H^{\neq}$ $KJ\ mol^{-1}$	$\Delta S^{\neq}$ $J\ mol^{-1}\ K^{-1}$	$\Delta G^{\neq}$ $KJ\ mol^{-1}$
C_2H_5Br	4.972	−19.24	10.807
C_3H_7Br	5.904	−19.73	11.885
C_4H_9Br	6.574	−20.39	12.755
$C_5H_{11}Br$	7.295	−21.02	13.668
$C_6H_{13}Br$	8.508	−19.79	14.507
$C_7H_{15}Br$	9.575	−19.04	15.346
$C_8H_{17}Br$	10.748	−17.86	16.162
$C_9H_{19}Br$	11.791	−16.89	16.910
$C_{10}H_{21}Br$	12.819	−15.80	17.609
$C_{11}H_{23}Br$	13.750	−15.03	18.312

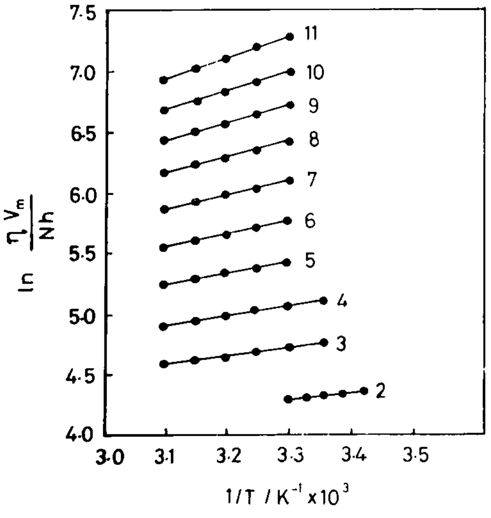

Figure 5 Plots of ln $(\eta V_m/Nh)$ against $1/T$ for 1-bromoalkanes.

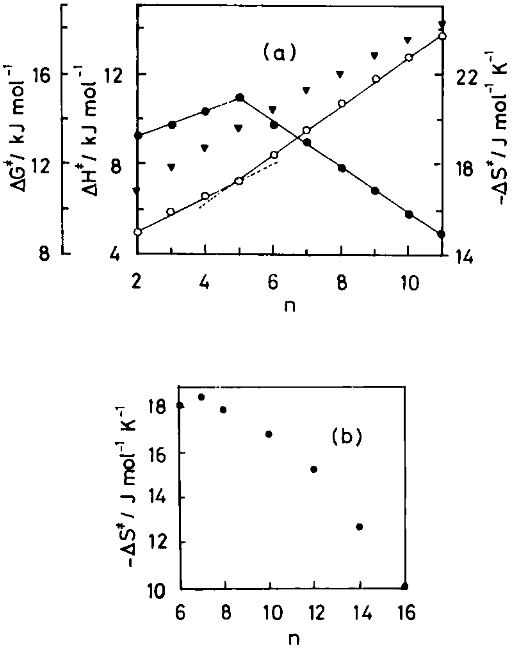

Figure 6 (a) Enthalpy, entropy and free energy of activition for viscous flow against n of 1-bromoalkanes. ○-$\Delta H^{\neq}$, ●-$\Delta S^{\neq}$ and- ▼$\Delta G^{\neq}$. (b) $\Delta S^{\neq}$ of n-alkanes as a function of n, calculated using data of references 3, 4, 9 and 10.

with slopes opposite in sign and intersect sharply at the same 1-bromopentane. The free energy however changes smoothly with respect to n. These behaviours have close resemblance with the work of smyth[1]. To see whether a similar entropy behaviour exists for n-alkanes, $\Delta S^{\neq}$ values for some n-alkanes ($n = 6$ to 16) have been calculated using literature data[3,4,9,10]. Although the results in Figure 6(b) depicted negative $\Delta S^{\neq}$ for n-alkanes as for the 1-bromoalkanes, the variation with respect to alkyl chain length is somewhat different. The maximum negative $\Delta S^{\neq}$ occurred for n-heptane compared to 1-bromopentane in the corresponding series. However, negative $\Delta S^{\neq}$ implies more orderedness of all these species in their activated states and, occurrence of negative maximum in $\Delta S^{\neq}$ either at 1-bromopentane or n-heptane indicates the maximum structural order in the transition state of the flow process for these two compounds in their respective series.

Acknowledgement

We greatly acknowledge with gratitude Dr. Ivan Cibulka, Institute of Chemical Technology, Prague, Czech Republic, for his useful comments.

References

1. C. P. Smyth, W. M. Heston and E. J. Hennelly, *J. Am. Chem. Soc.*, **70**, 4102 (1948).
2. W. M. Rutherford, *J. Chem. Eng. Data*, **33**, 234 (1988).

3. A. B. Adhikary, *M.Sc. Thesis*, Chittagong University, Chittagong, Bangladesh (1987).
4. N. U. A. Khan, *M.Sc. Thesis*, Chittagong University, Chittagong, Bangladesh (1992).
5. M. Garcia, C. Rey, V. P. Villar and J. R. Rodriguez, *J. Chem. Eng. Data*, **31**, 481 (1986).
6. *Ibid*, 33, 46 (1988).
7. H. Eyring, R. E. Powell and W. E. Roseweare, *Ind. Eng. Chem.* **33**, 837 (1941).
8. J. Ortega, *J. Chem. Eng. Data*, **30**, 462 (1985).
9. T. D. Vavanellos, A. A. Asfour and M. H. Siddique, *J. Chem. Eng. Data*, **36**, 281 (1991).
10. E. F. Cooper and A. A. Asfour, *J. Chem. Eng. Data*, **36**, 285 (1991).