Study of Molecular interaction in Binary Mixtures containing N, N-Dimethylformamide and n-Butanol

BISWAJIT SAMANTARAY¹, MANOJ KUMAR PRAHARAJ² and SMRUTI PRAVA DAS¹*¹

¹Department of Chemistry, Ravenshaw University, Cuttack, Odisha (India)
²Department of Physics, Ajay Binay Institute of Technology, Cuttack, Odisha (India)
*Corresponding AuthorE-mail: dassmrutiprava@yahoo.in
http://dx.doi.org/10.22147/juc/170101

Acceptance Date 30th April, 2021, Online Publication Date 4th May, 2021

Abstract

The acoustic studies of the interactions between alcohol molecules and water soluble polar solvent DMF are significant for understanding the relationships between structure and function of polar molecule like DMF, and for explaining the mechanisms of interaction of alcoholic OH group with an electronegative moiety. In this piece of work Ultrasonic velocity, density and viscosity have been measured at 298 K, 308 K, 318 K and 328 K for mixture of N,N-dimethylformamide (DMF) and n-butanol, the frequency being maintained at a constant value. The experimental data have been used to calculate the acoustical and thermodynamical parameters like adiabatic compressibility, free length, free volume, internal pressure, acoustic impedance, Gibbs free energy.

Key words: acoustic studies, electronegative moiety, N,N-dimethylformamide, thermodynamical parameters, adiabatic compressibility, free length, free volume, internal pressure, acoustic impedance.

Introduction

Ultrasonic studies provide a wealth of information about the state of liquids. The measurement of ultrasonic velocity in pure liquids and mixtures is an important tool to study the physiochemical properties of the liquids and also explain the nature of molecular interactions. The practical importance of liquid mixture rather than single component liquid systems has gained much importance during the last two decades in assessing the nature of molecular interactions and investigating the physio-chemical behaviour of such systems¹,². Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding the physical nature and strength of molecular interaction in the liquid mixtures³. For a better understanding of the physio-chemical
properties and the molecular interaction between the participating components of the mixtures, ultrasonic velocity together with density and viscosity are measured at different temperatures for different concentrations of the components in the mixture.

Ultrasonic velocity and the derived acoustical parameters like adiabatic compressibility, free length, relaxation time, acoustic impedance, etc., provide valuable information about the molecular environments. This has been studied for various binary and ternary mixtures with respect to variation in concentration of the liquids and temperatures.

In the present paper, variation of various parameters of binary mixtures containing n-Butanol and N,N-dimethylformamide (N,N-DMF) at different temperatures have been studied for different concentrations.

DMF (C₃H₇NO) is a versatile compound. It is a non-aqueous solvent which has no hydrogen bonding in pure state. Therefore, it acts as an aprotic, photophilic medium with high dielectric constant and it is also considered as a dissociating solvent. DMF being a polar molecule results in dipolar and induced dipolar interaction between it and chlorobenzene in addition to dipolar-dipolar interaction between its molecules. DMF is primarily used as an industrial solvent. DMF solutions are used to process polymer fibers, films and surface coating to permit easy spinning of acrylic fiber to produce wire enamels and as a crystallization medium in the pharmaceutical industry.

n-Butanol is a primary alcohol with the chemical formula C₄H₉OH and a linear structure. Butanol is used as a raw material for coating resins, butyl carboxylates such as butyl acetate, butyl acrylate, and glycol ethers. On the other hand, it is widely used as a solvent because many organic materials are soluble in it.

Experimental Section

The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay of 99.9% were obtained from E-Merk Ltd (India). Various concentrations of the binary liquid mixtures were prepared in terms of mole fraction.

Solution-1 (S₁) ⇒ n-Butanol : N,N-Dimethylformamide = 1:9
Solution-2 (S₂) ⇒ n-Butanol : N,N-Dimethylformamide = 2:8
Solution-3 (S₃) ⇒ n-Butanol : N,N-Dimethylformamide = 3:7
Solution-4 (S₄) ⇒ n-Butanol : N,N-Dimethylformamide = 4:6
Solution-5 (S₅) ⇒ n-Butanol : N,N-Dimethylformamide = 5:5.

(i) Velocity Measurement:

The velocity of ultrasonic wave in the binary mixture have been measured using multi-frequency ultrasonic interferometer with an high degree of accuracy operating at 11 different frequencies (Model M-84) supplied by M/s Mittal Enterprises, New Delhi. The measuring cell of interferometer is a specially designed double walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath (Model SSI-03spl) supplied by M/s Mittal Enterprises, New Delhi, operating in the temperature range -10°C to 85°C with an accuracy of ± 0.1 K has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid.

(ii) Density Measurement:

The densities of the liquid mixtures were measured using a digital meter named, “Microviscometer, Model-Lovis 2000 ME”.

(iii) Viscosity measurement:

The viscosities of the ternary mixture were measured using an Oswald’s viscometer calibrated with double distilled water. The Oswald’s viscometer with the experimental mixture was immersed in a temperature-controlled water bath. The time of flow was measured using a digital racer stop watch with an accuracy of 0.1 sec. The viscosity was determined using the relation,

\[ \eta_2 = \eta_1 \left( \frac{t_2}{t_1} \right) \left( \frac{\rho_1}{\rho_2} \right) \]
Where, $\eta_1$ = Viscosity of water, $\eta_2$ = Viscosity of mixture, $\rho_1$ = Density of water, $\rho_2$ = Density of mixture, $t_1$ = Time of flow of water, $t_2$ = Time of flow of mixture.

**Theoretical Aspect:**

The following thermodynamic parameters were calculated from Jacobson’s relation\(^8–10\).

(i) *Adiabatic Compressibility* ($\beta$):

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. It is calculated from the speed of sound (U) and the density ($\rho$) of the medium by using the equation of Newton Laplace\(^18\) as,

$$\beta = \frac{1}{U^2}\rho$$

(ii) *Intermolecular free length ($L_f$):*

The intermolecular free length is the distance between the surfaces of the neighbouring molecules. It is calculated by using the relation\(^19\),

$$L_f = K_T \beta^{1/2}$$

Where, $K_T$ is the temperature dependent constant and ‘$\beta$’ is the adiabatic compressibility.

(iii) *Free Volume* ($V_f$):

Free volume in terms of ultrasonic velocity (U) and the viscosity ($\eta$) of liquid\(^20\) is as follows

$$V_f = (M_{eff}.U/K.\eta)^{3/2}$$

Where ‘$M_{eff}$’ is the effective mass of the mixture, ‘K’ is a dimensionless constant independent of temperature and liquid.

Its value is 4.281 x 10\(^9\)\(^21\).

(iv) *Internal Pressure* ($\pi_i$):

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant of force of attraction and force of repulsion between the molecules. It is calculated by using the relation\(^22\),

$$\pi_i = bRT \left( k\eta(U)^{1/2} \left( \rho^{2/3}/M^{7/6} \right) \right)$$

Where, ‘b’ stands for cubic packing, which is assumed to be ‘2’ for all liquids, ‘k’ is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281 x 10\(^9\).

‘T’ is the absolute temperature in Kelvin’s is the effective molecular weight, ‘R’ is the Universal gas constant, ‘$\eta$’ is the viscosity of solution in N.S.m\(^{-2}\), ‘U’ is the ultrasonic velocity in m.s\(^{-1}\) and ‘$\rho$’ is the density in Kg.m\(^{-3}\) of solution.

(v) *Relaxation time* ($\tau$):

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and impurities. The relaxation time can be calculated from the relation,

$$\tau = 4/3. (\beta.\eta)$$

Where, ‘$\beta$’ is the adiabatic compressibility and ‘$\eta$’ is the viscosity of the mixture.

(vi) *Acoustic impedance* (Z):

The specific acoustic impedance is given by,

$$Z = U.\rho$$

Where, ‘U’ and ‘$\rho$’ are velocity and density of the mixture.

(vii) *Gibb’s free energy* :

The Gibb’s free energy is calculated by using the relation

$$\Delta G = kT.\ln (kT/\hbar)$$

Where, ‘$\tau$’ is the viscous relaxation time, ‘T’ is the absolute temperature, ‘k’ is the Boltzmann’s constant and ‘$\hbar$’ is the Planck’s constant.
(viii) Molar volume can be calculated by using the relation\(^{23}\)

\[
V_m = \frac{M_{\text{eff}}}{\rho}
\]  

(8)

Where, \(M_{\text{eff}}\) is the effective molecular weight and \(\rho\) is the density of the solution.

(ix) Available Volume:

Available volume is the direct measure of compactness and strength of binding between the molecules of liquid or liquid mixture. Schaffs et al.\(^{24}\) shown that the available volume can be obtained by the relation.

\[
V_a = V_m(1-U/Um)
\]  

(9)

(x) Rao’s Constant:

Rao’s constant is also known as molar sound velocity and it is an additive property. It has been found to be invariant with temperature and pressure for un-associated organic and inorganic liquid. R can be evaluated by an equation given by Bagchi et al.\(^{25}\)

\[
R = V_m U^{1/3}
\]  

(10)

11. Wada’s Constant:

Molar compressibility is also known as Wada’s constant, which is dependent on adiabatic compressibility and density, is given by the relation\(^{26}\)

\[
W = V_m \beta^{1/7}
\]  

(11)

12. Surface Tension:

Surface tension can be calculated by using the relation\(^{27}\)

\[
S = 6.3 \times 10^{-4} \cdot \rho \cdot U^{3/2}
\]  

(12)

Results and Discussion

The experimental data relating to density, viscosity and velocity at 298 K, 308 K, 318 K and 328 K for frequencies 2MHz for the mixtures are given in table-1. The calculated values of adiabatic compressibility (\(\beta\)), free length (\(L_f\)) and relaxation time (\(\tau\)) are reported in table-2. Acoustic impedance (Z), Gibb’s free energy (\(\Delta G\)) and Internal pressure (\(\pi_i\)) are reported in table-3. Surface tension (S), Rao’s constant (R) and Wada’s constant (W) are presented in table-4. Free volume (\(V_f\)), molar volume and available volume for the mixture are presented in table-5. The variation of different parameters with temperature are shown in fig.1-4.

**Table-1. Experimental values of density, viscosity and ultrasonic velocity at different temperatures**

| Solution | Density (Kg.m\(^{-3}\)) | Viscosity (N.s.m\(^{-2}\)) | Velocity (m.s\(^{-1}\)) |
|----------|----------------|----------------|----------------|
|          | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K |
| S\(_1\)  | 0.819 | 0.811 | 0.803 | 0.795 | 1.879 | 1.529 | 1.247 | 1.034 | 1266.4 | 1250.6 | 1239.8 | 1224.8 |
| S\(_2\)  | 0.8308 | 0.8225 | 0.8142 | 0.8058 | 1.546 | 1.276 | 1.065 | 0.901 | 1288.6 | 1276.4 | 1266.5 | 1251.4 |
| S\(_3\)  | 0.8438 | 0.8353 | 0.8267 | 0.8188 | 1.412 | 1.173 | 0.991 | 0.856 | 1322.5 | 1312.0 | 1306.6 | 1270.6 |
| S\(_4\)  | 0.8568 | 0.8482 | 0.8395 | 0.8307 | 1.256 | 1.059 | 0.903 | 0.784 | 1337.8 | 1315.9 | 1305.9 | 1279.7 |
| S\(_5\)  | 0.8739 | 0.8651 | 0.8562 | 0.8473 | 1.226 | 1.042 | 0.889 | 0.711 | 1351.5 | 1334.2 | 1313.0 | 1288.4 |

**Table-2. Calculated values of adiabatic compressibility, free length and relaxation time at different temperatures**

| Solution | Adiabatic compressibility x 10\(^{10}\) | Free length x 10\(^{10}\) | Relaxation time x 10\(^{12}\) |
|----------|----------------|----------------|----------------|
|          | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K |
| S\(_1\)  | 7.613 | 7.844 | 8.101 | 8.385 | 0.541 | 0.556 | 0.575 | 0.588 | 1.907 | 1.607 | 1.347 | 1.156 |
| S\(_2\)  | 7.249 | 7.463 | 7.657 | 7.925 | 0.528 | 0.541 | 0.559 | 0.572 | 1.494 | 1.270 | 1.087 | 0.952 |
| S\(_3\)  | 6.776 | 6.955 | 7.085 | 7.565 | 0.510 | 0.522 | 0.538 | 0.559 | 1.276 | 1.088 | 0.936 | 0.864 |
| S\(_4\)  | 6.521 | 6.809 | 6.985 | 7.351 | 0.501 | 0.517 | 0.534 | 0.551 | 1.092 | 0.962 | 0.841 | 0.769 |
| S\(_5\)  | 6.265 | 6.493 | 6.774 | 7.110 | 0.491 | 0.505 | 0.526 | 0.542 | 1.024 | 0.902 | 0.803 | 0.674 |
Ultrasonic velocity increases with increase in mole-fraction of DMF. Also, velocity decreases with increase in temperature. This is due to the structural changes occurring in the mixtures resulting in increase of intermolecular forces. Intermolecular free length is the distance between the surfaces of the neighbouring molecules in the mixture. Ultrasonic velocity in a solution depends on free length. As free length increases with temperature, ultrasonic velocity decreases with increase in temperature. Variation in free length indicates variation in molecular forces in the mixture which depends on the experimental density as well as temperature. It is found that free length decreases from s1 to s5 indicating increase in molecular interaction due to association in polar ends.

When the temperature is increased there is reduction in molecular interaction as they move away from each other. This reduces the cohesive force. Thus, a decrease in internal pressure and increase in free volume occurs with increases in temperature. In all the binary mixtures, internal pressure decreases with increase in temperature indicating weakening of interaction with higher temperature.

Contraction in volume leads to subsequent decrease in adiabatic compressibility as well as in intermolecular free length from s1 to s5 showing more cohesive forces as the concentration of n-butanol enhanced. These parameters increase with increase in temperature for a particular concentration as high temperature decreases the intermolecular force resulting in increase of volume.

Table-3. Calculated values of acoustic impedance, Gibb’s free energy and internal energy at different temperatures.

| Solution | Acoustic Impedance x 10^6 | Gibb’s free energy x 10^20 | Internal pressure |
|----------|---------------------------|---------------------------|------------------|
|          | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K |
| S1       | 1.037 | 1.104 | 0.996 | 0.974 | 1.196 | 1.231 | 1.267 | 1.303 | 3.123 | 2.914 | 2.714 | 2.550 |
| S2       | 1.071 | 1.105 | 1.103 | 1.008 | 1.186 | 1.122 | 1.258 | 1.294 | 2.836 | 2.660 | 2.505 | 2.376 |
| S3       | 1.116 | 1.096 | 1.108 | 1.040 | 1.200 | 1.215 | 1.251 | 1.290 | 2.703 | 2.542 | 2.403 | 2.324 |
| S4       | 1.147 | 1.116 | 1.096 | 1.063 | 1.173 | 1.210 | 1.247 | 1.285 | 2.560 | 2.437 | 2.318 | 2.238 |
| S5       | 1.181 | 1.154 | 1.124 | 1.092 | 1.171 | 1.128 | 1.245 | 1.279 | 2.550 | 2.432 | 2.323 | 2.151 |

Table-4. Calculated values of free volume, Rao’s constant and Wada’s constant at different temperatures.

| Solution | Surface tension | Rao’s constant | Wada’s constant |
|----------|-----------------|----------------|-----------------|
|          | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K |
| S1       | 23.25 | 22.60 | 22.09 | 21.47 | 194.5 | 195.6 | 197.0 | 198.1 | 134.5 | 135.2 | 136.0 | 136.7 |
| S2       | 23.61 | 23.63 | 23.12 | 22.47 | 192.8 | 194.2 | 195.6 | 196.9 | 133.5 | 134.3 | 135.2 | 135.9 |
| S3       | 25.57 | 25.01 | 24.60 | 23.36 | 191.5 | 192.9 | 194.7 | 194.7 | 132.7 | 133.6 | 134.6 | 134.7 |
| S4       | 26.41 | 25.51 | 24.96 | 23.96 | 189.3 | 190.2 | 191.7 | 192.4 | 131.4 | 132.0 | 132.8 | 133.3 |
| S5       | 27.35 | 26.56 | 25.66 | 24.69 | 186.3 | 187.3 | 188.3 | 189.1 | 129.6 | 130.3 | 130.8 | 131.3 |

Table-5. Calculated values of free volume, Molar volume and Available volume at different temperatures.

| Solution | Free volume x 10^-7 | Molar volume | Available volume |
|----------|---------------------|--------------|------------------|
|          | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K | 298K | 308K | 318K | 328K |
| S1       | 1.116 | 4.081 | 5.758 | 7.866 | 179.8 | 181.5 | 183.3 | 185.2 | 37.48 | 39.65 | 41.27 | 43.43 |
| S2       | 1.534 | 5.520 | 7.530 | 9.990 | 177.2 | 179.0 | 180.8 | 182.7 | 34.49 | 36.21 | 37.69 | 39.81 |
| S3       | 1.827 | 6.527 | 8.796 | 11.034 | 174.5 | 176.2 | 178.1 | 179.8 | 30.26 | 31.73 | 32.65 | 37.02 |
| S4       | 2.217 | 7.638 | 10.097 | 12.717 | 171.8 | 173.6 | 175.4 | 177.2 | 28.16 | 30.82 | 32.23 | 35.48 |
| S5       | 2.334 | 7.995 | 10.434 | 14.883 | 168.5 | 170.2 | 171.9 | 173.8 | 26.16 | 28.27 | 30.84 | 33.84 |
Relaxation time increases with an increase in mole fraction of DMF. Such a situation suggests that the molecules get rearranged due to cooperation process. When temperature increases, relaxation time decreases indicating the reverse process. As temperature increases, excitation energy increases and hence relaxation time decreases. Relaxation time is the time taken for the excitation energy to appear as translational energy. Further, since kinetic energy of the molecules increases, longer time is taken for rearrangement of molecules.

Molecular volume increases with a rise in temperature. This is because thermal energy facilitates increase in molecular separation. Molar volume should increase with molecular weight, which is evident in our observation. Available volume changes in the same way as molar volume. Available volume is a direct measure of the compactness and strength of bonding between the molecules of the liquid mixture.

Gibbs’ free energy increases with increase in temperature. Increasing value of Gibbs function suggests that the closer approach of unlike molecule is due to hydrogen bonding. The increase in Gibbs’ free energy also suggests shorter time for rearrangement of the molecules in the mixtures. Decreasing trend of Gibbs free energy with increase in concentration of alcoholic group due to intra molecular hydrogen bonding and force of attraction between polar heads.

Fig-1: Variation of adiabatic compr. with temperature

Fig-2: Variation of acou. impedance with temperature

Fig-3: Variation of internal pressure with temperature

Fig-4: Variation of relaxation time with temperature
The ratio of instantaneous excess pressure of any particle to the instantaneous velocity of that particle is known as specific acoustic impedance of the medium. This acoustic impedance decreases with increase in concentration of DMF as well as with increase in temperature. This indicates that there is a decrease in molecular concentration in both the cases.

The increasing trends of Rao’s and Wada’s constant with the increase of temperature suggest the availability of more number of components in a given region indicating close packing of the medium. With increase in temperature, surface tension decreases very slowly. This is also confirmed by the fact that the ultrasonic velocity increases slowly with temperature. This is because surface tension depends on density and velocity \( S \sim \rho U^{3/2} \).

**Conclusion**

Ultrasonic velocity studies on the system of binary mixture of DMF with n-Butanol shows that, when concentration of DMF increases, more rigid structure is formed due to bonding between the unlike molecules through dipole-dipole and dipole-induced dipole interaction. So acoustic parameters are highly affected at different temperatures due to dipole-dipole and dipole-induced dipole interaction between molecules. Dispersive forces along with intra molecular hydrogen bonding are also found to exist between the components of the mixture.

**Scope of Future Work :**

The present study has been done to measure the ultrasonic velocity and other acoustical parameters for the ternary mixture of n-Butanol, DMF and Water. This mixture is widely used as a running solvent in TLC for Peptides, Amino Acids and many other chemicals and also to monitor the progress of a reaction for studying structural–energetic properties of the mixed solvents. Different concentrations are used for different chemical mixtures. The behavior of parameters with variation in concentration will help to find out the most interacting ratio of concentrations and furthermore it will optimize the efficiency of work.

**Acknowledgement**

Authors are thankful to authorities of Ravenshaw University, College of Engineering & technology and ABIT, Odisha for providing infrastructure facility to do this piece of work.

**References**

1. Pushpalatha I M, Srinivasu C.H. and Narendra K., *Int. J. of res. in pharm. and chem.*, 13(1), 129 (2013).
2. Paikaray R and Mishra S., *J. of Acou. Soc. of India*, 37(1), 20 (2010).
3. Palani R and Balakrishnan S., *Indian J. of Pure and Applied Phy.*, 48: 544 (2010).
4. Panda S. and Mahapatra AP., *Int. J. of Chemical and Physical Sc.*, 5(5): 15 (2016).
5. Praharaj M. K and Mishra S., *J. of Chemical, Biological and Physical Sciences.*, 5(1), 686 (2015).
6. Praharaj M. K, SatapathyA, Mishra PR and Mishra S, *J of The and App Phy*, 7, 23 (2013).
7. Thirumaran. S, Job Sabu. K., *Ind J Pure &Appl Phys.*, 47, 87 (2009).
8. Praharaj M. K and S. Mishra, J. Therm. Anal. Calorim, 132 (2018).
9. M. J. Earle and R. Kenneth, *Pure Appl. Chem.*, 72, 1391 (2000).
10. Praharaj M. K., *Journal of Chemical and Pharmaceutical Research*, 5(1), 49-56 (2013).
11. Bagehi S, Nema S. K, and Singh R. P, *Eur. Polym. J.*, 22, 859 (1986).
12. Sahoo A. K., Das S. P. and Patnaik A.K., *Res Develop. Mater. 12*, 000776 (2019).
13. Sahoo A. K, Pradhan S. K., Patnaik A.K and Das S. P., *World Journal of Pharmaceutical Research 9(1)*, (2020).
14. Pradhan, S. K, Das S. P, Sahoo A. K, Das M., Patnaik A.K, *Int. J. Adv. Res.*, 5(6), 1534-1545 (2017).
15. Pradhan, S. K., Sahoo A. K, Das M, Das S. P, Patnaik A.K, Der Pharma Chemica, 9(24), 28-34 (2017).
16. Das M, Pradhan, S. K, Das S. P, Patnaik A.K, Am. Chem. Sci. J., 13(2), 1-7 (2016).
17. Das M, Pradhan, S. K, Das S. P, Patnaik A.K , Der Pharma Chemica, 7(12), 315-322 (2015).
18. Rao, D. N, Krishnaiah, A, Naidu, P. R, Acta.Chim. Acad. Sci. Hung, 107(1), 49–55 (1981).
19. Nikam, P. S, Hasan, M, Asian J. of Chem., 5(2), 319–321 (1993).
20. Prasad, N, J. Pure. App. Ultrason., 25, 25–30 (2003).
21. Palani, R, Balakrishnan, S, Ind. J. of pure & Appl. Phy., 48, 544–650 (2010).
22. Varada, R, Sreenivasulu, A, Raghuraman, G, Ind. J. of Chem. Tech., I, 302–304 (1994).
23. Sravana Kumar D and Krishna Rao D., Indian J Pure Appl Phys., 45, 210 (2007).
24. W. Schaaffs, Molecularakustik, Spinger-Verlag, Berlin (1963).
25. Rao M R., J Chem Phys., 9, 682 (1941).
26. Y. Wada, J. Phys. Soc. Jpn., 4, 280 (1949).
27. A. Ali, A. K. Nain, V. K. Sharma and S. Ahmad, Acoustics Letters, 23(3), (2001).