

where

$$C_1 = D(232.2 - 26.29 N_T^*)/a^4 \rho h, \quad (13)$$

$$C_2 = 187.57 D(A/h)^2/a^4 \rho h, \quad (14)$$

$$N_T^* = \frac{1}{a^2} \iint \frac{N_T}{D(1-\nu)} dx dy. \quad (15)$$

The solution of (12) with the initial conditions $F(0) = 1, dF(0)/dt = 0$ has been given by Nash and Modeer⁴ in terms of Jacobian elliptic functions of cosine type and obtained the ratio of the time-periods for nonlinear and linear vibrations of elastic plates. In the present case such ratio is given by

$$T^*/T = \frac{2\Theta}{\pi} (1 + C_2/C_1)^{-1/2} \quad (16)$$

in which T and T^* denote the time-periods for linear and nonlinear vibrations.

Numerical results and discussion: Variations of non-dimensional time-periods T^*/T for different values of non-dimensional amplitudes A/h and temperature parameter N_T^* have been computed and presented graphically. It is seen that the effect of increasing N_T^* is to diminish the relative time-periods. As expected, the nonlinear behaviour of plates due to elevated temperature, obtained here, is similar in nature to that of the plates subjected to in-plane compressive forces investigated by Biswas⁵.

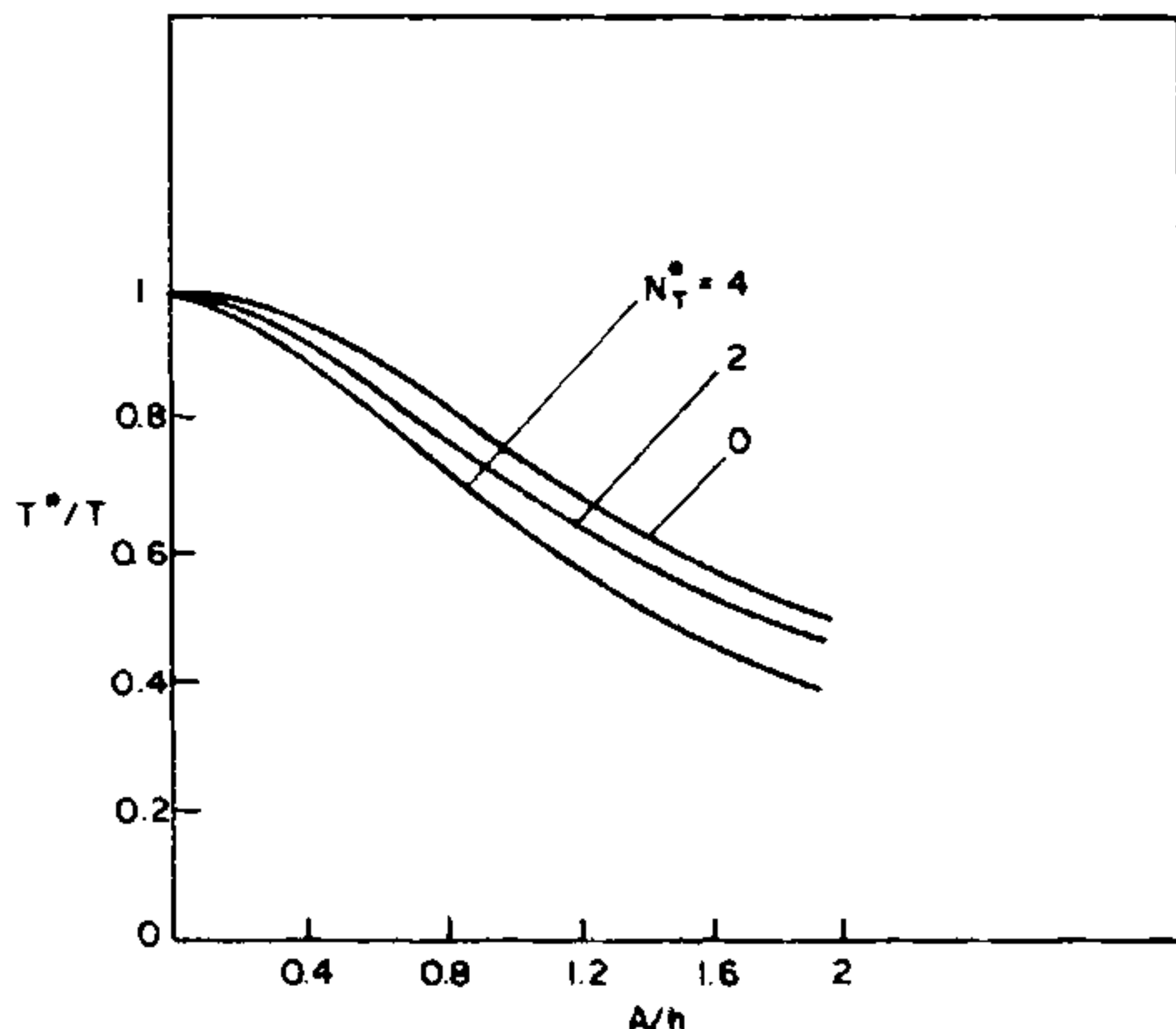


Figure 1. Variations of non-dimensional time-periods T^*/T for different values of non-dimensional amplitudes A/h and thermal loading parameter N_T^* .

The authors thank UGC, New Delhi for financial assistance.

1 January 1985; Revised 3 December 1985

1. Biswas, P. and Kapoor, P., *J. Indian Inst. Sci.*, 1984, **65**, 35.
2. Berger, H. M., *J. Appl. Mech. ASME*, 1955, **22**, 465.
3. Nowacki, W., *Thermoelasticity*, Pergamon Press, 1962, p. 439.
4. Nash, W. and Modeer, J. R., *Certain approximate analysis of the nonlinear behaviour of plates and shallow shells*, Engineering progress at the University of Florida, Tech. paper No. 193, Vol. XIV, 10, 1960.
5. Biswas, P., *J. Aero. Soc. India*, 1981, **33**, 103.

CORRECTIONS-TO-SCALING FROM LIGHT SCATTERING INTENSITY MEASUREMENTS IN A BINARY LIQUID MIXTURE

K. DEVANAND, P. CHANDRA SEKHAR and V. C. VANI

Department of Physics, Indian Institute of Science, Bangalore 560012, India.

ONE of the aims of light scattering studies near a critical point is to verify the universality hypothesis. Near the critical point, the susceptibility corresponding to the order-parameter fluctuations diverges as $t^{-\gamma}$ where $t = (T - T_c)/T_c$, is the reduced temperature, T_c being the critical temperature and γ a critical exponent. This exponent is obtained experimentally from the light scattering intensity measurements.

The true values of critical exponents are obtained by approaching very close to the critical point where $q\xi \gg 1$, q being the momentum transfer vector and ξ the correlation length. Away from T_c , in the hydrodynamic regime, where $q\xi < 1$, corrections-to-scaling terms may be present. Singular thermodynamic functions such as the order parameters, susceptibility etc are expected to be of the form

$$f - f_c = A|t|^\lambda (1 + B|t|^\Delta + \dots),$$

where the first term represents the 'pure' scaling term and the second and higher order terms, corrections to scaling. For instance, in binary liquid mixtures, λ corresponds to β , the order parameter exponent obtained from coexistence-curve measurements.

Correction-to-scaling is observed as an asymmetry in the coexistence curve giving rise to the diameter singularity¹. It has been shown theoretically, that if the temperature derivative of the coexistence curve should diverge at the critical point, then, the difference across the coexistence curve in the order parameter fluctuations should in general diverge at least as fast as the temperature derivative of the concentration difference. The coexistence curve of the binary liquid mixture, cyclohexane + acetic anhydride has been studied earlier². The diameter of the coexistence curve has been found to have a singularity. It is therefore expected that there be corrections-to-scaling terms associated with the order-parameter susceptibility. To verify the existence of such terms, light scattering intensity measurements were made on this system.

In the experiment, light from a He-Ne laser was focussed on the sample in the one-phase region kept in a thermostat controlled by a millidegree temperature controller. The light scattered at 90° falls on a RCA 31034-02 photomultiplier tube, cooled to -15°C where the dark counts are about 10/sec. The output of the PMT is fed to an ORTEC photon-counting system in which the output pulses are counted after amplifi-

Table 1 Reduced chisquare

Functional form	Run I	Run II	Run III	Run IV
$I_c/T = A_1 t^{-\gamma}$	16.64	0.5	1.1	56.80
$I_c/T = A_1 t^{-\gamma} + A_2 t^{-\gamma+\Delta}$	2.37	0.17	0.22	7.64
$I_c/T = A_1 t^{-\gamma} + A_2 t^{-\gamma+\Delta} + A_3 t^{-\gamma+2\Delta}$	2.03	0.14	0.22	4.0

Table 2 Sum of deviations

Functional form	Run I	Run II	Run III	Run IV
$I_c/T = A_1 t^{-\gamma}$	-317.7	-11.93	-22.16	-884.9
$I_c/T = A_1 t^{-\gamma} + A_2 t^{-\gamma+\Delta}$	-46.02	-4.42	-5.26	-343.32
$I_c/T = A_1 t^{-\gamma} + A_2 t^{-\gamma+\Delta} + A_3 t^{-\gamma+2\Delta}$	-39.9	-3.4	-5.2	-180.7

cation and suitable discrimination. The intensity of light is monitored by counting the number of photons for a given interval of time. Figure 1 shows a log-log plot of intensity (I_c/T) vs reduced temperature. It is evident, at a first glance, that the data do not fit a single power law going as $t^{-\gamma}$. Therefore, the data from four different runs were fitted to three different functional forms including one and then two corrections-to-scaling terms as in tables 1 and 2. In the analysis, γ and Δ were fixed at the standard values of 1.24 and 0.50 respectively and the coefficients of the terms were varied to obtain the best fits. The coefficients for the best fits are given in table 3. The improvement in fit on adding corrections-to-scaling terms is obvious from the values of variance and the sum of deviations. In runs II and III, it appears, from the value of the reduced chisquare, that the scaling term itself gives a good fit. But in both cases, the deviations of the data were not distributed equally on either side of the theoretical fit. The corrections-to-scaling fits were better, as seen from the lower values of the sum of deviations (table 2). It is essential that in looking for corrections-to-scaling terms, one has data sufficiently far away from $T_c^{3,4}$. The present experiment covers the range $10^{-4} < t < 10^{-1}$. Experiments with data only

Table 3. Table of coefficients

Functional form	Run I	Run II	Run III	Run IV
$I_c/T = A_1 t^{-\gamma}$	$A_1 = 0.067$	$A_1 = 0.003$	$A_1 = 0.007$	$A_1 = 0.025$
$I_c/T = A_1 t^{-\gamma} + A_2 t^{-\gamma+\Delta}$	$A_1 = 0.023$ $A_2 = 1.33$	$A_1 = 0.002$ $A_2 = 0.03$	$A_1 = 0.005$ $A_2 = 0.10$	$A_1 = 0.010$ $A_2 = 1.77$
$I_c/T = A_1 t^{-\gamma} + A_2 t^{-\gamma+\Delta} + A_3 t^{-\gamma+2\Delta}$	$A_1 = 0.009$ $A_2 = 2.00$ $A_3 = -5.27$	$A_1 = 0.003$ $A_2 = 0.076$ $A_3 = 0.340$	$A_1 = 0.005$ $A_2 = 0.10$ $A_3 = 0.007$	$A_1 = -0.017$ $A_2 = 2.34$ $A_3 = -8.65$

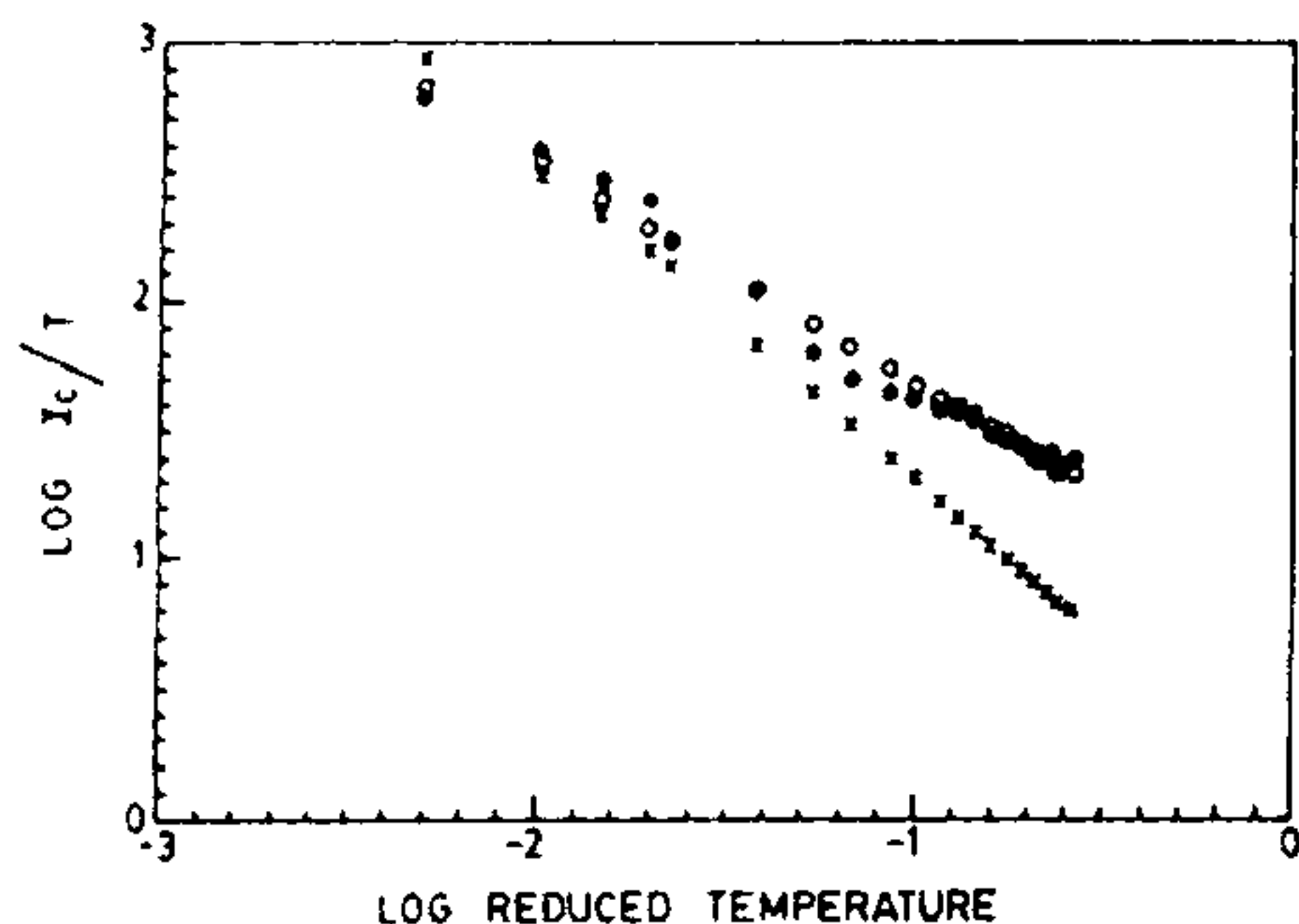


Figure 1. Intensity versus temperature (RUN I)
 ●—Experimental data points, ×—Theo fit to $I_c/T = A_1 t^{-\gamma}$, ○—Theo fit to $I_c/T = A_1 t^{-\gamma} + A_2 t^{-\gamma+\Delta}$.

very close to T_c may not show any evidence of corrections-to-scaling⁵. In figure 1, the fit with two correction terms is not shown, since, as seen from the tables, the improvement obtained with the second correction term $A_3 t^{-\gamma+2\Delta}$, is only marginal. It is also seen that the pure scaling term fits the data well much closer to T_c . Similar evidence of corrections-to-scaling terms in a binary liquid mixture has been found by A. Bourgou and D. Beysens⁶.

Thanks are due to Prof. P. S. Narayanan and Prof. E. S. Rajagopal for several useful discussions. One of the authors (KD) wishes to thank CSIR New Delhi for a research fellowship. Thanks are also due to the Department of Science and Technology for financial support.

27 December 1985

1. Mermin, N. D. and Rehr, J. J., *Phys. Rev.*, 1971, **A6**, 2408.
2. Gopal, E. S. R., Ramachandra, R., Chandra Sekhar, P., Govindarajan, K. and Subramanyam, S. V., *Phys. Rev. Lett.*, 1974, **32**, 284.
3. Marcos, L. K. and Green, M. S., *Phys. Rev.*, 1977, **A16**, 2483.
4. Cannell, D. S., *Phys. Rev.*, 1976, **A15**, 2053.
5. Chang, R. F., Burstyn, H. and Sengers, J. V., *Phys. Rev. Lett.*, 1979, **19**, 866.
6. Bourgou, A. and Beysens, D., *Phys. Rev. Lett.*, 1981, **47**, 257.

OROXINDIN, A RARE FLAVONE GLYCOSIDE FROM THE LEAVES OF *HOLMSKIOLDIA SANGUINEA*

G. A. NAIR and C. P. JOSHUA

Department of Chemistry, University of Kerala, Trivandrum 695 034, India.

PLANTS belonging to the family Verbenaceae¹ are important from the point of view of medicinal properties^{2,3} and the biosynthesis of rare and unusual flavonoids^{1,4}. The medicinal uses of plants belonging to Verbenaceae may be attributed to their flavonoid content to some extent and hence an examination of the flavonoids of plants of this family has been considered worthwhile. As there is no record of any detailed chemical work on *Holmskioldia sanguinea*^{5,6} (Verbenaceae), except the isolation of wogonin⁷ from the aerial parts of this plant, a systematic study was undertaken and the results are presented here.

Shade-dried leaves of *H. sanguinea* (1 Kg) were extracted with hot 90% EtOH (3 × 3 l). The combined extract was concentrated *in vacuo* to 300 ml and the aq. concentrate was then extracted with petroleum ether (60–80), ether and ethyl acetate in succession.

The petroleum ether extract yielded a waxy solid, identified after chromatographic purification [Al_2O_3 ; petrol-benzene (1:4) eluate] as sitosterol, colourless needles (180 mg) from MeOH, m.p. 136–37°, $[\alpha]_D^{28} = -37^\circ$ (c, 1.2, $CHCl_3$) (m.m.p., co-TLC and superimposable IR).

The ether extract yielded a yellow crystalline substance (120 mg), m.p. 202–204°. It gave pink colour with Mg-HCl and yellow colour with alkali. It was purple under UV and UV/ NH_3 and had UV (λ_{max}): 275, 340 (MeOH), 292, 333 sh, 395 ($AlCl_3$), 283, 355 (NaOAc) 275, 340 (NaOAc/ H_3BO_3) and 283, 375 nm (NaOMe); IR: 3200 (br), 1660, 1610, 1580, 1510, 1450, 1420, 1360, 1275, 1020, 840, 760, 680 and 660 cm^{-1} ; 100 MHz PMR spectrum in DMSO- d_6 : δ 12.52 (s, 1H, 5-OH), 7.9–8.2, centred at 8.0 (m, 2H, 2' and 6'-H), 7.4–7.8, centred at 7.6 (m, 3H, 3'4' and 5'-H), 7.01 (s, 1H, 3-H), 6.34 (s, 1H, 6-H) and 3.88 (s, 3H, 8-OCH₃); MS: (m/z) 284 (M^+ , 65), 269 ($M-CH_3$, 100), 241 (269–28, 42), 167 (A-ring fragment, 12), 139 (167–28, 70), 77 (B-ring fragment, 10%). With acetic anhydride and pyridine it yielded a diacetate, m.p. 150–52°, and identified as 5,7-dihydroxy-8-methoxyflavone (wogonin) which was confirmed by comparison (m.m.p., co-TLC, IR) with an authentic sample of wogonin.

Ethyl acetate extract gave a yellow substance which when crystallized from MeOH yielded yellow needles