Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric relaxation in coexisting nematic and smectic B phases

D. A. Dunmur[a]; S. P. Farnan[a]; C. I. Murray[a]
[a] Department of Chemistry and Centre for Molecular Materials, University of Sheffield, Sheffield, England

To cite this Article Dunmur, D. A. , Farnan, S. P. and Murray, C. I.(1995) 'Dielectric relaxation in coexisting nematic and smectic B phases', Liquid Crystals, 19: 6, 779 — 783
To link to this Article: DOI: 10.1080/02678299508031099
URL: http://dx.doi.org/10.1080/02678299508031099

LIQUID CRYSTALS, 1995, VOL. 19, NO. 6, 779–783

Dielectric relaxation in coexisting nematic and smectic B phases

by D. A. DUNMUR*, S. P. FARNAN and C. I. MURRAY
Department of Chemistry and Centre for Molecular Materials,
University of Sheffield, Sheffield S3 7HF, England

(*Received 6 January 1995; in final form 12 July 1995; accepted 31 July 1995*)

Mixtures of a polar solute 4-*n*-pentyl-4′-cyanobiphenyl in a non-polar nematic solvent exhibit two separated low frequency dielectric relaxations for concentrations of the solute between 2 mol% and 20 mol% over a limited temperature range. This behaviour is attributed to coexisting nematic and smectic B phases, in which the polar solute probe has different relaxation frequencies. The observed dielectric spectra can be accurately fitted to two Debye-like relaxations, and the strengths of the absorptions are proportional to the amounts of the coexisting phases. A microscopic determination of the phase diagram confirms the assignment of the coexisting phases, and it is concluded that there is a preference of the dipolar probe molecule for the smectic B phase, which is induced as a result of solute–solvent interactions.

1. Introduction

The physical properties of liquid crystals reflect their phase structures and symmetries. Different aspects of their structures can be probed by examining different properties, and dielectric properties can be used to investigate dipole organization, dipole–dipole interactions and molecular dynamics in liquid crystalline phases [1, 2]. In earlier studies of dipolar response and dipole–dipole interactions in liquid crystals, we have reported measurements of the static permittivity of solutions of polar mesogenic solutes in liquid crystalline solvents of low dielectric permittivity [3, 4]. Such solvents minimize the dielectric screening between dipoles, and so maximize the effect of electrostatic interactions. Variable frequency dielectric measurements reveal a number of dielectric relaxation processes [1, 2], which contribute differently to the different components of the permittivity tensor. For dipolar liquid crystals of positive dielectric anisotropy, a low frequency relaxation usually in the kHz/MHz region is observed for the permittivity component parallel to the director, which can be attributed to a reorientation of longitudinal molecular dipoles about a molecular short axis: so-called end-over-end rotation.

This paper is concerned with dielectric relaxation in a liquid crystal mixture. Previous workers have measured the dielectric relaxation in nematic mixtures [5], and in binary mixtures exhibiting nematic, smectic A and smectic B phases [6]. In the former case two separated low frequency relaxations corresponding to the solute and solvent were detected in the nematic phase of some mixtures. The end-over-end relaxations measured in nematic, smectic A and smectic C phases have similar frequencies, but in the more ordered smectic phases, the relaxation is observed to be of lower frequency with a higher activation energy [7, 8], consistent with the increased molecular organization. Counter-intuitively, the activation energy for the nematic phase is often higher than that for disordered smectic phases A and C [2], but this is not always the case [6]. A consistent interpretation of the low frequency dielectric relaxation in liquid crystal phases has yet to be developed. Most models for dielectric relaxation in nematics [9] or smectics [10] are based on single particle rotational diffusion in an anisotropic pseudo-potential, but mixtures of similar mesogens show a single relaxation, suggesting that it is a collective process involving a number of interacting molecules.

Although a full understanding of dielectric relaxation in liquid crystals may be lacking, the technique provides valuable information on the structure and dynamics of mesophases, and in particular on the various time-scales for different relaxation processes which directly determine the limiting response times for liquid crystal electro-optic applications. In this paper we report the application of dielectric relaxation as a technique to monitor phase behaviour in liquid crystalline mixtures. The use of probe molecules to study liquid crystal phases is well known in NMR, EPR, visible spectroscopy and fluorescence [11]. This paper describes the use of a dipolar

---

* Author for correspondence.

0267–8292/95 $10·00 © 1995 Taylor & Francis Ltd.

probe to examine the phase behaviour of a liquid crystal mixture in which the probe itself induces additional molecular organization.

2. Experimental

The system studied in this work was a mixture of the dipolar probe mesogen 4-*n*-pentyl-4′-cyanobiphenyl (CB5) with a nematic host mixture formulated by Merck UK Ltd. (17256, mixture N) to have a low dielectric constant ($\varepsilon = 2{\cdot}8$) and a low dielectric anisotropy ($\Delta\varepsilon = -0{\cdot}13$ at 30°C). The composition of the mixture N has not been disclosed, but it consists of a number of alkylphenyl alkylcyclohexanoates with bis-(alkylcyclohexyl)biphenyl additives to give a higher transition temperature; its liquid crystalline transition temperatures in the undoped state are crystal/nematic $T_{\mathrm{CrN}} < 0°\mathrm{C}$ and nematic/isotropic $T_{\mathrm{NI}} = 70°\mathrm{C}$. At moderate concentrations of dopant greater than 15 per cent CB5, a solute-induced smectic A phase formed. The phase diagram for the region of interest to this work, which is below 20 mol% CB5, is shown in figure 1. This phase diagram was determined from microscopic observations, and the formation of the smectic B phase from the nematic phase was accompanied by the appearance of characteristic butterfly dendrites [12], see figure 2. The phase behaviour for mixtures with less than 2% mol fraction of CB5 was difficult to establish experimentally, except that the crystal/nematic transition of mixture N (0 per cent CB5) super-cooled to less than − 20°C and a smectic B phase was not exhibited; phase boundary lines in this region are drawn on this basis.

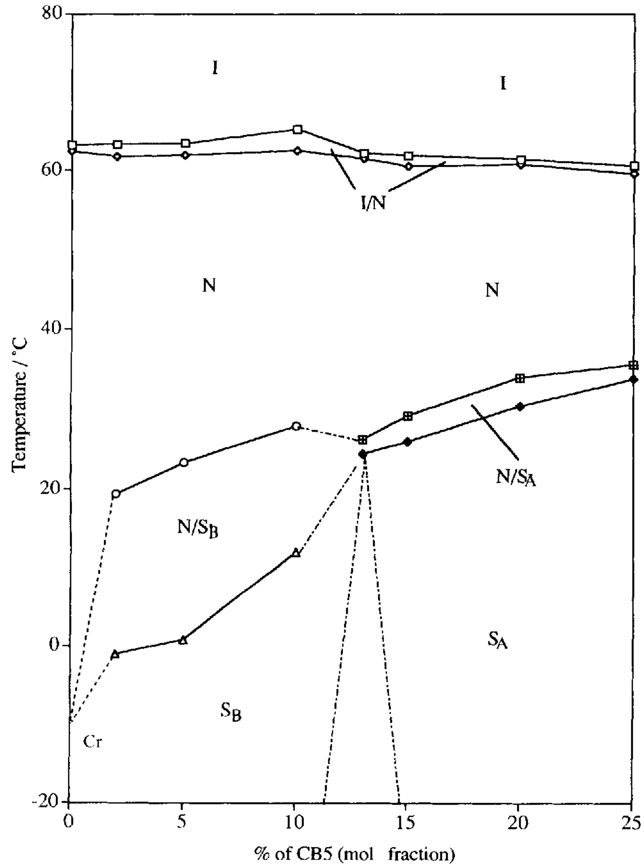


Figure 1. Phase diagram of 4-*n*-pentyl-4′-cyanobiphenyl (CB5) in Merck Ltd. mixture N, showing the two phase coexistence regions.

Figure 2. Butterfly dendrites of smectic B phase in coexistence with a nematic phase: 10 mol% CB5 in N at 24°C.

Dielectric relaxation measurements were made on 50 μm liquid crystal films sandwiched between gold-plated glass electrodes, having an overlapping area of 1 cm^2; edge-effects were avoided by using a guard-ring pattern of electrodes. A homeotropic (perpendicular) alignment was achieved and maintained by applying a d.c. bias of 10 V in the nematic phase. Capacitance and dissipation were measured using a Hewlett-Packard Impedance Analyser (HP 4192A) controlled by a PC, and the dielectric cell was thermostatted to ± 0·1° by circulating fluid from a Haake controller.

3. Results and discussion

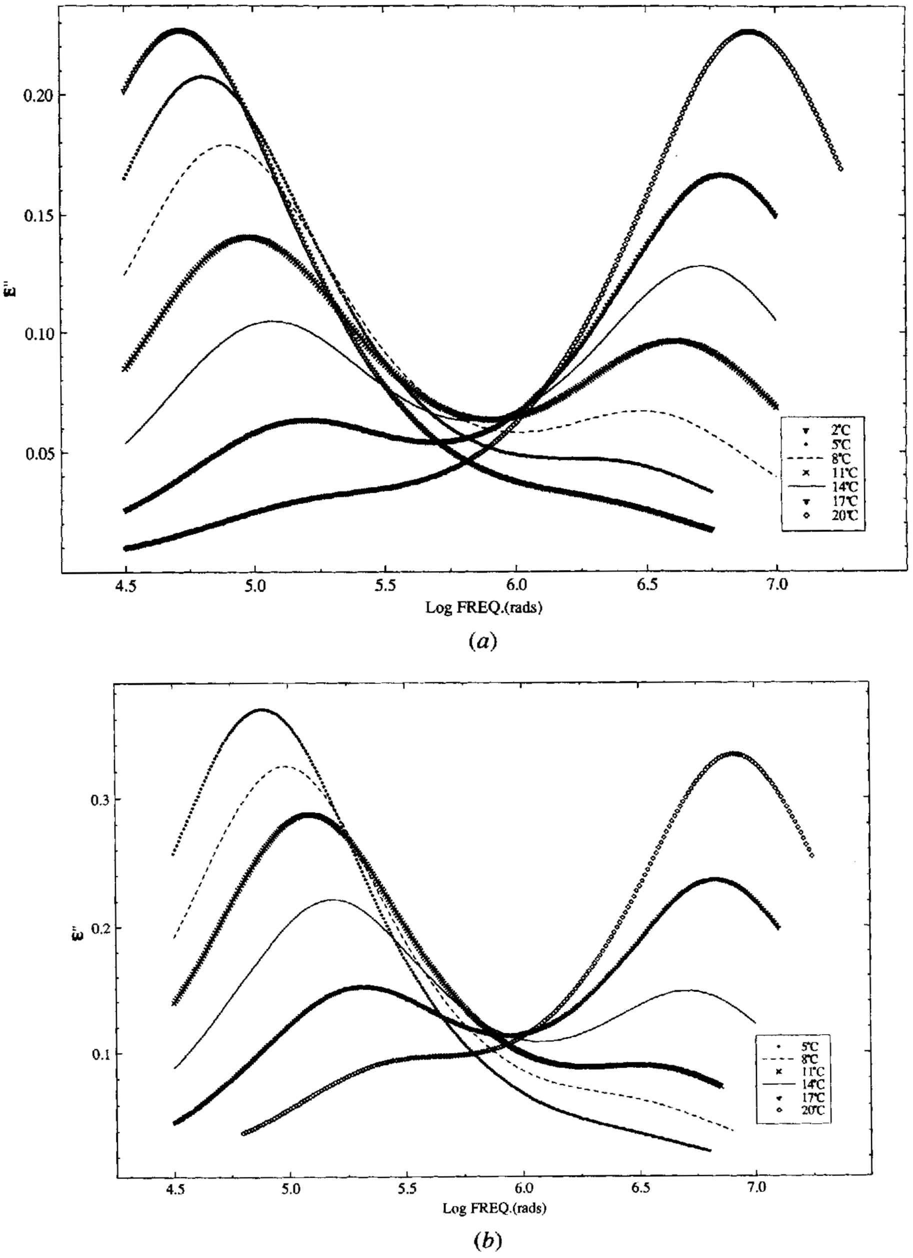
Measurements of the dielectric absorption (ε'') are given in figures 3 (*a*)–(*c*) for three concentrations of CB5 in mixture N. Two relaxations were observed, which are identified as being due to coexisting nematic and smectic B phases. The dipolar probe mesogen is distributed between the two phases, which are both present over temperature ranges of up to 20°. The lower frequency relaxation is ascribed to the end-over-end rotation of the probe molecule in the smectic B phase, while the higher frequency relaxation is due to the same process in the coexisting nematic phase. As the temperature is changed the relative amounts of the two phases present change, and this is reflected by the change in amplitude of the dielectric absorptions. The absorption curves can be accurately fitted by the expression:

$$\varepsilon''(\omega) = \frac{k_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{k_2\omega\tau_2}{1+\omega^2\tau_2^2} \qquad (1)$$

where $k_1 = \varepsilon'_{10} - \varepsilon'_{1\infty}$ and $k_2 = \varepsilon'_{20} - \varepsilon'_{2\infty}$ are the magnitudes of the real part of the permittivity which is being relaxed at each of the absorption processes. The subscript 1 refers to the low frequency relaxation (smectic B) and 2 refers to the higher frequency relaxation (nematic). Neglecting any specific influences of the different phases, nematic or smectic B, on the real part of the permittivity, the coefficients k_1 and k_2 can be expressed in terms of the relaxing end-over-end dipole component μ_1 as follows [1]:

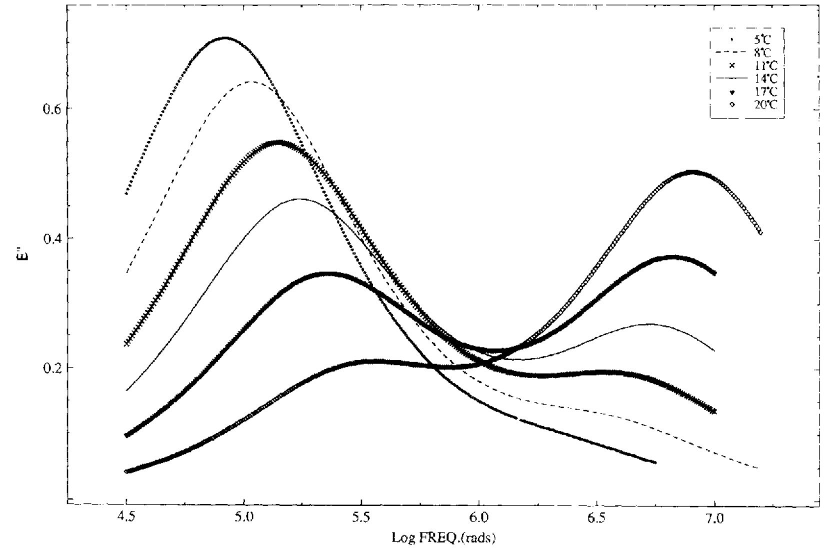
$$k_1 = \frac{N_1LF^2\mu_1^2}{3\varepsilon_0kT}(2S_1+1) \text{ and } k_2 = \frac{N_2LF^2\mu_1^2}{3\varepsilon_0kT}(2S_2+1) \qquad (2)$$

where L and F are macroscopic cavity and reaction field factors, respectively, assumed to be the same for both phases, and N_1 and N_2 are the respective number densities for the solute CB5 in the coexisting smectic B and nematic phases. The results shown in figure 3 have been fitted to equation (1); the fitted lines in the figure pass through all



(*a*)

(*b*)



(*c*)

Figure 3. Dielectric absorption as a function of frequency for mixtures of CB5 in N at various temperatures. (*a*) 4 mol%; (*b*) 6 mol%; (*c*) 8 mol%.

Table. Activation energies for dipole relaxation of CB5 in coexisting nematic and smectic B phases.

Concentration of CB5 mol%	E_{A1}(nematic)/ kJ mol^{-1}	E_{A2}(smectic B)/ kJ mol^{-1}
4·0	47·1	41·6
6·0	55·9	52·3
8·0	55·2	54·1

the data points, and we obtain values for the coefficients k_1 and k_2. These are plotted as functions of concentrations of CB5 for various temperatures in figures 4 (*a*) and (*b*). The apparent non-linear variation of k_1 and k_2 with concentration suggests that the order parameter of the solute is dependent on the concentration in coexisting phases.

Activation energies for coexisting phases were obtained from the temperature dependence of the relaxation times τ_1 and τ_2 corresponding to the nematic and smectic B phases, and these are listed in the table. The activation energies for end-over-end rotation are a little lower in the smectic B phase than in the nematic phase, and while this is counter-intuitive, it is in line with other reported measurements [2, 13] on other smectic phases.

4. Conclusions

A surprising result of this work is the formation of an induced smectic B phase in the mixture N for small dopant concentrations of the dipolar probe CB5. The induction of ordered phases by dipolar solutes from disordered liquid crystal phases is well known in a number of contexts. Mixtures of calamitic polar and non-polar nematogens frequently form induced smectic A phases [14, 15], while the addition of strongly polar solutes such as bromobenzene and *O*-dibromoxylene [16] or trinitrofluorenone [17] to discotic nematic phases results in the formation of ordered columnar phases. For these systems, the maximum stability of the induced phase occurs for approximately equimolar mixtures of solute and solvent. For the system studied here, the smectic B phase forms at concentrations of CB5 less than 20 mol%.

The detection of an additional coexisting smectic B phase in the system was initially achieved by observation of a second dielectric relaxation in the mixtures. Analysis of the results for the dielectric absorption indicate that the dipolar probe has a greater affinity for the smectic B phase, in which it appears to be more ordered. Since it is CB5 which causes the formation of the smectic B phase, it is perhaps reasonable that the free energy of the system is lowered by the increased concentration of the probe in the smectic B phase.

The observation of a low frequency relaxation in smectic B phases has been observed by a number of authors [7, 8], but a recent paper [18] suggests that in a chiral smectic B phase the end-over-end rotation is frozen. Our results certainly support the observations that reorientation about the molecular short axis can occur in non-chiral smectic B phases. The two relaxations observed by us in mixtures are separated by two decades of angular frequency, and microscopic evidence supports the assignment of the relaxations to nematic and smectic B phases.

In this work we have demonstrated the use of dielectric relaxation studies to investigate the phase behaviour of mixtures. The interpretation of the results for the system studied is complicated by the multicomponent nature of the solvent, and the discovery of similar behaviour in a simple two component system would enable a more detailed analysis to be carried out.

We are most grateful to the UK Science and Engineering Research Council and the University of Sheffield for the award of Research Studentships to SPF and CIM. The support of these studentships and this research through Industrial Studentships by Merck UK Ltd. is also gratefully acknowledged, as is the general supply of materials.

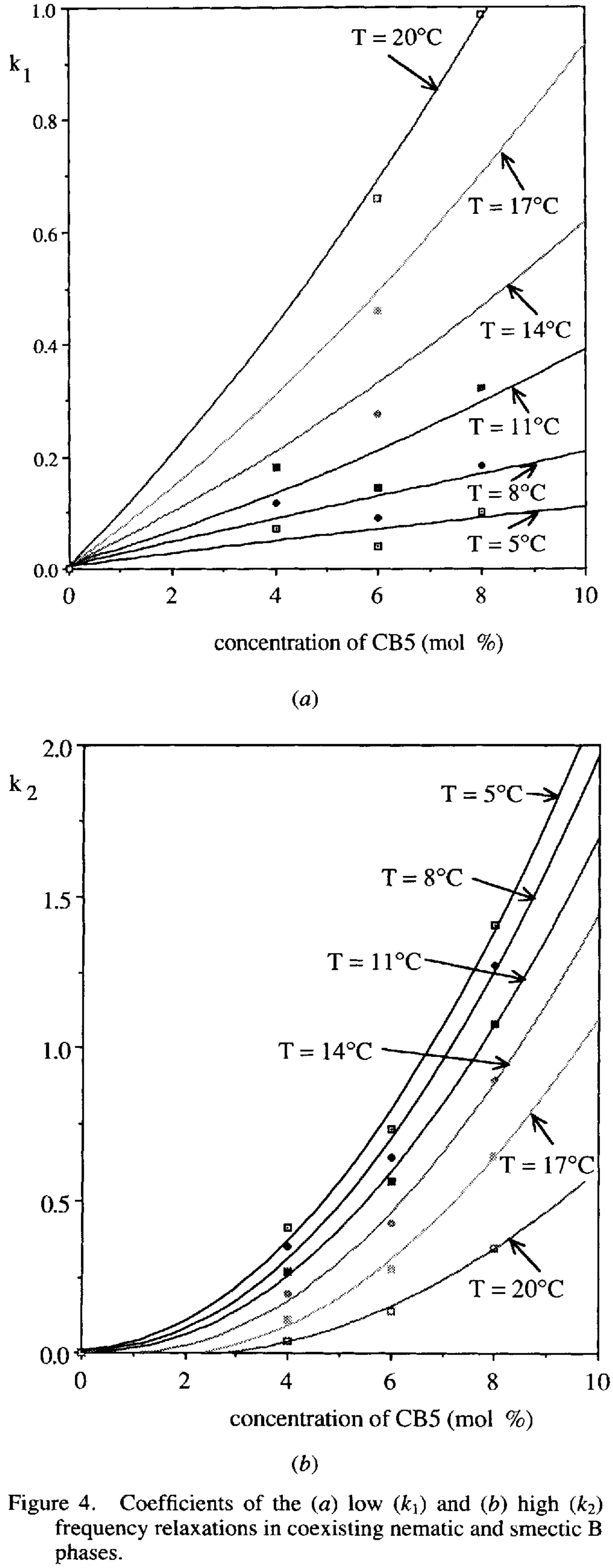


Figure 4. Coefficients of the (*a*) low (k_1) and (*b*) high (k_2) frequency relaxations in coexisting nematic and smectic B phases.

References

[1] Williams, G., 1994, *Molecular Dynamics of Liquid Crystals*, edited by G. R. Luckhurst and C. A. Veracini (Kluwer, Dordrecht), p. 431, and references therein.

[2] Kresse, H., 1982, *Fortsch. d. Phys.*, **30**, 507.

[3] Dunmur, D. A., and Toriyama, K., 1991, *Molec. Crystals liq. Crystals*, **198**, 201.

[4] Dunmur, D. A., and Toriyama, K., 1995, *Molec. Crystals liq. Crystals*, **264**, 131.

[5] Kresse, H., Rabenstein, P., and Demus, D., 1988, *Molec. Crystals liq. Crystals*, **154**, 1.

[6] Kresse, H., Stettin, H., and Tennstedt, E., 1986, *Cryst. Res. Technol.*, **21**, 1109.

[7] Pelzl, G., 1994, *Liquid Crystals*, edited by H. Stegemeyer (Springer), p. 76.

[8] Kresse, H., Selbmann, C., Demus, D., Buka, A., and Bata, L., 1981, *Cryst. Res. Technol.*, **16**, 1439.

[9] Nordio, P. L., Rigatti, G., and Segre, U., 1973, *Molec. Phys.*, **25**, 129.

[10] Bata, L., 1986, *Z. Chem.*, **26**, 27.

[11] Veracini, C. A., and Shilstone, G. N., 1994, *Molecular Dynamics of Liquid crystals*, edited by G. R. Luckhurst and C. A. Veracini (Kluwer, Dordrecht), p. 257.

[12] Buka, A., Katona, T. T., and Kramer, L., 1994, *Phys. Rev.* E, **49**, 5271.

[13] Kresse, H., and Gajewska, B., 1983, *Cryst. Res. Technol.*, **18**, 281.

[14] Dunmur, D. A., Walker, R. G., and Palffy-Muhoray, P., 1985, *Molec. Crystals liq. Crystals*, **122**, 321.

[15] Das, M. K., Paul, R., and Dunmur, D. A., 1995, *Molec. Crystals liq. Crystals*, **258**, 239.

[16] Praefcke, K., Singer, D., and Kohne, B., 1993, *Liq. Crystals*, **13**, 445.

[17] Praefcke, K., Singer, D., and Eckert, A., 1993, *Liq. Crystals*, **16**, 53.

[18] Gouda, F., Lagerwall, S. T., Skarp, K., and Stebler, B., 1994, *Liq. Crystals*, **17**, 367.