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**ÉTUDE EXPÉRIMENTALE DU COMPORTEMENT DE LA CONSTANTE
DIÉLECTRIQUE ET DE L'INDICE DE RÉFRACTION DE MÉLANGES
LIQUIDES BINAIRES À PROXIMITÉ DE LEUR POINT CRITIQUE DE
DÉMIXTION**

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*Cette thèse est dédiée à la mémoire de Marie B. Durocher (1942-2011),
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Résumé

Nous avons étudié la constante diélectrique statique et l'indice de réfraction dans le but de comprendre le comportement critique de mélanges liquides binaires à proximité de leur point critique de démixtion. La théorie la plus récente sur le comportement critique de la constante diélectrique des fluides énonce que l'anomalie observée au point critique est régie par deux contributions distinctes: une contribution extrinsèque, due à la divergence de la densité et proportionnelle à dT_c/dP , où T_c est la température critique de démixtion et P la pression, et une contribution intrinsèque proportionnelle à dT_c/dE^2 , où E^2 est le carré du champ local. Cette théorie, à l'échelle moléculaire, s'applique également à la description du comportement critique de l'indice de réfraction. Le but de notre étude vise à démontrer l'existence de cette contribution intrinsèque au comportement critique de la constante diélectrique et de l'indice de réfraction pour différents mélanges liquides binaires de composition critique.

Nous présentons dans cette thèse trois articles. Dans le premier article, nous avons étudié le comportement critique de la constante diélectrique statique du mélange liquide binaire triéthylamine-eau. Le choix de ce système vient du fait qu'il est le seul mélange liquide binaire où une anomalie intrinsèque dans le comportement critique de l'indice de réfraction ait effectivement été observée. Nous avons donc comparé nos résultats de la constante diélectrique statique avec les données expérimentales antérieures sur l'indice de réfraction et la densité, dans le but d'identifier toutes les contributions présentes dans la région critique de ce système. Nous avons trouvé que la contribution

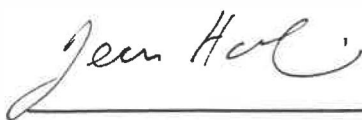
intrinsèque au comportement critique de la constante diélectrique est 5 fois plus importante que la contribution provenant de la densité, et de signe opposé.

Nous avons ensuite étudié le comportement critique de la constante diélectrique d'un mélange liquide binaire que l'on pourrait rendre isopycnique près de son point critique de démixtion, afin d'éliminer ou, à toutes fins pratiques, de réduire considérablement les fluctuations de densité qui apparaissent au point critique. Le but de cette procédure est de permettre une mesure exclusive de la contribution intrinsèque au comportement anormal de la constante diélectrique. Cette étude est l'objet de notre deuxième article. Nous avons choisi le mélange liquide binaire méthanol-cyclohexane car ces deux liquides possèdent des densités similaires à proximité de T_c . En ajoutant une faible quantité de cyclohexane deutéré dans le mélange méthanol-cyclohexane, on obtient un sous-système cyclohexane-cyclohexane deutéré qui possède la même densité que le méthanol au point critique. Nous avons donc étudié le comportement critique de la constante diélectrique statique du mélange liquide binaire méthanol-cyclohexane et celle du mélange liquide pseudo-binaire méthanol-cyclohexane-cyclohexane deutéré. En comparant le comportement critique de la constante diélectrique entre ces deux mélanges, on observe effectivement une diminution notable de l'anomalie au point critique.

Dans notre troisième article, nous présentons une étude du comportement de la chaleur spécifique, de la densité, de la constante diélectrique statique et de l'indice de réfraction à proximité du point critique de démixtion du mélange liquide binaire nitroéthane-cyclohexane dans le but de vérifier les relations qui existent entre ces quantités au point critique. Nous présentons aussi le résultat d'une étude sur la

dépendance en pression de la température critique de démixtion (dT_c/dP). Nous avons vérifié que nos résultats correspondaient bien aux prédictions faites par les théories d'échelle les plus récentes pour le modèle tridimensionnel d'Ising. Nous avons comparé la contribution principale à l'anomalie de la densité avec celle calculée à partir des données expérimentales de la chaleur spécifique et de dT_c/dP . Nous avons également comparé la contribution principale à l'anomalie de la densité avec celle obtenue des données expérimentales de l'indice de réfraction. Plus particulièrement, nous avons étudié le comportement critique de l'indice de réfraction de ce système dans le but d'observer la présence d'une contribution intrinsèque proportionnelle à dT_c/dE^2 . Nous avons choisi le mélange nitroéthane-cyclohexane parce que le comportement de la constante diélectrique de ce système au voisinage du point critique affiche une forte anomalie intrinsèque et parce que le comportement critique de la densité ainsi que la valeur de dT_c/dP sont connus. Cependant, la contribution intrinsèque à l'indice de réfraction proportionnelle à dT_c/dE^2 reste trop faible pour que nous puissions, à l'intérieur des marges de notre incertitude expérimentale, la mettre en évidence.

Ces trois articles représentent ensemble une étude détaillée du comportement diélectrique des mélanges liquides binaires près de leur point critique, contribuant à éclaircir le rôle des différentes contributions à l'origine de l'anomalie observée dans la constante diélectrique et l'indice de réfraction.



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Directeur de recherche

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Table des matières

Résumé	iii
Remerciements	vi
Introduction	1
Revue de la littérature	5
Constante diélectrique près du point critique de démixtion d'un mélange liquide binaire	7
Phénomène de Maxwell-Wagner	8
Relation entre chaleur spécifique, dT_c/dP et densité près du point critique de démixtion d'un mélange liquide binaire	11
Indice de réfraction près du point critique de démixtion d'un mélange liquide binaire ..	12
Description de la méthodologie	13
Résultats expérimentaux	14
Conclusion	17
Liste des références	20
Appendice A: Constante diélectrique du mélange triéthylamine-eau	22
Appendice B: Constante diélectrique du mélange méthanol-cyclohexane	25
Appendice C: Constante diélectrique du mélange méthanol-cyclohexane-cyclohexane deutééré (4.5%)	27
Appendice D: Constante diélectrique du mélange méthanol-cyclohexane -cyclohexane deutééré (9%)	29
Appendice E: Indice de réfraction du mélange nitroéthane-cyclohexane (première manipulation)	31

Appendice F: Indice de réfraction du mélange nitroéthane-cyclohexane (deuxième manipulation)	32
Appendice G: Indice de réfraction du mélange nitroéthane-cyclohexane (troisième manipulation)	33
Article I: Critical Behavior of the Dielectric Constant in the Triethylamine-Water Binary Liquid Mixture: Evidence of an Intrinsic Effect	779
Article II: Intrinsic Dielectric Constant Anomaly in Critical Liquid Mixtures	2733
Article III: The Specific Capacity Singularity and Related Weak Anomalies in the Critical Binary Liquid Mixture Nitroethane-Cyclohexane	A-1

Introduction

Au cours des 25 dernières années, plusieurs études théoriques,¹⁻⁶ appuyées par des mesures expérimentales,⁷⁻²³ ont été faites dans le but de comprendre le comportement anormal de la constante diélectrique statique (ϵ) près du point critique. Le comportement critique de ϵ pour la transition de phase liquide-liquide des mélanges liquides binaires obéit à la même loi d'échelle observée dans la transition de phase gaz-liquide, qui peut être décrite par un modèle mathématique appelé gaz-réseau, similaire au modèle d'Ising.²⁴ Au début de cette période, la situation expérimentale dans ce domaine n'était pas très claire. Les résultats publiés sur le comportement de $\epsilon(T)$ près de la température critique de démixtion T_c de plusieurs mélanges liquides binaires de propriétés diélectriques similaires étaient contradictoires. Certains auteurs^{8,10} observaient un accroissement marqué de ϵ tandis que d'autres^{9,11-13} observaient une faible décroissance. Les travaux de Thoen, Kindt et Van Dael¹⁴ et de Merabet et Bose¹⁵ ont montré que ces différences dans le comportement de ϵ étaient dues à la présence d'impuretés ioniques. Ces auteurs ont démontré que la conductivité ionique, combinée avec les fluctuations importantes de composition des mélanges binaires près du point critique, donnait naissance à une dispersion diélectrique du type Maxwell-Wagner. Par conséquent, seules les valeurs de la constante diélectrique mesurées à une fréquence plus haute que la limite supérieure de la fréquence de relaxation de Maxwell-Wagner (f_{MW}) peuvent être comparées aux prédictions théoriques.

Loin du point critique, une valeur précise de la densité (ρ) peut être obtenue grâce à une mesure de la constante diélectrique par l'entremise de la relation de Clausius-

Mossotti, ou encore de l'indice de réfraction (n) par l'entremise de la relation de Lorentz-Lorenz. Ces relations sont exactes loin du point critique mais inadéquates pour représenter le comportement de ϵ et de n près de T_c . Sengers et al.⁶ ont développé une théorie complète qui introduit une contribution intrinsèque au comportement critique de ϵ et n , proportionnelle à dT_c/dE^2 , où E^2 est le carré du champ local. Cette contribution intrinsèque se superpose à la contribution extrinsèque provenant de la densité et proportionnelle à dT_c/dP , où P est la pression. L'existence de cette contribution intrinsèque au comportement critique de ϵ pour les mélanges liquides binaires a été démontrée par Thoen et al.,¹⁴ Merabet et Bose,¹⁵ Jacobs et Greer¹⁶ et Hamelin, Bose et Thoen.²³ La contribution intrinsèque au comportement critique de n n'a été observée que pour le mélange liquide binaire triéthylamine-eau par Pépin, Bose et Thoen.²⁵ Bien qu'à l'extérieur du cadre de cet ouvrage, il faut mentionner que l'observation unique de la contribution intrinsèque au comportement anormal de n pour le système triéthylamine-eau par Pépin et al.²⁵ a suscité beaucoup de commentaires de la part de Beysens et Zalczer²⁶ qui n'avaient pas observé d'anomalie intrinsèque à n pour le même système. Il est donc très important d'obtenir le maximum d'informations sur ce dernier système par l'étude d'autres propriétés physiques qui le caractérise près du point critique.

Le but visé par notre étude est de mettre en évidence et de comprendre les mécanismes du comportement anormal de la dépendance thermique de ϵ et n à proximité de la température critique de démixtion (T_c), pour différents mélanges liquides binaires le long de leur isochore critique (X_c). Pour réaliser cet objectif nous avons étudié dans notre premier article ϵ en fonction de la température et de la fréquence à proximité de T_c pour le

mélange liquide binaire triéthylamine-eau. Nous avons montré que ce système possède une contribution intrinsèque au comportement critique de ε et de signe opposé à celle de la densité. Nous avons également comparé nos résultats avec ceux connus pour l'indice de réfraction²⁵ et la densité²⁷ dans la région critique, afin de montrer sur un même graphique toutes les contributions présentes.

Dans le deuxième article, nous avons choisi un mélange liquide binaire dont les densités des deux liquides sont similaires, soit le méthanol-cyclohexane. Notre idée était que si l'on pouvait rendre ce système isopycnique à proximité de T_c , cela aurait pour conséquence de réduire considérablement la contribution provenant de la densité, nous permettant d'obtenir directement la contribution intrinsèque au comportement critique de ε . Houessou et al.²⁸ ont démontré que l'ajout d'une faible quantité de cyclohexane deutéré, dans le mélange liquide binaire méthanol-cyclohexane, rendait effectivement ce système isopycnique près de T_c , tout en conservant son caractère de mélange binaire. Nous avons donc étudié ε en fonction de la température et de la fréquence à proximité de T_c , dans le mélange liquide binaire méthanol-cyclohexane, et dans le mélange liquide pseudo-binaire méthanol-cyclohexane-cyclohexane deutéré et nous avons observé une diminution de l'anomalie dans le comportement critique de ε . Pour nous assurer que cette diminution est bien réelle, nous avons ajouté suffisamment de cyclohexane deutéré pour que, au point critique, la phase riche en cyclohexane-cyclohexane deutéré soit plus lourde que la phase riche en méthanol. Nous avons observé, pour ce dernier système pseudo-binaire, une augmentation de l'anomalie dans le comportement critique de ε pratiquement aussi importante que pour le mélange liquide binaire méthanol-cyclohexane.

Finalement, pour notre troisième article nous avons choisi d'étudier le comportement critique de l'indice de réfraction (n) du mélange liquide binaire nitroéthane-cyclohexane dont le comportement de la constante diélectrique statique (ϵ) et de la densité (ρ) dans la région critique a été étudié par Thoen et al.²⁹ Ces derniers ont démontré que l'anomalie critique de ϵ est de beaucoup supérieure et de signe opposé à celle de ρ justifiant l'intérêt pour étudier le comportement critique de n . Nous avons comparé la contribution principale à l'anomalie de la densité²⁹ avec nos données expérimentales pour l'indice de réfraction mais, dans la limite de notre incertitude expérimentale, aucune contribution intrinsèque provenant de dT_c/dE^2 n'a pu être mise en évidence. Pour compléter cette étude, nous présentons de nouvelles données expérimentales sur le comportement critique de la chaleur spécifique à pression et composition constantes ($C_{p,x}$) qui, combinées avec des mesures de la variation de la température critique de démixtion avec la pression (dT_c/dP), nous ont permis de vérifier la relation d'échelle entre ceux-ci et le comportement singulier de la densité²⁹ près de T_c .

Mentionnons que la notation des coefficients des équations de cette thèse coïncident avec celles des deux premiers articles mais diffèrent de celles du troisième. Le premier article a également la particularité de présenter un mélange liquide binaire possédant un point critique de démixtion inférieur (*lower consolute point*) tandis que les mélanges des deux autres articles possèdent un point critique de démixtion supérieur (*upper consolute point*).

Revue de la littérature

Piekara⁷ fut le premier, en 1932, à mesurer le comportement anormal de la constante diélectrique près du point critique de démixtion du mélange liquide binaire nitrobenzène-hexane. Cependant, il fallut attendre jusqu'à 1973 pour que Mistura² élabore une théorie qui décrit avec succès le comportement critique de la constante diélectrique statique. Mistura a relié, par des arguments thermodynamiques et en utilisant le postulat de comportement monotone (*smoothness postulate*³), la partie singulière (critique) de la constante diélectrique statique à celle de l'énergie interne du système dont le comportement est caractérisé par l'exposant critique $1-\alpha$. La première étude expérimentale complète qui confirma cette théorie fut réalisée par Thoen, Kindt et Van Dael¹⁴ en 1980. Ils ont également observé que le comportement critique de la constante diélectrique était influencé par un phénomène de dispersion diélectrique à basse fréquence, qu'ils ont attribué à une relaxation interfaciale dite de Maxwell-Wagner. Également en 1980, suivant l'idée originale de Mistura,² Sengers et al.⁶ ont développé une théorie complète qui décrit les comportements critiques de la constante diélectrique statique et de l'indice de réfraction, théorie qui inclut des termes de correction d'échelle. Ils ont montré que le comportement critique de la constante diélectrique et de l'indice de réfraction possédait deux contributions distinctes: une contribution extrinsèque, due à la divergence de la densité et proportionnelle à dT_c/dP , et une contribution intrinsèque proportionnelle à dT_c/dE^2 . En 1982, Merabet et Bose¹⁵ ont vérifié cette dernière théorie par une étude détaillée du comportement critique de la constante diélectrique statique en tenant compte du phénomène de Maxwell-Wagner. Pépin, Bose et Thoen,²⁵ en 1988, ont

observé pour la première fois la contribution intrinsèque au comportement critique de l'indice de réfraction. Comme mentionné dans l'introduction, à une échelle réduite, l'indice de réfraction est soumis aux mêmes mécanismes critiques que la constante diélectrique. Une revue complète du comportement critique de la constante diélectrique statique, de la conductivité électrique et du phénomène de Maxwell-Wagner pour trois différents mélanges liquides binaires fut publiée en 1989 par Thoen et al.²⁹ Cet article incluait entre autre une première description théorique du comportement critique du phénomène de Maxwell-Wagner. Une autre étude expérimentale sur le comportement critique de la constante diélectrique statique, de la conductivité électrique et du phénomène de Maxwell-Wagner sur le mélange liquide binaire nitroéthane-3-méthylpentane fut réalisée par Hamelin, Bose et Thoen²³ en 1990 et confirma les résultats de Thoen et al.²⁹

La théorie décrivant le comportement critique des paramètres diélectriques des fluides s'étend également à d'autres systèmes comme par exemple les microémulsions. En effet, dans une région spécifique de leur diagramme de phase, les microémulsions se comportent comme des mélanges liquides binaires. Rebbouh, Hamelin, Bose et Thoen³⁰ ont vérifié ce phénomène en 1992, en étudiant le comportement critique de la conductivité électrique pour une microémulsion à quatre composantes. Finalement, les trois articles que nous présentons dans cette thèse forment un ensemble cohérent d'études qui ajoutent aux résultats expérimentaux disponibles obtenus jusqu'ici et qui permettent de mieux comprendre les mécanismes affectant les propriétés diélectriques au point critique.

Constante diélectrique près du point critique de démixtion d'un mélange liquide binaire

En se basant sur une idée initialement proposée par Mistura² sur l'applicabilité du caractère universel des phénomènes critiques au comportement des fluides en présence d'un champ électrique, Sengers et al.⁶ ont développé une théorie complète du comportement critique de ε et n qui incorpore les derniers résultats³¹ de la théorie du groupe de renormalisation sur la description des paramètres thermodynamiques près du point critique. Ils ont obtenu une équation complète [éq. (1) ci-dessous] décrivant ε près de T_c qui inclut les termes de correction d'échelle.³² Ils ont également démontré que la divergence de $d\varepsilon/dT$ lorsque $T \rightarrow T_c$ est régie par deux contributions distinctes: une contribution explicite due à la divergence de ρ^{-1} proportionnelle à dT_c/dP , ainsi qu'une contribution implicite proportionnelle à dT_c/dE^2 . Il est donc important de mesurer ε , n et ρ pour le même mélange liquide binaire de composition critique de manière à déterminer précisément et sans ambiguïté les différentes contributions au point critique.

La description complète de la dépendance en température de ε , obtenue par Sengers et al.⁶ le long de l'isochore critique et à pression constante, s'écrit:

$$\varepsilon \cdot \rho^{-1} = \varepsilon_c \cdot \rho_c^{-1} (1 + E_1 \cdot t + E_2 \cdot t^{1-\alpha} + E_3 \cdot t^{1-\alpha+\Delta_1} + \dots), \quad (1)$$

où $t = |T - T_c|/T_c$, $\alpha = 0.110 \pm 0.005$ et $\Delta_1 = 0.50 \pm 0.02$.³³ L'exposant α décrit le comportement anormal de la chaleur spécifique³⁴ à pression et composition constantes de la classe d'universalité $d = 3$ et $n = 1$ (modèle d'Ising) et Δ_1 est le premier exposant critique de correction d'échelle.³²

Le comportement critique du volume molaire (ρ^{-1}) s'écrit:

$$\rho^{-1} = \rho_c^{-1} (1 + R_1 \cdot t + R_2 \cdot t^{1-\alpha} + R_3 \cdot t^{1-\alpha+\Delta_1} + \dots). \quad (2)$$

Les paramètres critiques ε_c et ρ_c^{-1} ainsi que les E_i et R_i sont des paramètres nonuniversels qui dépendent du système physique. Des éqs. (1) et (2) on déduit la relation pour ε :

$$\varepsilon = \varepsilon_c (1 + D_1 t + D_2 t^{1-\alpha} + D_3 t^{1-\alpha+\Delta_1} + \dots), \quad (3)$$

où $D_1 = E_1 - R_1$, etc. Il existe donc deux contributions au comportement anormal en $t^{1-\alpha}$ de ε : (1) une contribution causée par la divergence de ρ^{-1} ($R_2 \neq 0$) et (2) un effet intrinsèque ($E_2 \neq 0$) pour ε , qui implique aussi que $D_2 \neq -R_2$. Pour l'analyse des données expérimentales, on utilise plus communément la relation suivante pour la densité:

$$\rho = \rho_c (1 + G_1 \cdot t + G_2 \cdot t^{1-\alpha} + G_3 \cdot t^{1-\alpha+\Delta_1} + \dots). \quad (4)$$

Phénomène de Maxwell-Wagner

Le phénomène de Maxwell-Wagner (MW) est un effet de dispersion diélectrique à basse fréquence qui se manifeste dans les milieux hétérogènes. Le modèle le plus simple pour expliquer ce phénomène nous est donné par Maxwell.³⁵ Il consiste en deux couches de matériaux de constante diélectrique et de conductivité électrique différentes insérées entre deux plaques parallèles d'un condensateur (fig. 1a). Du point de vue des impédances ce montage représente deux ensembles de capacitance et conductance en parallèle connectés en série (fig. 1b).

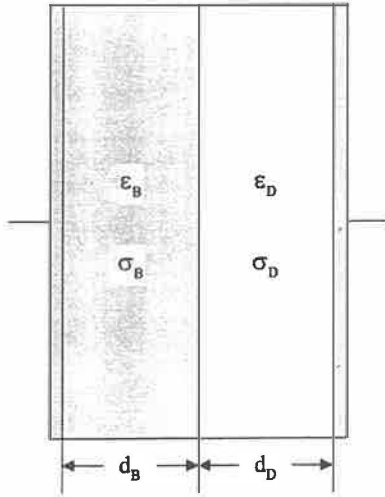


fig. 1a

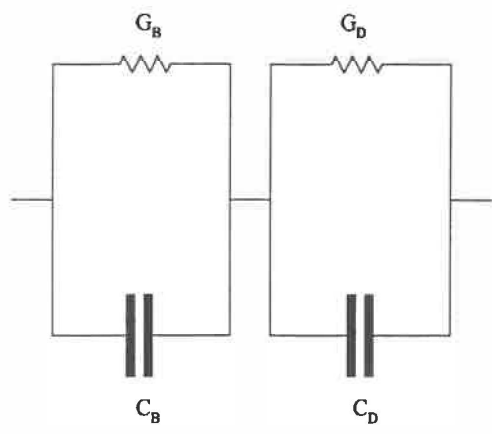


fig. 1b

Utilisant la définition pour la capacitance complexe $C^* = C + G/j\omega$ et la conductance complexe $G^* = G + j\omega C$ on obtient:³⁶

$$C^* = C_h + \frac{C_l - C_h}{1 + j\omega\tau} + \frac{G_l}{j\omega} \quad \text{et} \quad G^* = G_l + \frac{j\omega\tau(G_h - G_l)}{1 + j\omega\tau} + j\omega C_h, \quad (5)$$

où C_p , C_h , G_l et G_h (les indices l et h sont définis à la fig. 2b ci-dessous) ainsi que le temps de relaxation τ peuvent s'exprimer en terme de C_B , C_D , G_B et G_D en utilisant la relation pour la fraction de volume du matériel D, par exemple, et qui est donnée par $\phi = d_D / (d_D + d_B)$. L'éq. (5) peut se traduire en terme de la constante diélectrique et de la conductivité électrique comme suit:

$$\epsilon^* = \epsilon_h + \frac{\epsilon_l - \epsilon_h}{1 + j\omega\tau} + \frac{\sigma_l}{j\omega\epsilon_0} \quad \text{et} \quad \sigma^* = \sigma_l + \frac{j\omega\tau(\sigma_h - \sigma_l)}{1 + j\omega\tau} + j\omega\epsilon_0\epsilon_h, \quad (6)$$

où ϵ_h , ϵ_l , σ_h et σ_l et τ sont maintenant exprimés en terme de ϵ_D , ϵ_B , σ_D , σ_B et ϕ . ϵ_0 est la permittivité du vide. Wagner³⁷ a étendu la théorie décrivant cet effet aux systèmes

hétérogènes composés de micelles en phase dispersée dans un milieu continu (fig. 2a) et a prédit l'apparition d'un temps de relaxation unique $\tau_{MW} = (2\pi f_{MW})^{-1}$ où $f_{MW} = \omega_{MW}/2\pi$ sera presque entièrement déterminée par l'ordre de grandeur de la conductivité du milieu continu (indice B). Une représentation qualitative de la dépendance en fréquence de ϵ et σ est tracée à la fig. 2b.

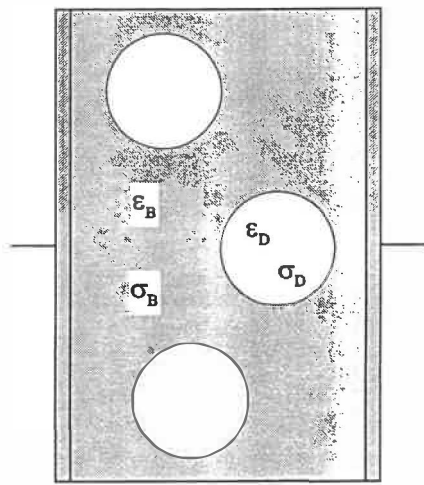


fig. 2a

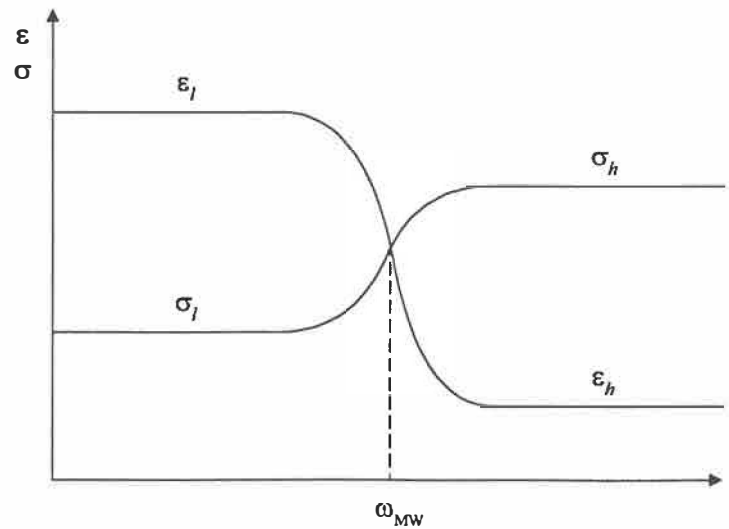


fig. 2b

Les fluctuations de concentration qui deviennent très importantes près du point critique peuvent être considérées comme des micelles. Dans presque tous les cas, on retrouve des impuretés ioniques dans les mélanges liquides binaires polaires-apolaires, provenant en grande partie du fait que les méthodes de purification ne sont pas efficaces à 100% ou, qu'avec le temps, des impuretés se développent de façon naturelle dans l'une des composantes. Lorsque présentes, ces impuretés ioniques interagiront de façon préférentielle avec une des composantes du mélange (e. g. le liquide polaire dans un mélange polaire-non-polaire) et les fluctuations (micelles) qui apparaissent au point

critique vont créer une hétérogénéité similaire au modèle de Wagner.³⁷ Lorsque $T \rightarrow T_c$, ce phénomène provoquera l'apparition d'une dispersion diélectrique²⁹ du type Maxwell-Wagner ayant pour effet, à basse fréquence, de faire croître ϵ . Par conséquent, si on veut mesurer ϵ , on devra déterminer le domaine d'influence de ce phénomène et analyser nos données expérimentales à une fréquence $f \gg f_{MW}$.

Relation entre chaleur spécifique, dT_c/dP et densité près du point critique de démixtion
d'un mélange liquide binaire

Au voisinage de T_c , les parties singulières de la chaleur spécifique $C_{p,x}$ et du coefficient d'expansion thermique $\alpha_{p,x} = \rho^{-1}(\partial\rho/\partial T)_{p,x}$ divergent³ avec le même exposant critique α , et sont reliées à la variation de la température critique avec la pression dT_c/dP par la relation suivante:[†]

$$G_2 = \frac{\rho_c C_2 dT_c}{1 - \alpha dP}, \quad (7)$$

où G_2 est la contribution principale à l'anomalie de la densité telle que définie à l'éq. (4), et C_2 est celle de la chaleur spécifique à pression et composition constantes telle que définie dans la relation suivante pour la phase homogène:

$$C_{p,x} = C_0 + C_1 t + C_2 t^{-\alpha} + C_3 t^{-\alpha+\Delta_1} + \dots \quad (8)$$

Dans la phase ordonnée on obtient:

[†] Il faut mentionner que l'éq. (7) suppose que le changement avec la température de la chaleur spécifique à volume et concentration constantes $C_{v,x}$ près de T_c peut être négligé en comparaison avec $C_{p,x}$.

$$C_{p,x} = C'_0 + C'_1 t + C'_2 t^{-\alpha} + C'_3 t^{-\alpha+\Delta_1} + \dots \quad (9)$$

L'universalité des phénomènes critiques prédit que les paramètres d'amplitude³⁸ des termes singuliers des éqs. (8) et (9) ne sont pas indépendants, mais sont reliés par le rapport universel C'_i/C_i . Les estimés numériques obtenus donnent $C'_2/C_2 = 1.91 \pm 0.04$ par des développements en ϵ du groupe de renormalization (a ne pas confondre avec la constante diélectrique ϵ), $C'_2/C_2 = 1.85 \pm 0.05$ par des méthodes de théorie des champs tridimensionnels et $C'_2/C_2 = 1.91 \pm 0.04$ par des développements en série et des simulations Monte Carlo.

Indice de réfraction près du point critique de démixtion d'un mélange liquide binaire

Le comportement singulier de la constante diélectrique implique aussi un comportement analogue pour l'indice de réfraction puisque $\epsilon = n^2$, pour un milieu de perméabilité magnétique $\mu_m = 1$. La relation décrivant le comportement de l'indice de réfraction au voisinage du point critique sera donc similaire à celle décrivant ϵ , soit:

$$n\rho^{-1} = n_c \rho_c^{-1} (1 + N_1 t + N_2 t^{1-\alpha} + N_3 t^{1-\alpha+\Delta_1} + \dots). \quad (10)$$

Des éqs. (2) et (10) on déduit la relation pour n :

$$n = n_c (1 + F_1 t + F_2 t^{1-\alpha} + F_3 t^{1-\alpha+\Delta_1} + \dots), \quad (11)$$

où les différents paramètres de cette équation sont définis comme dans l'éq. (3) et où $F_2 = N_2 - R_2$. Expérimentalement, il est plus pratique de mesurer la variation d'indice de réfraction Δn plutôt que sa valeur absolue. On utilisera donc la relation suivante:

$$\Delta n = n_0 + n_1 t + n_2 t^{1-\alpha} + n_3 t^{1-\alpha+\Delta_1} . \quad (12)$$

En se référant à la section V du troisième article, si on suppose que seule la densité contribue de façon significative au comportement critique de l'indice de réfraction, on obtient une relation exprimant le paramètre R_2 de l'éq. (2), contribution principale au comportement critique de ρ^{-1} , en terme du paramètre n_2 de l'éq. (12), contribution principale au comportement critique de Δn . Cette relation s'écrit

$$R'_2 = -\left(\frac{\partial \rho}{\partial n}\right)_{p,x}^{\text{reg}} n_2 / \rho_c , \quad (13)$$

où on suppose que le comportement de $\left(\frac{\partial \rho}{\partial n}\right)_{p,x}^{\text{reg}}$ ne dépend pas de la température. Si n possède une contribution intrinsèque près de T_c , nous aurons que $R'_2 \neq R_2$.

Description de la méthodologie

La présente étude consiste en la mesure de la constante diélectrique statique (ϵ) et de l'indice de réfraction (n) de mélanges liquides binaires à proximité de leur point critique de démixtion en fonction de la température (T) et de la fréquence (f) dans le cas de ϵ .

La cellule diélectrique que nous avons conçue pour les mesures de ϵ est décrite en détail dans le premier article. Cette cellule est immergée dans un bain thermostaté où la température est maintenue constante à mieux que ± 0.5 mK. Nous avons mesuré la constante diélectrique statique des mélanges liquides binaires que nous avons étudiés dans leur phase homogène, en commençant à une température suffisamment éloignée du régime critique. Nous nous sommes ensuite approché graduellement de T_c de manière à

obtenir le maximum d'information sur le comportement critique de ϵ . Pour chaque température, nous avons mesuré ϵ pour un ensemble de fréquences afin de situer, en fonction de la fréquence, le phénomène de Maxwell-Wagner.

L'interféromètre à double réseau et la cellule contenant le mélange liquide binaire de composition critique sont décrits en détail dans notre troisième article. La précision de cet interféromètre, $\lambda/256$, en plus de la grande stabilité de notre bain thermostaté, ± 1 mK, nous a permis d'obtenir une résolution de l'ordre du ppm pour Δn . Comme pour les mesures de ϵ , nous avons mesuré l'indice de réfraction du système nitroéthane-cyclohexane de composition critique et en phase homogène, en commençant la mesure à une température située à l'extérieur du régime critique. Nous nous sommes ensuite approché graduellement de T_c de manière à obtenir le maximum d'information sur le comportement critique de n .

Nous avons finalement procédé à une analyse statistique de nos résultats que nous avons tabulés dans nos articles.

Résultats expérimentaux

Tel que mentionné précédemment, les résultats pour la constante diélectrique statique ne sont valables que pour des fréquences supérieures à la région de dispersion du phénomène de Maxwell-Wagner. Ce phénomène est présent dans tous nos échantillons des deux premiers articles et c'est pourquoi nous avons dû étendre nos mesures de ϵ à la plage de fréquences de l'ordre du mégahertz. Une analyse minutieuse de la dépendance en fréquence^{14,29} de ϵ effectuée pour une seule valeur du temps de relaxation de Maxwell-

Wagner nous a confirmé que la différence entre ε mesuré à la fréquence la plus haute et les valeurs extrapolées de ε à plus haute fréquence est plus petite que la dispersion de nos données expérimentales.

Le premier résultat que nous avons obtenu de la paramétrisation des éqs. (3), (4), (8), (9) et (12) avec nos données pour ε , ρ , $C_{p,x}$ et Δn confirme que les exposants critiques^{33,34} obtenus correspondent bien à ceux du modèle d'Ising tridimensionnel, soit $1 - \alpha = 0.89$ et $1 - \alpha + \Delta_1 = 1.39$ (Tableau I de tous les articles).

Dans notre premier article nous avons obtenu pour le mélange liquide binaire triéthylamine-eau une valeur de E_2 égale à -3.70 ± 0.06 pour la contribution intrinsèque au comportement critique de ε [éq. (1)]. Furrow et Greer²⁷ ont obtenu $G_2 = 0.69 \pm 0.04$ pour la contribution provenant de la densité [éq. (4)]. Pépin et al.²⁵ ont également démontré l'existence d'une contribution intrinsèque au comportement critique de n . Ils ont obtenus une valeur de R'_2 [voir éq. (13)] 2 fois inférieure à la valeur de R_2 de Furrow et Greer²⁷, ce qui indique une contribution opposée et donc de même signe que notre valeur de E_2 . Ces contributions au comportement critique de ε et n sont plus aisément mises en évidence lorsque l'on porte en graphique les valeurs de $D_\varepsilon = (\varepsilon - \varepsilon_c)/t$, $(\partial\rho/\partial n)_{p,x}^{\text{reg}} [D_n = (n - n_c)/t]$ et $D_\rho = (\rho - \rho_c)/t$ en fonction de la température tel qu'illustré dans la fig. 7 de notre premier article.

Dans notre deuxième article, nous avons obtenus une valeur de $D_2 = 0.74 \pm 0.01$ [éq. (3)] pour l'échantillon isopycniquméthanol-cyclohexane-cyclohexane deutéré. Si l'on suppose que les fluctuations de densité sont absentes dans cet échantillon, nous

aurons que $D_2 = E_2$, où E_2 est la contribution intrinsèque au comportement critique de ε [éq. (1)]. Si on suppose de plus que cette valeur de E_2 est la même pour les échantillons nonisopycniques méthanol-cyclohexane et méthanol-cyclohexane-cyclohexane deutéré en phases inversées, on peut estimer les valeurs de R_2 de l'éq. (2) pour ces systèmes. Puisque nous avons obtenu $D_2 = 1.96 \pm 0.08$ pour le méthanol-cyclohexane, et $D_2 = 1.76 \pm 0.01$ pour le méthanol-cyclohexane-cyclohexane deutéré (phases inversées), ceci donne des valeurs de R_2 égale à -1.22 ± 0.09 et -1.02 ± 0.02 , respectivement, pour la contribution critique provenant de la densité de ces deux systèmes. Ces valeurs de R_2 pourraient éventuellement être vérifiées par des mesures de densité sur les systèmes méthanol-cyclohexane et méthanol-cyclohexane-cyclohexane deutéré en phases inversées. Cette diminution de la valeur de D_2 est plus apparente lorsque l'on porte en graphique les valeurs de D_ε en fonction de la température des échantillons isopycniques et nonisopycniques. En se référant à la fig. 4 de notre article, on observe une diminution dans la courbe de l'échantillon isopycnique.

Dans notre troisième article, nous avons obtenu comme résultat du rapport des amplitudes C'_2/C_2 une valeur de 1.92 ± 0.05 en accord avec les estimations numériques mentionnées plus haut pour la classe d'universalité du modèle d'Ising tridimensionnel. Nous avons ensuite vérifié l'éq. (7) en utilisant les résultats de notre paramétrisation des données expérimentales²⁹ sur la densité ρ et la chaleur spécifique $C_{p,x}$, la valeur théorique de α et la valeur obtenue pour dT_c/dP . Nous avons obtenu une valeur de $G_2 = -0.042 \pm 0.002$. La valeur que nous obtenons pour G_2 en paramétrisant l'éq. (4) avec les valeurs²⁹ de ρ est -0.034 ± 0.002 . Ces deux valeurs de G_2 sont considérées comme

identiques, malgré qu'il y ait une différence de 0.008 ± 0.004 . On doit considérer le fait qu'elles proviennent de trois expériences différentes faites sur trois échantillons différents. Pour l'indice de réfraction n , nous avons obtenu pour l'éq. (13) une valeur de $R'_2 = 0.037 \pm 0.001$ située entre $R_2 = 0.034 \pm 0.002$, de la paramétrisation de l'éq. (2) avec les données de ρ , et $R_2 = 0.042 \pm 0.002$ de l'éq. (7) où $R_2 = -G_2$. La présence d'une éventuelle contribution intrinsèque à n se situe donc à l'intérieur de notre incertitude expérimentale.

Conclusion

Dans notre premier article, nous avons présenté les résultats d'une étude expérimentale de la constante diélectrique à proximité du point critique de démixtion du mélange liquide binaire triéthylamine-eau. En comparant nos résultats avec les données disponibles sur la densité,²⁷ nous avons établi que la constante diélectrique statique possède une contribution intrinsèque 5 fois plus importante que la contribution extrinsèque provenant de la densité, et de signe opposé. Cette étude, avec celle de Pépin et al.²⁵ sur l'indice de réfraction ainsi que celle de Furrow et Greer²⁷ sur la densité, représente une analyse détaillée du comportement critique des propriétés diélectriques d'un mélange liquide binaire.

Dans notre deuxième article, nous avons présenté les résultats d'une étude expérimentale sur le comportement critique de la constante diélectrique du mélange liquide binaire méthanol-cyclohexane et de deux mélanges liquides pseudo-binaires méthanol-cyclohexane-cyclohexane deutéré dont les rapports cyclohexane-cyclohexane

deutérisé sont différents (l'un est isopycniqne et l'autre a les deux phases inversées comparativement au méthanol-cyclohexane). L'un des systèmes pseudo-binaires de composition critique (deuxième manipulation) a été rendu isopycniqne près de T_c , ce qui nous a permis d'étudier directement la contribution intrinsèque du comportement anormal de la constante diélectrique en réduisant substantiellement les fluctuations provenant de la densité. L'autre système pseudo-binaire (troisième manipulation) a les deux phases inversées, i.e. la phase riche en méthanol se retrouve au-dessus de la phase riche en cyclohexane-cyclohexane deutéré contrairement au système méthanol-cyclohexane. Une anomalie critique de ϵ substantiellement réduite a effectivement été observée dans le cas du système isopycniqne.

Notre troisième article présente plusieurs résultats provenant de l'analyse de nouvelles données expérimentales sur le comportement critique de la chaleur spécifique, de l'indice de réfraction et de la dépendance en pression de la température critique à proximité du point critique de démixtion du système nitroéthane-cyclohexane. Ces résultats, avec ceux déjà publiés²⁹ sur le comportement critique de la constante diélectrique statique et de la densité, nous ont permis de confirmer la validité des prédictions faites par les lois d'échelle. La relation entre la chaleur spécifique, dT_c/dP et la densité également prédite par ces théories d'échelle a été vérifiée. Par contre, la comparaison de nos résultats sur l'indice de réfraction avec les résultats expérimentaux sur la densité ne nous a pas permis de mettre en évidence la contribution intrinsèque au comportement anormal de l'indice de réfraction. Cette étude, avec celle de Thoen et al.²⁹ pour la constante diélectrique statique et la densité, représente une étude détaillée du

comportement critique des propriétés diélectriques, thermiques et mécaniques du système nitroéthane-cyclohexane.

Dans nos deux premiers articles, les études de comportement critique de la constante diélectrique statique que nous avons réalisées sur différents systèmes, nous ont permis de clarifier et de confirmer la validité des théories. Elles démontrent que toute étude rigoureuse de la constante diélectrique en régime critique doit tenir compte de la contribution intrinsèque proportionnelle à dT_c/dE^2 . Nous avons montré qu'en réduisant la contribution extrinsèque proportionnelle à dT_c/dP en utilisant un mélange isopycnique près de T_c , que l'on peut observer directement la contribution intrinsèque au comportement critique de la constante diélectrique. Cette méthode pourrait éventuellement s'appliquer pour observer la contribution intrinsèque au comportement critique de l'indice de réfraction. Il faut mentionner cependant que l'hypothèse de la réduction de la contribution provenant de la densité dans un mélange isopycnique au voisinage de T_c n'a pas été vérifiée expérimentalement. Jacobs et Greer³⁹ ont mentionné que l'hypothèse de la réduction de la contribution critique provenant de la densité dans un mélange liquide isopycnique ne s'appuie sur aucune théorie ou évidence expérimentale. Nous sommes tout à fait d'accord avec cette remarque et acquiesçons que nos résultats expérimentaux ne représentent en rien une preuve formelle de notre hypothèse de départ. Il serait donc intéressant de procéder à des mesures de densité pour ces systèmes de manière à confirmer notre hypothèse.

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Appendice A: Constante diélectrique du mélange triéthylamine-eau

freq (kHz) →		30000	26400	24000	22500	21500	21000	20000
No	T (° C)	ε						
1	12.834	53.823	53.823	53.823	53.823	53.823	53.823	53.823
2	13.338	53.736	53.727	53.730	53.745	53.730	53.727	53.726
3	13.836	53.644	53.640	53.630	53.652	53.634	53.633	53.636
4	13.984	53.615	53.625	53.635	53.643	53.648	53.658	53.657
5	14.328	53.552	53.549	53.546	53.567	53.558	53.555	53.544
6	14.337	53.560	53.557	53.565	53.601	53.596	53.592	53.590
7	14.682	53.494	53.481	53.491	53.510	53.515	53.503	53.509
8	14.941	53.459	53.443	53.434	53.441	53.456	53.457	53.458
9	15.034	53.436	53.422	53.426	53.456	53.448	53.453	53.452
10	15.347	53.390	53.376	53.379	53.388	53.398	53.396	53.401
11	15.740	53.329	53.310	53.321	53.340	53.346	53.344	53.349
12	16.038	53.291	53.267	53.287	53.322	53.306	53.316	53.322
13	16.331	53.253	53.234	53.249	53.284	53.273	53.285	53.290
14	16.582	53.228	53.204	53.234	53.264	53.247	53.259	53.279
15	16.837	53.195	53.192	53.213	53.231	53.242	53.247	53.267
16	16.838	53.200	53.187	53.202	53.221	53.221	53.241	53.260
17	17.084	53.178	53.161	53.186	53.223	53.222	53.219	53.254
18	17.333	53.166	53.162	53.182	53.221	53.207	53.222	53.257
19	17.333	53.161	53.149	53.185	53.227	53.217	53.224	53.242
20	17.533	53.152	53.150	53.175	53.195	53.209	53.218	53.250
21	17.629	53.152	53.163	53.177	53.198	53.208	53.224	53.244
22	17.629	53.149	53.143	53.165	53.186	53.204	53.200	53.247
23	17.733	53.153	53.152	53.165	53.211	53.207	53.208	53.244
24	17.886	53.159	53.159	53.164	53.206	53.210	53.227	53.245
25	17.928	53.156	53.150	53.170	53.221	53.225	53.227	53.260
26	17.978	53.159	53.156	53.172	53.218	53.231	53.231	53.279
27	18.007	53.166	53.168	53.180	53.224	53.244	53.245	53.280
28	18.030	53.174	53.164	53.179	53.232	53.245	53.252	53.287
29	18.054	53.175	53.178	53.184	53.240	53.244	53.258	53.294
30	18.077	53.182	53.178	53.186	53.264	53.272	53.276	53.309
31	18.087	53.181	53.179	53.180	53.252	53.250	53.262	53.287
32	18.097	53.188	53.187	53.192	53.247	53.244	53.250	53.302
33	18.109	53.185	53.192	53.200	53.255	53.254	53.260	53.313
34	18.122	53.191	53.198	53.211	53.260	53.276	53.277	53.328
35	18.134	53.190	53.192	53.199	53.263	53.272	53.279	53.334
36	18.144	53.196	53.201	53.203	53.268	53.284	53.284	53.336
37	18.154	53.197	53.213	53.210	53.268	53.271	53.293	53.340
38	18.164	53.203	53.211	53.216	53.271	53.264	53.282	53.336
39	18.174	53.203	53.229	53.211	53.244	53.263	53.280	53.341
40	18.184	53.211	53.237	53.215	53.273	53.281	53.294	53.351
41	18.199	53.216	53.255	53.232	53.286	53.307	53.309	53.353
42	18.210	53.210	53.249	53.233	53.285	53.306	53.301	53.352
43	18.218	53.218	53.256	53.243	53.286	53.308	53.309	53.355
44	18.221	53.226	53.255	53.235	53.296	53.308	53.316	53.365
45	18.228	53.220	53.262	53.242	53.293	53.313	53.319	53.368
46	18.236	53.234	53.269	53.236	53.292	53.299	53.321	53.367
47	18.242	53.230	53.262	53.234	53.299	53.317	53.339	53.367
48	18.253	53.349	53.271	53.234	53.354	53.381	53.393	53.435
49	18.263	53.356	53.265	53.238	53.362	53.387	53.402	53.452

	16400	14000	12500	11500	11000	10000	6400	4000
1	53.823	53.823	53.823	53.823	53.823	53.823	53.823	53.823
2	53.723	53.735	53.734	53.729	53.727	53.739	53.740	53.728
3	53.643	53.646	53.654	53.647	53.642	53.653	53.655	53.673
4	53.664	53.676	53.680	53.667	53.677	53.680	53.666	53.654
5	53.564	53.573	53.580	53.579	53.589	53.593	53.594	53.608
6	53.609	53.625	53.616	53.617	53.598	53.627	53.627	53.628
7	53.534	53.546	53.555	53.548	53.544	53.553	53.558	53.562
8	53.489	53.511	53.518	53.524	53.527	53.535	53.548	53.575
9	53.495	53.519	53.518	53.515	53.515	53.524	53.534	53.578
10	53.448	53.466	53.479	53.478	53.477	53.485	53.482	53.505
11	53.408	53.442	53.461	53.460	53.459	53.477	53.478	53.502
12	53.382	53.421	53.436	53.433	53.453	53.455	53.475	53.487
13	53.357	53.414	53.435	53.433	53.450	53.458	53.482	53.536
14	53.355	53.406	53.435	53.437	53.447	53.458	53.486	53.545
15	53.346	53.400	53.419	53.417	53.438	53.453	53.482	53.548
16	53.347	53.405	53.431	53.442	53.440	53.461	53.499	53.540
17	53.349	53.407	53.445	53.447	53.458	53.481	53.524	53.556
18	53.351	53.423	53.456	53.474	53.481	53.506	53.555	53.587
19	53.350	53.427	53.447	53.465	53.472	53.501	53.549	53.592
20	53.357	53.438	53.481	53.490	53.500	53.532	53.597	53.620
21	53.366	53.451	53.488	53.502	53.524	53.548	53.624	53.644
22	53.364	53.445	53.485	53.499	53.520	53.541	53.624	53.641
23	53.369	53.457	53.485	53.513	53.527	53.562	53.637	53.665
24	53.393	53.490	53.537	53.556	53.588	53.612	53.697	53.734
25	53.407	53.513	53.570	53.587	53.607	53.641	53.724	53.764
26	53.419	53.534	53.588	53.596	53.620	53.662	53.754	53.803
27	53.437	53.546	53.588	53.616	53.630	53.666	53.772	53.830
28	53.446	53.556	53.607	53.625	53.651	53.683	53.789	53.843
29	53.453	53.563	53.623	53.639	53.656	53.698	53.810	53.865
30	53.467	53.574	53.625	53.650	53.675	53.710	53.809	53.895
31	53.464	53.595	53.647	53.675	53.690	53.733	53.841	53.904
32	53.475	53.591	53.636	53.672	53.689	53.728	53.850	53.894
33	53.483	53.594	53.653	53.683	53.704	53.743	53.864	53.907
34	53.482	53.600	53.649	53.683	53.702	53.735	53.859	53.914
35	53.493	53.614	53.656	53.700	53.697	53.750	53.869	53.928
36	53.500	53.611	53.669	53.694	53.730	53.758	53.874	53.926
37	53.507	53.628	53.691	53.709	53.740	53.772	53.904	53.941
38	53.510	53.626	53.678	53.708	53.723	53.770	53.896	53.949
39	53.516	53.631	53.702	53.718	53.748	53.788	53.917	53.966
40	53.524	53.649	53.706	53.746	53.757	53.798	53.927	54.001
41	53.536	53.674	53.746	53.774	53.778	53.838	53.984	54.014
42	53.537	53.684	53.741	53.775	53.788	53.843	53.970	54.018
43	53.546	53.681	53.750	53.768	53.800	53.841	53.972	54.023
44	53.554	53.689	53.746	53.777	53.802	53.842	53.970	54.026
45	53.550	53.696	53.752	53.777	53.799	53.851	53.988	54.051
46	53.559	53.691	53.755	53.789	53.819	53.861	54.004	54.045
47	53.572	53.718	53.785	53.819	53.836	53.886	54.020	54.063
48	53.661	53.960	54.032	54.070	54.088	54.136	54.275	54.445
49	53.684	53.996	54.055	54.099	54.120	54.164	54.290	54.464

	2500	1500	1000	640	400	250	150	100
1	53.823	53.823	53.823	53.823	53.823	53.823	53.823	53.823
2	53.726	53.739	53.719	53.729	53.723	53.772	54.015	54.392
3	53.674	53.666	53.674	53.692	53.709	53.744	54.236	55.277
4	53.660	53.625	53.654	53.660	53.662	53.877	54.437	54.830
5	53.583	53.561	53.597	53.613	53.572	53.670	54.517	55.805
6	53.634	53.635	53.671	53.627	53.663	53.831	54.699	55.783
7	53.544	53.520	53.527	53.632	53.600	53.813	54.766	55.806
8	53.579	53.568	53.565	53.584	53.592	53.811	54.760	56.152
9	53.567	53.550	53.606	53.645	53.608	53.870	54.998	56.095
10	53.493	53.492	53.523	53.516	53.610	53.858	55.025	56.548
11	53.491	53.490	53.525	53.549	53.637	54.005	55.279	56.889
12	53.456	53.453	53.479	53.590	53.642	54.038	55.496	57.691
13	53.517	53.530	53.549	53.603	53.730	54.222	55.809	58.033
14	53.526	53.534	53.546	53.622	53.709	54.261	56.101	58.604
15	53.522	53.515	53.532	53.630	53.757	54.294	56.256	59.222
16	53.505	53.528	53.541	53.667	53.704	54.378	56.216	59.119
17	53.501	53.559	53.594	53.710	53.824	54.411	56.434	59.319
18	53.546	53.569	53.598	53.722	53.872	54.585	56.862	60.534
19	53.554	53.598	53.660	53.808	53.904	54.481	56.919	60.184
20	53.597	53.628	53.691	53.767	54.039	54.754	57.189	60.865
21	53.616	53.669	53.753	53.845	54.080	54.898	57.090	60.939
22	53.612	53.670	53.730	53.828	54.087	54.945	57.282	60.697
23	53.643	53.705	53.756	53.856	54.175	54.893	57.286	61.110
24	53.722	53.792	53.878	54.029	54.261	55.052	57.558	60.972
25	53.747	53.831	53.904	53.995	54.286	54.925	57.432	61.419
26	53.781	53.855	53.919	54.047	54.339	55.099	57.574	61.209
27	53.810	53.878	53.961	54.047	54.362	55.028	57.639	61.325
28	53.802	53.887	53.944	54.147	54.363	55.171	57.574	61.004
29	53.859	53.894	53.983	54.071	54.457	55.080	57.549	61.397
30	53.866	53.930	54.009	54.137	54.347	55.262	57.824	61.728
31	53.873	53.917	54.013	54.165	54.428	55.215	57.734	61.598
32	53.900	53.951	54.012	54.161	54.511	55.244	57.737	62.031
33	53.920	53.973	54.045	54.170	54.502	55.414	57.954	61.655
34	53.901	53.950	54.085	54.182	54.503	55.389	57.819	61.845
35	53.918	54.015	54.083	54.219	54.583	55.378	58.018	61.664
36	53.912	54.020	54.108	54.240	54.618	55.326	57.981	62.197
37	53.933	54.041	54.115	54.300	54.509	55.446	57.948	61.727
38	53.965	54.059	54.182	54.334	54.535	55.425	58.000	61.867
39	53.971	54.075	54.193	54.318	54.658	55.479	58.092	62.460
40	53.974	54.079	54.177	54.347	54.688	55.314	57.925	62.197
41	54.002	54.087	54.236	54.406	54.715	55.478	58.241	62.387
42	54.015	54.128	54.248	54.393	54.819	55.525	58.082	62.119
43	54.022	54.141	54.239	54.420	54.704	55.607	58.059	62.302
44	54.036	54.141	54.242	54.446	54.720	55.503	58.246	62.468
45	54.028	54.116	54.235	54.428	54.716	55.567	58.265	62.270
46	54.048	54.147	54.241	54.417	54.732	55.491	58.025	62.781
47	54.068	54.159	54.235	54.458	54.762	55.594	58.453	62.564
48	54.438	54.497	54.578	54.726	55.313	56.475	60.150	65.357
49	54.462	54.501	54.632	54.807	55.320	56.859	60.117	65.791

Appendice B: Constante diélectrique du mélange méthanol-cyclohexane

Freq (kHz)→		10	15	25	40	65	100	150	250
No	T (°C)	ε							
1	52.095	5.997	5.989	5.992	5.992	5.992	5.992	5.992	5.992
2	50.823	6.040	6.028	6.029	6.029	6.031	6.031	6.031	6.031
3	50.124	6.046	6.063	6.054	6.057	6.057	6.057	6.057	6.057
4	49.125	6.086	6.094	6.098	6.094	6.094	6.094	6.094	6.094
5	48.621	6.123	6.114	6.115	6.115	6.114	6.114	6.114	6.114
6	48.123	6.127	6.132	6.132	6.132	6.132	6.132	6.132	6.132
7	47.874	6.161	6.147	6.141	6.141	6.143	6.140	6.143	6.143
8	47.623	6.164	6.162	6.152	6.152	6.155	6.152	6.155	6.152
9	47.374	6.166	6.167	6.167	6.167	6.167	6.167	6.164	6.164
10	47.121	6.200	6.188	6.179	6.183	6.179	6.179	6.179	6.176
11	46.875	6.202	6.197	6.188	6.191	6.194	6.191	6.191	6.187
12	46.621	6.205	6.209	6.209	6.203	6.206	6.206	6.206	6.203
13	46.421	6.206	6.224	6.218	6.218	6.217	6.217	6.217	6.214
14	46.324	6.239	6.240	6.228	6.225	6.224	6.224	6.224	6.218
15	46.221	6.240	6.241	6.232	6.232	6.232	6.232	6.232	6.225
16	46.120	6.241	6.246	6.243	6.240	6.242	6.239	6.239	6.233
17	46.123	6.241	6.249	6.243	6.246	6.245	6.245	6.242	6.236
18	46.070	6.242	6.259	6.253	6.250	6.249	6.246	6.246	6.240
19	46.023	6.274	6.262	6.253	6.257	6.253	6.253	6.250	6.243
20	45.974	6.275	6.266	6.257	6.260	6.260	6.256	6.256	6.247
21	45.948	6.275	6.266	6.264	6.260	6.263	6.260	6.257	6.250
22	45.928	6.275	6.270	6.264	6.264	6.263	6.263	6.260	6.250
23	45.912	6.275	6.273	6.267	6.267	6.267	6.263	6.263	6.254
24	45.901	6.275	6.273	6.270	6.267	6.270	6.267	6.264	6.254
25	45.891	6.275	6.273	6.274	6.271	6.270	6.270	6.264	6.254
26	45.885	6.275	6.277	6.271	6.271	6.273	6.270	6.267	6.257
27	45.879	6.276	6.280	6.274	6.274	6.273	6.270	6.267	6.257
28	45.875	6.276	6.286	6.274	6.274	6.273	6.270	6.267	6.257
29	45.869	6.276	6.277	6.274	6.274	6.273	6.270	6.267	6.257
30	45.864	6.276	6.280	6.274	6.271	6.274	6.270	6.267	6.257
31	45.859	6.276	6.280	6.277	6.277	6.274	6.274	6.270	6.261
32	45.856	6.276	6.283	6.274	6.274	6.274	6.270	6.270	6.261
33	45.852	6.276	6.283	6.277	6.274	6.277	6.274	6.270	6.261
34	45.848	6.276	6.287	6.277	6.277	6.277	6.274	6.270	6.261
35	45.843	6.276	6.283	6.277	6.281	6.277	6.274	6.270	6.261
36	45.839	6.308	6.283	6.277	6.277	6.277	6.277	6.271	6.261
37	45.834	6.276	6.280	6.281	6.274	6.277	6.274	6.274	6.261
38	45.830	6.276	6.290	6.278	6.278	6.280	6.277	6.274	6.264
39	45.825	6.308	6.277	6.281	6.278	6.280	6.277	6.274	6.264
40	45.821	6.276	6.287	6.281	6.281	6.280	6.280	6.274	6.264
41	45.817	6.308	6.290	6.284	6.284	6.283	6.280	6.274	6.264
42	45.812	6.308	6.287	6.284	6.284	6.283	6.280	6.277	6.267

	400	650	1000	1500	2500	4000	6500	10000	13000
1	5.992	5.995	5.995	5.994	5.998	5.999	6.001	6.005	6.000
2	6.032	6.031	6.032	6.034	6.034	6.036	6.038	6.039	6.037
3	6.057	6.057	6.057	6.059	6.059	6.061	6.060	6.061	6.059
4	6.094	6.094	6.094	6.093	6.093	6.092	6.091	6.091	6.090
5	6.112	6.111	6.112	6.111	6.111	6.109	6.108	6.105	6.104
6	6.132	6.132	6.129	6.128	6.125	6.123	6.122	6.119	6.119
7	6.141	6.140	6.137	6.136	6.133	6.132	6.131	6.126	6.126
8	6.152	6.149	6.146	6.145	6.142	6.140	6.136	6.133	6.133
9	6.161	6.161	6.155	6.154	6.150	6.149	6.145	6.142	6.141
10	6.173	6.172	6.170	6.165	6.159	6.157	6.153	6.148	6.149
11	6.185	6.181	6.178	6.171	6.168	6.166	6.162	6.155	6.157
12	6.197	6.193	6.187	6.180	6.176	6.171	6.167	6.164	6.163
13	6.208	6.201	6.195	6.188	6.181	6.176	6.172	6.166	6.168
14	6.212	6.205	6.199	6.192	6.185	6.181	6.176	6.168	6.171
15	6.219	6.209	6.203	6.196	6.189	6.185	6.177	6.171	6.173
16	6.227	6.217	6.208	6.200	6.190	6.186	6.181	6.176	6.176
17	6.227	6.220	6.211	6.200	6.194	6.189	6.181	6.174	6.176
18	6.230	6.220	6.211	6.204	6.194	6.189	6.182	6.175	6.177
19	6.234	6.224	6.215	6.204	6.198	6.190	6.185	6.176	6.177
20	6.238	6.228	6.215	6.205	6.198	6.190	6.186	6.177	6.178
21	6.241	6.228	6.215	6.208	6.198	6.194	6.186	6.177	6.179
22	6.241	6.231	6.216	6.208	6.199	6.194	6.186	6.178	6.179
23	6.245	6.231	6.219	6.208	6.199	6.194	6.186	6.178	6.179
24	6.245	6.231	6.219	6.208	6.199	6.194	6.186	6.178	6.180
25	6.245	6.232	6.219	6.208	6.199	6.194	6.187	6.178	6.180
26	6.245	6.232	6.219	6.209	6.199	6.194	6.187	6.179	6.180
27	6.245	6.232	6.219	6.209	6.199	6.194	6.187	6.178	6.180
28	6.245	6.232	6.219	6.209	6.202	6.194	6.187	6.178	6.180
29	6.248	6.232	6.223	6.212	6.202	6.194	6.187	6.179	6.180
30	6.248	6.235	6.219	6.209	6.199	6.194	6.187	6.179	6.180
31	6.248	6.235	6.223	6.212	6.202	6.194	6.187	6.179	6.180
32	6.248	6.235	6.223	6.212	6.202	6.194	6.187	6.179	6.180
33	6.248	6.235	6.223	6.212	6.202	6.194	6.187	6.179	6.180
34	6.248	6.235	6.223	6.212	6.202	6.194	6.187	6.179	6.181
35	6.249	6.235	6.223	6.212	6.202	6.194	6.187	6.179	6.181
36	6.249	6.235	6.223	6.212	6.203	6.194	6.190	6.179	6.181
37	6.249	6.235	6.223	6.212	6.203	6.195	6.187	6.182	6.180
38	6.252	6.235	6.223	6.212	6.203	6.195	6.187	6.179	6.181
39	6.252	6.235	6.223	6.212	6.203	6.195	6.187	6.179	6.180
40	6.252	6.235	6.223	6.212	6.203	6.195	6.190	6.179	6.180
41	6.252	6.235	6.223	6.212	6.203	6.195	6.187	6.179	6.180
42	6.252	6.238	6.223	6.212	6.203	6.195	6.187	6.179	6.180

Appendice C: Constante diélectrique du mélange méthanol-cyclohexane-cyclohexane-
deutééré (4.5%)

Freq (kHz)→		10	15	25	40	65	100	150	250
No	T (°C)	ϵ							
1	51.738	6.016	6.026	6.021	6.022	6.024	6.025	6.025	6.025
2	51.123	6.055	6.043	6.044	6.045	6.043	6.044	6.044	6.044
3	50.696	6.060	6.057	6.058	6.059	6.058	6.058	6.058	6.058
4	50.123	6.066	6.080	6.078	6.078	6.080	6.078	6.078	6.078
5	49.622	6.104	6.095	6.099	6.097	6.095	6.096	6.096	6.096
6	49.123	6.109	6.110	6.111	6.112	6.114	6.115	6.115	6.111
7	48.400	6.150	6.137	6.142	6.139	6.138	6.139	6.142	6.139
8	48.123	6.153	6.150	6.148	6.152	6.151	6.151	6.151	6.148
9	47.821	6.156	6.163	6.158	6.165	6.164	6.161	6.161	6.161
10	47.620	6.191	6.175	6.173	6.174	6.173	6.173	6.170	6.170
11	47.422	6.193	6.174	6.182	6.183	6.181	6.182	6.179	6.179
12	47.222	6.195	6.189	6.187	6.191	6.190	6.191	6.187	6.187
13	47.024	6.197	6.204	6.196	6.200	6.199	6.199	6.199	6.196
14	46.922	6.231	6.202	6.204	6.204	6.203	6.204	6.204	6.200
15	46.821	6.232	6.213	6.208	6.212	6.211	6.211	6.208	6.205
16	46.722	6.233	6.221	6.219	6.216	6.215	6.216	6.212	6.209
17	46.617	6.234	6.219	6.220	6.221	6.223	6.220	6.220	6.214
18	46.527	6.235	6.226	6.227	6.228	6.227	6.224	6.224	6.221
19	46.472	6.236	6.233	6.231	6.232	6.231	6.228	6.228	6.225
20	46.424	6.236	6.234	6.235	6.232	6.234	6.232	6.232	6.225
21	46.385	6.237	6.234	6.242	6.236	6.238	6.235	6.232	6.229
22	46.351	6.237	6.235	6.236	6.236	6.235	6.236	6.236	6.229
23	46.323	6.237	6.238	6.239	6.237	6.239	6.239	6.236	6.233
24	46.307	6.238	6.238	6.243	6.240	6.239	6.240	6.240	6.233
25	46.297	6.238	6.245	6.246	6.247	6.242	6.243	6.240	6.236
26	46.292	6.238	6.248	6.246	6.243	6.245	6.243	6.243	6.236

	400	650	1000	1500	2500	4000	6500	10000	13000
1	6.026	6.026	6.026	6.026	6.029	6.029	6.030	6.030	6.031
2	6.045	6.045	6.045	6.046	6.045	6.045	6.046	6.047	6.048
3	6.060	6.060	6.060	6.060	6.060	6.060	6.060	6.060	6.060
4	6.076	6.076	6.076	6.076	6.076	6.076	6.076	6.075	6.075
5	6.094	6.094	6.094	6.092	6.091	6.091	6.088	6.089	6.088
6	6.109	6.109	6.109	6.107	6.106	6.106	6.104	6.103	6.101
7	6.137	6.134	6.134	6.131	6.127	6.127	6.125	6.122	6.119
8	6.146	6.143	6.140	6.137	6.137	6.137	6.131	6.129	6.125
9	6.156	6.153	6.153	6.147	6.147	6.143	6.141	6.137	6.134
10	6.165	6.162	6.158	6.156	6.152	6.149	6.146	6.143	6.138
11	6.174	6.170	6.164	6.161	6.157	6.157	6.152	6.148	6.144
12	6.182	6.176	6.173	6.170	6.166	6.163	6.157	6.154	6.150
13	6.191	6.184	6.178	6.175	6.168	6.165	6.163	6.158	6.153
14	6.195	6.189	6.182	6.177	6.173	6.170	6.164	6.161	6.156
15	6.200	6.193	6.187	6.181	6.177	6.171	6.168	6.163	6.158
16	6.204	6.198	6.191	6.185	6.178	6.175	6.169	6.166	6.161
17	6.208	6.199	6.192	6.187	6.183	6.179	6.174	6.168	6.163
18	6.213	6.203	6.197	6.191	6.184	6.181	6.175	6.170	6.165
19	6.216	6.207	6.200	6.191	6.188	6.181	6.175	6.171	6.166
20	6.217	6.207	6.201	6.195	6.188	6.182	6.176	6.173	6.166
21	6.221	6.211	6.201	6.196	6.189	6.185	6.180	6.174	6.167
22	6.221	6.211	6.205	6.196	6.189	6.186	6.180	6.174	6.168
23	6.225	6.215	6.205	6.196	6.189	6.186	6.180	6.175	6.168
24	6.225	6.215	6.206	6.200	6.193	6.186	6.180	6.176	6.169
25	6.225	6.215	6.209	6.200	6.193	6.186	6.181	6.177	6.176
26	6.225	6.215	6.209	6.200	6.193	6.190	6.181	6.177	6.176

Appendice D: Constante diélectrique du mélange méthanol-cyclohexane -cyclohexane deutéré (9%)

Freq (kHz)→		10	15	25	40	65	100	150	250
No	T (°C)	ϵ							
1	51.923	6.013	6.008	6.007	6.004	6.005	6.008	6.005	6.007
2	50.952	6.022	6.036	6.035	6.036	6.036	6.036	6.037	6.035
3	50.083	6.060	6.062	6.061	6.061	6.062	6.061	6.062	6.061
4	49.274	6.102	6.091	6.090	6.090	6.087	6.087	6.088	6.090
5	48.793	6.106	6.105	6.104	6.104	6.105	6.104	6.102	6.104
6	48.290	6.111	6.113	6.118	6.119	6.119	6.119	6.120	6.118
7	47.897	6.147	6.133	6.131	6.132	6.133	6.132	6.133	6.131
8	47.575	6.153	6.145	6.143	6.144	6.141	6.144	6.145	6.143
9	47.373	6.153	6.151	6.150	6.150	6.151	6.147	6.148	6.147
10	47.196	6.156	6.157	6.156	6.157	6.154	6.157	6.158	6.156
11	47.078	6.157	6.162	6.161	6.161	6.162	6.161	6.163	6.161
12	46.973	6.158	6.166	6.165	6.165	6.163	6.165	6.163	6.162
13	46.873	6.190	6.166	6.165	6.169	6.166	6.166	6.167	6.165
14	46.767	6.193	6.176	6.175	6.175	6.173	6.172	6.173	6.172
15	46.669	6.194	6.179	6.175	6.179	6.176	6.176	6.177	6.175
16	46.571	6.193	6.175	6.178	6.178	6.179	6.178	6.176	6.178
17	46.475	6.196	6.188	6.187	6.187	6.185	6.184	6.185	6.183
18	46.474	6.195	6.181	6.183	6.180	6.181	6.184	6.181	6.180
19	46.394	6.196	6.191	6.186	6.187	6.188	6.187	6.188	6.186
20	46.319	6.197	6.189	6.188	6.189	6.186	6.189	6.187	6.185
21	46.263	6.196	6.191	6.193	6.194	6.191	6.191	6.192	6.190
22	46.201	6.196	6.192	6.187	6.191	6.188	6.188	6.189	6.187
23	46.166	6.199	6.197	6.199	6.197	6.197	6.197	6.198	6.193
24	46.145	6.196	6.195	6.194	6.194	6.192	6.191	6.192	6.191
25	46.102	6.198	6.197	6.199	6.199	6.197	6.196	6.197	6.196
26	46.068	6.197	6.195	6.197	6.195	6.195	6.195	6.196	6.191
27	46.023	6.198	6.200	6.195	6.199	6.197	6.199	6.197	6.195
28	45.970	6.198	6.196	6.198	6.196	6.196	6.199	6.197	6.195
29	45.901	6.198	6.197	6.199	6.196	6.197	6.199	6.197	6.196
30	45.882	6.206	6.196	6.205	6.204	6.197	6.200	6.201	6.199

	400	650	1000	1500	2500	4000	6500	10000	13000
1	6.007	6.009	6.009	6.008	6.008	6.011	6.010	6.013	6.015
2	6.035	6.037	6.037	6.040	6.040	6.039	6.039	6.040	6.041
3	6.061	6.062	6.062	6.062	6.062	6.061	6.064	6.062	6.063
4	6.090	6.088	6.088	6.087	6.087	6.087	6.086	6.088	6.086
5	6.104	6.102	6.102	6.102	6.102	6.101	6.101	6.099	6.098
6	6.118	6.117	6.117	6.116	6.116	6.115	6.115	6.113	6.111
7	6.128	6.130	6.130	6.129	6.126	6.124	6.125	6.123	6.120
8	6.143	6.142	6.142	6.141	6.138	6.138	6.137	6.135	6.131
9	6.147	6.145	6.145	6.145	6.141	6.141	6.140	6.138	6.134
10	6.153	6.155	6.151	6.151	6.143	6.145	6.142	6.138	6.141
11	6.158	6.156	6.156	6.156	6.152	6.152	6.148	6.146	6.143
12	6.162	6.160	6.160	6.156	6.156	6.156	6.152	6.150	6.144
13	6.165	6.164	6.160	6.160	6.157	6.156	6.156	6.151	6.147
14	6.168	6.170	6.167	6.166	6.163	6.162	6.159	6.157	6.151
15	6.172	6.170	6.167	6.167	6.158	6.161	6.155	6.154	6.153
16	6.174	6.173	6.170	6.169	6.166	6.165	6.161	6.160	6.153
17	6.180	6.179	6.175	6.175	6.172	6.171	6.167	6.166	6.157
18	6.180	6.178	6.175	6.174	6.168	6.167	6.167	6.162	6.157
19	6.183	6.182	6.178	6.178	6.175	6.174	6.170	6.169	6.158
20	6.185	6.180	6.180	6.176	6.173	6.173	6.169	6.167	6.160
21	6.187	6.185	6.182	6.178	6.175	6.175	6.171	6.169	6.160
22	6.184	6.183	6.179	6.179	6.176	6.175	6.171	6.166	6.162
23	6.193	6.191	6.185	6.184	6.181	6.181	6.177	6.172	6.164
24	6.187	6.186	6.183	6.182	6.176	6.175	6.171	6.170	6.163
25	6.193	6.191	6.188	6.184	6.181	6.180	6.176	6.175	6.164
26	6.191	6.186	6.183	6.182	6.179	6.179	6.175	6.170	6.164
27	6.192	6.191	6.187	6.184	6.180	6.180	6.176	6.171	6.166
28	6.192	6.190	6.187	6.183	6.180	6.179	6.176	6.174	6.166
29	6.196	6.191	6.188	6.187	6.181	6.180	6.176	6.175	6.167
30	6.196	6.195	6.188	6.187	6.181	6.174	6.172	6.168	6.167

Appendice E: Indice de réfraction du mélange nitroéthane-cyclohexane (première manipulation)

No	T (°C)	K	Δn	No	T (°C)	K	Δn
1	29.634	0.00	0.000000	29	25.032	36.00	0.002490
2	29.433	1.52	0.000105	30	25.030	35.95	0.002486
3	29.234	3.03	0.000210	31	24.930	36.66	0.002535
4	29.041	4.55	0.000315	32	24.831	37.56	0.002598
5	28.832	6.15	0.000425	33	24.735	38.32	0.002650
6	28.633	7.68	0.000531	34	24.633	39.11	0.002705
7	28.435	9.26	0.000640	35	24.535	39.91	0.002760
8	28.232	10.88	0.000752	36	24.433	40.70	0.002815
9	28.032	12.44	0.000860	37	24.333	41.56	0.002874
10	27.832	13.99	0.000968	38	24.235	42.36	0.002930
11	27.632	15.52	0.001073	39	24.133	43.19	0.002987
12	27.431	17.07	0.001181	40	24.133	43.19	0.002987
13	27.231	18.60	0.001286	41	24.034	44.00	0.003043
14	27.030	20.20	0.001397	42	24.033	43.96	0.003040
15	26.832	21.73	0.001503	43	24.032	44.01	0.003044
16	26.634	23.33	0.001613	44	23.982	44.46	0.003075
17	26.632	23.30	0.001611	45	23.935	44.83	0.003100
18	26.429	24.90	0.001722	46	23.934	44.84	0.003101
19	26.429	24.84	0.001718	47	23.934	44.80	0.003098
20	26.236	26.43	0.001828	48	23.932	44.81	0.003099
21	26.032	27.99	0.001936	49	23.909	45.01	0.003113
22	25.834	29.54	0.002043	50	23.883	45.21	0.003127
23	25.633	31.12	0.002152	51	23.882	45.28	0.003131
24	25.533	31.93	0.002208	52	23.860	45.48	0.003145
25	25.434	32.69	0.002261	53	23.844	45.57	0.003152
26	25.331	33.56	0.002321	54	23.832	45.07	0.003117
27	25.231	34.41	0.002380	55	23.823	44.01	0.003044
28	25.137	35.10	0.002427				

Appendice F: Indice de réfraction du mélange nitroéthane-cyclohexane (deuxième manipulation)

No	T (°C)	K	Δn	No	T (°C)	K	Δn
1	29.636	0.00	0.000000	24	25.233	34.38	0.002378
2	29.433	1.62	0.000112	25	25.234	34.41	0.002380
3	29.233	3.05	0.000211	26	25.037	35.91	0.002483
4	29.036	4.65	0.000322	27	24.938	36.72	0.002539
5	28.833	6.20	0.000429	28	24.838	37.49	0.002593
6	28.635	7.68	0.000531	29	24.736	38.33	0.002651
7	28.435	9.36	0.000647	30	24.633	39.19	0.002710
8	28.234	10.83	0.000749	31	24.535	39.87	0.002757
9	28.034	12.40	0.000858	32	24.434	40.74	0.002818
10	27.834	14.04	0.000971	33	24.334	41.52	0.002871
11	27.634	15.56	0.001076	34	24.235	42.44	0.002935
12	27.633	15.46	0.001069	35	24.184	42.74	0.002956
13	27.436	17.00	0.001176	36	24.131	43.27	0.002992
14	27.234	18.67	0.001291	37	24.084	43.63	0.003017
15	27.035	20.16	0.001394	38	24.134	43.27	0.002992
16	26.834	21.83	0.001510	39	24.087	43.53	0.003010
17	26.636	23.33	0.001613	40	24.033	44.00	0.003043
18	26.437	24.95	0.001726	41	23.980	44.54	0.003080
19	26.234	26.40	0.001826	42	23.934	44.84	0.003101
20	26.034	28.04	0.001939	43	23.884	45.25	0.003129
21	25.834	29.54	0.002043	44	23.882	45.32	0.003134
22	25.635	31.15	0.002154	45	23.868	45.45	0.003143
23	25.434	32.83	0.002270				

Appendice G: Indice de réfraction du mélange nitroéthane-cyclohexane (troisième manipulation)

No	T (°C)	K	Δn	No	T (°C)	K	Δn
1	29.637	0.00	0.000000	25	25.236	34.34	0.002375
2	29.433	1.45	0.000100	26	25.136	35.16	0.002432
3	29.237	3.12	0.000216	27	25.034	36.00	0.002490
4	29.025	4.65	0.000322	28	24.935	36.69	0.002537
5	28.833	6.25	0.000432	29	24.834	37.44	0.002589
6	28.634	7.65	0.000529	30	24.732	38.38	0.002654
7	28.433	9.35	0.000647	31	24.636	39.02	0.002699
8	28.235	10.73	0.000742	32	24.535	40.01	0.002767
9	28.037	12.35	0.000854	33	24.435	40.69	0.002814
10	28.037	12.35	0.000854	34	24.335	41.47	0.002868
11	27.835	13.87	0.000959	35	24.235	42.43	0.002934
12	27.634	15.58	0.001077	36	24.183	42.70	0.002953
13	27.428	17.02	0.001177	37	24.137	43.17	0.002986
14	27.238	18.65	0.001290	38	24.086	43.52	0.003010
15	27.033	20.18	0.001396	39	24.031	44.11	0.003051
16	26.833	21.70	0.001501	40	23.985	44.47	0.003075
17	26.636	23.23	0.001607	41	23.958	44.65	0.003088
18	26.636	23.23	0.001607	42	23.933	44.81	0.003099
19	26.434	24.80	0.001715	43	23.916	45.04	0.003115
20	26.234	26.37	0.001824	44	23.895	45.17	0.003124
21	26.027	28.14	0.001946	45	23.885	45.27	0.003131
22	25.835	29.63	0.002049	46	23.874	45.35	0.003136
23	25.636	31.18	0.002156	47	23.869	45.14	0.003122
24	25.434	32.72	0.002263				

Critical behavior of the dielectric constant in the triethylamine-water binary liquid mixture: Evidence of an intrinsic effect

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Experimental data are presented for the dielectric constant in the homogeneous phase near the consolute point of the binary critical liquid mixture composed of triethylamine and water. From a comparison with existing mass density measurements, it is concluded that the critical anomaly in the static dielectric constant clearly shows a strong intrinsic effect opposite in direction from the one in the mass density. Moreover, a complete picture of the critical behavior of the dielectric properties for this system is drawn by including previously published refractive index measurements.

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I. INTRODUCTION

The large fluctuations which develop near the consolute point of binary liquid mixtures affect many physical properties, such as mass density, dielectric constant, and refractive index. The mass density ρ exhibits an anomaly which can be related to the singularity in the heat capacity at constant pressure and concentration $C_{P,X}$, which has a power-law divergence with the critical exponent α . An anomaly is also expected for the static dielectric constant ϵ and the refractive index n on the basis of thermodynamic [1,4] as well as microscopic theories [2,3]. Following an idea first proposed by Mistura [4] on the applicability of critical point universality to the behavior of fluids in the presence of an electric field, Sengers *et al.* [5] developed a complete theory to explain the anomaly in ϵ and n at the critical point. They showed that the divergent behavior of the temperature derivative of ϵ at the critical concentration is governed by two distinct contributions: an implicit contribution due to the divergence of the thermal expansion coefficient related to the rate of change of the critical temperature T_c with pressure P , and an intrinsic contribution related to the change of T_c with the square of the electric field, E^2 .

These two contributions have already been shown to exist by precision measurement of ϵ in the system nitroethane-3-methylpentane [6] and methanol-cyclohexane [7]. One can thus see that the anomalous behavior of the dielectric constant does not follow the same trend as the one of the mass density. The intrinsic anomaly for n has already been measured by Pépin, Bose, and Thoen [8] in the triethylamine-water binary liquid mixture, and, although its relative magnitude is smaller than the one in ϵ , it is nonetheless present and has the same sign.

The purpose of the present paper is to report precise experimental data on the dielectric constant as a function

of temperature in the one-phase region near the lower critical solution point of the binary liquid mixture composed of triethylamine and water (TE-WT). The static dielectric constant measurements for conductive critical mixtures have to be carried out at high frequencies (radio frequency region) beyond the dispersion region of the Maxwell-Wagner absorption. This type of precision measurement is only possible now because of the availability of the impedance meter up to 30 MHz, with a precision of 0.1%.

II. THEORETICAL BACKGROUND

A. Static dielectric constant

When the critical point of a binary liquid mixture at constant pressure is approached along the line of the critical concentration (X_c), all of the recent theories of critical phenomena predict, for the mass density ρ , the refractive index n , and the dielectric constant ϵ near the critical temperature T_c a leading behavior of the form

$$\rho \approx \rho_c + Rt^\theta, \quad (2.1)$$

$$n \approx n_c + Nt^\theta, \quad (2.2)$$

$$\epsilon \approx \epsilon_c + Dt^\theta, \quad (2.3)$$

where ρ_c , n_c , and ϵ_c are the values of the mass density, refractive index, and dielectric constant at the critical point, respectively, t is the reduced temperature $|T - T_c|/T_c$, and $\theta = 1 - \alpha$ is the critical exponent. Note that α characterizes the divergence of the specific heat at constant pressure and concentration $C_{P,X}$. The most recent and successful theory to date is the one from Sengers *et al.* [5]. They obtained a functional form for the static dielectric constant (and the refractive index) near the critical point that includes correction to scaling terms. They

applied critical-point universality to the thermodynamic behavior of fluids and mixtures in the presence of an electric field. They found that for $X = X_c$ the static dielectric constant in the one-phase region near a liquid-liquid critical point should have the functional form

$$\epsilon\rho^{-1} = \epsilon_c\rho_c^{-1}(1 + A_1t + A_2t^\theta + A_3t^{\theta+\Delta_1} + \dots). \quad (2.4)$$

In Ref. [5] they originally used $\tau = |T - T_c|/T$, but this has no bearing on the functional form. We have used T_c in the denominator of t to maintain the uniformity with the functional form used in the literature. For the mass density along the same $X = X_c$ line, a similar expression is obtained:

$$\rho^{-1} = \rho_c^{-1}(1 + B_1t + B_2t^\theta + B_3t^{\theta+\Delta_1} + \dots). \quad (2.5)$$

The correction-to-scaling exponent Δ_1 results from the Wegner [9] expansion for higher-order critical contributions. Renormalization group calculations [10] give $\alpha = 0.110 \pm 0.003$ and $\Delta_1 = 0.51 \pm 0.03$ for systems, like liquid mixtures, belonging to the three-dimensional Ising universality class. The critical parameters ϵ_c and ρ_c and the coefficients A_i 's and B_i 's are system-dependent nonuniversal parameters. From Eqs. (2.4) and (2.5) one deduces the dielectric constant ϵ itself:

$$\epsilon = \epsilon_c(1 + C_1t + C_2t^\theta + C_3t^{\theta+\Delta_1} + \dots), \quad (2.6)$$

where now $C_2 = A_2 - B_2$, etc. There are thus two possible contributions to the critical t^θ behavior of the dielectric constant: (1) a contribution due to the divergence of the thermal expansion ($B_2 \neq 0$), and (2) an intrinsic effect ($A_2 \neq 0$) for the dielectric constant, which also implies $C_2 \neq -B_2$. It is thus clear that the density must be included in the analysis in order to assess unambiguously the critical behavior of the dielectric constant.

B. Maxwell-Wagner effect

In the past the experimental situation on the behavior of the static dielectric constant near liquid-liquid critical points was rather confusing, until it was discovered [11] that this was mainly due to the presence of the Maxwell-Wagner effect in many systems. The Maxwell-Wagner (MW) effect is a low-frequency dielectric dispersion which can occur in heterogeneous systems. When two liquids A and B of conductivities σ_A and σ_B and dielectric constants ϵ_A and ϵ_B are mixed to form a single system, an additional contribution to the conductivity σ and the dielectric constant ϵ may result due to the accumulation of conducting charges at the interface in the boundary between two phases. This charge buildup has a frequency-dependent behavior. This is known as the Maxwell-Wagner dispersion effect. Binary liquid mixtures that might be completely homogeneous systems away from the critical point will show a certain degree of heterogeneity near T_c because of the occurrence of large-size concentration fluctuations. Thus the real static dielectric constant should only be considered at frequencies higher than the Maxwell-Wagner dispersion. The

details of the MW effect have been discussed in a previous publication [12].

III. EXPERIMENT

The present experiment consists in measuring the static dielectric constant of a critical triethylamine-water mixture as a function of temperature at several frequencies between 100 kHz and 30 MHz. Extended frequency measurements in the range 200 MHz–20 GHz have also been carried out with a network analyzer in order to locate the relaxation frequency of triethylamine in water. Details of the apparatus and the experimental procedure are given below.

A. Apparatus used

A sectional view of the sample cell is shown in Fig. 1. The container block has two holes (D) drilled at its bottom surface to facilitate sample filling. On the top surface, a groove is machined to accommodate a Teflon O ring (G). This serves as the seal for the liquids. The bore of the block is chamfered at the top at an angle of 60° to the horizontal. This is to assure that the axial positioning of the electrode assembly within the bore is retained upon dismantling and subsequent reassembly. This is important as it has a bearing on the C_0 of the cell. In contrast to some designs in the literature, the container block here does not serve as the outer electrode; instead it is connected to the ground potential to be used as a shield against noise pickup. A neoprene O ring (C) acts as a seal along with a bakelite cylinder (not in figure) to prevent fouling of the electrical connections atop the assembled cell by the thermostatic fluid. The top lid (B) is also machined out of a 316 stainless steel rod. Six

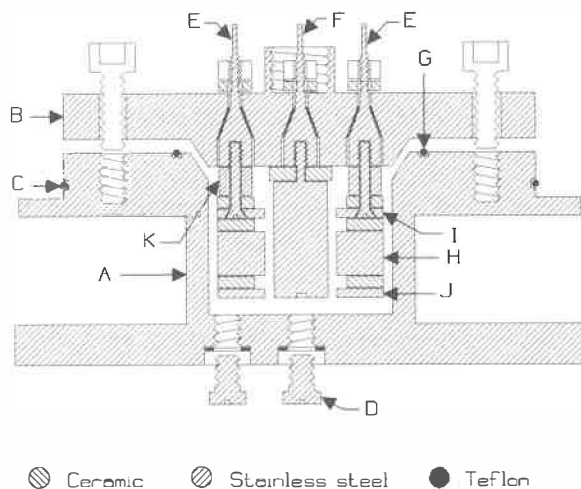


FIG. 1. Sectional view of the dielectric cell: I and J : upper and lower high electrodes, respectively; H : guard electrode; E : pair of feed-throughs for the upper high electrode; F : single feed-through for the low electrode; K : stand-offs (six of them); G : Teflon O-ring; D : two holes to fill the cell; A : cup; B : lid; C : neoprene O-ring for sealing off the electrode feedthroughs with another toplid (not shown). The two pairs of feedthroughs for J and H are not shown. A , B , and H are set to the ground. The cell is cylindrical.

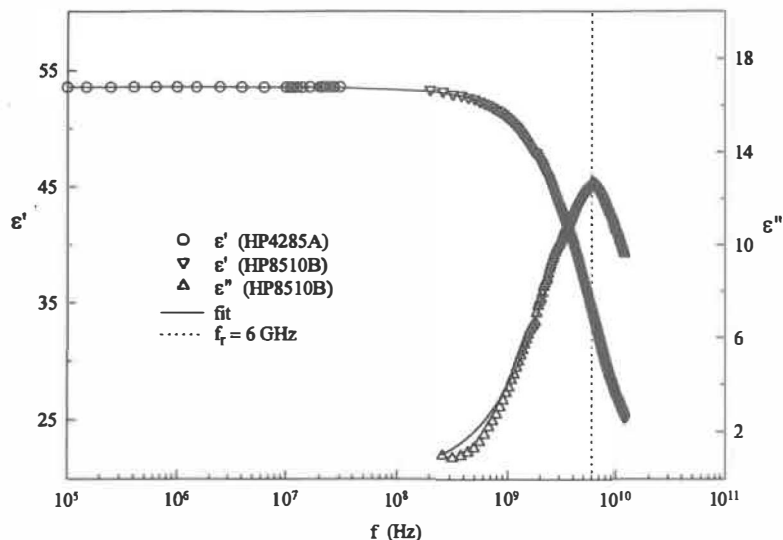


FIG. 2. Semilogarithmic plot of the frequency dependence of the dielectric constant for the critical TE-WT mixture at 10°C.

feedthroughs (E) are mounted radially on the lid to facilitate both mechanical fixture of, and electrical connections for, the outer electrodes. Each of these electrodes H , I , and J contain a central bore and are mounted using two diametrically opposite feedthroughs. The inner electrode is in turn mounted onto the centrally placed feedthrough (F). Atop the conical section of each feedthrough, a thin Teflon conical sleeve is inserted for electrical isolation from the lid. The feedthroughs are tightened onto the lid uniformly with a torque of approximately 2.5 N m. This causes the Teflon to be compressed, and rigidly fixes the feedthroughs in addition to providing a liquid tight seal. The electrodes are separated by discs made of Macor machinable glass ceramic [13] with a quoted zero porosity value. After the assembly of the electrodes and the separating ceramic plates, the capacitor assumes very good mechanical rigidity. The feedthroughs are electrically terminated at BNC connectors.

The capacitance in the range 200 MHz–12 GHz is measured with a Hewlett-Packard network analyzer model HP8510B. The capacitance in the range 100 kHz–30 MHz is measured with a Hewlett-Packard four-terminal impedance meter model HP4285A. The HP4285A, which is an improvement over the original model [14] (HP4275A), uses a state-of-the-art electronic automatic bridge technique and a 90° phase reference generator. A microprocessor controls the analog section that includes the bridge section and manipulates the data taken from the analog section to obtain the desired parameters. The maximum resolution and reproducibility that we could obtain was 0.001 pF at all frequencies, and we measured on the full range of the apparatus which is 75 kHz–30 MHz. The absolute precision for the capacity is $\pm 0.1\%$ (about ± 0.2 pF), but we have instead used the relative precision given from the statistical analysis of the experimental data (about ± 0.004 pF, depending on the data set) due to our interest in the relative values of the physical parameters rather than their absolute values. The temperature of the sample cell is controlled to within 0.5 mK over a period of at least 24 h by means of a

Tronac precision controller bath (model No. 41) filled with water. The temperature is measured with a Guildline platinum resistance thermometer (model No. 9540), which has a resolution of 1 mK and an absolute precision of ± 0.05 K.

B. Experimental procedure

The critical composition of our sample was 32.1 wt. % triethylamine, and T_c was situated between 18.242 and 18.253 °C which are, respectively, the temperature of the last data point taken in the homogeneous phase and the temperature of the first one in the separated phase. This is the same composition as used by Pépin, Bose, and Thoen [8] for the refractive index, Thoen and co-workers [15] for the heat capacity, and Furrow and Greer [16] for the mass density.

IV. RESULTS AND DISCUSSION

We have measured the dielectric constant of the critical mixture TE-WT, in the homogeneous phase, as a

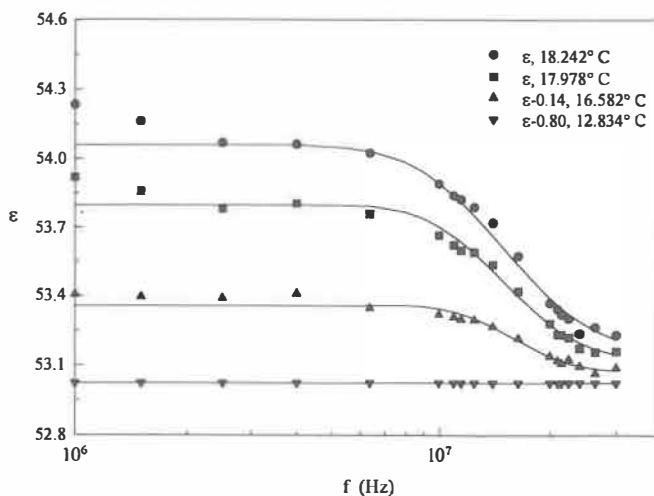


FIG. 3. Semilogarithmic plot of the frequency dependence of the dielectric constant for several temperatures above T_c for the critical TE-WT mixture.

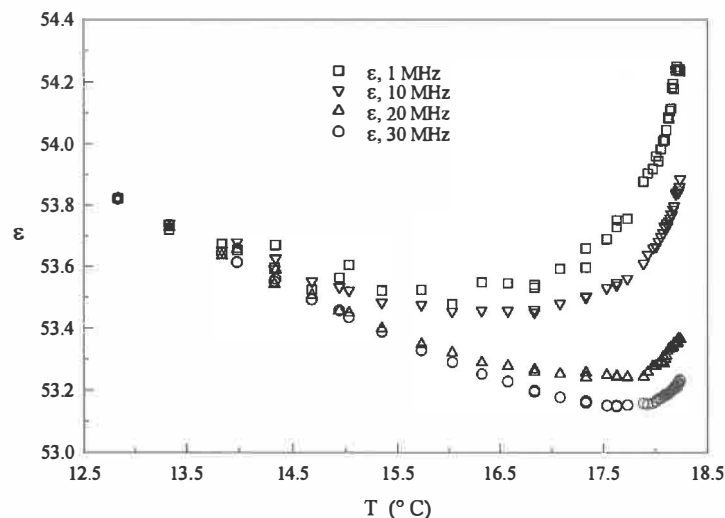


FIG. 4 Temperature dependence of the dielectric constant of the critical TE-WT mixture for four different measuring frequencies.

function of temperature in the range $0.0186 < t < 1.37 \times 10^{-5}$ and as a function of frequency between 100 kHz and 30 MHz. The critical temperature of demixing is situated between the last data point taken in the homogeneous phase (18.242 °C) and the first one in the separated phase (18.253 °C). We also verified that the dielectric constant was not affected by the normal relaxation of this system by measuring ϵ for a single temperature in the homogeneous phase in the frequency range 200 MHz–12 GHz.

The frequency dependence of the dielectric constant is given for a single temperature at 10 °C in Fig. 2. One can see that the relaxation mechanism of the triethylamine-water critical binary mixture has a relaxation frequency $f_r = 6$ GHz, and thus does not affect the value of ϵ in the frequency range 100 kHz–30 MHz. Figure 3 shows the frequency dependence of the dielectric constant for a set of temperatures in the homogeneous phase. An increasing dielectric dispersion, associated with the Maxwell-Wagner effect, is clearly visible as the temperature approaches T_c .

Although we have not looked specifically for the gravity effect by measuring ϵ as a function of height, we have shown in a previous publication [17] that no gravity effect could be detected within the experimental error, near T_c , in the one-phase region of a critical binary mixture composed of nitrobenzene and iso-octane. Greer, Block, and Knobler [18] studied the gravity effect for the system nitroethane-3-methylpentane extensively, and found that the density change close to the center of the sample, near T_c , was insignificant. We can therefore assume that the present measurements, carried out near the center of the sample, should be unaffected by gravity.

As pointed out above, the static dielectric constant data are only obtained at frequencies higher than the Maxwell-Wagner dispersion range. As already clearly demonstrated before [12], a completely different temperature dependence of the dielectric constant can be obtained for measuring frequencies too close to or below the MW relaxation frequency. This is clearly shown in Fig. 4, where we plotted our data for four fixed frequencies as a function of temperature. From Fig. 3 it can be seen

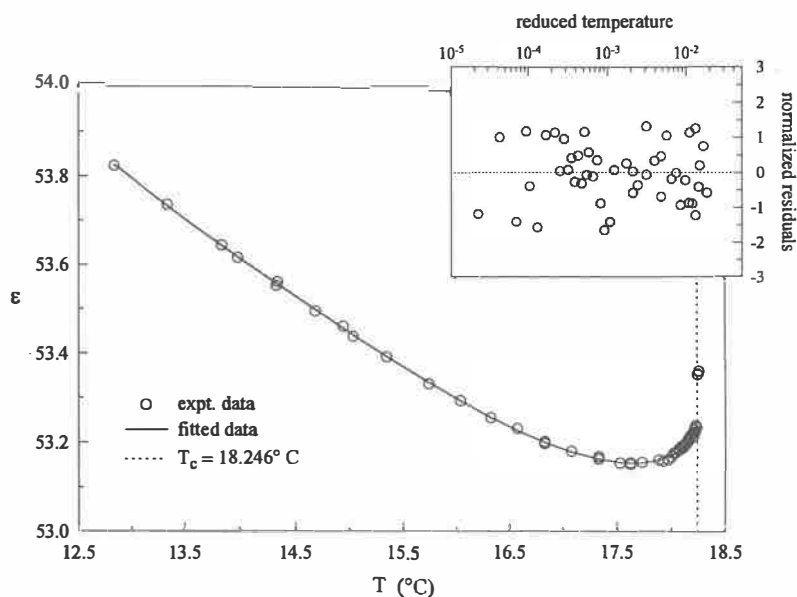


FIG. 5. Temperature dependence of the static dielectric constant (measured at 30 MHz) in the homogeneous phase of the critical TE-WT mixture. The inset shows the random dispersion of the normalized residuals resulting from the fit with Eq. (4.1).

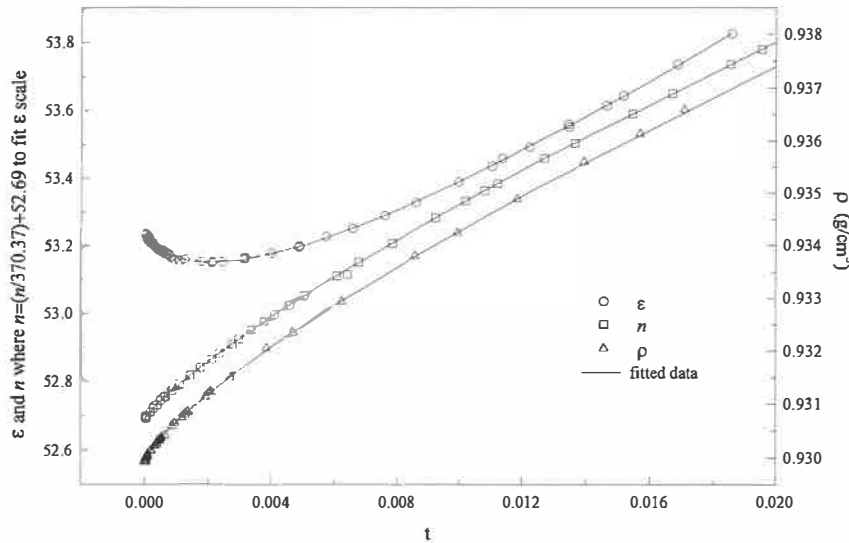


FIG. 6. Temperature dependence of the static dielectric constant (at 30 MHz), refractive index, and mass density in the homogeneous phase of the critical TE-WT mixture.

that the relaxation frequency is situated at about 15 MHz. It has been observed by numerical analysis that a possible contribution of the MW dispersion to our 30-MHz data was smaller than the experimental resolution. These 30-MHz data can then be considered as static dielectric constant values.

The ϵ data taken in the one phase region and at a frequency of 30 MHz are displayed in Fig. 5. The data were fitted to the following functional form:

$$\epsilon = \epsilon_c + D_1 t + D_2 t^\theta + D_3 t^{\theta + \Delta_1}, \quad (4.1)$$

which is identical to Eq. (2.6) with $D_1 = \epsilon_c C_1$, $D_2 = \epsilon_c C_2$, $D_3 = \epsilon_c C_3$, and $\theta = 1 - \alpha$. The analysis of the data was carried out with a modified computer program for non-linear equations called MINUIT, written originally by James and Roos [19]. In Table I, coefficients for the different fits are given. Uncertainties on the parameters correspond to three standard deviations. We have fixed T_c between the last point in the one-phase region and the first point in the two-phase region. We then varied T_c in the range given by these two data points, and looked for a minimum in the reduced chi square value χ_v^2 . This per-

mitted us to have a better resolution on the critical exponents since they are strongly correlated to the critical temperature. The parameters obtained by letting the exponents free in Eq. (4.1) compare very well with the ones obtained by fixing θ and $\theta + \Delta_1$ to the theoretical values¹¹ of 0.89 and 1.39, respectively.

Now, from the results shown in Table I and the parameters obtained by Furrow and Greer [16] for the mass density, we can calculate the value of A_2 in Eq. (2.4):

$$\begin{aligned} A_2 &= C_2 + B_2 = -4.44 \pm 0.02 + 0.74 \pm 0.04 \\ &= -3.70 \pm 0.06, \end{aligned}$$

which is five times larger than B_2 and opposite in sign. In their paper, Pépin, Bose, and Thoen [8] have also shown that the refractive index, for the same system, demonstrates an intrinsic $t^{1-\alpha}$ anomalous contribution which is also opposite in sign to the density contribution. By gathering all the data for ρ , ϵ , and n , we plot in Fig. 6 a complete picture of the different contributions at the critical point for the critical triethylamine-water binary liquid mixture. The refractive index data are from Pépin,

TABLE I. Results of least-squares fits with Eq. (4.1) to the experimental values of the dielectric constant at 30 MHz. The uncertainties quoted are three standard deviations. The values inside the parentheses are held constant for the fit.

T_c (°C)	ϵ_c	D_1	D_2	D_3	θ	$\theta + \Delta_1$	χ^2	χ_v^2
(18.248)	52.230 ± 0.006	279.8 ± 0.7	-159.3 ± 0.4		(0.89)		113.2	2.632
(18.246)	53.241 ± 0.006	442.6 ± 0.6	-236.5 ± 0.4	-211 ± 4	(0.89)	(1.39)	30.87	0.735
18.249 ± 0.025	53.242 ± 0.008	442.5 ± 0.7	-236.7 ± 0.4	-209 ± 4	(0.89)	(1.39)	30.50	0.744
(18.249)	52.243 ± 0.008	443.6 ± 0.7	-236.3 ± 0.8	-220 ± 15	0.889 ± 0.002	1.400 ± 0.008	30.28	0.757

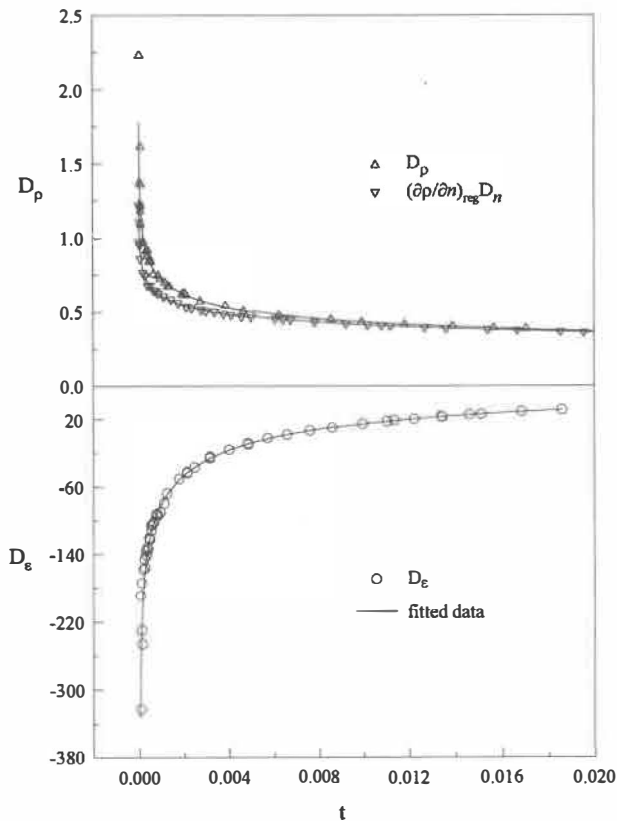


FIG. 7. Plot of the quantity $D_\epsilon = (\epsilon - \epsilon_c)/t$, $(\partial\rho/\partial n)_{\rho,x}^{\text{reg}} D_n \equiv (\partial\rho/\partial n)_{\rho,x}^{\text{reg}} (n - n_c)/t$, and $D_\rho \equiv (\rho - \rho_c)/t$ as a function of $t = (T_c - T)/T_c$ for the critical TE-WT mixture.

Bose, and Thoen [8], while the mass density data are taken from Furrow and Greer [16].

As discussed in previous papers [6–8,12], the comparison of the critical behavior of the dielectric constant and the refractive index with the mass density can be clearly elucidated if one plots $D_\epsilon \equiv (\epsilon - \epsilon_c)/t$, $(\partial\rho/\partial n)_{\rho,x}^{\text{reg}} D_n$

$\equiv (\partial\rho/\partial n)_{\rho,x}^{\text{reg}} (n - n_c)/t$, and $D_\rho \equiv (\rho - \rho_c)/t$ as a function of $t = (T_c - T)/T_c$ (Fig. 7). The comparison of the three curves near the critical point clearly shows that the behavior of the dielectric constant is opposite to that of the mass density, while that of the refractive index is in the same direction as that of the density but smaller in magnitude, thus suggesting an intrinsic critical contribution also opposite in sign from the density contribution.

V. SUMMARY AND CONCLUSION

In this paper we have presented the results of an investigation of the dielectric constant near the critical consolute point of the triethylamine-water binary liquid mixture. From a comparison with available mass density [16] measurements, we have established that the static dielectric constant possesses an intrinsic contribution to its critical behavior which is five times larger and opposite in sign than the extrinsic contribution coming from the mass density. This investigation, along with the refractive index results from Pépin, Bose, and Thoen [8] and the mass density results from Furrow and Greer [16] constitutes the only comprehensive dielectric study of the critical behavior of a binary liquid mixture so far, to our knowledge.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. We would like to thank the governments of Québec and Flanders for financial support for an exchange program between our two laboratories. We would also like to thank Jean-François Rouleau, who made the measurements for ϵ in the frequency range 200 MHz–12 GHz.

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Intrinsic Dielectric Constant Anomaly in Critical Liquid Mixtures

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Experimental data are presented for the dielectric constant ϵ near the consolute point of the binary liquid mixture methanol-cyclohexane and that of pseudobinary liquid mixtures of methanol-cyclohexane-deuterated-cyclohexane. One of the methanol-cyclohexane-deuterated-cyclohexane mixtures is made isopycnic at the critical temperature. This has permitted us to investigate more directly the intrinsic critical contribution to ϵ near the critical point by reducing the contribution resulting from the mass density fluctuations.

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Following an idea first proposed by Mistura [1] on the applicability of critical point universality to the behavior of fluids in the presence of an electric field, Sengers *et al.* [2] developed a complete theory to explain the dielectric constant anomaly at the critical point. They showed that the divergent behavior of the temperature derivative of the dielectric constant at the critical concentration is governed by two distinct contributions: an implicit contribution because of the divergence of the thermal expansion coefficient related to the rate of change of the critical temperature T_c with pressure P and an intrinsic contribution related to the change of T_c with the square of the electric field E^2 .

These two contributions have already been shown [3] to exist by combining precision measurement of the dielectric constant [3] and the mass density [4] on the same system. This way one can see that the anomalous behavior of the dielectric constant does not follow the same trend as that of the mass density. But, as far as we know, a direct attempt to measure the intrinsic contribution to the anomalous behavior of ϵ near T_c has never been made.

Since the contribution of the thermal expansion divergence is related to the mass density difference $\Delta\rho$ between the two phases, we have chosen a mixture in such a way that the mass density of each phase can be adjusted to become as close as possible to each other. In such a case one may expect to suppress the density-related implicit contribution to the critical behavior of the dielectric constant. Therefore we have decided to use the system methanol-cyclohexane since this system has been extensively studied by Houessou *et al.* [5] as a good contender for simulated microgravity measurements. The process of creating an isopycnic mixture is well known and has been well demonstrated by Houessou *et al.* [5] on the system methanol-cyclohexane and by Gopal *et al.* [6] on the system cyclohexane-acetonitrile. Addition of a spe-

cific amount of deuterated cyclohexane to the methanol-cyclohexane mixture makes the system isopycnic in the critical region while still retaining all the features of a critical binary liquid mixture.

The purpose of the present Letter is to report precise experimental data on the dielectric constant near the consolute point of three critical binary or pseudobinary mixtures: methanol + cyclohexane (ME-CH, run 1) and methanol + cyclohexane + deuterated cyclohexane (ME-CH-CH') with a proportion of 4.5% of CH' in the system CH-CH' (run 2) and ME-CH-CH' with a proportion of 9% of CH' (run 3). The particular interest in these systems stems from the fact that, while both critical contributions are expected to be present in the first and the third systems, the contribution from the fluctuations in the mass density is expected to be absent or substantially reduced in the second isopycnic one, allowing a direct measurement of the explicit contribution to ϵ in the critical region. This last system is also a simulation on Earth for conditions encountered in a microgravity environment.

When the critical point of a binary liquid mixture at constant pressure is approached along the line of the critical concentration, all of the recent theories predict for the static dielectric constant ϵ near the critical temperature T_c , a leading behavior of the form

$$\epsilon \approx \epsilon_c + At^\theta, \quad (1)$$

where ϵ_c is the static dielectric constant at T_c , $t = (T - T_c)/T_c$ is the reduced temperature, and $\theta = 1 - \alpha$, with the critical exponent α describing the singularity of the specific heat at constant pressure and concentration. The most recent and successful theory to date is the one from Sengers *et al.* [2]. They obtained a functional form for ϵ near the critical point that includes corrections to scaling terms. They applied the critical point universality to the thermodynamic behavior of fluids and mixtures in the presence of an electric field, and deduced that for $X = X_c$

(X being the mole fraction) the static dielectric constant in the one-phase region near a liquid-liquid critical point should have the functional form

$$\epsilon \rho^{-1} = \epsilon_c \rho_c^{-1} (1 + A_1 t + A_2 t^\theta + A_3 t^{\theta+\Delta_1} + \dots). \quad (2)$$

For the mass density ρ along the same $X = X_c$ line, a similar expression is obtained as

$$\rho^{-1} = \rho_c^{-1} (1 + B_1 t + B_2 t^\theta + B_3 t^{\theta+\Delta_1} + \dots). \quad (3)$$

The correction-to-scaling exponent Δ_1 results from the Wegner [7] expansion for higher-order critical contributions. Renormalization group calculations [8] give $\alpha = 0.110 \pm 0.003$ and $\Delta_1 = 0.51 \pm 0.03$ for systems like liquid mixtures, belonging to the three-dimensional Ising universality class. The critical parameters ϵ_c and ρ_c and the coefficients A_i and B_i are system-dependent nonuniversal parameters. From Eqs. (2) and (3) one deduces the dielectric constant ϵ itself:

$$\epsilon = \epsilon_c (1 + C_1 t + C_2 t^\theta + C_3 t^{\theta+\Delta_1} + \dots), \quad (4)$$

where now $C_2 = A_2 - B_2$, etc. There are thus two possible contributions to the anomalous t^θ behavior of the dielectric constant: (a) a contribution because of the divergence of the thermal expansion ($B_2 \neq 0$) and (b) an intrinsic effect ($A_2 \neq 0$) for the dielectric constant, which also implies $C_2 \neq -B_2$. It is thus clear that the mass density must be included in the analysis or its contribution should be diminished in order to assess unambiguously the intrinsic critical behavior of the dielectric constant.

In the past the experimental situation on the behavior of the static dielectric constant near liquid-liquid critical points was rather confusing until it was discovered [9] that this was mainly because of the presence of the Maxwell-Wagner (MW) effect in many systems. The MW effect is a low frequency dielectric dispersion which can occur in heterogeneous systems. When two liquids A and B of conductivities σ_A and σ_B and dielectric constants ϵ_A and ϵ_B are mixed to form a single system, an additional contribution to the conductivity σ and the dielectric constant ϵ may result because of the accumulation of conducting charges at the interfaces in the boundary between two phases. This charge buildup has a frequency-dependent behavior. This is known as the Maxwell-Wagner dispersion effect. Binary liquid mixtures that may well be completely homogeneous away from the critical point will show a certain degree of heterogeneity near T_c because of the occurrence of large-size concentration fluctuations. Thus the real static dielectric constant should be considered only at frequencies higher than the MW dispersion range. The details of the MW effect have been discussed in a previous publication [10].

The measurements of the dielectric constant as a function of frequency and temperature for the different mixtures have been carried out using a sample cell containing two vertical cylindrical symmetric capacitors. Full details of the measuring cell, sample preparation, and measuring procedure will be given elsewhere [11].

The capacitance is measured with a Hewlett-Packard four terminal LF impedance analyzer (Model No. HP4192A) with frequency capability ranging from 5 Hz to 13 MHz. Experimental data have been obtained in the frequency range between 10 kHz and 13 MHz. The maximum resolution and reproducibility that we could obtain was 0.001 pF at 13 MHz. The temperature of the sample cell is controlled to within 0.5 mK over a period of at least 24 h and measured with a platinum resistance thermometer, which has a resolution of 1 mK and an absolute precision of ± 0.05 K.

As pointed out above, the static dielectric constant data are obtained only at frequencies higher than the MW dispersion range. A completely different temperature dependence of the dielectric constant near the critical point can be obtained for measuring frequencies too close or below the MW relaxation frequency [9,10]. In all three critical mixtures the MW effect was present and measurements had to be extended into the MHz frequency range. This is clearly visible in Fig. 1 where for fixed measuring temperatures ϵ data are given as a function of temperature for all three critical mixtures. From a careful analysis of the frequency dependence and from fits with a single relaxation time expression [9,10] (solid curves in Fig. 1) it can be concluded that the differences between the ϵ (13 MHz) data and the extrapolated ϵ_∞ values are smaller than the scatter of the data points displayed in Fig. 1. Moreover, it should be realized, as can be seen in Fig. 1, that the MW relaxation frequencies (inflection points in the fitted curves) are nearly the same (around 1.5 MHz) for all three mixtures, resulting in almost identical very small deviations [at equal $(T - T_c)$ values] from the static values. For the purpose of further analysis our 13 MHz data can be considered as static dielectric constant values for all three systems.

The ϵ data taken in the one-phase region and at a frequency of 13 MHz for the three critical mixtures of

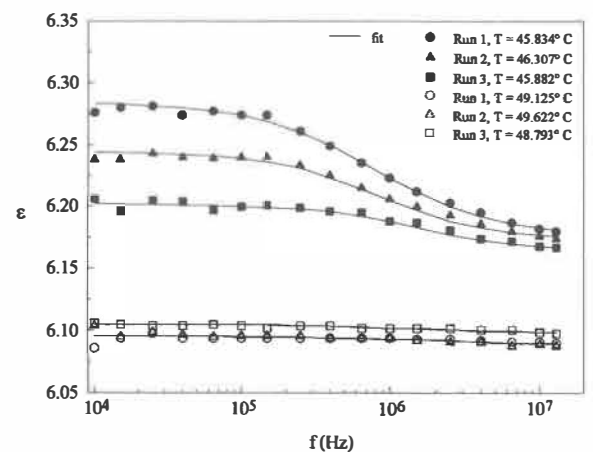


FIG. 1. Frequency dependence of the dielectric constant for several temperatures above T_c for the three different critical mixtures.

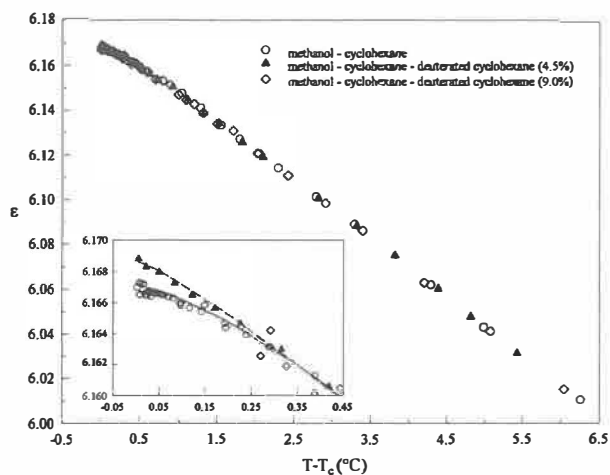


FIG. 2. Temperature dependence of the static dielectric constant (measured at 13 MHz) in the homogeneous phase of the critical mixtures investigated. The curves in the inset result from fits with the parameters given in Table I. Run 1 is the solid line, run 2 the dashed line, and run 3 the dotted line.

ME-CH or ME-CH-CH' are displayed in Fig. 2. The data were fitted to the following functional form:

$$\varepsilon = \varepsilon_c + D_1 t + D_2 t^\theta + D_3 t^{\theta + \Delta_1}, \quad (5)$$

which is identical to Eq. (4) with $D_1 = \varepsilon_c C_1$, $D_2 = \varepsilon_c C_2$, $D_3 = \varepsilon_c C_3$, and $\theta = 1 - \alpha$. The analysis of the data was carried out with a modified computer program for nonlinear equations called MINUIT, written originally by James and Roos [12]. In Table I, coefficients for the different fits are given. Uncertainties on the parameters correspond to three standard deviations. For each run we have fixed T_c between the last point in the one-phase region and the first point in the two-phase region. We then varied T_c in the range given by these two data points and looked for a minimum in the reduced χ^2 value χ_v^2 . This permitted us to have a better resolution on the critical exponents since they are strongly correlated to the reduced temperatures. The parameters obtained by letting the exponents free in Eq. (5) compare very favorably with the ones obtained by fixing θ and $\theta + \Delta_1$ to the theoretical values [8] of 0.89 and 1.40, respectively. In Fig. 3 experimental data are compared with the fitting curves in a semilogarithmic plot.

From the results shown in Table I, we can estimate the value of the critical parameter B_2 in Eq. (3). From run 2 we have $C_2 = D_2/\varepsilon_c = 0.74 \pm 0.01$. From run 1 and

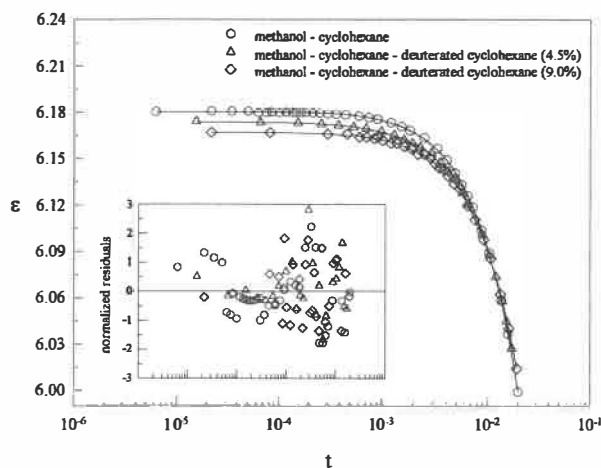


FIG. 3. Semilogarithmic plot of the temperature dependence of the static dielectric constant in the homogeneous phase of the three critical mixtures. Open symbols are the experimental data and the solid curves result from fits to Eq. (5) with the parameter values given in Table I.

run 3, respectively, we obtain $C_2 = 1.96 \pm 0.08$ and $C_2 = 1.76 \pm 0.01$. If we now assume that in the case of run 2, where we have an isopycnic mixture, the contribution from the density anomaly is absent we obtain that $C_2 = A_2$ and only because of the intrinsic critical effect in ε . If we now assume further that in the mixtures of run 1 and run 3 the intrinsic contribution is nearly identical to the one of run 2 we can estimate the coefficients B_2 in Eq. (3) for the nonisopycnic critical mixtures. For run 1 we obtain $B_2 = A_2 - C_2 \approx -1.22 \pm 0.09$ and for run 3 we obtain $B_2 = A_2 - C_2 \approx -1.02 \pm 0.02$.

As discussed in previous papers [3,10], the critical behavior of the dielectric constant as compared with the density can be clearly elucidated if one plots $D_\varepsilon \equiv (\varepsilon - \varepsilon_c)/t$ and $D_\rho \equiv (\rho - \rho_c)/t$ as a function of $t = (T - T_c)/T_c$. To the best of our knowledge, mass density data do not exist for these systems; thus we can compare only D_ε for the three different runs 1, 2, and 3 as shown in Fig. 4. The position of the lower curve for the ME-CH-CH' with 4.5% CH' in the system CH-CH' (run 2) as compared with run 1 and run 3 is again a clear indication of the absence or substantial reduction of the critical anomaly in the mass density.

In this Letter we have presented the results of an investigation of the dielectric constant near critical consolute points of the binary liquid mixture methanol-

TABLE I. Results of least-squares fits with Eq. (5) to the experimental values of the dielectric constant from runs 1 through 3 at 13 MHz. The uncertainties quoted are three standard deviations.

Runs	% CH'	ε_c	D_1	D_2	D_3	θ	$\theta + \Delta_1$	χ_v^2
1	0	6.1801 ± 0.0007	-30.90 ± 0.08	12.14 ± 0.08	20.2 ± 1.7	0.897 ± 0.003	1.44 ± 0.07	1.008
2	4.5	6.174 ± 0.001	-16.46 ± 0.07	4.56 ± 0.07	4.1 ± 2.2	0.89 ± 0.01	1.41 ± 0.03	1.072
3	9	6.167 ± 0.001	-29.2 ± 0.1	10.83 ± 0.07	17.8 ± 0.6	0.887 ± 0.003	1.36 ± 0.02	1.089

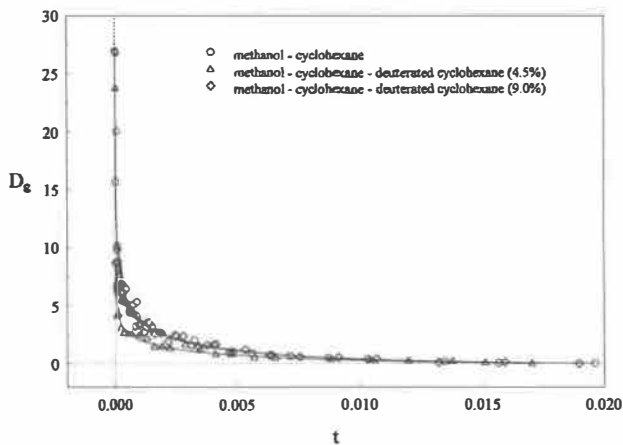


FIG. 4. Plots of the quantity $D_\epsilon \equiv (\epsilon - \epsilon_c)/t$ as a function of the reduced temperature $t = (T - T_c)/T_c$ for the three critical systems investigated.

cyclohexane and of pseudobinary liquid mixtures of methanol-cyclohexane-deuterated-cyclohexane. One of the critical pseudobinary systems (run 2) was made isopycnic. This permitted us to investigate more directly the intrinsic contribution to the static dielectric constant by reducing the critical contribution from the mass density. A substantially smaller critical anomaly in ϵ was indeed observed in the isopycnic case.

It would also be interesting to carry out careful density measurements in these three systems. Finally, it would also be important, but substantially more difficult, to see if the intrinsic contribution for the refractive index [13] could be isolated in the same manner.

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**THE SPECIFIC CAPACITY SINGULARITY AND RELATED WEAK ANOMALIES IN
THE CRITICAL BINARY MIXTURE NITROETHANE-CYCLOHEXANE**

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ABSTRACT

An adiabatic scanning calorimeter has been used to measure the specific heat capacity $C_{p,x}$ of a critical nitroethane-cyclohexane binary liquid mixture in the one-phase and two-phase region above and below the consolute point. The temperature dependence of the refractive index n has been measured with a grating interferometer. Also the change of the critical temperature with pressure has been measured. Combining these new results with existing results for the dielectric constant ϵ and the density ρ allowed a broad inspection of several relationships among these physical quantities. From our analysis it followed that the data are fully consistent with scaling predictions. The critical exponent α and the critical heat capacity amplitude ratio values agree very well with the theoretical values for the three-dimensional Ising universality class. Reasonable agreement was found between the critical amplitude from experimental density data and the value calculated from the specific heat capacity amplitude and the slope of the critical line. In contrast to the dielectric constant results, where a large intrinsic effect is present, a similar effect in the refractive index within the experimental uncertainties could not be detected.

I. INTRODUCTION

Intensive experimental and theoretical efforts during the last two to three decades have resulted in the concept of universality according to which the properties of a system near a critical point can be divided into a small number of universality classes. This concept of universality implies that the critical exponents describing critical behavior of macroscopic properties should only depend on the spatial dimension, the symmetry of the order-parameter, and the symmetry and range of interactions, but not on the details (like form and magnitude) of the interactions [1,2]. Both one-component pure fluids near their liquid-gas critical point and binary liquid mixtures near their consolute point belong to the same universality class as the three-dimensional Ising model [3,4]. In this universality class the critical behavior is determined by two relevant scaling fields, a strong ordering field related to the order-parameter fluctuations and a weak temperature like field related to the energy fluctuations.

We are concerned here with binary liquid mixtures near a consolute point in which case the order-parameter may be identified with the concentration and the strong scaling field with the chemical potential difference [5,6]. One of the consequences of the energy fluctuations is the weak divergence in $C_{p,x}$, the specific heat capacity at constant pressure and critical concentration $x = x_c$ for binary liquid mixtures [6,8]. Since binary liquid mixtures can be investigated at different pressures, there is a line of second-order consolute points with the critical temperature T_c varying with pressure. The work described further was carried out at or near a pressure of one atmosphere.

It can be shown [7] that, asymptotically close to the critical point, the singular part of $C_{p,x}$ and of the thermal expansion coefficient at constant pressure and composition $\alpha_{p,x} = \rho^{-1}(\partial\rho/\partial T)_{p,x}$ diverge with the same critical exponent α and are related to the change of the critical temperature with pressure dT_c/dp . Since the value for α is small ($\alpha = 0.110 \pm 0.002$) [9], the density will have a weak cusp near T_c , increasing or decreasing, depending on the sign of dT_c/dp . Besides the pressure field variable also other fields, e.g. and electric field, will give rise to lines of critical points. Exploring an argument proposed by Mistura [10], Sengers et al. [11] applied critical point universality to the thermodynamic behavior of fluids in the presence of an

electric field, and predicted that in addition to an anomalous contribution arising from the density behavior, there should also be an intrinsic $(1 - \alpha)$ anomaly in the dielectric constant ϵ and in the refractive index n related to the change of T_c with the square of the electric field dT_c/dE^2 .

In this paper we present for the binary liquid system nitroethane-cyclohexane (NE-CH) new data for the specific heat capacity $C_{p,x}$ along the critical composition line $x = x_c$ in the homogeneous phase and in the two-phase region, for the refractive index n in the homogeneous phase at $x = x_c$, and for dT_c/dp . Together with previously obtained results for the dielectric constant [12] and the density [13], this results in a rather complete characterization of this binary system, allowing to explore different relationships among the weak anomalies in a large set of physical parameters.

II. THEORETICAL BACKGROUND

The application of critical point universality to binary liquid mixtures by Sengers et al. [11] results in the homogeneous phase for the critical composition $x = x_c$ in the following functional forms for the energy U (per mole), the density, the dielectric constant and the refractive index:

$$U = U_c (1 + U_1 \tau^\theta + U_2 \tau + U_3 \tau^{\theta+\Delta_1} + \dots), \quad (1)$$

$$\rho^{-1} = \rho_c^{-1} (1 + R_1 \tau^\theta + R_2 \tau + R_3 \tau^{\theta+\Delta_1} + \dots), \quad (2)$$

$$\epsilon \rho^{-1} = \epsilon_c \rho_c^{-1} (1 + E_1 \tau^\theta + E_2 \tau + E_3 \tau^{\theta+\Delta_1} + \dots), \quad (3)$$

$$n \rho^{-1} = n_c \rho_c^{-1} (1 + N_1 \tau^\theta + N_2 \tau + N_3 \tau^{\theta+\Delta_1} + \dots), \quad (4)$$

where $\theta = 1 - \alpha$ and the index c refers to the value at the critical point of the corresponding quantity. $\Delta_1 = 0.50$ is the first correction-to-scaling exponent [9,14] and $\tau = |T - T_c|/T$ is only slightly different from the more commonly used reduced temperature difference $t = |T - T_c|/T_c$. From Eq. (1) one readily obtains for the specific heat capacity in the homogeneous phase:

$$C_{p,x} = C_0 + C_1\tau^{-\alpha} + C_2\tau + C_3\tau^{-\alpha+\Delta_1} + \dots \quad (5)$$

For the two-phase region, this corresponds to

$$C_{p,x} = C'_0 + C'_1\tau^{-\alpha} + C'_2\tau + C'_3\tau^{-\alpha+\Delta_1} + \dots \quad (6)$$

Since experimentally one does not measure $\varepsilon\rho^{-1}$ or $n\rho^{-1}$ but ε or n as a function of temperature, one normally uses, e.g. for fitting purposes, the following type of expressions:

$$\varepsilon = \varepsilon_c(1 + D_1\tau^\theta + D_2\tau + D_3\tau^{\theta+\Delta_1} + \dots), \quad (7)$$

$$n = n_c(1 + F_1\tau^\theta + F_2\tau + F_3\tau^{\theta+\Delta_1} + \dots), \quad (8)$$

where now $D_1 = E_1 - R_1$, $F_1 = N_1 - R_1$, etc. One thus recognizes two possible contributions to the leading anomalous τ^θ behavior of the dielectric constant ε or the refractive index n : (1) a contribution due to the thermal expansion divergence ($R_1 \neq 0$), and (2) an intrinsic effect for the dielectric constant ($E_1 \neq 0$) or the refractive index ($N_1 \neq 0$). In experimental data analysis it is also common practice to fit instead of ρ^{-1} directly the density ρ with an expression of the form:

$$\rho = \rho_c(1 + G_1\tau^\theta + G_2\tau + G_3\tau^{\theta+\Delta_1} + \dots). \quad (9)$$

As already pointed out in the introduction, there is a relationship between the leading singular part of the specific heat capacity and the thermal expansion coefficient in the limit $T \rightarrow T_c$. Indeed, using experimentally verified geometric analysis of phase diagrams of multicomponent systems and rigorous thermodynamic relations one arrives at the following relation between G_1 and C_1 in Eqs. (9) and (5) [7,15]:

$$G_1 = \frac{-\rho_c C_1}{1-\alpha} \frac{dT_c}{dp}. \quad (10)$$

It should also be pointed out that the amplitudes of the singular terms in the equations for $C_{p,x}$ above and below T_c are not independent but related by a universal ratio C'_1/C_1 , identical for all members of a given universality class. The ratio of the amplitudes C'_3/C_3 of the correction-to-

scaling terms (which are only important for large values of τ) is also considered to be a universal quantity.

III. EXPERIMENTAL METHODS

A. Specific heat capacity measurements

The $C_{p,x}$ measurements have been carried out by adiabatic scanning calorimetry previously also used to study binary and ternary liquid mixtures near consolute points [16] as well as several phase transitions in liquid crystal [17-19]. Full details on the construction of the calorimeters and possible modes of operation can be found elsewhere [20,21]. Here, only a brief account of some basic aspect of the measuring procedure will be given as far as needed for proper understanding of the reported results.

In the adiabatic scanning calorimetric method a measured heating power is continuously applied to (or extracted from) the sample and the sample holder. In such a dynamic mode the total heat capacity C_t is given by:

$$C_t = C_{p,x} + C_h = P_t / \dot{T} = (P_c + P_l) / \dot{T}. \quad (11)$$

In Eq. (11) the total heating power P_t has been divided into two parts : P_c the power applied electrically to a heater incorporated in the sample holder, and P_l representing leaks with an (adiabatic) shield surrounding the sample holder. For cooling runs, P_l has to be given a controlled negative value. By keeping P_t or \dot{T} constant, combined with increasing or decreasing the sample temperature, four practical modes of operation are obtained [20,21]. These modes require different settings for the servosystems controlling the temperature and maintaining adiabatic conditions, or a constant heat transfer between sample holder and shieldings. The most interesting operating conditions are the ones with constant heating or cooling power (P_t constant). It is sufficient to consider here only the constant heating mode. In this case, $P_t = P_c$ and P_l is kept negligibly small. In order to obtain the heat capacity of the sample one has to measure P_c , \dot{T} and C_h . P_c is easily obtained from a measurement of the current and the voltage drop across the heating resistor on the sample holder. The rate \dot{T} has to be obtained by numerical differentiation of the carefully measured time dependence of temperature with a sensor in close

thermal contact with the sample. Values of $C_h(T)$ can be derived from calibration runs without the sample or with calibration fluids in the sample holder.

B. Refractive index measurements

We have measured the variation of the refractive index with temperature by counting the fringe variation with a grating interferometer [22]. Fig. 1 gives a schematic diagram of the optical setup. The advantage of this grating interferometer is that it performs a reversible counting and generates a dc compensated signal from the interference fringes.

A linearly polarized He-Ne laser light passes through the first grating (G_1), producing numerous diffraction orders. Two symmetrical beams of the first diffraction order are selected such that one of them acts as a reference beam and the other as a measuring beam. One of the beams passes through a $\lambda/2$ plate (P_1) such that the planes of polarization of the two beams are now perpendicular to each other. The two beams made parallel by the first objective (O_1) then enter the optical cell where one goes through the measuring section and the other through the reference section. This ensures that to a great extent the variation in length due to change in pressure is compensated. The optical cell is embedded into a thermostat which controls the temperature to within $\pm 0.001^\circ$ C over a period of at least 24 hrs. A second objective (O_2) is used to focus the two beams on the second grating (G_2). The planes of polarization of the two beams are not affected by the two gratings. The beams focused on the second grating produce two diffraction patterns superimposed on one another. Among the resultant diffractions only three superposed orders ($0, \pm 2$) have enough contrast so that they can be converted to electrical signals at a later stage.

C. Measurements of dT_c/dp

The experiment consist in measuring the change of the critical temperature as a function of pressure. The sample was contained in a cell made of Pyrex and the change in the critical temperature T_c was noted visually. The precision in the measurements of pressure and temperature was better than 1 kPa and 10 mk. The same experimental setup has previously been

used to measure dT_c/dp for critical microemulsion systems, and full details can be found there [23,24].

D. Measurements of dielectric constant and density

For further analysis and discussion we will use our previously published results for the dielectric constant and the density for the critical binary nitroethane-cyclohexane mixture [12,13]. The constant dielectric data have been obtained with a measuring cell containing two vertically positioned cylindrical capacitors. Each capacitor was designed as a three-terminal system, i.e., both capacitor plates, were isolated from the ground, which included the can surrounding the capacitors and containing the mixture. The two-capacitor setup allowed simultaneous measurements in the two-phase region below T_c . Above T_c it allowed us to verify the absence of composition gradients in the cell. Further details on the construction of the cell, the temperature control and the measuring procedure can be found elsewhere [25]. The density data [26] were obtained with a A. PAAR, type DMA-02D, density meter, where density changes are derived from changes in the natural frequency of a hollow oscillating tube filled with the fluid.

IV. RESULTS

A. Specific heat capacity

Two different adiabatic scanning calorimetric runs have been carried out for a mixture of nitroethane-cyclohexane (NE-CH) with a critical mole fraction $x_c(\text{NE}) = 0.453 \pm 0.001$ as determined from dielectric measurements in the homogeneous phase and in the two-phase region for mixtures with different composition [26]. The first run had a scanning rate $\dot{T} \leq 0.04$ K/h, and the second run had $\dot{T} \leq 0.01$ K/h. In both cases the sample was slowly stirred in the same way as described elsewhere [17,20]. Fig. 2 gives an overview of the $C_{p,x}$ data of run 1, covering a temperature range between 19°C and 28°C. Run 2 only covered a temperature range of about 0.2°C below and above T_c . Fig. 3 gives $C_{p,x}$ results of run 2 in the immediate vicinity of T_c .

From simultaneous fits to the data of run 2 above and below T_c with Eqs. (5) and (6), under the restrains $C'_0 = C_0$, $C'_2 = C_2$ and $C'_3 = C_3 = 0$, the following values for relevant parameters have been obtained :

$$\alpha = 0.11 \pm 0.02, C_1 = 295 \pm 5 \text{ JK}^{-1}\text{kg}^{-1}, \text{ and } C'_1 = 567 \pm 8 \text{ JK}^{-1}\text{kg}^{-1}. \quad (12)$$

Separate fits to the data above and below T_c gave, within the quoted uncertainties, the same parameter values. Fits to the data of run 1 resulted in parameter values with somewhat larger uncertainties but consistent with (12). Including correction-to-scaling terms ($C_3 \neq 0$, $C'_3 \neq 0$) in these fits did not significantly improve the quality of the fits.

B. Refractive index

We have performed three runs with the same critical sample (mole fraction $x_c = 0.453 \pm 0.001$) to verify also its chemical stability. For run 1 the critical temperature was between 23.844°C (last point in the homogeneous phase) and 23.832°C (the first point in the two-phase region). For run 2 T_c was between 23.868°C and 23.852°C and for run 3 between 23.874°C and 23.869°C . Between run1 and run 3 there is a gradual increase of T_c by about 0.034°C , which is acceptable. We started each run from about 30°C , about 6°C above the critical temperature, and measured the fringe variation Δk by decreasing gradually the temperature steps toward T_c . The refractive index variation $\Delta n = n - n(T_0)$ is calculated from Δk by the relation

$$\Delta n = \Delta k \cdot \lambda / l, \quad (13)$$

where $n(T_0)$ is the refractive index value at the starting temperature of the run, $\lambda = 632.8 \text{ nm}$ the wavelength of the He-Ne laser, and l the sample thickness (9.15 mm). The Δn values for the three runs are displayed as a function of temperature in Fig. 4.

The data were fitted to the following functional form:

$$\Delta n = n_0 + n_1 t^\theta + n_2 t + n_3 t^{\theta + \Delta_1}, \quad (14)$$

The analysis of the data was carried out with a modified non-linear least-squares computer program called MINUIT, written originally by James and Roos [27]. In Table I, coefficients for the three different runs are given. Uncertainties on the parameters correspond to three standard deviations. We have limited T_c to the range between the last point in the one-phase region and the first point in the two-phase region. We varied T_c in the range given by these two data points and looked for a minimum in the reduced chi-square value χ^2_ν . For runs 1, 2 and 3 we obtained $T_c=23.834^\circ\text{C}$, 23.854°C and 23.871°C respectively. The parameters obtained by letting the exponents free in Eq. (14) compare very well with the ones obtained by fixing θ and $\theta+\Delta_1$ to the theoretical values [9] of 0.89 and 1.39 respectively. We also verified that replacing $t = |T - T_c|/T_c$ by $\tau = |T - T_c|/T$ in Eq. (14) did not significantly change parameter values.

C. Slope of the critical line

We have measured the change of the critical temperature with applied pressure for a critical mixture ($x_c = 0.453 \pm 0.001$) of nitroethane-cyclohexane in the way briefly described in Sec. III C. A graphical representation of the experimental values for the change in critical temperature $T_c(p) - T_c(p_0)$ for different values of $p - p_0$, with $p_0 = 1 \text{ atm}$, are given in Fig. 5. These data have been fitted with a straight line. The slope of this straight line corresponds to the desired quantity

$$dT_c/dp = (1.484 \pm 0.004) \times 10^{-7} \text{ K/Pa}. \quad (15)$$

D. Dielectric constant and density

For this paper we did not carry out new measurements for the dielectric constant ϵ and the density ρ , because we have done this already in the past and reported them in previous papers [12,13]. For the purpose of the discussion in the next section we briefly repeat here the elements needed there.

The ϵ data in the homogeneous phase, measured at sufficiently high frequency to avoid the low frequency Maxwell-Wagner relaxation phenomenon near the critical point [12,13], showed strongly nonlinear behavior as a function of temperature. Fitting these data with an expression of the form of Eq. (7) resulted in [12,29] :

$$\theta = 0.89 \pm 0.02 \text{ and } D_1 = 1.48 \pm 0.04 . \quad (16)$$

The density data [26] for a critical NE-CH mixture have been fitted [13] with Eq. (2). Good fits could be obtained for the range $\tau \leq 9 \times 10^{-3}$ with $\theta = 1 - \alpha = 0.89$ and $R_3 = 0$ imposed. This resulted in :

$$T_c = 23.7811 \pm 0.0001 \text{ } ^\circ\text{C} , \rho_c = 864.845 \pm 0.002 \text{ kg/m}^3 , \text{ and } R_1 = 0.034 \pm 0.002 . \quad (17)$$

V. DISCUSSION

The $\alpha = 0.11 \pm 0.02$ value given in (12), and obtained from the specific heat capacity data presented in Sec. IV A, fully agrees with the theoretical [9] $\alpha = 0.110 \pm 0.002$. This new result also confirms α results of previous high-resolution specific heat capacity measurements for critical mixtures of triethylamine-heavy water (TEA-D₂O) [16], 3-methylpentane-nitroethane (3MP-NE) [30], and 2,6 lutidine-water (2,6L-H₂O) [31]. The $\theta = 1 - \alpha$ values of (16) for the dielectric constant and of Table I for the refractive index confirm this conclusion.

Since also other critical exponents are in agreement with the theoretical values for the three-dimensional (3D) Ising model, it can be considered as a fact that consolute points of binary liquid mixtures belong to the 3D Ising universality class. Universality, however, not only predicts values for and relationships among critical exponents, but also gives specific predictions for ratios of critical amplitudes above and below T_c for a given physical quantity as well as among amplitudes of different quantities. These relationships have been experimentally investigated in far less detail. Since in the case of NE-CH we have detailed results available on several different quantities, we will further concentrate on these aspects.

Universality predicts that the amplitude ratio C_1'/C_1 of the leading singular terms of the specific heat capacity above and below T_c in Eqs. (5) and (6) is a specific number for each universality class [32]. There are no exact theoretical values available for this ratio, and in the past numerical estimates strongly depended on the calculation method. Recent results, reviewed by Privman et al. [32], seem to converge to a common value around 1.90. From ε -expansion calculations one finds $C_1'/C_1 = 1.91 \pm 0.04$, field theoretical calculations in 3D give 1.85 ± 0.05 , while $C_1'/C_1 = 1.91 \pm 0.04$ is now also obtained from series expansion and Monte Carlo calculations [32]. For NE-CH we obtain from (12) an experimental ratio $C_1'/C_1 = 1.92 \pm 0.05$, which is in very good agreement with the above theoretical values. Our value for NE-CH is somewhat larger than the previously reported value of 1.75 ± 0.03 for TEA-D₂O [16], 1.79 ± 0.06 for 3MP-NE [30], and 1.77 ± 0.09 for 2,6L-H₂O [31].

With Eq. (10) a value for G_1 , the amplitude of the leading singular term of the density in Eq. (9) can be calculated with the C_1 result in (12), the ρ_c value of (17) and dT_c/dp in (15). Further assuming $\alpha = 0.110 \pm 0.002$, we obtain $G_1 = -0.042 \pm 0.002$. From the $R_1 = 0.034 \pm 0.002$ value (17) from the fit to the direct density data, we have $G_1 = -0.034 \pm 0.002$. The two values of G_1 can be considered in satisfactory agreement, also in view of the fact that results from three different experiments with three different samples are involved in the calculations.

The existence of an intrinsic effect in the temperature dependence of the dielectric constant ε in the one-phase region on the critical concentration line of binary liquid mixtures is by now well documented since in 1980 [28] it was demonstrated that a low frequency Maxwell-Wagner relaxation (caused by the presence of ionic impurities) was the reason for quite often conflicting results previously published. Subsequently in 1981, published results of Thoen et al. [12] for NE-CH (briefly summarized in Sec. III D) showed a quite large intrinsic effect and fully confirmed the conclusions of Ref. 28. In fact in the case of NE-CH the intrinsic effect is much larger than and of opposite sign to the density related one (see Fig. 1 of Ref. 13). This can also be verified by comparing the amplitudes $E_1 = D_1 + R_1 = 1.51 \pm 0.04$ and $R_1 = 0.034 \pm 0.002$, obtained from (16) and (17). The existence of an intrinsic, dT_c/dE^2 related, critical contribution to

the temperature dependence of ε has also been observed for several other critical binary liquid mixtures [33-38].

Evidence for the presence of an intrinsic contribution to the refractive index critical behavior has so far only been obtained for the binary system triethylamine-water (TEA-H₂O). The existence of this intrinsic effect was first pointed out by Furrow and Greer [39] by comparing their density data with the existing refractive index of Beysens and Bourgois [40]. This was subsequently confirmed by Pépin et al. [41] on the basis of new refractive index data and the density data of Furrow and Greer. However, Beysens and Zalczer [42] carried out new density and refractive index data and claimed that the critical behavior of the refractive index can be entirely accounted for by the density effect.

Although the critical contribution to both the density and the refractive index for NE-CH are an order of magnitude smaller than for TEA-H₂O, a comparison between our new n results and the available ρ results is possible. From the exact relation

$$\left(\frac{\partial n}{\partial T}\right)_{p,x} = \left(\frac{\partial n}{\partial \rho}\right)_{p,x} \left(\frac{\partial \rho}{\partial T}\right)_{p,x}, \quad (18)$$

it follows that

$$\rho(T) - \rho(T_c) = \int_{T_c}^T \left(\frac{\partial \rho}{\partial n}\right)_{p,x} \left(\frac{\partial n}{\partial T}\right)_{p,x} dT \approx \left(\frac{\partial \rho}{\partial n}\right)_{p,x}^{\text{reg}} [n(T) - n(T_c)]. \quad (19)$$

In the last part of Eq. (19) the assumption of a regular temperature-independent $(\partial \rho / \partial n)_{p,x}$ is made. From a comparison of Eq. (19) with Eq. (14) one can define

$$Q_1 = \left(\frac{\partial \rho}{\partial n}\right)_{p,x}^{\text{reg}} n_1. \quad (20)$$

This quantity can be calculated from n_1 values of Table I provided a value for $(\partial \rho / \partial n)_{p,x}$ is available. This quantity is usually estimated from the ρ and n results far away from T_c [41]. For NE-CH we obtain $(\partial \rho / \partial n)_{p,x} = (1.98 \pm 0.02) \times 10^3 \text{ kg/m}^3$ in this way. Further comparing Eqs. (14), (2) and (20) it follows that

$$R_1 = -Q_1/\rho_c, \quad (21)$$

provided that the above assumptions are valid. An intrinsic contribution to n , which is large enough would, however, result in a R_1 value from Eq. (21) different from R_1 obtained from direct density data analysis. A calculation of R_1 with Eqs. (20) and (21) gives $R_1 = 0.037 \pm 0.001$, which falls in between $R_1 = 0.034 \pm 0.002$ from the direct density results in (17) and $R_1 = 0.042 \pm 0.002$ from $R_1 = -G_1$ and Eq. (10). From this one has to conclude that a possible intrinsic contribution to the critical behavior falls within the experimental uncertainty limits.

VI. SUMMARY AND CONCLUSION

In this paper we have presented new specific heat capacity $C_{p,x}$ and refractive index n data for the critical binary mixture of nitroethane-cyclohexane near the consolute point. Results for the slope of the critical line dT_c/dp have also been reported. The specific heat capacity and refractive index data have been analyzed in terms of the appropriate theoretical expressions (given in Sec. II). The data are fully in agreement with the scaling predictions. The critical exponent α values (for the specific heat capacity and the refractive index), and the amplitude ratio C'_1/C_1 (for the specific heat capacity) agree very well with the theoretical values for the 3D Ising universality class.

The results of the analysis of these new $C_{p,x}$, n and dT_c/dp data have been combined with our previously published results on the dielectric constant ϵ and density ρ , in an effort to investigate relations among several critical amplitudes of these physical quantities. Satisfactory agreement was found between the leading critical amplitude value calculated from the $C_{p,x}$ amplitude [with Eq. (10)] and the value obtained from the analysis of the direct ρ data. In contrast to the situation for the dielectric constant ϵ , where a quite large intrinsic contribution (related to dT_c/dE^2) is present, the possible intrinsic contribution to the critical behavior of the refractive index n does not exceed the uncertainty on the amplitude of the indirect density contribution.

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Table I. Results of least-squares fits with Eq. (14) to the experimental values of refractive index changes for the critical mixture of nitroethane-cyclohexane. The uncertainties quoted are three standard deviations. Parameter values between parentheses have been held constant in the fit.

run	n_0	n_1	n_2	n_3	θ	$\theta + \Delta_1$	χ^2_{G}
1	0.003116 ± 0.000004	-0.0162 ± 0.0002	-0.1382 ± 0.0003	0.006 ± 0.001	(0.89)	(1.39)	1.178
1	0.003159 ± 0.000002	-0.0162 ± 0.0002	-0.1381 ± 0.0003	0.006 ± 0.001	0.890 ± 0.002	1.36 ± 0.05	1.225
2	0.003150 ± 0.000005	-0.0162 ± 0.0002	-0.1381 ± 0.0004	0.006 ± 0.002	(0.89)	(1.39)	1.225
2	0.003150 ± 0.000007	-0.0161 ± 0.0007	-0.1378 ± 0.0009	0.004 ± 0.013	0.887 ± 0.007	1.3 ± 0.4	1.885
3	0.003140 ± 0.000007	-0.0163 ± 0.0003	-0.1381 ± 0.0005	0.007 ± 0.003	(0.89)	(1.39)	1.067
3	0.003140 ± 0.000005	-0.0164 ± 0.0003	-0.1382 ± 0.0005	0.008 ± 0.003	0.892 ± 0.004	1.45 ± 0.02	1.119

CAPTIONS FOR FIGURES

Fig. 1 Schematic diagram of the grating interferometer.

Fig. 2 The specific heat capacity results of run 1 for the critical binary liquid mixture of nitroethane-cyclohexane.

Fig. 3 The specific heat capacity results of run 2 for the critical binary liquid mixture of nitroethane-cyclohexane in a temperature range very close to the critical point.

Fig. 4 Temperature dependence of the refractive index for the critical binary liquid mixture of nitroethane-cyclohexane in a temperature range very close to the critical point for run 1, 2 and 3. The solid curve results from a fit to the data of run 1 with Eq. (14). The inset at the upper right shows the random dispersion of the normalized residuals resulting from the fit with Eq. (14).

Fig. 5 Change of the critical temperature with applied pressure for a critical mixture of nitroethane-cyclohexane.

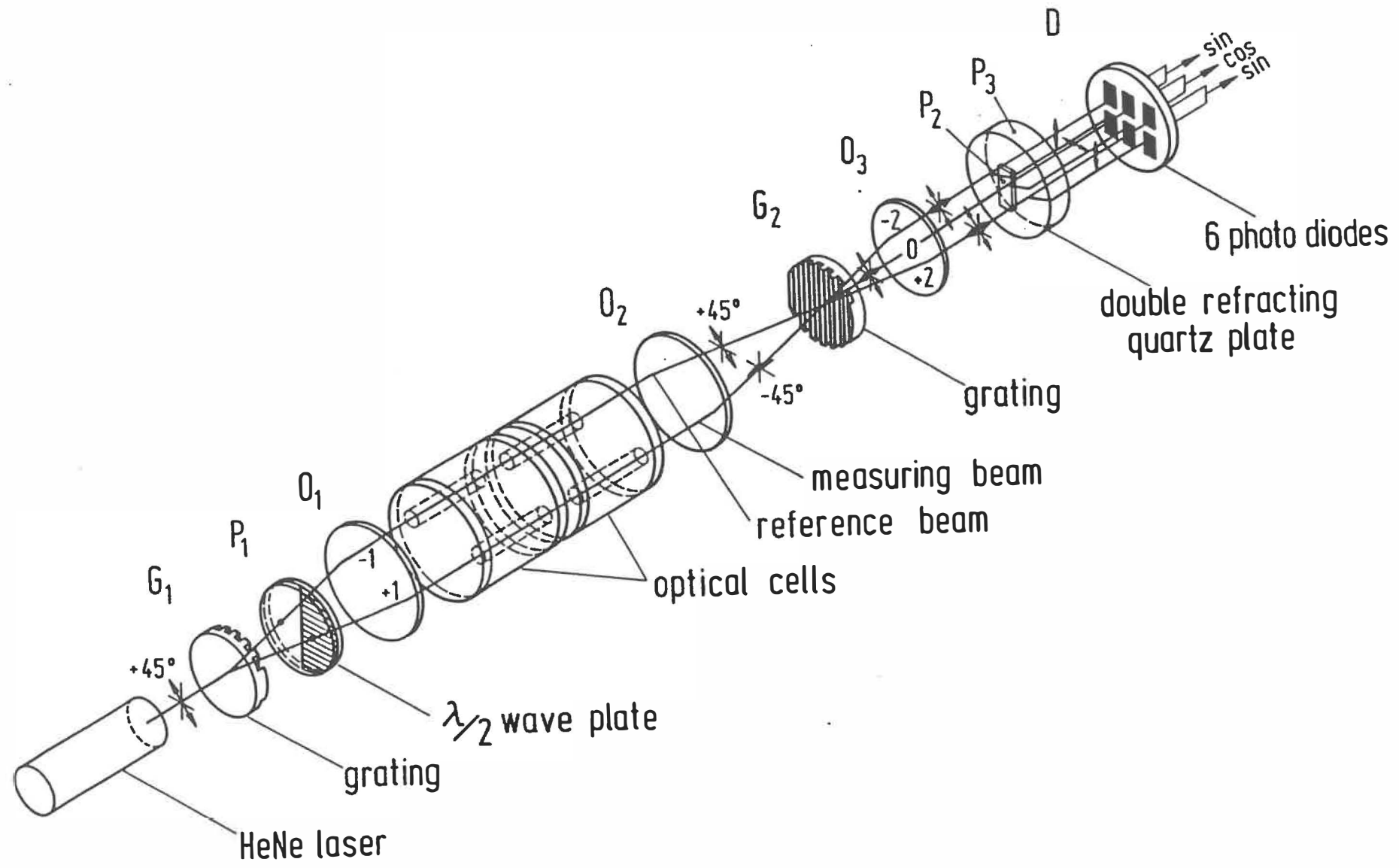


Fig. 2

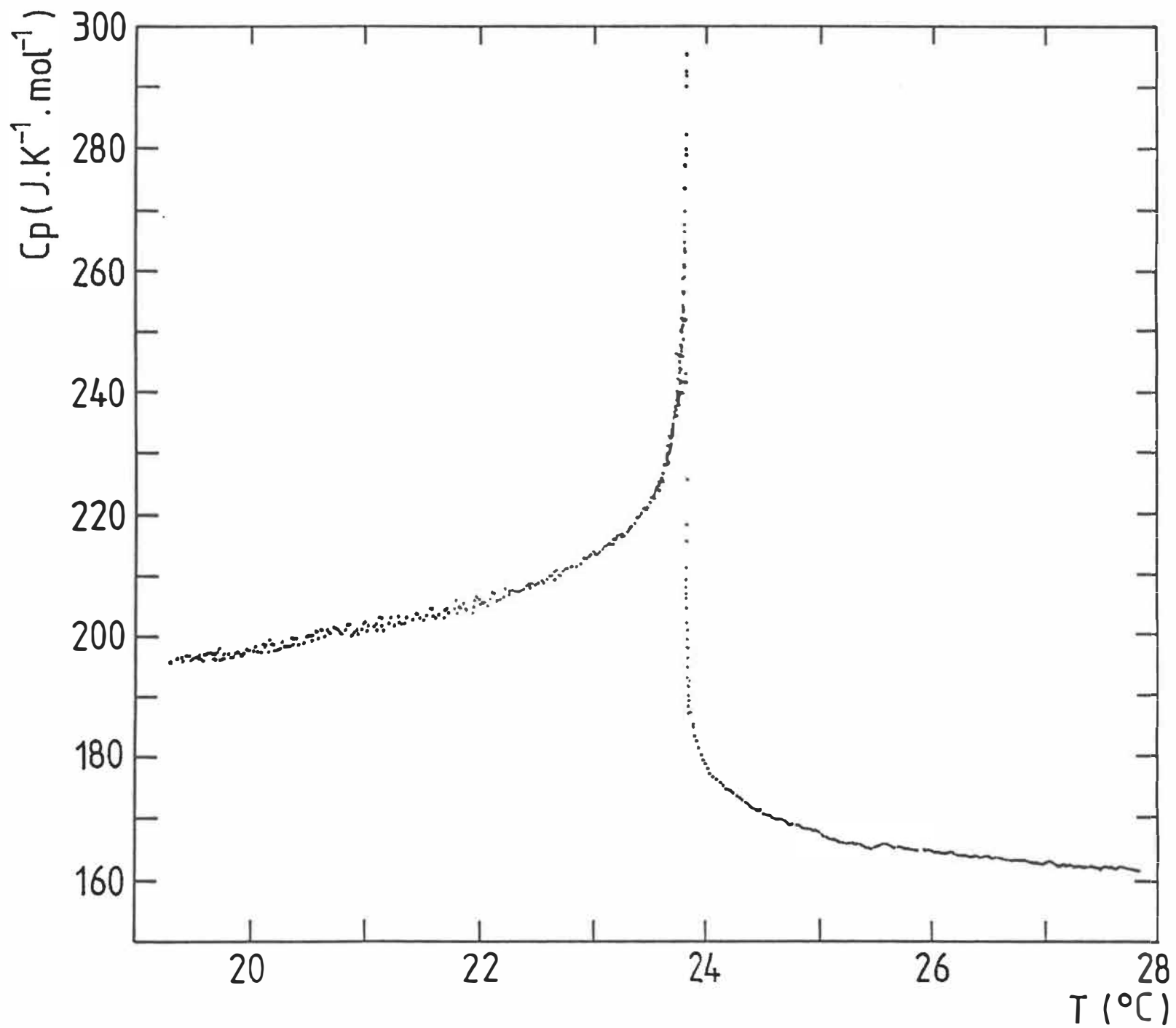
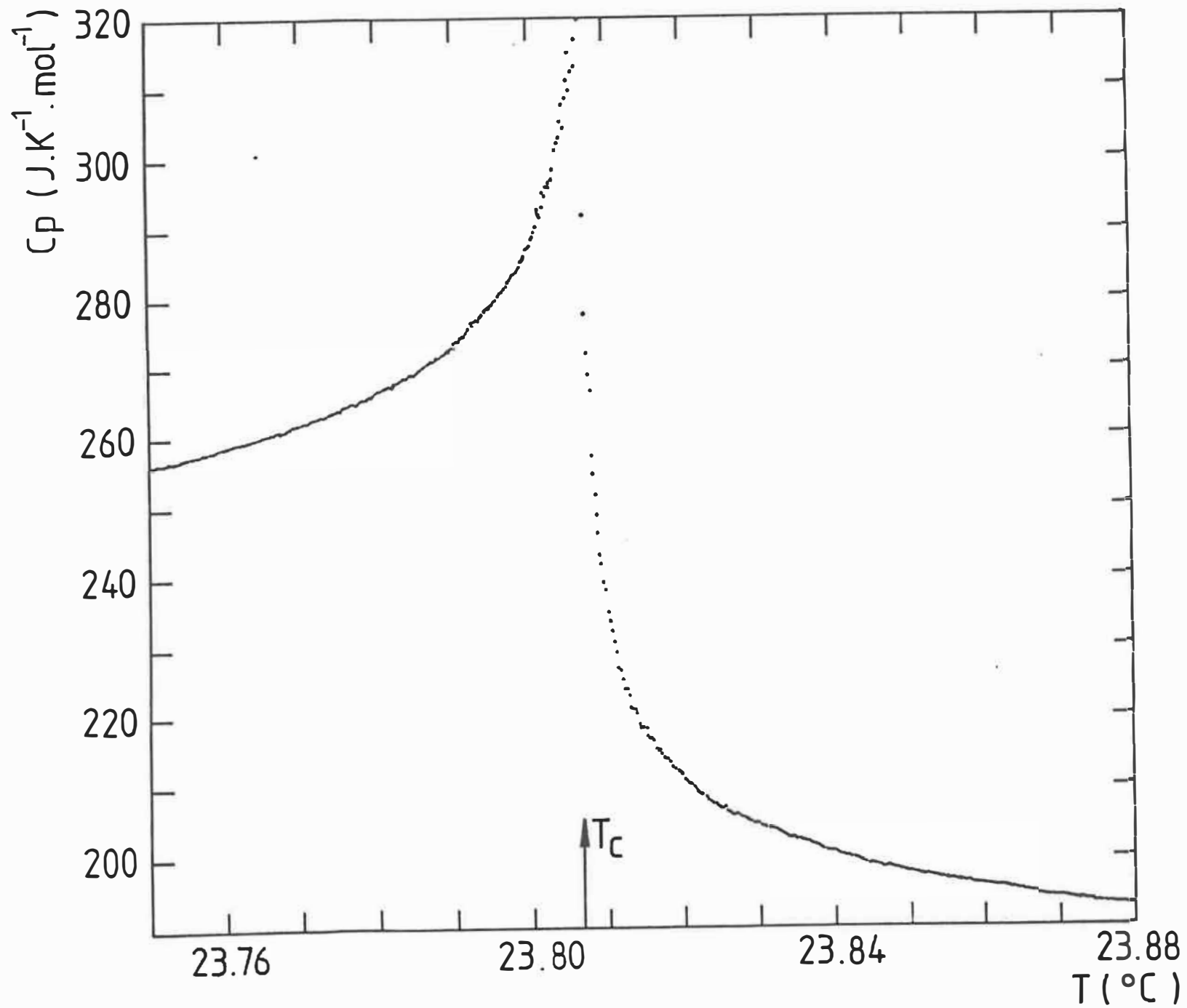
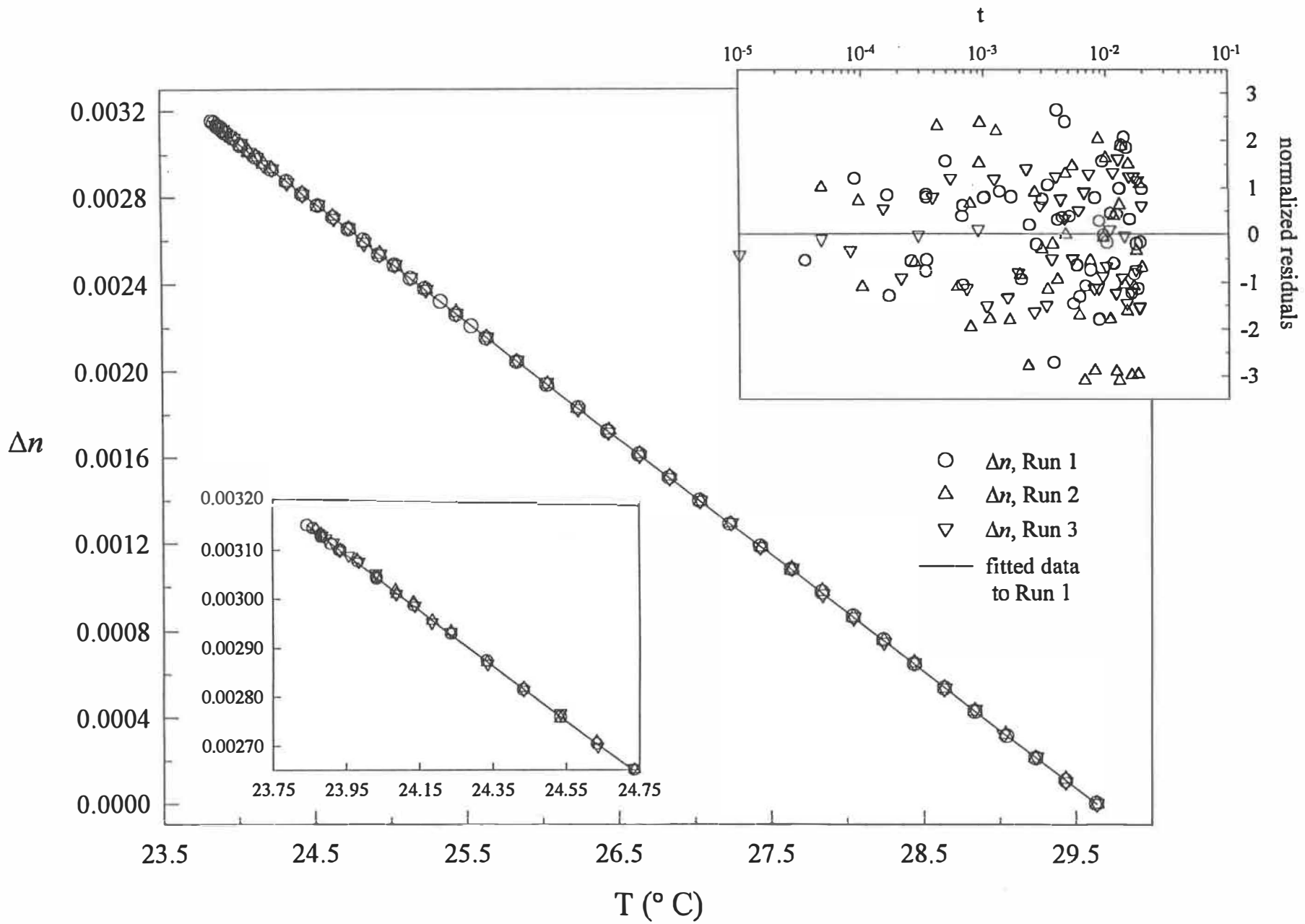


Fig. 3





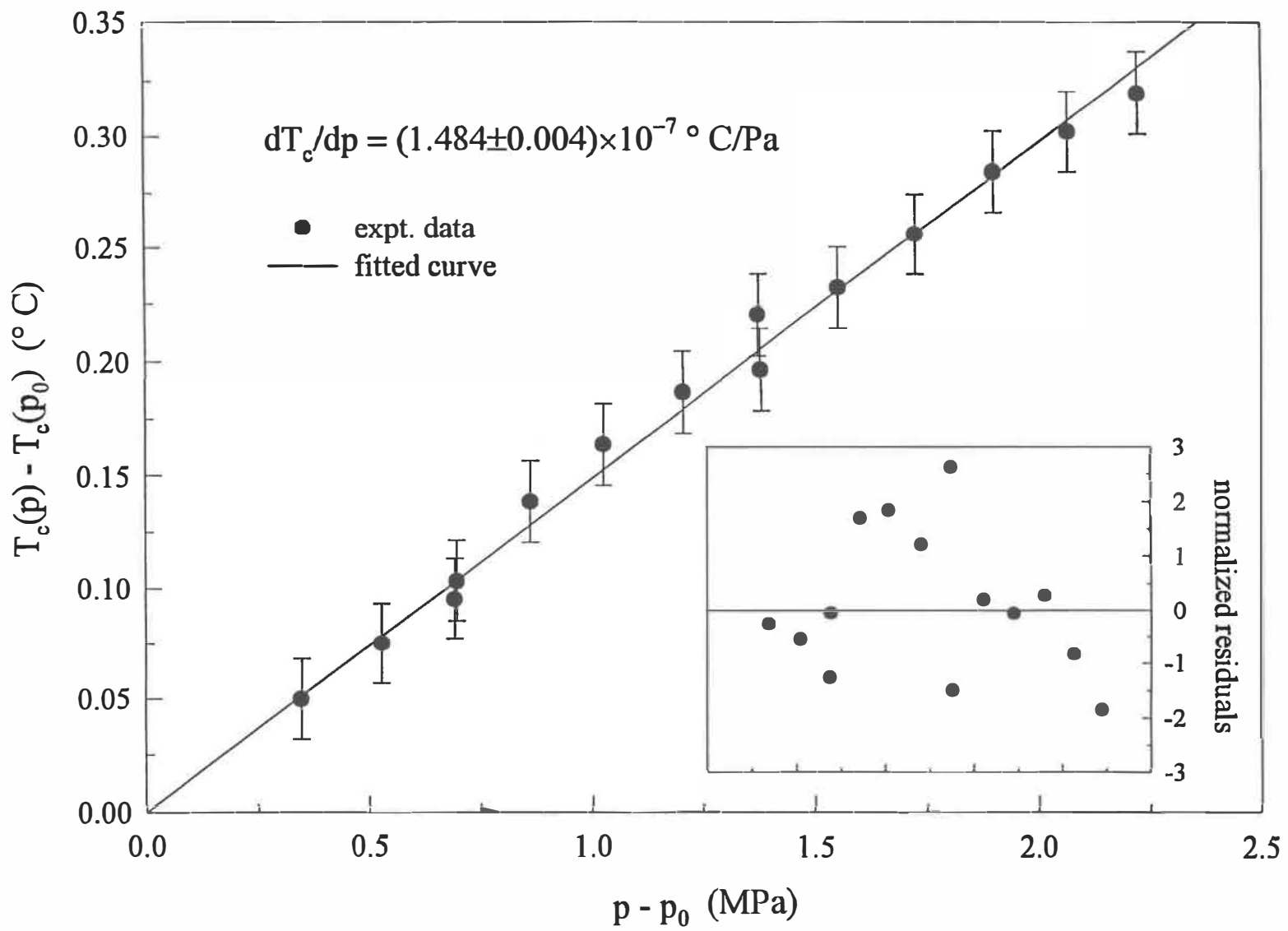


fig. 5