Thermochimica Acta, 151 (1989) 131–144
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMOKINETIC INVESTIGATION OF A REACTION WHICH INTERSECTS THE LIQUID-LIQUID COEXISTENCE CURVE NEAR THE CONSOLUTE POINT [1]

Christoph Müller, Alfred Steiger and Friedrich Becker [2]

Institut für Physikalische und Theoretische Chemie der
Universität, P.O.Box 11 19 32, D-6000 Frankfurt am Main, FRG

SUMMARY

The influence of the liquid-liquid phase transition on the rate of the stepwise esterification of 1,2-ethanediol by acetic anhydride in presence of catalytic amounts of trifluoroacetic acid is investigated at 298.15 K. The reaction starts in the two- phase and ends in the one-phase region. The heat production w(t) is measured by heat flow calorimetry which is equally well suited for obtaining data from heterogeneous and homogeneous media. The phase transition is indicated by a jump of w(t) which exhibits a minimum at the consolute point(C.P).In the neighbourhood of C.P. w(t) displays a fall-off which is virtually symmetric with respect to the phase transition point. From the shape of w(t) the critical exponents $\varphi' = 0.35 \pm 0.05$ in the one-phase and $\varphi'' = 0.50 \pm 0.05$ in the two-phase region are calculated. The contributions to φ' and φ'' of the divergence of the heat capacity and the viscosity and of the slowing down of the transport processes in the critical region are discussed.

INTRODUCTION

The influence of critical phenomena on chemical reactivity is a very recent subject which focuses much interest of both theoretical and experimental research. In a series of papers published in the last years by Procaccia and Gitterman (ref.1), Wheeler and Petschek (ref.2), Anderson and Greer (ref.3), Griffiths and Greer (ref.4), and others (ref.5), anomalies in chemical equilibria near the gas-liquid critical point resp. the consolute point (C.P.) in liquid mixtures are discussed. There is controversy with respect to the existence of a weak or strong 'critical slowing down' of the chemical reactivity in the critical region. Until now, all experiments being reported in the literature refer to the behaviour of systems very close to the chemical equilibrium, but

---

[1] Presented at the 10th IUPAC Conference on Chemical Thermodynamics, Prague, August 29 - September 2, 1988.

[2] to whom correspondence should be addressed

004-6031/89/$03.50

not to reaction rates far from equilibrium. Examples are the dissociation of weak acids, like isobutyric acid in aqueous solution, revealed by anomalies of conductance (ref.6), or the static dielectric constant in the system perfluoromethylcyclohexane + tetrachloromethane near the critical solution point, detected by anomalies of permittivity (ref.7). Our idea was to investigate the isothermal kinetics of a slow reaction in a liquid mixture in which the transition from the two-phase to the one-phase region results from the change of composition during the reaction, without any addition of reagents. The reaction rate is determined by measurement of the heat production w(t) as a function of time with a heat flow calorimeter. The advantage of this method is that it yields reliable results both from the heterogeneous and the homogeneous regimes. Thus the chemical reaction itself serves as a probe for obtaining information on the critical phenomena. A reaction is suited for investigations of this kind if it meets the following requirements: (1) It must start in the two-phase and end in the one-phase region, or vice versa, (2) the reaction enthalpy must be sufficiently great to allow detection of the heat production by heat flow calorimetry, (3) the reaction rate must be small for yielding a good resolution of the change of composition on the mole fraction scale which is essential for studying critical phenomena.

METHODS

Esterification of 1,2-ethanediol by acetic anhydride

The experiments were performed on the partially miscible system 1,2- ethanediole + acetic anhydride in which homogenization by esterification takes place at constant temperature and pressure in the materially closed system.

Using the abbreviations

$A = (CH_3CO)_2O \quad S = CH_3COOH \quad G = HOCH_2CH_2OH$

$E' = CH_3CO\text{-}O\text{-}CH_2CH_2OH \quad E = CH_3CO\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}COCH_3$,

the reaction mechanism can be formulated as a two-step esterification of 1,2-ethanediol, where the high reactivity of the acetic anhydride allows the back reactions to be ignored:

$$A + G \xrightarrow{k_1} E' + S \qquad (1)$$

$$A + E' \xrightarrow{k_2} E + S \qquad (2)$$

$$2A + G \longrightarrow E + 2S \qquad (3)$$

The rate laws in terms of the mole numbers n_A, n_G , $n_{E'}$, n_E and n_S of the reactants read

$$dn_{E'}/dt = k_1 n_A n_G - k_2 n_A n_{E'} \qquad (4)$$

$$dn_E/dt = k_2 n_A n_{E'} \qquad (5)$$

$$d(n_{E'} + n_E)/dt = k_1 n_A n_G \; . \qquad (6)$$

Denoting the single-step reaction enthalpies by ΔH_1 and ΔH_2, the total heat production of the reaction is

$$w = \Delta H_1 \, dn_{E'}/dt + \Delta H_2 \, dn_E/dt \qquad [W] \; . \qquad (7)$$

From eqns. (6) and (7) results that $w \sim d(n_{E'} + n_E)/dt$ is only valid if $\Delta H_1 = \Delta H_2$. This deviation of the heat production w from the simple second-order rate law, however, is not important for the study of critical phenomena. The reaction is subject to acid catalysis so that an autocatalytic acceleration of the reaction is observed when strong acids are absent. The uncatalysed reaction, however, is too slow. Weighted amounts of trifluoroacetic acid were added to adjust the half-life to about 100 to 120 minutes. In the presence of the catalyst, the autocatalytic effect of the acetic acid being formed during the reaction is negligible.

Heat flow calorimetry

The heat flow calorimeter made from gold-plated silver is of the same type as described earlier (ref.8). Both the cylindrical vessel, the capacity of which is 30 cm^3, and its conical lid are double-walled to obtain a fast heat exchange with the circulating water from a precision thermostat the temperature of which is controlled to ± 0.001 K. The time constant of the heat flow calculated from cooling curves is 11s. Changes of the temperature of the liquid in the vessel are measured by four symmetrically arranged thermistors being connected in a Wheatstone bridge. After amplification by a chopper amplifier (x 1000) the voltage signal of the bridge is fed to an AD converter and to a calculator which allows data acquisition in any desired time intervals. The liquid in the calorimeter is intensively stirred by a magnetic stirrer (700 rpm); the power dissipated by stirring is about 100 mW ± 2%. A heater serves for calibration of the heat flow signal and for establishing the linear relationship between the power input and the output signal under steady-state conditions. The resolution of ± 1 mW is mainly limited by the baseline noise arising from fluctuations of the thermostat temperature.

Products

Best reagent grade products (> 99%) were used. For further purification, 1,2-ethanediol was distilled at 7 Torr over an automatic Vigreux column with 10 theoretical plates. $Kp_7 = 89\,^{\circ}C$, $d_{20} = 1.1135$, $n_D^{20} = 1.4318$. The water content determined by Karl Fischer titration was 0.045 per cent. For eliminating traces of acetic acid, acetic anhydride was distilled at 100 Torr on the same column. $Kp_{100} = 80.7\,^{\circ}C$, $d_{20} = 1.0820$, $n_D^{20} = 1.3901$.

Kinetic experiments

Preliminary experiments were performed in a thermostated glass cylinder for determining visually the time elapsed between the start of the reaction and the homogenization of the mixture. If 0.16 to 0.22 mole percent of trifluoroacetic acid are added, the mixture becomes homogeneous after 60 to 120 minutes at 298.15 K. The slowness of the uncatalysed reaction (eqn. 1) allows the liquid-liquid coexistence curve to be determined approximatively. If, for instance, a 1:1 mixture of 1,2- ethanediol monoacetate + acetic acid is added to a 1:1 mixture of acetic anhydride + 1,2-ethanediol at 298.15 K, the clearing point is attained after 7.4 mole percent of the former mixture have been added . This means that the phase transition occurs far from equilibrium. It must be considered, however, that commercial 1,2-ethanediol monoacetate is not a pure component, but an equilibrium mixture of 1,2-ethanediol + 1,2-ethanediol monoacetate + 1,2-ethanedioldiacetate, which cannot be separated by distillation.

The thermokinetic experiments were performed by preparing mixtures of acetic anhydride + 1,2-ethanediol from the prethermostated components, the molar ratio being varied from 2:1 to 1:2. 25 cm^3 of this mixture was introduced into the calorimeter. After about five minutes, when the thermal equilibrium was attained, the reaction was started by addition of a weighted amount of trifluoroacetic acid from a syringe. The start of the reaction being indicated by an increase of the heat production by 200 to 300 mW is not precisely defined, but this does not affect the study of the influence of the phase transition on the reaction rate.

RESULTS

Some examples of heat flow curves versus time are presented in Fig.1. These curves differ by the initial mole fraction of acetic anhydride in the mixture, and by the mole fraction of trifluoroacetic acid. For a better comparison, the minimum of heat production is taken as zero of the time scales so that t becomes negative in the heterogeneous and positive in the homogeneous regions. The curve shapes are characterized by the following features:

(1) Far from the phase transition, the curves exhibit negative and virtually constant slopes which result from the decrease of the reactant concentrations with time, the contribution of the quadratic term (eqn. 6) during the time of observation being small.
(2) The transition from the heterogeneous to the homogeneous state is indicated by a jump of the heat production by 10 to 20 percent. This effect allows the instant of phase transition to be determined precisely.
(3) In the critical region, a fall-off of the heat production is observed which fades away when the phase transition occurs more and more distant from the consolute point. This fall-off is virtually symmetric with respect to the phase transition point.

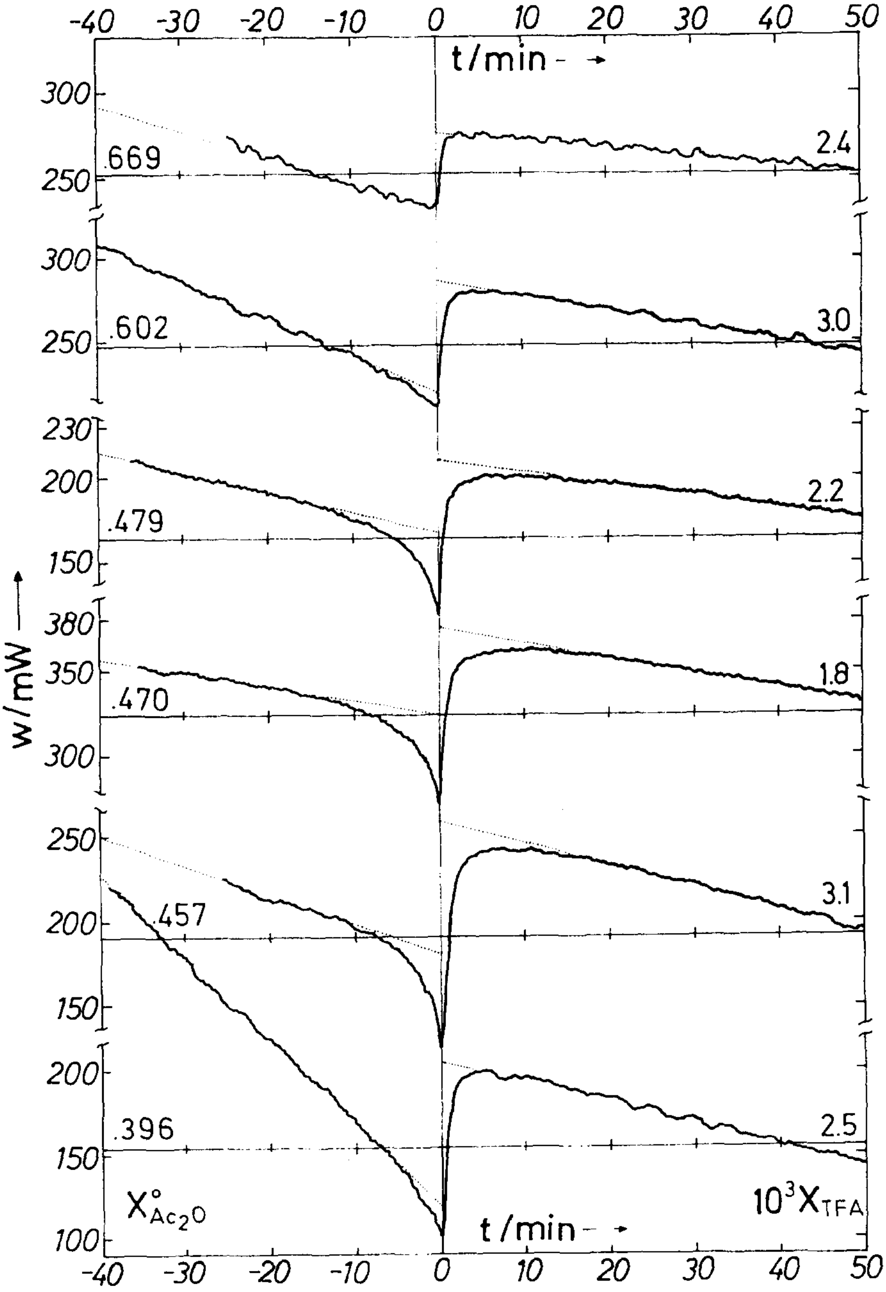

Fig. 1. Heat flow curves w(t) for the reaction of acetic anhydride (initial mole fraction $x^\circ_{Ac_2O}$ with 1,2-ethanediol at 298.15 K, catalysed by trifluoroacetic acid (mole fraction x_{TFA}). t<0 : two phases, t>0 : one phase.

DISCUSSION

Reaction path in the two-phase and one-phase regions

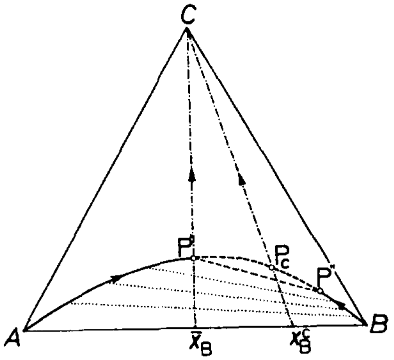

Fig.2. Path of the isothermal reaction A + B ⟶ C in the two-phase and one-phase regions. AP'P_cP"B coexistence-curve, ... tie-lines, P_c consolute point.

The path of an isothermal homogeneous reaction A + B ⟶ C is given by a straight line in the Gibbs phase triangle (Fig.2). In the heterogeneous region, however, the reaction takes place in two separated phases ' and ". If the reaction is slow and the mixture is intensively stirred, it is reasonable to assume that the material exchange between the phases ' and " is fast compared with the reaction rate, i.e. the material equilibrium between both phases is established throughout the reaction. Then the reaction path consists of two branches which follow the coexistence curve. This implicates that the reaction rates dn_C'/dt and dn_C''/dt depend one from another such that at any time the corresponding points on both branches of the reaction path must be end-points of a tie-line. It can be easily shown that for a second-order reaction half of the sum of the reaction rates in the coexisting phases ' and "

$$(dn_C'/dt + dn_C''/dt)/2 = k(n_A' n_B' + n_A'' n_B'')/2 , \qquad (8)$$

is always smaller than the rate of the homogeneous reaction in a mixture with the average composition,

$$d\bar{n}_C/dt = k\bar{n}_A \bar{n}_B , \qquad (9)$$

where

$$\bar{n}_A = (n_A' + n_A'')/2 \text{ and } \bar{n}_B = (n_B' + n_B'')/2 .$$

Putting

$$n_A' = \bar{n}_A (1+\delta) \qquad n_A'' = \bar{n}_A (1-\delta)$$

$$n_B' = \bar{n}_B (1-\varepsilon) \qquad n_B'' = \bar{n}_B (1+\varepsilon)$$

one obtains by subtraction of eqn.8 from eqn.9:

$$d\bar{n}_C/dt - (dn_C'/dt + dn_C''/dt)/2 = k\delta\varepsilon > 0 , \qquad (10)$$

which means that the advancement of the reaction in phase ' is delayed as long as phase " exists, or vice versa. If, for example, the initial mole fraction $\bar{x}_B$(Fig.2) is chosen such that the phase transition occurs at P' left from P_C , the mass of the phase " will decrease continuously until it vanishes at P' . In this case, the two branches of the reaction path on the coexistence curve do not join, but are separated by the tie-line P' P". After homogenization, the reaction path follows the straight line P' C which continues the fictitious "average path" $\bar{x}_B$ P' in the two-phase region. The length of the tie-line P' P" is a measure of the jump of the heat-production curve. If the initial mole fraction $x_B{}^c$ is chosen such that the "average path" intersects the coexistence curve exactly at P_C , the two branches of the actual reaction path join at P_C so that no jump of the heat production should occur. If this picture is right, the decrease of the jump should allow to locate precisely the consolute point. The results of this discussion on the three-component system A + B ⟶ C may be applied analogously to our five-component system A + G ⟶ E + E' + S (eqns. 1 and 2). Fig.3 shows a plot of the jump $\Delta w/(w' - w_{min})$ at the phase transition in the vicinity of C.P. versus the initial mole fraction x_G of 1,2-ethanediol. The fitting curve exhibits a rather sharp minimum at x_G = 0.519 , but the jump does not vanish at this point. The fact that a residual jump of about 40 mW persists at C.P. may be interpreted by the critical slowing down of the

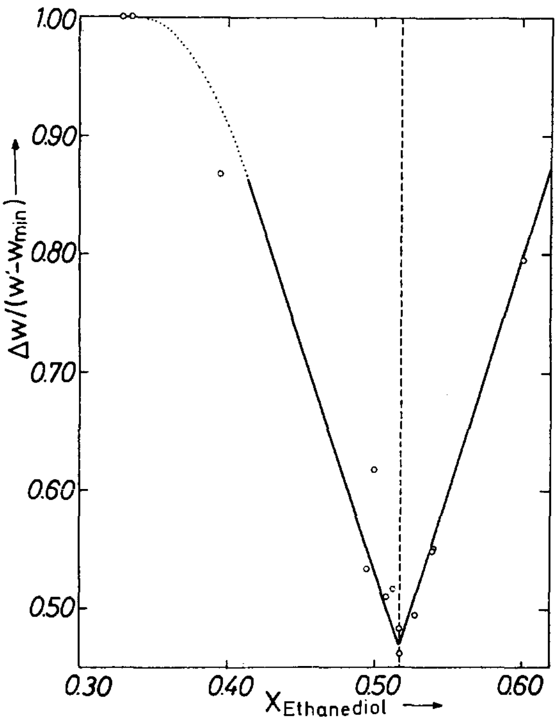

Fig. 3 Dependence of the relative jump of the heat flow, $\Delta w/(w'-w_{min})$, at the phase transition point on the initial mole fraction of 1,2-ethanediol

transport phenomena which prevents the two branches of the reaction path (Fig.2) from really joining at P_C. The assumption that the mass exchange between the phases' and " is fast compared with the reaction rate is no longer valid when the binary diffusion coefficients converge to zero.

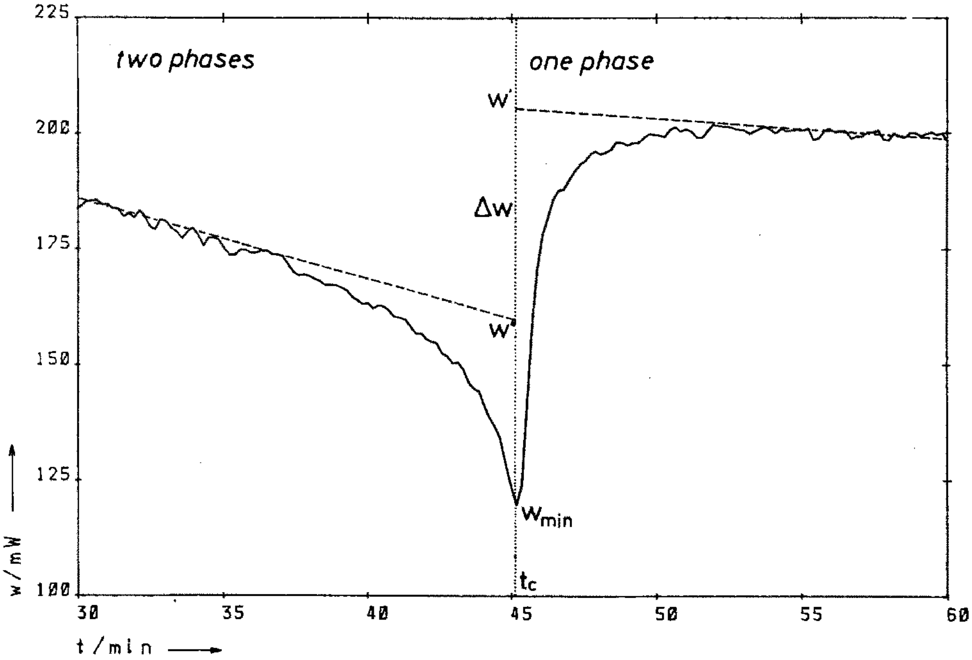

Fig. 4. Section of the heat flow curve w(t) in the neighbourhood of the phase transition point showing how the jump Δw and the critical exponents φ' and φ'' are determined.

Determination of the critical exponents φ' and φ''

In Fig. 4 a section of a plot w = f(t) in the vicinity of the phase transition point is presented to show how the critical exponents φ' and φ'' have been determined. Using the power law

$$|w - w_C|/w_C = [|t - t_C|/t_C]^{\varphi} \quad (T = \text{const.}) \quad , \qquad (11)$$

the double-logarithmic plot of the reduced heat production against the reduced reaction time,

$$\ln(|w - w_C|/w_C) = \varphi[\ln(|t - t_C|/t_C)] \qquad (12)$$

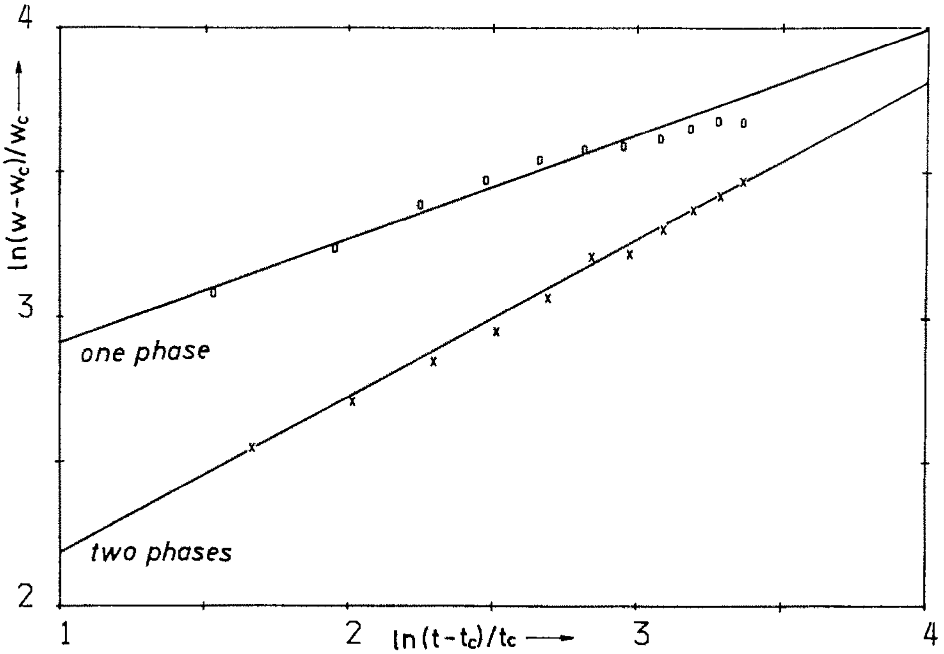

Fig. 5. Example of a linear plot $\ln(|w-w_c|/w_c) = \varphi \ln(|t-t_c|/t_c)$ in the one-phase and two-phase regions.

should yield a straight line with the slope φ. An example of such a plot is presented in Fig.5. The average values of the critical exponents of 10 runs in the vicinity of C.P. (see Table 1) are:

$\varphi' = 0.35 \pm 0.05$ homogeneous region
$\varphi'' = 0.50 \pm 0.05$ heterogeneous region .

The total heat production (= heat flow in the steady state) contains the contributions of the chemical reaction and of the power being dissipated by stirring,

$$w = w_r + w_{st} ,$$

where $w_{st} \approx 100$ mW at 700 rpm. The deviation from symmetry of the w(t) curves with respect to the phase transition point, being revealed by the difference between φ' and φ'', may be interpreted by the jump Δw. This jump is not rectangular but delayed according to the time constant of heat flow. Attempts for separating the true event signal from the time dependence of heat flow by a deconvolution procedure have not yet been undertaken until now.

Table 1: Reaction of acetic anhydride with 1,2-ethanediol (initial mole fraction x^o_{Et}) at 298.15 K. Heat flow data at the phase transition point (see Fig.4) (in mW), and critical exponents for some runs close to the consolute point.

x^o_{Et}	w_{min}	w''	w'	Δw	$\frac{\Delta w}{w'-w_{min}}$	φ'	φ''
0.3288	230	230	276	46	1.000	-	-
0.3340	182	182	215	33	1.000	-	-
0.3952	210	220	285	65	0.867	-	-
0.4950	342	420	509	89	0.533	0.46	0.30
0.5000	120	156	214	58	0.617	-	-
0.5091	144	170	197	27	0.509	0.29	0.44
0.5131	153	179	207	28	0.518	0.33	0.48
0.5186	118	165	209	44	0.483	0.38	0.54
0.5186	200	242	278	36	0.462	0.36	0.53
0.5283	268	322	375	53	0.495	0.35	0.27
0.5397	120	184	263	79	0.552	-	-
0.5400	144	184	233	49	0.551	-	-
0.6013	100	122	207	85	0.794	-	-

Discussion of the contributions to φ' and φ''

(a) Divergence of the heat capacity at C.P. The divergence of the heat capacity C_p of liquid mixture at C.P. is given by the power law

$$C_p \sim (|T - T_c|/T_c)^{-\alpha}, \qquad (13)$$

where $\alpha \approx 0.10$ (ref.9). In our experiments, however, C.P. is attained by change of composition at constant temperature. Precise data on the critical exponent of C_p along a path through C.P. perpendicular to the plane of the coexistence curve $T = f(x)$ are not reported in the literature. Recent investigations of Kohler et al. (ref.10) on the system bis(2-chloroethyl)ether + 2,2,4-trimethylpentane indicate that C_p diverges too, when C.P. is approached by changing the mole fraction at constant temperature.

Divergence of C_p should cause convergence of the heat flow signal to zero at C.P. Experimentally, this lower bound of w is not attained in a chemically reacting system because diffusivity and thermal diffusivity converge to zero at C.P., too.

(b) Divergence of the viscosity at C.P. The viscosity of binary liquid mixtures exhibits a weak divergence at C.P. which can be described by a power law,

$$\eta \sim [|x - x_c| / x_c]^{-\alpha} \quad (T = \text{const.}) , \qquad (14)$$

where α varies from 0.05 to 0.30 (ref.11). Because the magnetic stirrer is running at constant rpm, divergence of the stirring power w_{st} according to eqn. (14) is to be expected. Far from C.P., w_{st} is only 0.3 to 0.4 of w, but near the phase transition point w_{st} approaches w because of the critical slowing down of the reaction (see below). Thus, both effects (a) and (b) on the heat flow signal are opposite and partially cancel out.

(c) Critical slowing down of the reaction rate. From the above discussion follows that the main contribution to φ' and φ'' must be a 'critical slowing down' of the reaction rate. It is reasonable to make the convergence of the binary diffusion coefficients to zero at C.P. responsible for this effect. The theory of transport phenomena in the critical region (ref.12) relates the convergence of the transport coefficients to zero to the divergence of the correlation length,

$$\xi \sim (|T - T_c|/T_c)^{-\nu} , \qquad (15)$$

where $\xi \approx 0.64$. Although ξ is usually determined by variation of T at constant composition, a similar divergence of ξ is to be expected by variation of the composition at constant T. It should be noticed that the response of the temperature sensors of the calorimeter is not influenced by the convergence of the thermal diffusivitiy to zero at C.P., because, in a stirred system, the heat transport to the walls of the vessel is mainly effected by convection, and not by heat conduction.

The change of composition with time in a chemically reacting system needs continuous transport of matter for establishing the material equilibrium. This is especially important if the reaction takes place in the two coexisting phases of a partially miscible liquid mixture. The material equilibrium between both phases in the strongly agitated liquid can only be kept upright if the rate of transport of the reactants over distances which are large compared with the intermolecular distances is much faster than the reaction rate. This condition, however, is not fulfilled in the critical region. It is obvious from our experiments that the critical phenomena do not only occur in the immediate neighbourhood of C.P., but in a rather extended 'critical region' which comprises the mole fraction range of 0.52 ± 0.03 of 1,2- ethanediol. The slowing down of the transport processes prevents the C.P. from being exactly attained in dynamic experiments, like chemical reactions.

We do not attempt to give a quantitative interpretation of the values of φ' and φ'', for example in terms of other critical exponents, like α and ν, until experimental data on more reactions are available. Such an interpretation is complicated by the fact that the literature data on α and ν are usually obtained by variation of T at constant composition, whilst our experiments are performed along a path perpendicular to this path in the phase diagram, i.e. by variation of the composition at constant T.

Financial support of this work by the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, and the Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged.

REFERENCES

1 I.Procaccia, M.Gittermann, Anomalies in chemical equilibria near critical points, Phys.Rev. A 27 (1983) 555-557.
2 J.C. Wheeler, R.G. Petschek, Anomalies in chemical equilibria near critical points of dilute solutions, Phys.Rev. A 28 (1983) 2242-2248.
3 E.M.Anderson, S.C.Greer, Chemical reactions near critical points: dissociation of weak acids, Phys.Rev. A 30 (1984) 3129-3135.
4 R.B.Griffiths, J.C.Greer, Critical points in multicomponent systems Phys.Rev. A 2 (1970) 1047-1064. S.C.Greer, Thermal and chemical relaxations near the critical point of chlorine, Phys. Rev. A 31 (1985) 3240-3246.
5 J.L.Tveekrem, R.H.Cohn, S.C.Greer, The effect of critical fluctuations on chemical equilibrium, J.Chem.Phys. 86 (1987) 3602-3606.
6 J.C.Wheeler, Singularity in the degree of dissociation of isobutyric acid-water solutions at the critical solution point, Phys. Rev. A 30 (1984).
D.Jasnow, W.I.Goldburg, J.S.Semura, Resistance anomaly in weak acid near the critical point, Phys.Rev. A 9 (1974) 355-359.
H.A.Kolb, D.Woermann, Conductivity fluctuations in butyric acid/water and isobutyric acid/water mixtures, J.Chem.Phys. 80 (1984) 3781-3784.

7 R.H.Cohn, S.C.Greer, Dielectric constant near the liquid-liquid critical point in perfluoromethylcyclohexane + carbon tetrachloride, J. Phys. Chem. 90 (1986) 4163-4166.

8 F.Becker, M.Kiefer, H.Koukol, Kontinuierliche Bestimmung von Mischungswärmen durch quasi-isotherme Wärmeflußkalorimetrie, Z. physik. Chem. Chem. Neue Folge 80 (1972) 29-43.

9 F.Grønvold, Heat capacities in the critical region, Pure and Applied Chem. 47 (1976) 251-266.

10 H.Kaladi, F.Kohler, P.Svejda, Excess properties in the mixture bis(2-dichloroethyl)ether (chlorex) and 2,2,4-trimethylpentane (isooctane), Monatsh. Chem. 118 (1987) 1-18.

11 H.M.Leister, J.C.Allegra, G.F.Allen, Tracer diffusion and shear viscosity in the liquid-liquid critical region, J. Chem. Phys. 51 (1969) 3701-3708. A.Stein, J.C.Allegra, G.F. Allen, Shear viscosity of 3-methylpentane-nitroethane near the critical point, J. Chem. Phys. 55 (1971) 4265-4269.

12 J.V.Sengers, Transport processes near the critical point of gases and binary liquids in the hydrodynamic regime, Ber. Bunsenges. Phys. Chem. 76 (1972) 234-249.