

Difference between the Raman spectra near the upper and lower critical points in solution

S. V. Krivokhizha, I. L. Fabelinskii, and L. L. Chaikov

P. N. Lebedev Physics Institute, Russian Academy of Sciences, 117924, Moscow

(Submitted 2 December 1992)

Pis'ma Zh. Eksp. Teor. Fiz. **57**, No. 1, 21–24 (10 January 1993)

A difference has been observed between the Raman scattering spectra near the upper and lower critical points for layering in guaiacol–glycerol solutions.

Binary solutions, in particular, guaiacol–glycerol solutions, which exhibit a layering region and a double critical point have received comparatively little study, although they are interesting and important entities for research on the phase transitions and critical phenomena.^{1–4}

If a guaiacol–glycerol solution contains essentially no third component (water), it is homogeneous at an arbitrary concentration C and at an arbitrary temperature T .

When a small amount ($\sim 1\%$) of a third component is added, however, it gives rise to a closed region or loop in which the components do not mix. The size of this region in the T – C plane depends on the amount of the third component. An upper critical point for layering (T_c^U) and a lower one (T_c^L) exist simultaneously in such a solution. The binodal in the coordinates T , C , and C_w (C_w is the concentration of water) is a crater-shaped three-dimensional surface.¹ The upper and lower critical points convert into lines of upper and lower critical points. A double critical point forms where these lines intersect at the minimum of the binodal surface.

Walker and Vause⁵ have derived a theoretical description of the phase diagrams of solutions which have upper and lower critical points on the basis of renormalization-group theory.

At a purely qualitative level one can see why the solution becomes homogeneous above the upper critical temperature T_c^U and below the lower critical one T_c^L by working from the general thermodynamic principle that upon a change in the state of a system the system tends to occupy the position with the lowest free energy $\Phi = E - TS$. This free energy is determined by a competition between the energy (E) of the system and its entropy (S).

With increasing temperature near T_c^U , the entropy increases, and the product TS becomes substantial, with the result that Φ falls off sharply, and the solution becomes homogeneous.

At temperatures below T_c^L , the appearance of a homogeneous phase of the solution cannot be explained in the same way, since at small values of T a slight increase in S cannot lead to a sufficiently large value of the product TS . In an effort to explain the homogeneous solution observed below T_c^L , Walker and Vause⁵ invoked hydrogen-bond forces, which should lead to a decrease in E which is far greater at a low temperature ($< T_c^L$) than at a high one ($> T_c^U$).

If that suggestion is correct, then one might think that hydrogen-bond forces would act in different ways on, for example, the OH vibration near T_c^U and T_c^L . This difference should in turn be reflected in Raman scattering spectra. In this letter we are reporting a purely qualitative experimental observation of the Raman spectrum near the upper and lower critical points of a guaiacol–glycerol solution.

We studied the test solutions with layering regions $T_c^U - T_c^L = \Delta T = 39.65^\circ\text{C}$ and 0.29°C , a “dry” solution, and a solution with $\Delta T = 2.8^\circ\text{C}$ to which 0.7% ethanol was added to achieve $\Delta T = 0$. In the two latter solutions, critical phenomena were not observed (the correlation radius of the concentration fluctuations in these solutions was smaller than 30 \AA).

The Raman spectra were measured by a Koderk LRDH-800 double spectrometer with holographic gratings. The spectrum was excited by light at $\lambda = 5145\text{ \AA}$ and 15 mW from an argon laser.

Raman-scattering spectrograms were measured as the upper and lower critical layering temperatures were approached from the side of the homogeneous phase and in the immediate vicinity of these critical temperatures.

The spectrograms in Figs. 1 and 2 have been normalized to the same ordinate at the frequency 3150 cm^{-1} .

From these spectra we can draw some conclusions. In the solutions with layering regions $\Delta T = 39.65^\circ\text{C}$ and 0.29°C , at temperatures $T - T_c^U = 10$ and 0.5°C , there is a clearly defined, deformed peak of a band of OH vibrations of water in the spectra⁶ (curves 3 and 4 in Figs. 1 and 2). The spectrograms of the same solutions, in the same frequency interval but near the lower critical point, look completely different (curves 1 and 2 in Fig. 1). In this case, we do not see a peak of the band in the solution with $\Delta T = 39.65^\circ\text{C}$.

The spectrograms recorded in a study of the solution with $\Delta T = 7^\circ\text{C}$ are very similar to those found for a solution with $\Delta T = 39.65^\circ\text{C}$.

The spectrograms for temperatures 10 and 0.5°C above T_c^U are thus the same. For the same temperature intervals below T_c^L , the spectrograms are again the same. The spectrograms above T_c^U and below T_c^L , however, are very different.

In a solution with $\Delta T = 0.29^\circ\text{C}$ we see no substantial difference between the nature of the spectrograms measured at temperatures above T_c^U and below T_c^L .

In a “dry” guaiacol–glycerol solution and in a solution to which ethanol has been added, we see no deviations from a monotonic behavior in the frequency interval $3200\text{--}3700\text{ cm}^{-1}$ at any temperature (curves 6 and 7 in Figs. 1 and 2).

In the solutions with $\Delta T = 39.65$ and $\Delta T = 0.29^\circ\text{C}$, we can clearly see a group of Raman lines in the frequency interval $2843\text{--}3069\text{ cm}^{-1}$ which belong to the guaiacol molecule. The intensity of these lines increases appreciably as we go from T_c^L to T_c^U . We do not see this increase in the dry solution or in the solution with ethanol in the same temperature interval.

We can offer a purely qualitative explanation for these observations.

In the dry guaiacol–glycerol solution, the hydrogen bonds between the compo-

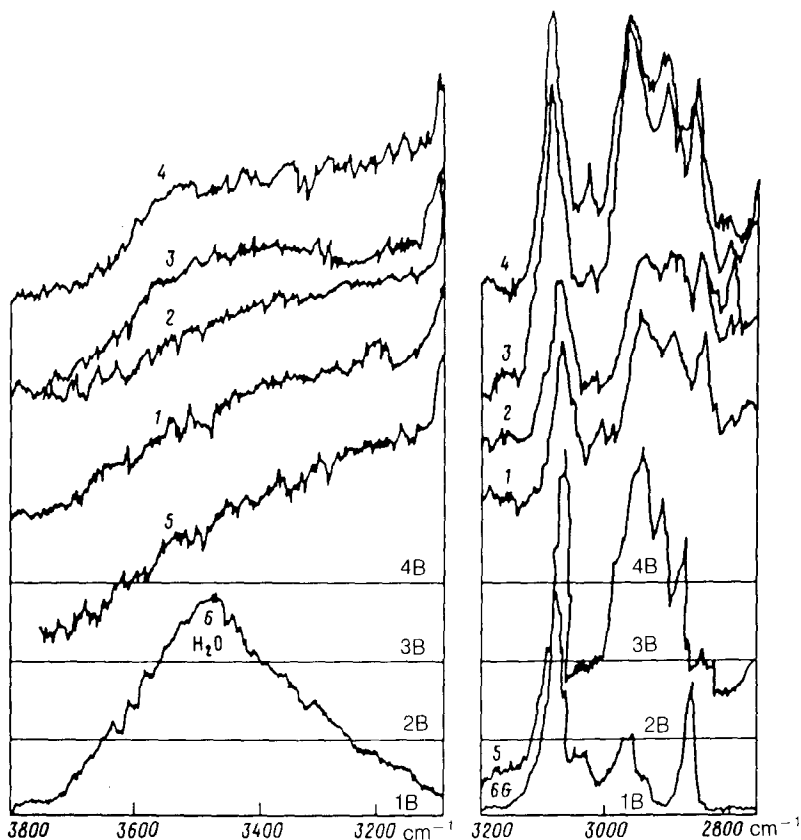


FIG. 1. Spectra of the Raman scattering of light in a guaiacol-glycerol solution with a layering region $\Delta T=39.65^\circ\text{C}$ (1-4), in a dry solution at $T=44.3^\circ\text{C}$ (5), in water (6 H_2O), and in guaiacol (6 G). 1, 2—Raman spectra at depths of 10 and 0.5° in the homogeneous phase ($T_1=32.08$, $T_2=41.47^\circ\text{C}$) as the lower critical temperature for layering is approached; 3, 4—Raman spectra at depths of 0.5 and 10° in the homogeneous phase ($T_3=82.26$ and $T_4=91.46^\circ\text{C}$) as the upper critical temperature for layering is approached. Here 1B-4B are the zero lines of spectra 1-4, respectively.

nents are very strong, and they cause the free energy to decrease. The solution is homogeneous at arbitrary C and T . When a sufficient amount of water is added to the solution, the hydrogen bonds between the major components weaken, with the result that a layering region appears.^{1,5}

The difference between the spectrograms near the upper critical point T_c^U and near the lower one T_c^L in the solution with a layering region $\Delta T=39.65^\circ\text{C}$ is clear evidence that the hydrogen-bond forces are having different effects in these regions. If we assume that an increase in the importance of the hydrogen bond flattens out a spectrogram, as in the dry solution (curve 5 in Fig. 1), then we might be led to believe that the role of the hydrogen bonds is larger near T_c^L than near T_c^U , in confirmation of a theoretical prediction.⁵

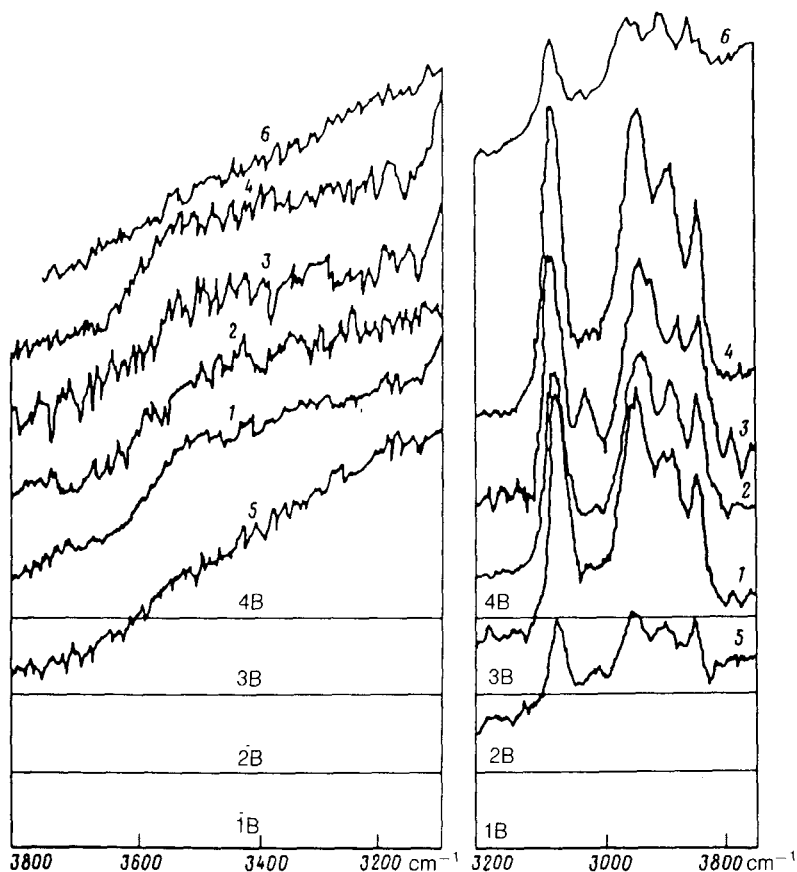


FIG. 2. Raman spectra in a solution with a layering region $\Delta T=0.29^\circ\text{C}$ (1-4), in a solution with a layering region of 2.8° , to which 0.7% of ethanol has been added to achieve $\Delta T=0$. 5—At a temperature of 43.97° ; 6— 78.24°C . 1, 2) Raman spectra at depths of 10 and 0.5° in the homogeneous phase ($T_1=50.51^\circ\text{C}$, $T_2=61.69^\circ\text{C}$) from the side of the lower critical temperature; 3, 4) Raman spectra at depths of 0.5 and 10° in the homogeneous phase ($T_3=63.1$, $T_4=72.89^\circ\text{C}$) from the side of the upper critical temperature. Here 1B-4B are the zero lines of spectra 1-4, respectively.

The disappearance of the layering region in the solution with $\Delta T=2.8^\circ\text{C}$ when 0.7% of ethanol is added (the layering region also disappears in solutions with other values of ΔT) can apparently be explained on the basis that the formation of hydrogen bonds between the water and the ethanol is preferred from the energy standpoint over the formation of bonds with other molecules. The solution then becomes "dehydrated" and homogeneous, like the dry solution.

The behavior of the intensity of the group Raman lines belonging to the guaiacol molecule in solutions having layering regions can apparently be linked with a difference between the nature of the upper and lower critical points. The intensity of this

group of lines is essentially the same in the dry solution and in the solution with ethanol in the same temperature interval.

The solutions which exhibit both upper and lower critical points are of considerable research interest. They deserve further study, particularly by spectral methods.

We are sincerely thankful to Yu. N. Polivanov for interest and assistance and to N. I. Krindach for assistance in the experiments.

¹S. V. Krivokhizha, O. A. Lugovaya, I. L. Fabelinskiĭ, and L. L. Chaĭkov, *Zh. Eksp. Teor. Fiz.* **89**, 85 (1985) [*Sov. Phys. JETP* **62**, 48 (1985)].

²V. P. Zaitsev, S. V. Krivokhizha, O. A. Lugovaya *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* **43**, 85 (1986) [*JETP Lett.* **43**, 112 (1986)].

³S. V. Krivokhizha, N. A. Fabelinskiĭ, and L. L. Chaĭkov, *Usp. Fiz. Nauk* **149**, 328 (1986) [*Sov. Phys. Usp.* **29**, 572 (1986)].

⁴R. G. Jonston, N. A. Clark, P. V. Wiltzius, and D. S. Cannel, *Phys. Rev. Lett.* **54**, 49 (1985).

⁵J. S. Walker and C. A. Vause, *J. Chem. Phys.* **79**, 2660 (1983).

⁶G. S. Landsberg, *Selected Works*, Izd. Akad. Nauk SSSR, 1958.

Translated by D. Parsons